

Contents lists available at [ScienceDirect](http://www.sciencedirect.com/science/journal/13858947)

# Chemical Engineering Journal

Chemical Engineering Journal

journal homepage: [www.elsevier.com/locate/cej](http://www.elsevier.com/locate/cej)

# Study of critical flux in ultrafiltration of seawater: New measurement and sub- and super-critical flux operations

## Jia Xu, Congjie Gao<sup>∗</sup>

Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao, Shandong 266100, China

### article info

Article history: Received 15 June 2010 Received in revised form 30 August 2010 Accepted 30 August 2010

Keywords: Ultrafiltration Critical flux Seawater Sub- and super-critical flux operations Nature flux mode

#### **ABSTRACT**

The concept "critical flux" allows for a relatively new operation optimization of ultrafiltration (UF) in fouling control strategies. The present studies mostly pay attention to colloids, organic solution and surface fresh water, which are of a less complex chemistry than that of seawater. In this work, "critical flux" was applied into the field of seawater desalination to investigate the utility of this concept for dealing with UF membrane fouling. Firstly, the nature flux mode, a new measurement for the critical flux, was proposed for UF in treating seawater and compared favorably with other measurements such as constant flux mode and constant pressure mode. Secondly, the definition (strong form  $J_{cs}$  and weak form  $J_{cw}$ ) of critical flux for UF of seawater was evaluated to make sure whether or not the perfect operating condition (without UF fouling) is in existence. Thirdly, the effects of sub- and super-critical flux operations using different operating modes on the extent of membrane fouling were investigated by measuring hydraulic resistance. Moreover, a brief analysis of the economic feasibility of sub-/super-critical flux operations was covered. The results showed that the highest  $E<sub>p</sub>$  was yielded when operating in constant pressure mode with higher TMP under super-critical flux conditions, while the lowest  $E<sub>p</sub>$  in constant/nature flux mode with higher permeate flux under sub-critical flux conditions. When operating in constant/nature flux modes, lower  $E<sub>p</sub>$  was achieved under sub-critical flux conditions than under super-critical flux conditions.

© 2010 Elsevier B.V. All rights reserved.

#### **1. Introduction**

Ultrafiltration (UF) has already been used extensively as an efficient pretreatment technique to produce consistent and high quality seawater for seawater reverse osmosis (SWRO) [\[1\]. H](#page-8-0)owever, the most knotty problem tempering with the performance of UF is membrane fouling, which leads to the elevation of the hydraulic resistance and the transmembrane pressure (TMP), the reduction of recovery and flux during filtration, as well as the increasing operational cost. An enormous amount of research has been done to identify robust membranes and appropriate operating conditions and modes, but there is still a long way to go.

Critical flux  $(J_{\text{crit}})$  defined as the flux of a membrane system, under which fouling does not occur or is relatively slow, formally proposed in 1995 [\[2–4\]. T](#page-8-0)herefore, it might be a good indicator for the membrane system to maintain its constant productivity with the advantage of operational cost. This concept provides a logically theoretical combination of membrane fouling and UF operation, such as the transition of phase from concentration polarization to fouling adjacent to membrane surface [\[5\].](#page-8-0) This research area is expanding and now represents a significant fraction around 10% of works dealing with fouling [\[6\].](#page-8-0)

However, some loopholes and disputes in the previous studies on critical flux are as follows:

- Various methods involved in flux-stepping or pressure-cycling [\[7–9\],](#page-8-0) particle mass balance [\[10,11\]](#page-8-0) and direct observation through membrane [\[12\]](#page-8-0) were mainly applied to determine the value of critical flux. However, for a certain feed and membrane system, how to choose a proper method still seems to be an open question.
- The operating mode generally using either constant flux or constant pressure is crucial for the UF performance and the measurement of the critical flux. Most researchers [\[13\]](#page-8-0) considered that operation in constant flux mode was superior to that in constant pressure mode due to lower resistance and larger volume of product water, while some researchers [\[7\]](#page-8-0) preferred the constant pressure mode due to less irreversible resistance. Therefore, the optimum operating mode still appears to be another open question.
- The critical flux of UF membrane depends mostly on the feed chemistry. The feed water studied was generally focused on col-

<sup>∗</sup> Corresponding author. Tel.: +86 532 66781872; fax: +86 532 66781872. E-mail addresses: [qdxujia2007@gmail.com](mailto:qdxujia2007@gmail.com) (J. Xu), [gaocjie@mail.hz.zj.cn](mailto:gaocjie@mail.hz.zj.cn) (C. Gao).

