Effects of chemical coagulation and particle cut-off on reverse osmosis membrane fouling during municipal solid waste leachate filtration

Weerapong Rukapan, Chart Chiemchaisri*, Wilai Chiemchaisri

Department of Environmental Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand, Tel.: +6626790730; emails: fengccc@ku.ac.th (C. Chiemchaisri), johnny_johnest@hotmail.com (W. Rukapan), fengwlc@ku.ac.th (W. Chiemchaisri)

Received 26 January 2020; Accepted 12 May 2020

ABSTRACT

Particulate fouling on reverse osmosis (RO) membrane during its application to municipal solid waste (MSW) leachate filtration was investigated. The feed water was obtained from raw and ferric chloride coagulated leachates from full-scale leachate treatment plant at an MSW disposal site in Thailand. The particle fraction in the feed water was fractionated into different size range using microfiltration (MF) and ultrafiltration (UF) membrane with different particle cut-off sizes as suspended solids (>1.2 µm), coarse colloids (1.2 µm–0.45 µm), fine colloids (0.45 µm–1 kDa), and dissolved matter (<1 kDa). Each particle fraction was evaluated for their fouling characteristics on the RO membrane. Foulant layer resistance obtained from coagulated water was found lower than that of raw leachate when the same particle cut-off treatment was applied. The cake layer resistance \( R_c \) derived from resistance in the series model and Kozeny–Carman equation was compared and good agreement was found for all particle fractions.

Keywords: Cake filtration; Solid waste leachate; Particulate fouling; RO; Size fractionation

1. Introduction

Globally, the majority of municipal solid waste (MSW) is currently disposed of in landfills or open dumps [1]. One of the main environmental problems associated with land disposal of MSW is the generation of leachate from excessive moisture in wastes, mostly resulted from the intrusion of rainwater into the waste layer. Several technologies including advanced processes such as membrane processes have been applied to the treatment of MSW leachate to meet more stringent regulations [2,3]. Generally, the removals of dissolved solids, mainly inorganic salts, from leachate require an application of membrane processes with narrow pore sizes such as nanofiltration or reverse osmosis [4–6]. Nevertheless, one of the main obstacles in the application of this advanced technology is the fouling of membrane caused by the deposition of foulants on the membrane surface [7,8]. The foulants may include organic and inorganic substances both in particulate and dissolved forms. The gradual development of membrane fouling not only reduces the permeability of the membrane but may also cause deterioration in treated water qualities [6]. To minimize membrane fouling, pre-treatment of wastewater before membrane systems has been proven as an effective operation strategy of the membrane systems.

To identify appropriate pre-treatment systems, characterization of potential foulants including particle and dissolved matter in feed water is essential. In MSW leachate, the organic matter associated with different particle size fractions separated by sequential filtration of molecular weight cut-off (MWCO) membrane has been investigated [9-12] and the study revealed that only small amount of organic matter was available in particulate fraction (size >0.45 µm) and mostly they were in small colloidal for dissolved forms [9,10,12]. The molecular and particle size of organic matter in truly-dissolved (size <0.001 µm, approximately equal to apparent molecular weight <1 kDa and
colloidal fractions (0.001–0.45 µm) were found varied with the duration of waste deposition in landfills [10]. Therefore, it is important to understand the main components of leachate, including their molecular weight and particle size distributions, taking advantage of membrane technologies [11]. In our previous research, the main fouling observed at the full-scale leachate treatment plant was identified as a particulate type [7]. Previous research has also revealed that the molecular weight percentage distribution in leachate varied as the leachate was treated in the biological treatment stages with fine colloid fractions increased while those of dissolved fraction decreased [10,13]. The positive impact of colloid and suspended particles cut-off on RO membrane treatment was also observed using chemical coagulation and microfiltration membrane as pretreatment [14].

