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Effects of operating conditions on hollow fiber membrane systems used as pretreatment for spandex wastewater reverse osmosis

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ABSTRACT

Three different types of ultrafiltration (UF) membranes were investigated to treat the effluents of secondary sedimentation tank of spandex wastewater. The main parameters studied consist of the UF membrane pore size, the backwash frequency and duration time, filtration mode and the stability of the UF system. The results showed that (1) the cross-flow filtration was better in restoring K decline than the dead-end filtration; (2) the optimized backwash frequency and duration were 30 min and 2 min, respectively; (3) the modified polysulfone (PSf) UF membrane (100 kDa) was determined to be the appropriate membrane; (4) the continuous operation experiment showed that this UF system was stable.

Keywords: Spandex wastewater; UF membrane; Backwash frequency; Backwash duration; Cross-flow filtration; Dead-end filtration

1. Introduction

UF is a pressure-driven process to separate macromolecules from the smaller species in the feed solution. Nowadays, UF membrane has been applied and studied extensively to water treatment, such as, dye wastewater treatment and reuse, oily wastewater treatment and reuse, papermaking wastewater treatment, seawater/brackish water desalination pretreatment, medical distilled water (except viruses, bacteria) preparation, water purification in food industrial and so on [1–5].

In a water treatment process, engineering companies usually choose mature commercial membranes in the market, where the options are limited. As a result, many different kinds of wastewater are treated by the same type of membranes. However, membranes with different materials and pore sizes usually have different treatment efficiencies. A number of researches have studied the role of membrane pore size in membrane fouling, such as, Gitis etc. [6], who used five different PSf and polyether sulphone (PES) membranes with molecular weight cutoff (MWCO) of 2, 10, 20, 50 and 100 kDa to treat the secondary effluent from municipal wastewater treatment. They found that membranes with lower MWCO made a greater contribution to total organic carbon (TOC) reduction, the values for TOC reduction increasing from 20.5% for PSf-100 through 33.4% for PSf-50 to almost similar retention levels of 45.9, 45.5 and 44.6% for PSf-20, PES-10 and PES-2 membranes, respectively. Lin [7] found dissolved organic carbon mass retained in 10 kDa membranes was about 1.0 g/m^2 and that in 100 kDa membranes was more than 3 times higher (3.6 g/m^2) for a 24 h period. It is highly likely that some dissolved organic matters (DOMs) bind or aggregate together to form surface gel layer in the smaller 10 kDa UF system; those DOMs largely present in inner pore and serving as pore blockage on a loose membrane (100 kDa) are responsible for severe flux decline.

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The operating conditions of a UF system are also very important to the membrane lifetime and system stability. In a dead-end filtration, fluid feed flows through the membrane vertically, so the particles deposit on the membrane surface and form a gradually thickening filtration cake. But in a cross-flow filtration, fluid feed flows horizontally crossing the membrane surface, the shear force and buoyancy induced by cross-flow can effectively reduce the organic accumulation on the membrane surface. When the concentration of separated substances is high, the membrane filtration resistance increase rapidly, the cross-flow filtration is a much more reasonable choice [8,9]. Backwashing conditions such as pressure and duration were studied in order to maximize the net flux per cycle. It was found that the efficiency of backwashing was more dependent on backwashing time than pressure [10].

In secondary effluents of wastewater stream, there are more than 200 different chemical compounds – many of which may be acutely or chronically toxic to organisms. Optional tertiary treatment upgrades the quality of secondary effluents can serve as a substitute for freshwater sources for industrial needs. A number of researches have discussed that flocculation, adsorption on powdered activated carbon (PAC) are as pretreatment for UF process for municipal wastewater [11–15]. This study was potential optimization part of tertiary (industrial wastewater) treatment, initiated by Zhejiang Huafon Spandex Co. Ltd., and aimed to select the appropriate UF membrane and UF system operating parameters for pretreatment effluents of secondary sedimentation tank of spandex wastewater. Namely, the UF membrane with optimal MWCO was expected not to develop significant fouling, and to offer maximal turbidity removal. At the same time, effects of filtration mode (cross-flow and dead-end), backwash frequency, backwash duration time and UF system stability were investigated.