<sup>1385-8947/\$ –</sup> see front matter © 2010 Elsevier B.V. All rights reserved. doi:[10.1016/j.cej.2010.08.071](dx.doi.org/10.1016/j.cej.2010.08.071)

<span id="page-1-0"></span>

**Fig. 1.** Schematic flow diagram of testing UF system.

loids such as silica particles and latex, organic solutions such as humic substances and proteins, and surface water such as rivers and lakes [\[14–19\].](#page-8-0) All of the above represent a less complex nature and chemistry compared to seawater characterized by relatively higher content of nature organic matter (NOM), turbidity and salinity. Till now, little attention is paid to the critical flux of UF in clarifying seawater to relieve the membrane fouling.

The purpose of this study was to explore and optimize UF operation from a critical flux perspective, which allows for a more robust and effective pretreatment of seawater desalination. Based on the above three limitations, a new measurement of critical flux was tested and compared with other existing measurements to verify its feasibility and superiority. To ascertain whether the operating condition without fouling exists, form (either strong form  $J_{cs}$  or weak form  $J_{\text{cw}}$ ) of the critical flux for UF of seawater was evaluated via flux-pressure profile or hydraulic resistance. If the initial flux-pressure curve of seawater superposes the one of pure water, or the hydraulic resistance maintains constant, it indicates that the perfect operating condition without fouling does exist. Moreover, the effects of sub- and super-critical flux operations using different operating modes on UF performance and membrane fouling were investigated. In addition, a brief analysis of the economic feasibility of UF operations under sub- and super-critical flux conditions was reported. The results obtained in this study are expected to supply a potential understanding of the utility of the concept "critical flux" and its contribution to the optimum operation of UF in treating seawater.

#### **Table 1**

Chemistry of raw seawater of the Yellow Sea.





**Fig. 2.** Flux-stepping measurement using nature flux mode for the critical flux assessment.

<span id="page-2-0"></span>

Fig. 3. Flux-stepping measurement using constant flux mode for the critical flux assessment.

#### **2. Experimental**

#### 2.1. Testing membrane system

The pilot-scale UF membrane system with capacity of  $72 \text{ m}^3/\text{d}$ used in the present study was installed near the Yellow Sea of China in May 2007. The flow diagram of this system is shown in [Fig. 1, w](#page-1-0)hich mainly consists of feed diving pump (Gaobang glass fiber reinforced plastic centrifugal pump), sand filter (quartz sand with filter fineness 50  $\mu$ m), 1 m<sup>3</sup> cylindrical feed tank, feed pump with pressure transducer (Grundfos multiple centrifugal pump), hollow fiber UF module (Lanlv, China), flux and pressure measurement system, backwash system with solenoid pilot actuated valve, and a peristaltic permeate pump. The UF membrane was made of modified polyether sulfone (PES) and its molecular weight cut-off was 80–100 kDa. The effective filtration area for each UF module padded with 4900 fibers was 11  $m<sup>2</sup>$ . The feed tank was fed with prefiltered seawater (temperature  $26-28$ °C) by a feed diving pump immersed in shore of Jiaozhou Bay. Continuous feed was circulated to the UF module by a feed pump which was switched on and off automatically by the water level gauge installed in the feed tank. The TMP and flux were measured by rotameter and pressure gauge and periodically recorded manually. The peristaltic permeate pump was utilized to control flux when the constant flux mode was needed to determine critical flux. Backwash and in situ cleaning procedures when needed, were fully automated and controlled by a programmable logic controller (PLC). All water sources such as UF permeate, concentrate, and backwash waste were collected and returned back to the sea through the injection well on site.

#### 2.2. Chemistry of raw seawater

The characteristics of raw seawater of Yellow Sea are listed in [Table 1.](#page-1-0) Turbidity characterizing inorganic particles and  $UV_{254}$ related directly to the aromatic fraction of NOM in seawater were measured using a turbidity meter (LP2000-11, HANNA, Italy) and an ultraviolet spectrophotometer (UV-2540, SHIMADZU, Japan), respectively. Ion concentrations (Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>−</sup> and SO<sub>4</sub><sup>2–</sup> in seawater) were analyzed using ion chromatograph (Dionex90, DIONEX, USA).

#### 2.3. New measurement for the critical flux and testing procedure

A new measurement for critical flux called nature flux mode was proposed to treat seawater using UF modules, which also adopted flux-stepping procedure and was determined by flux-pressure profile. The critical flux tests using flux-stepping (constant flux mode) and pressure-cycling (constant pressure mode) methods as well as



**Fig. 4.** Pressure-cycling measurement using constant pressure mode for the critical flux assessment.

<span id="page-3-0"></span>

**Fig. 5.** Qualitative models of foulant layer build-up under different operating modes.

this new measurement, were carried out in order to understand the impact of various operating modes on UF performance and find out an appropriate one for UF of seawater.

