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Experimental test for high saline wastewater treatment in a submerged membrane bioreactor

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ABSTRACT

A submerged membrane bioreactor was used to treat wastewater containing 50% seawater with the conditions as follows: chemical oxygen demand (COD) was 300–2600 mg/L, ammonium-N was 50–300 mg/L, pH was 6.0–9.0, mixed liquor suspended solids (MLSS) was 7,000 mg/L, dissolved oxygen (DO) was 2–4 mg/L, temperature was 20–25°C. The results showed that both COD and ammonium-N removal efficiencies could reach 90% with the optimal conditions as follows: organic loading rates and ammonium-N loading rates were less than 3.2 kg COD m^{-3} d^{-1} and 0.35 kg N m^{-3} d^{-1}, respectively, pH value was between 7.5 and 8.5, hydraulic retention time (HRT) was more than 12 h. Membrane fouling was aggravated because the viscosity of high saline wastewater was higher than that of fresh water. The trans-membrane pressure (TMP) increased from 5 to 44 kPa during first 180 days but dropped dramatically to 8 kPa after the chemical and physical cleaning, and the filtration capacity of the membrane was almost recovered normally.

Keywords: **A** submerged membrane bioreactor; Organic loading rates; Ammonium-N loading rates; pH; HRT; Membrane fouling

1. Introduction

In 2025, two thirds of the world's population will suffer from water scarcity unless a large scale action is taken [1]. Moreover, half of the world's population lives less than 200 km away from the coast and this number may rise to 75% by 2025 [2]. It is necessary to save significant amounts of fresh water by utilizing seawater. For instance, lavatory flushing by seawater instead of tap water is a good way to save the fresh water. In general, about 30% of urban water supply is for domestic consumption, among which lavatory flushing water accounts for 35%. Although it could save 10.5% urban water supply by seawater lavatory flushing, the domestic sewage contains 35% seawater. When such effluent is discharged into the environment without prior treatment, inevitably it can cause severe contamination in soils, surface water and groundwater. As far as saline wastewater treatment is concerned, physicochemical means are adopted usually. However, physicochemical techniques were energy-consuming and their startup and running costs were high [3]. Biological treatment of saline wastewater usually resulted in low chemical oxygen demand (COD) removal

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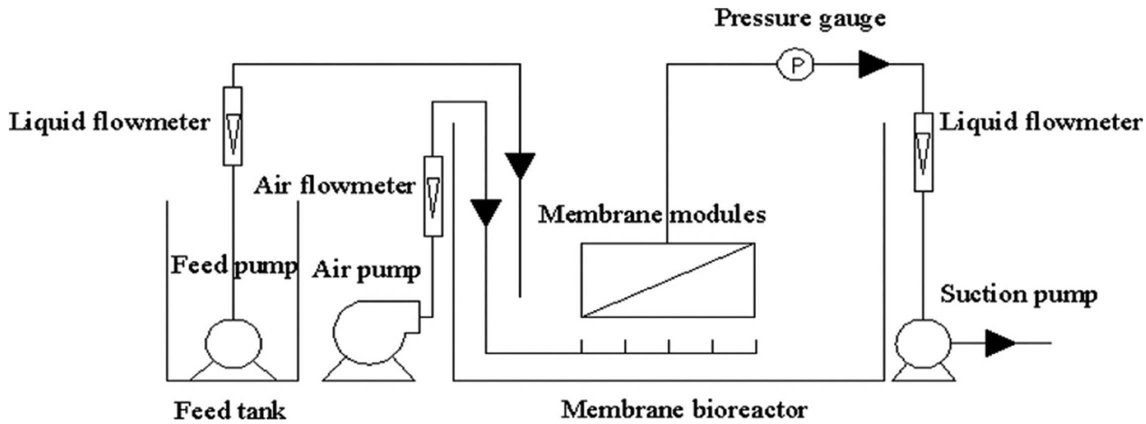

Fig. 1. Schematic diagram of membrane bioreactor.

performance because of adverse effects of salt on microbial flora [4]. High salt concentration (>1% salt) caused plasmolysis and loss of activity of the cells [5]. Other major reports stated that rapid shifts in salt concentrations have more adverse effects than gradual shifts [6–11]. Although biological treatment was inhibited by high salt levels, many studies proved that it was feasible to use salt-adapted microorganisms capable of withstanding high salinities and degrading the pollutants [12]. Moreover, high salinity was known to compromise the correct operation of conventional aerobic wastewater treatment processes only above chloride concentrations of 5–8 g L^{-1} [13]. Also, a variety of processes were applied to treat saline wastewater, such as a conventional aerobic wastewater treatment process [13], a process with aerobic rotating discs [4], a sequencing batch reactor (SBR) [14], a sequencing batch biofilm reactor (SBBR) [15], an anaerobic/anoxic/aerobic process [16], an anaerobic filter [17–19], an upflow anaerobic sludge blanket (UASB) [20] and an anaerobic contact system [21]. The COD and ammonia removal efficiencies obtained with this type of wastewater varied largely.