2. Experimental

2.1. Raw effluent quality

Secondary effluent was obtained from Zhejiang Huafon Spandex Co. Ltd. wastewater treatment plant (Zhejiang province, China). This plant typically treats 800 m^3/d of spandex wastewater by the activated sludge process (including: pretreatment + hydrolytic acidification + anaerobic-aerobic biological treatment + sedimentation + sand filtration). The effluent of UF system will be as the influent of reverse osmosis system, and tertiary effluent will be applied as industrial circulating cooling water. The secondary effluent, directly sent to the UF system on-the-spot, were characterized in terms of COD, NH_3–N, electrical conductivity, pH, turbidity, etc (Table 1).

2.2. Membrane modules

Three different MWCO modified PSf membranes manufactured by Shanghai Megavision Membrane Tech. & Eng. Co. LTD. were investigated. The membranes were supplied as membrane modules, UFH-90-1 (50 kDa), UFH-90-2 (100 kDa) and UFH-90-3 (300 kDa), and effective membrane area of each module was 5 m^2.

2.3. UF system

At room temperature, the water flux was measured for 2 membrane modules (*A* and *B*), and the total membrane area was 10 m^2. The permeability (*K*) and the water recovery rate (*R*) are defined as follows, respectively:

$$K = \frac{\Delta V}{A \times \Delta t \times TMP} = \frac{J}{TMP} \quad (1)$$

where, K denotes the permeability (l/m^2·h·bar), ΔV is the change in volume of the permeate sample (l), Δt is the time difference (h), A is the effective membrane area (m^2), J is the observed permeate flux (l/m^2·h) and TMP denotes the transmembrane pressure (bar).

$$R = \frac{Q_i - Q_e}{Q_i} \times 100\% \quad (2)$$

where, R denotes the water recovery rate (%), Q_i is the influent flow of UF system (l/h), Q_e is the effluent flow of UF system (l/h).

Under the normal operation, V2 was used to adjust the inflow rate and V1 was closed. V10 was used to adjust the water recovery rate. And the other valves were used in backwashing and chemical washing operation modes (Fig. 1). The permeate stream of module B was used to backwash module A, and the permeate stream of module A was used to backwash module B. The backwash sequence was: (1) backwashing module A; (2) crossflushing module A; (3) backwashing module B; (4) crossflushing module B.

Table 1
Characteristics of the secondary effluent from spandex wastewater treatment plant

Water quality	COD (mg/l)	NH3–N (mg/l)	Electrical conductivity (ms/cm)	pH	Turbidity (NTU)	BOD5 (mg/l)	Hardness (mg/l)	Alkalinity (mmol/l)
Average value	35 ± 15	35 ± 25	1050 ± 100	7.5 ± 1.0	<5	11.5	32.64	9.17

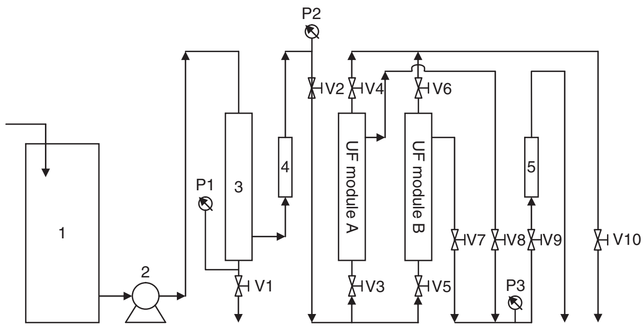

Fig. 1. Schematic diagram of the UF system. 1 tank; 2 pump; 3 micro-filtration pretreatment; 4, 5 flow meter; V1~V10 control valve; P1~P3 pressure gauge.

The fouling material was removed from the membrane surface and then discharged. The parameters were recorded after the UF system was stable.

