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Study on treating of NH_3–N wastewater by membrane technology in a pilot plant

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ABSTRACT

Reverse osmosis (RO) and activated zeolite and three types of tertiary treatment pilot systems were evaluated to treat the effluents of secondary sedimentation tank of spandex waste water. For RO system, when NH_3–N concentration of RO influent was less than 28 mg/l, NH_3–N concentration of RO effluent was below 1 mg/l; when NH_3–N concentration was 62 mg/l, the NH_3–N removal rate of RO system was 90%. For activated zeolite, the lower NH_3–N concentration of the feed, the lower NH_3–N removal rate. Compared to UF/RO system and UF/RO/NH_3–N remover system, the multimedia filter/UF/RO/NH_3–N remover combined system was the most suitable to treat the spandex secondary effluent.

Keywords: Multimedia filter; UF; RO; NH_3–N remover; Spandex waste water; NH_3–N

1. Introduction

Ammonia nitrogen is an important indicator in wastewater discharge, because it not only leads to considerable eutrophication and an increase in the frequency of toxic algae blooms, but also is toxic to organism (such as, fish) and erodes metal (such as, Cu) [1,2]. Great efforts have been devoted to the removal of ammonia nitrogen from wastewater. Traditional methods include: biological denitrification [3,4], ammonia-stripping [5], chemical precipitation with magnesium ammonium phosphate [6], electrochemical conversion [7], microwave radiation [8,9], ultrasound [10] and so on. Biological denitrification is the most common process in the treatment of ammonia nitrogen wastewater. However, ammonia concentration after biological treatment is still high because the high concentration of ammonia leads to the low ratio of C/N [11]. Ammonia stripping method needs a large stripping tower and consumes much energy, and the ammonia concentration in effluent is not low. Chemical precipitation needs additional reagents, which may introduce new pollutants to water body. Electrochemical method often uses expensive metal or metal oxide as electrodes, and also consumes large quantity of energy. Microwave radiation and ultrasound methods are not suitable large-scale treatment. Thus, it is necessary to develop cost-effective method for the removal of ammonia nitrogen from wastewater.

In recent years, reverse osmosis (RO) technology has been widely used in wastewater reclamation [12]. However, according to our knowledge, there are no reports on the removal of ammonia nitrogen from wastewater by RO. Ali [13] ever studied asymmetric polyethersulfone (PES) nanofiltration (NF) membranes to remove ammonia nitrogen. The pore size of RO is smaller than that of NF, so this study is to investigate the ability of removal ammonia nitrogen for RO system. In addition, zeolite used as the filter media has high ability to preferentially remove ammonium ions from wastewater.

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Unlike synthetic ion exchange resins, zeolite is known to possess a higher selective ion-exchange capability for ammonium ion than Ca^{2+} and Mg^{2+}, even when the concentration of the latter is higher than the former [14–16]. Zeolite was mainly used to remove ammonium ions from secondary effluent by selective ion exchange, but it was rarely tested for the RO permeate of low ammonium nitrogen level.

This study, initiated by Zhejiang Huafon Spandex Co. Ltd., aimed to select the appropriate tertiary treatment process for treating effluents of secondary sedimentation tank of spandex waste water as industrial circulating cooling water. Three types of membrane processes----UF/RO system, UF/RO/NH_3–N remover system and multimedia filter/UF/RO/NH_3–N remover combined system were studied in detail.

2. Experimental

2.1. Raw effluent quality

Spandex wastewater treatment plant (Zhejiang Huafon Spandex Co. Ltd., Zhejiang province, China) 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 wastewater includes DMAc purification wastewater, spinning wastewater, rinse wastewater, floor washing wastewater of production department and domestic sewage. The influent and effluent of this biological treatment system were characterized in terms of COD, NH_3–N, pH, etc (Tables 1 and 2). Comparing Table 1 and Table 2, it shows that the biological treatment system can greatly remove COD and part of NH_3–N.

