

# Comparison of reverse osmosis membrane fouling characteristics in full-scale leachate treatment systems with chemical coagulation and microfiltration pre-treatments

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## ABSTRACT

Fouling characteristics of reverse osmosis (RO) membrane with chemical coagulation and microfiltration (MF) pre-treatment were investigated at full-scale leachate treatment systems. In chemical coagulation pre-treatment, solid separation from stabilized leachate was performed by ferric chloride coagulation followed by sand filtration. Meanwhile, MF pre-treatment and the RO system utilized direct filtration using a 0.03 µm membrane without chemical addition. MF pre-treatment yielded better pollutant removals in terms of organics and nitrogen. The study on effect of pre-treatment on RO membrane fouling revealed that accumulated foulant on the RO membrane in MF pre-treatment was significantly lower than that of chemical coagulation. Nevertheless, NaOH cleaning of the fouled RO membrane after chemical coagulation pre-treatment could better recover its permeate flux, thus suggesting that the formation of a loose-structure cake layer by chemical coagulation pre-treatment could allow effective penetration of chemical cleaning and detachment of foulant layer from the membrane surface.

**Key words** | chemical cleaning, fouling characteristics, leachate treatment, RO pre-treatment

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## INTRODUCTION

In developing countries, low-cost treatments such as stabilization ponds are usually applied to the treatment of leachate from municipal solid waste disposal sites. In most cases, the treatment efficiencies were not sufficient as the natural treatment system cannot produce treated water that meets stringent effluent standards (Abbas *et al.* 2009). This was mainly due to ineffective treatment capacity of stabilized leachate, which contains recalcitrant compounds and toxic contaminants such as heavy metals and ammonia (Cho *et al.* 2009; Renou *et al.* 2008). Therefore, advanced treatment of this complex wastewater is considered necessary in order to purify this wastewater until it does not create negative impact on the natural environment.

The reverse osmosis (RO) membrane has been applied for leachate treatment in some developed countries when the compliance with strict discharge regulations is required. In general, the RO system yields high pollutant retention efficiency (Linde *et al.* 1995; Ushikoshi *et al.* 2002); however, the high osmotic pressure and fouling of the RO membrane

were major drawbacks, yielding flux decline and increased applied pressure. High organic content presented in municipal solid waste leachate both in dissolved and particulate forms would easily lead to severe fouling of RO membranes. A pre-treatment to the RO membranes is considered necessary to reduce the membrane fouling and to increase the membrane lifetime. Nevertheless, there is no individual physico-chemical treatment technique which is universally applicable to leachate treatment. Among the treatment techniques, adsorption and chemical precipitation are mostly frequently used (Kurniawan *et al.* 2006).

In our previous investigation, a full-scale advanced leachate treatment system using chemical coagulation as pre-treatment to the RO membrane could be successfully operated at a solid waste disposal site in Thailand (Rukapan *et al.* 2012). Nevertheless, frequent routine membrane cleaning was required to mitigate particulate fouling on the RO membrane surface. As a part of an improvement project at the site, a new microfiltration (MF) membrane unit has been

installed as pre-treatment in a separate pre-treatment stream in order to minimize particulate fouling on the RO membrane and reduce chemical cost of the operation. It was anticipated that the application of direct filtration instead of chemical coagulation would yield different fouling characteristics on the downstream RO membrane unit. Thus, a comparative study of fouling on an RO membrane when applied to the treatment of the effluent from chemical coagulation and MF pre-treatment systems was carried out in this study.

## MATERIALS AND METHODS

### Full-scale advanced leachate treatment plant

The schematic of the chemical-coagulation–RO system with a treatment capacity of 1,000 m<sup>3</sup>/d is shown in Figure 1(a).

