

# Effects of mixed liquor pH on membrane fouling and micro-pollutant removals in membrane bioreactors for municipal landfill leachate treatment

Samunya Sanguanpak, Chart Chiemchaisri, Wilai Chiemchaisri and Kazuo Yamamoto

## ABSTRACT

This research investigated the membrane fouling and micro-pollutant removals in treatment of municipal landfill leachate at various pH levels (i.e. 5.5, 6.5, 7.5, and 8.5) using membrane bioreactors. The findings revealed that membrane fouling was influenced by the pH level of mixed liquor, with pH 5.5 exhibiting the most severe membrane fouling. At pH 5.5, proteins and carbohydrates were predominant in the membrane foulants, while at pH 8.5 humic-like and inorganic substances constituted the largest proportion of the foulants on the membrane surface. The removal efficiencies of micro-pollutants (bisphenol-A; 2,6-di-tert-butylphenol and 2,6-di-tert-butyl-4-methylbutylphenol) were nevertheless insignificantly influenced by the pH levels of mixed liquor. In addition, the removal rates of the compounds at pH 5.5 were slightly lower vis-à-vis at the higher pH levels. The micro-pollutant retention on the fouled membranes was also significant and highest under the mixed liquor pH of 8.5. Furthermore, the experiments demonstrated that the varying degrees of rejection by the fouled membranes could be attributed to the alteration of foulant characteristics as a result of the pH variations.

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

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## INTRODUCTION

Landfill leachate is the putrid liquid that drains or leaches from a landfill. The composition of landfill leachate typically includes biodegradable and recalcitrant organic compounds, nutrients, dissolved salts and heavy metals. Leachate might also contain toxic compounds that could harm aquatic organisms and the ecosystem of the natural water bodies. To mitigate the environmental impact of leachate, it is necessary to deploy effective leachate treatment technologies for removal of the pollutants prior to discharge into the receiving environment. Of the existing treatment techniques, the membrane bioreactor (MBR) technique is a new approach with high potential for landfill leachate treatment. In Chiemchaisri *et al.* (2011) and Boonyaroj *et al.* (2012), a two-stage MBR was applied to treat landfill leachate for a period of over 3 years. According to Sipma *et al.* (2010), the MBR technology improved the removal efficiencies of several toxic compounds due to the enhancement of bio-sorption and degradation induced by

the higher concentration of biomass under a longer sludge age condition in relation to the conventional activated sludge. Membrane fouling in the MBR, attributable to organic substances and inorganic elements (i.e. calcium and magnesium), was a major obstacle for the MBR operation (Sanguanpak *et al.* 2013). The MBR membrane fouling contributed to decreased productivity and a reduced membrane lifespan, thereby leading to a rise in the operation costs (Ahmed & Lan 2012). Nevertheless, the fouling layer could help capture certain micro-pollutants in the wastewater. The degree of membrane fouling is greatly influenced by a number of factors, including pH levels. pH is a factor that significantly influences the activated sludge characteristics, membrane fouling, and the removal efficiencies of pharmaceutical and personal care products during the treatment (Gao *et al.* 2010; Tadkaew *et al.* 2010; Wu *et al.* 2010; Zhang *et al.* 2014). Most research focused on the effects of mixed liquor pH on either membrane fouling

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or micro-pollutant removal in MBR treating synthetic wastewater or low-strength wastewater. In contrast, this current research has attempted to investigate the concurrent effects on both the membrane fouling and micro-pollutant removal of the pH variations in the highly organic-loaded MBR operation for leachate treatment.

In this research, two identical laboratory-scale MBR tanks were utilized, one of which was for the experiments under the mixed liquor pH 5.5 and 6.5 conditions, while the other was for those under the pH 7.5 and 8.5 conditions. The entire experimental period was 150 days. The fouling behaviors, sludge properties, and changes in the membrane foulant characteristics were systematically investigated. The removal efficiencies of the micro-pollutants, i.e. bisphenol-A (BPA), 2,6-di-tert-butylphenol (2,6-DTBP) and 2,6-di-tert-butyl-4-methylbutylphenol (BHT), by biodegradation and adsorption were also evaluated on a batch scale for the entire experimental pH range (i.e. 5.5, 6.5, 7.5, and 8.5). Furthermore, the retention efficiencies of the compounds by the fouled membranes were examined to determine the relations between the foulant characteristics and mixed liquor pH.

## MATERIALS AND METHODS

### Laboratory-scale MBR setup and operation

This research utilized two identical 12 L laboratory-scale MBRs individually fitted with submerged hollow-fiber microfiltration membrane modules (Mitsubishi Rayon, Japan), as shown in Figure 1. The membranes were of polyvinylidene fluoride material, with a membrane surface

