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Submerged membrane bioreactor (sMBR) for the treatment of contaminated raw water

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ABSTRACT

The mini-pilot experiments of submerged membrane bioreactor (sMBR) for the drinking water treatment from a slightly polluted surface water supply was conducted for more than 110 days, with a hydraulic retention time of 0.5 h. Perfect ammonia removal (by 89.4%) were achieved by the sMBR through the biological nitrification. However, the capacity of the sMBR for organic matter removal was demonstrated to be low. The average removal efficiencies for TOC, COD_{Mn}, DOC, UV_{254}, and corresponding THMFP and HAAFP were 28.6%, 33.5%, 21.5%, 15.1%, 34.1% and 24.7%, respectively, though much higher removal of 51.7% and 54.9% were obtained for BDOC and AOC, respectively. A sludge layer was observed on the UF membrane surface in the sMBR. The sludge layer could provide additional filtration for dissolved organic matter (DOM) in the mixed liquor, especially for organic molecules in the range of 5000–500 Da. Fractionation of DOM indicated that the sludge layer together with the UF membrane had the ability to reject hydrophobic neutrals, hydrophobic acids, and weakly hydrophobic acids by 45.0%, 42.7% and 48.1%, respectively; whereas hydrophobic bases and hydrophilic organic matter were separated mainly by the UF membrane, with the efficiencies of 11.3% and 14.6%, respectively.

1. Introduction

Due to the rapid economic development and shortage of stringent environmental protection regulations, many domestic and industrial wastewaters have been discharged into natural water bodies without sufficient treatment, which has led to serious pollution situation of the surface water supplies in developing countries, with organics and ammonia nitrogen (NH_3–N) as the main pollutants. Organic matter including natural organic matter and synthetic organic chemicals has always been one of the major concerns in drinking water treatment. Organic impurities could cause the problems of color and odor in drinking water, and result in the formation of disinfection by-products when reacting with chemical disinfectants such as chlorine [1]. Furthermore, biodegradable organic matter (BOM) also provides substrate for microbial regrowth in the distribution system [2]. As a result, elimination of organic pollutants in the raw water is of great importance for the production of potable water. However, the capacity of conventional treatment processes (coagulation, sedimentation, filtration, and disinfection) for organics removal seems to be limited when treating polluted surface water [3].

In drinking water treatment, it has been established that biological processes can effectively remove organic matter and ammonia content from raw water [4,5]. Biological pre-treatment as well as biological activated carbon substituting sand-filter have been widely applied in China, which result in the decrease of bio-film formation potential in the distribution system and the enhancement of bio-stability of the finished water [6]. Unfortunately, Morin and Camper [7] found that colonized carbon fines could be released from the filters, and these fines may transport bacteria to the distribution networks.

Membrane filtration technology including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) has been rapidly developed in the past decades. Traditionally, NF and RO are able to remove the majority of dissolved organic matter (DOM) and inorganic constituents in water. However, high feed pressure is required for the operation [8]. Whereas new generations of low-pressure NF membranes and ultra-low-pressure RO membranes could significantly reduce the operating pressure and thus the costs while producing the similar permeate water quality [9,10]. These low-pressure NF and RO processes might be promising technologies for advanced drinking water treatment. On the other hand, MF and UF processes are able to separate the majority of particles and microorganisms from raw water, and considered as the alternative to conventional clarification and filtration units [11]. However, both of them cannot remove DOM effectively [12–14]. As

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a result, a variety of pre-treatment processes have been integrated into the MF/UF systems to enhance the DOM removal as well as alleviate membrane fouling, such as coagulation [15], adsorption [16], photocatalysis [17], and so on.

In recent years, membrane bioreactor (MBR) technology has gained unprecedented popularity in the field of wastewater treatment. MBR, i.e. the combination of membrane and activated sludge, offers many advantages over conventional biological treatment such as small footprint, excellent treated water quality, and complete solids/liquid separation. One of the major obstacles for its widespread application is membrane fouling, which could cause severe loss of membrane permeability and thus the increase of energy consumption. Many researches have focused on the fouling behaviors and the factors influencing membrane fouling [18,19]. It was reported that the membrane fouling might be reduced when adopting appropriate strategies and operating parameters. For example, operating a MBR with the flux below its critical flux leads to no fouling; periodical physical and chemical cleaning could also mitigate the membrane fouling [20].

Although MBR has been widely studied and applied on full-scale in wastewater treatment [21–24], it is considered as a new technology in drinking water treatment. Up to now, only a few literatures could be found on this subject and the conclusions seem to be controversial. Williams and Pirbazari [25] found that MBR was effective for the removal of BOM and trihalomethane precursors when combined with ozone and powdered activated carbon (PAC). Li and Chu [26] achieved over 60% of total organic carbon (TOC) removal and 95% of ammonia removal in their submerged MBR for treating simulated polluted surface water; However, the results reported by Sagbo et al. [27] was not so exciting, the TOC removal efficiency they obtained was only 25%, though the MBR perform well in the elimination of ammonia in their study. Moreover, the mechanisms of MBR for inorganic and organic pollutants removal in drinking water treatment have not been seriously dealt with yet.

As compared with MF, UF is able to reject influent bacteria completely. In this paper, a submerged membrane bioreactor (sMBR) with UF membrane was brought forward and investigated for the drinking water treatment from slightly contaminated surface water. Meanwhile, PAC had been used as the carrier for bacterial growth in the bioreactor. The effectiveness of the sMBR for the removal of inorganic and organic contaminants was evaluated, and the relevant mechanisms were also discussed.

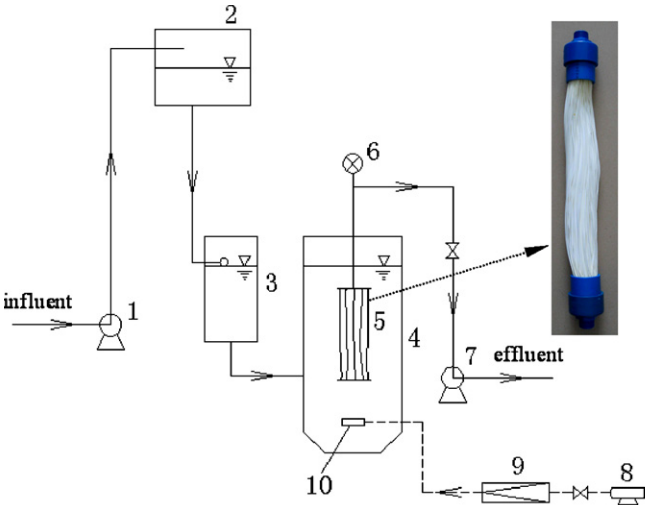

Fig. 1. Schematic diagram of the experimental set-up (1) feed pump; (2) high level water tank; (3) constant level water tank; (4) sMBR; (5) UF membrane module; (6) manometer; (7) suction pump; (8) air blower; (9) air flowmeter; (10) air diffuser. The photo shows the submerged hollow fiber UF membrane module (Litree China) with a total surface area of 0.4 m^2 and a nominal pore size of 0.01 μm.