The system consists of an open-jet clarifier, pressure sand filter, and an RO filtration unit. In the open-jet clarifier, ferric chloride was added into the raw leachate at the pre-determined optimum dose of 2.0–2.5 g/l, after which suspended solids were removed by the pressure sand filter. Prior to the RO filtration, a cartridge filter (5 µm) was used to polish the remaining suspended solids. In the RO unit, LFC3-LD spiral-wound modules (Nitto Denko Corp.) were contained in seven pressure vessels, each of which has six RO membrane modules. The recovery rate and operating pressure were maintained between 20% and 50% and 1.5 and 2.5 MPa, respectively. Anti-scalant and biocide were dosed into the feed stream at 3–5 and 1–2 mg/l, respectively.

The MF pre-treatment and RO system (Figure 1(b)) has a treatment capacity of 500 m<sup>3</sup>/d. The system consists of 15 units of capillary tube polyvinylidene fluoride (PVDF) MF membrane (0.03 µm, Norit X Flow) operated with a feed

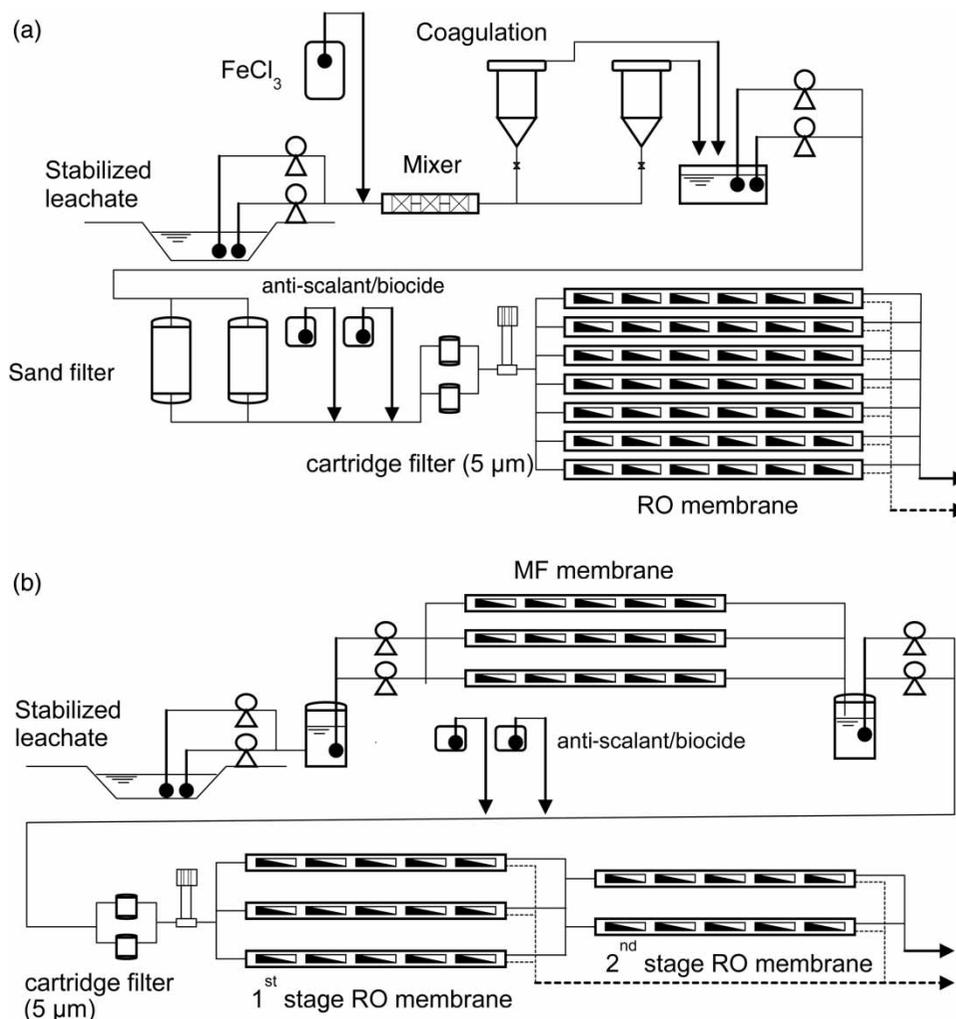


Figure 1 | Schematic of advanced leachate treatment systems with (a) chemical coagulation pre-treatment and (b) MF pre-treatment.

