Short- and long-term fouling characteristics of reverse osmosis membrane at full scale leachate treatment plant

Weerapong Rukapan, Benyapa Khananthai, Chart Chiemchaisri, Wilai Chiemchaisri and Thirdpong Srisukphun

ABSTRACT

This research is focused on characterizing the foulants on a reverse osmosis (RO) membrane taken from a full-scale leachate treatment plant in Thailand. The system consists of a physico-chemical pre-treatment unit and RO system and has been in operation for 2 years. Ferric chloride (FeCl3) was added to the open-jet sedimentation tank at 2.0–2.5 g/l dosage for chemical coagulation. The supernatant from the sedimentation tank was polished using a pressurized sand filter prior to entering the RO system. The RO unit consists of seven pressurized vessels and 42 membrane elements (6 elements in each vessel). The recovery ratio and operating pressure in the RO system were maintained at 50% and 1.5–2.5 MPa. Fouled membranes obtained from short-term (6 months) and long-term operation (2 years) were taken from the system and analyzed by autopsy and sequential cleaning methods. The analysis of foulants on the membrane surfaces revealed that Fe deposits at 3.11 g/m². For short-term operated membranes, water cleaning could recover 32.14 and 7.45% of initial pure water flux on the 1st and 6th membrane elements. NaOH cleaning, however, recovered more than 90% of initial flux, much higher than that of HCl solution in both elements. For long-term operated membranes, pure water flux recovery was below 5% for both 1st and 6th elements. Sequential cleaning by NaOH followed by HCl yielded the best results. Nevertheless, flux recovery through sequential cleaning of long-term operated membranes was only 35.3 and 19.1% for the 1st and the 6th elements, respectively.

Key words | flux recovery, fouling, leachate treatment, reverse osmosis, sequential cleaning

INTRODUCTION

Landfill is the most popular method for disposing solid wastes in developing countries because it is the least expensive alternatives. Nevertheless, biological and chemical transformation processes in landfills produce solid, liquid, and gaseous by-products. The degradation of the organic portion of the waste, in combination with percolating rain water, leads to the production of a highly contaminated leachate. Appropriate treatment of leachate depends on leachate characteristics. Raw leachate from young landfills contains most of organic substances in biodegradable form thus can be easily treated by biological processes. For old landfills, most of the leached organic compounds are hardly or non-biodegradable forms and they should be treated by physico-chemical processes or a combination of biological and physico-chemical processes (Baumgarten & Seyfried 1996; Ahn et al. 2002; Renou et al. 2008). Among the treatment processes, membrane filtration especially reverse osmosis has been successfully applied to stabilized leachate (Bilstad & Madland 1992; Linde et al. 1995; Chianese et al. 1999; Trebouet et al. 2001; Chan et al. 2006). However, membrane fouling is still the main task to overcome (Peters 1998; Agenson & Urase 2007; Tang et al. 2007; Sioutopoulos et al. 2010). Specifically, fouling of reverse osmosis membrane applied to leachate treatment differs from one site to another due to the fact that chemical composition of leachate is very complex and varies widely depending on landfill operating conditions. For effective prevention of membrane fouling, short-term and long-term fouling characteristics of pollutants which deposited on membrane surface needs to be clearly understood.
Nevertheless, such information is very limited especially on a full-scale operating leachate treatment system. This study attempts to investigate short-term and long-term fouling characteristics of reverse osmosis membrane applied to leachate treatment at full scale operation in Thailand.

