Development of Anti-Fouling High Pressure RO and Application to ZLD process

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EXTENDED ABSTRACT

In order to alleviate freshwater scarcity and environmental pollution problems common in industrial water treatment, maximizing the recovery and recycling efficiencies of industrial wastewater has become a growing trend in recent years. However, wastewater treatments that yield very high recovery could result in the generation of high salinity wastewater containing high concentrations of organic foulants.

Conventional seawater reverse osmosis (SWRO) membranes have mainly been developed for seawater desalination, but they have also seen development and use for the treatment of industrial wastewater with high concentrations of salinity and high organic foulants.

This paper reports on the study of a novel anti-fouling high pressure RO (HPRO) membrane that has been developed by modifying its membrane surface to get neutral and hydrophilic properties. A comparison test between the anti-fouling HPRO and a conventional SWRO membranes was performed in India at a common effluent treatment plant (CETP) where the effluent contains high concentrations of organic foulants and salinity. As the result, anti-fouling HPRO has showed higher fouling resistance compared to the conventional SWRO. It means, neutral charge and hydrophilic surface contribute the improvement of anti-fouling property and suitable for high COD high salinity wastewater applications.

Keywords: Fouling, Anti-fouling RO membrane, Industrial wastewater, Zero liquid discharge, High chemical oxygen demand,

I. INTRODUCTION

Rising demand for fresh water as a result of rapid industrialization and urbanization has brought about water scarcity and environmental pollution in the world, which are becoming critical global issues. Over the past decade, wastewater recovery and its recycling has been drawing more and more attention. Wastewater reuse contributes not only to minimize the volume of freshwater intake from nature but also to alleviate pollution of aquatic ecosystems. From this perspective, zero liquid discharge (ZLD) can also be regarded as a technology to reduce water pollution and to augment water supply [1].

Early technologies of the conventional ZLD systems were based on thermal processes, where wastewater was fed to an evaporator for evaporation follow by a brine crystallizer or an evaporation pond. One of the major challenges of implementing ZLD is high cost of operation. For this reason, the early thermal based ZLD system has only been applied to the limited cases. However, in recent years, thermal ZLD technologies have been developed with combination of reverse osmosis (RO) membrane systems to improve energy and cost efficiencies. For thermal ZLD solutions, RO membrane is used at pre-concentration in order to minimize the volume of concentrated brine to be fed to evaporators for the reduction of the energy consumption [2][3].

In recent years, India and China have already been experiencing water scarcity resulted from depleting freshwater resources and increasing water contamination. These two countries have enforced rigid environmental regulations that made ZLD wastewater treatment is mandatory for various industries. In India, a large part of industrial wastewater comes from textile and tannery industries in which most factories are small scale and cannot afford to have their own effluent treatment plant (ETP). Therefore, local government authorities have taken the initiative to promote installation of common effluent treatment plants (CETP) at numerous industrial clusters throughout India to treat wastewater from these plants collectively [4]. The wastewater collected from various plants has a wide range of feedwater salinities from 2,000 to 15,000 mg/L of TDS with various types of contaminants that can be represented as water quality parameters: suspended solids (SS), turbidity, chemical oxygen demand (COD), biochemical oxygen demand (BOD), silt density index (SDI) and hardness in high value. They are indicators of fouling potential of water treatment. RO membrane system is usually designed with two to five stages based on the system recovery, and the brine water of this kind of multi-stage system contains the highly concentrated contaminants mentioned above. This could pose potential problems of heavy fouling and scaling of RO membrane.

Membrane fouling is one of the biggest problems for the wastewater treatment. When TDS concentration in wastewater is higher than 10,000 mg/L, SWRO would be suitable to be used considering the maximum pressure limit and membrane performance. So far, majority of ZLD wastewater plants have been using conventional SWRO membranes to concentrate high-salinity wastewater prior to evaporator; however, these SWRO membranes were originally developed for seawater desalination, not for industrial wastewater treatment. So, we have developed a novel anti-fouling HPRO membrane named PRO-LF1 targeting at treatments of high salinity wastewater. PRO-LF1 is designed to withstand high pressure up to 1200psig and has modified the membrane surface with neutral charge and a hydrophilic coating layer that can minimize fouling rate.