flow rate of 80–90 m<sup>3</sup>/h and applied pressure of 0.1–0.18 MPa followed by 25 RO membrane modules (Filmtech NF270-400, Dow Chemical) operated with recovery rate and operating pressure of 30–50% and 0.5–2.1 MPa, respectively. The RO unit was designed having three pressure vessels in the first stage followed by two vessels in the second stage connected in series. Each vessel contains five RO membrane modules. Anti-scalant and biocide were dosed into the feed stream at 3–5 and 1–2 mg/l, respectively.

Figure 2 shows variation of feed and permeate flow together with osmotic and transmembrane pressure of RO membranes along the treatment train in both systems. Total recovery rate of the RO membrane was set at 50%. In chemical coagulation pre-treatment, feed flow varied from 5.5 m<sup>3</sup>/h in the first module to 3.5 m<sup>3</sup>/h in the sixth module of the same RO vessel. The transmembrane pressure was determined from the difference between applied pressure and osmotic pressure, and it decreased from 1,084 kPa in the first module to 214 kPa in the sixth module. In the MF pre-treatment system, feed flow rate and transmembrane pressure varied from 6.9 m<sup>3</sup>/h and

1,303 kPa in the first module to 3.68 m<sup>3</sup>/h and 216 kPa in the fifth module of the first stage, and from 5.4 m<sup>3</sup>/h and 134 kPa in the first module to 5.22 m<sup>3</sup>/h and 4 kPa in the fifth module of the second stage, respectively.

## RO membrane fouling study

The performance of both systems was monitored regularly over 7 months of continuous operation. The monitoring parameters included pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), suspended solids (SS), and total dissolved solids (TDS) according to *Standard Methods for the Examination of Water and Wastewater* (APHA 1998). Moreover, particle size distributions in feed water to the RO unit (from both pre-treatment units) were also analyzed using a particle analyzer (Hydro 2000 MU, Malvern Instruments) to determine the potential for fouling from particulate matter on the RO membrane surface. The study of RO membrane fouling was performed when the system was temporarily stopped for routine chemical cleaning in place (CIP) of RO membrane.

A cross-flow membrane filtration set used for this test is shown in Figure 3. In the RO membrane fouling study, the used membrane was taken off the filtration vessels of the full-scale systems (the first and the sixth modules in the same vessel after chemical coagulation pre-treatment and the first module of the first and second stages after MF pre-treatment) and subjected to sequential cleaning procedures using pure water, alkali, and acid solutions to determine the type of foulant deposited on the membrane surface and to evaluate the effectiveness of each chemical cleaning stage (Table 1). The RO membrane was unfolded and cut into a flat sheet with an area of 12.68 cm<sup>2</sup>. The operating pressure and feed flow rate were adjusted using a bypass valve in order to simulate the operating conditions in the spiral-wound module. Firstly, the pure water flux of the fouled membrane was examined to determine the total