Nature flux mode means that elevation of pressure or reduction of flux due to membrane fouling is in the natural state during UF operation without permeate pump, neither imposing a flux to measure a changing pressure (constant flux mode) nor imposing a pressure to measure a changing flux (constant pressure mode). Compared to constant flux/pressure modes reported in literature [\[7–9\],](#page-8-0) the most distinction in nature flux mode is that no additional external force is imposed except for hydraulic force and lateral force during cross-flow operation. One hypothesis is that the additional external force derived from the feed pump with pressure transducer formaintaining a constant pressure or the peristaltic permeate pump formaintaining a constant flux, can probably result in the formation of more compact fouling layer, which could increase the hydraulic resistance and hence lower the real critical flux.

The duration of each step in flux/pressure-stepping procedure was usually less than 10 min. It might be questioned whether such a short time would be sufficient to indicate the critical flux and whether the critical flux indicated would be stable over a longer testing duration. This point, however, was neglected in most previous studies [\[20,21\]. I](#page-8-0)n our work, the duration of one step was expanded to 25 min to ensure the accuracy and validity of the results obtained. The critical flux was estimated according to the average permeability (the slope of flux–pressure curve) during each step. At the end of each test, hydraulic washing with deionized water and chemical cleaning with 5% NaClO solution were performed in turn for UF fouling removal and permeability recovery. As the feed temperature was stable (26–28 $\degree$ C), it is needless to take into consideration the temperature effect on seawater viscosity, and thus on flux.

A small fouling rate can be tolerated or even non-detectable when operating at a small time scale, whereas it becomes unacceptable (and therefore unsustainable) for long filtration times [\[6\].](#page-8-0) Tests over a relatively long-term operating period under a wide range of sub-/super-critical flux conditions were carried on to evaluate the utility of critical flux and superiority of nature flux mode for UF of seawater by measuring the hydraulic resistance. In addition, it has been reported that the accumulation of foulants might occur even UF operating under the sub-critical flux conditions [\[6\].](#page-8-0) Therefore, under sub-critical flux (sub- $J_{\text{crit}}$ ) conditions, two initial fluxes (80 and  $100 \text{ L/m}^2$  h) were applied in both nature flux and constant flux modes, which were lower than the corresponding critical flux estimated, and the TMPs of 0.2 and 0.4 bar were chosen in constant pressure mode. As to super-critical flux (super- $J_{\rm crit}$ ) conditions, both the initial fluxes of 110 and  $130 L/m<sup>2</sup>$  h were tested in nature flux and constant flux modes, and the TMPs of 0.6 and 0.7 bar were tested in constant pressure mode.

#### **3. Results and discussion**

#### 3.1. Comparison of different measurements

Operations based on flux-stepping (nature flux and constant flux mode) and pressure-cycling (constant pressure mode) measurements were performed for estimating the values of critical flux. The results were shown in [Figs. 2–4.](#page-1-0) Unless otherwise specified, the following identical test conditions were applied: cross-flow velocity around 0.11 m/s, feed turbidity 3.01-4.50 NTU, feed UV $_{254}$ 0.016–0.021 cm−1.

[Fig. 2](#page-1-0) shows the result of the critical flux assessment using fluxstepping measurement in nature flux mode. In the operation where the initial flux was increased step by step, both flux and pressure in each step could vary spontaneously. In other words, it is in a natural manner, solely due to the membrane fouling. It is normally known that the initial flux of a given membrane is proportional to its transmembrane pressure (TMP), and serious flux loss typically occurs at higher initial flux. Similar information can be found in [Fig. 2. W](#page-1-0)hen the initial flux was increased from 27.8 to  $105.7$  L/m<sup>2</sup> h, the corresponding flux and TMP maintained nearly constant in each step. When the initial flux was set to 111.3  $L/m<sup>2</sup>$  h, the flux and TMP varied slightly during the testing duration with the flux reduction of 1.2  $L/m<sup>2</sup>$  h and the TMP elevation of 0.002 MPa, respectively. It indicates the commence and trace of the membrane fouling. A further increase in initial flux (higher than  $111.3 \text{ L/m}^2$  h) resulted in more serious changes in both flux and TMP. Therefore, the critical flux is estimated to be  $105.6$  L/m<sup>2</sup> h.