This paper describes the properties of PRO-LF1 comparing with a conventional SWRO and benefits expected from PRO-LF1 based on the pilot test results collected from the actual ZLD plant, industrial CETP in India.

II. MATERIALS AND METHOD

2.1 RO Membrane

In this study, two types of RO membranes were tested. **Fig. 1** shows the membrane cross section structure of PRO-LF1. Conventional SWRO membrane has 3 layers structure include non-woven fabric (Poly Ester), support layer (Poly Sulfone), skin Layer (Poly Amide). On the other hand, PRO-LF1 membrane has another layer which consist of hydrophilic polymers on the top. It means PRO-LF1 membrane has 4 layers structure.

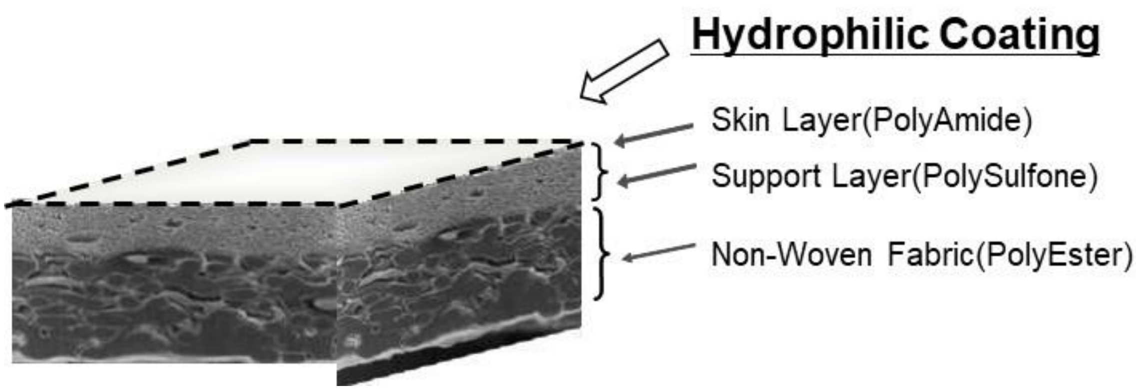

Fig. 1. Membrane cross section structure of PRO-LF1

2.2 Membrane characterization

2.2.1 water contact angle

The water contact angle was evaluated using a drop shape analysis system (Drop Master DM 500, Kyowa). The water contact angle was automatically measured using θ/2 method of computer image analysis. The contact angle of distilled water droplet deposited on the membrane surface (1.5 uL) was measured 10 seconds after the start.

2.2.2 Zeta potential measurements

Zeta potential of the membrane surface was determined by latex electrophoresis method using a laser doppler method (ELS-Z, Otsuka Electronics) A sheet of membrane was attached on a quartz cell, and monitoring particle solutions were circulated to measure the zeta potential at pH 3, 4, 5.5, 7, 9.

2.3 Trial in a real-scale industrial CETP

2.3.1 Description of a real-scale plant

To evaluate the performance of PRO-LF1, a pilot trial was carried out at a real CETP in India. The plant's water treatment process consists of equalization tank, flash mixer primary clarifier, aeration tank, secondary clarifier, dual media filter (DMF), ultrafiltration (UF), three stages RO follow by evaporator.

The RO system information is summarized on **Table 1**. In the trial, two RO trains with the same configuration were used. Each train has three stages with 4 pressure vessels, the array of the pressure vessels is as follows: two vessels in 1st stage, single vessel in 2nd stage and in 3rd stage respectively, and each vessel accommodates six membranes. The 1st stage of both trains was used for the trial. PRO-LF1 elements were installed in one train, and the same number of conventional SWRO were installed in the other at the same time.

