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Effect of powdered activated carbon on Chinese traditional medicine wastewater treatment in submerged membrane bioreactor with electronic control backwashing

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Abstract

Chinese traditional medicine wastewater, rich in macromolecule and easy to foam in aerobic biodegradation such as Glycosides, was treated by two identical bench-scale aerobic submerged membrane bioreactors (SMBRs) operated in parallel under the same feed, equipped with the same electronic control backwashing device. One was used as the control SMBR (CSMBR) while the other was dosed with powdered activated carbon (PAC) (PAC-amended SMBR, PSMBR). The backwashing interval was 5 min. One suction period was about 90 min by adjusting preestablished backwashing vacuum and pump frequency. The average flux of CSMBR during a steady periodic state of 24 d (576 h) was 5.87 L/h with average hydraulic residence time (HRT) of 5.97 h and that of PSMBR during a steady periodic state of 30 d (720 h) was 5.85 L/h with average HRT of 5.99 h. The average total chemical oxygen demand (COD) removal efficiency of CSMBR was 89.29% with average organic loading rate (OLR) at 4.16 kg COD/($m^3 \cdot d$) while that of PSMBR was 89.79% with average OLR at 5.50 kg COD/($m^3 \cdot d$). COD concentration in the effluent of both SMBRs achieved the second level of the general wastewater effluent standard GB8978-1996 for the raw medicine material industry (300 mg/L). Hence, SMBR with electronic control backwashing was a viable process for medium- strength Chinese traditional medicine wastewater treatment. Moreover, the increasing rates of preestablished backwashing vacuum, pump frequency, and vacuum and flux loss caused by mixed liquor in PSMBR all lagged compared to those in CSMBR; thus the actual operating time of the PSMBR system without membrane cleaning was extended by up to 1.25 times in contrast with the CSMBR system, and the average total COD removal efficiency of PSMBR was enhanced with higher average OLR.

Key words: electronic control backwashing; powdered activated carbon; membrane bioreactor; aerobic process; wastewater treatment

Introduction

Membrane bioreactor (MBR) is an improvement on the activated sludge process in which solid separation is achieved without the requirement of a secondary clarifier, and it is now widely used for municipal and industrial wastewater treatment (Benitez *et al*., 1995; Buisson *et al*., 1998; Cote *et al*., 1998; Cornelissen *et al*., 2002; Rosenberger *et al*., 2002). Although MBRs offer many advantages over conventional processes, such as small footprint and better effluent quality, membrane fouling remains a major drawback. Membrane fouling is mainly associated with the deposition of a filter cake or fouling layer onto the membrane surface, thus limiting the permeate flux. Fouling leads to frequent cleaning or replacement of membranes, which in turn increases operating costs (Gander *et al*., 2000).

Various methods have been adopted to control fouling during the operational cycle of the MBR process. Since the bubbles generated by aeration are essential for suppressing the build-up of the cake, most submerged MBRs (SMBRs) adopt a configuration allowing the membrane surface to contact intimately with the air bubbles, which then induce a moderate shear stress (Benitez *et al*., 1995; Wen *et al*., 1999; Hong *et al*., 2002; Chua *et al*., 2002). Periodic backwashing improves membrane permeability and reduces fouling, thus leading to optimal, stable hydraulic operating conditions (Bouhabila *et al*., 2001; Albasi *et al*., 2002). Adding powdered activated carbon (PAC) to a SMBR with intermittent suction reduces membrane fouling effectively in a long-term operation, and operating intervals can be extended about 1.8 times compared to that without PAC (Li *et al*., 2005).

This study focused on an understanding of the feasibility of operating SMBR with an electronic control backwashing on Chinese traditional medicine wastewater treatment, which is difficult to be treated by aerobic biodegradation because it is rich in the easy-to-foam medium that leads to solid loss and because of the presence of molecules

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with large molecular weight that are hard to biodegrade. The effect of adding PAC was also explored by comparing filtration characteristics of the SMBRs with and without PAC, in bulk under the same feed.

