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Ultrafiltration of humic acid and surface water with tubular ceramic membrane

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ABSTRACT

In recent years, the ceramic membrane filtration has become increasingly attractive for drinking water production. The flux evolution and retention performance of a tubular ceramic membrane with nominal pore size of 0.01 μm was systematically investigated. Filtration experiments were carried out on a pilot-scale crossflow unit using humic acid (HA) solution and surface water as feed by varying transmembrane pressure (TMP). Measurements such as total organic carbon (TOC), ultraviolet absorbance at 254 nm (UV254), fluorescence excitation emission matrices (EEMs), pH, and conductivity were made on both raw water and the permeate. During filtration, flux declined drastically in the beginning stage due to fouling and proceeded to a pseudostable flux. In the low HA concentration, the flux decreased in the first 30 min for about 36, 48, 50 and 51% with the TMP of 0.5, 0.8, 1.0, and 1.2 bar, respectively, while it came to 47, 52, 57, and 65%, respectively for relatively high concentrations; the steady flux increased with increasing TMP from 0.5 to 1.2 bar at the specific concentration of feed water studied. Finally, the effectiveness of the membrane treatment was determined by evaluating the removal efficiency of TOC, UV254, and EEM. The rejection efficiency decreased with increasing TMP in low organic concentration of feed water, while increased in relatively high feed concentration. In addition, filtration in HA and surface water showed a different retention performance, rejection efficiency for HA (>50%) was higher than that for surface water (<20%), which may have a relevance to nature organic matter molecular weight distribution.

Keywords: Ceramic membrane: Ultrafiltration: Permeate flux: Retention: Water treatment

1. Introduction

In recent decades, due to the extremely high water quality in respect to hygiene and microbiological safety, advanced membrane technology, especially ultra- and microfiltration membranes have become increasingly attractive for drinking water production. Compared with conventional treatment processes, low-pressure membranes are highly efficient, easy to operate, economical and satisfy more stringent supply limitations [1]. Furthermore, they provide the possibility of fully automatic operation, a compact system design in connection with good space utilization and

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flexibility in system enlargement, modernization and new installations [2].

However, the effectiveness of membrane separation processes is greatly affected by membrane fouling, which is characterized as a reduction in permeate flux through the membrane or higher trans-membrane pressures (TMP) across the membrane, as a result of increased flow resistance due to the accumulation of colloidal matter, organic molecules, sparingly soluble inorganic compounds, and microorganisms on membrane surfaces and in membrane pores during filtration [3]. Membrane fouling results in the reduction in the productivity of the membrane, a significant requirement for increase in transmembrane pressure (driving force), biodegradation of membrane materials and system failure, and ultimately increases the cost of operation [4]. The problem of membrane fouling has been a major impediment to the application of membrane separation technology in water treatment.

Currently, the study of ultrafiltration (UF) in water treatment was almost exclusively focused on polymeric membranes, while less researches were conducted with ceramic membranes. It is well known that ceramic membranes have some unique advantages when compared to polymeric ones, for instance, (i) a relatively narrow pore size distribution and higher porosity, resulting in better separation characteristics, (ii) a higher mechanical stability (allowing higher pressures), (iii) a higher chemical stability resulting in longer membrane lifetimes, and (iv) higher hydrophilicity resulting in high fluxes at low pressures [5]. Higher hydrophilicity is also associated with lower fouling. Nevertheless, it is rare for them to be used in water treatment compared with usage of polymeric membranes.

This study focuses on the performance evolution of a tubular ceramic membrane with respect to fouling and removal efficiency. The objectives in this study are the following: (1) analysis of flux decline during crossflow UF and (2) carrying out comparison of performance under different operation conditions.

2. Materials and methods

2.1. Membrane and pilot-scale filtration system

The tubular 2-channel aluminum–titanium oxide membrane ($L = 0.25$ m, $\varnothing_{int} = 4$ mm, filtration area = 6.28×10^{-3} m^2) used for filtration experiment were obtained from Kaimi Membrane Tech Co. Ltd in Jiangsu, China. The nominal pore size was 10 nm. In this configuration, permeate flows from inside to outside of the membrane. The membrane module shell was made of stainless steel. The virgin membrane was cleaned by soaking in a sodium hydroxide solution (0.1 M) overnight, then rinsing with MilliQ water for 2 h.

