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Pilot Study on Treatment of Wastewater from an Ethylene Plant with Membrane Bioreactor Technology

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Abstract: Pilot studies were conducted with an anoxic/aerobic concept membrane bioreactor (MBR) technology and a hollow fiber Petro® MBR system with capacity of 12 m^3/d was operated continuously (24-hour) during the study. Trials on different membrane fluxes were conducted to obtain the sustainable flux while mixed liquor suspended solid (MLSS) was maintained at 9-11 g/L. The results of the MBR pilot trials showed that no obvious fouling of the membrane was found when the plant was operated at the flux of 12 L /m^2/h (LMH) over 3 months and 15 LMH over one month during the pilot study. Design guidelines such as hydraulic retention time (HRT), sludge retention time (SRT), anoxic and aeration volume ratio, re-circulation flow rate and air scouring were obtained for a full-scale plant. It was concluded that treatment of wastewater from an ethylene plant without addition of any chemicals using MBR technology is feasible. The product quality consistently met the requirement for discharge and was suitable for the feed of further reverse osmosis (RO) post-treatment.

Keywords: Membrane bioreactor, ethylene wastewater, COD removal, nitrification, wastewater treatment and reuse.

INTRODUCTION

Advanced membrane bioreactor (MBR) which is a combination of the conventional activated sludge process (ASP) and Microfiltration/Ultrafiltration membrane separation has been widely used in treatment of domestic sewage as MBR has advantages of consistently high quality of effluent, small footprint, reduced sludge production and simple system operation and facility management over ASP [1-14]. Stephenson *et al.* [2] have introduced a number of MBRs for treatment of municipal wastewater. Various commercial MBRs have proven both robustness of the process and reliable and simple operation. Gander *et al.* [4] have studied different types of commercial MBRs for domestic wastewater treatment with cost considerations and indicated that the submerged configuration with sucking the product from the inside of membranes would be more cost effective in operation than the side-stream configuration with pressuring the product from the inside to outside of membranes. Judd [9] has reviewed the MBR technology with focus on principles and applications of MBRs. Tao *et al.* [12,13] have investigated different types of submerged MBRs under the tropical conditions and demonstrated the advantages of MBR technology for reclamation of the domestic sewage.

Very recently, Viero *et al.* [15] have studied the effect of long-term feeding of high organic loading in a submerged MBR treating oil refinery wastewater and showed high removal efficiency for both organic and phenols that proved the ability of the MBR technology to tackle high strength feed. However, there are limited studies of MBR technology on the treatment and reuse of petrochemical wastewater [16, 17]. Especially, challenges exist to deal with the ethylene wastewater with high concentrations of ammonia or oil & grease (O&G) and shock-loading of sulphide. Nevertheless, tightening effluent regulations have generated interest in the treatment of petrochemical wastewater with the advanced MBR process. An existing wastewater treatment facility in a ExxonMobil Chemical Operations Private Limited (Singapore) facility consists of oil-water separation, equalization, additional oil-water separation and conventional activated sludge process. Waste activated sludge treatment includes aerobic digestion and dewatering on a belt filter press. The treated water is discharged to sea in compliance with Singaporean effluent limitations. The facility wanted to investigate enhancement of its existing effluent treatment system. MBR was considered to be a viable solution for achieving better treated water quality and possible product water recycling. The objectives of this study were to evaluate the feasibility of treating the ethylene wastewater to meet the applicable discharge limits consistently using a submerged Petro® MBR and further to evaluate whether the quality of the treated water would meet reuse requirements.

MATERIALS AND METHODS

The feed water for the MBR pilot plant was tapped from a point after the equalization tank and before the conventional activated sludge process at the waste water treatment

