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Evaluation of ultrafiltration membranes with the multimedia filter/ultrafiltration/reverse osmosis/NH_3-N remover system to treat surface water

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ABSTRACT

This study discussed the feasibility for the multimedia filter/UF/RO/NH_3-N remover system to treat river Tang surface water, and three different polysulfone (PSf) membranes with molecular weight cut off of 80, 100, and 300 kDa were tested to select a UF membrane for low membrane fouling, higher flux, low transmembrane pressure and better quality of the permeate. The results showed that the multimedia filter/UF/RO/NH_3-N remover combined system was able to remove all unwanted elements and to produce consistent and high-quality water. For the whole experiment, K of RO system basically stabilized at 2.8 L/m^2 h·bar. RO system could effectively remove NH_3-N and conductivity. Comparing results from three UF membranes experiments, it was found that three UF membranes could remove particles (colloids) and the 100 kDa PSf membrane was the most suitable membrane to treat the river Tang.

Keywords: UF membranes; Multimedia filter; RO; NH_3-N remover; Surface water

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1. Introduction

Nowadays, membrane technology has been applied extensively to wastewater treatment and surface water treatment. Surface water always has low turbidity, high color, and high natural organic matter (NOM) content, which is a primary contributor to membrane fouling. NOM includes particulate and soluble NOM. The former can be removed by conventional methods easily, but the latter is a kind of complex mixture of aromatic, aliphatic hydrocarbons, including amide, carboxyl, hydroxyl, ketone, and various other functional groups, which may form membrane fouling and are difficult to be removed.

Membrane fouling is ineluctable in membrane process. At present, flocculation and adsorption on powdered activated carbon have been studied as pretreatment methods for reducing membrane fouling in UF process [1,2]. In comparison with aluminum coagulants, the use of ferric coagulants under slightly acidic condition was identified as an effective method to achieve a stable performance for the UF system in

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treating river Spree [3]. Powdered activated carbon which adsorbs DOM showed significant decrease in membrane fouling. However, the powdered activated carbon addition could not stop the ongoing fouling. And the high concentration of powdered activated carbon showed a potential of adverse effects on membrane performance [2,4]. A set of experiments showed that the removal of floc aggregates after coagulation and powdered activated carbon was critical to maintain high water flux in the membrane system.

At a fixed water intake point of the river, the water quality is usually stable. Then, the material and the pore size of the membrane are more important to membrane fouling and usually affect treatment efficiencies, for example, hydrophilic membranes are less sensitive than hydrophobic membranes to organic fouling. The engineering cases [5] have proved that the operating pressure and chemical cleaning frequency of hydrophobic membranes are higher than that of hydrophilic membranes. After chemical cleaning, the flux of hydrophilic membranes can nearly recover 100% but that of hydrophobic membrane just recover 80–90%. The reason is that the fouling materials, just like colloid, oil and protein, adhering to the hydrophobic membrane surface as pie-sharp are hard to clean out by water backwash, but fouling materials adhering to the hydrophilic membrane as ball-sharp are easily cleaned by water backwash. A number of researches have studied the role of both material and membrane pore size in membrane fouling, such as Goren et al. [6] used five different polysulfone (PSf) and polyethersulfone (PES) membranes with molecular weight cut offs (MWCOs) of 2, 10, 20, 50, and 100 kDa to treat the secondary effluent from municipal wastewater treatment facility. Lin et al. [7] found that dissolved organic carbon mass retained in 10 kDa PSf membranes was about $1.0\,g/m^2$ and that in 100 kDa PSf membranes was more than three times higher ($3.6\,g/m^2$) for a 24 h period. However, the literatures that compared different membranes material and pore sizes to treat surface water are seldom seen. Guo et al. [8] used the modified polyvinylchloride UF membrane (80 kDa) to treat six DOM model compounds and their mixtures. It was found that neutral DOM compounds, especially hydrophobic neutral compounds, fouled the membrane more severely. But the hydrophilic fraction caused fouling faster than the hydrophobic fraction. Brehant et al. [9] found that UF provided permeate water with high and constant quality resulting in a higher reliability of the RO process than with a conventional pretreatment in seawater desalination.

This study discussed the feasibility for the multimedia filter/UF/RO/NH_3-N remover system to treat river Tang surface water (the multimedia filter was used as pretreatment for UF system), and three different PSf membranes with MWCOs of 80, 100, and 300 kDa were tested to select a UF membrane for low membrane fouling, higher flux, low transmembrane pressure (TMP), and better quality of the permeate.