For effective prevention of membrane fouling, the particle characteristics in the feed water, as well as their effect on fouling layer formation on the membrane surface, needs to be clearly understood. Nevertheless, such information is very limited especially for those obtained from the operation of full-scale membrane filtration systems. In this research, the relationship between particle size in feed solution and fouling behavior of the RO membrane using different particle cut-off sizes was studied and explained using cake filtration theory. For the application of the cake filtration model, fundamental characteristics of particles were determined for different feed water using leachate samples obtained from an operating full-scale leachate treatment system in Thailand. The effect of different particle cut-off size chemical pretreatment on flux decline and foulant layer formed on the RO membrane surface were investigated. Then, the cake filtration model was used to explain the observed experimental data.

2. Materials and methods

2.1. Leachate sampling and analysis

MSW leachate was obtained from an operating landfill site in Thailand. The leachate was feeding to an advanced leachate treatment system utilizing chemical coagulation followed by sand and microfiltration for pre-treatment of RO membrane units. Detailed performance of the leachate treatment system is described elsewhere [7,14]. For chemical coagulation, ferric chloride (FeCl3) was applied at 2.0–2.5 g/L dose. The water samples collected at the inlet of the leachate treatment plant and the outlet of chemical coagulation unit were used for the study of their fouling potential on the RO membrane in the laboratory. The chemical characteristics of raw and treated leachate including pH, chemical oxygen demand (COD), total organic carbon (TOC), total kjeldahl nitrogen (TKN), total phosphorus, suspended solids (SS), and total dissolved solids (TDS) were determined according to the Standard Methods for the examination of water and wastewater [15]. The particle size distribution in the samples was also determined using a particle analyzer (Hydro 2000 MU, Malvern Instruments).

2.2. Preparation of samples with different particle size fractions

The leachate samples were sequentially filtrated using membranes with different particle cut-off sizes, that is, 1.2, 0.45 µm, and 1 kDa. The 1.2 µm glass fiber membrane filter (Whatman, GF/C, Merck, Germany) was made of borosilicate glass while 0.45 µm and 1 kDa membranes were made of regenerated cellulose (RC). The use of a glass fiber membrane filter allows a direct comparison of its filtrate to SS-free water conditions. The filtered residues retained by the 1.2, 0.45 µm, and the 1 kDa MWCO membranes were defined as SS, coarse colloids, and fine colloids, respectively whereas the filtrate from the 1 kDa MWCO filtration is considered as a truly dissolved matter [11].

2.3. RO filtration experiment

The filtration module (C40-B, Nitto Denko Corp., Japan) is a stirring batch-type cell with a 75 mm diameter flat-sheet membrane. The N2 gas pressure is applied for the permeation of the feed solution. The stirrer bar is used to prevent concentration polarization. Besides, the stirrer is rotated at a high speed of 300 rpm. The RO filtration experiments were designed to evaluate the effects of chemical coagulation and particle cut-off on RO membrane fouling that resembled the operation of full-scale leachate treatment plant where leachate samples were obtained. The operating pressure and feed flow rate of the RO filtration experiment were adjusted using a by-pass valve to simulate the operating conditions in the RO spiral wound module. The RO flux and electrical conductivity (EC) of RO filtrate was monitored over 48 h. For cleaning of fouled membranes, NaOH followed by HCl cleaning procedure was used. The feed flow and cross-flow speeds were set at 3 mL/min and 0.15 m/s, respectively. After the cleaning, the pure water flux and resistance of foulants were measured using the cross-flow module under the prescribed condition while setting the percent recovery and operating pressure at 50% and 1.5–2.0 MPa.

After the end of the filtration experiment, surface morphology and elemental composition of the fouled and cleaned membranes (1 cm² size) were analyzed by scanning electron microscopy-energy dispersive X-ray spectrometer (SEM-EDX).

2.4. Determination of membrane fouling and cake model parameters

The fouling resistance was determined by comparing the pure water flux of the virgin membrane and the fouled membrane. First, the pure water flux was determined for virgin membrane normalized to a temperature of 25°C. After the RO membrane was fouled, the pure water flux was again measured for fouled membrane normalized to the same temperature. The degree of RO membrane fouling is described using a cake filtration model [16]. The fouling resistance was obtained by using the resistance in a series model as shown in Eq. (1).