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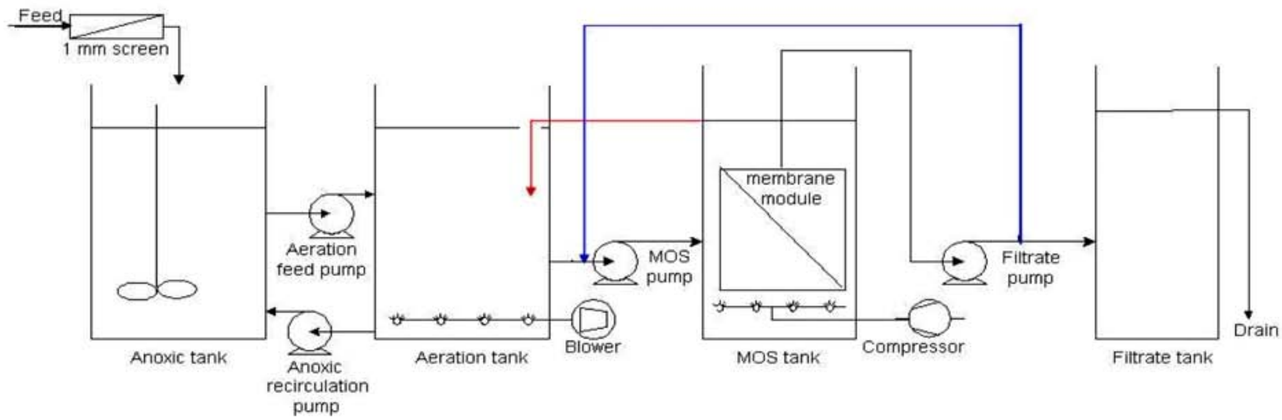

Fig. (1). Schematic process flow diagram of MBR pilot plant.

plant (WWTP) of the facility. Fig. (**1**) shows a schematic process flow diagram with an anoxic/aerobic concept. In the process, denitrification happens and nitrate is converted to nitrogen in the anoxic tank, and nitrification takes place and ammonium is converted to nitrate in the aeration tank while BOD and COD are biologically digested in both tanks. The membranes as filters allow clean water to pass but retain the activated sludge in the membrane operation system (MOS) tank. Hollow fibre membranes from Siemens Water Technologies were used for the trials. Specification of the MBR pilot plant is given in Table **1**. The operating conditions of MBR system are shown in Table **2**. The MBR pilot plant was operated continuously (24-hour) during the study and the operation was controlled by a programmable logic controller (PLC).

Table 1. Specification of MBR Pilot Plant

Item	Specification
Membrane type	Hollow fibre
Membrane material	Polyvinylidene Fluoride (PVDF)
Membrane pore size	0.04 μm (nominal)
Inner diameter/outer diameter of fibre	0.7 mm / 1.2 mm
Membrane area	37.5 m^2
Effective volume of anoxic tank	1.87 m^3
Effective volume of aeration zone	4.63 m^3

Trials on different membrane fluxes were conducted to obtain the sustainable flux. On Day 1, the MBR pilot plant was seeded from the existing activated sludge system. On Day 3, full operation of the pilot plant started at the net membrane flux of 6 LMH which was then gradually increased to 8, 10 and 12 LMH with zero sludge wastage on Day 5, Day 12 and Day 33, respectively. After that, the pilot plant continued the operation at the net flux of 12 LMH until Day 75 with wasting excess MLSS from the aeration tank at 300L/day from Mondays to Fridays. Due to an unexpected accident on the first membrane module which was replaced with a new one on Day 107, the pilot plant was operated at the net flux of 15 LMH with the second module from Day 113 onward. Maintenance clean (MC) with 200 mg/L of NaOCl solution was done twice per week during the operation.

MLSS in the aeration tank started from 4.5 g/L, gradually increased to 9 g/L, and was then maintained at 9-11 g/L during the study. Air flow for the aeration tank was 1.6 m^3/min or 2.56 m^3/h per m^2 membrane area, which was relatively high. It could be attributed to the high ***chemical oxygen demand*** (COD) in the influent, small effective aeration tank depth of 2.3m and low limit run of the aeration tank blower at 68% which resulted in an overcapacity run state (most of the time). Optimization of this condition in a full scale plant would be expected. Air scouring for the membrane was provided at 0.264 m^3/h per m^2 membrane area, which is commonly acceptable in a full scale plant.

RESULTS AND DISCUSSION

Membrane Permeability at Different Fluxes

Fig. (**2**) shows the membrane relative permeability (which is the ratio of specific flux at the time over that on Day 3) of the first membrane vs. time. The data before Day 10 were not presented. When the operation started at the flux of 6 LMH, the initial membrane relative permeability was 1.0 with MLSS concentration of 4512 mg/L in the aeration tank. When the flux was enhanced to 10 LMH on Day 12, MLSS was increased to 7280 mg/L. As a consequence, the relative permeability dropped to about 0.6. When the flux was increased to 12 LMH on Day 33 while MLSS was 8800 mg/L, the permeability further decreased to about 0.5. After that, the flux was kept at 12 LMH, the permeability remained stable at around 0.5 until Day 70. However, permeability declined quickly toward 0.36 on Day 78. The pilot plant was out of operation after Day 83 for a few days. The product was found to be contaminated with MLSS on Day 89. Thus, Clean-in-place (CIP) with hypo solution was conducted on Day 91 and membrane module was taken out for inspection. Loose connections between the cap and the module were found. Thus, a spring washer was added to secure the connection. When the pilot plant was restarted, permeability was recovered to 0.53 on Day 93 and quickly reduced to 0.35 on Day 102. When CIP was conducted again with citric acid solution, permeability only reached 0.48. The quick reduction of the membrane permeability on both Day 78 and Day 93 as well as the poor efficiency of CIP might be due to