2.2. The characteristic of membrane modules

The modified PSf UF membrane module with molecular weight cutoff (MWCO) of 100 KDa was manufactured by Shanghai Megavision Membrane Tech. & Eng. Co. LTD., whose effective membrane area is 5 m^2. The properties of the RO membrane module (DOW) are: 97% NaCl rejection (25°C), 7.2 m^2 effective membrane area.

Table 2
Characteristics of the secondary effluent from spandex wastewater treatment plant

Items of water quality	Data	Items	Data
CODcr (mg/l)	<50	SS (mg/l)	70–90
NH_3–N (mg/l)	<60	BOD_5 (mg/l)	11.5
Conductivity (μs/cm)	1000	Hardness (mg/l)	32.64
pH	7.7–9.0	Alkalinity (mmol/l)	9.17

2.3. Pilot system

The combined pilot tertiary treatment system consists of multimedia filter, UF, RO and NH_3–N remover as shown in Fig. 1. The secondary effluent was directly sent to the tertiary treatment system on-the-spot, and the tertiary effluent will be applied as industrial circulating cooling water.

The permeability (*K*) and the water recovery rate (*R*) are defined as follows, respectively:

$$K = \frac{\Delta V}{A \times \Delta t \times \text{TMP}} \tag{1}$$

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) and TMP denotes the transmembrane pressure (bar).

$$R = \frac{Q_i - Q_e}{Q_i} \times 100\% \tag{2}$$

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).

In the tertiary treatment system, the total membrane area of UF modules and RO module were 10 m^2 and 7.2 m^2, respectively. The water recovery rate of RO system was 15%. For UF system, cross-flow filtration, 80% water recovery rate and 1800 l/h initial inflow

Table 1
Properties of the influent wastewater

Items of water quality	CODcr (mg/l)	NH_3–N (mg/l)	pH	SS (mg/l)
DMAc purification process	5000–15000	90–100	9–11	40–60
Spinning process	300–500	60–65	8–9	40–60
Cleaning process	2000–3000	70–75	8–9	1–5
Sanitary wastewater	200–300	20–30	7–8	80–100
Composite wastewater	300–500	60–80	8–9	60–70