2.4. Water-quality measurement

Organic content was analyzed qualitatively and quantitatively by a COD detector (HH-6 COD measuring instrument, Jiangyan Yinghe Instrument Factory, China). The concentration of NH_3–N was conducted with NH_3–N detector (5B-6D NH_3–N measuring instrument, Lian-hua Technology Co. LTD., China). Electrical conductivity, pH and turbidity were measured directly with a conductivity meter (DDS-304 conductivity meter, Shanghai Precision & Scientific Instrument Co. LTD., China), a pH meter (PHSJ-3F pH meter, Shanghai Precision & Scientific Instrument Co. LTD., China) and a scattering light turbiditor (WGZ-3 turbidity measuring instrument, Zhenzhou North-south Equipment Co. LTD., China), respectively.

3. Results and discussions

3.1. Basic operating parameters

The module UFH-90-1 (50 kDa) was used to measure basic operating parameters and these data were recorded after the UF system was stable.

When maintaining *R* at 80% and adjusting the inflow rate to 1200, 1500 and 1800 l/h, respectively, effects of the inflow rate on *K* and *TMP* were shown in Fig. 2. It was found that (1) *K* declined with runtime extension; (2) *K* decline increased with decreasing inflow rate; (3) *TMP* of 1800 l/h increased with runtime obviously, however, *TMP*s of 1200 and 1500 l/h were nearly stable. An increase in cross-flow velocity leads to higher shear stress acting on the membrane surface, as a result, less membrane fouling. However, this impact becomes less significant under higher cross-flow velocity. At the same time, higher *TMP* induces more serious membrane fouling, but a higher flux is obtained due to the higher resulting filtration driving force [6,7]. In this pilot, the inflow rate increase means the cross-flow velocity increase. When the cross-flow velocity increased, *K* decreased, but considering *TMP* increase, the observed permeate flux increased oppositely. In pseudo-steady, the observed permeate fluxes were 42, 60 and 66 l/ m^2·h for 1200, 1500 and 1800 l/h inflow rates, respectively. Because it is difficult to keep constant *TMP* (or *J*) for this pilot-scale experiments, so we mainly investigated *K* for the following experiments in the same initial operation conditions (*R*: 80%, the inflow rate: 1800 l/h).

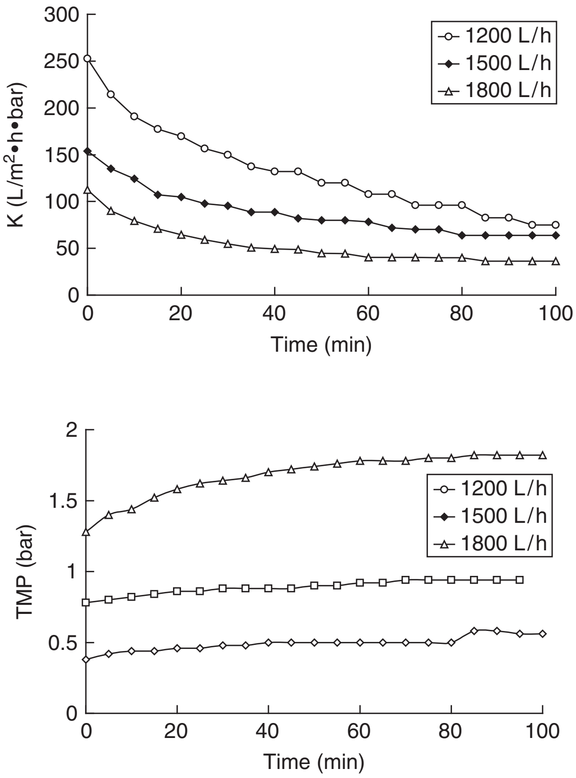

Fig. 2. *K* and *TMP* profile for different inflow rates.

3.2. UF backwash frequency and duration time

Backwashing is known to be effective in controlling fouling and necessary for ensuring UF system stable running. Lower backwash frequency can not effectively mitigate membrane fouling, while higher frequency will bring down the operational efficiency. Different backwash frequencies, duration times and operation modes were studied for 480 min of continuous filtration. The membrane module UFH-90-1 (50 kDa) was chose to test. The recovery rate and initial inflow rate were 80% and 1800 l/h, respectively.