Table 2. Operating Conditions of the MBR Pilot Plant

Parameter	Test 1	Test 2	Test 3
Desired net membrane flux (L/m²/h)	10	12	15
Feed flow rate (m³/h)	0.375	0.450	0.450
Desired product flow rate (m³/h)	0.406	0.570	0.687
Flow rate of re-circulated filtrate (gallon/min)	0	0	0.6
HRT (h)	17.3	14.4	14.4
Dissolved oxygen in the aeration tank (mg/L)	>2		
Re-circulation ratio from aeration to anoxic tank	3:1		
Re-circulation ratio from MOS to aeration tank	7:1		
pH in the anoxic tank	7.8 – 8.3		
pH in the aeration tank	7.4-7.9		
SRT (d)	28 (N/A for 10 LMH)		
Anoxic volume ratio (%)	30		
MLSS in aeration tank (mg/L)	9000~11000 (N/A for 10 LMH)		
Operation mode of membrane unit	On : Idle = 12 min : 1min		
Air flow for the aeration tank (m³/min)	1.6		
Membrane scouring air flow (standard ft³/h)	350		
Temperature (ºC)	35 ± 3		

plugging of MLSS into fibers caused by an unexpected accident of the loose connections mentioned above.

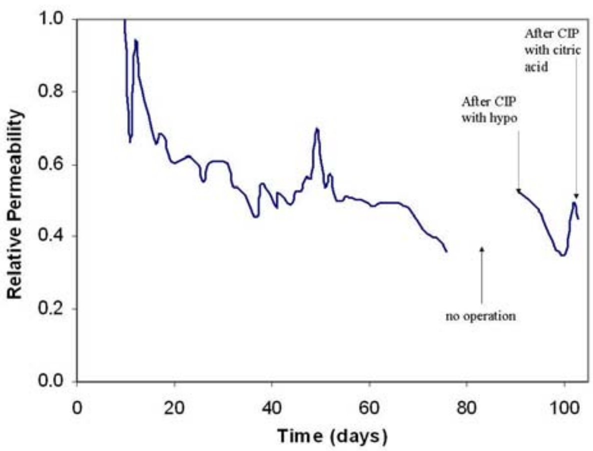

Fig. (2). Relative permeability of the 1st membrane *vs*. time.

Because of unsatisfactory recovery of permeability after CIP with hypo and citric acid, it was decided to install the second membrane module to replace the first one on Day 107. Initial membrane net flux of the second membrane module was 10 LMH on Day 109. The net flux was increased to 12 LMH on Day 111 and 15 LMH on Day 113. HRT was maintained at 14.4 hours during the operation at 15 LMH by re-circulating the product to the feed line of the MOS pump while the feed flow rate remained the same at 0.450 m^3/h. Fig. (**3**) shows the relative permeability vs. time. Permeability reduced from 1.0 at the beginning of 15 LMH on Day 113 to 0.56 on Day 132. Then, permeability seemed to be stable at 0.56 for about one week until Day 148. As the trans-membrane pressure (TMP) was <0.08 bar, which was really low compared to the target 0.4 bar for CIP, there would not be sufficient fouling to test the effectiveness of CIP. Encouraging results were observed at the flux of 15 LMH under the desired operating conditions during the five weeks.

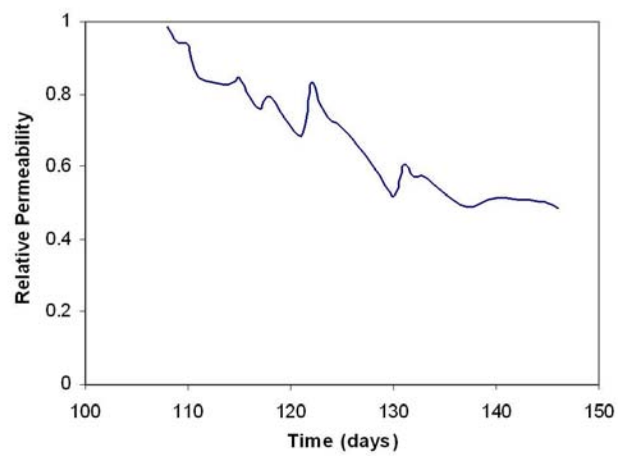

Fig. (3). Relative permeability of the 2nd membrane *vs*. time.