area of  $0.07 \text{ m}^2$  per module and a nominal pore size of  $0.4 \mu\text{m}$ . To maintain the dissolved oxygen (DO) concentration within a range of  $3\text{--}4 \text{ mg L}^{-1}$ , two sets of air pumps were employed to supply air through diffusers at the base of the MBR tanks at an air flow rate of  $5 \text{ L min}^{-1}$ . A hydraulic retention time of 1.5 days was selected, which corresponded to an approximate  $4.5 \text{ L m}^{-2} \text{ h}^{-1}$  permeate flux. To maintain a constant volume in both MBRs, the influent pumps were regulated with level sensors. The feed leachate was prepared by diluting fresh leachate with tap water in a ratio of 1:10 ( $\text{v v}^{-1}$ ), resulting in an organic loading (biochemical oxygen demand (BOD) and chemical oxygen demand (COD)) of approximately  $3.7 \pm 0.5 \text{ kg BOD m}^{-3} \text{ day}^{-1}$  and  $5.4 \pm 0.9 \text{ kg COD m}^{-3} \text{ day}^{-1}$ . Both MBR tanks were seeded with activated sludge from an integrated MBR-reverse osmosis pilot plant in Thailand. The initial mixed liquor suspended solids (MLSS) concentration was  $7 \text{ g L}^{-1}$  and was subsequently maintained within a range of  $10\text{--}15 \text{ g L}^{-1}$  throughout the MBR process without sludge wastage operation except for sampling purposes. The initial ambient pH of mixed liquor in both experimental MBR tanks (i.e. MBRs 1 and 2) was  $7.9 \pm 0.1$ . The experiments were divided into two successive phases of 75 days each. In MBR 1, the mixed liquor pH was first reduced from the ambient pH (i.e.  $7.9 \pm 0.1$ ) to  $\text{pH } 6.5 \pm 0.3$  during the first phase (days 1–75) and subsequently lowered to  $\text{pH } 5.5 \pm 0.3$  during the second phase (days 76–150). Conversely, in MBR 2 the pH was raised to  $\text{pH } 8.5 \pm 0.2$  in the first phase and then adjusted to  $\text{pH } 7.5 \pm 0.1$  in the subsequent phase.

The pH of the MBRs was manually adjusted to the targeted pH levels using analytical-grade HCl (1 M) and NaOH (1 M) solutions, and the measurements of mixed

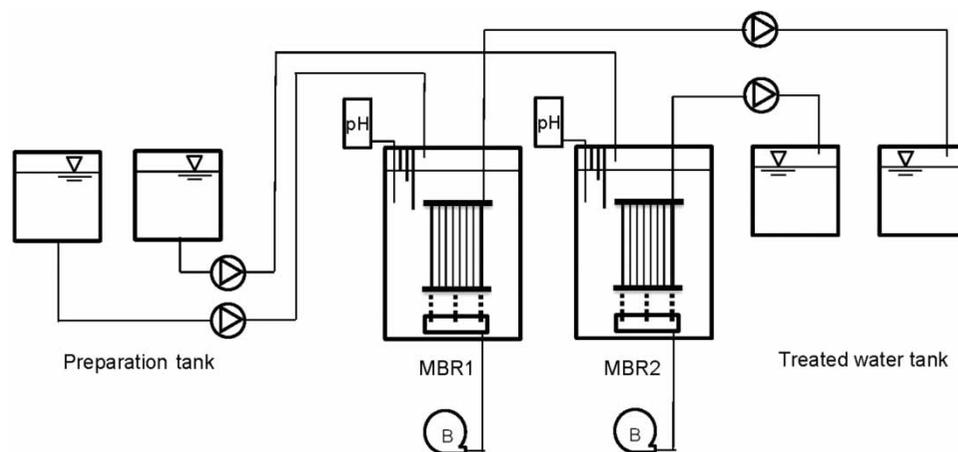


Figure 1 | The schematic of experimental MBR aeration tanks.

liquor pH were taken every hour using a digital pH meter. In addition, the permeate flux was monitored volumetrically and the trans-membrane pressure (TMP) was measured with a pressure gauge on a daily basis. The operation of the treatment system was continuous and under ambient conditions (27–30 °C). Membrane cleanings were individually performed at the end of each experimental run (i.e. 75 days for each pH operation), whereby the membrane modules were removed and rinsed with tap water to wash off the foulants on the membrane surface. Furthermore, chemical cleaning was undertaken by soaking the membranes in a 0.1% sodium hypochlorite solution (pH ~ 12) for 60 min, followed by 0.1% hydrochloric acid (pH ~ 2) for another 60 min.

### Determination of micro-pollutant removals

The aim of the batch experiments was to investigate the effects of mixed liquor pH on the removals of micro-pollutants through the biodegradation, adsorption and membrane filtration mechanisms. Three organic contaminants of phenolic compounds (BPA, BHT, and 2,6-DTBP) were studied due to their high concentrations in the raw leachate. Table 1 presents the physicochemical properties of these compounds. The stock solution of micro-pollutants was prepared at a concentration of 10 mg L<sup>-1</sup> in pure methanol prior to dilution with distilled water to obtain an initial concentration of 3,000 µg L<sup>-1</sup> for the batch experiments.

To distinguish between the removals of the micro-pollutants through biodegradation and through adsorption, the experiments utilized both active and inactivated MBR sludge. The inactivation of sludge was performed by sterilization at 121 °C for 15 min in triplicate. The batch experiments were carried out using a 500 mL glass vessel containing MLSS with an initial concentration of 3 g L<sup>-1</sup> suspended in the micro-pollutants-containing water. The micro-pollutant removals through biodegradation were determined using the active sludge under continuous

aeration to maintain the DO level of 3–4 mg L<sup>-1</sup>, similar to the MBR operation, whereas the adsorption capacity was determined using the inactivated sludge. The samples were taken hourly for the first 6 hours and subsequently every 6 hours for an entire period of 24 hours for determination of the remaining concentrations.

