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Membrane cleaning in membrane distillation of reverse osmosis concentrate generated in landfill leachate treatment

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ABSTRACT

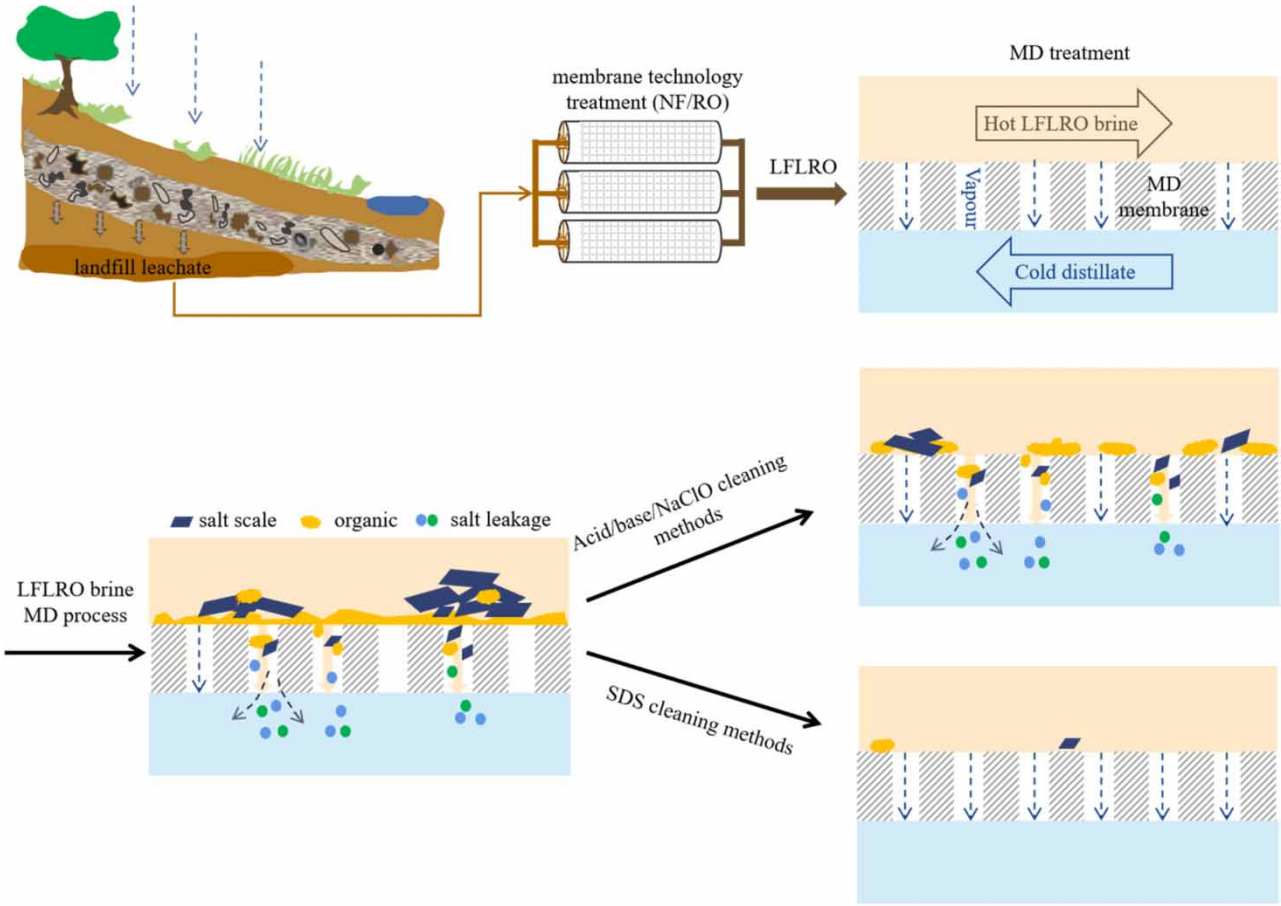
As a thermally induced membrane separation process, membrane distillation (MD) has drawn more and more attention to the advantages of treating hypersaline wastewaters, especially the concentrate from the reverse osmosis (RO) process. One of the major obstacles in widespread MD application is the membrane fouling. We investigated the feasibility of direct contact membrane distillation (DCMD) for landfill leachate reverse osmosis concentrate (LFLRO) brine treatment and systematically assessed the efficiency of chemical cleaning for DCMD after processing LFLRO brine. The results showed that 80% water recovery rate was achieved when processing the LFLRO brine by DCMD, but membrane fouling occurred during the DCMD process, and manifested as the decreasing of permeate flux and the increasing of permeate conductivity. Analysis revealed that the serious flux reduction was primarily caused by the fouling layer, which consisted of organic matter and inorganic salts. Five cleaning methods were investigated for membrane cleaning, including hydrogen chloride (HCl)-sodium hydroxide (NaOH), ethylene diamine tetraacetic acid (EDTA)-NaOH, citric acid, sodium hypochlorite (NaClO) and sodium dodecyl sulphate (SDS) cleaning. Among the chemical cleaning methods investigated, the 3 wt.% SDS cleaning showed the best efficiency at recovering the performance of fouled membranes.