Table 1. RO system information in CETP

Total number of Trains	3
Number of stages per train	3
Array of vessel at each stage	2 : 1 : 1
Number of membranes per vessel	6
Designed permeate recovery	65%
Designed Feed flow	13.0 m3/h

2.3.2 RO feed water parameters

Typical RO feed water parameters are listed in **Table 2**. Since the wastewater treated at the CETP was collected from about 20 facilities, some of water parameter values slightly fluctuated during the operation. TDS values were around 15,000 to 23,000 mg/l, and COD were around 500 to 1,500 ppm.

Table 2. Typical RO feed water parameters in CETP

Parameters	value
TDS	15,000 – 23,000 mg/L
Calcium as Ca	120 mg/L
Magnesium as Mg	180 mg/L
Total alkalinity as CaCO3	2,000 mg/L
COD	500 – 1,500 mg/L
pH	7.0 - 8.4

2.2.3 RO system performance normalization

RO systems are expected to operate under steady conditions over the long term with constant operating parameters such temperature, operation pressure, permeate flow and recovery. In actual operations, some of parameters do change due to membrane fouling and changed feed conditions. RO system performance normalization is a technique that takes account of factors of temperature, pressure and feed TDS to normalize equations used for comparing operations at a specific set of conditions with the initial stable conditions. The normalized data would help us to analyze whether changes in flow or rejection have been caused by fouling or simply by different operating parameters. In this study, the normalized data was calculated by Nitto Denko/Hydranautics software RODataXL

III. RESULTS AND DISSCUTION

3.1 Membrane characterization

As shown in **Fig. 2**, the water contact angle of the conventional SWRO membrane is 45 degree, in comparison, the contact angle of PRO-LF1 is 25 degree, which is smaller than that of conventional SWRO. It means PRO-LF1 membrane has higher hydrophilic surface compared with the conventional SWRO.

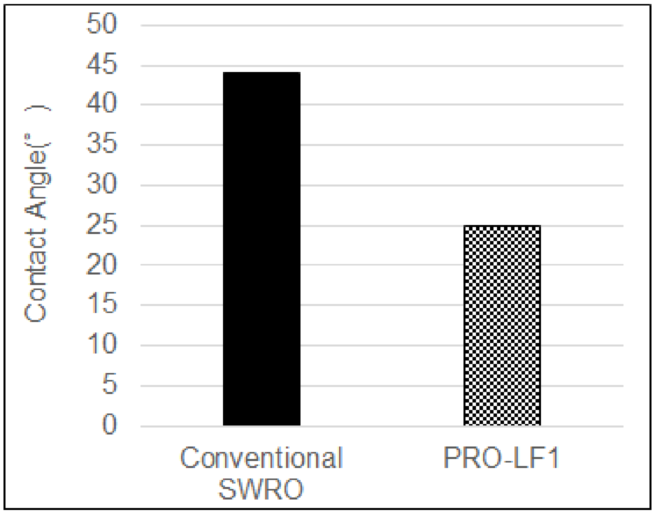

Fig. 2. Water contact angle as a measurement of hydrophilicity of the membrane surface.

Zeta potential of the membrane surface is shown in **Fig. 3**. Normally, Zeta potential of RO membranes changes from positive to negative when pH increases. When the pH range was between 6 and 10, which is normally seen in actual wastewater treatment, PRO-LF1 shows a narrow range of zeta protentional near the range of zero mV, which means the membrane charge keeps neutral. On the other hand, the conventional SWRO membrane has a negative zeta potential at the pH range of 6-10.