In the filtration experiments, 20 mL of membrane foulants collected from the experimental MBR tanks were filtered through a cellulose acetate membrane with 0.45 µm nominal pore size to imitate the foulant layer on the membrane surface. The rejection tests were conducted using new and pre-fouled membranes to compare the retention efficiency at a constant TMP of 30 kPa. The target micro-pollutants were spiked through each membrane specimen. At the experiment termination, the permeate samples were taken for concentration measurement. The micro-pollutant removal performance (*R*) through filtration was determined by:

$$R(\%) = \left(1 - \frac{C}{C_0}\right) \times 100 \quad (1)$$

where *C* is the remaining concentration and *C*<sub>0</sub> is the initial concentration.

### Analytical methods

The characteristics of the feed and treated leachate were constantly monitored throughout the experiment. BOD<sub>5</sub> and COD were determined in accordance with *Standard Methods* (APHA 2005) without pre-treatment. Dissolved organic carbon (DOC) was measured using the Shimadzu TOC-5000. UV<sub>254</sub> was determined by a spectrophotometer (Thermo Scientific™ Evolution 60S) and the results were employed to calculate specific UV absorbance (SUVA<sub>254</sub>), i.e. scaling UV<sub>254</sub> by DOC. The ion concentrations of calcium and magnesium were quantified using a Shimadzu HIC-10A ion chromatograph.

The microbial floc size was measured by a Malvern Mastersizer 2000 particle size analyzer. The surface charges of supernatant samples were determined as zeta potential in 0.01 N NaCl at pH 7.0 using an electrophoresis measurement apparatus (Zetasizer nano ZS, Malvern Instruments). Soluble microbial products (SMP) and extracellular polymeric substances (EPS) were extracted from the mixed liquor using the heat treatment method (Le-Clech et al. 2006). The extracted solutions were analyzed for total proteins and carbohydrates in accordance with the folin and phenol-sulfuric acid methods, respectively.

**Table 1** | The physicochemical properties of the micro-pollutants under study

Compounds	CAS no.	Mol. wt (g mol <sup>-1</sup> )	Log <i>K</i> <sub>ow</sub> <sup>a</sup>	p <i>K</i> <sub>a</sub> <sup>a</sup>
BPA	80-05-7	228.29	3.32	9.73
2,6-DTBP	128-39-2	206.33	4.92	12.16
BHT	128-37-0	220.35	5.10	12.76

<sup>a</sup>The values were from the SciFinder Scholar (American Chemical Society) database.

To investigate the foulant properties, the fouled membranes were retrieved from the MBR tanks at termination and desorbed with 2 L of deionized water for foulants. The foulant properties with respect to suspended solids (SS), DOC, proteins, carbohydrates, and inorganic content were analyzed in accordance with the aforesaid analytical methods. Fluorescence excitation–emission matrix (EEM) spectroscopy of the dissolved membrane foulants was determined with a Jasco FP-8200 spectrofluorometer. The surface morphology and element composition of the fouled membranes were characterized by scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS, JEOL model JSM-5410). The hydrophobicity of the fouled membranes was determined by measuring the contact angles of water droplets onto the membrane surface. The measurement of contact angles was carried out using a Ramé-hart contact angle goniometer with DROP image Standard v2.4.

The organic contaminants were analyzed according to the method described in Boonnorat *et al.* (2014). Solid phase extraction (SPE) and gas chromatograph–mass spectrometry (GC-MS) were used to identify the compounds in the water samples. To determine the compounds' concentrations, 50 mL of the filtered samples were fed through C18-SPE tubes at an approximate flow rate of 1 mL min<sup>-1</sup>. Afterward, the adsorbed organic micro-pollutants in SPE sorbent were eluted by 10 mL dichloromethane:methanol in a 1:9 mixing ratio. The extracted samples were subsequently concentrated to 1 mL volume by a nitrogen evaporator. Detection and quantification of the toxic contaminants were performed by GC-MS (Shimadzu, GC-MS-QP2010 plus). The organic micro-pollutants in the water samples were identified by comparing with GC/MS library (Wiley 7) developed from standard substances with the detection limits of 1.0 µg L<sup>-1</sup>.

## RESULTS AND DISCUSSION

### Effect of mixed liquor pH on treatment performance and fouling behaviors

Table 2 presents the characteristics of the influent and the treated leachate of MBR for the entire experimental mixed liquor pH. At the pH levels of 6.5, 7.5, and 8.5, the removal efficiencies of COD, BOD, and DOC were on average 99%, 99% and 97%, respectively, but slightly decreased when pH was 5.5. Variations in pH were reported to influence the microbial metabolism, e.g. the utilization of carbon and substrate degradation efficiency (Baily & Ollis 1986). A slight decrease in the removal performance of organic matters at pH 5.5 mixed liquor could be attributed to the decreased microbial activities in the MBRs. Some micro-organisms in the activated sludge reactors became inactive under mildly acidic conditions (i.e. pH 5.5). Conversely, the inorganic removal efficiencies of Ca and Mg were varied within the ranges of 1–4%, 12–14%, 30–60%, and 68–74% for the pH levels of 5.5, 6.5, 7.5, and 8.5, respectively, indicating a positive correlation between the inorganic removals and the pH levels of mixed liquor. A higher percentage of inorganic removal efficiency as the pH level of mixed liquor increased could be attributed to the increased precipitation of Ca and Mg inside the MBRs.

