



Membrane Fouling and Cleaning by Hybrid Membrane Bioreactor Treating Mustard Tuber Wastewater

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When treating a typical mustard wastewater by hybrid membrane bioreactor, membrane fouling was unavoidable. To investigate this problem, an experimental study was carried out to compare the performances of the aerobic membrane bioreactor and anoxic/aerobic membrane bioreactor. Membrane cleaning experiments were studied as well. The results showed that, the initial flux of the two bioreactor was 17.6 and 15.4 L/m² h and the final flux was 15.4 and 8.3 L/m² h, respectively. In addition, their flux tended to be steady at 30 and 65 min, respectively. Therefore, the aerobic membrane bioreactor has a relative efficient operation. Soaking in 0.5 % hydrochloric acid following 0.5 % sodium hypochlorite could make the flux recovered with 82 % and it was the most effective way of membrane cleaning.

Keywords: Mustard wastewater, Hybrid membrane bioreactor, Fouling, Cleaning.

INTRODUCTION

With the rapid development of the three Gorges Reservoir economy, the level of intensive producing of its pillar business mustard is getting higher; its scale is getting larger and larger with more and more producing enterprises. But organic wastewater with high concentration of salt and nitrogen from some pickle processing enterprises is discharged directly without effective treatment. As a result, the ecosystems of many rivers in the reservoir are facing a real danger and the life of local inhabitants is caused tremendous harmful.

As an efficient technology for municipal and industrial wastewater treatment, membrane bioreactors (MBRs) played an increasingly important role in the past decade^{1,2}. But a major problem hindering the widespread application of membrane bioreactors for wastewater treatment is the rapid decline of the permeation flux with time as a result of membrane fouling³. Fouling results in degradation of membrane performance (such as permeate water flux and quality) and ultimately shortens membrane life⁴. Besides, membrane fouling decreases water production rate and increases complicacy of membrane filtration operations since the system has to be ceased frequently to restore the flux by back-flushing⁵. Therefore, studying causes of membrane fouling and membrane cleaning are major

challenges. The formation of membrane fouling is divided into two steps: (1) membrane flux decline at initial stage caused by concentration polarization; (2) long term membrane flux decline caused by particle deposition and solute adsorption.⁵ Many factors that might influence membrane fouling of MBRs have been reported, but the main factors are shown as following: (1) membrane materials⁶; (2) mixture characteristics⁷⁻⁹; (3) operating conditions¹⁰⁻¹². Cleaning is one of the most pivotal steps for maintaining membrane performance, such as permeability and selectivity. In general, cleaning should be efficient, easy and fast, with no damage to the membrane and the installation and must satisfy sanitary requirements¹³. Membrane cleaning methods usually include physical, chemical, physico-chemical and biological methods¹⁴⁻¹⁶. There are number of studies about membrane cleaning until now and the chemical methods proved to be the relative effective ways¹⁷⁻²⁰. But it is a difficult and hot spot to seek the optimum combinations of chemical agents on different conditions.

The purpose of this study was to seek an economical and efficient system through the different membrane fouling level between aerobic membrane bioreactor and anoxic/aerobic membrane bioreactor. In addition, the cleaning methods had been studied and an efficient method was put forward when treating mustard wastewater.

EXPERIMENTAL

Experiment set-up: (1) The schematic of the aerobic membrane bioreactor in this study is shown in Fig. 1(a). The effective volume of the reactor was 400 L, with a size of 108 cm × 75 cm × 60 cm (length × width × height). The reactor was divided into biota zone and diaphragm zone. The biota zone was filled with semi-soft biofilm filler and the biofilm density was 30 %. The diaphragm zone was filled with hollow fiber membrane module. (2) The schematic diagram of the anoxic/aerobic membrane bioreactor in this study is shown in Fig. 1(b). The effective volume of the reactor was 650 L, with a size of 100 cm × 50 cm × 138 cm (length × width × height). The reactor was divided into anoxic zone, aerobic zone and diaphragm zone. The anoxic zone was provided with mixing device and its size was 20 cm × 50 cm × 138 cm (length × width × height). The aerobic zone was filled with semi-soft biofilm filler and the biofilm density was 15 %, its size was 50 cm × 50 cm × 138 cm (length × width × height). The diaphragm zone was filled with hollow fiber membrane module.