In view of the stringent discharge criteria, increasing space constraints and desired flexibility for future expansion and upgrade, membrane bioreactor (MBR) process emerged as an innovative and promising solution for wastewater treatment and reclamation. Compared to the conventional activated sludge process, the advantages of MBR were obvious, such as excellent effluent quality, high biomass, low sludge production, small footprint, the separation of solids retention time (SRT) and hydraulic retention time (HRT), and flexibility for future expansion and upgrade [22,23]. However, the performance of high saline wastewater treatment by MBR process was less studied. By employing a MBR to treat saline sewage wastewater, all the biomass could be retained inside the reactor and acclimate to saline surroundings better.

The aim of this work was to study the performance of a MBR treating wastewater which contained 50% seawater (17,500 mg/L salt) and investigate the variation of the COD and ammonium-N removal efficiencies with impact factors such as organic loading rates, ammonium-N loading rates, pH value and HRT.

2. Materials and methods

2.1. Experimental set-up and operating conditions

Fig. 1 shows a flow chart of submerged MBR used in this study. Continuous operation was carried out during the whole experiment. The reactor was equipped with eight hollow-fiber microfiltration (MF) membrane modules (provided by Korean KMS company) which were made of polyethylene with a total surface area of 2.57 m^2 and a nominal pore size of 0.4 μm, and its working volume was 257 L. In the MBR, aeration was continuously carried out, and filtration was intermittently carried out (7 min filtration and 3 min pause) using suction pump. The bubbles pushed the sludge to flow upward between the membrane modules to minimize membrane fouling. The MLSS concentration in the MBR was maintained at 7,000 mg/L by extracting excess sludge. Dissolved oxygen and temperature sustained at 2–4 mg/L and 20–25°C, respectively. The flowrate varied between 17 and 45 L/h, and the aeration intensity was 5–7 m^3/h. The HRT was changed by modifying influent flowrate. When the HRT varied between 6 and 15 h, the influent flowrate was modified as shown in Table 1. However, if the flowrate was changed, the organic and ammonium-N loading rates were changed as well. In order to fix the organic and ammonium-N loading rates (3.2 kg COD m^{-3} d^{-1} and 0.35 kg N m^{-3} d^{-1}) as

Table 1
Variation of influent flowrate, COD and ammonium-N concentration with different HRT

HRT (h)	6	7	8	9	10	11	12	13	14	15
Flowrate (L/h)	42.8	36.7	32.1	28.5	25.7	23.4	21.4	19.8	18.4	17.1
COD (mg/L)	798	931	1064	1197	1330	1463	1596	1729	1862	1995
Ammonium-N (mg/L)	90	105	120	135	150	165	180	195	210	225

Part 3.4 required, the influent COD and ammonium-N concentrations were modified. Corresponding to the different HRT, the modifying influent COD and ammonium-N concentrations are shown in Table 1.

2.2. Composition of synthetic wastewater

The synthetic feed was prepared with seawater, soybean milk, NH_4Cl, KH_2PO_4 and Na_2CO_3. In this study, varying organic and NH_3-N loading rates were obtained by changing COD and NH_3-N concentrations which were 300–2600 mg/L and 50–300 mg/L respectively. The seawater accounted for 50%, and correspondingly the salinity and chloride content were 17,500 and 9,500 mg/L, respectively.

2.3. Analytical methods

Samples were withdrawn from the liquid media at the beginning and at the end of each treatment period and were centrifuged at 6,000 rpm for 30 min to remove microorganisms from the liquid medium. Sufficient amounts of $HgSO_4$ were added to precipitate chloride ions into $HgCl_2$ in order to avoid chloride ion interfering with COD measurement. The COD, NH_3-N contents of the supernatants were analyzed according to standard methods [24]. Samples were analyzed in triplicate and mean values were reported. DO and pH measurements were done by using the relevant probes and analyzers (METTLER TOLEDO FiveGo^{TM} DO meter and METTLER TOLEDO FE20 pH meter). Samples were centrifuged to separate saline water from the biomass and the washed salt-free organisms were used to determine the biomass concentrations. The biomass was determined by filtering the washed salt-free samples through 0.45 μm membrane filter and drying the washed salt-free organisms in an oven at 105°C to constant weight.