**MATERIALS AND METHODS**

**Full-scale leachate treatment plant**

The schematic of the leachate treatment process is illustrated in Figure 1. The treatment capacity of the leachate treatment is 1,000 m³/d. The leachate treatment plant consists of an open-jet sedimentation unit, pressurized sand filter, and a reverse osmosis (RO) membrane. The open-jet sedimentation unit consists of two tanks. The diameter, height, and volume of each tank are 6 m, 6.6 m, and 112 m³, respectively. Ferric chloride was dosed to the raw leachate as coagulant at a concentration of 2.0 – 2.5 g/l. After leaving the sedimentation tank, the treated leachate was fed into the pressurized sand filter. The main function of the pressurized sand filter is to remove suspended solids from the supernatant from sedimentation tank. The pressurized sand filter consisted of two tanks. The diameter, height, volume, and cross-sectional area of the sand filter were 2.9 m, 1.5 m, and 6.6 m² respectively. The experiment found that the filters required back flush every 2 days because of the increased inlet pressure (>0.45 MPa). Thirty (30) minutes were required to clean the filter. Forty-two (42) membrane elements and 6 vessels were used. An LFC3-LD spiral wound module from Nitto Denko Corp. was used throughout the study. The recovery rate and operating pressure were maintained in the range of 20–50% and 1.5–2.5 MPa, respectively. Anti-scalant and biocide were dosed into the feed stream at concentrations of 3–5 and 1–2 mg/l, respectively. The RO membrane was routinely cleaned by clean-in-place (CIP) methodology at 1–1.5 time/month interval. Average of cross flow velocities employed during operation and CIP were 0.10 and 0.12 m/s, respectively. The chemical used for the cleaning was hydrochloric (HCl) acid, and sodium hydroxide (NaOH). The chemical was fed into six vessels with a controlled flow of 60 m³/h. The pH was controlled at 2 and at 10 for acid solution and alkali solution, respectively. The membrane was soaked under static condition for 30 min after which the solution was re-circulated across the membrane surface for another 30–60 min.

Raw leachate and treated water from the treatment plant were sampled on monthly basis during two years study period. The samples were sent for analysis at Kasetsart University’s laboratory on the collection date. The analytical parameters include pH, SS, TDS, BOD, COD, TKN and heavy metals (nickel, cadmium, manganese, ferric, copper, lead, zinc). All chemical analyses were performed according to the procedures described in *Standard Methods for the Examination of Water and Wastewater* (APHA 1998). In addition to chemical analyses, particle size in leachate was also determined using a particle analyzer (Hydro 2000 MU, Malvern Instruments). Table 1 shows the characteristics of the leachate and treated water from leachate treatment plant at the landfill site. After the treatment, effluent (RO permeate) is utilized for non-potable (mainly washing) purposes on-site whereas the RO concentrate is...
pumped back for irrigation on topsoil and vegetation at the closed landfill cell. Land application of concentrate can take advantage of nutrients extracted from the wastes and could be used for the production of additional biomass (Jenkins et al. 2003). The performance of each treatment unit and bio-toxicity reduction of treated water can be found elsewhere (Theeparaksapan et al. 2011).

**Membrane fouling determination**

Resistance in a series model was used to determine the resistance on the RO membrane. After the RO membrane was fouled, the fouled membrane was cleaned via the procedures illustrated in Table 2. These procedures were applied to distinguish the type of foulant deposited on the membrane surface and to evaluate the effectiveness of chemical cleaning. A cross-flow membrane filtration set (Figure 2) was used for this test. Firstly, pure water flux of the fouled membrane was examined to determine the total resistance of the fouled membrane. The fouled membrane was then subjected to sequential cleaning procedures (Table 2) using pure water at cross flow velocity of 0.05 and 0.15 m/s, NaOH at 0.15 m/s and HCl at 0.15 m/s, respectively.

The resistance of RO membrane was determined using the resistance in a series model as follows:

\[
J = \frac{\Delta P - \Delta \pi}{\eta(Rm + Rf)}
\]

where \(J\) = permeate flux (m/d), \(\Delta P\) = pressure difference between feed and permeate side (MPa), \(\Delta \pi\) = osmotic