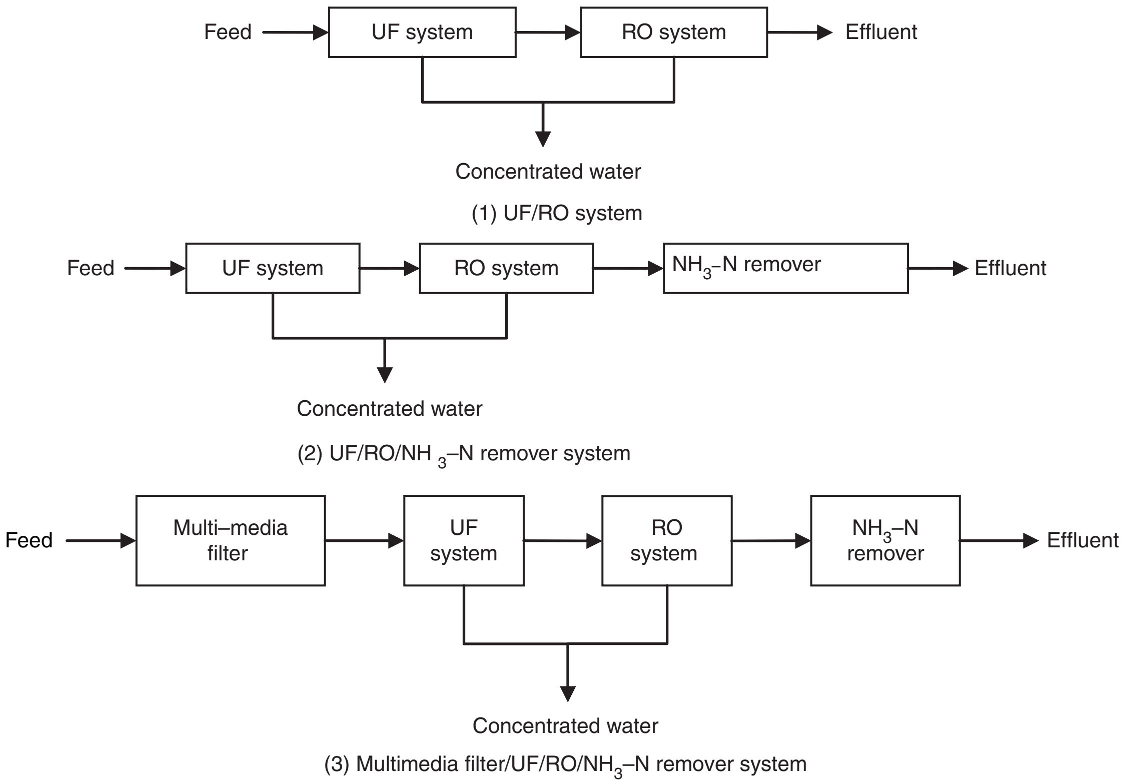


Fig. 1. The schematic diagram of pilot system.

rate were adopted. UF membranes were cleaned with both physical and chemical wash. The chemical wash employed 100 ppm sodium hypochlorite (NaClO) to wash membrane modules for 10 min. The physical wash included 6 min of backwashing and 4 min of crossflushing. The RO module was only crossflushed by deionized water for 5 min. Multimedia filter and NH_3–N remover were not washed during the whole experiments period.

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

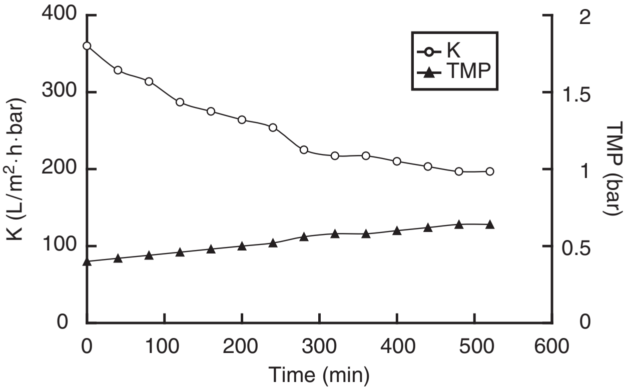
3.1. UF/RO system

During the operation process and after the experiment, UF system did not carry out physical and chemical cleaning and RO system did not execute chemical cleaning and physical crossflushing.

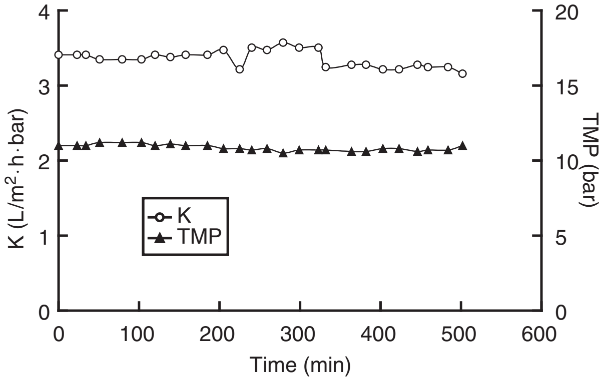
With the extension of the runtime, it is found in Fig. 2 that K of UF system decreased from 360 to 197 $l/m^2 \cdot h \cdot bar$ when TMP gradually increased from 0.40 to 0.64 bar, however, K and TMP of RO system basically stabilized at 3.3 $l/m^2 \cdot h \cdot bar$ and 11.0 bar, respectively.

Table 3 shows that RO system had strong ability in removal of ammonia nitrogen. By adjusting the operation conditions in the biological treatment system and increasing the NH_3–N concentration of secondary effluent, it is confirmed further that most of the NH_3–N could be removed by RO membranes (Table 4). In wastewater, ammonia nitrogen refers to two chemical species (NH_3, un-ionized and NH_4^+, ionized). When dissolved in water, normal ammonia (NH_3) reacts to form an ionized species called ammonium (NH_4^+).

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad (3)$$



UF system



RO system

Fig. 2. The running experiment of the UF/RO system.