The result of the critical flux using flux-stepping measurement in constant flux mode is illustrated in [Fig. 3. C](#page-2-0)ompared to operation in constant pressure mode, operation in constant flux mode was preferred especially when the feed is so wispy that it is very difficult to control the TMP at a value low enough to measure critical flux. As shown in [Fig. 3, t](#page-2-0)he TMP varied slightly from 0.050 to 0.052 MPa with the corresponding flux around  $109.1 \text{ L/m}^2$  h, and increased rapidly in each following steps when the flux was elevated to 130.1 and  $140.3 \frac{\text{L}}{\text{m}^2}$  h. Based on the above, the critical flux is determined to be 102.7  $L/m<sup>2</sup>$  h. [Fig. 4](#page-2-0) presents the result of the critical flux assessment using pressure-cycling measurement in constant pressure mode, which involves a series of up-and-down steps of constant TMP proposed by Wu et al. [\[13\]](#page-8-0) and further developed by Espinasse et al. [\[22\]. A](#page-8-0)ny extent of decline in flux observed indicated the membrane fouling when the TMP was increased and then <span id="page-4-0"></span>decreased back to a previous value in a series of steps. In [Fig. 4, w](#page-2-0)hen the TMP was set to 0.060 MPa, the corresponding flux decreased from 97.5 to 95.4 L/m<sup>2</sup> h during the testing duration; between the previous step of TMP 0.05 MPa and the next step of TMP 0.05 MPa which was set beck from TMP 0.060 MPa, a reduction in flux of  $7-8$  L/m<sup>2</sup> h was recorded. It clearly demonstrates the membrane fouling and the critical flux is estimated to be  $91.3 \text{ L/m}^2$  h.

Comparing the results of the critical flux determined, sequence of various measurements (the values of the critical flux from high to low) is nature flux, constant flux and constant pressure mode, among which quite similar results with nature flux and constant flux mode were obtained. As illustrated in [Figs. 2–4,](#page-1-0) below the critical flux values in flux–TMP curves, the slopes representing membrane permeability obtained by operations in nature flux, constant flux and constant pressure mode are 249.94, 240.71, 188.46 L/(m<sup>2</sup> h bar), and the coefficients  $(R^2)$  are 0.9997, 0.9891, 0.9874, respectively. High values of  $R^2$  (>0.9850) present the rationality and accuracy of these measurements due to the experimental definition of the critical flux which is the point where the flux–TMP relationship becomes non-linear. From filterability point of view, permeability of high value represents outstanding performance as reported in the previous work [\[23\]](#page-8-0) and becomes an integrative parameter to evaluate the performance of a fixed membrane or a fixed operating mode. It can be observed that one given membrane system under the uniform testing conditions but in different operating modes was performed diversely. It indicates that the operating mode is preliminarily considered to be the main reason for the difference in the critical fluxes. Thus, nature flux mode is superior to other operating modes because of the highest permeability value of  $249.94 \text{ L/(m}^2 \text{ h bar})$ . In addition, from operability point of view, operations in constant flux/pressure modes, which require feed and permeate pump with pressure transducer to control flux and TMP in a constant state, are more complicated than operation in nature flux mode. Based on the above, flux-stepping measurement using nature flux mode is considered to be the optimum operating mode for the critical flux assessment in this study.

In constant flux/pressure modes, filtration force perpendicular to membrane surface is enhanced by an external force from the feed/permeate pump with transducer. And the external force increases with filtration time to guarantee the invariant production volume or driving force, resulting from the gradual build-up of concentration polarization layer and/or cake layer. Filtration in nature flux mode, on the other hand, does not yield such a rapid change in permeation flux or TMP as observed in the above experiments [\(Figs. 2–4\).](#page-1-0) It might show that the concentration polarization layer or cake layer related to the hydraulic resistance is less developed in the nature flux operation. This hypothesis is illustrated in [Fig. 5.](#page-3-0)

#### 3.2. Form type of the critical flux of UF in treating seawater

Generally speaking, the critical flux can be classified into strong form  $(J_{cs})$  and weak form  $(J_{cw})$  [\[2\],](#page-8-0) both of which are typically defined as the flux leading to the first deviation from a linear variation of flux–TMP curve from an experimental point of view. For different feed and membrane, different forms of the critical flux result from the behavioral discrepancy of solute migration due to surface interactions between solute and membrane. As to the strong form, when flux is below the critical flux at which the TMP starts to deviate from the pure water line, adsorption between solutes and membrane is negligible and thus presents a non-deposition condition. Hence the strong form can differentiate the states between zero-fouling and any kind of fouling. As to the weak form, membrane fouling on start-up, due to the strong interaction of solute–membrane, results in that flux–TMP curve is lower than the pure water line. It can distinguish whether the



**Fig. 6.** Type of the critical flux for UF of seawater.

fouling phenomena are driven by the solvent transfer through the membrane.

