Effect of organic fouling on micro-pollutant rejection in membrane bioreactor treating municipal solid waste landfill leachate

Samunya Sanguanpak, Chart Chiemchaisri, Wilai Chiemchaisri and Kazuo Yamamoto

ABSTRACT

Effect of membrane fouling on the removal of micro-pollutants from municipal solid waste landfill leachate, i.e. 4-methyl-2,6-di-tert-butylphenol (BHT), bisphenol A (BPA), and bis(2-ethylhexyl)phthalate (DEHP), in membrane bioreactor (MBR) was investigated. Modifications of membrane surface properties were analyzed to determine their relationship with their removals. Membrane fouling was simulated with foulants of different particle sizes on cellulose acetate (CA) microfiltration membrane to investigate the effect of foulant characteristics on BHT, BPA, and DEHP retention in the filtration experiment. The rejection efficiencies of the organic micro-pollutants in the MBR were 82–97% by fouled membrane, and 70–90% by cleaned membrane. The fouled membrane provided higher rejection of micro-pollutants from about 5% for BPA and BHT to 19% for DEHP. These improvements were due to the modification of membrane surface characteristics in terms of surface morphology, and contact angle after membrane fouling. The degree of rejection was found to be dependent upon the characteristics of foulant deposited on CA membrane surface. Increasing foulant particle size and its density shifted the mechanism of micro-pollutant rejection from membrane pore narrowing to pore blocking and cake formation while increasing pollutant adsorption capacity onto the foulant layer.

Key words | landfill leachate, membrane bioreactor, membrane fouling, micro-pollutants

INTRODUCTION

Landfill leachate is a complex wastewater containing a large number of organic micro-pollutants from solid wastes discarded in landfill. Among them, phenolic compounds and phthalic acid esters have been frequently detected in landfill leachate (Asakura et al. 2004). These compounds may affect human and animal health even at trace concentrations (Slack et al. 2005). Membrane bioreactor (MBR) has been applied to various types of wastewater including landfill leachate (Ahmed & Lan 2012). The removals of several micro-pollutants in MBR were better than conventional activated sludge process due to enhanced biosorption and biodegradation by biomass cultivated under longer sludge age condition (Sipma et al. 2010). Nevertheless, the removal efficiencies of trace organic contaminants also depended on their physico-chemical properties (Xu et al. 2006). Effects of hydrophobicity, chemical structure, operating pH and types of membranes on their removals were observed (Urase et al. 2005; Tadkaew et al. 2011; Dolar et al. 2012).

Membrane fouling in MBR is complex phenomena comprising adsorption of solute or colloid particles, deposition and formation of cake layer on the membrane surface and changes in deposited foulant properties (Meng et al. 2009). The deposition and accumulation of foulants can significantly modify membrane surface characteristics such as pore size, surface roughness, and hydrophobicity, and influence the removal of organic contaminants (Le-Clech et al. 2006). The membrane fouling could enhance the rejection of micro-organisms by submerged microfiltration (MF) membrane in MBR (Wu et al. 2010; Marti et al. 2011). Previous studies (Xu et al. 2006; Jermann et al. 2009) have determined the effect of membrane fouling on rejection of trace organic contaminants in ultrafiltration (UF) membrane.
and suggested that solute rejection was governed by hydrophobic interactions between membranes and solutes, pore blocking, and cake-enhanced concentration polarization phenomena. Most of those previous studies are focusing on the MBR treating low strength municipal wastewater. There are very limited studies on the effect of membrane fouling on micro-pollutant rejection in highly organically loaded MBR specifically during leachate treatment. Moreover, the relationship between fouling characteristics of the membrane and their effect on micro-pollutant retention are not well understood.