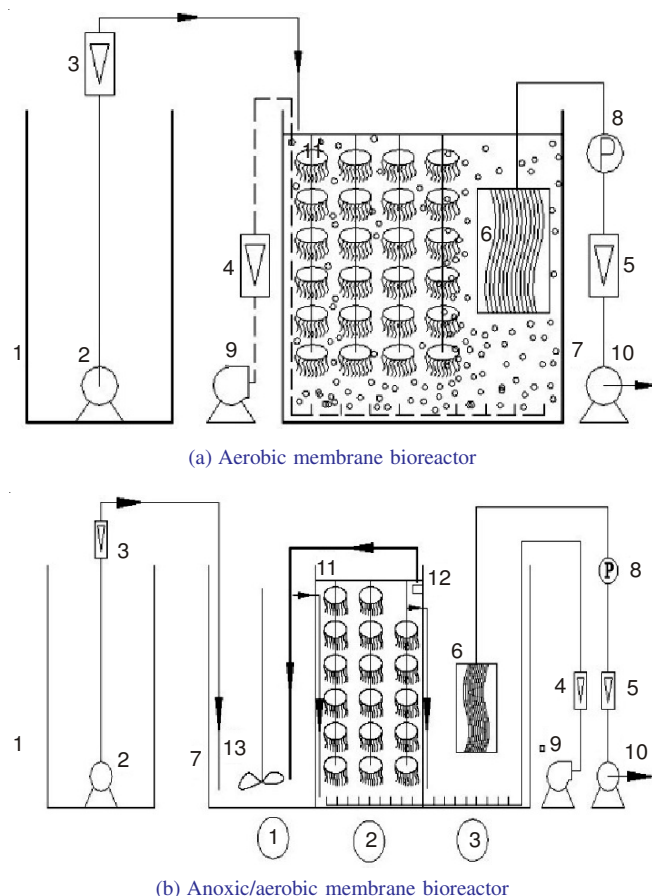


Fig. 1. Schematic diagram of the membrane bioreactors. 1-regulation tank 2-influent pump 3-5-flowmeter 6-membrane module 7-Mixed MBR 8-pressure gage 9-aerator pump 10-suction pump 11-biofilm filler 12-reflux pump 13-mixing pump. (1) anoxic zone (2) aerobic zone (3) diaphragm zone

The two reactors adopted continuous inflow of raw wastewater and intermittent discharge of effluent. In these two reactors, each membrane module was provided with a valve to control inflow. The suction pumps worked in intermittent operation mode and the suction/cease time was controlled by programmable logic controller (PLC) electric cabinet. The membrane flux was measured by flowmeter and transmembrane pressure was measured by negative pressure meter. The bottoms of the reactors were provided with perforated aerator pipe (the diameter was 20 mm). In this experiment, the wastewater flow can form counter-clockwise circulation through controlling the aeration intensity of biota(aerobic) zone and diaphragm zone. The treated wastewater was extracted through collecting pipes at last.

Wastewater composition: The experimental wastewater used in this study was anaerobic tank effluent of the wastewater treatment plant provided by Fuling Mustard Tuber Group Co., Ltd, Chongqing, China. The quality of the influent is given in Table-1.

Analytical methods: Parameters were tested periodically and analyzed according to monitoring and analysis method of water and wastewater¹ and the standard methods for the examination of water and wastewater which was published by American public Health Association².