SUVA<sub>254</sub> is a parameter indicating the presence of aromatic carbon and biodegradable-recalcitrant organic matters, e.g. humic substances, in dissolved organic matter (DOM). In Table 2, SUVA<sub>254</sub> of the influent was low, suggesting DOM with low aromatic molecular structure. In contrast, SUVA<sub>254</sub> of the effluent significantly increased, suggesting the biodegradation of non-aromatic molecular structure in the MBRs. SUVA<sub>254</sub> in the effluent sample at

**Table 2** | The influent and effluent characteristics of MBR as a function of mixed liquor pH

Parameter	Influent	Permeate at pH = 5.5	Permeate at pH = 6.5	Permeate at pH = 7.5	Permeate at pH = 8.5
pH	5.47 ± 1.0	5.66 ± 0.30	6.61 ± 0.23	7.96 ± 0.10	8.79 ± 0.06
COD (mg L <sup>-1</sup> )	5445 ± 900	104 ± 40	41 ± 2	59 ± 11	51 ± 23
BOD (mg L <sup>-1</sup> )	3659 ± 476	53 ± 8	18 ± 9	23 ± 5	20 ± 10
DOC (mg L <sup>-1</sup> )	1154 ± 205	48 ± 2	26 ± 10	25 ± 2	30 ± 2
UV <sub>254</sub> (cm <sup>-1</sup> )	4.11 ± 0.09	0.79 ± 0.10	0.74 ± 0.12	0.74 ± 0.05	0.85 ± 0.05
SUVA <sub>254</sub> (Lmg <sup>-1</sup> m <sup>-1</sup> )	0.35 ± 0.06	1.70 ± 0.04	2.88 ± 0.03	2.96 ± 0.01	2.84 ± 0.02
Calcium (mg L <sup>-1</sup> )	410 ± 105	392 ± 27	354 ± 33	164 ± 17	106 ± 12
Magnesium (mg L <sup>-1</sup> )	195 ± 35	193 ± 14	171 ± 18	136 ± 11	69 ± 9

No. of samples = 12.

**Table 3** | The effects of pH on TMP increasing rate and mixed liquor characteristics

	pH = 5.5	pH = 6.5	pH = 7.5	pH = 8.5
TMP increasing rate (kPa day <sup>-1</sup> )	0.91	0.33	0.31	0.64
Floc characteristics				
Mean floc size (µm)	55 ± 2.3	58 ± 2.1	54 ± 2.1	55 ± 2
Zeta potential (mV)	-13 ± 1.8	-14 ± 1.5	-18 ± 1.9	-21 ± 2.0
SMP-protein (mg L <sup>-1</sup> )	119.1 ± 10	99.6 ± 10	98.8 ± 4	132.2 ± 12
SMP-carbohydrate (mg L <sup>-1</sup> )	44.6 ± 4	24.3 ± 6	27.0 ± 5	27.7 ± 3
EPS-protein (mg gSS <sup>-1</sup> )	68.3 ± 5	50.4 ± 3	51.7 ± 3	53.9 ± 3
EPS-carbohydrate (mg gSS <sup>-1</sup> )	29.4 ± 1.2	20.8 ± 1.2	22.8 ± 1.1	18.4 ± 1.1

No. of samples = 6.

pH 5.5 was slightly lower than those at pH 6.5, 7.5, and 8.5. The finding indicated that the removal and transformation efficiencies of non-aromatic compounds decreased with the acidity of the mixed liquor.

The TMP increasing rates in the MBR tanks varied significantly in response to variations in the mixed liquor pH, with the mildly acidic condition of pH 5.5 the most severe. Since the feed leachate and the operating conditions were identical, the differences in the fouling rates could thus be attributed to the differing mixed liquor properties. Table 3 presents the TMP increasing rates and the characteristics of mixed liquor for the four experimental pH levels. The mean microbial floc sizes were relatively similar (54–58 µm), while the absolute values of zeta potential of the mixed liquor supernatants were positively correlated with the levels of pH. According to Zhang et al. (2014), a lower absolute value of zeta potential at a low pH increased the adherence capacity of sludge flocs on the membrane surface to form a cake layer, thereby resulting in more severe membrane fouling. Taking into account EPS either in a soluble form (SMP) or bound to sludge flocs, the largest amounts of SMP in terms of protein and carbohydrate concentrations were found at pH 8.5 and 5.5, respectively. The extracted EPS exhibited the highest concentrations of proteins and carbohydrates at pH 5.5. The increase in the contents of SMP and EPS could be attributed to the microbial activity during unstable conditions. Thus, large pH adjustments in the MBRs apparently induced the generation of more SMP and EPS.

To better understand the correlation between the mixed liquor characteristics and TMP increasing rate at each pH level, a statistical analysis of linear correlation was performed to identify the key factors contributing to membrane fouling. The analysis results indicated that EPS protein (Pearson's correlation coefficient ( $r_p$ ) = 0.862) was significantly positively correlated to the TMP increasing

rate, whereas EPS carbohydrate ( $r_p$  = 0.611), SMP protein ( $r_p$  = 0.63), and SMP carbohydrate ( $r_p$  = 0.769) were moderately correlated to the TMP increasing rate. Nonetheless, no correlation was detected between the TMP increasing rate and the mean particle size of sludge flocs ( $r_p$  = -0.110) and the zeta potential of supernatants ( $r_p$  = 0.218).