Scanning electron microscopy (SEM) observations were also performed. For SEM observation, the samples were fixed in a 2.5% (v/v) glutaraldehyde solution, dehydrated in grading water-ethanol solutions, dried under vacuum conditions and then sputter-coated with gold before SEM pictures were taken with a JEOL JSM-500LV microscope.

The cooling extraction method, which is described as follows, was applied for the extraction of the extracellular polymeric substances (EPS) from the sludge. For the EPS analysis, 2 mL of sludge were centrifuged, removed of supernatant, added with 10 ml of 0.85% NaCl solution and 60 mL formalin. The EPS in this mixed liquor was extracted with ultrasonication for 300 s while being cooled in ice water. After being centrifuged at 12,000 rpm for 30 min, the supernatant was analyzed for polysaccharide and protein, which were regarded as the main parts of EPS materials. Polysaccharide was determined by a sulphuric acid-anthrone method and protein was analyzed according to the Lowry Folin method [25].

2.4. Inoculum

The seed sludge was taken from Qingdao Municipal Wastewater Treatment Plant (Tuandao Road, Shinan District). The mixed microbial community was composed of heterotrophic organisms which were capable of oxidizing carbonaceous compounds and denitrification and autotrophic nitrifying organisms. Microbial culture and acclimation could be divided into five phases according to the seawater percentage (10%, 20%, 30%, 40% and 50%) in the wastewater, and the salinities in the five phases were 3,500, 7,000, 10,500, 14,000 and 17,500 mg/L, respectively. One phase did not start until the last phase was performed steadily. The duration of each phase varied from three to five weeks. The organic loading rates and ammonium-N loading rates were below 3.2 kg COD m^{-3} d^{-1} and 0.35 kg N m^{-3} d^{-1} respectively.

2.5. Membrane cleaning

Membrane fouling occurred inevitably during the MBR process, and it could be indexed by an increase of trans-membrane pressure (TMP). When the TMP was above 40 kPa, membrane cleaning was performed. First of all, a sludge cake was flushed out by tap water. Secondly, membrane modules were cleaned chemically by mixed solution of NaClO and NaOH (effective Cl 3,000 mg L^{-1}, NaOH 500 mg L^{-1}, pH = 11.5). Finally, the modules were dipped into distilled water for 8 h.

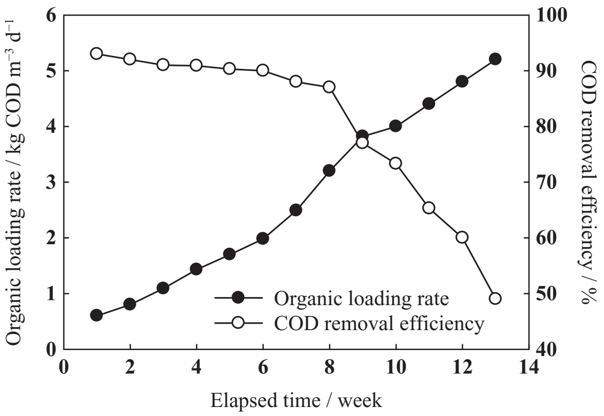

Fig. 2. COD removal efficiency with different organic loading rates.

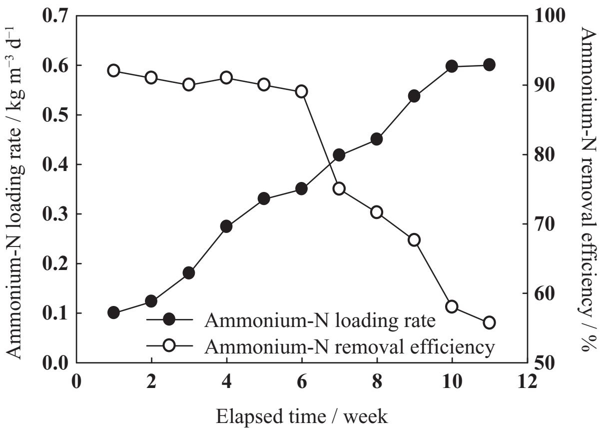

Fig. 3. Ammonium-N removal efficiency with different ammonium-N loading rates.