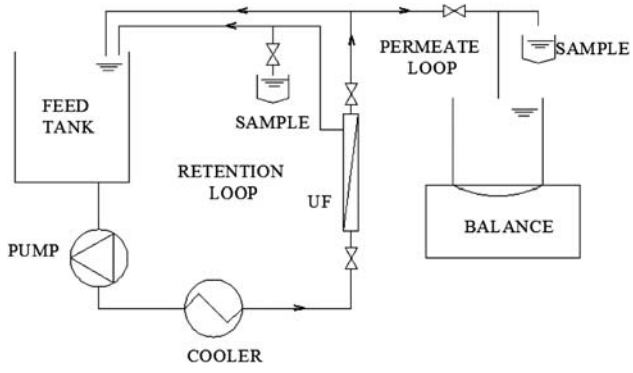


Fig. 1. General scheme of the UF setup.

Experiments were conducted in a pilot plant including three major parts: the feed tank ($V = 10$ L), the retentate loop and the permeate loop, (Fig. 1). The raw water was circulated through the filtration unit by a diaphragm pump (SEISUN®, DP-125, China). By adjusting the control valves appropriately, various modes with different TMP (0.5, 0.8, 1.0, and 1.2 bar respectively) were achieved. A constant temperature was provided for feed stream by using water fed heat exchanger/chiller. The permeate flux was measured through weighting the permeate mass in 2 min using a digital balance (OHAUS® SE6001F, America, accuracy ±0.1 g)

2.2. Feed water

Two sources of water, including humic acid (HA) solution and surface water, were used to perform crossflow UF tests. As HA is easily obtained and well characterized, it has been widely used as a model foulant by many membrane researchers [6]. In this study, HA was obtained from Jufeng Chemical Corporation (Shanghai, China). HA stock solution was prepared by dissolving weighted amounts of powder HA in 1 M NaOH solution with constant stirring for some time to give a final concentration of about 1 g dry HA/L solution. After complete dissolution of HA, the pH of solution was adjusted to 7 by the slow addition of HCl (3 M) with steady swirling. The solution was then filtered through 0.45 μm pore size filter papers (New Asia Purification Technology Corporation, China) to remove possible undissolved materials. The stock solution was stored at 4℃. HA working solution was prepared from the stock solution, with a dilution of 50, 100 and 200 times, respectively.

Table 1
Water quality in experiments

Type	pH	Conductivity (μS/cm)	Turbidity (NTU)	TOC (mg/L)	UV254
Low HA	6.28	103	–	2.78	0.252
Medium HA	6.36	201	–	5.65	0.500
High HA	6.41	384	–	9.91	0.902
Surface water	7.95	480	4.0	3.90	0.067

Another type of feed water, surface water was obtained from Lake Sanhaowu (Shanghai) and stored at 4℃ prior to the use after raw water had been pre-filtered by 0.45 μm filtration, corresponding to the specification for dissolved organic carbon (DOC). Table 1 shows the water quality data obtained for the water used in this study.

2.3. Filtration and cleaning procedures

In the first step, the intrinsic membrane resistances were determined by measuring its flux with Milli-Q water under controlled temperature and pressure. Then, the filtration test started after adjusting the feed temperature at 17 ± 0.5℃. The feed flow-rate and TMP were controlled using the retentate valves. About 8 L of raw water was used in the feed tank and the filtration was conducted for 3 h duration at a constant TMP of 0.5–1.2 bar. The permeate flow rate was measured at regular intervals of 15 min, while analytical samples were collected every 30 min.

Finally, specific membrane cleaning methods were utilized. After filtration, the loops was emptied and rinsed with Milli-Q water. The membrane was cleaned by ultrasonic vibration for 5 min, soaking in sodium hypochlorite (800 ppm). The chemical cleaning procedure was repeated for 2 times, afterwards the membrane was rinsed with Milli-Q water and stored in Milli-Q water until next experiment. Before starting a new test, the ceramic membrane was characterized with Milli-Q water at the very TMP (0.5, 0.8, 1.0 or 1.2 bar) to verify the initial flux. A new experiment was started only if the initial flux had not changed.