From the doubled headed arrow the reaction can go either way, ammonia and water could combine to form hydroxyl ions and ammonium ions. This is precisely what happens as the pH of water increases. At same time, it is also observed that RO membranes could also reduce the pH level in water. The reduction in pH value was caused by the carbonic acid balanced reaction, the balance would move to H_2CO_3 decomposition when a lot of ions in water were removed by RO system. CO_2 of the air would be more soluble in water to produce carbonic acid, as a consequence, the pH value declined.

$$CO_2 + H_2O{=}H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-} \tag{4}$$

In waste water, hydroxyl ions and hydrogen ions form water, which is a very weak electrolyte and difficult to ionize.

$$H^+ + OH^- \rightleftharpoons H_2O \tag{5}$$

Therefore, the equilibriums of Eqs. (3) and (4) are pushed to the right and more ionized ammonium is formed. RO membrane is easy to remove ionized ammonium by sieve mechanism, so NH_3–N concentration decreased.

Some un-ionized NH_3 and ionized NH_4^+ maybe absorb on the particles (colloids). While particles (colloids) were removed during UF treatment, this NH_3–N could be removed. The rejection of COD by RO membranes was low as shown in Tables 3 and 4, which was probably due to the properties of spandex wastewater. The spandex wastewater contains large amount of DMAc (C_4H_9ON, molecular weight of 87.12) which is commonly used as solvent for membrane preparation. The biological treatment system cannot guarantee fully degradation of DMAc during the activated sludge process, therefore it is common that some residuals will be in water, and RO membranes do not have good separation performance on these organics, thus the COD value appeared to be higher in the permeate flux of RO membranes.

Table 3
Running results of the UF/RO system

Items	CODcr (mg/l)	NH_3–N (mg/l)	Conductivity (μs/cm)	pH	Turbidity (NTU)
Feed	4.5	3.25	880	7.64	0.51
The permeate of UF system	1.9	3.16	880	7.52	0.03
The permeate of RO system	1.6	0.12	5.6	6.2	0.01

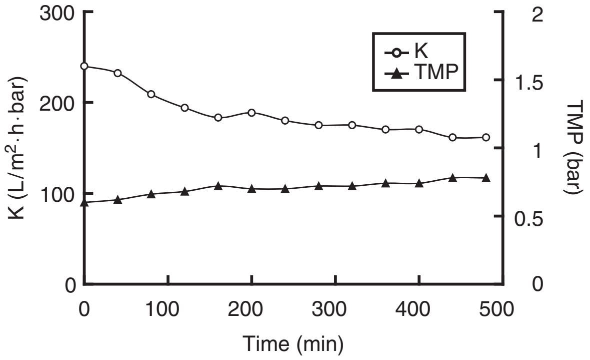
Table 4
Running results of the UF/RO system (high NH_3–N concentration)

Items	CODcr (mg/l)	NH_3–N (mg/l)	Conductivity (μs/cm)	pH	Turbidity (NTU)
Feed	41.7	45.42	1000	6.50	3.23
The permeate of UF system	18.4	28.66	1000	6.96	0.05
The permeate of RO system	11.4	0.58	14	5.75	0.01

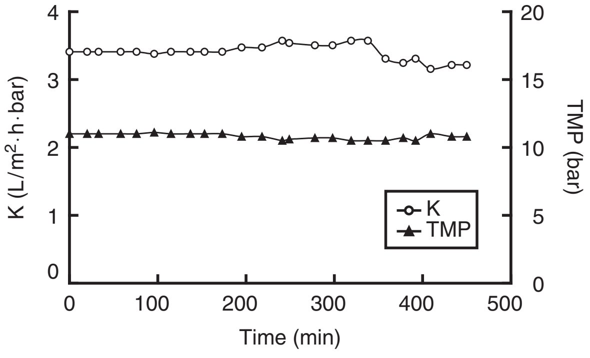
3.2. UF–RO–NH_3–N remover system

For UF system, *K* decreased from 240 to 162 l/m²·h·bar and TMP gradually increased from 0.6 to 0.78 bar in the first day (Fig. 3). Results from second day experiment are shown in Fig. 4, *K* decrease and TMP increase were from 164 to 119 l/m²·h·bar and 0.88 to 0.94 bar, respectively. Because UF system didn't carry out physical and chemical cleaning during 3.1 and 3.2 experiments, the membrane fouling was gradually serious as the days passed by, which induced further TMP increase and *K* decrease. For RO system, TMP basically stabilized at 11.0 bar, however *K* of the first day was higher than that of the second day.