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

where \(J\) is the permeate flux (m/d); \(\Delta P\) is the pressure difference between feed and permeate side (MPa); \(\Delta \pi\) is the Osmotic pressure difference between feed and permeate side.
(MPa); $\eta$ is the viscosity of solution (MPa/d); $R_m$, $R_c$ is the resistance of membrane and foulants ($m^{-1}$).

In this study, the viscosity of solution and resistance of membrane was assumed constant, therefore, the $R_c$ can be calculated from Eq. (2).

$$R_c = \frac{\Delta P - \Delta \tau}{\eta}$$

(2)

The cake resistance is expressed as a function of deposited solid mass and specific cake resistance ($\alpha$) as follow:

$$R_c = \alpha \cdot M_s$$

(3)

where $M_s$ is the accumulated solid mass per unit area on the membrane surface. This parameter was also determined experimentally during the filtration experiment. Moreover, $\alpha$ can be expressed in terms of particle size and cake porosity ($\varepsilon$) following the Kozeny–Carman equation.

$$\alpha = \frac{45(1 - \varepsilon)^2}{\rho a_p^2 \varepsilon^3}$$

(4)

where $\rho$ is the particle density and $a_p$ is particle radius. The size of particles in the foulant layer was determined experimentally from particle size analyzer whereas the porosity of the cake layer formed with different particle sizes was estimated using Autodesk 3D program.

3. Results and discussion

3.1. Pollutants associated with different particle size fractions

Table 1 shows the characteristic of leachate after filtration through membranes with different particle size cut-offs. The COD concentration of raw leachate was reduced from 3,000 to 1,283 mg/L after sequential filtration through membranes with different pore sizes to 1 kDa. The majority of the COD reduction took place when the 0.45 mm filtrate was applied to the 1 kDa membrane there indicating that organic matter is predominantly associated with colloidal particle fraction in raw leachate. The only minority (17%) of organic matter was contributed from suspended solids (>1.2 $\mu$m). This is in agreement with the previous study reporting that only a small fraction of organic matter was presented in the particulate form [7]. After FeCl$_3$ coagulation, COD originally presented in raw leachate was reduced by 45% to 1,639 mg/L (Table 2). Then, a total COD reduction of more than 60% was achieved after sequential filtration through membranes with different pore sizes to 1 kDa. Along with COD reduction, TDS was simultaneously reduced by 32% and 21% for raw leachate and FeCl$_3$ coagulated water after filtration through 0.45 $\mu$m membrane. More than 80% of TDS was then removed by the 1 kDa membrane. Meanwhile, TOC and TKN of raw leachate decreased from 1,083 to 585 mg/L and 124 to 80 mg/L after sequential separation with total removal of 46% and 47%, respectively. The pre-treated leachate with ferric chloride had TOC and TKN removed by 49% and 46%, respectively.

The particle size distribution in raw and pre-treated leachate was determined. In raw leachate, particle sizes were classified into two groups ranging between 0.01–1 and 1–150 $\mu$m (Fig. 1). After FeCl$_3$ coagulation, the particle sizes were enlarged to 0.5–150 and 1,000 $\mu$m, respectively. Further filtration through 1.2 and 0.45 $\mu$m membranes, the remaining particle sizes were ranged between 0.05–1 and 0.01–1 $\mu$m. As described earlier, COD containing in the filtrate from 0.45 $\mu$m represented are the majority of the organic matter presented in leachate, therefore they would possibly