2.4. Analytical method

Permeate and feed samples, stored at 4℃ until analysis, were used to determine total organic carbon (TOC, Elementar, Germany), UV Absorbance at 254 nm (UV765, PRECISION&SCIENTIFIC, China) and fluorescence materials (Cary Eclipse Fluorescence Spectrophotometers, Varian, Australia). TOC and UV254 rejection are defined as the observed rejection:

$$R = \frac{c_b - c_p}{c_b} \times 100\%$$

where R is the observed rejection for some materials, c_b is the concentrations in the bulk solution, and c_p is the concentrations in the permeate.

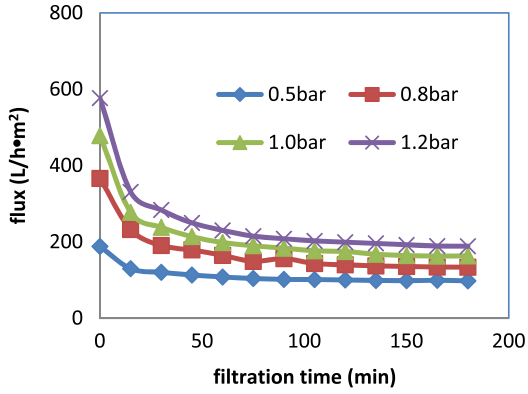
3. Results and discussion

3.1. Filtration of HA feed

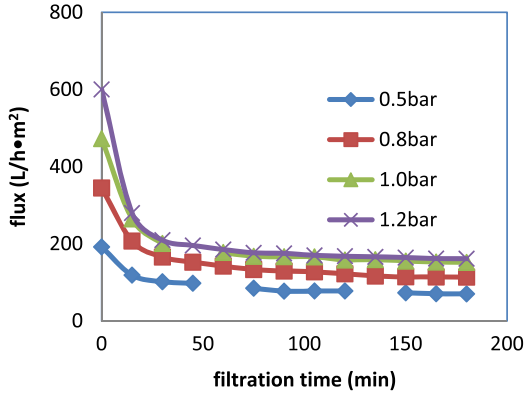
3.1.1. Effect of TMP and HA concentration on the membrane flux

Membrane fouling is one of the most significant issues affecting the development of membrane applications in drinking water treatment [7-10], resulting in poor membrane performance by decreasing the specific permeate flux. In this study, the membrane flux decline within HA feed was investigated using tubular ceramic membrane. It was observed that the flux decreased over time regardless of TMP adopted and strength of HA feed water used in Fig. 2. According to Fig. 2, permeate flux declined drastically at the beginning stage of filtration and finally preceded to a pseudostable flux. The results suggested that pore blocking and adsorption of the substance onto the membrane surface was intense during the initial stage, followed by concentration polarization and cake formation dominated in the later stage. This fouling mechanism was confirmed by previous investigation of Yazdanshenas [11] and Zydney [8] as well as Muthukumaran et al. [12]. They found that during the initial stage of filtration, while the membrane was clean, the particulate pollutants were rejected by the size of the membrane pores, afterwards the particles started to accumulate near the membrane surface to form a cake layer. Both the pore blockage and cake layer decreased the permeate flux which are key factors governing the application of membrane system.

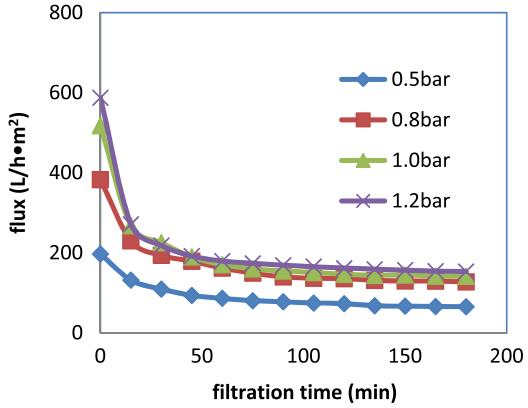
With regard to the effect of feed concentration on the membrane performance, the rate of flux decline increased with increasing foulant concentration under a specific TMP. As shown in Fig. 2, in the low concen-



(a). effect of TMP on membrate flux at low HA concentration



(b). effect of TMP on membrane flux at medium HA concentration



(c). effect of TMP on membrane flux at high HA concentration

Fig. 2. Flux evolution in the HA feed.

tration of HA solution, the flux decreased in the first 30 min for about 36, 48, 50, 51% with the TMP of 0.5, 0.8, 1.0, and 1.2 bar, respectively. But when it came to relative high strengths, the rate increased to 47, 52, 57, and 65%, respectively. Particularly, one interesting finding should be noted that the difference of the flux decline rates between medium and high-strength feed was not so significant. When it came to the later stage of pseudostable flux, a similar result was obtained. The result indicated that during a low range of feed concentration, increasing concentration of foulant would accelerate and assist in pore blockage and particle accumulation on the membrane surface, lead to a more severe membrane fouling, thus result in a more rapid and extensive flux decline. As to a relative high-concentration range, increasing feed strength did not affect flux under the various TMP studied, which is consistent with another study by Defrance et al. [13].