### Effect of mixed liquor pH on membrane fouling characteristics

Table 4 shows the effects of mixed liquor pH on the characteristics of membrane foulants. SS were the most significant contributing factor to membrane fouling, followed by inorganic elements and soluble organic substances. The results indicated that at pH 8.5 the fouling layer was mostly made up of SS and inorganic elements, while the soluble organic substances, i.e. DOC, protein and carbohydrate, were more abundant in the fouling layer at pH 5.5. It is important to note that the fouling behavior is governed by the characteristics of activated sludge. The differences in the composition of membrane foulants were attributable to variations in the mixed liquor pH. Thus, the abundance of

**Table 4** | Characteristics of the desorbed membrane foulants as a function of mixed liquor pH

Parameter	pH = 5.5	pH = 6.5	pH = 7.5	pH = 8.5
SS (g m <sup>-2</sup> )	11.286	6.571	7.429	18.429
DOC (g m <sup>-2</sup> )	2.463	0.947	0.917	2.183
Protein (g m <sup>-2</sup> )	0.996	0.417	0.368	0.628
Carbohydrate (g m <sup>-2</sup> )	0.243	0.077	0.083	0.225
Mg <sup>2+</sup> (g m <sup>-2</sup> )	0.786	0.834	1.500	1.937
Ca <sup>2+</sup> (g m <sup>-2</sup> )	2.000	2.880	2.629	6.320

The values are averages of triplicate measurements.

proteins and carbohydrates in EPS in pH 5.5 mixed liquor contributed to the highest amount of soluble organic substances in the membrane foulants. The rises in SS and inorganic matters in the membrane foulants at pH 8.5 were attributed to a higher propensity for chemical precipitation on the membrane surface under the alkaline condition. At pH 8.5, DOC and proteins were increasing again, a phenomenon attributable to the alkalinity of mixed liquor following the introduction of NaOH, which subsequently resulted in a greater amount of SMP produced.

Based on the fluorescence EEMs of DOM in landfill leachate obtained by Lu *et al.* (2009), two main peaks relevant to aromatic protein-like substances (Peak A) and tryptophan protein-like substances (Peak B) were identified from the fluorescence spectra of the foulants of pH 5.5 (Figure 2). With the increasing pH levels of mixed liquor, two additional fluorescence peaks (Peaks C and D) representing humic-like substances were detected. Both Peaks C and D were red-shifted (5–50 nm) along the excitation and emission axes,

where a red shift was associated with the increases in molecular size, aromatic poly-condensation, and humification (Huo *et al.* 2009). This demonstrated that the variations in mixed liquor pH in the MBRs contributed to the diverse organic structure and components of the membrane foulants. Under the mildly acidic conditions (pH 5.5, 6.5), the soluble foulants were mainly composed of protein-like substances in various structures, but humic-like substances predominated for the pH level beyond 7.5.

Figure 3 illustrates the SEM images of the fouled and cleaned membranes, in which the significant differences in the microstructure of membrane fouling attributable to the variations in mixed liquor pH could be observed. The morphology of the cake layer formed on the membrane surface at pH 5.5 was relatively smooth, while that at pH 8.5 was rough due to larger particles. Even though the fouling layer at the low pH was relatively dense, it could be easily removed vis-à-vis that at the high pH. This phenomenon was attributable to an increase in the irremovable