Key words: concentrated brine, landfill leachate, membrane cleaning, membrane distillation, membrane fouling

HIGHLIGHTS

- The performance of LFLRO treatment using MD process was evaluated.
- The membrane fouling was primarily caused by a mixture of salts and organic matters.
- Removal of pollutants inside membrane pores was key to avoiding membrane wetting.
- The SDS solution cleaning was most effective in recovering membrane performance.

GRAPHICAL ABSTRACT



ABBREVIATIONS

DCMD	direct contact membrane distillation
EDS	energy dispersive spectroscopy
FO	forward osmosis
ICP-AES	inductively coupled plasma-atomic emission spectrometry
LFLRO	landfill leachate reverse osmosis
MD	membrane distillation
MSW	municipal solid waste
MVR	mechanical vapor recompression
NF	nanofiltration
PVDF	polyvinylidene fluoride
RO	reverse osmosis
SDS	sodium dodecyl sulphate
SEM	scanning electron microscope
TDS	total dissolved solids
UPVC	unplasticized polyvinyl chloride

1. INTRODUCTION

Sanitary landfill is one of the most common methods for the ultimate disposal of municipal solid wastes (MSW) nowadays due to its economic advantages, and the MSW generation is increasing due to the growing population and industrialization processes. Thus, the leachate released from sanitary landfills has also increased and become the subject of interest as highly

contaminated wastewater. Landfill leachate is defined as a mixture of rainwater percolation through wastes, water produced from wastes by a series of physical, hydrolytic and fermentative degradation, and the inherent water content of wastes (Renou *et al.* 2008). Landfill leachate contains a high concentration of organic and inorganic contaminants, including humic acid, ammonia nitrogen, heavy metals, and inorganic salts. With the increasingly strict discharge standard for landfill leachate, the treatments based on membrane technology become the feasible alternative to the conventional physico-chemical methods of landfill leachate treatment (Li *et al.* 2010). Reverse osmosis (RO) has been used more and more in recent years due to its great advantages in inorganic salts rejection and water recovery (Ince *et al.* 2010; Kuusik *et al.* 2014; Rukapan *et al.* 2015).

During the RO process, a kind of brown solution will be produced continuously – the landfill leachate reverse osmosis concentrate (LFLRO) brine, which represents typically 13–30% of total landfill leachate entering the treatment system and contains a high concentration of refractory organic and inorganic salt contaminants (Van der Bruggen *et al.* 2003). Discharge of LFLRO brine without effective treatment would cause substantial environmental pollution. Currently, common treatment methods for LFLRO brine include further treatment to remove contaminants (Labiadh *et al.* 2006; Wang *et al.* 2016; Fernandes *et al.* 2017; Mojiri *et al.* 2017; Chen *et al.* 2019), thermal incineration or drying (Ye *et al.* 2017; Bai *et al.* 2021) and re-infiltration into the landfills (Calabro *et al.* 2010). However, there are many limitations and disadvantages to these methods. For example, recycling back to landfills will increase leachate salinity and cause negative effects on the leachate treatment system. During mechanical vapor recompression (MVR), the high salinity may lead to severe scaling of treatment facilities and reduce the heat transfer efficiency.

Membrane distillation (MD) is an emerging technology that combines thermally driven distillation and membrane separation and has shown great promise in the treatment of hypersaline solutions. The MD process may be used as a substitute for conventional separation processes such as multistage vacuum evaporation, RO, and distillation (Lawson & Lloyd 1997). Compared to MVR and incineration, MD process requires lower operating temperature, vapor space and energy consumption (Alkhudhiri *et al.* 2012). Besides, unlike RO, MD is hardly affected by osmotic pressure, thus it can further recover pure water from RO brine. Other advantages of MD include potential for 100% rejection of nonvolatile solutes and compact configuration (Ding *et al.* 2006a, 2006b; Khayet 2011; Chung & Wang 2015). In recent years, there have been extensive studies on the application of MD in water desalination and treatment (Gryta 2005, 2015; Martinetti *et al.* 2009; Hickenbottom & Cath 2014; Chew *et al.* 2019). Thus, MD might be an effective method for the further treatment of LFLRO brine. However, membrane fouling and membrane wetting are the major technical challenges, which can cause several negative consequences on MD performance, including flux reduction and salt leakage (Zou *et al.* 2018; Chang *et al.* 2021).