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw water</th>
<th>1.2 $\mu$m filtrate</th>
<th>0.45 $\mu$m filtrate</th>
<th>1 kDa filtrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.90 ± 0.07</td>
<td>8.73 ± 0.12</td>
<td>8.81 ± 0.06</td>
<td>8.51 ± 0.16</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>3,000 ± 600</td>
<td>2,497 ± 704</td>
<td>2,268 ± 373</td>
<td>1,283 ± 136</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>1,083 ± 192</td>
<td>1,021 ± 62</td>
<td>994 ± 84</td>
<td>585 ± 14</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>637 ± 401</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>14,767 ± 2,549</td>
<td>12,637 ± 1,347</td>
<td>10,060 ± 1,320</td>
<td>1,760 ± 205</td>
</tr>
<tr>
<td>TKN (mg/L)</td>
<td>124 ± 25</td>
<td>121 ± 24</td>
<td>109 ± 12</td>
<td>80 ± 22</td>
</tr>
<tr>
<td>TP (mg/L)</td>
<td>8.03 ± 0.97</td>
<td>7.11 ± 0.54</td>
<td>4.82 ± 0.70</td>
<td>2.77 ± 0.60</td>
</tr>
</tbody>
</table>

After FeCl$_3$ coagulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw water</th>
<th>1.2 $\mu$m filtrate</th>
<th>0.45 $\mu$m filtrate</th>
<th>1 kDa filtrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.22 ± 0.70</td>
<td>7.44 ± 0.11</td>
<td>7.73 ± 0.34</td>
<td>8.20 ± 0.30</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>1,639 ± 34</td>
<td>1,183 ± 145</td>
<td>1,078 ± 141</td>
<td>961 ± 12</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>194 ± 33</td>
<td>170 ± 52</td>
<td>157 ± 63</td>
<td>99 ± 0.86</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>263 ± 52</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>18,566 ± 2,453</td>
<td>18,238 ± 2,963</td>
<td>14,603 ± 1,150</td>
<td>893 ± 416</td>
</tr>
<tr>
<td>TKN (mg/L)</td>
<td>57 ± 22</td>
<td>55 ± 11</td>
<td>35 ± 4</td>
<td>31 ± 2</td>
</tr>
<tr>
<td>TP (mg/L)</td>
<td>5 ± 0.6</td>
<td>5.2 ± 0.5</td>
<td>3.8 ± 0.3</td>
<td>3.4 ± 1.1</td>
</tr>
</tbody>
</table>

No. of samples = 5
associate with fine colloidal particles with the size range between 0.01 and 0.05 µm in this study.

3.2. Effect of particle cut-off to RO membrane fouling

The flux of RO membrane normalized by applied and net pressure during cross-flow filtration of raw and treated leachate after FeCl₃ coagulation and filtrate through 1.2, 0.45 µm, and 1 kDa membranes are illustrated in Figs. 2 and 3, respectively. RO membrane flux was rapidly decreasing when applied to raw leachate especially during the first hour whereas gradual reduction was observed for FeCl₃ coagulated leachate. This was possibly due to the formation of loose structure cake layer formed during the deposition of larger flocculated particles on the membrane surface [16] and adsorptive removals of fouling materials such as humic-like substances during FeCl₃ coagulation [17]. The previous study [18] also reported similar observations suggesting that leachate pretreated with FeCl₃ yielded a much lower RO membrane fouling index (MFI-RO) than that of original raw leachate. In all cases, the filtrate from 1 kDa gave higher flux than the others. It was anticipated that FeCl₃ coagulation helped to retard but not eliminate the formation of foulant on the RO surface. Nevertheless, the particle cut-off from feed water helped to increase RO flux to some extent.