1 Materials and methods

1.1 Membrane and bioreactor

Experiments were carried out with two identical SMBRs equipped with same electronic control backwashing device operating in parallel. Both were set to the same effective volume with the same feed tank and the same water-level equilibrium box. One SMBR was used as the control (control SMBR, CSMBR) while the other was dosed with PAC (PAC-amended SMBR, PSMBR). Bench-scale rigs (Fig.1) of each SMBR comprised a rectangular tank of 500 mm × 200 mm × 500 mm having an effective volume of 35 L, with a vertical-mounted submerged hollow fiber membrane module (Hangzhou Zheda Hyflux Hualu Membrane Tec. Co., Ltd., China). The membrane was made of polypropylene with a pore size of 0.1 μm, and its molecular weight cut-off was approximately 80 kDa. Each membrane module had a filtration area of 1 m^2. Both membrane modules had been used for several months prior to this study, they were thoroughly washed and backwashed in situ with a 1.5% (w/v) NaClO solution until results from the tap water trials showed that the two SMBR systems had almost the same initial filtration resistance before the operation commenced.

1.2 Sewage

Settled sewage was a dilution of the Chinese traditional medicine industrial wastewater collected directly from the product line in the Harbin No.2 Chinese Traditional Medicine Plant. The wastewater was rich in macromolecule that was difficult to be treated and easy to foam in aerobic biodegradation, such as Glycosides, so it was diluted with tap water before feeding to the reactors in view of the fact that the aerobic SMBRs would be foaming sharply and avoid overloading with strong feed. Chemical oxygen demand (COD) concentration in the wastewater ranged from 143682.2 to 586479.8 mg/L, and was diluted to 574.8–3201.3 mg/L as required in feed. pH value of the wastewater ranged from 6.75 to 7.54 and the dilution showed a relatively stable neutral pH without regard to dilution rates. BOD/COD fluctuated between 0.32 and 0.37 in both the wastewater and the dilution, while the COD:TN:TP remained about 258:3:1.

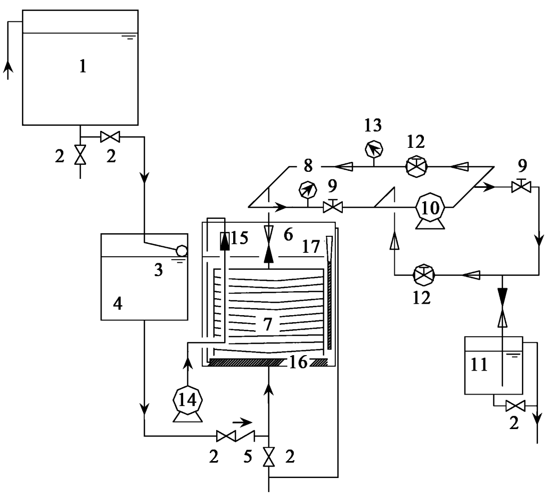

Fig. 1 Schematic diagram of the experimental device. (1) highly placed feed tank; (2) gate valve; (3) float-controlled valve; (4) water-level equilibrium box; (5) rewound valve; (6) bioreactor; (7) hollow-fiber membrane module; (8) triggered vacuum gauge; (9) normally open solenoid valve; (10) pump; (11) backwashing tank; (12) normally closed solenoid valve; (13) pressure gauge; (14) air compressor; (15) air flow meter; (16) diffuser; (17) electric heater.

1.3 Seed sludge

The reactors were seeded with the activated sludge collected from the return-sludge line of the conventional activated sludge process in the Harbin No. 2 Chinese Traditional Medicine Plant. It was introduced evenly into PSMBR and CSMBR. Each 35 L SMBR contained 12.5 L sludge and the remaining parts were filled with tap water. An electric heater inside the reactor was opened, to maintain the bioreactor temperature at 25±1°C. An air-diffuser was placed under the membrane modules so that an uplifting two-phase flow of bubbling air and mixed liquor could remove the fouling layer formed on the membrane. In order to abate solids loss caused by foam, airflow was controlled using a flow meter (Model LZB, Tianjin Wuhuan, China), with an airflow rate fixed at approximately 12–15 L/min. PAC was sieved (100–120 mesh) and rinsed several times to remove impurities. After seeding the reactors, 87.5 g PAC was added to PSMBR immediately; hence the initial PAC concentration was 2500 mg/L. The reactors were then allowed to stabilize for 6 h without further modification before starting the experiments.

