Evaluation of a Low-fouling High-pressure RO Membrane for ZLD System Compared with a Conventional SWRO

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Abstract: To relieve the freshwater scarcity and environmental pollution, maximizes recovery and recycling of industrial wastewater has been required. Such high recovery of wastewater results in high salinity wastewater including high organic foulants. Conventional seawater RO (SWRO) membranes have been used to treat them. However, SWRO membranes are mainly designed for seawater desalination, which present challenges in the treatment of the industrial wastewater with high salinity and high organic foulants. A low-fouling high-pressure RO (HPRO) membrane has been developed by modifying the membrane surface with neutral changed and hydrophilic features. A comparison test between the low-fouling HPRO membrane and a conventional SWRO membrane were carried out in a tannery common effluent treatment plant (CETP) where the effluent quality characterizes high organic foulants and high salinity. The low-fouling HPRO showed a higher permeate flow and lower chemical cleaning frequency than the SWRO membrane during the trial.

Keywords: Zero liquid discharge; Low-fouling high-pressure RO; Tannery wastewater

Introduction

Recovery and recycling of wastewater has been receiving more and more attention in the past decade. Wastewaters reuse not only minimizes the volume of intake of freshwater from nature, but also alleviates the pollution of the aquatic ecosystems. In this perspective, zero liquid discharge (ZLD) is reconsidered as a promising technique to reduce water pollution and augment water supply (Yaqub, M., and Lee, W., 2019). For example, the water situation in India has already overstressed with the depleting freshwater resources and increasing water contamination. Environmental regulations have mandated true ZLD wastewater treatment in many industries, including textile, tannery, pulp & paper, pharmaceutical and distillery in certain locations (Virpan *et al.*, 2016). A large part of industrial wastewater such as textile and tannery which generated in India comes from small size factories, which is unaffordable to install standard effluent treatment plant (ETP). Therefore, public authorities have taken the initiative to promote an approach is together the wastewater from the small industrial plants in CETP to treat the wastewater (Singh, A., *et al.*, 2008). These wastewaters combined in 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 such as suspended solids (SS), turbidity, COD, biochemical oxygen demand (BOD), silt density index (SDI) and hardness in high value. They are indicated fouling potential of water treatment. RO membrane system usually designed from two to five stages based on the system recovery and contaminants. These contaminants will be concentrated in brine water of RO which cause the fouling and scaling potential of RO membrane.

In recent years, China has faced a similar situation to India. In China, water shortages and environmental pollution due to rapid economic development and urbanization are becoming severe, and some regions are demanding the introduction of ZLDs to thermal power plants. Also, to reduce dependence on oil imports from overseas, coal chemical industry using abundant coal reserves has been booming in China. Coal chemical industry is an industry that produces chemical raw materials by liquification or gasification of coal as a substitute for chemical raw materials derived from petroleum and natural gas. Inner Mongolia, Shanxi Province, Xinjiang such regions where coal chemical industry is thriving, on the other hand, these regions are suffering from water shortages. Since coal chemical plants consume a large amount of water, the coal chemical industry is required to improve the water reuse rate and ZLD.

In conventional early 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. The main challenge of implementing ZLD is the high cost of operation. For this reason, the early thermal based ZLD system has been applied only in limited cases. Recently, ZLD technology has been developed for combination of reverse osmosis (RO) membranes system into the thermal ZLD system to improve energy and cost efficiencies (Tong,T., and Elimelech, M., 2016). However, majority of ZLD wastewater plants have been using conventional SWRO membrane to concentrate high-salinity wastewater prior to evaporator. Those SWRO membrane were developed for seawater desalination but for treatment of industrial wastewater. Therefore, Nitto Denko /Hydranautics developed a new low fouling and high-pressure RO (HPRO), PRO-LF1, to treat the high salinity industrial wastewater (Tomi *et al.*, 2021). The membrane surface is modified with a neutrally charged and hydrophilic coating layer which minimizes fouling rate.

This paper is explored the performance of the low fouling HPRO membrane, PRO-LF1, compared with a conventional SWRO to estimate the benefit of the low fouling membrane. Actual plant tests were carried out at a tannery CETP in India.

Material and Methods

Two types of RO membranes were tested in the study: an low-fouling HPRO, PRO-LF1, and a conventional polyamide composite SWRO membrane. The 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 has another layer on the membrane surface by using a surface coating method. The membrane surface has a neutrally charged hydrophilic coating layer, which minimizes membrane fouling. The SWRO membrane has a negative charged on the membrane surface. **Table 1** lists the properties of the elements.