The form type of the critical flux of UF for seawater was determined by both the pure water line and the flux–TMP curve of seawater using nature flux mode, and the results are shown in Fig. 6. According to the definition, the weak form of the critical flux was observed, which indicates that a rather low but non-zero rate of membrane fouling is detected even under sub-critical flux conditions due to the coupling interactions of components (such as NOM, inorganic particles) in seawater and UF membrane. Such fouling is nothing more than a lower extent compared to the fouling under super-critical flux conditions. According to resistance-inseries model of Darcy law, it can be seen that the total resistance involved in membrane instinct resistance and adsorption resistance was maintained constant when UF was operated under sub-critical flux conditions. Meanwhile, it shows that the membrane fouling is ineluctable under whatever operating conditions for UF in treating seawater.

### 3.3. Relative long-term of sub- and super-critical flux operations

The membrane fouling is considered to have its own fouling mechanism in a real water purification system, which might be detected or ignored in a period of the experimental operation. A flux appears to be steady over a short time scale, but in reality over a few days or a longer time scale it might be not. In fact, all of the measurements of critical flux could only detect the fouling rate which is below a threshold of sensitivity for the method and the time scale used [\[6\]. T](#page-8-0)herefore, the longer time scale is of importance for the experimental study of critical flux, and needs to be held in mind especially for evaluating the performance of UF and the utility of the concept "critical flux". In this study, each run of UF for seawater lasted a relatively long period (2 days) in sub-/supercritical flux operations by adjusting flux or TMP, which usually applied a few minutes in the literatures [\[6\]. T](#page-8-0)he UF performance in treating seawater was investigated under the following identical test conditions: cross-flow velocity around 0.11 m/s, feed turbidity 2.40–2.79 NTU, feed UV<sub>254</sub> 0.023–0.026 cm<sup>-1</sup>, feed conductivity around 44.2 ms/cm.

### 3.3.1. UF performance under sub-critical flux conditions

As the results discussed in Section [3.1,](#page-3-0) the critical fluxes of UF in treating seawater were 91.2, 102.7 and  $105.6 \frac{\text{L}}{\text{m}^2}$  h using constant pressure, constant flux and nature flux mode, with the corresponding TMP of 0.052, 0.047 and 0.044 MPa, respectively. [Fig. 7](#page-5-0) shows the performance of UF in different operating modes under sub-critical flux conditions. It can be seen that no matter which

<span id="page-5-0"></span>

**Fig. 7.** UF performance for seawater vs. time under sub-J<sub>crit</sub> conditions: (a) constant pressure mode; (b) constant flux mode; (c) nature flux mode.

operating mode was applied, no obvious variations of flux and TMP were observed with operating time under sub-critical flux conditions, which qualitatively confirms the concept "critical flux" of UF. The impact of the initial flux or initial TMP on the stability of UF performance is so tiny that the operation is considered to be stable at whatever values of initial flux or TMP, as long as under sub-critical flux conditions.

Membrane fouling with the operations in different operating modes was evaluated via hydraulic resistance ( $\sum \! R$ ) calculated. These trends of  $\sum$ R are shown in Fig. 8.  $\sum$ R appears to be constant in every applied operating mode, indicating that the UF performance can be in a stable state under sub-critical flux conditions for a certain UF system in a certain operating mode. The results from Fig. 8 show that the highest and lowest hydraulic resistances of  $2.22 \times 10^{12}$  and  $1.74 \times 10^{12}$  m<sup>-1</sup> were obtained with the operations in constant pressure and nature flux mode, respectively. Membrane intrinsic resistance is  $1.60 \times 10^{12}$  m<sup>-1</sup> by measuring the pure water flux–TMP curve of a fresh UF membrane. Thus, the resistances solely owing to fouling (adsorption,  $R_{ad}$ ) are the ultra low values of  $0.62 \times 10^{12}$ ,  $0.22 \times 10^{12}$ ,  $0.14 \times 10^{12}$  m<sup>-1</sup>, and the contributions to the total resistance are 27.9, 12.1, 8.0% with the corresponding operation in constant pressure, constant flux and nature flux mode, respectively.

According to the previous conclusion from Section [3.2, a](#page-4-0)dsorption rather than accumulation of foulants on the membrane surface is predominately responsible for the membrane fouling when operating under sub-critical flux conditions. Adsorption is expected to



Fig. 8. Membrane fouling of UF treating seawater vs. time under sub-J<sub>crit</sub> condition.



