# Test of membrane bioreactor for waste water treatment of a petrochemical complex *

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**Abstract**—Membrane bioreactor (MBR) used in water and waste water treatment is a developing technique for water pollution control and water reuse. This paper described a membrane bioreactor for treatment of waste water in a petrochemical complex. The experimental MBR was a lab scale one composed of an activated sludge bioreactor unit and an ultrafiltration membrane unit. The relationship of COD removal with MLSS and HRT in this MBR was studied. The effects of crossflow velocity, backwash interval and volume of flush liquid on the flux were discussed. The results showed that average removal of COD, oil, SS and turbidity in petrochemical waste water by the MBR was 91%, 86%, 92% and 99%, respectively. The average removal of $NH_3$-N and total phosphorous was 85% and 82% respectively. A coefficient of COD removal, $k$, was 0.017—0.080 L/(mg.d). The membrane flux maintained higher than 60 L/hm$^2$ bar for 34 days without chemical cleaning when the velocity of crossflow was 3.5—3.9 m/s and the backwash interval was 30 minutes and backwash duration at 20 seconds. The results indicated that it is feasible for MBR technology to be used in petrochemical waste water treatment. The treated water could be considered as a source of to make up water for industrial cooling system or to be reused for other purposes.

**Keywords**: membrane bioreactor; petrochemical waste water; biological process; water treatment; activated sludge.

## 1 Introduction

The development of membrane technology has expanded its application field to water and waste water treatment for more than 30 years. The membrane bioreactor (MBR) for treatment of domestic waste water (Smith, 1969; Chart, 1994; Vigneswaran, 1991), oily waste water (Knoblock, 1994) and drinking water (Chang, 1993) has been studied in some countries, such as in Japan, USA and France. Extractive membrane bioreacter used for detoxifying chemical industrial wastewater has been reported (Livingston, 1994). These studies showed that MBR had high efficiency of pollutants removal and could produce high quality of treated water for reuse. Reports about MBR for petrochemical waste water treatment and reuse were very few. Water pollution and water shortage are serious environmental problems in China, specially in the cities and big industrial districts such as the petrochemical complexes in northern China. The techniques for water pollution control and water reuse have been studied for many years, but limited work has been done on MBR as a water treatment method in China. The purpose of this work is to test the feasibility of the MBR for petrochemical wastewater treatment and for reuse for the treated waste water.

## 2 Materials and methods

### 2.1 Experimental system

The experimental MBR was consisted of three parts: bioreactor unit, membrane separation

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unit and an operation control unit. The bioreactor unit contained a feed tank, an air pump and an aeration tank. The membrane unit was composed of a membrane module, a recirculation pump, a backwash pump and two flow meters. The control unit was consisted of two controllers, one for water level control of aeration tank and the another for backwash time control of the membrane. A schematic diagram of the experimental setup is shown in Fig.1.

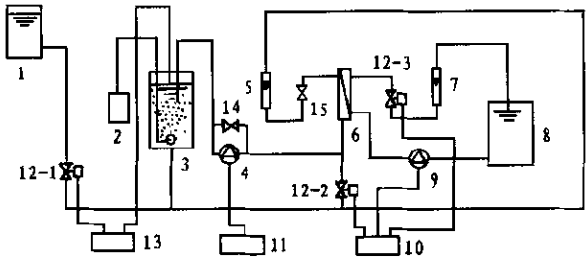


**Fig.1** Schematic of MBR experimental setup
1. Elevated feed tank; 2. Air pump; 3. Biorcactor; 4. Circulation pump; 5,7. Flow meter; 6. Membrane module; 8. Purified water tank; 9. Backwash pump; 10. Backwash timer; 11. Recirculation timer; 12. Electromagnetic valves; 13. Water level controller; 14,15. valves

In bioreactor unit, the aeration tank was an activated sludge tank with volume of 20 litters. Air was blown into the mixed liquid of the tank through a sand molding diffuser.