1.4 Suction and backwashing

The electric switch box used was composed of two digital display-timing relays, two microminiaturized counter-type electronic timer totalizers, and eight switches.

Suction flow is indicated with solid arrowheads in Fig.1. Constant-flux filtration was carried out using an electromagnetic metering pump (ES-B30, Iwaki, Japan) on the permeate stream. The reading of the triggered vacuum gauge mounted up while membrane fouling got worse. A connection signal was send out when the reading pointer touched the upper limit, which pointed at the preestablished backwashing vacuum, and then the normally open solenoid valves closed while the normally closed solenoid valves opened, hence the pipeline was switched from suction flow to backwashing flow. Counter-type electronic timer stopped at the same time and the reading showed the time of one suction period.

Hollow arrowheads in Fig.1 show the flow of backwashing. Backwashing was completed using effluent stored in a backwashing tank. The backwashing interval was controlled by the display-timing relay, which sent out a connection signal at the end of backwashing. Then the normally open solenoid valves opened while the normally closed solenoid valves closed. Thus the pipeline was switched from backwashing flow to suction flow, and the counter-type electronic timer restarted to count time once again.

Bubbling is only partially efficient, as bubbles are capable of limiting particle deposition and polarization phenomena, but not internal fouling. For given conditions of aeration, periodic backwashing gave an additional efficiency by decreasing internal fouling (Bouhabila *et al*., 2001; Albasi *et al*., 2002). Pump frequency and aeration rate was not increased but remained unchanged during backwashing considering economy and facilitation. Thus membrane fouling was lightened by the cooperation of aeration and backwashing, which was an optimal way to reduce fouling. The backwashing interval was 5 min.

1.5 Sampling

Three samples were collected everyday, namely: influent, supernatant, and effluent. The supernatant was obtained by filtering a sample of mixed liquor through a filter paper of 1.6 μm. The role of the supernatant was to distinguish between microbial removal that occurred within the activated sludge itself, and removal that was attributable solely to the membrane (which includes fouling layer). Thus, the difference in microbial concentration between the influent and the supernatant represents microbial removal by activated sludge, while the difference between the supernatant and the effluent represents microbial removal by membrane. Group data that comprised pump frequency, flux, vacuum, preestablished backwashing vacuum and reading of counter-type electronic timer recorded at 10 min after a suction period began, as the suction period was going to end, and at 10 min after the next suction period began, was collected twice a day at different time. The data collection interval between CSMBR and PSMBR was less than 30 min.

No wasting of biomass took place except for sampling, thereby giving an infinite solid retention time (SRT). Dissolved oxygen (DO) concentration in the both SMBRs was maintained at 2.54–3.90 mg/L. Microscopic observation confirmed that there was no bulking sludge rudiment caused by filamentous organisms in both SMBRs throughout the trial.

1.6 Analytical items and methods

All items on the quality of the influent, supernatant, and effluent, together with the mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were measured according to the standard methods (American Public Health Association, 1995). Bacteria in the bioreactors were observed with a light-level microscope (CX31PTSF, Olympus, Philippines). DO and the temperature in the bioreactors were measured with a DO meter (Oxi 330i, WTW, Germany). Scanning electron microphotographs of the fouled membrane fiber were taken by a scanning electron microscope (JSM-840, JEOL, Japan) after preparation following the standard procedure.

2 Results and discussion

2.1 Flux, pump frequency, and preestablished backwashing vacuum

Membrane was fouled in bioreactor by the accumulation of mixed liquor components on the internal and external structures of the membrane. By means of optimizing the control of backwashing interval, preestablished backwashing vacuum and pump frequency, flux and hydraulic residence time (HRT) could be fluctuated within a range, and thus fouling could be remedied by the cooperation of backwashing and aeration. As time went by, the greater the membrane fouling, the greater the readings of the triggered vacuum gauge, and the smaller the flux. Hence, suction period became shorter and backwashing frequent, as preestablished backwashing vacuum and pump frequency remained stable. Thus the total effluent quantity fell quickly, which was definitely uneconomical. Therefore it was necessary for preestablished backwashing vacuum and pump frequency to be adjusted in time according to the variation of flux and vacuum. Owing to the wastewater characteristics, long HRT was required to keep low organic loading rate (OLR). One suction period was about 90 min by adjusting preestablished backwashing vacuum and pump frequency. The average flux of CSMBR during a steady periodic state of 24 d (576 h) was 5.87 L/h and that of PSMBR during a steady periodic state of 30 d (720 h) was 5.85 L/h (Fig.2a). Therefore, the average HRT of CSMBR was 5.97 h, while the average HRT of PSMBR was 5.99 h.