Fig. 9. UF performance for seawater vs. time under super-J<sub>crit</sub> conditions: (a) constant pressure mode; (b) constant flux mode; (c) nature flux mode.

be divided into the internal fouling [\[24\]](#page-8-0) that standard blockage results from the adsorption of foulants to the inside of membrane pores, and the surface fouling that the foulants are adsorbed on the membrane surface [\[25\].](#page-8-0) Whatever adsorption type is,  $R_{ad}$  is assumed to be constant and commences once the membrane and seawater are in contact when operating under sub-critical flux conditions, resulting in the constant total resistance. In contrast, the extent of membrane fouling such as accumulation is indeed related to the difference between the rate of transport of foulants towards a membrane surface, which is a function of the permeate flux, and the rate of back transport of particles away from a membrane surface, which is a function of the system hydrodynamics such as cross-flow velocity [\[26\]. W](#page-8-0)hen operating at a proper cross-flow velocity under sub-critical flux conditions, the rate of foulants transport away from the membrane surface can be theoretically faster than that towards the membrane surface, indicating the accumulation of foulants on the membrane surface might not happen.

#### 3.3.2. UF performance under super-critical flux conditions

Tests were conducted with the operations in three operating modes under super-critical flux conditions. The UF performance was investigated and the results are shown in Fig. 9. In constant pressure mode (Fig. 9(a)), when TMPs were preformed at 0.060 and 0.075 MPa which were higher than the  $\text{TMP}_{\text{crit}}$  (the TMP at critical flux), flux declined rapidly during the first 0–500 min of operation. More serious reduction in the higher initial flux was observed at higher TMP. And, flux at lower initial TMP was always higher than that at higher initial TMP after about 250 min of filtration. It should be noted that the fluxes are higher than critical flux (91.3 L/m<sup>2</sup> h) under the above super-critical flux conditions. It is contrary to the results reported in the previous work [\[6\]](#page-8-0) which concluded that UF operation under super-critical conditions could result in less water production than that if the system were operated initially at a sub-critical flux. As shown in Fig. 9(b), with operation in constant flux mode, TMP increased nearly linearly with operating time  $(0-2900 \text{ min})$  at the super-critical flux of 110 and 130 L/m<sup>2</sup> h, and the higher flux of 130 L/m<sup>2</sup> h is responsible for a higher initial TMP (0.064 MPa). It qualitatively indicates that the operation at higher flux could lead to the enhanced transport of particles and NOM to the membrane surface and the more compact accumulated layer, resulting in the higher operating pressure compared to sub-critical operations. Concerning nature flux mode in Fig.  $9(c)$ , the initial fluxes of 110 and 130 L/m<sup>2</sup> h were related to the initial TMP of 0.049 and 0.064 MPa, respectively. Variations of both flux and TMP are much slighter than those in other operating modes although membrane fouling was observed in the same way, indicating that



Fig. 10. Membrane fouling of UF treating seawater vs. time at super-J<sub>crit</sub> condition.

operation in nature flux mode might yield the less fouling potential.

Fig. 10 illustrates the membrane fouling of UF in treating seawater with different operating modes under super-critical flux conditions, which could verify the efficiency of fouling detection as well as the concept of critical flux. Compared to the operation under sub-critical flux conditions ([Fig. 8\),](#page-5-0) the initial total resistances ( $\sum \! R$ ) are evidently higher and are elevated to different extents with the continuously prolonged operating time. At super-critical flux, transport of particles and NOM to the membrane surface is enhanced, and thus the concentration polarization layer and/or cake layer will become thicker and more compact, leading to the higher hydraulic resistance. The overall highest value of  $\sum\! R$  is observed in constant pressure mode, while  $\sum\!R$  remains relatively stable after 500 min of operation. The lower values of initial  $\sum\!R$ are yielded in both constant flux mode and nature flux mode, while the elevation rates are higher than that in constant pressure mode. Comparatively speaking, operation in nature flux mode is superior to that in constant flux mode due to lower membrane fouling potential and its elevation rate with the operating time. Note that after 2900 min of operation, the similar values of  $\sum$ R are achieved at a TMP of 0.060 MPa in constant pressure mode and at a flux of 130 L/m<sup>2</sup> h in nature flux mode. Thus, operation in nature flux mode might not yield the lower membrane fouling under super-critical flux conditions, which should be investigated in a further longer experimental period.

#### 3.4. Economic feasibility of sub- and super-critical flux operations

Although the performance of UF in treating seawater under subcritical flux conditions has proven to be able to achieve a minimum fouling potential by applying a lower TMP or flux, as shown in the above experiments, operations at such low fluxes might not be favorable since larger quantity of membrane modules would be required and this subsequently results in higher investment costs. Therefore, it is essential to assess the economic feasibility of the filtration process of these membranes under different operating conditions using different modes. The energy consumption of the filtration process is a significant factor for proving the viability of an industrial application [\[27\]. I](#page-8-0)n this study, the values of specific energy consumption per unit volume of permeate  $(E_n)$  were calculated to determine the performance of membrane system under sub-/super-critical flux conditions from an economical point of view.  $E_p$  is defined in Eq. (1) [\[28\]:](#page-8-0)

$$
E_{\rm p} = \frac{P_{\rm l} Q}{J S} \tag{1}
$$

where  $P_1$  is the axial pressure drop along the hollow fiber membrane module, Pa; Q is the feed flow velocity,  $m^3/h$ ; J is the permeate flux through the membrane,  $m/h$ ; S is the effective membrane area,  $m^2$ .