Tables 5 and 6 show the turbidity of UF effluent was less than 0.2 NTU and RO system could reject salt and NH_3–N effectively. For studied further the consequences of high NH_3–N concentration, the operation conditions in the biological treatment system were adjusted to increase the NH_3–N concentration of secondary effluent. It is found in Table 7 that NH_3–N concentration of RO effluent was 5.63 mg/l when that of RO influent was 68.24 mg/l, which was further confirmed that NH_3–N could be removed by RO membranes.

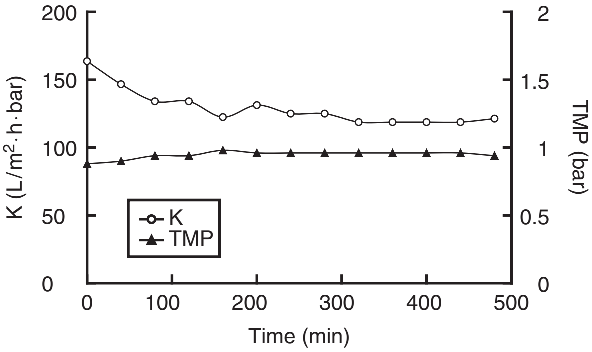


UF system

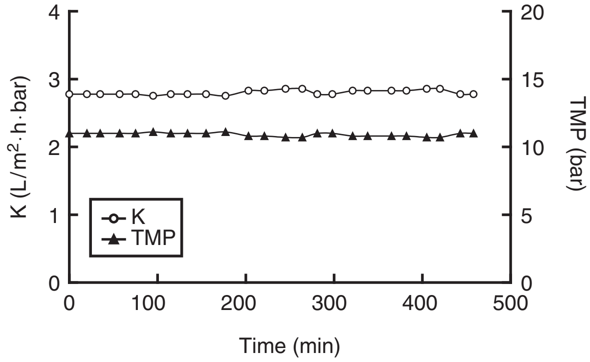


RO system

Fig. 3. The running experiment of the UF/RO/NH_3–N remover system (First day).



UF system



RO system

Fig. 4. The running experiment of the UF/RO/NH_3–N remover system (Second day).

In NH_3–N remover, activated zeolite possesses a high selective ion-exchange capability for ammonium ion. The ion-exchange equilibrium between the NH_4^+ ion in the solution and the Na^+ ion attached to the zeolite can be expressed as stoichiometric reaction [15,16]:

$$\text{Z-Na}^+ + NH_4^+ \rightarrow \text{Z-NH}_4^+ + Na^+ \tag{6}$$

where Z = zeolite. When NH_3–N concentration of NH_3–N remover influent was lower than 0.3 mg/l, NH_3–N removal efficiency of activated zeolite was much low (Tables 5 and 6). When NH_3–N concentration of NH_3–N remover influent was 5.63 mg/l, NH_3–N concentration of NH_3–N remover effluent was 0.26 mg/l and rejection of NH_3–N was 95% (Table 7). At the same time, activated zeolite particles were reliably crushed by gravity force and

Table 5
Running results of the UF/RO/NH$_3$–N remover system (First day)

Items	CODcr (mg/l)	NH$_3$–N (mg/l)	Conductivity (μs/cm)	pH	Turbidity (NTU)
Feed	8.2	2.79	750	7.69	0.60
The permeate of UF system	7.3	2.17	770	7.57	0.03
The permeate of RO system	5.4	0.22	5.2	6.42	0.01
The output of NH$_3$–N remover	0.6	0.20	15	7.39	0.73

Table 6
Running results of the UF/RO/NH$_3$–N remover system (Second day)