In addition, the effect of TMP on flux evolution could be studied through Fig. 2. Apparently the steady flux increased with increasing TMP at the very concentration of feed water studied. In contrast, Gan et al. [14] found that increasing TMP from 1.5 to 2.5 bar showed no response in the steady-state permeate flux when tubular ceramic membrane was used for the treatment of sewage effluents. One possible explanation for the difference is that higher TMP (i.e. >1.2 bar) could lead to a more compact cake formation and greater in-pore plugging when

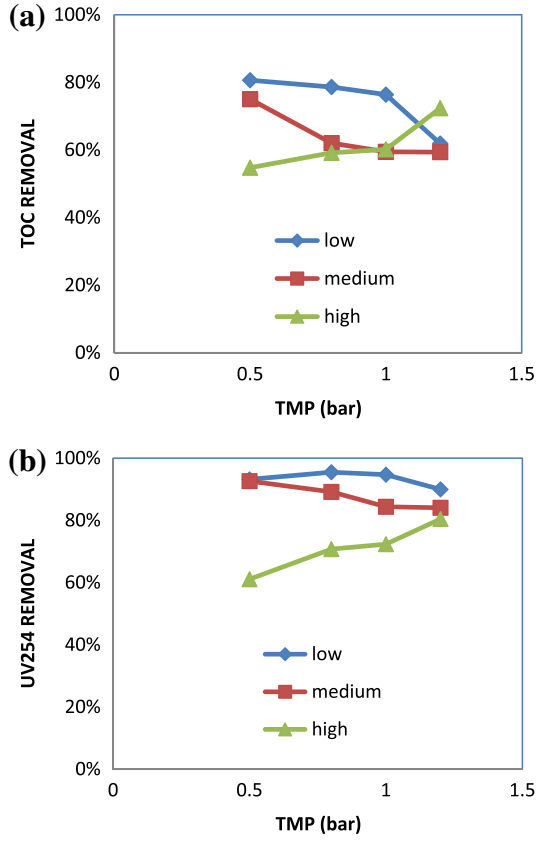


Fig. 3. Rejection efficiency of the tubular ceramic membrane with HA. (a) TOC and (b) UV254.