2. Experimental

2.1. Raw effluent quality

The surface water used in the investigation came from river Tang, Zhejiang, China. This river does not always flow freely and its water quality varies with changes in weather condition. When it rains, the water becomes muddy and water quality is poor. Some relevant properties of the surface water are listed in Table 1.

2.2. Characteristic of membrane modules

Three different MWCOs UF membrane modules (UFH-90-1, UFH-90-2, and UFH-90-3) assembled by

Table 1
Characteristics of the surface water

Water quality	COD (mg/L)	NH_3-N (mg/L)	Electrical conductivity (μs/cm)	pH	Turbidity (NTU)
Average value	<25	<2.5	<1,100	7.4–7.8	<15

Table 2
Properties of the membrane modules

Module	UFH-90-1	UFH-90-2	UFH-90-3	BW30-4040
Material	PSf	PSf	PSf	–
MWCO	80 kDa	100 kDa	300 kDa	NaCl rejection > 97%
Membrane effective area	$5\,m^2$	$5\,m^2$	$5\,m^2$	$7.2\,m^2$

Shanghai Megavision Membrane Tech. and Eng. Co. LTD and one RO membrane module (BW30-4040) manufactured by Dow were investigated, whose properties are shown in Table 2.

2.3. Pilot system

The system consisted of multi-media filter, UF, RO, and NH_3-N remover is shown in Fig. 1. Firstly, the surface water was directly sent to multi-media filter and UF system for removing the turbidity; secondly, the salt was separated by the RO system; thirdly, NH_3-N was removed by NH_3-N remover. For UF, RO, and NH_3-N remover, the connection between every two systems was direct, that is, the permeate of the former was the feed of the latter.

Because it is difficult to keep constant TMP (or J) for these pilot-scale experiments, so we mainly investigated K for the following experiments under the same initial operation conditions. The permeability (K) and the water recovery (R) for UF system are defined as follows, respectively:

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

where K denotes the permeability ($\mathrm{L/m^2 \cdot h \cdot bar}$), ΔV is the change in volume of the permeate sample (L), Δt means the time difference (h), A implies the effective membrane area (m^2), and TMP expresses the transmembrane pressure (bar).

$$R = \frac{Q_\mathrm{i} - Q_\mathrm{e}}{Q_\mathrm{i}} \times 100\% \tag{2}$$

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

In this system, the total membrane effective areas of UF modules and RO module were 10 and 7.2 m^2, respectively. R of RO system was 15%, because only one RO module was used in RO system. For the UF crossflow filtration system (Fig. 2), 80% R and 1,800 L/h initial inflow rate were adopted. UF membranes were cleaned with both chemical and physical wash every day after ending operation. 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 permeate stream of

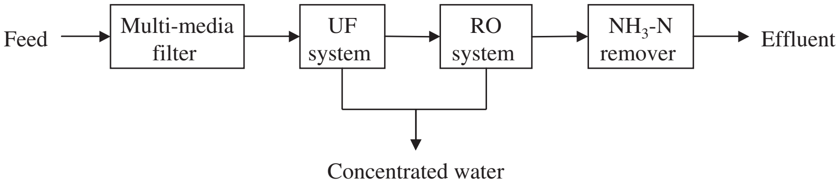


Fig. 1. Schematic diagram of the multimedia filter/UF/RO/NH_3-N remover system.