MATERIALS AND METHODS

Pilot-scale experimental system

Pilot-scale two-stage MBR (Figure 1) with 1 m³ anoxic and 1 m³ aerobic reactors was used. An inclined tube module was installed in the anoxic reactor as sludge separator whereas two hollow fiber membrane modules (0.4 μm, polyethylene membrane, 9 m² surface area each) were provided for solid–liquid separation in the aerobic reactor. Aeration was provided at specific aeration demand (SAD) of 0.33 Nm³ (m² h)⁻¹ in order to maintain dissolved oxygen (DO) concentration of 3–4 mg L⁻¹. Hydraulic retention time of MBR was set at 24 hours corresponding to membrane permeate flux of 0.11 m³ m⁻² day⁻¹ or 4.58 L m⁻² h⁻¹. The MBR was operated without sludge wastage except for sampling purposes. Internal recirculation was performed between anoxic and aerobic reactors at 100% of feed flow rate. When transmembrane pressure (TMP) was exceeding the pre-set upper limit (i.e. 20 kPa), the operation was temporarily stopped for membrane cleaning. The membrane module taken out from the MBR was rinsed with 1m³ of tap water to remove foulants from the membrane surface. Solid mass accumulated on the membranes was determined from the mass of solids removed by water cleaning divided by membrane surface area. Then, a few hollow fibers from each fouled and cleaned membrane module were sampled for further characterization. The fouled and cleaned membranes were stored in a glass Petri dish at room temperature for 24 hours prior to surface characterization. Surface morphology and element composition were characterized by scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS, JEOL model JSM-5410). Fourier transform infrared (FTIR) spectroscopy was employed in order to obtain the functional groups on membrane samples by a Perkin-Elmer spectrum spotlight FTIR Imaging system with Micro-ATR (ATR: attenuated total reflectance) technique. The FTIR spectra were examined in a mid-infrared wavenumber of 4,000–600 cm⁻¹. The hydrophobicity characteristic of membranes was identified by measurement contact angle of water droplet onto membrane surface. The contact angle was performed using a Ramé-hart contact angle goniometer with DROP image Standard v2.4. Both sides of at least 5 water droplets were measured in each membrane sample.

Membrane characterization

For characterizing the membrane in the MBR, the membrane module taken out from the MBR was rinsed with 1 m³ of tap water to remove foulants from the membrane surface. Solid mass accumulated on the membranes was determined from the mass of solids removed by water cleaning divided by membrane surface area. Then, a few hollow fibers from each fouled and cleaned membrane module were sampled for further characterization. The fouled and cleaned membranes were stored in a glass Petri dish at room temperature for 24 hours prior to surface characterization. Surface morphology and element composition were characterized by scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS, JEOL model JSM-5410). Fourier transform infrared (FTIR) spectroscopy was employed in order to obtain the functional groups on membrane samples by a Perkin-Elmer spectrum spotlight FTIR Imaging system with Micro-ATR (ATR: attenuated total reflectance) technique. The FTIR spectra were examined in a mid-infrared wavenumber of 4,000–600 cm⁻¹. The hydrophobicity characteristic of membranes was identified by measurement contact angle of water droplet onto membrane surface. The contact angle was performed using a Ramé-hart contact angle goniometer with DROP image Standard v2.4. Both sides of at least 5 water droplets were measured in each membrane sample.
Study of micro-pollutant rejection by fouled membrane

Two liters of mixed liquor taken from the MBR was separated into different fractions and used for simulation as foulant layer on membrane surface to investigate the effect of particle size in foulant layer on the rejection of the selected organic micro-pollutants (BPA, BHT, and DEHP, whose chemical properties are shown in Table 1). The first separation step was the centrifugation of mixed liquor for 15 minutes at 4,000 rpm to obtain supernatant fraction. The fine particles of supernatant were prepared by sequence filtration fractionation through 1.2, 0.45, and 0.2 μm membrane filters. For the coarse particles, gravitational sedimentation of the mixed liquor after 30, 90, and 120 minutes was employed to separate particles having different sizes.