Stability of Biological Process

Fig. (**4**) indicates nitrification efficiency, sulfide and O&G contents in the feed during the pilot plant operation. Within one week from starting of the plant operation, the nitrification efficiency reached almost 100%. The nitrification efficiency was low at 54% and 22% on Day 76 and Day 97, respectively. The upset nitrification could be related to both the spikes of sulphide (more than 50 mg/L) and O&G in the MBR feed. However, the impact did not last long and nitrification recovered within few days.

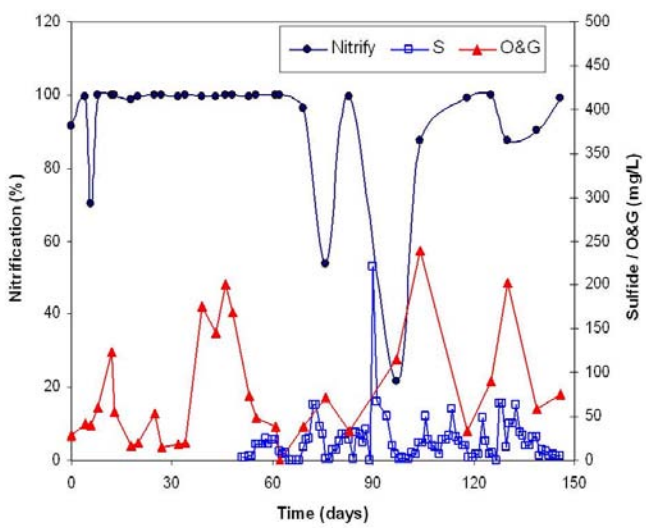

Fig. (4). Nitrification efficiency, sulphide and O&G content s in the feed *vs*. time.

Table **3** shows the ranges of the biologically degradable or convertible parameters in feed, anoxic tank, aeration tank and product. It can be seen that COD and biological oxygen demand (BOD) in the feed fluctuated in the range of 940-1600 mg/L and 290-885 mg/L, respectively. NH_3-N and TKN in the feed were at high levels and fluctuated in the range of 54.4-114 mg/L and 57-122 mg/L, respectively. When the operation was stable, BOD and COD in the anoxic tank were in the range of 13-32 mg/L and 108-371 mg/L, respectively. If nitrification was disturbed, BOD and COD were higher with maximums at 65 and 574 mg/L, respectively. During the stable operation, NH_3-N in the anoxic tank was 11.25-33.9 mg/L. NH_3-N reached 88.7 mg/L in the anoxic tank when nitrification was upset. It might be due to high sulphide content in feed as shown in Fig. (**4**). Nitrite did not inhibit both nitrification and de-nitrification throughout the study because nitrite levels in both anoxic and aeration tanks were very low at <0.1 mg/L (most of time). It is further confirmed that de-nitrification was not a concern because NO_3-N in the anoxic tank was less than 1.1 mg/L throughout the study. NH_3-N and NO_3-N in the aeration tank were in the range of 0.7-6.52 mg/L and 1.3-16.8 mg/L, respectively, indicating nitrification was satisfied. As a result, product COD and NH_3-N are in the range of 31-74 mg/L and 0.1-2.83 mg/L which are well within the water reuse specification indicated in Table **4** later.

In summary, biological process was generally quite stable during the study. There were a few occasions of sulphide spikes in the feed water which caused the upset of nitrification, however, nitrification in MBR system could be recovered within few days. Moreover, high concentration of oil & grease in the feed did not show an impact on the biological process and membrane fouling.

Analytical Results of Feed and Product Water

Typical quality of feed and MBR product water is summarized in Table **4**. Requirement for discharge and specification for water reuse are also given in Table **4**. The data shows that the MBR can produce a stable effluent even when the feed quality varies significantly. When the operation of MBR system was stable, COD and BOD concentrations in the product were 31-74 and 2-5 mg/L, respectively. Oil & grease in the product was less than 10 mg/L. NH_3-N was < 3 mg/L. Phosphate in the product was at <0.80-3.98 mg/L. It should be pointed out that pH of product was narrow in the range of 7.8-8.5 without addition of any chemical in the treatment process although the feed pH varied in a wide range of 6.9-9.4. TSS and turbidity of the product were <2.5 mg/L and 0.1-0.3 NTU, respectively. As a consequence, the product quality in terms of the biologically degradable parameters and characterization related to the MF membrane filtration well met the requirement not only for discharge but also for reuse because good biological processes were achieved and the integrity of the membranes was good. In addition, silt density index (SDI) of the MBR product was 2.9, indicating the product was suitable for RO feed.