### Table 1 | Characteristics of leachate and treated water from leachate treatment plant

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Leachate Range</th>
<th>Average</th>
<th>Effluent Range</th>
<th>Average</th>
<th>Effluent standard*</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>–</td>
<td>8.58–8.96</td>
<td>8.76</td>
<td>7.2–8.3</td>
<td>7.9</td>
<td>5.5–9.0</td>
</tr>
<tr>
<td>SS</td>
<td>mg/l</td>
<td>180–1,186</td>
<td>451</td>
<td>ND – 2</td>
<td>0.01</td>
<td>–</td>
</tr>
<tr>
<td>TDS</td>
<td>mg/l</td>
<td>11,214–11,466</td>
<td>217</td>
<td>1.2–5.6</td>
<td>1.6</td>
<td>20</td>
</tr>
<tr>
<td>BOD</td>
<td>mg/l</td>
<td>65–298</td>
<td>3,892</td>
<td>10–90</td>
<td>50</td>
<td>120</td>
</tr>
<tr>
<td>COD</td>
<td>mg/l</td>
<td>218–260</td>
<td>270</td>
<td>1.2–5.6</td>
<td>4.3</td>
<td>100</td>
</tr>
<tr>
<td>Nickel</td>
<td>mg/l</td>
<td>ND – 0.484</td>
<td>0.242</td>
<td>ND – 0.01</td>
<td>0.004</td>
<td>1</td>
</tr>
<tr>
<td>Cadmium</td>
<td>mg/l</td>
<td>ND – 0.03</td>
<td>0.015</td>
<td>ND</td>
<td>ND</td>
<td>0.03</td>
</tr>
<tr>
<td>Manganese</td>
<td>mg/l</td>
<td>0.079–0.375</td>
<td>0.227</td>
<td>0.012–0.085</td>
<td>0.026</td>
<td>4</td>
</tr>
<tr>
<td>Ferric</td>
<td>mg/l</td>
<td>ND – 3.78</td>
<td>1.89</td>
<td>0.26–0.78</td>
<td>0.31</td>
<td>–</td>
</tr>
<tr>
<td>Copper</td>
<td>mg/l</td>
<td>0.002–0.059</td>
<td>0.0305</td>
<td>ND</td>
<td>ND</td>
<td>0.2</td>
</tr>
<tr>
<td>Lead</td>
<td>mg/l</td>
<td>ND – 0.01</td>
<td>0</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Zinc</td>
<td>mg/l</td>
<td>0.025–0.268</td>
<td>0.1465</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

Remark: ND: Not Detected.

*Industrial effluent standard of Thailand.

### Table 2 | Procedures for determination of foulant type

<table>
<thead>
<tr>
<th>No.</th>
<th>Condition</th>
<th>Target foulant</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cleaning with pure water at CFV of 0.05 m/s</td>
<td>Total resistance of attached foulants on membrane surface</td>
</tr>
<tr>
<td>2</td>
<td>Cleaning with pure water at CFV of 0.15 m/s</td>
<td>Particulate fouling</td>
</tr>
<tr>
<td>3</td>
<td>Cleaning with NaOH at CFV 0.15 m/s</td>
<td>Organic fouling</td>
</tr>
<tr>
<td>4</td>
<td>Cleaning with HCl at CFV at 0.15 m/s</td>
<td>Inorganic fouling</td>
</tr>
</tbody>
</table>

![Figure 2](http://iwaponline.com/wst/article-pdf/65/1/127/443539/127.pdf) | Schematic diagram of the cross flow membrane test cell.
pressure difference between feed and permeate side (MPa), \( \eta \) = viscosity of solution (MPa/d), \( R_m, R_f \) = resistances of membrane and foulants (m\(^{-1}\)).

To determine the extent of membrane fouling, a recirculation mode RO experiment proposed by Pervov (1999) was used. Membrane fouling was also investigated using the autopsy method for the optimization of the cleaning chemical and observation of the foulant on the RO membrane surface. Firstly, the 1st and 6th RO membranes were removed from the vessels and placed in the lab-scale cross-flow membrane test cell (Figure 2). Each RO membrane was unfolded and cut into a flat sheet with an area of 12.68 cm\(^2\). The operating pressure and feed flow rate were adjusted using a by-pass valve in order to simulate the operating conditions in the spiral wound module. For cleaning, the feed flow and cross flow speed were set at 3 ml/min and 0.15 m/s. After cleaning, the pure water flux and resistance of foulants were measured using the cross flow module under the previously described conditions with the percent recovery and operating pressure at 50% and 1.5–2.0 MPa, respectively. Both the permeate and concentrated water were returned back into a feed tank. The flux decline was observed over 48 hours. The conductivity and permeate flux were measured by EC meter and cylinder volume.

Analysis of deposited foulant

Two methods were used to quantify the amount of deposited foulants. Firstly, the sample of deposits on the RO membrane (12.68 cm\(^2\) unit) was extracted using hydrochloric acid and sulfuric acid. The extract sample was measured by using an inductively coupled plasma atomic emission spectrometry analyzer (ICP/AES, ICPS-7000, Shimadzu). The general wavelength scan was covered by Al, Ba, Ca, Fe, Mg, Mn, Si, Sr, and Zn. The amount of deposit element was then expressed as mass of deposited element per unit area of the membrane surface. Secondly, membrane samples were scanned with a scanning electron microscope (JSM-5600, LV, Japan) at 15 kV acceleration magnitude at 100×, 1,000×, 5,000× and 10,000×. The size of deposited particles on the membrane surface was estimated from the SEM image. Subsequently, the analysis of the elements on membrane was performed using the energy dispersive X-ray spectroscopy (EDS) to determine the percentage of deposited elements on the membrane surface. The samples were sputter-coated with gold in an Eiko Engineering 1B-Z ion coater.