In membrane unit, the membrane module has 20 centimeters long with 0.03 $m^2$ membrane surface area. The hollow fiber ultrafiltration membrane in the module was made of PAN (polyacrylonitrile) with 50000 molecular weight cutoff. The inner diameter of each membrane fiber was 1 millimeter and 55 pieces of the fibers were packed in the module. The membrane and the module were made and provided by the Polymer Membrane Laboratory of Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

In order to keep liquid level in the aeration tank, a level control unit consisted of a water level sensor and an electromagnetic valve was used to control the inflow of the tank. In order to remove the deposition and internal clogging of the membrane, a backwash control unit was designed to control the membrane backwash frequently. The backwash pump and electromagnetic valves were controlled by two timers regularly so that backwash operation could be run automatically. The backwash interval or filtration period (Tf) and the duration of backwash (Tb) could be adjusted manually with the timers.

### 2.2 Petrochemical wastewater

The experiment was carried out at a waste water treatment plant in a petrochemical complex. The wastewater to be treated in the MBR was taken from the influent of an aeration tank of activated sludge process in the plant. This influent was a mixture of one third of domestic wastewater and two thirds of petrochemical industrial wastewater. COD, SS, oil and turbidity of the waste water was 120—900 mg/L, 26—399 mg/L, 2.2—56.5 mg/L and 7.3—74.0 NTU, respectively.

### 2.3 Experimental procedure and analytical methods

Waste water was filled to the elevated feed tank (Fig.1) twice a day. From the tank, waste water flowed into the aeration tank and it was the influent of the MBR. The influent flow was controlled by a water level controller of the aeration tank. Mixed liquor of the aeration tank was pumped into the membrane module, where a part of water permeated through the membrane and the mixed liquor was concentrated. From the module, the permeated water flowed to the purified water tank. It was the effluent of the MBR. The concentrated mixed liquor returned back to the aeration tank. This circulation of mixed liquor went round and round. Backwash of the membrane was carried out frequently with the treated water as the backwash water.

The samples of influent and effluent were taken once a day. Water quality parameters measured in this study were COD (chemical oxygen demand, mg/L), SS (suspended solids, mg/L), pH, $NH_3$-N, P (phosphorous, mg/L), turbidity and oil. The parameters of the MBR operation condition were DO (dissolved oxygen, mg/L), HRT (hydraulic retention time, h), SRT (sludge retention time, h), MLSS (mixed liquor suspended solid, mg/L), $T$ (temperature, ℃), Tf, Tb, Pb (backwash pressure, bar), f (flux of membrane, L/(hm$^2$ · bar)) and v (crossflow velocity, m/s).

**Table 1 Parameters and analytical methods**

| Parameter | Analytical method |
|---|---|
| pH | UC-23 pH meter |
| T | Glass thermometer |
| DO | HDO-22 DO meter |
| MLSS | Weight method |
| $NH_3$-N | Nesslerization method |
| P | Stannous chloride method |
| COD | Dichromate reflux method |
| SS | Weight method |
| Turbidity | Model 8391-37 turbidimeter |

Table 1 shows the analytical methods of some water quality parameters mentioned above (Table 1).

## 2.4 Operation conditions

Operation conditions are shown in Table 2.

**Table 2 Operation conditions**

| Parameter | $T$, ℃ | pH | Air flow, L/min | DO, mg/L | MLSS, mg/L | HRT, h | SRT, h |
|---|---|---|---|---|---|---|---|
| Maximum | 39 | 8.4 | 4.5 | 7.4 | 3.496 | 28.9 | 435 |
| Minimum | 16 | 7.0 | 1.0 | 0.3 | 0.724 | 7.4 | 145 |
| Average | 29 | 7.6 | 2.8 | 3.6 | 1.543 | 10.7 | 288 |

Temperature of the water in the MBR was higher than that of influent by 10℃ to 20℃ because of high circulation of the mixed liquor and was subject to the change of ambient temperature. The dissolved oxygen in mixed liquid waved with the flow rate of air blew into the aeration tank and with the concentration of pollutants in the influent. Activated sludge of the aeration tank was not discharged or wasted in the experiment, except be taken for sludge sampling. The sludge retention time (SRT) was calculated on the basis of volume of sludge sample only taken from the aeration tank for MLSS measurement. Because of the reason mentioned above, SRT was longer than HRT and it was separated from HRT in the MBR. MLSS of the MBR maintained at a lower concentration range comparing with that of the aeration tank treating the same waste water as the MBR in the waste water plant.