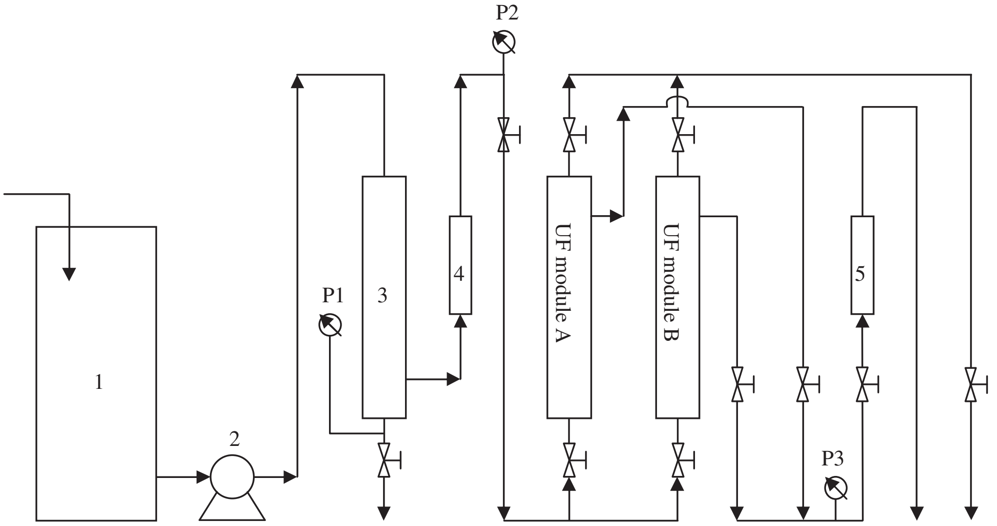


Fig. 2. Schematic diagram of the UF system. (1) Tank; (2) pump; (3) micro-filtration pretreatment; (4, 5) flow meter; and (P1)–(P3) pressure gauge.

module *B* was used to backwash module *A*, and on the contrary, the permeate stream of module *A* was used to backwash module *B*. The backwash sequence was as follows: (1) backwashing module *A*; (2) crossflushing module *A*; (3) backwashing module *B*; (4) crossflushing module *B*. The RO module was only crossflushed every day after ending operation by deionized water (DI water) for 5 min. Activated zeolite, possessing a selective ammonium ion-exchange capability, was filled in NH_3-N remover, which was not washed and regenerated during the whole experiments period. The multimedia filter plays the major role in removing of suspended solids and solid particles, which includes the layered anthracite coal, sands, and fine garnet. 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 was cleaned every day. The parameters were recorded after the system was stable.

2.4. Water quality measurement

Organic content in the effluents 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 measured by a NH_3-N detector (5B-6D NH_3-N measuring instrument, Lian-hua Technology Co. Ltd., China). Electrical conductivity, pH, and turbidity were measured by 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.

2.5. Morphology of the hollow fiber membranes

The membrane cross-section morphology was observed with a JSM-6301 field emission scanning electron microscope (SEM, JEOL Ltd.). To avoid destroying the structure of the cross-sections of the hollow fiber membranes, the membrane samples were first immersed in liquid nitrogen, then fractured, and finally sputtered with metallic gold.

3. Results and discussions

3.1. UFH-90-1 (80 kDa)

It is found in Fig. 3 that K of UFH-90-1 decreased gradually from 180 to 91 L/m^2 h·bar on the first day and from 103 to 63 L/m^2 h·bar on the next day. Comparing two days' data, the turbidities of the first day were lower than those of the second day, and the pseudo-steady *K* of the first day was higher than that of the second day. In general, two factors can induce the UF membrane fouling, one was small particles (colloids) accumulation on the membrane surface, and the other was particles (colloids) lodged inside the membrane pores. Internal pore adsorption (or clogging) is attributed to irreversible fouling, but the fouling cake deposited on membrane surface can easily be removed by backwashing [7]. These experimental results mean that UFH-90-1 had formed irreversible fouling in two days operation.

K of the RO system basically stabilized at 2.8 L/m^2 h·bar in the whole experiment process. Table 3 shows that UFH-90-1 membrane module could remove particles (colloids), and the rejections of RO system to salt and NH_3-N were more than 99 and 90%, respectively. It was found that pH of the effluent of RO system was lower than that of the influent of RO system.

In water, 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^+).

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

From the doubled-headed arrow, the reaction can go either way, ammonia and water could combine to form hydroxyl ions and ammonium ions. This precisely explained what happened as the pH of water increased. At the same time, it is also observed that RO membranes could also reduce the pH level in water. The reduction in pH value is caused by the carbonic acid balanced reaction, and the balance would move to H_2CO_3 decomposition when a lot of ions in water are removed by RO system. RO membranes could not reject CO_2 but reject HCO_3^- and CO_3^{2-}. The

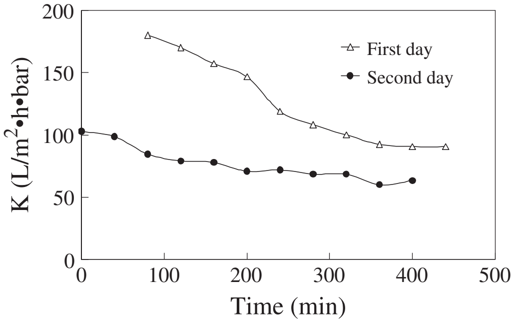


Fig. 3. *K* profile for UFH-90-1 modules.