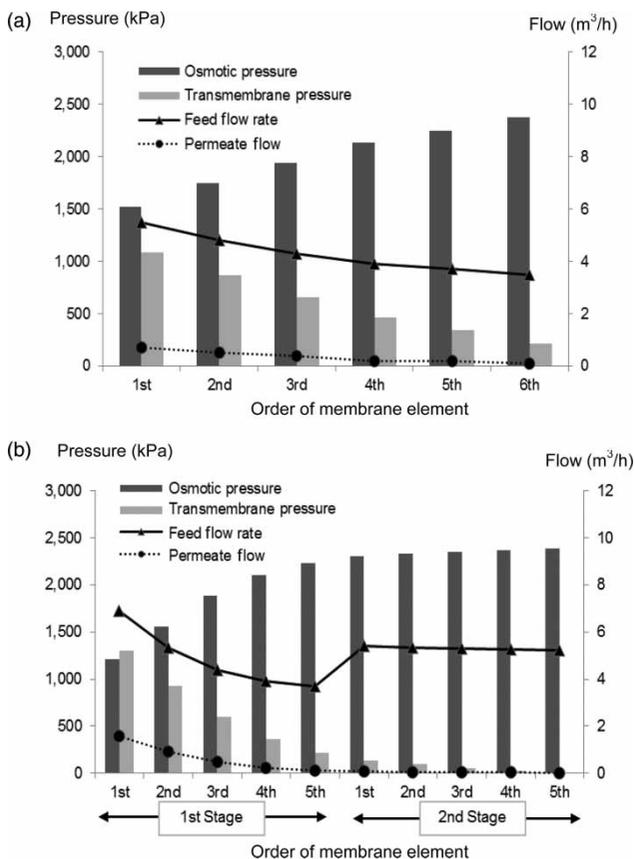


Figure 2 | Variation of flow and pressure of RO membrane modules along the treatment train in (a) chemical coagulation and (b) MF pre-treatment systems.

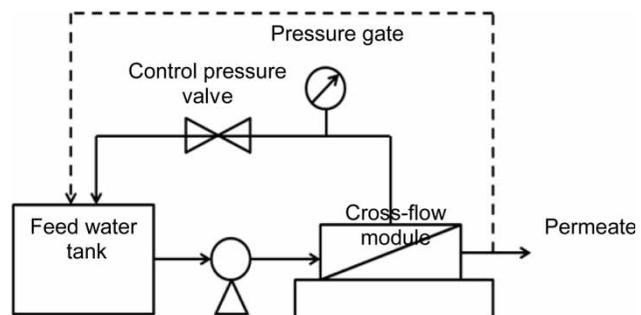


Figure 3 | Schematic diagram of the cross-flow membrane test cell.

resistance of the fouled membrane. The membrane module was then subjected to a cleaning test using pure water at cross-flow velocity of 0.05 m/s (normal cross-flow operation) and 0.15 m/s (high cross-flow operation) followed by NaOH cleaning at 0.15 m/s and HCl cleaning at 0.15 m/s, consecutively. This chemical cleaning sequence was found the most effective for the removal of filtration resistances in our trial test especially when compared to HCl followed by NaOH cleaning. After each cleaning step, the pure water flux of the cleaned RO membrane modules was determined. The resistance of the RO membrane was determined using the resistance in a series model as follows:

$$J = \frac{\Delta P - \Delta \pi}{\eta(R_m + R_f)} \quad (1)$$

where  $J$  = permeate flux;  $\Delta P$  = pressure difference between feed and permeate side;  $\Delta \pi$  = osmotic pressure difference between feed and permeate side;  $\eta$  = viscosity of water/

solution;  $R_m$ ,  $R_f$  = resistances of membrane and foulants, respectively.

## RESULTS AND DISCUSSION

### Pollutant removals during pre-treatment and RO filtration

Table 2 shows the characteristics of the leachate and treated water from both leachate pre-treatment systems. BOD and COD removals in chemical coagulation pre-treatment unit were about 70% and 30% whereas they were 88% and 20% in the case of MF pre-treatment, respectively. The difference in organic removal efficiencies was possibly related to the association of organic compounds with small colloidal particles as the particle size cuts off in the chemical coagulation unit, and the sand filter after the chemical coagulation unit is different from the MF pre-treatment system (0.03  $\mu\text{m}$ ). A previous study has demonstrated that little organic matter was present in the particulate fraction of larger size than 0.45  $\mu\text{m}$  (Jensen *et al.* 1999). The size fractionation of organic matter in truly dissolved form also varied with the age of landfill (Li *et al.* 2009). Sequential ultrafiltration experiments conducted by Insel *et al.* (2013) revealed that most of the organics were below 2 nm filter mesh size. Another possibility is the effect of enhanced coagulation, which helped remove large organic macromolecules from water, yielding higher COD removal efficiency in the chemical pre-treatment case (Singh *et al.* 2012). Nevertheless, the addition of coagulant increased TDS in water after this pre-treatment step. When the pre-treated water