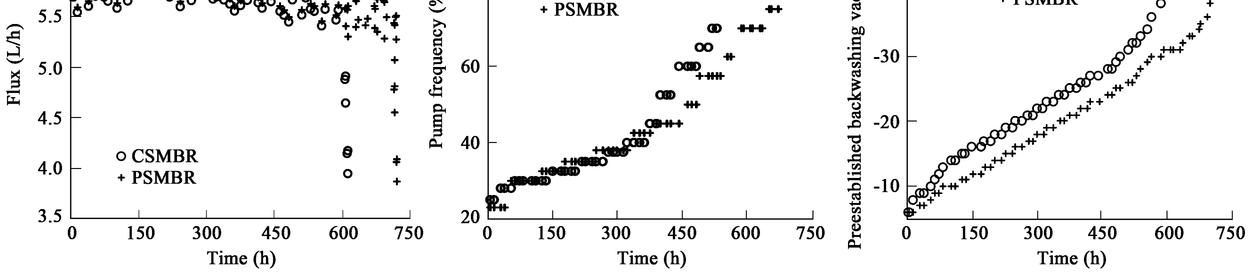

Fig. 2 Flux (a), pump frequency (b) and preestablished backwashing vacuum (c) in PSMBR and CSMBR.

Because of long-term contact, with almost zero wastage except for sampling, the combination of deposited foulants and membrane material became more consolidated, which led to a progressive blocking of membrane pores, thus reducing the effective filtration area. Moreover, a loss of effective filtration area by fouling would increase local flux in some regions of the membrane, which might reach critical local filtration conditions. A rapid deposition of particles and colloidal aggregation on the membrane led to the formation of a cake layer and a sharp increase in preestablished backwashing vacuum. Finally, the cake layer became thicker and more compact with long-term operation, leading to a rapid increase in hydraulic filtration resistance. In this case, the cake is the real filtering barrier, providing a hydraulic filtration resistance, which is much higher than that of the membrane. On day 25, flux of CSMBR descended sharply even as pump frequency rose to 100%, which meant the membrane inside needed to be regenerated, so CSMBR stopped with preestablished backwashing vacuum at –48 kPa. However, PSMBR continued operating for the next 6 d and stopped on day 31 with preestablished backwashing vacuum at –50 kPa for the same reason. The actual operating time of the PSMBR system without membrane cleaning was extended by up to 1.25 times in contrast with the CSMBR system under long-term operation conditions. And both preestablished backwashing vacuum and pump frequency of CSMBR were higher than those of PSMBR (Figs.2b and 2c)) during the first 25 d. This indicated that adding PAC into the SMBR could reduce the accumulation of foulants on the membrane surface and prevent the reduction of permeate flux.

2.2 COD removal effect

COD removal effect both in CSMBR and in PSMBR are shown in Fig.3. After the stopping of CSMBR on day 25, COD concentration in influent of PSMBR kept on increasing till the end. The average total COD removal efficiency of CSMBR was 89.29% with average OLR at 4.16 kg COD/(m^3·d) while that of PSMBR was 89.79% with average OLR at 5.50 kg COD/(m^3·d). COD concentration in effluent of both SMBRs achieved the second level of the general wastewater effluent standard GB8978-1996 for the raw medicine material industry (300 mg/L). Hence, SMBR with electronic control backwashing was a viable process for medium-strength Chinese traditional medicine wastewater treatment. Moreover, addition of PAC could prolong the operation time and enhance the average total COD removal efficiency. However, to reduce COD level in effluent, combined anaerobic treatment processes before aerobic SMBR with electronic control backwashing was needed in the case of high-strength Chinese traditional medicine wastewater treatment.