3. Results and discussion

3.1. COD removal in different organic loading rates

Organic loading rate which affects microbial growth and activity is a key factor during the wastewater treatment process. Experiments were performed at different COD loading rates varying from 0.6 to 5.2 kg COD m^{-3} d^{-1}. Fig. 2 depicted the variation of COD removal efficiency with feed organic loading rates. Obviously, COD removal efficiency decreased when organic loading rates increased. The decrease was steeper at high COD loading rates. When organic loading rates were no more than 3.2 kg COD m^{-3} d^{-1}, COD removal efficiency could be kept at 90%. On one hand, MBR featured higher MLSS which consisted of a variety of microorganisms, so the system could resist salt inhibition better. On the other hand, refractory matters could be rejected both by membrane and biofilm affiliated on the membrane surface, so the COD removal by the whole system was more than that by microbes only. However, COD removal efficiency dropped to 49% when the organic loading rate arrived at 5.2 kg COD m^{-3} d^{-1}. In order to make the COD removal efficiency above 90%, organic loading rate should maintain below 3.2 kg COD m^{-3} d^{-1}.

3.2. Ammonium-N removal in different ammonium-N loading rates

Salinity and ammonium-N loading rate are two major factors in terms of ammonium removal. With fixed salinity (17,500 mg/L), experiments were performed at different ammonium loading rates varying from 0.1 to 0.6 kg N m^{-3} d^{-1}. Fig. 3 showed that ammonium removal efficiency decreased with increasing ammonium loading rates. When ammonium loading rates were lower than 0.35 kg N m^{-3} d^{-1}, ammonium removal efficiency could arrive at 90%. Nitrifying bacteria belonged to autotrophic organisms which reproduced much slower than heterotrophic ones. Therefore their generation cycles were far longer than heterotrophic organisms'. In conventional activated sludge process, they were prone to be washed out and difficult to enrich. Although the membrane which was utilized by MBR failed to reject ammonia, it could hold all nitrifiers in the reactor. As a result, autotrophic nitrifying bacteria could be enriched in the reactor and take longer time to acclimate to the saline surroundings than they were in conventional activated sludge process. However, ammonium removal efficiency decreased noticeably with increasing loading rates, and finally removal efficiency dropped to 55% when the ammonium loading rate attained 0.6 kg N m^{-3} d^{-1}.

3.3. Effect of pH value on COD and ammonium-N removal

Both microbial activity and metabolism are affected by pH value, which in turn affects wastewater treatment process. Experiments were performed at fixed salinity (17,500 mg/L), and organic and ammonium-N loading rates were kept at 3.2 kg COD m^{-3} d^{-1} and 0.35 kg N m^{-3} d^{-1}, respectively. Fig. 4 depicted the COD and ammonium-N removal efficiency with pH value. Effect of pH value on COD removal was less than that on ammonium-N removal. When pH value fluctuated between 6.5 and 8.5, COD removal efficiency could remain 90% steadily. However, COD removal efficiency decreased obviously when pH value was below 6.5 or above 8.5. When pH value fluctuated between 7.5 and 9.0, ammonium-N removal efficiency could be kept at 90%. However, ammonium-N removal efficiency decreased noticeably with decreasing pH value, and dropped to 35% when the pH value was 6.0. Considering comprehensive effect on COD and

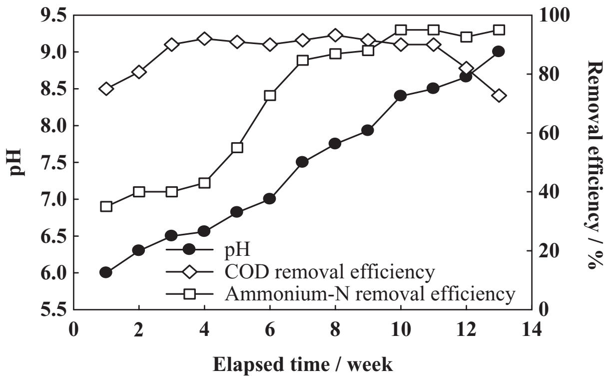

Fig. 4. COD and ammonium-N removal with different pH value.

ammonium-N removal, pH value should be controlled between 7.5 and 8.5 when MBR process was adopted to treat wastewater containing 50% seawater.