Table 1
The physical characteristics of the UF membrane module

Parameters	Membrane module
Type	Hollow fiber
Material	PVC
Nominal pore size (μm)	0.01
Length of fibers (mm)	300
Number of fibers	300
Inner diameter of the fibers (mm)	0.85
Outer diameter of the fibers (mm)	1.45
Total membrane area (m^2)	0.4

2. Materials and methods

2.1. Experimental set-up

A mini-pilot-scale sMBR was constructed and used in this study (Fig. 1). A hollow fiber UF membrane module (Litree China) with a nominal pore size of 0.01 μm and a total membrane area of 0.4 m^2 was employed in the sMBR, which was specified in Table 1. The membrane module was directly immersed inside the activated sludge reactor (effective volume of 2 L). The reactor was fed with raw water through a constant level tank, and the effluent was drawn directly from the membrane module by using a suction pump. A manometer was set between the membrane module and the suction pump to monitor the trans-membrane pressure (TMP). Continuous aeration was provided at the bottom of the reactor to supply dissolved oxygen (DO) for the activated sludge and generate strong turbulence for membrane scouring.

2.2. Operation conditions

The effluent suction pump was controlled by a timer based on a time sequence of 8 min on and 2 min off in each cycle. The air was continuously supplied at the bottom of the sMBR through a diffuser with the flow rate of 80 L h^{-1}.

The UF membrane flux was set at 10 L m^{-2} h^{-1}, corresponding to a hydraulic retention time (HRT) of 0.5 h. In drinking water treatment plants, the total HRT is usually in the range of 0.5–1.5 h. The longer the HRT is, the larger the footprint would be. As one kind of the advanced treatment technologies in drinking water treatment, sMBR might be able to achieve satisfactory treatment efficiencies at low HRT. So the HRT of 0.5 h was selected and tested in this study.

The membrane was occasionally taken out of the reactor and physically or chemically cleaned. Except for mixed liquor sampling and membrane cleaning, no sludge discharge was performed during the experiments, which corresponded to a sludge retention time (SRT) of more than 80 days. In this study, the raw water had low suspended solids content (1.88 ± 0.62 NTU of turbidity, as shown in Table 3), and the BOM concentration in the raw water was much lower than that in wastewater (Table 3). Therefore, there might be not the problem of excess suspended solids accumulation in the bioreactor when selecting the long SRT. On the other hand, long SRT might promote the accumulation of some slowly growing microorganisms in the bioreactor. Thus, the SRT of 80 days was selected for the sMBR.

A predetermined amount of PAC (1.5 g L^{-1}) was added in the reactor at the beginning of the start-up to support bacterial growth.

Table 2
Analyses of conventional water quality parameters

Water quality parameters	Pre-treatment	Analytical methods or apparatus
Turbidity	–	Turbidimeter (TURBO550, WTW, Germany)
Ammonia nitrogen (NH_3–N)[a]	0.45 μm membrane	Colorimetric method, spectrometer (UV754, CANY, China)
Nitrite nitrogen (NO_2^-–N)	0.45 μm membrane	Colorimetric method, spectrometer (UV754, CANY, China)
Total organic carbon (TOC)	–	TOC analyzer (TOC-VCPH, Shimadzu, Japan)
Permanganate index (COD_{Mn})	–	The potassium permanganate oxidation method
Dissolved organic carbon (DOC)[a]	0.45 μm membrane	TOC analyzer (TOC-VCPH, Shimadzu, Japan)
UV absorbance at 254 nm (UV_{254})[a]	0.45 μm membrane	Spectrometer (UV754, CANY, China)
Dissolved oxygen (DO)	–	DO electrometer (pH/Oxi 340i, WTW, Germany) with a probe (Cellox® 325)
Mixed liquor suspended solids (MLSS)	–	The drying method
Mixed liquor volatile suspended solids (MLVSS)	–	The burning method

[a] As for the analyses of NH_3–N, DOC and UV_{254} in the mixed liquor, the samples were first centrifuged at 5400 rpm for 5 min, and then filtered through 0.45 μm membranes.

There was no further PAC addition during the following experimental period. When considering the lower BOM content in the raw water, it was inferred that the 1.5 g L^{-1} of PAC might be sufficient to support the microbial growth in the bioreactor. Natural start-up was selected for the sMBR when considering it was for drinking water treatment. The sMBR had been in stable operation before this investigation was conducted.

2.3. Simulated raw water

Domestic sewage was added to the local (Harbin China) tap water with a volumetric ratio of 1:30 to simulate a surface water supply slightly polluted by sewage discharge. The domestic sewage had average COD_{Cr}, TN and NH_3–N concentrations of 242.0 ± 93.0, 48.7 ± 8.1 and 39.1 ± 4.1 mg L^{-1}, respectively. Furthermore, 1 mg L^{-1} of humic acid was also added to the raw water, and the NH_3–N concentration was maintained at 3–4 mg L^{-1} by dosing NH_4Cl (analytical grade). Before feeding to the sMBR, the simulated raw water was stabilized at room temperature for 2 days. During the experimental period, the raw water had average temperature of 25.2 ± 2.5 °C, pH of 7.17 ± 0.16. Other water quality parameters could be found in Table 3 as given below.

2.4. Analytical methods

Conventional water quality analyses were conducted following the standard methods [28], as elaborated in Table 2.

Trihalomethanes formation potential (THMFP) and haloacetic acids formation potential (HAAFP) were determined following US EPA Method 551.1 and 552.2, except that the incubation time after chlorine dosing was shortened from 7 to 3 days. The THMFP presented here was the sum of $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$; and HAAFP was the sum of $CH_2ClCOOH$, $CH_2BrCOOH$, $CHCl_2COOH$, CCl_3COOH, $CHBrClCOOH$, $CBrCl_2COOH$, $CHBr_2COOH$, $CBr_2ClCOOH$, and CBr_3COOH.