The TMP, flux (J), pressure loss and specific energy consumption of UF in treating seawater are summarized in Table 2. The highest value of  $E_p$  is 918.5 J/m<sup>3</sup> obtained by operating in con-





<sup>a</sup> 0 represents the beginning of ultrafiltration; t represents the end of each run ultrafiltration.

<span id="page-8-0"></span>stant pressure mode with higher TMP under super-critical flux conditions, while the lowest value of  $247.8$  J/m<sup>3</sup> obtained by operating in constant/nature flux mode with higher permeate flux under sub-critical flux conditions. In constant/nature flux modes, lower  $E_p$  is produced by operating under sub-critical flux conditions than under super-critical flux conditions. However, higher  $E_p$ of 510.6  $J/m<sup>3</sup>$  is obtained, interestingly, by operating in constant pressure mode with lower TMP under sub-critical flux conditions, which might be attributed to the lowest permeate flux (36 L/m<sup>2</sup> h). An increasing  $E_p$  is observed in each run of UF under super-critical flux condition, and the maximum differences in  $E<sub>p</sub>$  of 196.20 and 170.90 J/ $m<sup>3</sup>$  are achieved using constant pressure mode with higher TMP and constant flux mode with higher permeate flux, respectively.

#### **4. Conclusions**

From the tests on critical flux of UF in treating seawater in this study, the following conclusions can be drawn:

- The new measurement for the critical flux called nature flux mode has proven to be superior compared to other measurements.
- The weak form of the critical flux is observed, indicating that the membrane fouling is ineluctable even under the optimum operating conditions. Adsorption is responsible for the dominate membrane fouling under sub-critical flux conditions.
- For operation under sub-critical flux conditions, flux, TMP and hydraulic resistance ( $\sum$ R) remain constant in each applied operating mode. A minimum  $\sum \! R$  is yielded by operating in nature flux mode. The adsorption resistance is ultra low compared to the total resistance.
- For operation under super-critical flux conditions, TMP and flux varies evidently using whatever a operating mode. In constant pressure mode, the higher TMP leads to a higher initial and less steady flux. In constant flux mode, TMP increases nearly linearly with operating time, and a higher flux yields a higher initial TMP. In nature flux mode, lower fouling potential is observed by the small variations of flux and TMP. From the point of hydraulic resistance, operation in nature flux mode is superior to that in constant flux mode.
- From an economic point of view, the highest and lowest  $E<sub>p</sub>$  are yielded by operating in constant pressure mode under super-critical flux conditions and constant/nature flux mode under sub-critical flux conditions, respectively. In constant/nature flux modes, lower  $E<sub>p</sub>$  is produced by operating under sub-critical flux conditions than under super-critical flux conditions. Operation under super-critical flux conditions leads to an increasing  $E_p$  of each run of UF, and the maximum differences in  $E_p$  are achieved using constant pressure mode with higher TMP and constant flux mode with higher flux, respectively.

#### **Acknowledgements**

The authors would like to express their appreciations to China Huangdao Power Plant for their contribution to the pilot tests. This work was supported by technological project in Shandong Province (No. 2007GG10005001).