Membrane characterizations were investigated by using methods of water contact angles, membrane surface zeta potentials and atomic force microscopy (AFM).

To evaluate the performance, a real-scale trial was carried out in a tannery wastewater CETP ZLD process in India. Both SWRO and PRO-LF1 were installed in individual RO trains. The process consists of equalization tank, primary clarifier, aeration tank, dual media filter, UF, three stages RO follow by an evaporator unit. **Figure 1** shows the schematic diagram of the ZLD process. The wastewaters combined in a wide range of feedwater salinities from 15,000 to 20,000 mg/L of TDS with various types of contaminants that can be represented as water quality parameters such as turbidity, COD, silt density index (SDI) and hardness in high value.

Results and Discussion

The effect of the pH changes on the zeta potential of the membrane surface has been measured. The effect of the pH changes on the zeta potential of the membrane surface as shown **in Figure 2**. The Zeta potential of the RO membranes change from positive to negative as the pH of the solution is increased. At the pH range of 6 to 9, where normally to be represented in actual wastewater treatment, PRO-LF1 shows a narrow range of zeta protentional near the range of zero mV, which means the membrane characterize natural change on the membrane surface. On the other hand, the conventional SWRO membrane has a negative zeta potential at the pH range of 6-9.

The water contact angle as a measurement of hydrophilicity of the membrane surface was evaluated using a drop shape analysis system. As shown **in Figure 3**, the water contact angle of the conventional SWRO membrane has 45°, in comparison, the contact angle of PRO-LF1 has 25°It indicate that PRO-LF1 not only has a more neutral surface charge, but also it shows more hydrophilic compared with the conventional SWRO. It is known that surface charge properties on membrane have a significant influence on membrane performance. The negatively charged membranes surface would be easily adsorbed by cationic and amphoteric surfactants that leads to the water flux of membrane drastically decreases because of fouling. To investigate the effect of the neutral changed membranes on different species surfactants, cationic, anionic, ampholytic and non-ionic surfactants have been used the comparison test between PRO-LF1 and the conventional SWRO membrane. The effect of different species surfactants on the permeate flux retention as shown in **Figure 4**. Both of nonionic changed membranes and conventional negative charged membranes are stable with Anion surfactant. On the cationic, ampholytic and neutral surfactants, the neutral changed membranes show more stable permeate flow retention compared with that of negative charged membranes.

To investigate benefits of the low fouling high pressure membrane 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. **Figure. 5** shows the normalized permeate flow with operating time. 1^{st} 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. At the 2^{nd} CIP, PRO-LF1 maintain the permeate flow higher than that of the conventional SWRO.

The actual permeate TDS changes with operating data as shown in **Figure 6**. The feed water TDS are fluctuated between 14,500 mg/L and 18,500 mg/L, and is nearly maintained at 16,000 mg/L. Initially permeate TDS was in the range of 280ppm to 300 ppm, after few weeks, permeate TDS was maintained in the range of 220 to 260 ppm. Both permeate solution have shown good qualities with the TDS lower than 300 mg/L. It is indicated the permeate TDS is seldom influenced from the reduction of the permeate flow due to the organic fouling.

Conclusions

In this study, an HPRO membrane, PRO-LF1, has been developed by modifying the membrane surface with neutral charged and hydrophilic characteristics. Results indicated that HPRO membranes could achieve a stable plant performance while treating high organics laden wastewaters compared with a conventional SWRO. A comparison test between the HPRO membrane and SWRO membrane were carried out in a CETP in India. As a result, the HPRO showed a lower fouling rate than the SWRO for treating wastewater with high COD and high salinity such as tannery.

Lower permeate flow reduction, lower chemical cleaning frequency and lower downtime increased the plant productivity realizing cost benefits compared to the SWRO membranes.

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Figures and Tables

Table 1 Specified performance description and properties of RO membranes.

Parameter	low fouling HPRO (PRO-LF1)	Conventional SWRO
Nominal Salt Rejection*)	99.8 %	99.8 %
Nominal Permeate flow*)	29.1 m^3/d	34.1 m^3/d
Materials	Composite polyamide	Composite Polyamide
Membrane surface	Neutral	Negative
Active area	37.2 m^2	37.2 m^2
Configuration and size	8-inch Spiral wound	8-inch Spiral wound
Maximum pressure	8.3 MPa	8.3 MPa
Manufacturer	Nitto Denko/Hydranautics	Nitto Denko/Hydranautics
*Test conditions	32,000 mg/L NaCl solution; 5.5 MPa;25 Degree C; 10% recovery	