Items	CODcr (mg/l)	NH$_3$–N (mg/l)	Conductivity (μs/cm)	pH	Turbidity (NTU)
Feed	15.0	3.13	1100	7.63	0.55
The permeate of UF system	9.9	3.20	1100	7.47	0.05
The permeate of RO system	4.0	0.30	6	7.2	0.01
The output of NH$_3$–N remover	0.4	0.14	20	7. 69	1.48

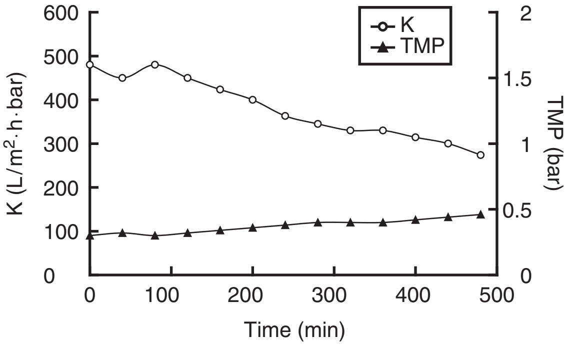
Table 7
Running results of the UF/RO/NH$_3$–N remover system (high NH$_3$–N concentration)

Items	CODcr (mg/l)	NH$_3$–N (mg/l)	Conductivity (μs/cm)	pH	Turbidity (NTU)
Feed	35.6	68.24	900	7.61	2.64
The permeate of UF system	24.9	62.79	900	7.75	0.13
The permeate of RO system	14.1	5.63	19	5.60	0.05
The output of NH$_3$–N remover	0.9	0.26	150	6.72	2.74

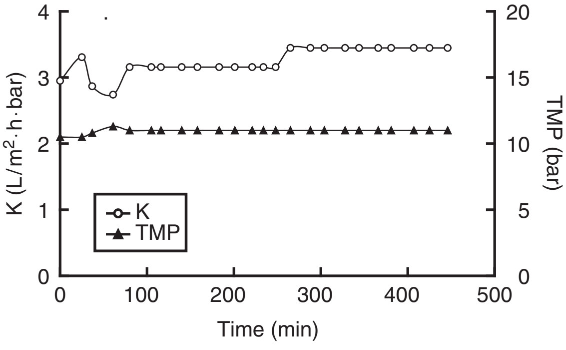
current wallop, and the powders of activated zeolite were easily taken by fluid, so the turbidity of NH$_3$–N remover permeate was higher than that of RO permeate. On the other hand, zeolite could release some ion to water, which induced electrical conductivity of NH$_3$–N remover influent was lower than that of NH$_3$–N remover effluent.

3.3. Multimedia filter/UF/RO/NH$_3$–N remover system

The multimedia filter plays the major role in removing of suspended solids and solid particles. The layered anthracite coal, sands and fine garnet are the beds of the multimedia filter. The top of the bed is formed by the lightest and thickest materials while the heaviest and finest materials are put on the bottom of the bed. The separation principle of the multimedia filter is that the larger particles in the water are removed in the top, and the smaller particles are removed in the more depth of the filter media. The multimedia filter has the virtue of low construction cost and operation costs, simplicity of operation. This experiment was used to detect whether the multimedia filter could reduce the content of small particles in the water and slow down the UF membrane fouling or not.



UF system



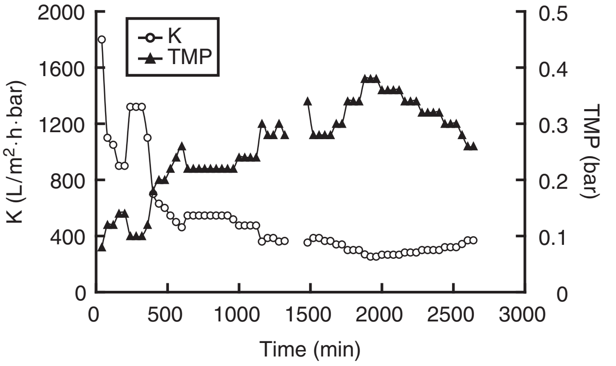
RO system

Fig. 5. The experiment of the multimedia filter/UF/RO/NH$_3$–N remover system.