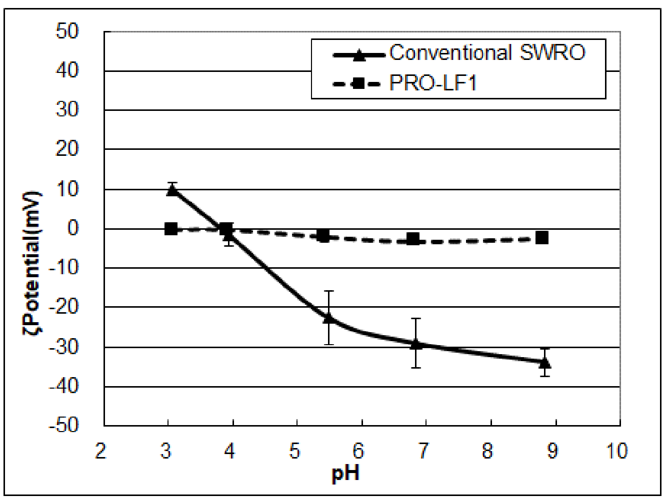

Fig. 3. Effect of pH changes on the zeta potential of the membrane surface.

3.2 Trials in real-scale industrial CETP plant

In order to investigate benefits of PRO-LF1 compared with the conventional SWRO, both were installed in the first stage of the respective trains and operated in parallel at same condition and period. **Fig. 4** shows the normalized permeate flow with operating time of the two membranes. 1st chemical cleaning in place (CIP) was conducted both trains at same time due to the normalized permeate flow dropped after operating 3 weeks.
The CIP restored permeate flow of PRO-LF1 better than that of conventional SWRO. PRO-LF1 normalized permeate flow has been restored to the level of the initial operation. In contrast, the normalized permeate flow of conventional SWRO has been restored to 80% of the level of the initial operation. Before a 2nd CIP, PRO-LF1 maintain the permeate flow higher than that of the

conventional SWRO. During the pilot trials, PRO-LF1 were conducted 4 times CIPs. In contrast, the conventional SWRO were conducted 8 times CIPs due to the reduction of the permeate flow. The frequency rate of the CIP of PRO-LF1 is reduced 50% compared with conventional SWRO during the same period. There is approximated 10 % higher permeate flow for PRO-LF1 compared to the conventional SWRO during the period of the trial.

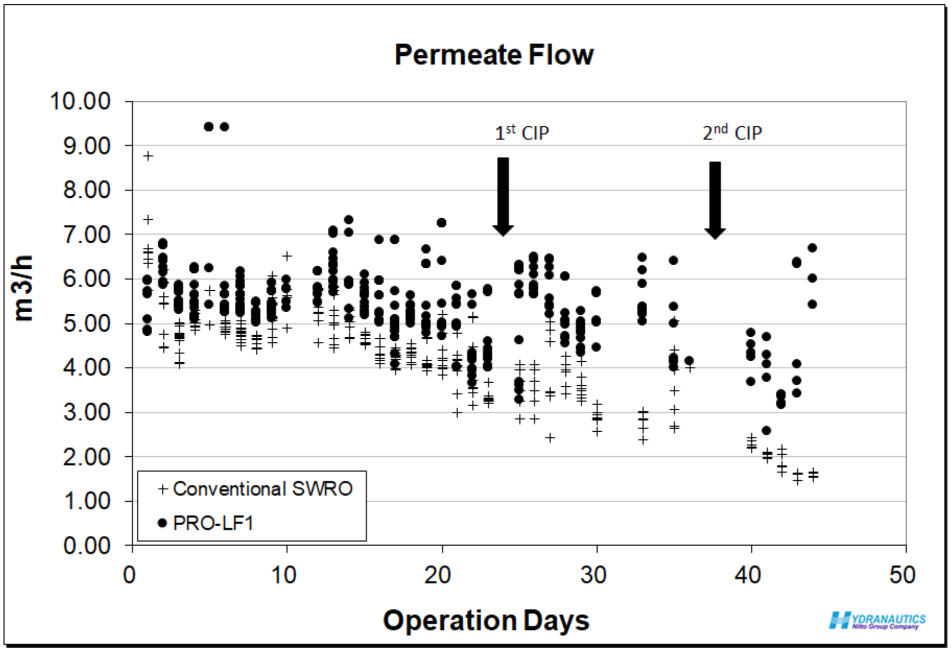

Fig. 4. Normalized permeate flow with operating time of the two membranes.

