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A pilot scale anoxic/oxic membrane bioreactor (A/O MBR) for woolen mill dyeing wastewater treatment

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Abstract: A pilot-scale(10 m³/d) anoxic/oxic membrane bioreactor(A/O MBR) was tested for dyeing wastewater treatment of woolen mill without wasting sludge in 125 days operation. Results showed that the effluent quality was excellent, i.e. effluent COD less than 25 mg/L, BOD₅ under 5 mg/L, turbidity lower than 0.65 NTU, and colour less than 30 DT, and met with the reuse water standard of China. The removal rates of COD, BOD₅, colour, and turbidity were 92.4%, 98.4%, 74% and 98.9%, respectively. Constant-flux operation mode was carried out in this study, and backwash was effective for reducing membrane fouling and maintaining constant flux. Membrane fouling had heavy impact on energy consumption. More attention should be paid on pipe selection and design for the sidestream MBR system, too.

Keywords: activated sludge; backwash; constant flux; dyeing wastewater treatment; membrane bioreactor (MBR); woolen mill

Introduction

The dyeing wastewater of woolen mill contains a lot of kinds of pollutants, such as acidic dyes, disperse dyes, mordant dyes, auxiliaries, salts. Dyes include a broad spectrum of different chemical structures, such as aromatic amine (C_6H_5 -NH $_2$), carcinogen phenyl (C_6H_5 -CH $_2$) and naphthyle (NO $_2$ -OH). A large number of dyes are azo compounds (-N-N-1), and are recalcitrant for biodegradation (Talarposhti, 2001). Conventional approaches of dealing with textile-dyeing wastewater consist of combinations of biological, physical and chemical methods such as oxidation, adsorption, or coagulation by aluminum or iron salts (Vlyssides, 2000). Because of the large variability of the composition of textile-dyeing wastewater, the use of conventional wastewater treatment processes becomes increasingly challenged with the identification of more and more contaminants, rapid growth of population and industrial activities, and diminishing availability of water resources.

Along with aggravation of water pollution and water shortage in China, it is more and more important to develop higher efficient technologies for dyeing wastewater treatment with recalcitrant pollutants. Some emerging treatment technologies, including membrane filtration, advanced oxidation processes, and electrochemical method, hold great promise to provide alternatives for better protection of public health and the environment. Ozonation and photooxidation have been proposed as alternatives in recent years. But the high cost of these methods impedes their applications. Electrochemical method has been successfully tested to deal with dyeing wastewater (Sheng, 1994). However, it has little effect to treat wastewaters with dyes, which have good water solubility and small molecule weight.

Over the years, more attention has been paid to the membrane bioreactor technology for wastewater treatment because of its higher efficiency of pollutant removal and excellent effluent quality. Membrane bioreactor (MBR), a process involving membrane filtration combined with biological treatment, have demonstrates that membrane processes may offer a number of advantages over conventional treatment processes, including (1) high-quality effluent over a wide range of raw water sources; (2) no chemical addition except when organic removal is practiced; (3) a small amount of solids requiring disposal; (4) very compact installations; (5) simpler automation and control; and (6) reduced operation and maintenance requirements (Zhou, 2001). Different kinds of membrane bioreactor systems are recently

studied or applied for bathing wastewater (Liu, 2001), restaurant wastewater (Ning, 2002), high concentration wastewater (Cheng, 2000), hospital wastewater (Ding, 2001), oil-containing wastewater (Bao, 2002) and other industrial wastewater treatment in China(Zheng, 2002). Hence, the purpose of this work is to study the feasibility of membrane bioreactor for dyeing wastewater treatment and to determine whether the treated water could be reused. Our previous bench-scale research showed it was necessary for this kind of wastewater treatment to adopt anoxic process in order to improve its biodegradability (Fan, 2000). An anoxic/oxic membrane bioreactor (A/O MBR) were tested in this study.