**Table 1** | Procedures for determination of foulant type

No.	Condition	Target foulant
1	Cleaning with pure water at cross-flow velocity (CFV) of 0.05 m/s	Total resistance of attached foulants on membrane surface
2	Cleaning with pure water at CFV of 0.15 m/s	Particulate fouling
3	Cleaning with NaOH at CFV 0.15 m/s	Organic fouling
4	Cleaning with HCl at CFV at 0.15 m/s	Inorganic fouling

**Table 2** | Qualities of feed and treated water from both treatment systems

Parameter (unit)	Sampling along the treatment system					
	Raw leachate	After chemical pre-treatment <sup>a</sup>	After MF pre-treatment	RO permeate after chemical pre-treatment	RO permeate after MF pre-treatment	Effluent standard <sup>b</sup>
pH (–)	8.9 ± 0.1	7.1 ± 0.5	8.7 ± 1	7.9 ± 0.10	8.8 ± 0.02	5.5–9.0
BOD (mg/l)	400 ± 99	120 ± 112	47 ± 23	1.6 ± 2.0	2 ± 0.3	20
COD (mg/l)	3,441 ± 500	2,424 ± 123	2,736 ± 277	50 ± 20	27 ± 11	120
TKN (mg/l)	269 ± 107	36 ± 13	32 ± 2.7	4.3 ± 1.2	3.2 ± 2.8	100
SS (mg/l)	570 ± 167	ND	ND	ND	ND	–
TDS (mg/l)	20,191 ± 2,242	21,653 ± 2,365	19,276 ± 1,496	736 ± 102	1,197 ± 247	3,000

ND: not detected, the numbers show average ± standard deviation values.

<sup>a</sup>Samples were collected after 5  $\mu\text{m}$  cartridge filter.

<sup>b</sup>Industrial effluent standard of Thailand.

Sampling and analysis were performed once a month over a 7-month period.

was subsequently filtered in the RO unit, good qualities of treated water that satisfied effluent discharge standards could be achieved. Comparing both pre-treatment methods, MF pre-treatment yielded better effluent qualities in terms of COD and TKN. Nevertheless, chemical pre-treatment provided RO permeate with lower TDS than MF pre-treatment. Nystrom *et al.* (1995) found that humic acid retention by the membrane decreases when filtered together with FeCl<sub>3</sub>. Meanwhile, Trebouet *et al.* (2001) reported that Fe<sup>3+</sup> ions contribute to change the characteristics of organic matter and surface charges of the membrane but do not enhance the retention and permeate flux of the membrane. It was found that the chemical pre-treatment yielded higher deposition of solid particles and the formation of a cake layer on the RO membrane surface. The improvement of TDS rejection of the RO membrane after chemical pre-treatment could be due to higher adsorption of dissolved solids onto solid particles during filtration through the cake layer on the RO membrane surface.

### Operating condition and fouling of RO membrane

The operating conditions of RO membranes located at the upstream and downstream ends of the chemical and MF pre-treated leachate treatment systems are shown in Table 3. While the feed flow to RO membrane modules was decreasing from 5.5 m<sup>3</sup>/h at the first element to 3.5 m<sup>3</sup>/h at the sixth element in the same RO vessel of the chemical pre-treated RO leachate treatment system, recovery of RO permeate was reduced from 12.7 to 2.9%. Meanwhile, recovery percentages were reduced from 14.5% at stage 1 to 3.4% at stage 2 of the MF pre-treated system. This reduction in recovery percentages was mainly due to the decrease in transmembrane pressure of the RO membrane during the operation. Whereas applied pressure to the inlet of the RO pressure vessel was kept constant, the driving force through the membrane was determined from the difference between applied pressure and osmotic pressure ( $\Delta P - \Delta \pi$ ). The osmotic pressure of chemical pre-treated water was higher than that of MF pre-treated water due to the increase in TDS