Table 3
Experimental results for UFH-90-1 modules

Items	CODcr (mg/L)	NH_3-N (mg/L)	Conductivity (μs/cm)	pH	Turbidity (NTU)
The permeate of UF system	–	1.94	1,050	7.69	0.72
The permeate of RO system	0.01	0.14	5	6.42	0.01
The output of NH_3-N remover	0.02	0.12	17	7.32	0.98

resulting increase in ratio of CO_2/HCO_3^- in the permeate is responsible for the increase in concentration of hydrogen ion and reduction in pH of permeate.

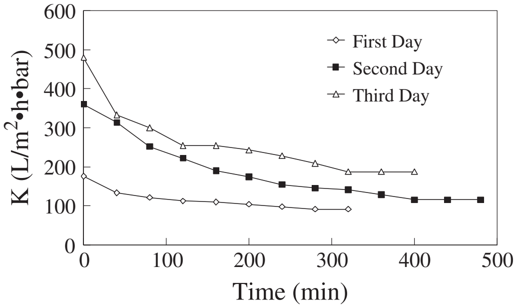


Fig. 4. *K* profile for UFH-90-2 modules.

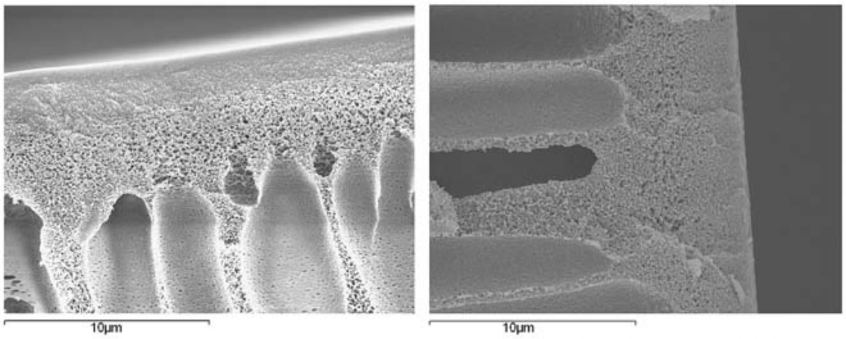
$$CO_2 + H_2O = H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad (4)$$

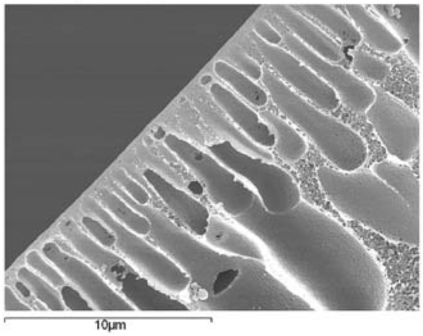
In surface water, hydroxyl ions and hydrogen ions form water, which is a very weak electrolyte and difficult to ionize.

$$H^+ + OH^- = H_2O \quad (5)$$

Therefore, the equilibriums of Eqs. (3)–(5) 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.



UFH-90-1 modules (80 kDa) UFH-90-2 modules (100 kDa)



UFH-90-3 modules (300 kDa)

Fig. 5. Cross-section SEM micrographs of the different membranes.

Table 4
Experimental results for UFH-90-2 module

Time	Items	CODcr (mg/L)	NH_3-N (mg/L)	Conductivity (μs/cm)	pH	Turbidity (NTU)
First day	The permeate of UF system	0.10	0.76	1,050	7.57	0.04
	The permeate of RO system	0.01	0.04	5	6.23	0.01
	The output of NH_3-N remover	0.01	0.12	18	7.21	0.20
Second day	The permeate of UF system	4.40	0.50	1,060	7.61	0.03
	The permeate of RO system	0.01	0.03	5	6.37	0.01
	The output of NH_3-N remover	0.01	0.12	16	6.81	0.08
Third day	The permeate of UF system	4.90	0.36	1,100	7.47	0.10
	The permeate of RO system	0.01	0.16	6	6.24	0.07
	The output of NH_3-N remover	0.01	0.19	50	7.23	1.13

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 [10,11]:

$$Z - Na^+ + NH_4^+ \rightarrow Z - NH_4^+ + Na^+ \quad (6)$$

where Z = zeolite. When NH_3-N concentration of NH_3-N remover influent was lower than 1 mg/L, NH_3-N removal efficiency of activated zeolite was much lower (Table 3).