In the fouling experiment, 30 ml feed solution of each mixed liquor fraction was filtered through a cellulose acetate (CA) membrane with 0.45 μm nominal pore size, 47 mm diameter, and 17.3 cm² filtration area in order to simulate the foulant layer on the membrane surface. The fouled CA membrane was prepared with deposited suspended solids (SS) mass at about two times of that determined during MBR membrane cleaning by water to account for attached biomass on the membrane surface as well as accumulated biomass between fibers within the hollow fiber modules. Rejection tests were conducted with virgin and fouled membrane to compare the retention of BPA, BHT, and DEHP in dead-end filtration mode at constant TMP of 50 kPa. Prior to the tests, the filtration unit was rinsed with deionized water to remove the attached impurities. Thirty milliliters of the target organic micro-pollutants from stock solution with initial concentration of 1,000 μg L⁻¹ were filtered through each membrane specimen until there was no residual solution remaining. After that, the permeate samples were taken for concentration measurement at the end of the experiment. The rejection performances of BPA, BHT, and DEHP through virgin and pre-fouled membrane were calculated by the following equation:

\[
R(\%) = \left(1 - \frac{C_{\text{per}}}{C_{\text{feed}}}\right) \times 100
\]

where \(C_{\text{per}}\) is the concentration of the permeate, and \(C_{\text{feed}}\) is the initial concentration.

After the filtration experiment, virgin and pre-fouled CA membranes were also characterized in terms of surface morphology and hydrophobicity in accordance with the analytical methods described above. The blocked surface of the virgin and pre-fouled membranes were determined following Silvestri et al. (2007) by using SEM for later comparison of pore blocked area using imaging software (Media Cybernetic, Inc. Image Pro Plus® Version 5.1 for Windows).

**Water sample analyses**

Leachate and the mixed liquor samples were regularly analyzed for their characteristics during the experiment. Electrical conductivity (EC) and pH were measured by EC and pH meters. SS, BOD, and COD were performed following Standard Methods (APHA 2005) without any pretreatment. DOC was measured using Shimadzu TOC-5000 total organic carbon analyzer. \(U_{254}\) was determined by spectrophotometer (Hach DR/4000 U) with a quartz cell. \(U_{254}\) analytical results were employed to calculate SUVA₂₅₄, i.e. \(U_{254}\) divided by DOC. The mixed liquor fractions were characterized for particle size distribution with a particle size analyzer (Mastersizer 2000, Malvern Instruments), and absolute density using helium pycnometer (Ultrapycnometer 1000, Quantachrome).

The organic micro-pollutants in samples were analyzed following the method described in Boonyaroj et al. (2012). In brief, the compounds were determined by solid phase extractions (SPEs) using C18-Bond Elut® (Varian, Inc.). One-hundred milliliters of water samples was fed through C18-SPE columns at approximate flow rate of 1 mL min⁻¹. Afterward, the adsorbed organic micro-pollutants in SPE sorbent were eluted by 10 ml dichloromethane: methanol in 1:9 mixing ratio. The extracted samples were concentrated to 0.5 ml volume by nitrogen evaporator/concentrator. Detection and quantification of the selected toxic organic contaminants were performed using a gas chromatograph equipped with a mass spectrometer (Shimadzu, GC-MS-QP2010 plus), RTX-55 MS capillary column, and helium used as a carrier gas. Detection limit for the analyzed compounds was 1.0 µg L⁻¹.

**Table 1** Chemical properties of the selected organic micro-pollutants in this study

<table>
<thead>
<tr>
<th>Compounds</th>
<th>CAS no.</th>
<th>Formula</th>
<th>Molecular weight (g/mol)</th>
<th>Log K(_{ow})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Methyl-2,6-di-tert-butylphenol (BHT)</td>
<td>128-37-0</td>
<td>C₁₅H₂₅O</td>
<td>220.35</td>
<td>5.10</td>
</tr>
<tr>
<td>Bisphenol A (BPA)</td>
<td>80-05-7</td>
<td>C₁₃H₁₄O₂</td>
<td>228.29</td>
<td>3.32</td>
</tr>
<tr>
<td>Bis(2-ethylhexyl) phthalate (DEHP)</td>
<td>117-81-7</td>
<td>C₂₄H₃₄O₄</td>
<td>390.56</td>
<td>7.54</td>
</tr>
</tbody>
</table>