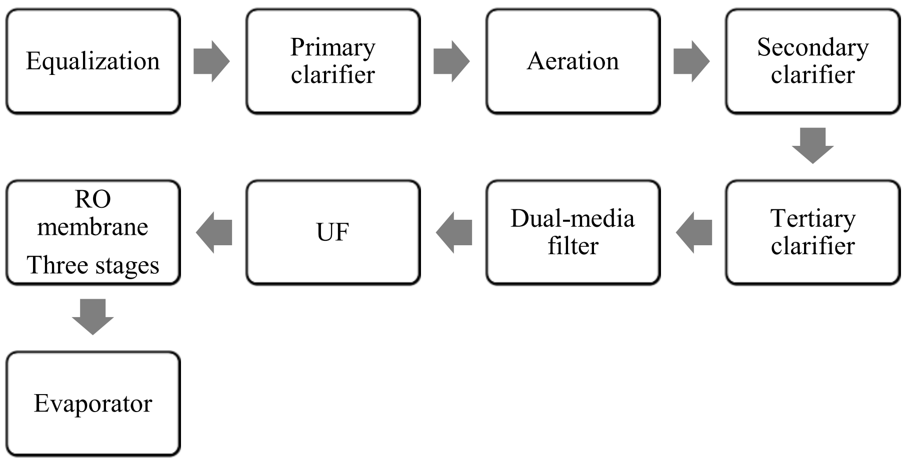

Figure 1 Schematic diagram of the tannery ZLD process.

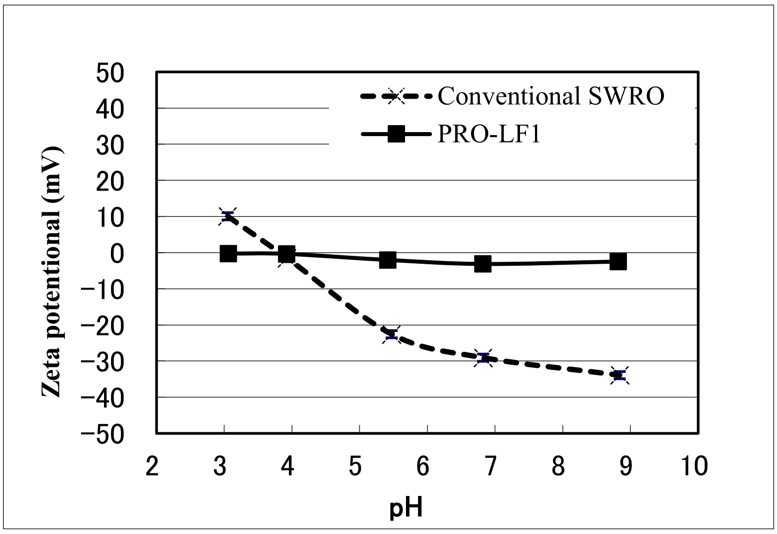

Figure 2 Effect of pH on the zeta potential of the membrane surface

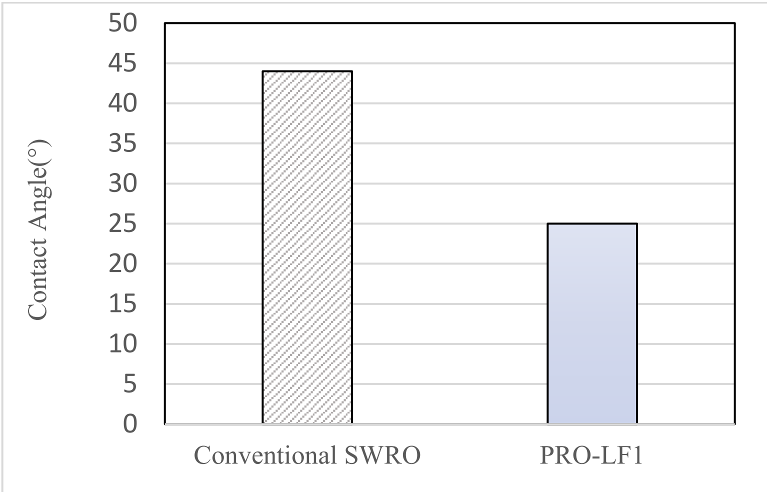

Figure 3 Water contact angle as a measurement of hydrophilicity of the membrane surface.