In saline surroundings, both the activity and growth of organisms were inhibited. In order to combat the salt inhibition, microbes secreted extracellular polymeric substances (EPS) to protect themselves. At the beginning, the activated sludge was inoculated into the reactor, and the MBR was operated without seawater. During this period, the EPS content was about 0.28 g/gMLVSS, and the activated sludge structure was loose as Fig. 5(left) shown. When the reactor was run for 35 weeks with 50% seawater, however, the EPS content was 0.57 g/gMLVSS. This agreed with early research that high salinity greatly increased EPS content [26]. Extracellular polymeric substances made microorganisms adhere to each other tightly, and the activated sludge structure was kept compact as Fig. 5(right) shown. This could resist the salt inhibition better. What's more, the activated sludge which formed compact structure could also endure higher pH value. However, in regard with the optimum pH for ammonium removal, the range of pH in which good ammonium removal was achieved in the MBR was seemed to be slightly higher than in usual biological ammonium removal systems treating municipal wastewater. This was interesting and deserved further study.

3.4. Effect of HRT on COD and ammonium-N removal

HRT is a key parameter in MBR process, not only because system performance but because reactor volume is associated with it. Salinity was fixed at 17,500 mg/L, and organic and ammonium-N loading rates remained at 3.2 kg COD m^{-3} d^{-1} and 0.35 kg N m^{-3} d^{-1} respectively. Fig. 6 showed the COD and ammonium-N removal efficiency with HRT. COD removal efficiency could be kept at 90% steadily, when HRT was above 9 h. However, when HRT decreased, COD removal efficiency dropped steeply. Otherwise, Ammonium-N removal efficiency was more affected than COD removal efficiency by HRT. It could not attain 90% when HRT was below 12 h. When the wastewater contained lots of organic substrates, heterotrophic organisms which were capable of oxidizing carbonaceous compounds could outcompete autotrophic nitrifying organisms. COD was removed prior to ammonium. When most organics were degraded, nitrifiers became active and ammonium-N removal was efficient. The ammonium-N removal lagged behind the COD removal. Therefore, in view of comprehensive effect on COD and ammonium-N removal, HRT should be above 12 h.

3.5. Membrane fouling and cleaning

Membrane fouling occurred inevitably during the MBR process. Viscosity of high saline wastewater is much higher than that of fresh water. In order to achieve steady flux, operating pressure had to be enhanced. This aggravated membrane fouling. The membrane fouling of the MBR could be indexed by an increase of

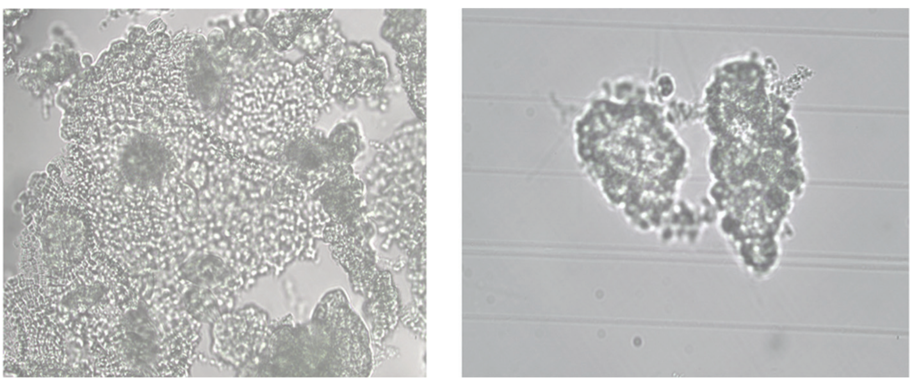

Fig. 5. Micrographs of sludge structure in wastewater without seawater (left) and with 50% seawater (right).

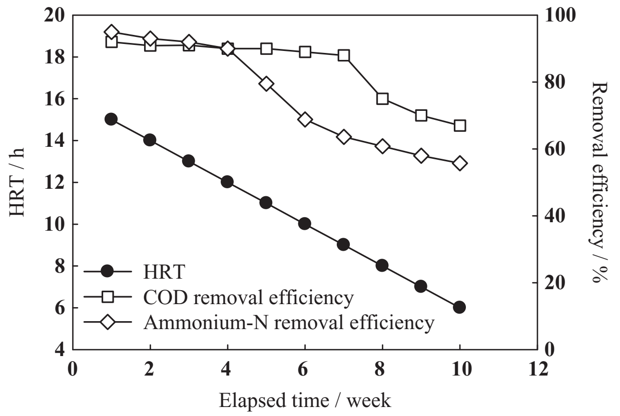

Fig. 6. COD and ammonium-N removal with different HRT.