Assimilable organic carbon (AOC) measurement was carried out using a method modified by Liu et al. [29], which was developed based on the procedures of Van der Kooij et al. [30]. The bioassay procedure employed two strains of microorganisms: *Pseudomonas fluorescens* (P17) and *Aquaspirillum* (NOX). AOC concentration was calculated by comparing the cell formation unit number and the yield coefficient, and the total AOC was the sum of AOC_{P17} and AOC_{NOX}.

Biodegradable dissolved organic carbon (BDOC) was measured with the method established by Servais et al. [31] with some modifications: the incubation was conducted in the dark at 22 °C for 3 days. The BDOC was defined as the difference between the original DOC and final DOC after incubation.

Size exclusion chromatography (SEC) was used to determine the apparent molecular weight (MW) distribution of UV-active substances in the waters from the sMBR. The measurement was carried out on a high performance liquid chromatography (LC-10A, Shimadzu, Japan) with UV detection (SPD-10A) at 254 nm, using a Waters Ultrahydrogel 250 column (7.8 mm × 300 mm). To suppress the nonsize exclusion effects (electrostatic repulsion and specific adsorption), the mobile phase was comprised of Milli-Q (MQ) water buffered to pH 6.8, containing 0.1 M NaCl, 0.002 M KH_2PO_4, and 0.002 M Na_2HPO_4 [32]. The flow rate was set at 0.4 mL min^{-1}. Polyethylene glycols (PEG) were employed to calibrate the relationship between the MW and the retention time. Injection volume of water samples were 50 μL.

DOM was fractionated into five fractions by using Amberlite XAD-8 and XAD-4 resins according to Qiao et al. [33]: hydrophobic bases (HoB); hydrophobic neutral fraction (HoN); hydrophobic acids (HoA); weakly hydrophobic acids (WHoA); hydrophilic organic matter (HiM). DOM fractions were subjected to DOC analysis. The resins were cleaned and conditioned as described by Leenheer [34] and Imai et al. [35].

2.5. Microscopic observations

At the end of the study, scanning electron microscopy (SEM) was employed to observe the surface of the UF membrane in the sMBR and a clean one. The experimental membrane sample together with the clean one was first fixed with 3.0% glutaraldehyde in 0.1 M phosphate buffer (pH 7.2) for 3 h. This was followed by the dehydration in a graded ethanol series (50%, 70%, 80%, 90%, 100%, 100%, and 100%; 15 min each). After that, the samples were gold-coated by a sputter and observed under a scanning electron microscopy (SEM) (HITACHI S4800 HSD, Japan).

The sludge layer attached to the membrane surface was observed using a confocal laser scanning microscopy (CLSM) (LSM 510 META, Carl Zeiss, Germany). For polysaccharide and bacteria staining, two probes were collectively applied: ConA-FITC (100 μg mL^{-1}, Sigma) to target the polysaccharide with D-glucose or D-mannose and rhodamine (50 μM, Sigma) to target all bacteria. After staining, the sample was washed gently with a phosphate buffer to remove unbound probes. After that, the treated sample was immediately observed under the CLSM.

Atomic force microscopy (AFM, Digital Instruments, Veeco, USA) was also employed to determine the surface morphology of the experimental UF membrane. The tip of the AFM is made of etched single crystal silicon, with a curvature radius of 5–10 nm. Before observations, both the used membrane sample and a clean one were gently washed with MQ water, followed by drying at room temperature. The membrane samples were fixed on a slide glass and scanned over 10 μm × 10 μm. AFM was performed under tapping mode with a scanning rate of 0.5 Hz. Data obtained were analyzed with the software of Nanoscope V5.30; images were in the height mode.

Table 3
Pollutants removal efficiencies of the sMBR process

Water quality parameters	Influent	sMBR		Tap water
		Effluent	Removal (%)	
Turbidity (NTU)	1.88 ± 0.62	0.07 ± 0.02	96.2 ± 1.8	0.51 ± 0.09
NH_3–N (mg L^{-1})	3.49 ± 0.49	0.38 ± 0.14	89.4 ± 3.4	0.32 ± 0.09
NO_2^-–N (mg L^{-1})	0.096 ± 0.117	0.042 ± 0.066	41.4 ± 68.9	0.000 ± 0.000
TOC (mg L^{-1})	5.952 ± 0.711	4.225 ± 0.460	28.6 ± 7.3	4.135 ± 0.463
COD_{Mn} (mg L^{-1})	4.79 ± 0.56	3.18 ± 0.42	33.5 ± 6.3	2.76 ± 0.38
DOC (mg L^{-1})	5.398 ± 0.517	4.225 ± 0.460	21.5 ± 7.0	3.965 ± 0.376
UV_{254} (cm^{-1})	0.086 ± 0.008	0.072 ± 0.005	15.1 ± 4.1	0.067 ± 0.007
THMFP (μg L^{-1})	249.1 ± 18.7	163.7 ± 19.7	34.1 ± 8.5	205.1 ± 20.0
HAAFP (μg L^{-1})	168.3 ± 10.9	126.8 ± 12.3	24.7 ± 3.9	167.2 ± 13.7
BDOC (mg L^{-1})	0.576 ± 0.214	0.259 ± 0.114	51.7 ± 12.9	0.221 ± 0.141
AOC (μg L^{-1})	771.3 ± 145.9	344.4 ± 61.1	54.9 ± 7.5	176.8 ± 30.5

For turbidity, the measurements number $n = 17$; for NH_3–N and NO_2^-–N, $n = 31$; for TOC and DOC, $n = 36$; for COD_{Mn}, $n = 33$; for UV_{254}, $n = 39$; for THMFP, HAAFP, BDOC and AOC, $n = 9$.

3. Results and discussion

3.1. Effectiveness of the sMBR for inorganic and organic pollutants removal

3.1.1. Turbidity removal

The sMBR experiments for treating a slightly polluted surface water supply were conducted for more than 110 days under the stable operating conditions. The efficiencies of the sMBR for inorganic and organic pollutants removal were summarized and listed in Table 3. In general, more than 96% of the particles in the influent were removed by the sMBR through the rejection of the UF membrane, as demonstrated by the decrease of turbidity from 1.88 ± 0.62 NTU in the raw water to 0.07 ± 0.02 NTU in the effluent.