CAS: conventional activated sludge; \(K_{ow}\): octanol-water partition coefficient.
RESULTS AND DISCUSSION

Membrane fouling and organic micro-pollutant removal in MBR

Pilot-scale MBR was operated under constant flux condition at about 4.58 L (m² h⁻¹) for more than 300 days. Low permeate flux of membrane was used in this study as the MBR was directly fed with high organic strength leachate. Similar operating range of permeate flux was reported in previous studies (Laitinen et al. 2006; Ahmed & Lan 2012). During the MBR operation, it was found that TMP increased from 8 to 25 kPa corresponding to the reduction in permeability from 57 to 16 L (m² h⁻¹) bar⁻¹ within 100 days of operation (Figure 2). This flux decline was caused by the accumulation of SS and soluble substances on the membrane surface and/or within membrane pore induced membrane fouling. Thereafter, chemical cleaning with 0.2% sodium hypochlorite, followed by 2% citric acid was performed. The cleaning of membrane by sodium hypochlorite could efficiently eliminate most of membrane foulant indicating that the fouling was mainly caused by organic substances. The performance of fouled and cleaned membrane on pollutant rejection are compared in Table 2. For organic matter removal, the feeding leachate had average COD, BOD, and DOC values of 9,240, 5,816, and 3,694 mg L⁻¹, respectively. After treatment the effluent concentrations of COD, BOD, and DOC were reduced to average values of 1,204 mg L⁻¹, 180 mg L⁻¹, and 646 mg L⁻¹ when filtered through the fouled membrane, and 1,209 mg L⁻¹, 187 mg L⁻¹, and 658 mg L⁻¹ for the cleaned membrane, respectively. Accordingly, average removals of 87% of COD, 97% of BOD, and 82% of DOC were achieved. SUVA₂₅₄ is a parameter representing the presence of aromatic carbon and hardly biodegradable organic matter. An increase in SUVA₂₅₄ after treatment indicates the presence of higher aromatic organic carbon content and increased dissolved organic matter (DOM) removal (Comstock et al. 2010). SUVA₂₅₄ of effluent showed a significant increase in comparison with that of influent from 0.65 to about 2.70 L mg⁻¹ m⁻¹ by the cleaned membrane and 2.74 L mg⁻¹ m⁻¹ by the fouled membrane suggesting the biodegradation of non-aromatic molecular structure within the MBR. The foulant layer formed on the membrane surface only slightly improved COD, BOD, DOC and non-aromatic DOM rejection compared to the cleaned membrane. The improvement was also observed in previous research (Chang et al. 2001; Kang et al. 2006); however, it was found to a lower degree in this study.

For micro-pollutant removal, the influent leachate contained 21.7 μg L⁻¹ of BPA, 7,331 μg L⁻¹ of BHT, and 22.3 μg L⁻¹ of DEHP. After the treatment, the effluent concentrations of BPA, BHT, and DEHP operated with the fouled membrane were reduced to 1.2, 1,183, and 2.1 μg L⁻¹ and 2.2, 1,545, and 6.5 μg L⁻¹ for the cleaned membrane, respectively. The removal efficiencies of the toxic compounds were between 84 and 94% by the fouled membrane, and 70–90% by the cleaned membrane. For this study, it was found that the fouled membrane provided additional removal of the toxic compounds, ranging from about 4% difference for BPA, 5% difference for BHT, and 19% difference for DEHP. The result is consistent with previous studies reporting that the deposition of mixed liquor activated
sludge on MF membrane acting as the additional barrier enhanced the retention of micro-pollutants during filtration process (Urase et al. 2005). Major mechanisms responsible for micro-pollutant removal in MBRs are adsorption and biodegradation by SS. An increase in rejection of the fouled membrane could be explained by enhanced adsorption capacity of the dynamic foulant layer and biofilm that was deposited on the membrane surface. In addition, modification of membrane surface properties by foulant layer may also influence micro-pollutant retention.