RESULTS AND DISCUSSION

Fouling characteristics of RO membrane modules

Figure 3 shows the variation of flow rate, driving force, total dissolved solids (TDS) in feed flow and corresponding osmotic pressure along the membrane vessel (each RO vessel consists of 6 membrane modules). The recovery rate of the RO membrane was initially set at 50% and it reduced along the treatment plant operation to 20% in long term (2 years). As shown in Figure 3, the permeate flow was set constant and thus due to the fouling of RO membrane, feed flow was increased to provide sufficient driving force.

![Figure 3](image-url)
resulting in the reduction in recovery rate. The feed flow decreased from 5.5 m$^3$/h in the 1st membrane module to 3.5 m$^3$/h in the 6th RO membrane modules during short-term (6 months) operation and 4.7 to 2.7 m$^3$/h during long-term (2 years) operation respectively. The driving force across membrane was calculated from the difference in pressure applied between the inlet and outlet using osmotic pressure ($\Delta P - \Delta \pi$). The driving force also decreased along the position of the membrane module in the same vessel. The feed flow rapidly decreased from the 1st to the 3rd membranes. For the 4th, 5th, and 6th membranes, the feed flow decreased slightly. This could be explained by the decreased driving force of subsequent membranes. The decrease in applied pressure also affected the decrease in permeate flow. In addition, the feed flow also decreased with each subsequent membrane. As per water and mass balance calculations, this decreasing feed flow lead to an increase in TDS in the concentrate flow due to the rejection rate of the RO membrane. Moreover, the increasing TDS in the feed flow was associated with increasing osmotic pressure. The total pressure drop in the vessel was 200 and 300 kPa for short-term and long-term when osmotic pressure was increased from 1.5 to 2.4 MPa and 1.3 to 2.4 MPa for short-term and long-term operation respectively.

After the applied pressure of RO membranes increased up to 2.5 MPa, the 1st and the 6th RO membranes were removed from the vessel to measure the resistance of the RO membranes. The resistance was determined in the laboratory using cross-flow unit. The average osmotic pressure in and resistance of the membranes for LFC3-LD membrane were 2.4 MPa and $1.67 \times 10^{13}$ m$^{-1}$, respectively.

The fouling experiment was done both for short-term (6 months) and long-term (24 months) operation. Table 3 shows the resistance to fouling over different time periods. In the short-term period, the resistance of the 1st RO membrane was higher than the 6th RO membrane. The main factors resulting in those differences in observed membrane resistances are operating conditions such as feed flow rate, filtration rate, and TDS of the feed. For long-term operation, the resistance was much greater than for short-term operation. However, the difference in resistance to fouling for long-term operation between the 1st and 6th membranes is less than that for short-term operation.

**Table 3**  Filtration resistance ($\times 10^{10}$ m$^{-1}$) over different time periods

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Short-term (6 months)</th>
<th>Long-term (2 years)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>SD</td>
</tr>
<tr>
<td>1st</td>
<td>137</td>
<td>32</td>
</tr>
<tr>
<td>6th</td>
<td>58</td>
<td>35</td>
</tr>
</tbody>
</table>

**Foulant determination on the RO membrane**

The foulants were classified into three groups, i.e. particulate, organic and inorganic types, by the cleaning procedures (Table 2). The filtration resistances of 1st and 6th RO membrane after each cleaning procedure are presented in Table 4. The NaOH cleaning showed itself to be the most effective chemical at removing the foulant from RO membranes for short-term and long-term operation. In the case of a short-term operated membrane, water cleaning could recover 32.14 and 7.45% of pure water flux on the 1st and the 6th membrane element compared to that of virgin membrane. The NaOH cleaning could remove major part of foulant deposit on membrane surface result by recovery of 97.8 and 98.3% of pure water flux of virgin membrane. In the case of long-term operation, the effectiveness of chemical cleaning decreased. The pure water flux of cleaned membrane was only 76.8 and 74.7% of pure water flux of virgin membrane on the 1st and the 6th membrane element, respectively. It was found that irreversible fouling of the membranes increased along the operation time and the degree of fouling was strongly related to the feed concentration above the membrane surface. Lui et al. (2008) reported that regular chemical cleaning every 100 h to 500 h was required to maintain smooth operation of RO system applied to leachate treatment.