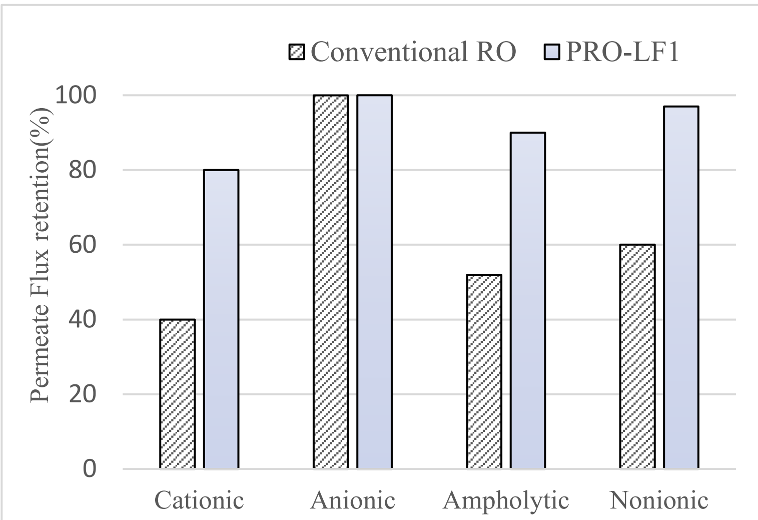

Figure 4 Effect of different species surfactants on the permeate flux retention.

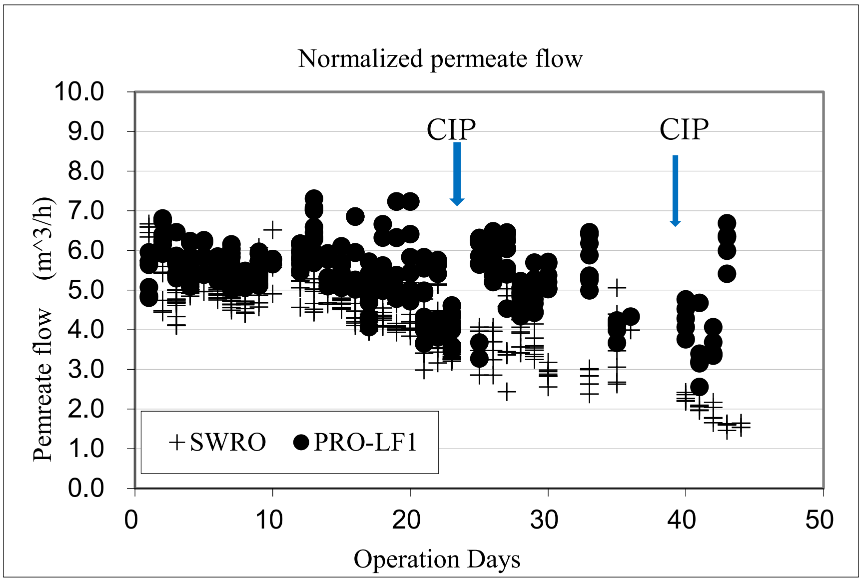

Figure 5 Normalized permeate flow data present with operating time.

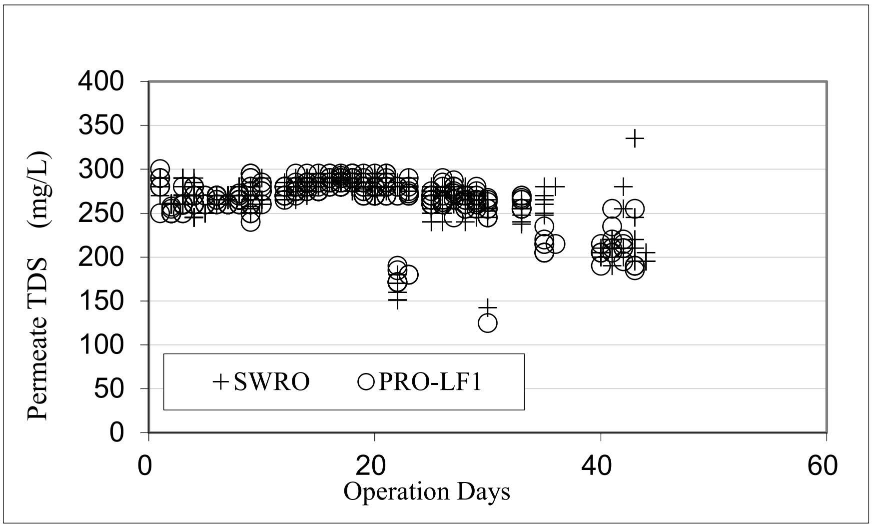

Figure 6 Actual permeate and Feed TDS change with operating time.