from coagulant addition. Nevertheless, the chemical pre-treatment system was operated at higher net driving pressure than the MF pre-treated system by about 80%. Comparing both pre-treatment cases, specific fluxes of MF pre-treatment were found to be about 2.6–3.6 times those of the chemical pre-treatment. Low specific flux of the RO membrane receiving chemical pre-treated water was due to formation of a dense foulant layer having higher filtration resistance on the RO membrane surface. The foulant was found largely deposited on the upstream (first element) rather than the downstream end. In the case of MF pre-treatment, specific flux of the RO membrane was kept relatively constant even though filtration resistance was found higher in the latter stage of the RO element train. This was due to the second stage RO that received the concentrated water from the first stage RO.

The main factor governing filtration resistances of the RO membrane was the cake layer formed after deposition of solid particles. Applying different pre-treatment methods led to the different particle size and TDS available in the RO feed water and the mass deposited on the membrane surface. As suggested in Figure 4, the particle size contained in feed water after chemical pre-treatment largely ranged between 1 and 100  $\mu\text{m}$  whereas it was 0.01–0.04  $\mu\text{m}$  after MF pre-treatment. Higher filtration resistances in the case of chemical coagulation resulted from higher mass deposited on the membrane surface even though the particle sizes of deposited solids were larger than for the MF pre-treatment case. Park *et al.* (2008) demonstrated that increase of particle size in feed water led to a decrease of RO flux decline. It was also found that most of the flocculated particles formed after chemical pre-treatment were identified as organic–iron complex substances, which subsequently deposit onto the RO membrane surface (Rukapan *et al.* 2012).

### Foulant characteristics and cleaning efficiencies of RO membrane

The fouling characteristic on the RO membrane surface was studied using scanning electron microscopy (SEM) and

Table 3 | Operating condition of RO within the treatment systems

Location		Permeate flux ( <i>J</i> ) m <sup>3</sup> /h	Transmembrane pressure ( $\Delta P$ ) kPa	$J/\Delta P$ m/(d × kPa) × 10 <sup>4</sup>	Foulant resistance ( <i>R</i> ) 10 <sup>10</sup> m <sup>-1</sup>
Chemical pre-treatment	1st element	0.45	1,084	0.42	137
	6th element	0.06	214	0.30	58
MF pre-treatment	1st element of stage 1	0.65	590	1.10	30
	1st element of stage 2	0.13	120	1.08	45