#### **References**

- [1] J. Xu, G.L. Ruan, X.L. Gao, X.H. Pan, B.W. Su, C.J. Gao, Pilot study of inside-out and outside-in hollow fiber UF modules as direct pretreatment of seawater at low temperature for reverse osmosis, Desalination 219 (2008) 179–189.
- [2] R.W. Field, D.Wu, J.A. Howell, B.B. Gupta, Critical flux concept formicrofiltration fouling, J. Membr. Sci. 100 (1995) 259–272.
- [3] P. Bacchin, P. Aimar, V. Sanchez, Model for colloidal fouling of membranes, AIChE J. 41 (1995) 368–377.
- [4] J.A. Howell, Sub-critical flux operation of microfiltration, J. Membr. Sci. 107 (1995) 165–171.
- [5] J.C. Chen, M. Elimelech, A.S. Kim, Monte Carlo simulation of colloidal membrane titration: model development with application to characterization of colloid phase transition, J. Membr. Sci. 255 (2005) 291–305.
- [6] P. Bacchin, P. Aimar, R.W. Field, Review critical and sustainable fluxes: theory, experiments and applications, J. Membr. Sci. 281 (2006) 42–69.
- [7] G. Gesan-Guiziou, R.J. Wakeman, G. Daufin, Stability of latex crossflow filtration: cake properties and critical conditions of deposition, Chem. Eng. J. 85 (2002) 27–34.
- [8] S. Milcent, H. Carrere, Clarification of lactic acid fermentation broths, Sep. Purif. Technol. 22–23 (2001) 393–401.
- [9] M. Manttari, M. Nystrom, Critical flux in NF of high molar mass polysaccharides and effluents from the paper industry, J. Membr. Sci. 170 (2000) 257–273.
- [10] D.Y. Kwon, S. Vigneswaran, A.G. Fane, R. Ben Aim, Experimental determination of critical flux in cross-flow microfiltration, Sep. Purif. Technol. 19 (2000) 169–181.
- [11] W.R. Bowen, T.A. Doneva, H.-B. Yin, Separation of humic acid from a model surface water with PSU/SPEEK blend UF/NF membranes, J. Membr. Sci. 206 (2002) 417–429.
- [12] H. Li, A.G. Fane, H.G.L. Coster, S. Vigneswaran, An assessment of depolarisation models of crossflow microfiltration by direct observation through the membrane, J. Membr. Sci. 172 (2000) 135–147.
- [13] D.X. Wu, J.A. Howell, R.W. Field, Critical flux measurement for model colloids, J. Membr. Sci. 152 (1999) 89–98.
- [14] W. Yuan, A. Kocic, A.L. Zydney, Analysis of humic acid fouling during microfiltration using a pore blockage-cake filtration model, J. Membr. Sci. 198 (2002) 51–62.
- [15] Y. Bessiere, N. Abidine, P. Bacchin, Low fouling conditions in dead end filtration: evidence for a critical filtered volume and interpretation using critical osmotic pressure, J. Membr. Sci. 264 (2005) 37–47.
- [16] C. Bourchard, J. Serodes, M. Rahni, D. Ellis, E. Laflamme, M. Rodriquez, Membrane fouling in ultrafiltration and coagulation ultrafiltration of surface water, J. Environ. Eng. Sci. 2 (2003) 139–148.
- [17] H. Chapman, S. Vigneswaran, H.H. Ngo, S. Dyer, R. Ben Aim, Preflocculation of secondary treated wastewater in enhancing the performance of microfiltration, Desalination 146 (2002) 367–372.
- [18] Y. Bessiere, P. Bacchin, B. Jefferson, Dead-end filtration of natural organic matter: experimental evidence of critical conditions, Desalination 175 (2005) 29–36.
- [19] P. Choksuchart, M. Heran, A. Grasmick, Ultrafiltration enhanced by coagulation in an immersed membrane system, Desalination 145 (2002) 265–272.
- [20] G. Guglielmi, D.P. Saroj, D. Chiarani, G. Andreottola, Sub-critical fouling in a membrane bioreactor formunicipal wastewater treatment: experimental investigation and mathematical modeling, Water Res. 41 (2007) 3903–3914.
- [21] P. Le-Clech, B. Jefferson, I.S. Chang, S.J. Judd, Critical flux determination by the flux-step method in a submerged membrane bioreactor, J. Membr. Sci. 227 (2003) 81–93.
- [22] B. Espinasse, P. Bacchin, P. Aimar, On an experimental method to measure critical flux in ultrafiltration, Desalination 146 (2002) 91–96.
- [23] J. Xu, G.L. Ruan, X.Z. Chu, Y. Yao, B.W. Su, C.J. Gao, A pilot study of UF pretreatment without any chemicals for SWRO desalination in China, Desalination 207 (2007) 216–226.
- [24] P.R. Bérubé, H. Lin, Y. Watai, Fouling in air sparged submerged hollow fiber membranes at sub- and super-critical flux conditions, J. Membr. Sci. 307 (2008) 169–180.
- [25] H. Li, A. Fane, H. Coster, S. Vigneswaran, Observations of deposition and removal behavior of submicron bacteria on membrane surface during cross-flow microfiltration, J. Membr. Sci. 217 (1/2) (2003) 29–41.
- [26] P. Gui, X. Huang, Y. Chen, Y. Qian, Effect of operating parameters on sludge accumulation on membrane surfaces in submerged membrane bioreactor, Desalination 151 (2) (2003) 185–194.
- [27] J.W. Stairmand, B.J. Bellhouse, Mass transfer in a pulsating turbulent flow with deposition onto furrowed walls, Int. J. Heat Mass Trans. 28 (1985) 1405–1408.
- [28] F.J. Garcia Garcia, T.Y. Chiu, Economic aspects of critical flux operability in star shaped microfiltration membranes: influence of some operating conditions, J. Membr. Sci. 325 (2008) 641–646.