3.1.2. Ammonia and nitrite removals

Ammonia removal through biological oxidation in the sMBR was found much better than that of organic matter, i.e. nearly complete nitrification was achieved by the sMBR. It could be seen from Fig. 2a that in despite of the fluctuation of NH_3–N concentrations from 2.17 to 4.24 mg L^{-1} (3.49 ± 0.49 mg L^{-1} on average) in the raw water, only 0.38 ± 0.14 mg L^{-1} was detected in the effluent (removed by 89.4 ± 3.4%). Although nitrite accumulation was occasionally observed in the effluent of the sMBR, the average effluent

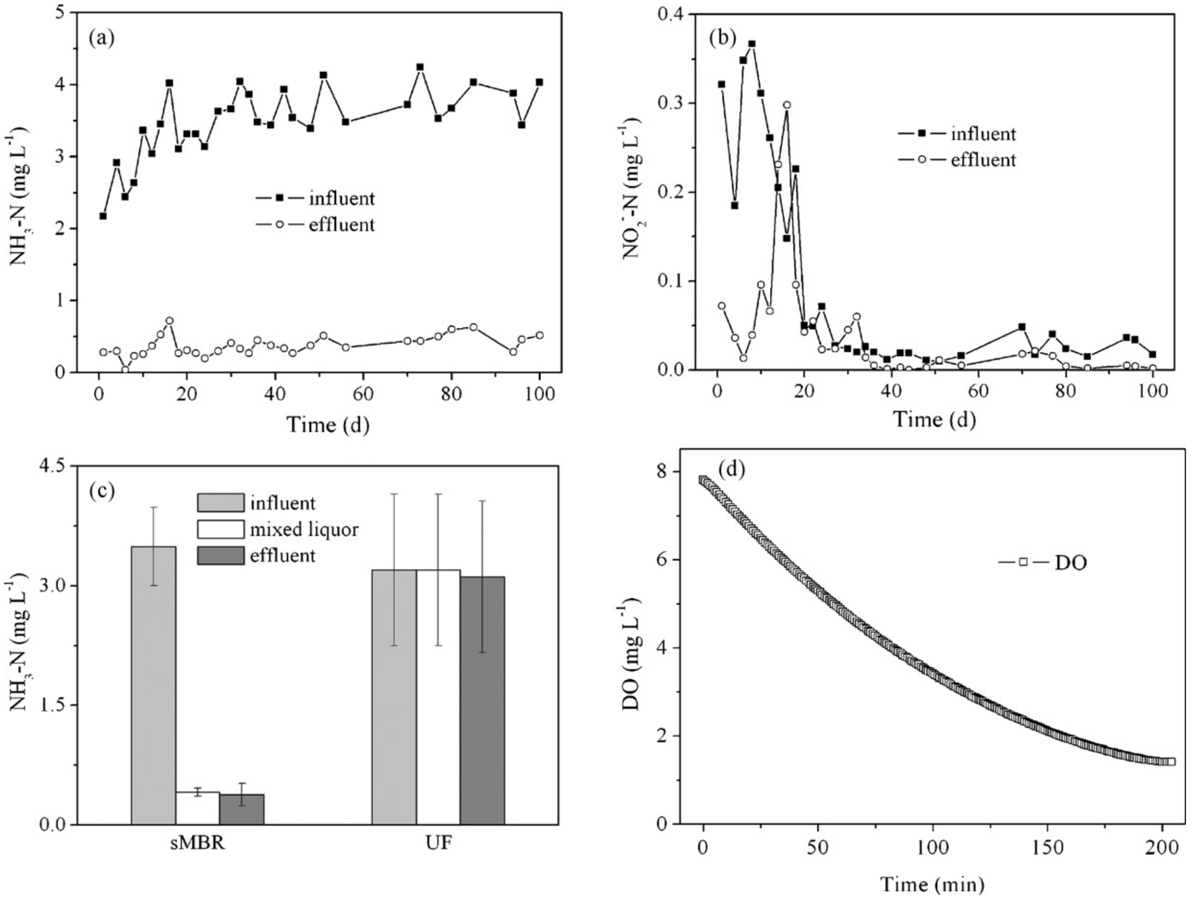

Fig. 2. Removals of NH_3–N (a) and NO_2^-–N (b) by the sMBR; NH_3–N rejection by the UF membrane in the sMBR and a clean one (c); OUR by the nitrifying bacteria in the sMBR (d).

concentration of NO_2^-–N was still as low as 0.042 ± 0.066 mg L^{-1}, which was in comparison with the 0.096 ± 0.117 mg L^{-1} in raw water (Fig. 2b).

To illustrate the removal mechanism of ammonia in the sMBR, the ammonia concentration in the mixed liquor was also investigated. As illustrated in Fig. 2c, 0.41 ± 0.05 mg L^{-1} of NH_3–N was detected in the mixed liquor of the sMBR. This concentration was essentially at the same level of the 0.38 ± 0.14 mg L^{-1} in the effluent, while much lower than the 3.49 ± 0.49 mg L^{-1} in the raw water. Besides, results of the individual UF experiment indicated that the UF membrane used in this study had no capacity for rejecting NH_3–N. Thus, it is reasonable to infer that NH_3–N was eliminated through biological nitrification by the ammonia oxidizing bacteria and nitrite oxidizing bacteria when considering the high DO concentration (7.32 ± 0.17 mg L^{-1}) maintained in the bioreactor of the sMBR.

To determine the activity of nitrifying bacteria in the sMBR, the oxygen uptake rate (OUR) by the nitrifying bacteria was measured in this study. 50 mL of mixed liquor was taken out of the bioreactor and transferred into a conical flask (1 L). Then the flask was fully filled with the pre-aerated NH_3–N solution (4 mg L^{-1}); meanwhile, a DO probe was immediately inserted into the flask. After that, the conical flask was completely sealed. Samples were mixed during the measurement by using a magnetic stirrer at 150 rpm. The DO concentration was recorded with time, which was shown in Fig. 2d. It could be seen that the DO in the flask decreased from initial 7.81 to 1.41 mg L^{-1} after 200 min of DO consumption. Based on the difference of DO concentrations at 2 and 30 min, it might be calculated that the OUR by the nitrifying bacteria in the sMBR amounted to 1.06 μg O_2 mL^{-1} mixed liquor h^{-1}.