# 3 Results and discussion

## 3.1 Pollutants removal and water quality of effluent

Fig.2 shows the figures of COD, turbidity, SS, oil, ammonia nitrogen ($NH_3$-N) and phosphorus (P) in the influent and effluent of the MBR system.

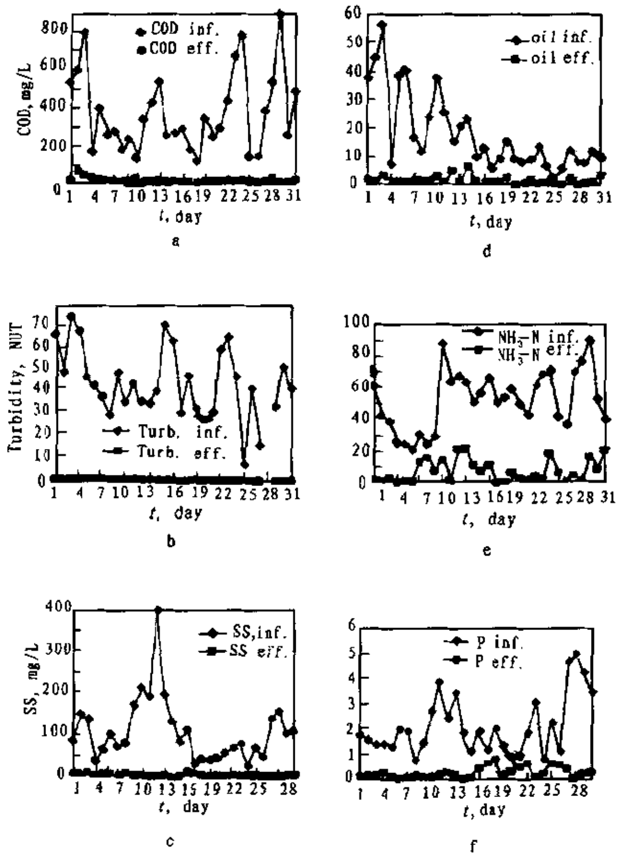


Fig.2 Pollutants in influent and effluent of the MBR unit: (a), (b), (c), (d), (e) and (f)

Removal of COD was from 74% to 98% and the average was 91%. Although COD of influent ranged from 135 mg/L to 900 mg/L with standard deviation (SD) 210 mg/L, COD of effluent was down to an average of 27.9 mg/L with SD 10.3 mg/L. This result showed that the MBR could provide a high removal efficiency of COD for this kind of petrochemical wastewater and the quality of the treated water was quite stable (Fig.2(a)).

Turbidity removal was very high ranging from 98% to 100%, with average being 99% (Fig.2(b)). The turbidity in effluent was from 0.06 to 0.11 NUT when the turbidity in influent fluctuated from 7 to 74 NUT. The effluent from MBR was so clear that looking like tap water.

Removal of SS was from 80% to 99%, with average being 92%. The SS in effluent was 1.2 mg/L to 7.9 mg/L while it was 36 mg/L to 399 mg/L in influent. SD of SS in effluent was 1.7 mg/L (Fig.2(c)).

Oil is one of the important items considered in petrochemical waste water treatment and reuse. The average removal of oil was 86% by the MBR. When average concentration of oil in influent was 19.6 mg/L (SD = 13.0 mg/L), that in effluent was down to 2.7 mg/L (SD = 3.7 mg/L; Fig.2(d)).