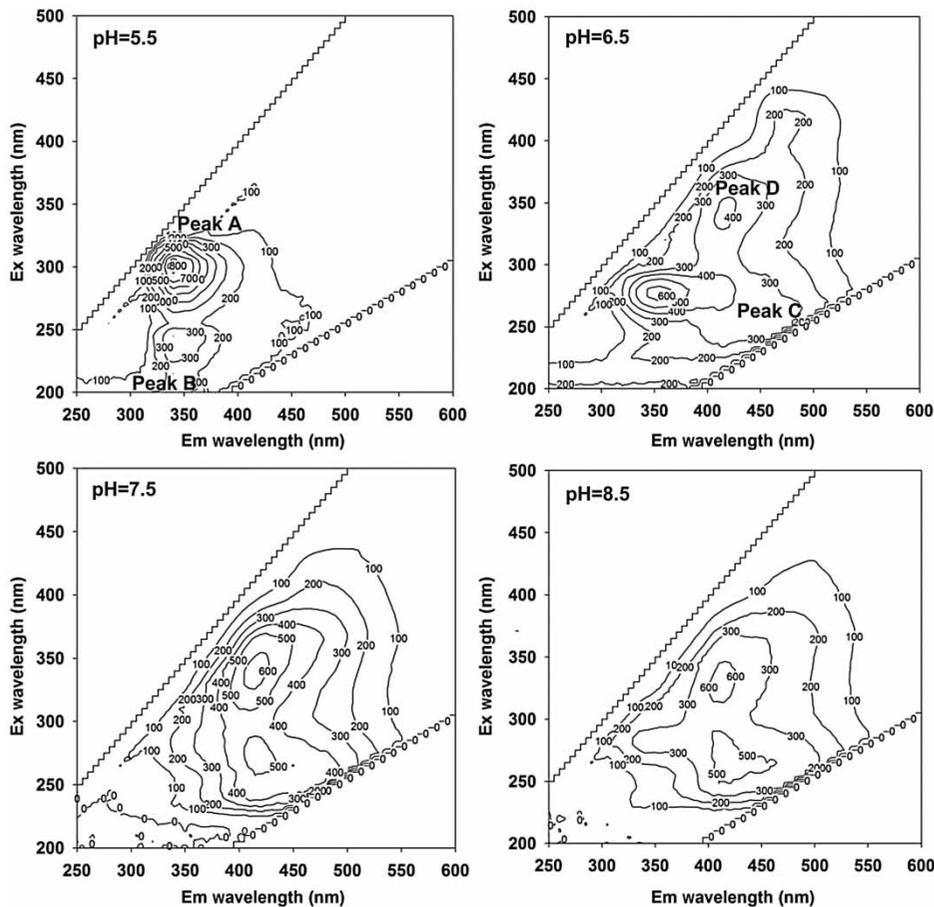
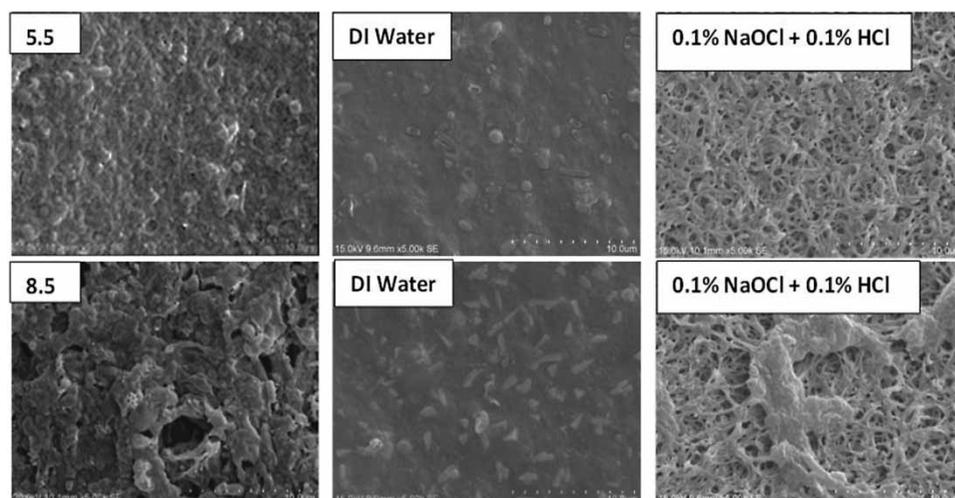


Figure 2 | Fluorescence EEMs of the desorbed membrane foulants as a function of mixed liquor pH.



**Figure 3** | SEM micrographs (x5000) of the fouled and cleaned membranes of pH 5.5 and 8.5.

fouling as the cohesion of organic fouling and the chemical precipitation on the membrane surface and/or within membrane pores increased with the alkalinity in the MBRs (Meng *et al.* 2009). The inorganic elements of the foulant layers through EDS elemental analysis consisted of C, O, Ca, Mg, Na, K, Cl, and Fe, with their contents relatively higher at pH 8.5. In addition, the changes in membrane surface morphology as a result of variations in the mixed liquor pH altered the hydrophobicity of the membranes. Typically, the hydrophobicity of a fouled membrane is determined from the contact angle between water and the membrane surface. The larger the contact angle, the greater the hydrophobicity. In the experiments, it was observed that the contact angles of the fouled membranes for pH 5.5, 6.5, 7.5, and 8.5 were 61, 59, 72, and 75°, respectively, indicating a slight increase in hydrophobicity with the increase in pH. The slight increase in hydrophobicity at the higher pH was attributed to the increased hydrophobic fractions of the foulant layers formed on the membrane surface.

### Effect of mixed liquor pH on micro-pollutant removal in batch experiments

This research also investigated the effects of mixed liquor pH on the BPA, 2,6-DTBP, and BHT removal efficiencies by the MBR sludge on a batch scale. In Table 5, the total removal efficiencies for BPA, 2,6-DTBP, and BHT were 97–98%, 93–96%, and 90–95%, respectively. The removals of BPA, 2,6-DTBP, and BHT through the adsorption mechanism were 15–20%, 25–29%, and 34–39%; and their respective removal through biodegradability were 77–82%, 65–71%, and 53–61%, indicating that the main compound-removal mechanism was biodegradation. According to Tadkaew *et al.* (2011), the contributions of adsorption and biodegradation to total removal efficiency were unequal, subject to the properties of the compounds. In this current research, BPA had the highest removal efficiency through better biodegradation in relation to the other compounds. Table 5 also presents the removal efficiencies of toxic

**Table 5** | Removal efficiencies of BPA, 2,6-DTBP, and BHT and kinetic constants as a function of mixed liquor pH

pH	BPA			2,6-DTBP			BHT		
	Total	Ads	Bio	Total	Ads	Bio	Total	Ads	Bio
	$k_{1st\ order} (h^{-1})$	(%)	(%)	$k_{1st\ order} (h^{-1})$	(%)	(%)	$k_{1st\ order} (h^{-1})$	(%)	(%)
5.5	0.17	98	77	0.12	93	65	0.10	90	53
6.5	0.17	97	79	0.14	96	71	0.12	92	55
7.5	0.18	98	80	0.14	96	69	0.13	95	61
8.5	0.17	97	82	0.14	94	65	0.12	93	54

The values are averages of triplicate measurements.