Further analysis of the MBR product for inorganic parameters as shown in Table **5** indicates that sodium and sulphate in the product were the main components which caused high total dissolved solids (TDS). The TDS in the effluent precludes the use of all the MBR effluent for cooling water makeup. The final percentage of reuse will be determined after startup and the specific chemical program for the cooling water circuit is defined. In addition, total organic carbon (TOC) in the product was higher than the requirement for cooling tower makeup.

Table 3. Range of BOD, COD, NH_3-N and NO_3-N in Feed, Anoxic Tank, Aeration Tank and Product

Sampling Point	BOD (mg/L)	COD (mg/L)	NH_3-N (mg/L)	TKN (mg/L)	NO_3-N (mg/L)	NO_2-N (mg/L)
Feed	290 - 885	940 - 1600	54.4 - 114	57 – 122	0.02 – 2.8	-
Anoxic tank	13- 32	108 – 371	11.25 – 33.9	-	0.01– 1.1	0.01– 0.1
Aeration tank	9 – 28	52 – 162	0.7 – 6.52	-	1.3 – 16.8	0.01– 0.1
Product	2– 5	31 – 74	– 2.83	0.15 – 4.2	8.6 – 28.4	0.01– 0.1

Table 4. Typical Quality of Feed and Product

Parameter	Feed	Product	Requirement for Discharge	Specifications of Water Reuse for Cooling Tower Makeup
COD (mg/L)	940 - 1600	31 – 74	<100	-
BOD (mg/L)	290 - 885	2 – 5	<50	<5
Oil & grease (mg/L)	15 - 239	<10	<10	-
NH_3-N (mg/L)	54.4 - 114	0.1 – 2.83	-	<5
PO4 (mg/L)	<0.80 – 14.3	<0.80 – 3.98	<5	-
pH	6.9 - 9.4	7.8 - 8.5	6-9	-
TSS (mg/L)	12-511	<2.5	<30	<5
Turbidity (NTU)	--	0.1 – 0.3	-	-
SDI		2.9	-	<3 (as RO feed)
TDS (mg/L)	3190 - 6470	2916 - 6540	-	<1000
TOC (mg/L)	313 - 475	13.4 – 26.6	-	<10

Table 5. Product Quality (Inorganic)

Parameter	Unit	Value
Arsenic	mg/L	0.013 – 0.020
Calcium	mg/L	8.89 - 12.7
Chloride	mg/L	137 - 169
Chromium	mg/L	<0.007
Copper	mg/L	<0.002
Iron	mg/L	0.017 - 0.023
Lead	mg/L	<0.013
Magnesium	mg/L	5.48 – 6.40
Mercury	mg/L	0.032 - 0.047
Nickel	mg/L	0.004 - 0.006
Phosphate	mg/L	<0.80 – 3.98
Sodium	mg/L	1570 - 1830
Sulphate	mg/L	2410 - 3195
Si as SiO_2	mg/L	2.57
Total alkalinity as CaCO3	mg/L	365 - 406
Zinc	mg/L	<0.004

CONCLUSIONS

From the results of the MBR pilot trials, the conclusions can be drawn as follows: (1) it is feasible to treat petrochemical wastewater using MBR technology. The product quality consistently met the requirement for discharge and was suitable for the feed of further RO post-treatment; (2) during the pilot study, no obvious fouling of the membrane was found when the plant was operated at the flux of 12 over 3 months and 15 LMH over one month; (3) HRT of 14 hours and SRT of 28 days, anoxic and aeration volume ratio of 30:70, re-circulation flow rate from the aeration tank to anoxic tank being 3 times of the feed flow rate, air scouring for the membrane at 0.264 $m^3/h/m^2$ could be used as design guide for full-scale plant; (4) MC with 200 mg/L of hypo solution at the frequency of twice per week was found reasonable.

Recommendations in future work include to optimise air flow for the aeration tank, to verify low fouling tendency at higher flux for enhancement of production, to conduct RO post-treatment for reuse of the treated water and to conduct economic evaluation of the new process.

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