Experimental procedure: The experiment was divided into two stages. The first stage was aimed at studying the different membrane fouling situations and the second stage was seeking the most efficient cleaning method. Four groups of experiments were designed to study on treating mustard wastewater by aerobic membrane bioreactor using PVDF membrane. On the condition of different feed loadings and normal temperature and on the condition that the bio-film density was 15 %, salinity was 2-3 % DO was 4-5 mg/L, HRT was 2.7 h, suction pumps were operated for 10 minutes and closed for 3 min each time, TMP was 15KPa, studied the membrane fouling levels. Four groups of experiments were designed to study on treating mustard wastewater by anoxic/aerobic membrane bioreactor. On the condition of different feed loadings and normal temperature and on the condition that the bio-film density was 15 %, salinity was 2-3 %, DO was 1 mg/L and MLSS was 2000 mg/L in the anoxic zone, the bio-film density was 15 %, HRT was 2.7 h, DO was 4-5 mg/L and MLSS was 6000 mg/L in the aerobic zone, the ratio of recycling the mixture was 200 %, suction pumps were operated for 10 min and closed for 3 min each time, TMP was 15 KPa, studied the membrane fouling levels.

RESULTS AND DISCUSSION

Different membrane fouling situations between aerobic membrane bioreactor and anoxic/aerobic membrane bioreactor: Fig. 2 shows the flux decline regularity when the two reactors operated with their own optimum operating feeding load. At the beginning, the membrane flux of aerobic

TABLE-1
QUALITY OF THE INFLUENT

Parameter	Salinity (%)	COD (mg/L)	Ammonia nitrogen (mg/L)	Total nitrogen (mg/L)	Total phosphorus (mg/L)	Suspended solids (mg/L)
Value	2-3	770-1240	103-191	207-409	21-48	237-525

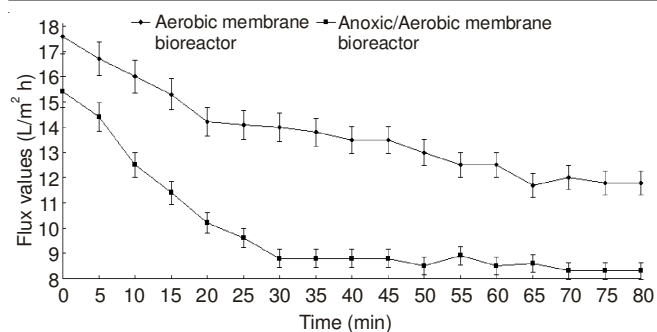


Fig. 2. Contrast on the decline of membrane fluxes

membrane bioreactor and anoxic/aerobic membrane bioreactor was 17.6 and 15.4 L/m² h, respectively. However, the flux value was reduced to 11.8 and 8.3 L/m² h, respectively at 80 min. Analysis showed that the difference of the environment which the membrane of the two systems may be the main reason for the difference. In the aerobic membrane bioreactor, the concentration of suspended solids was 2000 mg/L. However, the sludge concentration was 6000 mg/L in the anoxic/aerobic membrane bioreactor. So, its microbial quantity was far more than that in the anoxic/aerobic membrane bioreactor. Analysis showed that the extracellular polymeric substances (EPS) concentration increased with the sludge concentration and EPS was considered as the most significant factor membrane fouling¹. Therefore, the fouling degree of aerobic membrane bioreactor was lower than that of the anoxic/aerobic membrane bioreactor with the same operating time and the aerobic membrane bioreactor operated more effectively.

Chemical cleaning: The recovery rates after different chemical cleaning methods were shown in Table-2: (1) Soaking in hydrochloric acid aimed to remove the inorganic materials in the membrane pores. It can be found that the flux recovery rate was slightly higher than that of physical cleaning alone. But the physical cleaning contributed 20 % of the recovery

rate and the HCl contributed only 8 %. Studies identified that some metals such as Fe and Al could cause the irreversible membrane fouling and acid cleaning method had a significant effect on it²⁴, nevertheless, the concentrations of such metals in mustard wastewater were quite low. As a result, only 8 % removal rate was obtained by HCl cleaning; (2) soaking in sodium hypochlorite aimed to remove the organic foulants in the pores. The result showed that the NaClO exhibited an excellent performance for the fouled membrane and the flux could be greatly improved and it could be recovered to 73 % of initial flux. Another similar study showed that, the permeability recovery was 64.5 % using 0.05 % NaClO and 55.1 % using 0.5 % H₂SO₄ after the same soak time²⁵, it indicated that NaClO was more effective than acid in membrane cleaning. Analysis showed that the EPS could form a cake layer on membrane surface and NaClO could efficiently destroy the cake layer structure with its oxidizing characteristic, besides, NaClO sometimes entered the pores and increased their effective diameter²⁶⁻²⁸; (3) after soaking in HCl and NaClO, the flux could be recovered to 82 % of the initial flux. In addition, most of the recovery attributed to NaClO. An experimental result showed that the > 97 % flux recovery was achieved by 0.5 wt % NaClO solution on certain conditions²⁹.