3.1.3. Organic matter removal

Total organic matter in water might be classified into particulate organic fraction and dissolved organic fraction. Particulate organic matter (POM) could be easily removed even through the conventional treatment chain (coagulation, sedimentation, and sand-filtration); whereas DOM is one of the major concerns in drinking water treatment due to its difficulty to be removed. During the experiments, the raw water had average DOC and UV_{254} concentrations of 5.398 ± 0.517 mg L^{-1} and 0.086 ± 0.008 cm^{-1}, respectively. As shown in Fig. 3a and b, DOC was reduced to 4.225 ± 0.460 mg L^{-1} (by 21.5 ± 7.0%) through the sMBR treatment; by contrast, only 15.1 ± 4.1% of the influent UV_{254} was removed, with 0.072 ± 0.005 cm^{-1} still remained in the effluent. Furthermore, it could be observed that the removal efficiency of the sMBR for DOM was rather stable during the 110 days of operation. Therefore, it was reasonable to infer that the DOM was removed mainly through biodegradation in the sMBR when taking into account the long SRT of 80 days. On the other hand, some of the refractory organics might also be removed through the sludge withdrawal during mixed liquor sampling and membrane cleaning.

TOC and COD_{Mn} as the surrogate parameters representing the content of total organic substances are widely used in the field of drinking water treatment. Through sMBR treatment, TOC was decreased from 5.952 ± 0.711 mg L^{-1} in raw water to 4.225 ± 0.460 mg L^{-1} in the effluent, with an overall removal efficiency of 28.6 ± 7.3% (Fig. 3c). Furthermore, 4.79 ± 0.56 mg L^{-1} of COD_{Mn} in the raw water was reduced to 3.18 ± 0.42 mg L^{-1} (removed by 33.5 ± 6.3%, Fig. 3d) by the sMBR. It was obvious that the removal efficiency of the sMBR for total organic matter was higher than that for DOM, due to the complete rejection of POM by the membrane.

As the nitrification of ammonia took place in the bioreactor of sMBR, the chlorine demand of the treated water was substantially reduced [26]. Together with the DOM biodegraded by the heterotrophic bacteria as well as the POM rejected by the UF membrane, disinfection by-product formation potential (DBPFP) in the sMBR effluent must be depressed. As illustrated in Fig. 3e, the raw water had average THMFP and HAAFP concentrations of 249.1 ± 18.7 and 168.3 ± 10.9 μg L^{-1}, respectively. 34.1 ± 8.5% of THMFP removal was achieved by the sMBR, with 163.7 ± 19.7 μg L^{-1} as the effluent concentration. While a relatively lower removal efficiency of 24.7 ± 3.9% was obtained for HAAFP, there was still 126.8 ± 12.3 μg L^{-1} in the sMBR effluent.

In order to further investigate the removal of organic matter in relation with the biological stability of finished water and bacterial regrowth in the distribution system, AOC and BDOC in both the influent and the effluent of the sMBR were also examined (Fig. 3f). It could be seen that AOC was decreased from 771.3 ± 145.9 μg L^{-1} in the raw water to 344.4 ± 61.1 μg L^{-1} in the effluent (by 54.9 ± 7.5%); Meanwhile, BDOC was removed by 51.7 ± 12.9% with the reduction from initial 0.576 ± 0.214 to 0.259 ± 0.114 mg L^{-1} in the effluent. The biological stability of the treated water was significantly improved. The results of AOC and BDOC removal by the sMBR may serve as another evidence for the fact that biological process is especially efficient for the elimination of BOM.

From Fig. 3a–d, it could be seen that the sMBR exhibited low organic removal efficiencies in this study. The reason might be that the organic matter in drinking water source is usually bio-refractory in nature. Furthermore, the low HRT (0.5 h) might also contribute to the low organics removal. However, the removal of bio-refractory organic matter is often accomplished by enhanced coagulation and PAC adsorption in drinking water treatment, and the sMBR might be regarded as the substitute to conventional filter. The sMBR could provide additional removal of turbidity, ammonia and BOM, and also provide physical disinfection for the finished water.

3.2. MLSS and MLVSS in the sMBR

The MLSS and MLVSS in the bioreactor of the sMBR were shown in Fig. 4. It could be seen that the MLSS and MLVSS were rather stable during the experimental period, with the average concentrations of 2.85 ± 0.16 and 1.91 ± 0.15 g L^{-1}, respectively. In this investigation, the MLSS was consisted of the PAC, the organic matter adsorbed on the PAC, biomass and inorganic components. No significant accumulation of MLSS in the bioreactor was observed due to the relatively low suspended solids content in the raw water (1.88 ± 0.62 NTU for turbidity), as well as the MLSS withdrawal when membrane cleaning and mixed liquor sampling.

The MLVSS was consisted of not only the biomass, but also the PAC (PAC could be burned to ashes at the temperature of 600 °C for MLVSS measurements) and the organic matter adsorbed on it. Because of the PAC loss when membrane cleaning and mixed liquor sampling, it was difficult to quantify the content of PAC in the mixed liquor and thus the biomass during the experiments. However, from the stable performance of the sMBR for ammonia (Fig. 2a and b) and organic matter (Fig. 3a–d) removal, it might be inferred that the biomass in the bioreactor was also stable.

3.3. TMP developments in the sMBR

In the experiments, the UF membrane flux was set at the constant value of 10 L m^{-2} h^{-1}. The TMP development of the sMBR was shown in Fig. 5. It could be seen that the initial TMP was rather high when compared with that on the 61st day after chemical cleaning of the membrane. The reason was that the sMBR had been operated for a period of time before this investigation was conducted,