The removal of $NH_3$-N was from 35% to 100%, with average being 85%, and that of P was from 45% to 99%, with average being 82% (Fig.2(e) and Fig.2(f)). The removal efficiency of

$NH_3$-N and P was less than that of COD, SS and turbidity, and it usually changed with that of COD. This phenomenon imply that there are some relations among removals of COD, $NH_3$-N and P, and it will be discussed below.

### 3.2 Kinetic parameters and ratios among COD/$NH_3$-N/P

Ratio of food to microorganism (F/M) in this MBR was from 0.1 to 1.5 (g COD/g MLSS day), the average was 0.6 (g COD/g MLSS day). The *F/M* ratio of the MBR was about twice of that in the aeration tank of the waste water treatment plant, where the MBR research work was carried out. During the experiment, the MBR treated the same influent as the waste water treatment plant did, but the MLSS in MBR was only one half of that of the plant. At this MLSS condition, the MBR had higher removal of COD and better quality of effluent than that of the plant. The result showed that the activated sludge in the MBR had higher ability of removing COD than that of the aeration tank in the waste water treatment plant.

Based on the data measured in the experiment, we got a coefficient of COD removal, $k$, which was derived from a kinetics equation showed below.

In a continuous activated sludge process, at a constant ratio of food to microorganism, a kinetics equation is expressed as

$$\frac{S_0 - S_e}{t \times x} = k \times (S_e - S_n) = Us, \qquad (1)$$

where $S_0$ is the concentration of COD in influent; $S_e$ is the concentration of COD in effluent; $S_n$ is non-biodegradable COD concentration in effluent; $t$ is hydraulic retention time; $x$ is MLSS; $Us$ is sludge loading; $k$ is the coefficient of the COD removal (Gu, 1993). $k$ was calculated with the experiment data. For this MBR and this kind of petrochemical wastewater, $k$ was from 0.017 to 0.080 L/(mg·d). The calculation results of kinetics equation and $k$ are shown in Table 3. In Table 3, $r$ means the correlation coefficient of the kinetics equations.

**Table 3 COD removal coefficients ($k$) and kinetics equations**

| Data | Kinetics equations | $k$, L/(mg·d) | $r$ |
|---|---|---|---|
| Mar. 17—22 | $Us = k(S_e - 0.4)$ | 0.0178 | 0.89 |
| Mar. 23—29 | $Us = k(S_e - 17.8)$ | 0.0800 | 0.90 |
| June 2—13 | $Us = k(S_e - 4.0)$ | 0.0167 | 0.90 |

Fig. 3 shows the variation of MLSS in the aeration tank of the MBR. Comparing Fig. 3 with Fig. 2(a), we found that MLSS varied positively with COD of influent in many days. It means that when COD in influent increased, population of bacteria in the aeration tank would grow fast, so MLSS increased, and that when COD in influent decreased, population of bacteria would decline, so MLSS was getting low. This may be the reason why a high efficiency on COD removal and a stable quality of effluent could be got and less exceed sludge produced in the MBR.

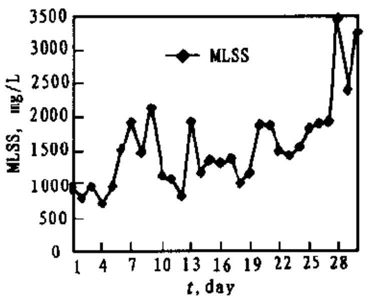


Fig. 3 MLSS of the MBR unit

From the experimental results, we noticed that the removal of ammonia and phosphorus varied with that of COD. According to the statistic results, the ratios of average removals of COD/$NH_3$-N/P in influent was 100/13.5/0.6.

Nitrogen and phosphorus are very important nutrients in biosynthesis. More or less of the nutrients of nitrogen or phosphorus can reduce the efficiency of waste water treatment. Adjusting and keeping the ratios at the values measured above, a higher removal of COD, $NH_3$-N and phosphorus can be expected for petrochemical waste water treatment with the MBR.