Fouling through the formation of a dynamic layer at the membrane surface might be expected to reach equilibrium once the adhesive forces between the layer and the membrane substrate are balanced by the shear forces at the layer-solution interface. When the dynamic fouling layer was thick enough to format a biofilm, the COD removal efficiency of membrane was strengthened, but membrane fouling became worse. Then, the thicker the layer became, the higher the COD removal efficiency of membrane achieved. In CSMBR, COD removal efficiency of bioreactor was lower than that in PSMBR, while COD removal efficiency of membrane was higher. This indicated that PAC served as a filter to reduce foulants in the bulk solution by adsorption and flocculation in PSMBR, which decreased the foulants loading the membrane surface and alleviated membrane fouling by reducing the thickness of the cake layer.

2.3 MLSS, MLVSS, and VSS/SS

As there was no wastage of biomass except in sampling, similar rising trends in MLSS and MLVSS concentration were observed both in CSMBR and in PSMBR (Fig.4). Although both MLSS and MLVSS grew more and more slowly, MLSS grew faster than MLVSS, while VSS/SS in CSMBR descended on the whole during the operation. The addition of PAC made VSS/SS in PSMBR much lower than that in CSMBR. MLVSS concentrations of both CSMBR and PSMBR were almost the same during the period of the first 25 d. Because the PAC distribution in

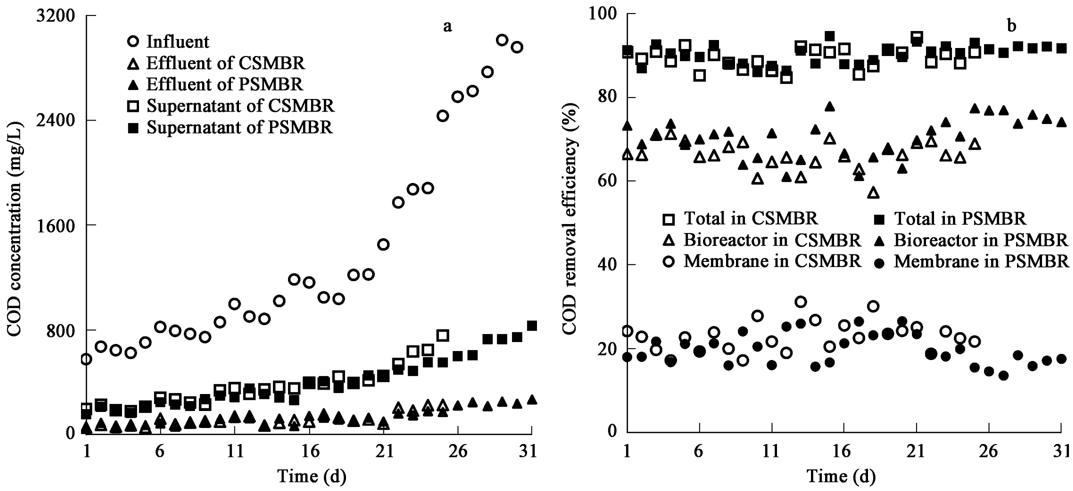

Fig. 3 COD variation (a) and removal efficiency (b) in PSMBR and CSMBR.

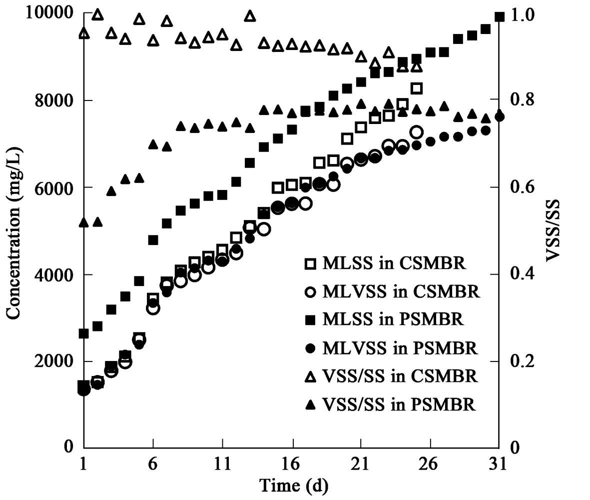

Fig. 4 MLSS, MLVSS, and VSS/SS variations in PSMBR and CSMBR.