When considering the normalized flux by net pressure without osmotic pressure (Fig. 3), it was found that the flux obtained from 1.2 µm membrane filtrate was highest especially in the case of FeCl₃ coagulated leachate. These results reveal that the particle cut-off through 1.2 µm membrane filtration would be sufficient to eliminate the formation of the foulant layer on the membrane surface after chemical coagulation was performed. In comparison to 0.45 µm membrane filtrate, the presence of cake layer from the deposition of coarse colloids (0.45-1.2 µm particle size) helped to minimize the formation of dense foulant layer (<0.45 µm particle size) with high filtration resistance. Meanwhile, the lower net filtration pressure attained under this condition due to high osmotic pressure of 0.45 µm membrane filtrate resulted in the higher normalized flux.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental filtration resistance (\times 10^{10} \text{ m}^{-1})</th>
<th>(M_d) (g/m²)</th>
<th>Cake porosity</th>
<th>Cake density (\times 10^{-7} \text{ m})</th>
<th>Particle radius (\times 10^{10} \text{ m/kg})</th>
<th>Specific cake resistance (\times 10^{10} \text{ m/kg})</th>
<th>Calculated filtration resistance (\times 10^{10} \text{ m}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Raw leachate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Original</td>
<td>74.0</td>
<td>35.0</td>
<td>0.511</td>
<td>1,200</td>
<td>19.5</td>
<td>1.7</td>
<td>62.0</td>
</tr>
<tr>
<td>1.2 µm filtrate</td>
<td>48.0</td>
<td>12.0</td>
<td>0.641</td>
<td>1,800</td>
<td>6.0</td>
<td>3.3</td>
<td>41.0</td>
</tr>
<tr>
<td>0.45 µm filtrate</td>
<td>28.0</td>
<td>1.0</td>
<td>0.591</td>
<td>2,400</td>
<td>2.25</td>
<td>30.0</td>
<td>30.0</td>
</tr>
<tr>
<td><strong>After FeCl₃ coagulation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Original</td>
<td>49.0</td>
<td>35.0</td>
<td>0.643</td>
<td>1,200</td>
<td>97.0</td>
<td>1.3</td>
<td>44.0</td>
</tr>
<tr>
<td>1.2 µm filtrate</td>
<td>42.0</td>
<td>13.0</td>
<td>0.641</td>
<td>1,800</td>
<td>6.0</td>
<td>3.3</td>
<td>41.0</td>
</tr>
<tr>
<td>0.45 µm filtrate</td>
<td>35.0</td>
<td>1.0</td>
<td>0.591</td>
<td>2,400</td>
<td>2.25</td>
<td>32.0</td>
<td>30.0</td>
</tr>
</tbody>
</table>

Fig. 1. Distribution of particle size in raw leachate, supernatant after FeCl₃ coagulation, and filtrates through 1.2, 0.45 mm membranes.
Fig. 2. Normalized flux with applied pressure for raw (upper) and FeCl₃ coagulated leachate (lower).

Fig. 3. Normalized flux with net pressure of raw (upper) and FeCl₃ coagulated leachate (lower).
Fig. 4. SEM images of foulant on RO membranes (a) fouled membrane by raw leachate, (b) cleaned membrane (raw leachate), (c) fouled membrane by 1.2 µm filtrate, (d) cleaned membrane (1.2 µm filtrate), (e) fouled membrane with 0.45 µm filtrate, (f) cleaned membrane (0.45 µm filtrate), (g) fouled membrane with 1 kDa filtrate, and (h) cleaned membrane (1 kDa filtrate).
Fig. 5. SEM images of foulant on RO membranes (a) fouled membrane with FeCl$_3$ coagulated leachate, (b) cleaned membrane (FeCl$_3$ coagulated leachate), (c) fouled membrane fouled with 1.2 µm filtrate, (d) cleaned membrane (1.2 µm filtrate), (e) fouled membrane with 0.45 µm filtrate, (f) cleaned membrane (0.45 µm filtrate), (g) fouled membrane with 1 kDa filtrate, and (h) cleaned membrane (1 kDa filtrate).
3.3. Effect of chemical pre-treatment to RO fouling