### 3.3 Flux and its stability

Flux and its stability are two very important parameters for application of MBR and it is expected at a high and a stable level for a practicable MBR. For this purpose, some cleaning methods of the membrane, such as backwash and high crossflow velocity, were used in this work.

Fig.4 shows the flux of the MBR. Before the 15th day, the flux fall very obviously, when backwash parameters were set, Tf (backwash interval) at 30 minutes, Tb(duration of backwash), at 20 seconds, Pb(backwash pressure) at 2.4 bar, and the crossflow velocity at 2.3—3.2 m/s. The membrane was cleaned at 4th, 8th, and 15th day with chemical cleaning agent and tap water. After the 15th day, at the same backwash condition mentioned above, the crossflow velocity was increased to 3.5—3.9 m/s. At this operation condition, the flux tended to be stable and maintained at no lower than 60 L/($hm^2$ bar) for 34 days till the experiment was stopped (Fig.4). This result means that, as MLSS at 0.7—3.5 g/L, for a stable flux of the MBR, the crossflow velocity should set at a level not less than 3.5 m/s.

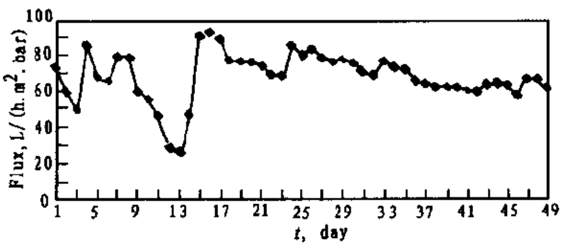


Fig.4 Flux of the MBR unit

Because of the backwash, a part of purified water was driven back through the membrane to the bioreactor tank. The ratio of backwash water to flux water was about 2.4%.

## 4 Conclusion

The results showed that membrane bioreactor composed of a hollow fiber ultrafiltration membrane (MW cutoff 50000) and an activated sludge reactor can be used for treatment of complex petrochemical wastewater. The efficiency of pollutants removal and effluent water quality were satisfactory. The average removal of COD, SS, turbidity was 91%, 92% and 99%, respectively. The average removal of oil, $NH_3$-N and phosphorus was 86%, 85% and 82%, respectively. The treated water was very clear and no smell like tap water. It may be considered as a kind of water source for making make-up water for industrial recycling cooling system, or for fire fighting, street showering, car washing and so on.

The coefficient of COD removal was from 0.017 to 0.080 L/(mg·d) according to COD removal and MLSS in the experiment. The rate of average removals of COD/$NH_3$-N/P was 100/13.5/0.6. HRT was about 11 hours and separated from SRT. SRT in the MBR was about 288 hours. No exceed sludge was discharged, MLSS samples excepted, in the experimental period. At backwash interval (Tf) 30 minutes, backwash time (Tb) 20 seconds, backwash pressure (Pb) 2.4

bar and cressflow velocity 3.5—3.9 m/s, flux of the MBR tended to stable and maintained larger than 60 L/$hm^2$ bar for more than 800 hours.

The experiment results show that the MBR process discussed in this work has technical feasibility for petrochemical waste water treatment and reuse.

## References

AOHA-AWWA-WPCF. Standard methods for the examination of water and wastewater, 15th edition. Washington, DC.: American Public Health Association, 1980

Chang J, Manem J, Beaubien A. J Membr Sci, 1993, 80:233—242

Chart C, Yamamoto K. J Membr Sci, 1994, 87: 119—129

Gu X S. Mathematical models of biological wastewater treatment, Beijing: Tsinghua University, 1993. 45—51

Knoblock M D, Sutton P M, Mishra P N, Gupta K A, Janson A. Water Environmental Research, 1994, 66:133—139

Livingston A G. J Chem Tech Biotachnol, 1994, 60:117—124

Smith C V Jr, Gregorio D D, Talcott R M. The use of ultrafiltration membranes for activated sludge separation. Paper presented at 24th annual Purdre industrial waste conference, 1969. 1300—1310

Vigneswaran S, Vigneswaran B, Aim R B. Environmental Sanitation Reviews, 1991, 31:117

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