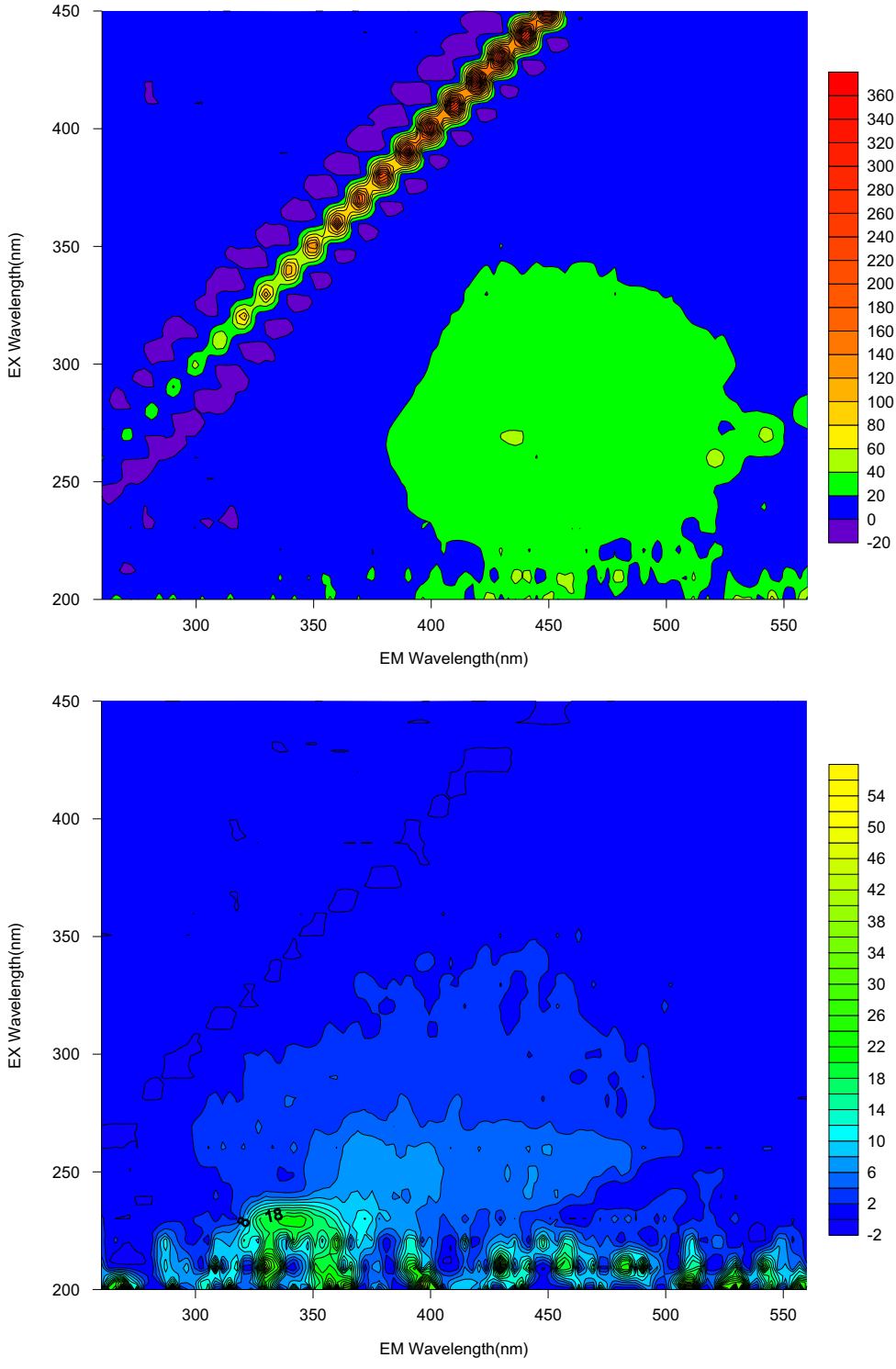


Fig. 4. A comparison for the feed and permeate with low strength HA feed at 0.5 bar.

tubular ceramic membrane was used. Thus, this result confirmed less fouling in the tubular ceramic membrane under the range of TMP adopted in this study.

3.1.2. HA removal by ceramic UF membrane

The efficiencies of ceramic UF membrane in removing HA, with respect to TOC and UV254 for three levels of HA concentration and four different

TMP studied, were shown in Fig. 3. As shown in Fig. 3, The nature organic matter (NOM) removal removal efficiencies, as determined by UV254, were higher than those obtained by TOC for all cases, indicating that aromatic/hydrophobic compounds can be preferentially removed over the entire range of membrane pore size, which were in agreement with previous investigations made by many researchers [15,16].

The effect of feed concentration and TMP on the rejection performance was investigated. Generally, the rejection efficiency of organic matter decreased with increasing feed concentration regardless of different TMP. As to the effect of TMP on HA removal, a slight difference was observed. The rejection efficiency decreased with increasing TMP in low and medium concentration of feed water, while increased in relatively high concentration of HA. Thus, both pore size and TMP contributed major influences on NOM removal.

Typical fluorescence excitation–emission matrices (EEMs) observed during the HA filtration were shown in Fig. 4. When excited by ultraviolet and visible light, NOM fluoresces and the characteristics and intensity of the fluorescence varies depending on the fluorophores present [17]. The composition of NOM can be visualized as a pattern of fluorescence peaks within an EEM. Fluorescence peaks can be attributed to both humic-like fluorescences, defined as peaks C located in the region of 300–360 nm and excitation 400–480 nm emission wavelength, and protein-like fluorescences, defined as peaks T located in the region around 280 nm excitation and 350 nm emission [18]. In this filtration test, the feed was HA, it can be seen from Fig. 4 that peaks C dominated over all the other areas of the EEM, therefore discussion focused on peaks C. Apparently humic-like fluorescences were significantly removed by the ceramic membrane, which confirmed the results obtained in TOC and UV254 analyses that the membrane pore size plays an critical role in the ceramic UF.