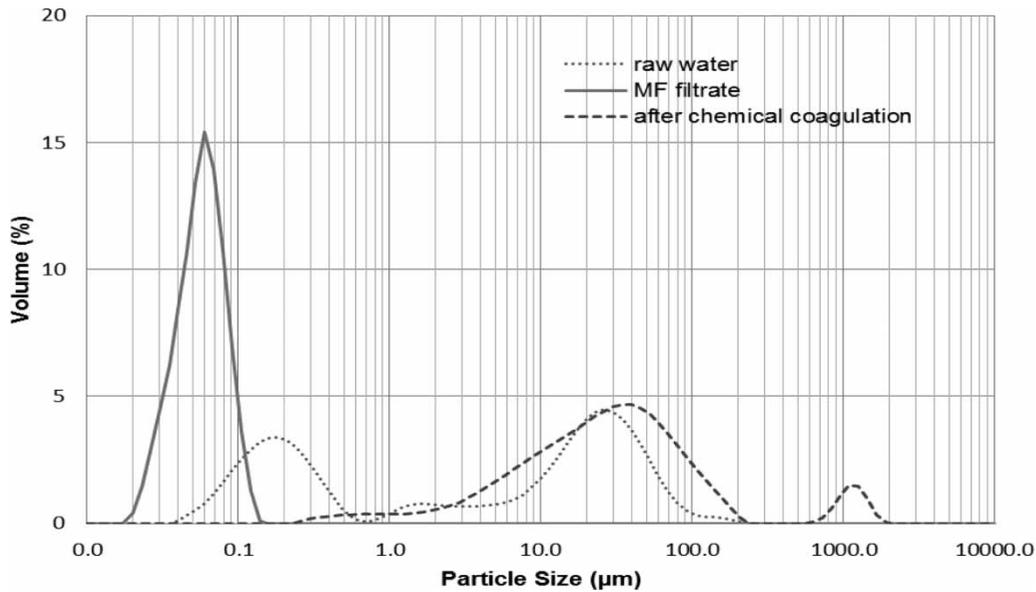


Figure 4 | Distribution of particle size in feed water to the RO membrane.

energy dispersive X-ray spectroscopy for elemental analyses. Figure 5 shows the SEM images and predominant element found on the RO membrane surface. For the chemical pre-treatment case, the presence of Fe and Mg on the surface along with other compounds such as Mn, Al, Zn, Sr, Ba, Si, and Ca was revealed. Meanwhile, the formation of a cake layer, in which deposited particle size of 0.45–0.70 µm was

estimated from the SEM images, was found. For MF pre-treatment, the deposition of inorganic foulant was not significant. Deposition of a thin biofilm foulant later was observed.

Table 4 presents the filtration resistance of fouled and cleaned membrane during sequential chemical cleaning. The fouled RO membrane from the chemical pre-treatment system had higher filtration resistance when compared