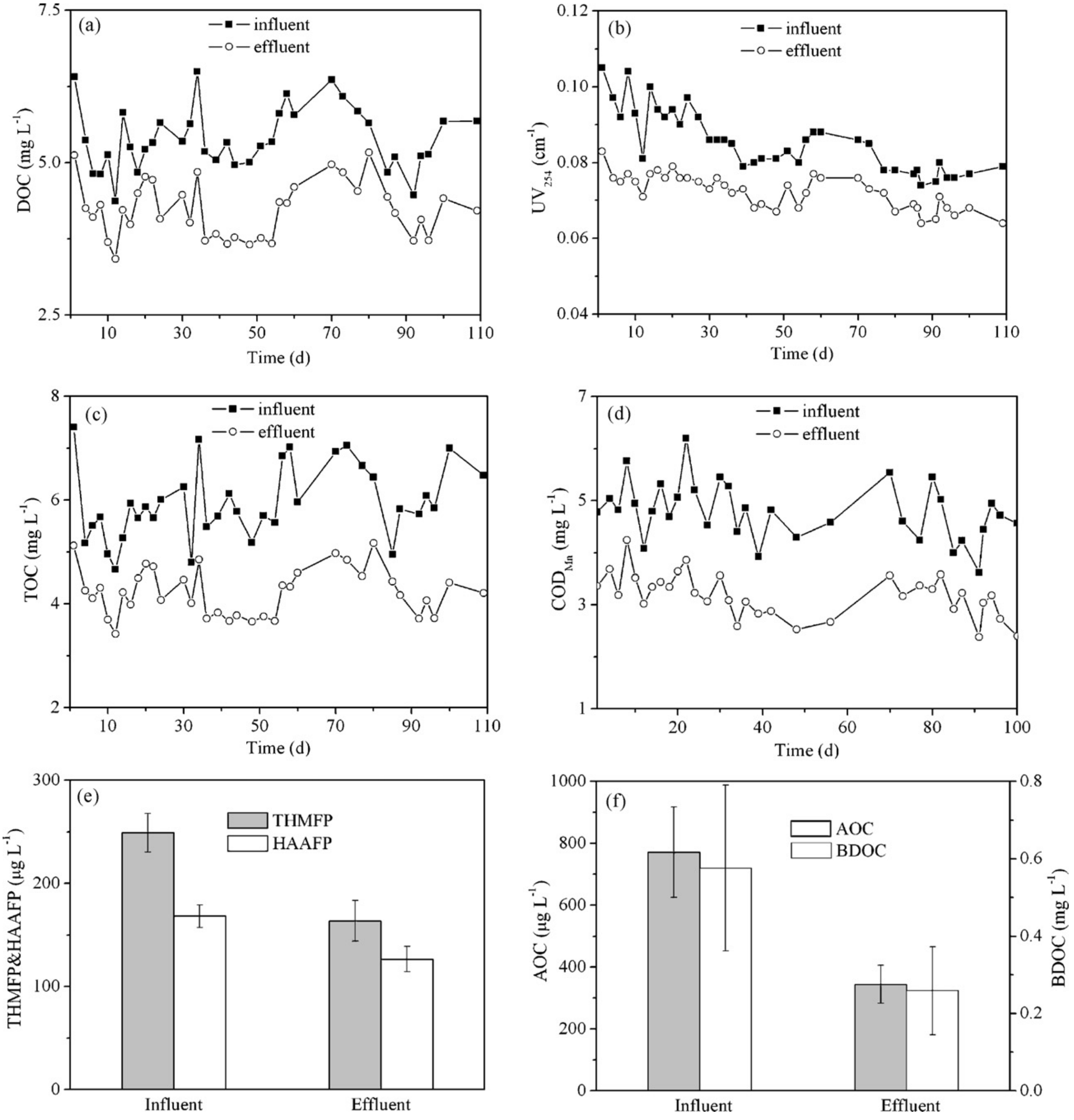

Fig. 3. Removals of DOC (a), UV_{254} (b), TOC (c), and COD_{Mn} (d), as well as THMFP and HAAFP (e), AOC and BDOC (f) by the sMBR.

and the membrane fouling had already been formed on the UF membrane. On the 7th and 34th day, the UF membrane was taken out of the sMBR and physically cleaned by thoroughly flushing and backwashing.

On the 61st day of this investigation, the UF membrane in the sMBR was first physically cleaned, which resulted in the decrease of TMP from 27 to 19 kPa. Then, the membrane was chemically cleaned with the combination of NaOH ($5.0\,g\,L^{-1}$) and NaClO ($200\,mg\,L^{-1}$). The TMP was further decreased to 13 kPa. Based on these values, it could be approximately calculated that the reversible fouling (8 kPa of TMP) accounted for 57.1% of the total membrane fouling (14 kPa of TMP); while irreversible fouling (6 kPa of TMP) contributed to 42.9% of the total fouling. After that, the TMP of the sMBR gradually increased to 28.5 kPa at the end of the study. The TMP developing rate might be calculated as $0.33\,kPa\,d^{-1}$ on average.

3.4. *Mechanism of sMBR for DOM removal*

3.4.1. *Additional filtration function of the sludge layer on the membrane surface*

Apart from in the influent and effluent of the sMBR, DOM in the mixed liquor was also investigated and expressed in terms of DOC and UV_{254}. From Fig. 6, it can be seen that the DOM in the mixed liquor was much higher than that in the effluent. The rejection of the membrane in the sMBR for DOC and UV_{254} reached to 32.3 ± 12.9% and 20.6 ± 5.9%, respectively. However, additional UF experiment showed that clean UF membrane (the same as the one used in the sMBR) only removed 11.1 ± 2.4% of influent DOC and 11.4 ± 1.3% of UV_{254}, which were coincident with the results achieved by other researchers [12–14,36]. This indicated that an enhanced organic removal mechanism might be involved in, which

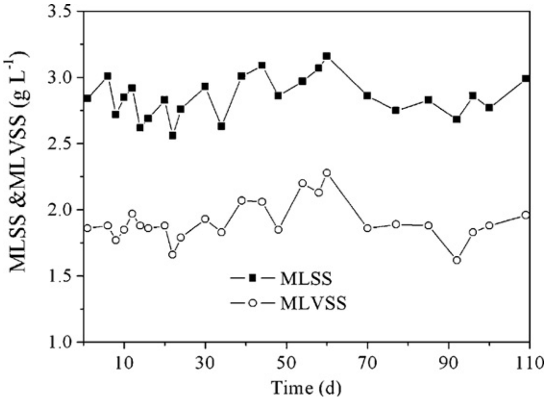

Fig. 4. MLSS and MLVSS in the bioreactor of the sMBR.

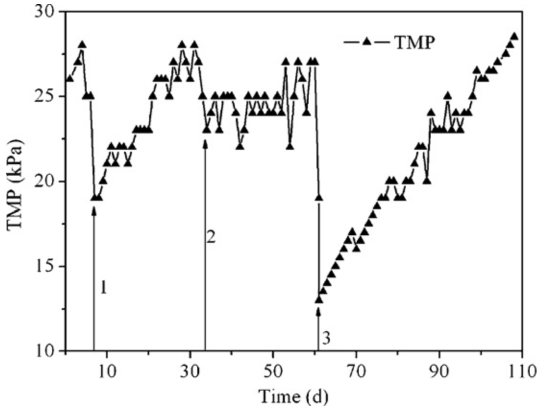

Fig. 5. TMP development in the sMBR (1 and 2: physical cleaning of the UF membrane; 3: chemical cleaning of the UF membrane).