3.2. Filtration of surface water

3.2.1. Flux variation with different TMP

In the case of UF with surface water, the flux variation with different TMP was showed in Fig. 5. Unlike the HA solution, surface water contains a wide variety of suspended, colloidal and dissolved particles, leading to a irreversible fouling resistance which cannot get a complete recovery by the chemical cleaning procedure. Similar to results obtained in HA solution, the permeate flux with surface water declined drastically at the beginning stage of filtration and finally preceded to a pseudosteady value, while the steady flux increased with increasing TMP from 0.5 to 1.2 bar. It can be seen from Fig. 5 that flux decline increased from 46 to 77% as TMP increased from 0.5 to 1.2 bar, indicating that higher TMP could lead to a more compact cake formation and greater in-pore plugging [9].

3.2.2. NOM removal by ceramic UF membrane

The effectiveness of ceramic membrane in removing organic matter, with respect to DOC, UV254 and EEM for surface water at four different TMP, was shown in Figs. 6 and 7, respectively. Generally, the removal efficiency was much lower compared to the results with HA solution. All removal efficiencies were below 20% and even down to only 8% for DOC at 0.8 bar. Meanwhile, the EEM pictures showed no significant difference of peak C and peak T intensity for the raw water and permeates. Taking the flux decline into consideration, the fouling was so remarkable while rejection for organic materials was quite poor, and thus, it can be predicted that the surface

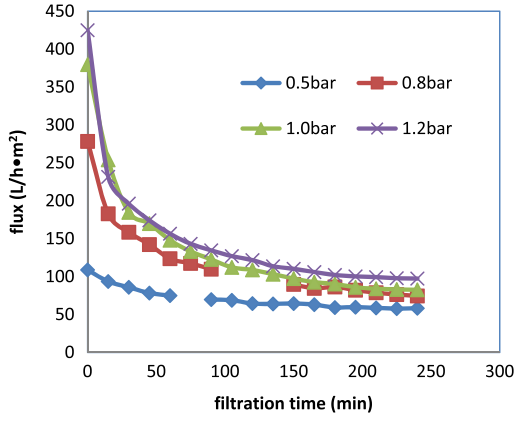


Fig. 5. Flux evolution with surface water.

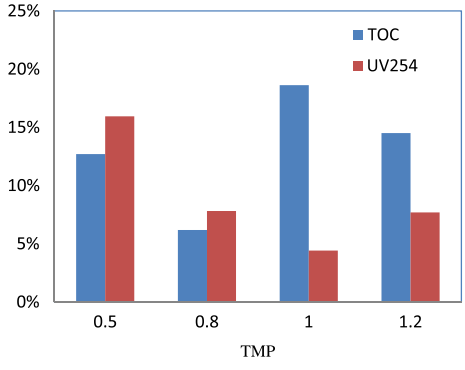


Fig. 6. Rejection efficiency of the tubular ceramic membrane with surface water.

water used in experiments contained large variety of inorganic foulant, including suspended, colloidal and dissolved particles or some sparingly soluble inorganic compounds. In addition, most of NOM in the feed may have a molecular weight smaller than the pore size of the ceramic membrane. This study indicates that the ceramic membrane alone will not be adequate for removing NOM in surface water treatment. Employing pretreatment such as coagulation or powder activated carbon adsorption should be suggested to form the hybrid pretreatment—UF process for surface water treatment.