Six groups of cross-flow filtration experiments were shown in Fig. 3, it was found that (1) *K* decreased in

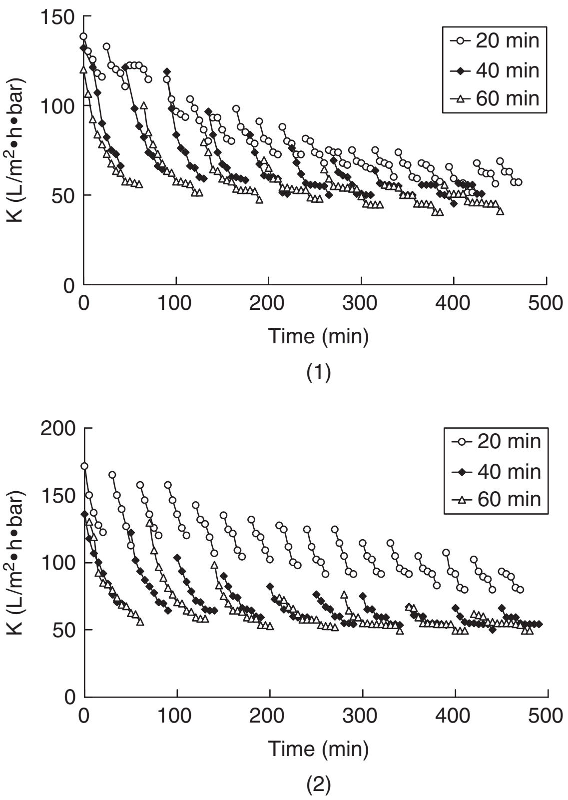

Fig. 3. Effects of backwash frequencies on *K*. Backwash duration time: (1) 1 min, (2) 2 min.

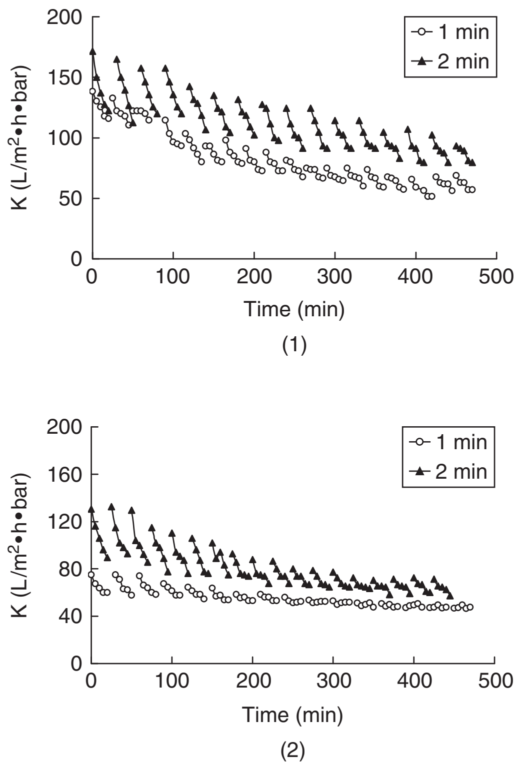

Fig. 4. Effects of backwash duration time on *K*. Backwash frequency: 20 min, (1) cross-flow filtration, (2) dead-end filtration.

the same backwash duration time when the backwash frequency increased from 20 to 60 min; (2) *K* decreased gradually and then finally stabilized with runtime extension. When backwash duration time was 2 min, there is a larger difference of *K* for 20 and 40 min of backwash frequency, but *K* is same for 40 and 60 min of backwash frequency. In general, *K* is not totally reversible by backwashing, over long periods of operation would increase the degree of irreversible fouling [8–10]. 20 min of backwash frequency was too short, 40 min had formed irreversible, and thus 30 min maybe was suitable.

Theoretically, sufficient backwash duration time for the removal of particles accumulated in the membrane induces high flux restoration [13,15]. Comparing 1 and 2 min of backwash duration time in Fig. 4, it is apparent that longer backwashing time improved *K* significantly regardless of cross-flow or dead-end filtration when backwash frequency was 20 min. However, for backwash frequencies of 40 and 60 min, *K* had not a decided change for different backwash duration times (Fig. 3). This phenomenon may be due to the fact that the contamination deposit grows with time of filtration and much of which induces to form irreversible fouling.