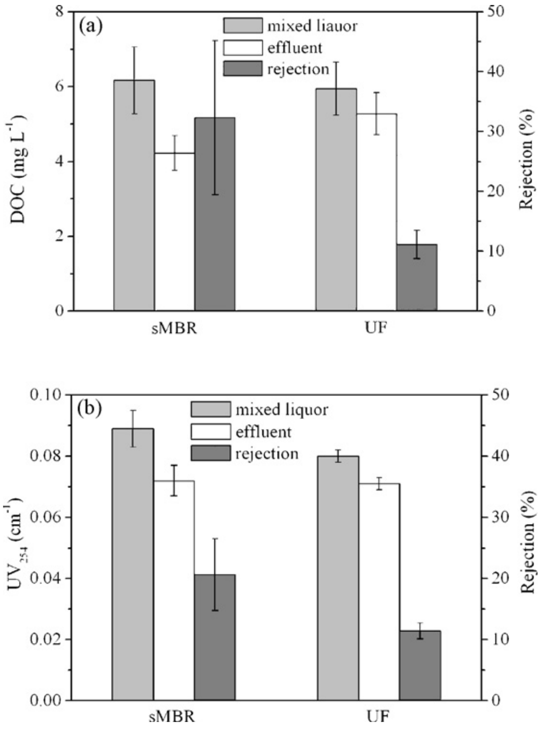

Fig. 6. DOC (a) and UV$_{254}$ (b) in the waters from both the sMBR and the UF systems.

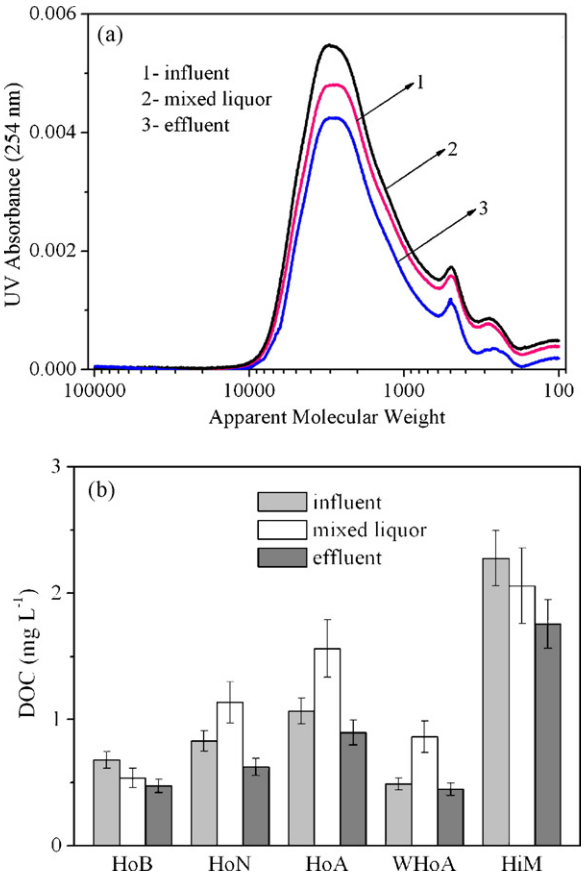

Fig. 7. MW distribution (a) and fractionation (b) of DOM in the waters of sMBR.

was possibly provided by the additional filtration function of the sludge layer formed on the membrane surface during the filtration of the mixed liquor. The sludge layer including a cake layer and a gel layer has been well known as the secondary or dynamic membrane, and been demonstrated to be able to enhance the removal of organic matter and particles in wastewater treatment [37,38]. Here it is also inferred that the sludge layer has the ability to enhance the rejection of the UF membrane for DOM in drinking water treatment.

3.4.2. MW distribution and fractionation of DOM in waters from the sMBR

The apparent MW distributions of DOM in the influent, mixed liquor and effluent of the sMBR were measured by using SEC and given in terms of UV absorbance at 254 nm. As can be seen in Fig. 7a, the intensity of the absorbance peaks in the sMBR effluent was decreased as compared with that in raw water. Whereas the absorbance intensity of UV-active substances in the mixed liquor was much higher than that in the effluent, and even higher than that in the raw water, especially for organic molecules with the MW range of 5000–500 Da. However, the UF membrane used in the sMBR had much larger nominal pore size of 0.01 μm, which approximated to a MWCO of 100,000 Da. Thus, it could be concluded that organic molecules in the range of 5000–500 Da could be effectively rejected by the sludge layer and accumulated in the mixed liquor of sMBR, for further biodegradation by the microorganisms in the bioreactor.

Fractionation of DOM was also conducted for the waters of the sMBR, and the results were illustrated in Fig. 7b. It was obvious that HoN, HoA, and WHoA could be efficiently rejected by the UF membrane together with the sludge layer. These three fractions were in much higher concentrations in the mixed liquor than in the effluent (45.0%, 42.7%, and 48.1% higher, respectively). On the other hand, HoB and HiM in the mixed liquor were only 11.3% and 14.6% higher than that in the effluent, which were at the same level of the rejection capability of clean UF membrane for DOC (11.1%) and UV_{254} (11.4%). Therefore, the conclusion could be drawn that HoN, HoA, and WHoA were effectively retained in the bioreactor by the sludge layer, while HoB and HiM were separated mainly through the UF membrane.

3.4.3. Microscopic observations of the sludge layer

SEM observations of the membrane in the sMBR and a clean one were conducted at the end of the investigation, as shown in Fig. 8. It should be noted that most of the cake layer and even a