Characteristics of MBR fouled and cleaned membranes

Changes in MBR membrane surface properties between the fouled and the cleaned membrane were characterized to determine its relationship with micro-pollutant removals. The SEM pictures (Figure 3) indicated a significant difference between the fouled and cleaned membrane surfaces. An elemental analysis elucidated that Ca, Mg, Na, K, and Cl were the major inorganic elements in the foulant layer. Through the FTIR spectra analysis (Figure 4), the fouled membrane showed the absorption band at about 1,649, 1,540, and 1,412 cm\(^{-1}\) relating to protein structure (amides I, II, and amino acids), and the absorption band at about 1,040 cm\(^{-1}\) corresponding to polysaccharides or polysaccharide-like substances (Meng et al. 2010). For the cleaned membrane, typical absorption bands of the original polyethylene membrane appeared at 2,916, 2,850, 1,472, and 720 cm\(^{-1}\). The residue absorption bands similar to those of the fouled membrane were observed at 1,646, 1,540 and 1,412 cm\(^{-1}\). The SUVA\(_{254}\) (L mg\(^{-1}\) m\(^{-1}\)) of the fouled membrane was 2.70 (0.01), while that of the cleaned membrane was 2.74 (0.01). The SEM micrographs (Figure 3) showed the significant difference between the fouled and cleaned membranes.

### Table 2 | Removal performance of MBR treatment plant operated with fouled and cleaned membrane

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Influent</th>
<th>Effluent of fouled membrane</th>
<th>Removal (fouled membrane)</th>
<th>Effluent of cleaned membrane</th>
<th>% Removal (cleaned membrane)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Organic matter</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>6.8</td>
<td>9.2</td>
<td>-</td>
<td>9.1</td>
<td>-</td>
</tr>
<tr>
<td>EC (mS cm(^{-1}))</td>
<td>26.8 (1.0)</td>
<td>25.0 (0.1)</td>
<td>-</td>
<td>25.2 (0.1)</td>
<td>-</td>
</tr>
<tr>
<td>BOD (mg L(^{-1}))</td>
<td>5,816 (155)</td>
<td>180 (10)</td>
<td>96.91</td>
<td>187 (6)</td>
<td>96.78</td>
</tr>
<tr>
<td>COD (mg L(^{-1}))</td>
<td>9,240 (416)</td>
<td>1,204 (40)</td>
<td>86.97</td>
<td>1,209 (98)</td>
<td>86.92</td>
</tr>
<tr>
<td>DOC (mg L(^{-1}))</td>
<td>3,694 (26)</td>
<td>646 (2)</td>
<td>82.51</td>
<td>658 (2)</td>
<td>82.19</td>
</tr>
<tr>
<td>UV(_{254}) (cm(^{-1}))</td>
<td>23.92 (0.01)</td>
<td>17.72 (0.05)</td>
<td>25.92</td>
<td>17.79 (0.03)</td>
<td>25.63</td>
</tr>
<tr>
<td>SUVA(_{254}) (L mg(^{-1}) m(^{-1}))</td>
<td>0.65</td>
<td>2.74 (0.01)</td>
<td>-</td>
<td>2.70 (0.01)</td>
<td>-</td>
</tr>
<tr>
<td><strong>Toxic micro-pollutant</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPA (µg L(^{-1}))</td>
<td>21.7 (1.2)</td>
<td>1.2 (0.2)</td>
<td>94.32</td>
<td>2.2 (0)</td>
<td>89.85</td>
</tr>
<tr>
<td>BHT (µg L(^{-1}))</td>
<td>7,331 (137)</td>
<td>1,183 (6)</td>
<td>83.86</td>
<td>1,545 (17)</td>
<td>78.92</td>
</tr>
<tr>
<td>DEHP (µg L(^{-1}))</td>
<td>22.3 (1.9)</td>
<td>2.1 (0.2)</td>
<td>90.57</td>
<td>6.5 (0.3)</td>
<td>70.96</td>
</tr>
</tbody>
</table>