Ads: adsorption; Bio: biodegradation.

contaminants as a function of mixed liquor pH. It could be observed that variations in the pH level of mixed liquor had little effect on the removals of the toxic compounds. Once the  $pK_a$  and log octanol–water partition coefficients ( $\log K_{ow}$ ) of BPA, BHT, and 2,6-DTBP from the American Chemical Society database were taken into account, the degrees of hydrophobicity of the compounds were relatively constant in relation to the variations in pH. A slight variation in the removal efficiencies could thus be attributed to the relatively constant properties of the compounds.

Furthermore, this research examined the effects of mixed liquor pH on the concentrations of micro-pollutants over time. First-order kinetics was used to determine the difference in overall removal mechanisms (Boonnorat *et al.* 2014). In Table 5, the kinetic constants from the experimental plot of  $\ln(C/C_0)$  relative to time ( $t$ ) were  $0.10$ – $0.18 \text{ h}^{-1}$ , but the total removal rate of the compounds at pH 5.5 was slightly lower in comparison with those of the other pH levels. This was probably due to the dissimilar microbial community and/or the weakening microbial activity as the mixed liquor pH declined toward pH 5.5 (Wu *et al.* 2010).

### Effect of mixed liquor pH on micro-pollutant removal through fouled membranes

In Figure 4, the removal efficiencies of BPA, 2,6-DTBP, and BHT through filtration for the new membrane were, respectively, 11%, 35%, and 33%. The micro-pollutant removals of the fouled membranes lay between 25 and 59% for pH 5.5,

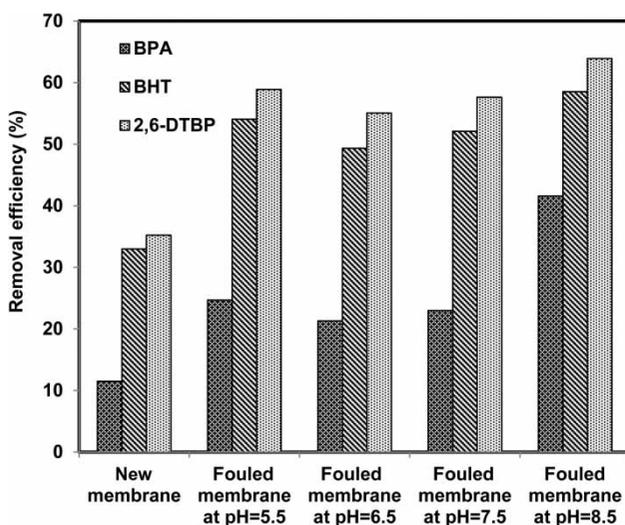


Figure 4 | Removal efficiency of BPA, BHT, and 2,6-DTBP for pre-fouled and fouled membranes at pH 5.5, 6.5, 7.5, and 8.5.

21 and 55% for pH 6.5, 23 and 58% for pH 7.5, and 42 and 64% for pH 8.5. Of the three micro-pollutants, BPA had the lowest removal performance, consistent with its lowest  $\log K_{ow}$ , which explained the lower hydrophobic adsorption of BPA to membrane relative to BHT and 2,6-DTBP. An increase in the retention of fouled membranes could be attributed to the elevated adsorption capacity of foulant layer on the membrane surface (Urase *et al.* 2005). With regard to the influence of pH on the toxic compound removal, the pre-fouled membrane at pH 8.5 exhibited the highest retention, suggesting the effect of foulant layer characteristics on the retention capacity. Nghiem & Hawkes (2007) documented that membrane fouling could significantly alter the charge surface, pore restriction, and cake-enhanced polarization properties of the membrane and thus influence the removal efficiencies of toxic contaminants. However, changes in the membrane charge surface were unrelated to the rejection capacity of this current research because the compounds were neutral for pH between 5.5 and 8.5.

The highest retention of the toxic contaminants by the fouled membrane at pH 8.5 was thus possibly due to: (i) the maximum SS accumulation on the membrane surface which may induce a higher adsorption capacity and thereby reduce the micro-pollutants' mass transport through the membrane; (ii) an abundance of humic and inorganic substances in the foulants at pH 8.5, which could act as a glue to form a denser cake layer, resulting in an increase in the pore-blocked area; and (iii) the highest hydrophobicity produced by an abundance of hydrophobic components on the membrane surface that allows a higher amount of the hydrophobic micro-pollutant compounds to be adsorbed by the foulant layer, resulting in less diffusion across the membrane (Hajibabania *et al.* 2011). The fouling-induced changes in the membrane surface properties, including the SS mass accumulation, pore-blocked area and hydrophobic solutes–membrane interactions at the various mixed liquor pH levels, could probably act as an additional micro-pollutant removal mechanism.