PSMBR was so uneven that some PAC might deposit in/at the corners in the bioreactor even after aeration, MLSS concentration in PSMBR was higher than that in CSMBR, and ranged from 1135 to 1655 mg/L during operation, although the initial addition concentration of PAC was 2500 mg/L. However, this did not disturb the research to contrast PSMBR with CSMBR. For a more stable long-term operation, PAC would be added to the bioreactor intermittently and not once at the very beginning. Sludge discharge was proposed, and fresh PAC with an amount equal to that lost from the discharged sludge would be supplied sporadically to keep a stable PAC concentration in the bioreactor.

2.4 Vacuum and flux loss caused by mixed liquor

Results from the tap water trials showed that both the relationship between tap water vacuum (z) and pump frequency (x) and the relationship between tap water flux (y) and pump frequency (x) were linear with the adjusted R-square statistic obtained on the fittings, 0.99 in both PSMBR ($z = -13.286x - 0.6238$, $y = 24.974x + 0.4762$) and CSMBR ($z = -11.686x - 0.1571$, $y = 24.004x + 0.5217$). To a certain extent, tap water vacuum and flux were both in direct ratio with pump frequency. Slight differences between them illustrated the dissimilarity of head loss from pipeline in both PSMBR and CSMBR system during a suction period.

Permeability of SMBR in long-term operation was always found to be lower than that attained for tap water, because of the existence of biomass. Therefore the following terms were defined in this paper. For a certain pump frequency, the readings of the triggered vacuum gauge minus the tap water vacuum gained from the relationship between tap water vacuum (z) and pump frequency (x) was the vacuum loss caused by mixed liquor, which was caused by the mixed liquor without regard to effects of pipeline. Similarly, for a certain pump frequency, the flux minus the tap water flux gained from the relationship between tap water flux (y) and pump frequency (x) was the flux loss caused by mixed liquor. Vacuum and flux loss caused by mixed liquor increased during operation (Fig.5) in both PSMBR and CSMBR, and vacuum and flux loss caused by mixed liquor in CSMBR was higher than those in PSMBR during the first 25 d. Since both SMBRs had same feed and similar MLSS and MLVSS concentration, the difference in vacuum and flux loss was possibly due to other factors such as EPS concentration, colloid sizes, molecular forces, etc. among these substances. In general, activated sludge in CSMBR consists of weak flocs, which break easily in a turbulent environment. The destruction of flocs could promote the release of colloidal and some soluble components such as EPS and soluble microbial products, from the inner side of microflocs to the bulk solution, causing an increase in the viscosity of the mixed liquor. PAC can serve as an adsorbent and coagulant, leading to continuous depletion of fine colloids and EPS in the bulk phase by adsorption and flocculation. Li *et al.* (2005) has reported that adding of PAC could lower the mean apparent viscosity of the SMBR system by nearly 45%. This result in a decrease in growth of vacuum and flux loss caused by mixed liquor in PSMBR.

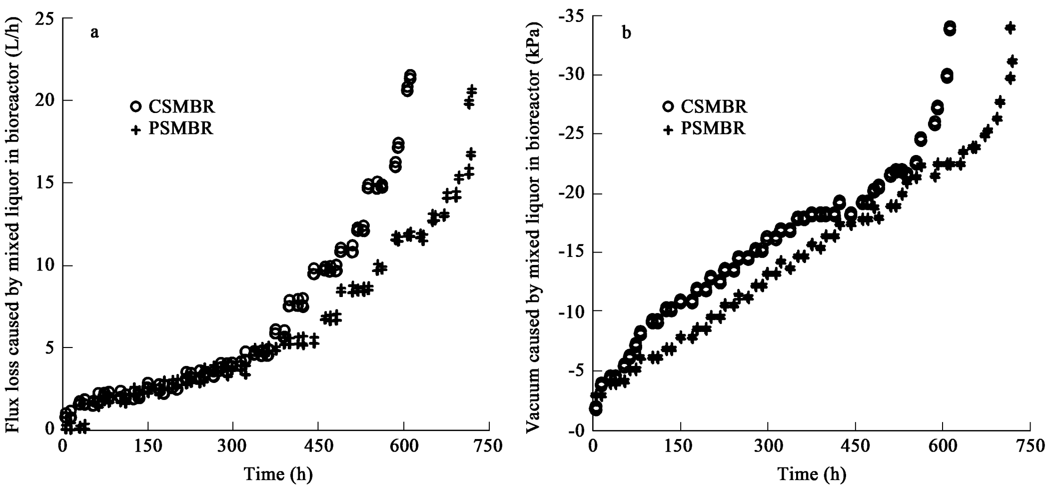

Fig. 5 Flux loss (a) and vacuum (b) caused by mixed liquor in bioreactor of PSMBR and CSMBR.