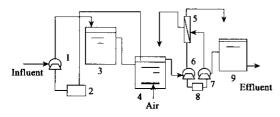


Fig. 1 The schematic diagram of A/O MBR for dyeing wastewater treatment

feed pump;
level control;
anoxic tank;
aeration tank;
membrane module;
recycle pump;
backwash timers;
treated water tank

1 Materials and methods

1.1 Pilot scale plant

The pilot scale experiment setup(Fig.1) was composed of an anoxic $tank(4.8 \text{ m}^3)$ and a side stream membrane bioreactor(MBR), in which an ultrafiltration membrane module (hollow fiber, PAN, molecular weight cut-off 60000 Dalton), supplied by the Membrane Technology Center, RCEES, was coupled with an activated sludge aeration $tank(3 \text{ m}^3)$.

Wastewater was brought into anaerobic tank from a condition tank by pump controlled by a

level sensor, which maintained a constant level in the reactors. A loop was constituted by the aeration tank, centrifugal pump and membrane module. The membrane was regularly backwashed with treated water to alleviate membrane fouling. Transmembrane pressure (TMP) is calculated as $(P_{in} + P_{out})/2$.

Table 1 shows the characteristics of influent and effluent in A/O MBR, and the operational parameters are listed in Table 2. The experiment was carried out at the wastewater treatment plant of Beijing Woolen Mill. Initially, the bioreactors were filled with activated sludge sampled from a wastewater treatment plant and then fed with settled dyeing wastewater in a condition tank. The raw wastewater entered the condition tank after through two sieves for removal of suspended solid and wool.

Table 1 Characteristics of influent and effluent in A/O MBR

	COD, mg/L	BOD_5 , mg/L	Turbidity, NTU	NH_3 - N , mg/L	Colour, DT	SS, mg/L
Inf.						
$(Av. \pm s.d)$	256.5 ± 47.8	94.8 ± 50.3	45.65 ± 7.8	1.05 ± 0.56	64 ± 20	58.7 ± 58.9
(Range)	179.0-358.0	44.8-206.0	34.0-98.0	0.51 - 1.74	50-240	11—94
Eff.						
$(Av. \pm s.d)$	20.2 ± 9.5	1.6 ± 2.3	0.51 ± 0.05	0.56 ± 0.32	25 ± 6	n.d.
(Range)	11.9-44.9	0-4.8	0.45-0.65	0.07-1.08	15—40	n.d.
Removal rate, %						
$(Av. \pm s.d)$	92.4 ± 3.4	98.4 ± 1.6	98.9 ± 0.2	52.0 ± 26	74 ± 9	100
(Range)	81.4-96.2	83.7-100.0	98.2-99.2	20.0-80.0	56-89	100
Reuse water						
standard ** (a)	50	10	10	20	30	10
(b)	50	10	5	10	30	5

Notes: * NTU: nephelometric turbidity units; DT: dilution times; * * water reuse standard for (a) flush water (b) car washing, land watering etc., in China (CJ25.1—89)

MBR system was operated at 6—8 h hydraulic retention time(HRT), and the membrane module was periodically backwashed(20 s every 30 minutes) using treated wastewater. There was no sludge wasting in MBR system during 125 days operation.

Table 2 Operating parameters of aeration tank in A/O MBR									
T, C	pН	DO, mg/L	MLSS, g/L	HRT, h	$Q, m^3/d$				
Max	35.0	8.2	10.4	2.82	9.4	13.4			
Min	9.0	6.5	0.2	0.66	5.4	7.7			
Av. $\pm s.d$.	24.9 ± 6.1	7.4 ± 0.4	3.3 ± 2.2	1.55 ± 0.72	7 ± 0.7	10.3 ± 1.1			

1.2 Analytical methods

The performance of reactors was monitored by analyzing influent and effluent samples for selected parameters according to standard procedures. The pH was measured by pH meter (pHS-3C, China). Chemical oxygen demand(COD) was measured by a CTL - 12 COD meter (Huatong Company, China). Five-day biochemical oxygen demand (BOD_5) was determined by a $BODTrak^{TM}$ (Hach Company, USA) . Turbidity was measured by a turbidity meter (Model 8391-37 Turbidity, USA). Dissolved oxygen (DO) and temperature were registered with a portable DO meter combined with a temperature probe (JBP-607 DO, China). Ammonia nitrogen (NH₄ -N), colour, suspended solids (SS) and volatile suspended solids (VSS) were conducted by standard methods.