### CONCLUSION

This research has discovered that the variations in mixed liquor pH greatly influenced the membrane fouling behaviors in the MBR tanks for landfill leachate treatment. In addition, the pH levels of 6.5 and 7.5 were the optimum pH levels for the MBR operation with regard to the mitigation of membrane fouling. The removals of micro-pollutants

(i.e. BPA, BHT, and 2,6-DTBP) through adsorption and biodegradation were subject to the properties of the compounds but independent of the pH levels of mixed liquor. The micro-pollutant retention efficiencies of the foulant layer were relatively different between pH levels and were correlated to the pH levels of mixed liquor. The retention capacity could also be attributed to the changes in the membrane foulant characteristics as a result of the pH variations.

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## REFERENCES

- Ahmed, F. N. & Lan, C. Q. 2012 [Treatment of landfill leachate using membrane bioreactor: a review](#). *Desalination* **287**, 41–54.
- APHA 2005 *Standard Methods for the Examination of Water and Wastewater*. 21st edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA.
- Baily, J. E. & Ollis, D. F. 1986 *Biochemical Engineering Fundamentals*. 2nd edn, McGraw-Hill, New York.
- Boonnorat, J., Chiemchaisri, C., Chiemchaisri, W. & Yamamoto, K. 2014 [Microbial adaptation to biodegrade toxic organic micro-pollutants in membrane bioreactor using different sludge sources](#). *Bioresource Technology* **165**, 50–59.
- Boonyaroj, V., Chiemchaisri, C., Chiemchaisri, W. & Yamamoto, K. 2012 [Removal of organic micro-pollutants from solid waste landfill leachate in membrane bioreactor operated without excess sludge discharge](#). *Water Science and Technology* **66** (8), 1774–1780.
- Chiemchaisri, C., Chiemchaisri, W., Nindee, P., Chang, C. Y. & Yamamoto, K. 2011 [Treatment performance and microbial characteristics in two-stage membrane bioreactor applied to partially stabilized leachate](#). *Water Science and Technology* **64** (5), 1064–1072.
- Hajibabania, S., Verliefe, A., Drewes, J. E., Nghiem, L. D., McDonald, J., Khan, S. & Le-Clech, P. 2011 [Effect of fouling on removal of trace organic compounds by nanofiltration](#). *Drinking Water Engineering and Science* **4**, 71–82.
- Huo, S. L., Xi, B. D., Yu, H. C. & Liu, H. L. 2009 [Dissolved organic matter in leachate from different treatment processes](#). *Water and Environment Journal* **23**, 15–22.
- Gao, W. J., Lin, H. J., Leung, K. T. & Liao, B. Q. 2010 [Influence of elevated pH shocks on the performance of a submerged anaerobic membrane bioreactor](#). *Process Biochemistry* **45**, 1279–1287.
- Le-Clech, P., Chen, V. & Fane, A. G. 2006 [Fouling in membrane bioreactors used in wastewater treatment](#). *Journal of Membrane Science* **284**, 17–53.
- Lu, F., Chang, C. H., Lee, D. J., He, P. J., Shoa, L. M. & Su, A. 2009 [Dissolved organic matter with multi-peak fluorophores in landfill leachate](#). *Chemosphere* **74**, 575–582.
- Meng, F., Chae, S. R., Drewes, A., Kraume, M., Shin, H. S. & Yang, F. 2009 [Recent advances in membrane bioreactors \(MBRs\): Membrane fouling and membrane material](#). *Water Research* **43**, 1489–1512.
- Nghiem, L. D. & Hawkes, S. 2007 [Effect of membrane fouling on the nanofiltration of pharmaceutically active compounds \(PhACs\): mechanisms and role of membrane pore size](#). *Separation and Purification Technology* **57**, 182–190.
- Sanguanpak, S., Chiemchaisri, C., Chiemchaisri, W. & Yamamoto, K. 2013 [Removal and transformation of dissolved organic matter \(DOM\) during the treatment of partially stabilized leachate in membrane bioreactor](#). *Water Science and Technology* **68** (5), 1091–1099.
- Sipma, J., Osuna, B., Collada, N., Monclus, H., Ferrero, G., Comas, J. & Roda, I. R. 2010 [Comparison of removal of pharmaceuticals in MBR and activated sludge system](#). *Desalination* **250**, 653–659.
- Tadkaew, N., Sivakumar, M., Khan, S. J., McDonald, J. A. & Nghiem, L. D. 2010 [Effect of mixed liquor pH on the removal of trace organic contaminants in a membrane bioreactor](#). *Bioresource Technology* **101**, 1494–1500.
- Tadkaew, N., Faisal, I. H., McDonald, J. A., Khan, S. J. & Nghiem, L. D. 2011 [Removal of trace organics by MBR treatment: the role of molecular properties](#). *Water Research* **45**, 2439–2451.
- Urase, T., Kagawa, C. & Kikata, T. 2005 [Factors affecting removal of pharmaceutical substances and estrogens in membrane bioreactors separation bioreactors](#). *Desalination* **178**, 107–113.
- Wu, J., Zhuang, Y., Li, H. & Huang, X. 2010 [pH adjusting to reduce fouling propensity of activated sludge mixed liquor in membrane bioreactor](#). *Separation Science and Technology* **45**, 890–895.
- Zhang, Y., Zhang, M., Wang, F., Hong, H., Wang, A., Wang, J., Weng, X. & Lin, H. 2014 [Membrane fouling in a submerged membrane bioreactor: effect of pH and its implications](#). *Bioresource Technology* **152**, 7–14.

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