Average (SD) values from \(n = 5\).
1,040 cm\(^{-1}\) demonstrating the presence of irreversible fouling. The accumulation and precipitation of the inorganic and organic foulants on the membrane surface may act as a secondary membrane resulting in a narrowing pore size and increase in adsorption capacity, which might be one of the reasons for the enhancement in the rejection efficiencies of the micro-pollutants. The contact angles of the fouled and cleaned membrane were 64 and 62°, respectively and contributed to a slight increase in hydrophobic character after the membrane fouling. A slightly higher hydrophobicity caused by the foulant layer could probably help rejecting and adsorbing hydrophobic micro-pollutants such as BPA, BHT, and DEHP. The octanol-water partition coefficient (K\(_{ow}\)) of the studied compounds was found to be related to their removals by the fouled membrane. The membrane fouling yielded significant increase in rejection of DEHP (19%), whereas it provided less impact for BPA (4%) and BHT (5%).

**Particle size fractions in mixed liquor and their fouling potential**

The particle size distributions based on volume of fine and coarse particle fractions are presented in Figure 5(a) and 5(b). It was found that fine particles of <0.2, <0.45, and <1.2 \(\mu\)m had narrower size distribution ranging between 0.03 and 1.0 \(\mu\)m with average particle size of 0.22, 0.26, and 0.54 \(\mu\)m, respectively, while the distribution of the fine particles >1.2 \(\mu\)m was featured with two broader peaks at...
0.3 and 36 μm with average particle size of 21 μm. The particle size of coarse particles was mainly distributed from 0.5 μm to 100 μm, with average particle sizes of 40 μm, 44 μm, and 51 μm for the coarse particles settled after 120 minutes, 90 minutes, and 30 minutes, respectively. The larger particles shared higher SS and COD in leachate as well as contribution of deposited SS on the membrane surface (Table 3).

The SEM images (Figure 6) indicated significant difference in surface morphology of fouled CA membrane when

**Table 3** | Characteristics of the mixed liquor fractions

<table>
<thead>
<tr>
<th>MBR mixed liquor fractions</th>
<th>pH</th>
<th>EC (mS cm⁻¹)</th>
<th>SS (mg L⁻¹)</th>
<th>COD (mg L⁻¹)</th>
<th>Volume average diameter (μm)</th>
<th>Absolute density (g cm⁻³)</th>
<th>SS mass per areaa (g m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBR membrane foulants</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fine particles</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;0.2 μm</td>
<td>8.8</td>
<td>25.2 (0.1)</td>
<td>0 (0)</td>
<td>1,098 (11)</td>
<td>0.22 (0.06)</td>
<td>1.0123</td>
<td>0.00 (0)</td>
</tr>
<tr>
<td>&lt;0.45 μm</td>
<td>8.8</td>
<td>25.2 (0.1)</td>
<td>0 (0)</td>
<td>1,148 (18)</td>
<td>0.26 (0.04)</td>
<td>1.0129</td>
<td>0.00 (0)</td>
</tr>
<tr>
<td>&lt;1.2 μm</td>
<td>8.9</td>
<td>25.3 (0.1)</td>
<td>10 (1)</td>
<td>1,483 (15)</td>
<td>0.54 (0.09)</td>
<td>1.0138</td>
<td>0.17 (0.03)</td>
</tr>
<tr>
<td>&gt;1.2 μm</td>
<td>8.9</td>
<td>25.4 (0.1)</td>
<td>320 (15)</td>
<td>1,512 (10)</td>
<td>21.33 (0.87)</td>
<td>1.0150</td>
<td>5.47 (0.26)</td>
</tr>
<tr>
<td>Coarse particles</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Settled in 120 minutes</td>
<td>8.9</td>
<td>25.3 (0.1)</td>
<td>370 (10)</td>
<td>1,554 (15)</td>
<td>40.05 (0.48)</td>
<td>1.0152</td>
<td>6.39 (0.17)</td>
</tr>
<tr>
<td>Settled in 90 minutes</td>
<td>8.9</td>
<td>25.4 (0.1)</td>
<td>2,630 (40)</td>
<td>2,002 (21)</td>
<td>44.45 (0.67)</td>
<td>1.0235</td>
<td>46.14 (0.69)</td>
</tr>
<tr>
<td>Settled in 30 minutes</td>
<td>8.8</td>
<td>25.5 (0.2)</td>
<td>3,110 (20)</td>
<td>2,146 (19)</td>
<td>51.05 (0.71)</td>
<td>1.0287</td>
<td>53.74 (0.35)</td>
</tr>
</tbody>
</table>