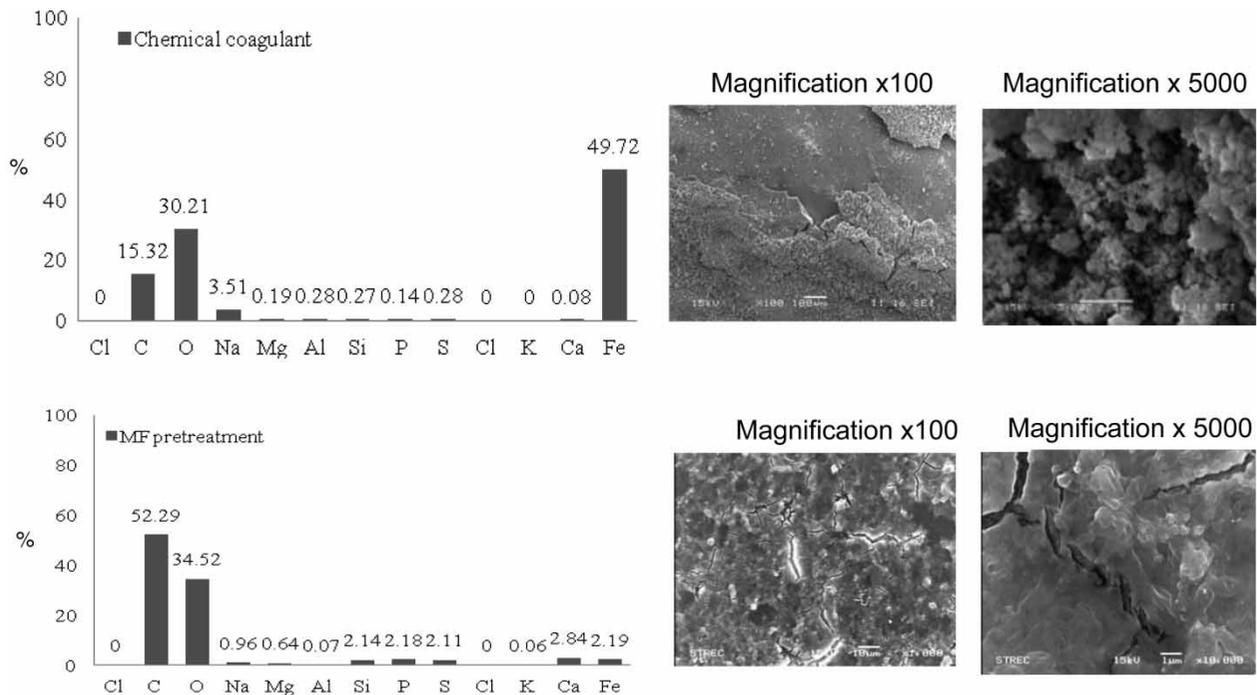


Figure 5 | SEM images and extracted elements from foulants on the RO membranes.

**Table 4** | Filtration resistance ( $10^{10} \text{ m}^{-1}$ ) of fouled and cleaned membrane

Membrane sample	Chemical coagulation pre-treatment				MF pre-treatment			
	1st element		6th element		1st element of the 1st stage		1st element of the 2nd stage	
	Avg	SD	Avg	SD	Avg	SD	Avg	SD
Fouled membrane	137	73	58	32	30	12	45	21
After water cleaning	108	69	50	24	17	8	20	12
After NaOH cleaning	1.3	0.2	8.3	0.4	15	5	18	8
After HCl cleaning	1.1	0.1	1.7	0.8	12	4	16	5

with that from the MF pre-treatment system. During high cross-flow water cleaning to remove deposited particulate matter, the filtration resistances could be reduced by only 14–20% for the chemical pre-treatment case, but they were up to 44–55% for MF pre-treatment. These results suggested that some of the biofilm layer, which was loosely attached on the RO membrane surface, could be easily removed by water shear force in the case of MF pre-treatment. Meanwhile, a bonded cake layer consisting of complex organic-iron substances formed on the RO membrane in the case of chemical pre-treatment. After subsequent NaOH cleaning, the majority of remaining foulant on the RO membrane in the case of chemical pre-treatment was removed. The remaining filtration resistance became even lower than those in the MF pre-treatment case. These results suggest that NaOH cleaning helped detach most of the organic-constituted cake layer from the RO membrane surface, and there was only little foulant remaining after this chemical cleaning step. It is anticipated that the filtration of chemical coagulated water containing larger particle sizes could lead to the formation of a loose-structure cake layer on the membrane surface, thus allowing effective penetration of cleaning (NaOH) agent for detachment of organic foulant from the membrane surface. Meanwhile, the removal of a thin 'gel-like' layer in the MF pre-treatment was not so effective, as the penetration of chemical cleaning agent into the layer is limited due to its small pores. The subsequent acid (HCl) cleaning step reduces the filtration resistance further, but its effect was significant only for the downstream RO unit (sixth element) of the chemical pre-treatment.

Overall, chemical cleaning recovered 99% and 97% of the original flux for the first and sixth RO element in the chemical pre-treatment system, respectively. However, the

flux was only at 60% and 64% for the first and second stage of MF pre-treatment, respectively. The results indicated that irreversible fouling of the membranes increased based on the development of small (submicron) particle fouling in relation to the feed concentration above the membrane surface.

## CONCLUSION

The effect of chemical coagulation and MF pre-treatment on RO membrane fouling characteristics applied to stabilized leachate treatment was analyzed. Pollutant removal efficiencies were higher in MF pre-treatment yielding better water qualities in terms of COD and TKN. Accumulation of foulant in MF pre-treatment was significantly lower than that of chemical coagulation. A thin biofilm foulant layer on the RO membrane surface receiving feed water after MF pre-treatment was observed in contrast to a complex organic-iron cake layer formed in the case of chemical pre-treatment. Sequential chemical cleaning of the fouled RO membrane from the chemical coagulation pre-treatment case was more effective as NaOH solution could penetrate through the cake layer and help detach the foulant from the membrane surface better than it could the 'gel-like' layer in the MF pre-treatment case.

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