Fig. 3 showed the membrane states after different chemical ways: (1) after HCl solution cleaning, there existed *Bacillus*-like substances on the membrane surface. The pores were clogged with foulants and the average size of the pores was 0.087 μm (Fig. 3a); (2) after NaClO solution cleaning, the amount of *Bacillus*-like substances decreased and the foulants in the pores reduced as well. Besides, the pore size was recovered well and the average size was 0.13 μm (Fig. 3b); (3) after combined HCl + NaClO cleaning, the membrane surface was relatively clean and the average pore size was 0.15 μm (Fig. 3c). Therefore, an HCl + NaClO method can solve the flux decline effectively. It can remove the foulants on the

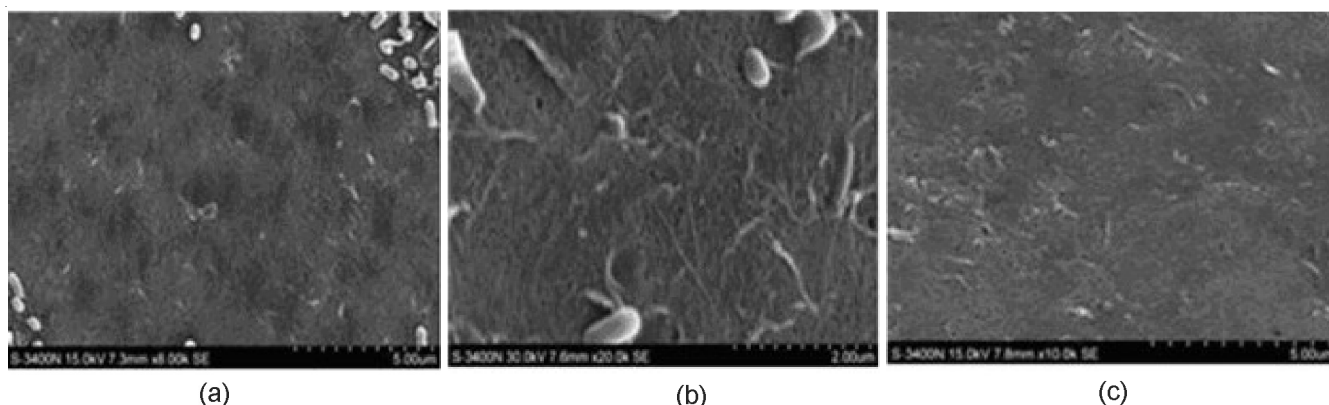


Fig. 3. SEM photograph after different chemical cleaning ways

TABLE-2
RECOVERY RATES AFTER DIFFERENT CHEMICAL CLEANING WAYS

Item	Flux (L/m ² ·h)	Recovery rate
Initial flux	30	–
Flux before cleaning	5	–
Physical cleaning + 0.5 wt % HCl	8.4	28
Physical cleaning + 0.5 wt % NaClO	21.9	73
Physical cleaning + 0.5 wt % HCl + 0.5 wt % NaClO	24.6	82

membrane surface and foulants in the pores as well and then prolong the membrane life.

Conclusion

When treating mustard wastewater, the aerobic membrane bioreactor can operate more effectively than the anoxic/aerobic membrane bioreactor. In order to defer the growth rate of membrane fouling and control the resistance accumulation, it is always necessary to carry out membrane cleaning. Combined use of 0.5 % HCl and 0.5 % NaClO was the most effective chemical way to remove membrane foulants.

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