Average values (SD) from n = 3.

aDetermined as mass of solids per membrane area.

**Figure 6** | SEM micrographs (magnification × 3,500) and % blocked area of the virgin CA membrane (a) and pre-fouled CA membranes with the fine particle fractions <0.2 μm (b), <0.45 μm (c), <1.2 μm (d), >1.2 μm (e), and coarse particle fractions settled in 120 minutes (f), 90 minutes (g), 30 minutes (h).
being fouled with different particle size fraction. The fouled membrane with (i) fine particles smaller than the membrane pore size (<0.45 μm) generated internal deposition, and a reduction in pore size of approximately 8–20% (Figure 6(b) and 6(c)), (ii) the fine particles larger than the membrane pore size produced an effect of pore blocking by increasing blocked area by 78 to 88% (Figure 6(d) and 6(e)), and (iii) the coarse particles in mixed liquor yielded cake formation and augmentation of blocked area by more than 89% (Figure 6(f)–6(h)). Table 4 also presents the modification of CA membrane surface properties through its contact angle. Comparing between the virgin CA membrane and the pre-fouled CA membrane, their contact angles were not different in case of fouling with the fine particles smaller than the membrane pore size, but there was a slight increase in hydrophobicity after fouling with particles larger than the membrane pore size. This observation suggested that the deposition of mixed liquor comprising soluble hydrophobic components (e.g. proteins and humic substances) and sludge particles led to a hydrophobic characteristic of the membrane surface. Lee et al. (2005) demonstrated that the increased hydrophobic properties of microbial floc and supernatant in submerged MBR were related to higher sludge retention time employed during the reactor operation.

### Effect of the foulant characteristics on BPA, BHT, and DEHP rejection

Figure 7 shows the removal efficiencies of BPA, BHT, and DEHP by the virgin CA membrane and the pre-fouled CA membranes with different size fractions of mixed liquor.

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Contact angle of the virgin CA membrane and the pre-fouled CA membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>Contact angle (°)</td>
</tr>
<tr>
<td>Virgin CA membrane</td>
<td>46.9 (1.4)</td>
</tr>
<tr>
<td>Pre-fouled CA membranes with the fine particles</td>
<td></td>
</tr>
<tr>
<td>&lt;0.2 μm</td>
<td>42.9 (1.8)</td>
</tr>
<tr>
<td>&lt;0.45 μm</td>
<td>46.6 (3.7)</td>
</tr>
<tr>
<td>&lt;1.2 μm</td>
<td>47.5 (1.9)</td>
</tr>
<tr>
<td>&gt;1.2 μm</td>
<td>50.0 (2.4)</td>
</tr>
<tr>
<td>Pre-fouled CA membranes with the coarse particles</td>
<td></td>
</tr>
<tr>
<td>Settled in 120 minutes</td>
<td>50.3 (2.1)</td>
</tr>
<tr>
<td>Settled in 90 minutes</td>
<td>54.7 (2.1)</td>
</tr>
<tr>
<td>Settled in 30 minutes</td>
<td>56.7 (2.8)</td>
</tr>
</tbody>
</table>

Average (SD) values from n = 5.