Backwashing has the limitation of consuming permeate and increasing down time, both of which reduce the overall system efficiency. 30 min of backwash frequency and 2 min of backwash duration time maybe were appropriate for this kind of wastewater.

3.3. Comparative experiments for different UF membrane modules

Three kinds of UF modules — UFH-90-1 (50 kDa), UFH-90-2 (100 kDa) and UFH-90-3 (300 kDa) were compared in 30 min of backwash period. Same conditions in experiments were maintained as mentioned before.

Comparing different membranes in Fig. 5, the initial *K* values were seen to be clearly dependent on membrane pore size. *K* decline was faster and more severe in the loose pore UF system, particularly during the first 200 min filtration. In general, two factors can induce the UF membrane fouling, one is small particles (colloids) accumulation on the membrane surface, and the other is particles (colloids) lodged inside the membrane pores. Internal pore adsorption (or clogging) was attributed to irreversible fouling, and the fouling cake deposited on membrane surface can easily be removed by backwashing [7]. Fig. 5 means that (1) the pore size of 50 kDa membrane is so small that the majority of contaminants deposited to form surface gel layer with very little inner pore adsorption (or clogging); (2) a large fraction of

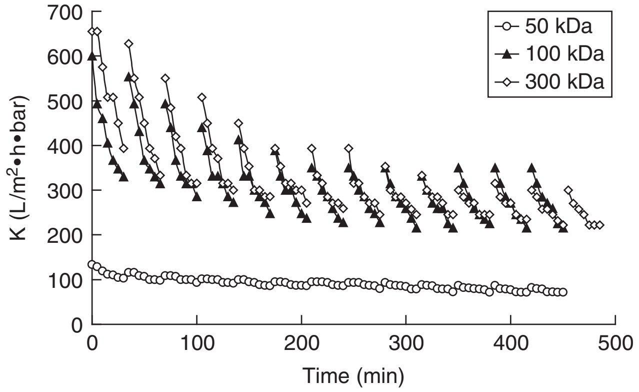

Fig. 5. Results of different membranes comparison experiments. Cross-flow; backwash frequency: 30 min; backwash duration time: 1 min.

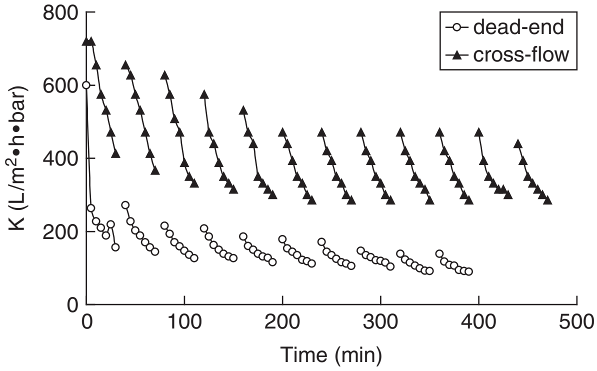

Fig. 6. Effects of filtration modes on K (UHF-90-2). 30 min of backwash frequency, 2 min of backwash duration.

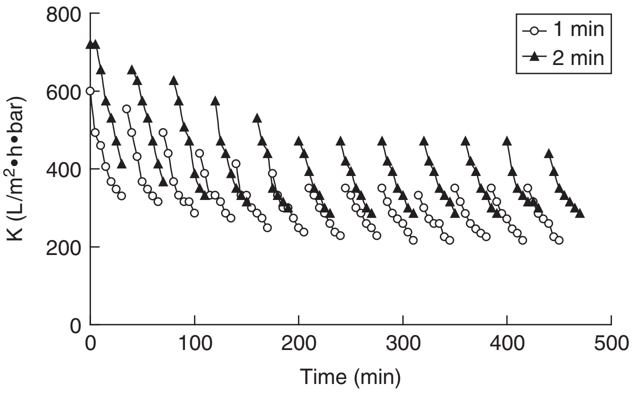

Fig. 7. Effects of backwash duration time on *K* (UHF-90-2). Cross-flow, 30 min of backwash frequency.

contaminants having the molecular size <300 kDa is able to enter 300 kDa membrane pore and subsequently aggregate and stick together in the pore channel. The permeate quality of UFH-90-2 (100 kDa) was more stable than that of UFH90-3 (300 kDa) (Table 2). Based on these results, it is justifiable to state that the pore size is the most important factor of affecting *K* and the comprehensive properties of 100 kDa membranes were higher than these of 50 and 300 kDa membranes.