Results and discussion

2.1 Performance of MBR

2.1.1 Pollutants removal efficiency

The characteristics of influent and effluent of A/O MBR is shown in Fig.2 and Table 1. It shows that the effluent quality of A/O MBR was excellent and met with water reuse standard in China. The influent COD was fluctuated from 179 to 358 mg/L, however, the effluent COD was maintained at a low level, i. e. lower than 43 mg/L and the average effluent COD was only 20.2 mg/L. The average COD and BODs removal efficiency were 92% and 98.4%, respectively. The effluent BOD, was down to about 0 mg/L to 4.8 mg/L as influent was from 44.8 mg/L to 206 mg/L. It implied that the biodegradable pollutants in dyeing wastewater of Beijing Woolen Mill were almost removed by A/O MBR. The BOD₅/COD ratio is usually used to express the biodegradability of the wastewater in engineering. In this study, the BOD₅/COD ratio varied from 0.13 to 0.5 after anoxic treatment.

A/O MBR had an excellent performance on colour and turbidity for dyeing wastewater treatment. Colour of the effluent was down to an average of 25 dilution times (DT) when colour of the influent was from 50 DT to 240 DT. The effluent turbidity was lower than 0.65 NTU, and its average was 0.51 NTU, although the turbidity of influent varied from 34 to 98 NTU.

It can be concluded that the removal of organic pollutant by the A/O MBR was very high in terms of COD and BOD, , and an excellent effluent quality can meet with reuse water standard during the long-term operation.

2.1.2 Sludge and volumetric loading rate

Fig. 3a shows profiles of sludge and volumetric loading rate of A/O MBR for dyeing wastewater treatment in Beijing Woolen Mill. The average sludge and volumetric loading rates were 1.48 kgCOD/ (kgSS·d) and 1.67 kgCOD/(m³·d), respectively. The sludge and volumetric loading rates of A/O MBR corresponded with the influent COD fluctuations during the long-term operation. The sludge loading rate on day 55 went up to the maximum value of 3.67 kgCOD/(kgSS·d) because of the influent COD sudden increase. However, the effluent COD still remained as low as 45 mg/L. It clearly showed that A/O MBR had a strong shock buffer capacity. Compared with conventional activated sludge plants (CASP), the average volumetric loading rate was about 2 to 4 times that of CASP (Stephenson, 2000), and this indicated that use of MBR could not only eliminate the secondary clarified but also reduce the size of the bioreactor by two to three times in comparison with the CASP. Therefore, the A/O MBR was considered as one of the cost-effective solutions for dyeing wastewater treatment.

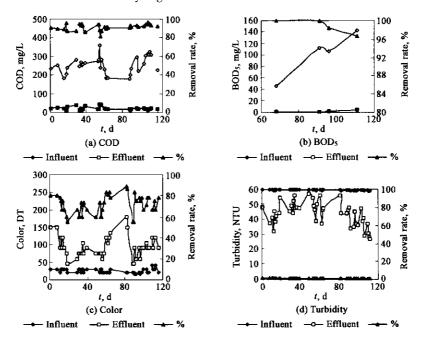


Fig. 2 Performances of A/O MBR for dyeing wastewater treatment

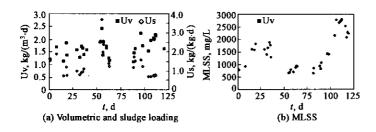


Fig. 3 Profiles of sludge and volumetric loading rates of A/O MBR

In the operating period of over 120 day, except some sludge was lost because something is wrong with pump from 30th to 45th day, no any sludge was drawn from the A/O MBR (Fig. 3b). The ratio of VSS/SS of sludge was in the range of 0.85 to 0.9 from 110th to 125th day, almost being constant. This

implied no accumulation of inorganic matter in the MBR even at operation without sludge discharge. The above results demonstrated that high sludge activity is the important reason why MBR is efficient for treating dyeing wastewater.