Figure 7 | Removal of BPA, BHT, and DEHP under the virgin CA membrane and the pre-fouled CA membranes by different size fractions of MBR mixed liquor.
The removals of BPA, BHT, and DEHP were 15, 22, and 25%, respectively, by the virgin membrane corresponding to initial adsorption capacity of 0.26, 0.38, and 0.43 μg cm\(^{-2}\), respectively. When the membranes were fouled, average removals of BPA, BHT, and DEHP compared to the virgin membrane were not significantly increased for the fouling with fine particles of smaller size than the membrane pores (<0.2 and <0.45 μm). The fouled membranes with fine particles larger than the membrane pores (>1.2 and >1.2 μm) increased the removals of BPA, BHT, and DEHP by approximately 5, 17–23, and 11–25%, respectively. Meanwhile, those of the fouled membrane with coarse particles significantly increased by approximately 28–36, 27–32, and 36–42%, respectively. DEHP with higher log \(K_{ow}\) (7.54) was more effectively retained by the fouled membrane compared to BPA and BHT. Boonyaroj et al. (2022) also reported an increase in BPA, BHT, and DEHP retention by 20–50% due to the presence of gel and cake layer on the membrane surface. Urase et al. (2005) found that the deposit layer on the membrane surface helped increase the removal of pharmaceuticals by 10–40%. In this study, increase in BPA, BHT, and DEHP removals by the fouled membrane could be explained by the following phenomena: (i) the increase in solid particles accumulation on the membrane surface could induce higher adsorption capacities leading to reduction of micro-pollutant transport through the foulant layer; (ii) increased coverage of pore blocked area could result in an enhanced steric exclusion and less partitioning of micro-pollutant transport through the membrane; and (iii) higher hydrophobic characteristic of membrane surface could yield high rejection of hydrophobic compounds. Figure 8 shows the correlation (using best fit mathematical expression from least squares method) between BPA, BHT, and DEHP removal efficiencies and the changes of membrane surface properties when the membranes were fouled with different size fractions of mixed liquor. It can be seen that the amount of solid mass accumulation, pore blockage area, and contact angle of membrane surface increased with fouling.
were related to micro-pollutant removals ($R^2$ of 0.69–0.95). The results indicated that the presence of deposited solid mass significantly affected the rejection of BPA, BHT, and DEHP. Meanwhile, the modification of membrane surface properties in terms of blockage pore area and hydrophobicity improved the removals proportionally.

\section*{CONCLUSIONS}

The effect of membrane fouling on BPA, BHT, and DEHP rejection in MBR during municipal landfill leachate treatment was examined. The characterization of membrane foulants indicated presence of proteins and carbohydrates and inorganic foulants such as Ca, Mg, Na, K, and Cl. The fouled membrane improved micro-pollutant rejection, from about 4% for BPA, 5% for BHT, and 19% for DEHP compared to the cleaned membrane. The modification of membrane surface characteristics after fouling significantly affects the rejection of micro-pollutants. The removal of micro-pollutants was more pronounced when the membrane was fouled by particles larger than the membrane pore size as a result of an increase of adsorption capacity by SS mass accumulation as well as hydrophobic interaction between micro-pollutants and the foulant layer.

\section*{ACKNOWLEDGEMENTS}

This research was carried out under the Research and Development for Water Reuse Technology in Tropical Regions (WaterIntro) project supported by Japan International Cooperation Agency (JICA) and Japan Science and Technology Agency (JST). Granted research from the Kasetsart University Research and Development Institute (KURDI) is also acknowledged.

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First received 3 February 2015; accepted in revised form 5 May 2015. Available online 20 May 2015.