**Table 4**  Filtration resistance ($10^{10}$ m$^{-1}$) of fouled and cleaned membranes

<table>
<thead>
<tr>
<th>Membrane sample</th>
<th>Short-term 1st element</th>
<th>6th element</th>
<th>Long-term 1st element</th>
<th>6th element</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>SD</td>
<td>Average</td>
<td>SD</td>
</tr>
<tr>
<td>Fouled membrane</td>
<td>137</td>
<td>73</td>
<td>58</td>
<td>32</td>
</tr>
<tr>
<td>After water cleaning</td>
<td>108</td>
<td>69</td>
<td>50</td>
<td>24</td>
</tr>
<tr>
<td>After NaOH cleaning</td>
<td>1.3</td>
<td>0.2</td>
<td>8.3</td>
<td>0.4</td>
</tr>
<tr>
<td>After HCl cleaning</td>
<td>1.1</td>
<td>0.1</td>
<td>1.7</td>
<td>0.8</td>
</tr>
</tbody>
</table>
The foulant after cleaning was extracted in order to quantify the amount of deposited elements (Fe, Mg, Mn, Al, Zn, Sr, Ba, Si, and Ca) on the membrane surface. Fe element was found as predominated deposited elements on the membrane surface. The mass of total ferric elements in the 1st membrane increased from 3.11 to 35.31 g/m² or about 10 fold from short-term to long-term operation, respectively (Table 5). The mass of total ferric elements in the 6th membrane increased from 3.01 to 20.66 g/m² (about 7 fold) during the same period. These results show that the total accumulation of ferric element increases in the long term. Thörneby et al. (2003) also reported the possibility of precipitation of iron salts on RO membrane even without chemical pre-treatment. Trebouet et al. (2001) reported that deposited ferric ions contributed greatly to change of organic matter and the surface charges of membranes.

When the surface of the membrane was magnified, the foulant on the surface of the RO membrane was clearly visible. Figure 4 shows the optical images and extracted elements of the foulant on the RO membranes. The surfaces of fouled membranes were covered with particles. For analysis of the elements on each membrane, the energy dispersive X-ray spectroscopy (EDS) indicates the dominant presence of Fe and Mg on the surface along with other compounds such as Mn, Al, Zn, Sr, Ba, Si, and Ca. After water cleaning, some deposited particulates disappeared and Fe and Mg content decreased. This result suggest that the water could remove particles containing Fe and Mg. Acid cleaning gave the best performance in term of removing deposited Fe and Mg. With alkali cleaning, the surface of the RO membrane also showed slight roughness. The elements C, Mg, and Fe were removed. Moreover, the size of particulate foulant could be determined in the SEM image. It is in the range of 0.45–0.70 μm.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Deposit mass per unit area (g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Short-term</td>
</tr>
<tr>
<td>1</td>
<td>3.11 ± 0.1</td>
</tr>
<tr>
<td>6</td>
<td>3.01 ± 0.1</td>
</tr>
</tbody>
</table>

Table 5 | Deposition of ferric element on the RO membranes

Figure 4 | The optical images and extracted elements from foulants on the RO membranes (1st membrane module, short-term operation).
The particle size distribution of feed water to the RO membranes is shown in Figure 5. According to the results, the particle size of the feed ranged from 0.01 to 100 μm. Moreover, only particles of 0.45–0.70 μm in size were attached to the RO membrane surface.

CONCLUSION

Short-term and long-term characteristics of reverse osmosis (RO) membrane applied to leachate were investigated. In long-term operation for 2 years, it was found that deposited foulants on RO membrane increased by 7–10 fold when compared to those of short-term operation (6 months). Analyses of deposited foulants using various techniques revealed major particulate fouling of ferric element with particle size of 0.45–0.70 μm. The degree of fouling was higher on the first membrane module when compared to the last membrane module in the same vessel. Sequential chemical cleaning using alkaline followed by acid solution was effective in removing foulants on the membrane surface in which NaOH helped reducing filtration resistance substantially. Pure water flux of cleaned membrane up to 97.8–98.3% of pure water flux of virgin membrane for short-term operated membrane module and 74.7–76.8% for long-term operated membrane module were achieved.

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REFERENCES


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