2.2 Membrane fouling and counter-measures

2.2.1 Constant flux mode

As most membrane process operates, it was recognized that fouling was most rapid at the start of the filtration. Lots of research work reported that the clogging of pore inside the membrane matrix, which could be a function of the flux, would contribute significantly to the membrane resistance increase (Stephenson, 2000). The higher the initial flux, the faster the clogging inside the membrane matrix. Hence, it is very important to initiate and operate the membrane at a proper TMP at which the flux remains stable or decreases slowly, reducing the backwash frequency of the membrane. For this study, the constant flux mode was carried out, and shown to be effective to control membrane fouling. Since a constant membrane flux was maintained during the operation, the TMP exerted on the membrane would inevitably increase if membrane fouling occurred. Therefore, the membrane fouling state during operation could be observed in time by continuously monitoring the TMP.

No.4

Fig. 4 shows the variations of membrane permeate flux and TMP with time. The TMP was increased slowly in the beginning from day 1 to day 20, from 19 kPa to 45 kPa; and the average membrane permeate flux tended to decreased slightly and maintained a constant value of $40 \pm 5 \text{ L/(m}^2 \cdot h)$. From 21th to 125th day, the membrane flux was maintained at a constant value of $35 \pm 5 \text{ L/(m}^2 \cdot h)$, and TMP correspondingly increased from 45 kPa to 75 kpa.

In all practical membrane filtration applications, as the resistance increases the flux will decline. The following equation can be used to describe the overall characteristics of membrane fouling.

 $R = \Delta P/\mu J = R_{\rm m} + R_{\rm f} + R_{\rm p} = R'_{\rm m} + \Phi P$, where R is the hydraulic resistance of the membrane (m^{-1}) , $R_{\rm m}$ is intrinsic resistance (m^{-1}) , $R_{\rm f}$ is the fouling resistance (m^{-1}) , and $R_{\rm p}$ is the cake layer resistance $(m^{-1})(R_{\rm p} = \Phi P)$, where Φ is an adjustable parameter). ΔP is the transmembrane pressure across the membrane (N/m^2) , μ is the absolute viscosity of the water (N/m^2) , and J is the permeate flux $(m^3/(m^2 \cdot s))$. Fig. 5 shows the

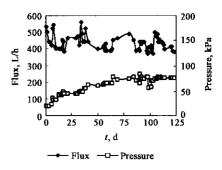


Fig. 4 The relationship of permeate and TMP in A/O

changes of membrane resistance (R'_{m}). The membrane resistance increased along with pressure increasing because the constant flux mode was adopted in this study.

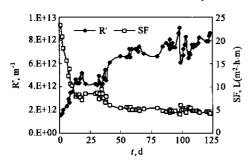


Fig. 5 Membrane fouling in A/O MBR for dyeing wastewater treatment

To enable direct comparison of the flux caused in different TMP(1 m $H_2O = 9.8$ kPa), the performance of the membranes was quantified in terms of specific flux (SF), the permeate flux produced per unit pressure applied (in $L/(m^2 \cdot h \cdot m)$). The average membrane flux was maintained at a constant value of 5 $L/(m^2 \cdot h \cdot m)$ from 21st to 125th day. However, the membrane special flux decreased from 23.2 $L/(m^2 \cdot h \cdot m)$ to 6.3 $L/(m^2 \cdot h \cdot m)$ during the first 20 days operation, which can be explained by the membrane initial plugging and pollution. As shown in Fig.6, SF

decreased with increasing TMP, while flux was increasing. We find that the SF decrease faster with increasing TMP in first 11th and 33th day than in 81th and 98th day. This implied that more and more particles are deposited on the membrane during greater TMP and corresponding high flux. The resistance of the forming cake layer influences the flux more and more especially at the beginning of the filtration. Therefore, it is very important to choose the correct TMP during the operation of MBR.