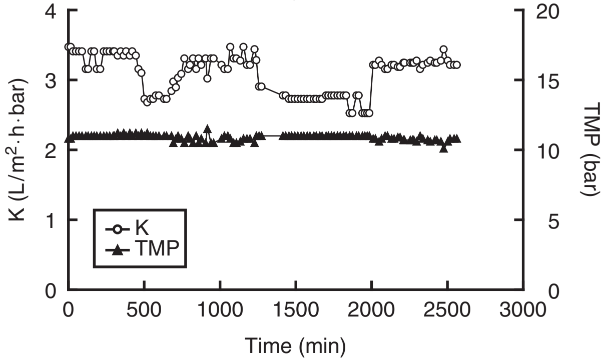
Comparing Figs. 2, 3, 4 and 5, it is found that K of UF system was higher with multimedia filter than

Table 8
Running results of the multimedia filter/UF/RO/NH_3–N remover system

Items	CODcr (mg/l)	NH_3–N (mg/l)	Conductivity (μs/cm)	pH	Turbidity (NTU)
Feed	23	3.20	890	7.64	0.43
The permeate of UF system	20.2	3.20	890	7.53	0.20
The permeate of RO system	18.5	3.20	890	7.53	0.03
The output of NH_3–N remover	2.9	0.20	14	7.83	0.57



UF system



RO system

Fig. 6. The continuous operation experiment.

without multimedia filter and TMP of UF system was lower with multimedia filter than without multimedia filter. This phenomenon illuminated multimedia filter could protect UF system. Table 8 shows some COD could be removed during multimedia filter process. The other experiment results in Table 8 had the same regularity as mentioned before. For the whole experiments, *K* of UF system decreased from 480 to 274 l/m²·h·bar when TMP gradually increased from 0.3 to 0.46 bar, *K* and TMP of RO system stabilized at 3.4 l/m²·h·bar and 11.0 bar, respectively (Fig. 5).

3.4. The continuous operation experiment

The long term effectiveness of the multimedia filter/UF/RO/NH_3–N remover combined system was evaluated by *K* (or TMP) restoration over a period of 2640 min runtime. The UF 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. The water recovery rate of RO system was 15% and the RO membrane was not cleaned with both physical and chemical cleaning.

Fig. 6 shows that *K* and TMP of the UF system basically were 369 l/m²·h·bar and 0.3 bar at the pseudo-steady and *K* and TMP of the RO system basically stabilized at 3.2 l/m²·h·bar and 11.0 bar. Table 9 shows that the multimedia filter/UF/RO/NH_3–N remover system could effectively remove COD, NH_3–N, electrical conductivity. These experiment results are clear that the multimedia filter/UF/RO/NH_3–N remover system was not only effective in restoring *K* decrease or TMP increase even in "long term" operation and but also a suitable advanced treatment system for spandex wastewater reuse.

Table 9
Results of the continuous running experiment

Items	CODcr (mg/l)	NH_3–N (mg/l)	Conductivity (μs/cm)	pH	Turbidity (NTU)
Feed	15.6	0.16	950	7.90	0.36
The permeate of UF system	12.3	0.14	950	7.74	0.21
The permeate of RO system	10.0	0.13	950	6.17	0.07
The output of NH_3–N remover	1.0	0.10	28	6.59	1.45

4. Conclusions

When NH_3–N concentration was less than 28 mg/l, RO membrane could remove NH_3–N effectively, and the NH_3–N concentration of RO effluent was below 1 mg/l. When NH_3–N concentration was 68 mg/l, the NH_3–N removal rate of RO system was 90%. Activated zeolite possesses a high selective ion-exchange capability for ammonium ion. It is found for activated zeolite that the lower NH_3–N concentration of the feed, the lower NH_3–N removal rate. RO membranes did not have good separation performance on COD because of large amount of DMAc in spandex wastewater. Compared to UF/RO system and UF/RO/NH_3–N remover system, the multimedia filter/UF/RO/NH_3–N remover combined system not only could effectively remove NH_3–N, COD, electric conductivity and turbidity but also was effective in restoring *K* decrease or TMP increase.

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