During raw leachate filtration, the osmotic pressure determined from TDS concentrations was 1.01, 0.81, and 0.14 MPa for 1.2, 0.45 µm, and 1 kDa membranes. For FeCl₃ coagulated leachate, they were 1.14, 1.17, and 0.07 MPa, respectively. The normalized flux with net pressure (applied pressure minus osmotic pressure) through different membranes was not much different in the case of raw leachate as compared to those of FeCl₃ coagulated leachate. The pre-treatment by FeCl₃ coagulation helped to reduce the fouling of the RO membrane even though an increase in osmotic pressure reduced net transmembrane pressure yielding indifferent observed permeate flux from the others. The SEM images of the fouled membrane using raw and treated leachate are presented in Figs. 4 and 5. They are used to illustrate cake layer conditions with enlarged images of cake fracture or deposited particle flocs and their removals after the chemical cleaning process. For raw leachate case (Fig. 4), the SEM images suggest that the foulant on the RO membrane was in the form of dense but scatter spotted solid particles directly deposited on the membrane surface (Figs. 4a and c) when 1.2 and 0.45 µm membrane filtrate was applied. The foulant layer was mostly disappeared when the filtrate from 1 kDa membrane was applied compared to the other pre-treatment cases (Fig. 4g). However, in the case of FeCl₃ coagulated leachate, the deposition of an agglomerated solid mass with fractured and highly porous structure was visualized (Figs. 5a and c). The differences in the foulant layer structure deposited on the membrane surface also led to its chemical cleaning efficiencies. A loose structure cake layer formed under FeCl₃ coagulation was found effectively removed and therefore favorable for chemical cleaning (Figs. 5b and d) when compared to those of raw leachate condition (Figs. 4b and d). Nevertheless, the removals of foulant from the fouled membrane by 1 kDa filtrate of raw leachate (Fig. 4g) was found to be slightly better than those of FeCl₃ coagulated leachate condition (Fig. 5g).

3.4. Application of cake model to explain filtration resistance under different particle cut-off condition

The filtration resistance of raw and FeCl₃ coagulated leachate is presented in Table 2. The filtration resistance was determined from Eq. (1). During the filtration experiment, the accumulated solid mass per unit area (M_d) obtained by extraction of the foulant from the RO membrane applied to raw leachate was found to be 30, 12, 1, and 1 g/m² for filtrate from 1.2, 0.45 µm, and 1 kDa membranes. They were 32, 13, 1, and 1 g/m² for FeCl₃ coagulated leachate. The presence of deposited solids was confirmed by larger filtration resistance. It was found that M_d was significantly reduced when the leachate was filtrated through 0.45 µm and 1 kDa membranes.

The cake resistance was determined by Eq. (3) for raw and FeCl₃ coagulated leachate with different particle cut-off levels. They were calculated as 7.1 × 10⁹, 4.1 × 10⁹, 3.0 × 10⁹, and 1.8 × 10¹⁷ m⁻¹ for raw leachate after filtered through 1.2, 0.45 µm, and 1 kDa membranes. The good agreement (R² = 0.96) between observed resistances from filtration experiments and cake resistance was found for all particle sizes (Fig. 6). For FeCl₃ coagulated leachate, the filtration resistances were found to be 6.2 × 10⁹, 3.7 × 10⁹, 3.2 × 10⁹, and 1.6 × 10¹⁷ m⁻¹ with moderate agreement (R² = 0.75) with the experimental observation. Their results suggested that the cake model could be used to verify filtration resistances created from the colloids deposition of suspended particles, coarse colloids, and fine colloids during leachate filtration.

Successful application of cake filtration model to filtrates of 1.2 and 0.45 membranes also confirmed that chemical cleaning agents could be transported more effectively from bulk water to the membrane surface through loose or porous cake structure rather than pore-less dense structured foulant layer observed in case of 1 kDa membrane filtrate. For the recovery of fouled RO membrane, the chemical cleaning mechanism relies on chemical agent diffusion into deposited cake layer followed by chemical reactions (hydrolysis, dissolution, and dispersion) between cleaning agents and substances in the cake layer resulting in the removals of fouling materials from the membrane surface [19].
4. Conclusions

The cake model was applied to explain RO membrane fouling phenomena applied to raw and FeCl₃ coagulated leachate. The filtration of leachate through 1.2 and 0.45 µm membranes helps mitigate particulate fouling on the RO membrane while removing only small percentages of organic and dissolved pollutants from leachate as they were mainly associated with fine colloids (0.01–0.05 µm size). The filtration resistances determined from the filtration experiment was related well with the calculated resistances from the cake model from the observed deposited solid mass and particle size in the foulant layer.

References