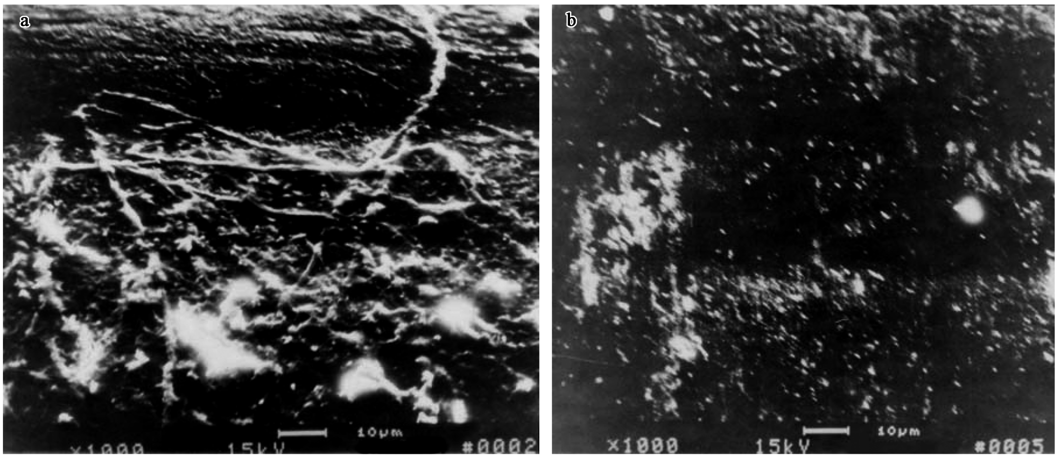

Fig. 6 SEM photomicrographs (×1000) of external membrane surface in CSMBR (a) and PSMBR (b).

2.5 SEM photomicrographs of external membrane surface

Figure 6 shows the SEM photomicrographs of external membrane surface both in CSMBR and in PSMBR immediately after they were stopped. There was a great deal of filamentous contamination on the external surface of the membrane from CSMBR, while there was only a spot of contamination on the external surface of the membrane from PSMBR. In the CSMBR, the released macromolecule organic solutes and colloids accumulate on the membrane and effectively fill the void space between the biomass particles in the cake layer. As a result, a dense cake layer adsorbed by bacteria was formed on the membrane surface, leading to a higher filtration resistance of the membrane. However, in the PSMBR, PAC could adsorb and coagulate dissolved organics, fine colloids and free bacteria, and thus reduce the amount of foulants adsorbed and attached onto the surface or filled in the membrane pores.

3 Conclusions

SMBR with electronic control backwashing was a viable process for treatment of a medium-strength Chinese traditional medicine wastewater that was rich in macromolecule, and easy to foam in aerobic biodegradation. The backwashing interval was 5 min. One suction period was about 90 min by adjusting preestablished backwashing vacuum and pump frequency. The average flux of CSMBR during a steady periodic state of 24 d (576 h) was 5.87 L/h with average HRT of 5.97 h and that of PSMBR during a steady periodic state of 30 d (720 h) was 5.85 L/h with average HRT of 5.99 h. The average total COD removal efficiency of CSMBR was 89.29% with average OLR at 4.16 kg COD/(m^3·d), while that of PSMBR was 89.79% with average OLR at 5.50 kg COD/(m^3·d). COD concentration in effluent achieved the second level of the general wastewater effluent standard GB8978-1996 for the raw medicine material industry (300 mg/L).

CSMBR and PSMBR equipped with the same electronic control backwashing device were operated in parallel under the same feed. The increasing rates of preestablished backwashing vacuum, pump frequency, and vacuum and flux loss caused by mixed liquor in PSMBR were all lagged compared to that in CSMBR. Thus, the actual operating time of the PSMBR system without membrane cleaning was extended by up to 1.25 times compared to the CSMBR, and the average total COD removal efficiency of PSMBR was enhanced with higher average OLR.

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