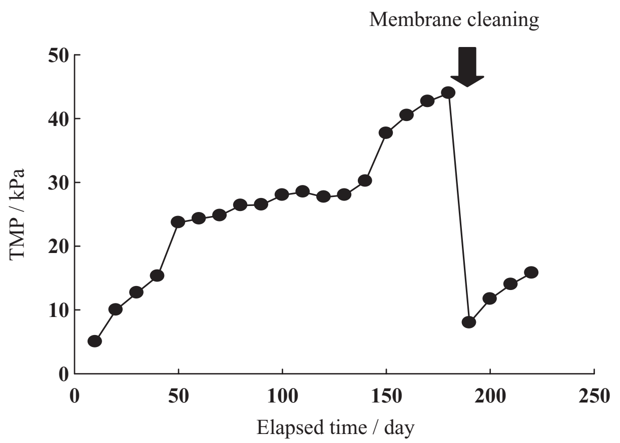

Fig. 7. Variation of TMP with operating days.

TMP. Fig. 7 showed that the TMP increased from 5 to 44 kPa during first 180 days of operation. Then membrane cleaning was performed. After the physical and chemical cleaning, the TMP dropped dramatically to 8 kPa and the filtration capacity of the membrane was almost recovered completely. SEM images of fouled membrane surface were taken before and after cleaning shown as Fig. 8. Before cleaning, the membrane pores were not clear and many organics and microorganisms deposited on the membrane surface. After cleaning, the organics and microorganisms deposited on the membrane surface decreased greatly and the membrane pores were nearly visible again. Therefore, the results proved that microorganisms and organics contributed to the membrane fouling.

4. Conclusions

This study focused on the long-term performance of a continuously fed and aerated MBR treating wastewater containing 50% seawater. COD and ammonium-N removal efficiencies were evaluated when several key factors like organic loading rates, ammonium-N loading rates, pH value and HRT varied. The optimal conditions for the MBR process were as follows: (a) organic and ammonium-N loading rates should be lower than 3.2 kg COD m^{-3} d^{-1} and 0.35 kg N m^{-3} d^{-1} respectively; (b) pH value should be controlled between 7.5 and 8.5; (c) HRT should be no less than 12 h. Under the optimal conditions, COD and ammonium-N removal efficiencies could be kept at 90% steadily. Membrane fouling was aggravated because viscosity of high saline wastewater was much more than that of fresh water. The TMP increased obviously from 5 to 44 kPa during first 180 days. After chemical and physical cleaning, the TMP dropped dramatically to 8 kPa and the filtration capacity of the membrane could recover again.

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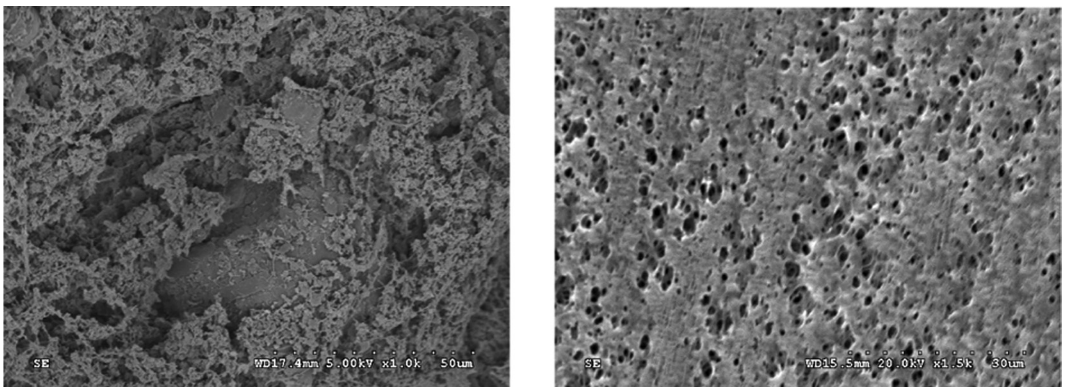

Fig. 8. SEM images of membrane surface before (left) and after (right) membrane cleaning.

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