Although dead-end filtration enhances the water recovery rate of the UF system, the higher membrane fouling induces the increase frequency of chemical cleaning which reduces the membrane lifetime and increases the membrane replacement. It was found in Fig. 6 that cross-flow filtration resulted in more significant restoration of *K* than dead-end filtration. Therefore, the dead-end filtration was not recommended to treat this kind of wastewater. In Fig. 7, the same conclusion as mentioned before, longer backwashing time improved *K* restoration significantly.

3.4. Evaluation of membrane module UFH-90-2 in long term operation

The long term effectiveness of UFH-90-2 (100 kDa) was evaluated by *K* (or TMP) restoration over a period of 44 h runtime. The experiment conditions were kept constant as follows: 1800 l/h initial inflow rate, 80% the water recovery rate, 30 min of backwash frequency and 2 min of backwash duration time. A multimedia filter was used as pretreatment for UF system.

It is clear that backwashing conditions was effective in restoring *K* decline even in "long term" operation and UF system can effectively remove turbidity and some COD (Fig. 8 and Table 3). These results indicated that UFH-90-2 (100 kDa) was a suitable membrane module to treat the effluents of secondary sedimentation tank of spandex wastewater.

Table 2
Effluent qualities of different UF membranes (Cross-flow; backwash frequency: 30 min; backwash duration time: 1 min)

Water quality	COD (mg/l)	$N–NH_3$ (mg/l)	Electrical conductivity (μs/cm)	Turbidity (NTU)
UFH-90-1	8.7	0.11	980	0.01
UFH-90-2	11	1.45	920	0.01
UFH-90-3	31.1	11.23	1000	0.01

Table 3
Effluent quality of the continuous operation UF experiment

Water quality	COD (mg/l)	NH_3–N (mg/l)	Electrical conductivity (μs/cm)	Turbidity (NTU)
Effluent of the multimedia filter	12.3	0.14	950	0.21
Effluent of UF	10.0	0.12	950	0.07

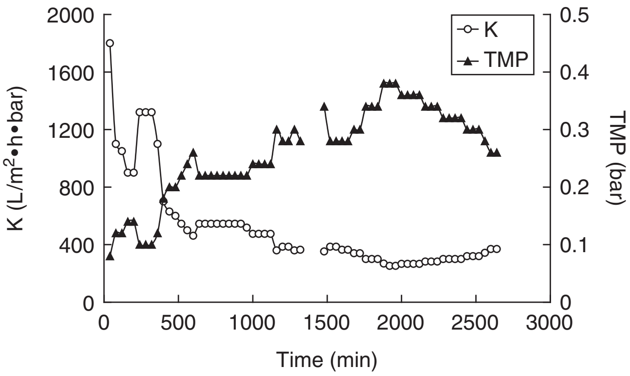

Fig. 8. Results of the continuous operation experiment. UHF-90-2; cross-flow; backwash frequency: 30 min; backwash duration time: 2 min.

4. Conclusions

Compared to three different modified PSf membranes with MWCO of 50, 100 and 300 kDa, it was found that 100 kDa membranes were suitable to be used as pretreatment for RO process in treating the secondary effluents of spandex wastewater. *K* decline was faster and more severe in the loose pore UF system, particularly during the first 200 min of filtration. 40 or 60 min period of operation would increase the degree of irreversible fouling. However, longer backwashing time could improve *K* restoration. The cross-flow filtration resulted in more significant restoration of *K* than dead-end filtration. It is clear that backwashing conditions (30 min of backwash frequency and 2 min of backwash duration time) was effective in restoring *K* decline even in "long term" operation.

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