3.2. *UFH-90-2 (100 kDa)*

K decreased gradually from 176 to 92 L/m^2 h·bar on the first day. Results of the second-day operation are shown in Fig. 4, *K* decreased from 360 to 115 L/m^2 h·bar. The results of the third-day operation using the same UFH-90-2 module found that *K* decreased from 480 to 188 L/m^2 h bar (Fig. 4). Depending on the above data, the sequence of *K* value was as follows: the third day > the second day > the first day. Comparing three membranes from the SEM micrographs (Fig. 5), UFH-90-1 membrane had the densest and thickest inner surface layer, and UFH-90-3 membrane surface layer was the thinnest, but UFH-90-2 membrane had the moderate surface layer with more sponge-like holes. The phenomenon of *K* value with time becoming larger is different with the conventional thought, the possible reason maybe is that physical and chemical wash processes are most likely contributed to the increase of effective filtration pore number on the UFH-90-2 membrane.

For RO system, *K* stabilized at 2.8 L/m^2 h·bar in the whole three-day experiment. Table 4 shows that the turbidity of UF permeates was lower than 0.1 NTU, and the rejections of RO system to salt, NH_3-N, and COD were more than 99, 90, and 99%, respectively. NH_3-N remover was not washed during all experiments period. In UFH-90-1 experiments, activated zeolite had absorbed ammonium ions from the RO permeate. However, in UFH-90-2 experiments, the NH_3-N concentration was lower than 0.1 mg/L, so some ammonium ions released to the effluent water of NH_3-N remover. That was the reason why the NH_3-N remover had adverse effect on NH_3-N. At the same time, activated zeolite particles were reliably crushed by gravity force and 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. It is also found that pH of the influent of RO system was higher than that of the effluent of RO system.

3.3. *UFH-90-3 (300 kDa)*

Two days experiments were executed. Because NH_3-N removal efficiency of NH_3-N remover was not

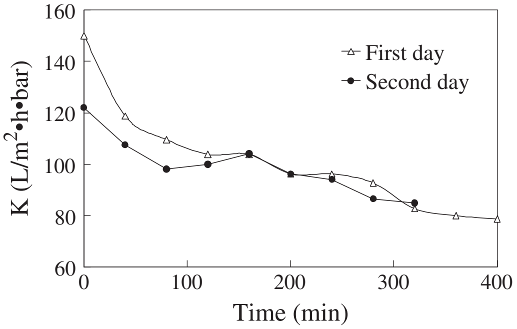


Fig. 6. *K* profile for UFH-90-3 modules.

Table 5
Experimental results for UFH-90-3 modules

Items	CODcr (mg/L)	NH_3-N (mg/L)	Conductivity (μs/cm)	pH	Turbidity (NTU)
The permeate of UF system	13.20	1.32	900	7.62	0.17
The permeate of RO system	2.8	0.05	5	6.54	0.01
The output of NH_3-N remover	0.01	0.20	20	7.36	0.84

significant for low concentration of NH_3-N (<1 mg/L), NH_3-N remover did not run on the second day. The other experimental conditions were the same as before (in Section 3.1.)

K of UFH-90-3, decreased gradually from 150 to 79 L/m^2 h·bar on the first day, had a little fluctuation during the early operation and finally stabilized at 85 L/m^2 h·bar on the second day (Fig. 6). Comparing two days' data of UF system, it was found that the pseudo-steady *K* of the first day was similar to that of the second day. These phenomena showed clearly that the UFH-90-3 had not formed irreversible fouling in two days operation.

For the whole experiments, *K* of RO system stabilized at 2.8 L/m^2 h bar. Table 5 shows that the UFH-90-3 membrane module could remove particles (colloids), the turbidity of UF permeates was lower than 0.2 NTU; RO system had removed 99% of COD, 97% of NH_3-N, and 99% of conductivity. The reasons of other parameters variation in Table 5 were the same as mentioned in Sections 3.1. and 3.2.

4. Conclusions

Comparing results from three UF membranes experiments, it was found that the UFH-90-1 had the lowest *K*, the UFH-90-3 came second and the UFH-90-2 had the highest *K*. Interestingly, the UFH-90-2 modules increased final K by 20% on the second day and 200% on the third day relative to the first day. The possible reason is that the physical and chemical wash processes were most likely contributed to the increase in effective filtration pore number on the UFH-90-2 membrane.

The multimedia filter/UF/RO/NH_3-N remover combined system was able to remove all unwanted elements and to produce consistent and high quality water. For the whole experiments, *K* of RO system basically stabilized at 2.8 L/m^2 h bar. RO system could effectively remove NH_3-N and conductivity. Three UF membranes could remove particles (colloids). And the 100 kDa PSf membrane was the most suitable membrane to treat the river Tang.

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