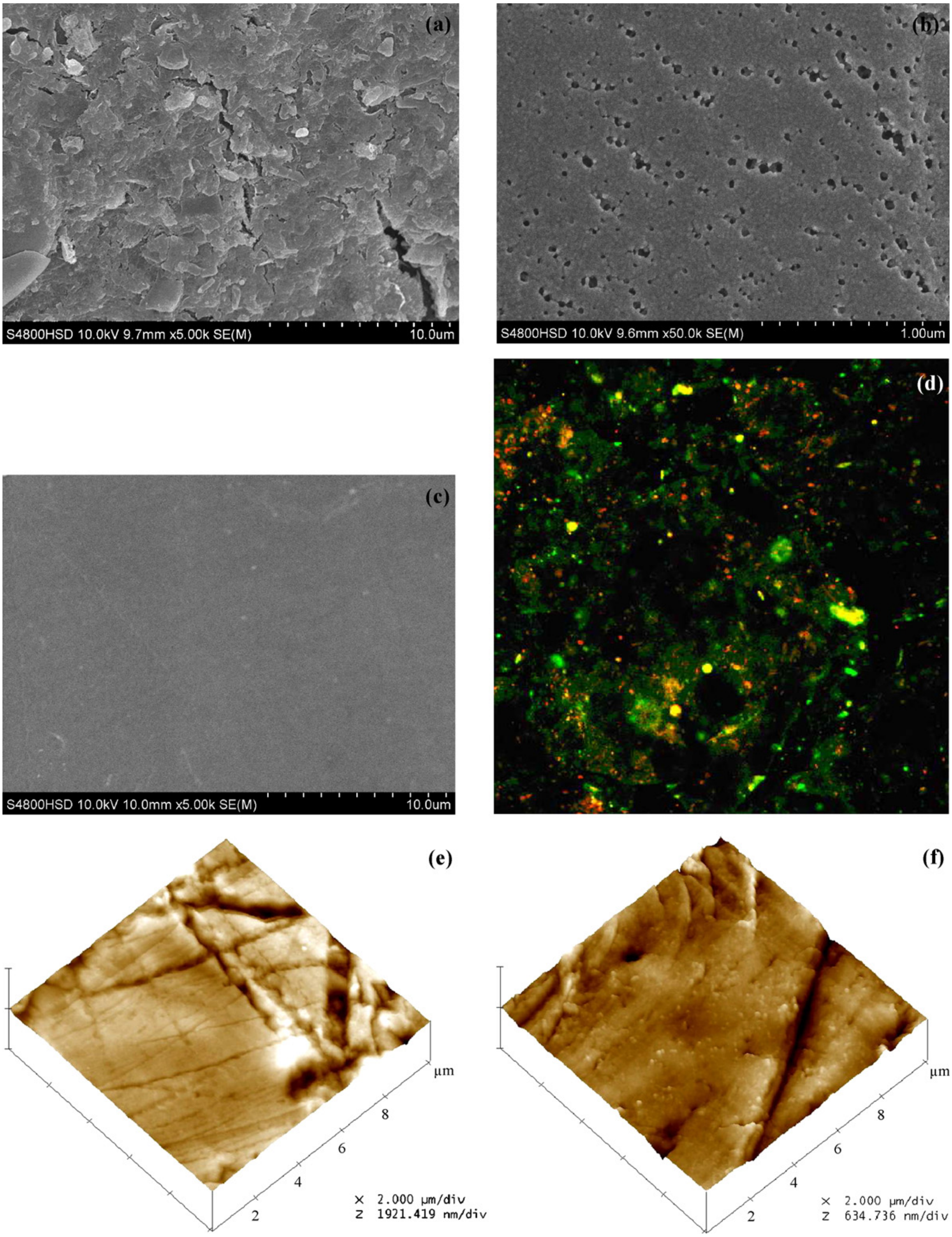

Fig. 8. SEM image of the membrane surface in the sMBR (a); SEM images of clean membrane surface (b) and (c); CLSM image of the sludge layer on membrane surface in the sMBR (d); AFM images of the clean membrane (e); the membrane in the sMBR (f). (For interpretation of the references to color in the text, the reader is referred to the web version of the article.)

part of the gel layer might have been broken off during the samples preparation due to their loose attachment to the membrane, and the sludge layer in the image was mainly comprised of the gel layer. From Fig. 8a, it could be seen that an irregular and rough gel layer was extensively distributed on the surface of the membrane in the sMBR, which was in comparison with the smooth and flat surface of the clean membrane (Fig. 8b and c). The gel layer was found to be mainly consisted of abiotic matter with some microorganisms scattering on it, which appeared to be dense and nonporous.

The result of CLSM observation was shown in Fig. 8d. It could be found that the membrane surface in the sMBR was covered with a polysaccharides (green) layer. Some bacteria (red) was also scattered on it. The polysaccharides might be derived from the metabolic activity of microorganisms in the bioreactor. During the filtration operation, the polysaccharides in the mixed liquor were adsorbed on the membrane surface and formed the gel layer. However, the CLSM image provided support for the observations made from the SEM images.

Three-dimensional AFM images of the clean membrane and the membrane in the sMBR were also taken and compared in Fig. 8e and f. It was clear that the used membrane provided a higher topography than the clean one, which appeared to be covered with a dense gel layer (cake layer might be washed away by MQ water before AFM observation). The evidence from the AFM images was in coincidence with the observations taken from the SEM and CLSM images.

The SEM, CLSM and AFM observations all showed that the membrane surface in the sMBR was covered with an irregular and dense sludge layer. The sludge layer had been demonstrated to be able to provide additional filtration function for the DOM in the mixed liquor in the aforementioned sections. On the other hand, the sludge layer was also known as the fouling layer, which would increase the filtration resistance of the membrane and result in the loss of the membrane permeability, as reflected by the development of TMP (shown in Section 3.3).

During the filtration operation, the sludge layer would inevitably be formed on the membrane surface, which could be controlled through periodically physical and chemical cleaning. From the practical point of view, it is important to optimize the cleaning strategies to take the advantage of the sludge layer and maintain membrane permeability simultaneously.

4. Conclusions

The sMBR experiments for treating a slightly polluted surface water supply were conducted for more than 110 days with a HRT of 0.5 h. The following conclusions could be made:

(1) Nearly complete turbidity removal was exhibited by the sMBR due to the physical separation of the UF membrane.
(2) Perfect ammonia removal (by 89.4 ± 3.4%) was also achieved through the biological nitrification carried out in the bioreactor of the sMBR.
(3) The sMBR decreased influent organic matter by 21.5 ± 7.0%, 15.1 ± 4.1%, 28.6 ± 7.3%, and 33.5 ± 6.3% for DOC, UV_{254}, TOC, and COD_{Mn}, respectively. THMFP and HAAFP were reduced by 34.1 ± 8.5% and 24.7 ± 3.9%, correspondingly. The much higher removal efficiencies of 54.9 ± 7.5% and 51.7 ± 12.9% were obtained by the sMBR for AOC and BDOC.
(4) Through SEM, CLSM, and AFM examinations, a sludge layer was observed to be formed on the membrane surface in the sMBR during the filtration operation. The sludge layer could provide additional filtration function for DOM in the mixed liquor, especially for organic molecules in the MW range of 5000–500 Da. Fractionation of DOM by XAD-8/4 resins indicated that the UF membrane together with the sludge layer was able to reject HoN, HoA, and WHoA by 45.0%, 42.7%, and 48.1%, respectively; while HoB and HiM were separated mainly through the UF membrane, with the efficiencies of 11.3% and 14.6%.
(5) The sludge layer was also known as the fouling layer, which would result in the loss of membrane permeability. Optimization of the cleaning strategies is necessary for maintaining the membrane flux and simultaneously making use of the sludge layer.

Acknowledgments

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