The permeate and reject TDS during the pilot trials as shown in **Fig. 5**. Both permeate water have good qualities with the TDS lower than 300 mg/L at same. We could achieve the return and reuse the permeate water to the facility's process and smooth concentrate the TDS before evaporator.

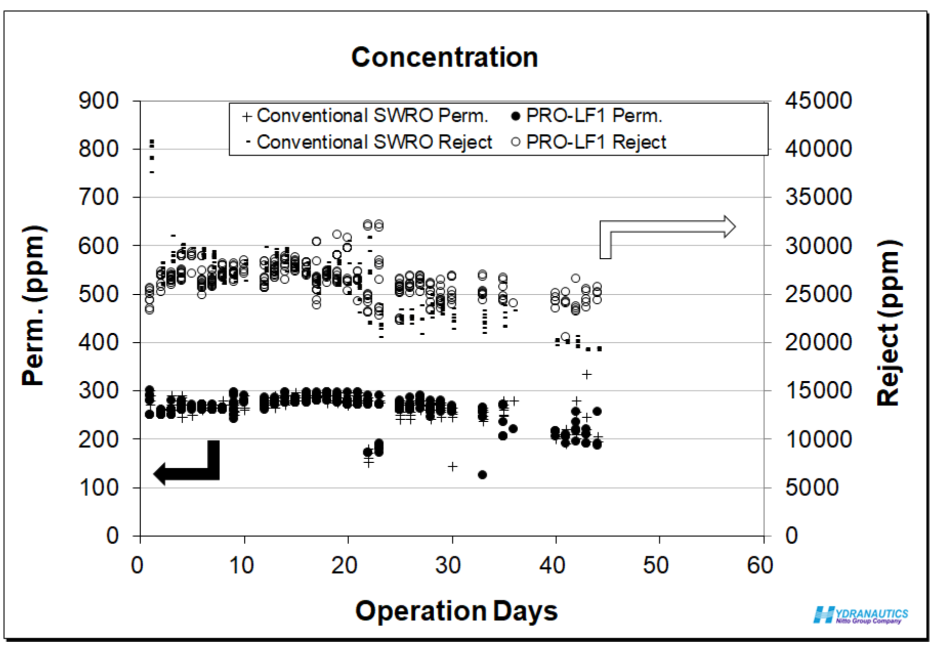

Fig. 5. Permeate and reject TDS with operating time of the two membranes.

IV. CONCLUSIONS

In this study, a novel anti-fouling high pressure RO membrane (PRO-LF1) has been developed by modifying the membrane surface with neutral changed and hydrophilic features.
A comparison test between PRO-LF1 and a conventional SWRO membrane were carried out in industrial common effluent treatment plant (CETP) in India around 150 days. As the result, PRO-LF1 has showed higher fouling resistance compared to the conventional SWRO. PRO-LF1 showed lower fouling rate than the conventional SWRO, which is suitable for with high COD high salinity wastewater applications. It means, neutral charge and hydrophilic surface contribute the improvement of anti-fouling property. PRO-LF1 provides cost benefits that consist of better productivity because of lower flow reduction, less chemical cleaning frequency and higher plant availability by downtime reduction compared to the conventional SWRO.

V. REFERENCES

[1] Tiezheng Tong and Menachem Elimelech, The Global Rise of Zero Liquid Discharge for Wastewater Management: Drivers, Technologies, and Future Directions, Environ. Sci. Technol. 2016, 50, 6846−6855

[2] Yasuhiro Tomi, Toshiyuki Kawashima, Shunsuke Nomi, Cutting-edge of Membrane Development for Water Treatment. 2020, 182-192

[3] Salt works HP https://www.saltworkstech.com/news/zero-liquid-discharge-and-minimal-liquid-discharge-become-lower-cost-through-reverse-osmosis-innovation/

[4] Anju Singh, Richa Gautam and Rajan Sharma, Performance evaluation of a common effluent treatment plant (CETP) treating textile wastewaters in India, Jr. of Industrial Pollution Control 24(2) (2008)111-121.