2.2.2 Backwash operation

Sludge particles being filtered often foul the membrane by blocking the membrane pores and/or by forming a cake layer on the membrane. Typical methods to reduce fouling effects include control over operating conditions (low pressure, high turbulence, and intermittent filtration), backwash (with permeate or air or both), and chemical

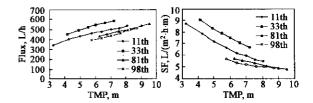


Fig. 6 Performances of flux and SF for dyeing wastewater treatment

cleaning (Visvanathan, 2000). Backwash with treated wastewater was used to alleviate membrane fouling in this study. Fig. 7 shows the characteristics of membrane permeate with and without backwash. Permeates with and without backwash were the same in the first 40 minutes operation, however, permeate without backwash decreased sharply after 40 minutes, i.e. dropped almost 65% within 90 min. Thus, 40 minutes was considered the limit for permeation without backwash. It is important to determine backwash time and frequency because backwash at too high frequency does not allow for adequate permeate collection, whereas backwash at too low frequency results in significant flux decline due to cake or gel buildup during each period of filtration. Backwash time and frequency should be optimized for maximizing the permeate flux, and was determined (30 minutes filtration and 20 seconds backwash) based on the method (Fan, 1997). About 90% of the permeate flux was restored after backwash. Permeate remained stable and decreased slowly during 125 days without chemical cleaning, which showed such way of backwash operation was effective technique for inhibiting membrane fouling.

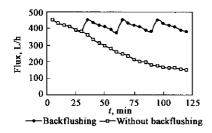


Fig. 7 Comparison of permeate with/without backwash in A/O MBR

Clearly, the negative effect of the cake layer on membrane performance was so serious that the flux was decreased sharply without backwashing. Deposition of sludge on the surface of membrane increase the risks of channel clogging, which is difficult to be removed. Backwashing is effective in removing the layer deposited on the membrane, decreasing cake layer resistance; at the same time, it is beneficial in reducing long-term membrane fouling.

2.3 Energy consumption

Membrane bioreactor power requirements come from pumping feed water, recycling retenate, backwash and aeration (Owen,

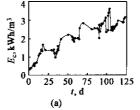
1995). Recycling retentate is the main factor of energy consumption ($E_{\rm c}$) for sidestream MBR because it has large pumping requirements to circulate biomass around the membrane loop at sufficiently high pressures and velocities. In this study, the energy consumption of the recirculation pumps was calculated from the measured values of flow and pressure through the system using the following equations:

Power (kW) =
$$[flow (m^3/s) \times pressure (N/m^2)]/1000;$$

Energy consumption (kWh/m³) = power (kW)/permeate flux (m³/h).

The pump efficiency should usually be considered (70% is used in this study). The results showed the energy consumption was $0.3-0.7 \text{ kWh/m}^3$ from day 1 to day 10, and increased significantly in following days compared to that in initial days due to TMP increasing. TMP should be increased in order to maintain constant permeate flux because membrane fouling inevitably occurred during operation. Energy consumption was $2.6-3.6 \text{ kWh/m}^3$ from day 65 to day 125 (Fig. 8a). As shown in Fig. 8b, E_c is dependent on flux. At a given TMP, the lower the flux, the higher the E_c . In other word, membrane fouling had heavy impact on energy consumption.

However, energy consumption obtained from power meter(3—5 kWh/m³) was higher than that in calculation. Such phenomenon may be explained that the energy consumption calculated did not include energy loss in pipe system due to frication, and in this study, a part of energy consumption was consumed in the pipe system, which means more attention should be paid on pipe selection and design



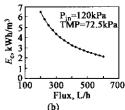


Fig.8 Theoretical energy consumption in A/O MBR

for the sidestream MBR system.

3 Conclusions

A/O MBR was feasible and effective for treating dyeing wastewater. The quality of treated water was excellent and met with the reuse water standard.

The permeate water quality was consistently high in this pilot scale MBR tested, i.e. effluent COD less than 25 mg/L, BOD₅ under 5 mg/L, turbidity lower than 0.65 NTU, and colour less than 30 DT, and met with the water reuse standard. The result showed that A/O membrane bioreactor could be used to treat dyeing wastewater.

Constant-flux operation was carried out in this study, and regular backwash was proved to be effective for reducing membrane fouling and maintaining constant flux.

Membrane fouling had heavy impact on energy consumption. In addition, more attention should be paid on pipe selection and design for the sidestream MBR system because a part of energy consumption was consumed in the pipe system.

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