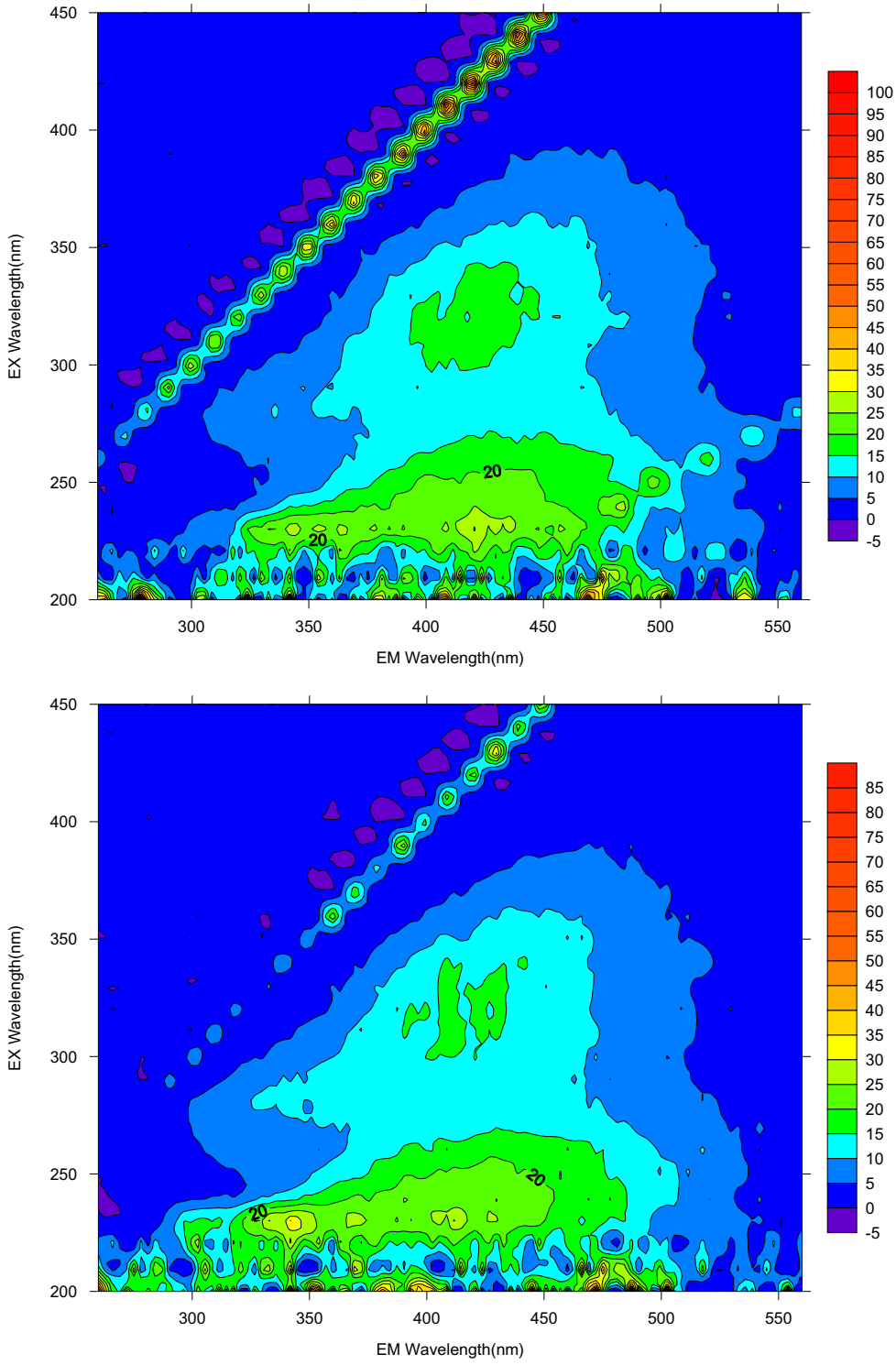


Fig. 7. A comparison for the feed and permeate with surface water at 0.5 bar.

4. Conclusion

The flux evolution and rejection performance of a tubular ceramic membrane with nominal pore diameter of 0.01 μm in treating HA solution and surface water was systematically investigated to understand how the TMP and feed concentration influence the permeate quality and flux in a cross-flow mode filtration. This study arrives at the following conclusions:

(1) During a low range of feed concentration, increasing concentration of foulant would accelerate and assist in pore blockage and particle accumulation on the membrane surface, lead to a more severe membrane fouling, thus result in a more rapid and extensive flux decline. As to a relative high-concentration range, an increase in HA concentration will adversely affect the permeate flux over the range of TMP studied.
(2) The steady flux increases with increasing TMP from 0.5 to 1.2 bar due to a more compact cake formation and greater in-pore plugging at higher TMP, while for surface water the increasing degree is not so pronounced compared with HA solution.
(3) The removal efficiency of HA decrease with increasing feed concentration regardless of various TMP. As to the effect of TMP, the removal efficiency decrease with increasing TMP in low and medium concentration of HA, while increase in relatively high concentration.
(4) The removal efficiency for surface water is much lower compared to the results with HA solution. All rejections are below 20% and even down to only 8% for TOC at 0.8 bar. Such a difference may have a close connection with feed composition and molecular size.

Acknowledgments

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