To achieve long stable operation of the MD process in LFLRO brine treatment, effective membrane cleaning methods will be necessary. The potential pollutants in LFLRO brine that may cause membrane fouling include inorganic and organic matters. For inorganic pollutants, acids such as hydrogen chloride (HCl), oxalic acid and citric acid have been proven to achieve effective removing (Gryta 2008). Elena *et al.* reported that the mixed cleaning solution composed of 0.1 wt.% oxalic acid and 0.8 wt.% citric acid can remove the sodium chloride (NaCl) scale layer that covered the fouled membranes (Guillen-Burrieza *et al.* 2014). Besides, ethylene diamine tetraacetic acid (EDTA) forms a strong complex with Ca^{2+}, thus can be used to remove Ca^{2+} precipitation on the membrane. Peng *et al.* used five cleaning agents to washing calcium sulfate ($CaSO_4$) deposits on the fouled membrane and found that the flux recovery rate after cleaning followed an order of ethylene diamine tetraacetic acid tetrasodium (EDTA-4Na) > NaCl > citric acid > NaOH > KCOOH (Peng *et al.* 2015). The pollutants in LFLRO brine are more complicated than pure inorganic salts (Van der Bruggen *et al.* 2003), especially the organic pollutants that may cause serious membrane fouling in the MD process. Thus, it is necessary to consider the removal of organic pollutants.

For organic pollutants, sodium hypochlorite (NaClO) has been proved to be an effective cleaning solution (Paugam *et al.* 2010; Porcelli & Judd 2010; Lee *et al.* 2013). Due to its oxidizability, NaClO can react with the foulants on the membrane surface (Cai & Liu 2016). Besides, Wang *et al.* found that large organic colloids can be disintegrated into fine particles and/or soluble organic matters at caustic conditions (Wang *et al.* 2014). More important, Ca^{2+} can greatly enhance organic matter fouling by complexation and subsequent formation of intermolecular bridges among organic foulant molecules (Li & Elimelech 2004; Srisurichan *et al.* 2005), thus, breaking the Ca^{2+}-organic complexation is also important for the removal of organic pollutants (Li & Elimelech 2004). Study showed that sodium dodecyl sulphate (SDS) and ethylene diamine tetraacetic acid (EDTA) were effective in disrupting the complexes formed by the organic foulants with Ca^{2+} when cleaning organic fouled membranes, including RO, nanofiltration (NF) and forward osmosis (FO) membranes (Li & Elimelech 2004; Ang *et al.* 2006, 2011; Beyer *et al.* 2010; Wang *et al.* 2015).

Given the absence of cleaning methods for direct contact membrane distillation (DCMD) treatment of LFLRO brine. The objective of this study was to investigate the feasibility of DCMD for LFLRO brine treatment and evaluate the cleaning efficiency of different cleaning methods. First, during the DCMD treatment of LFLRO, the permeate flux and conductivity variations were studied. In addition, the membrane fouling was also investigated. For the membrane cleaning, five cleaning methods were evaluated and the effects of each membrane cleaning method on membrane performance were analyzed in detail.

2. MATERIALS AND METHODS

2.1. Water source

The municipal landfill considered in this study locates in the north of Beijing, China, which has been in operation since 1996. Leachate treatment process flow diagram for this plant is shown in Figure 1, the treatment system contains a biological treatment process and advanced membrane separation processes. In membrane separation processes, landfill leachate is pumped to the first stage RO membrane module units (RO1) after ultrafiltration. The RO1 permeate is fed to the second stage RO membrane module units (RO2) for purifying and the RO2 permeate is discharged to Wenyu River at last. Concentrate from the RO2 units is fed back to the RO1 units and mixed with landfill leachate as the feed solution of RO1, and the RO1 concentrate is sent to the concentrate tank for further treatment. The recovery rate of the RO1 units is 50–80%, which is adjusted in accordance with the total salinity of the inlet water. The RO2 units are operated under the recovery rate of 80–90%. The total recovery rate of the whole landfill leachate treatment system is in the range of 70% to 85%. The chemical physical characteristics of the RO concentrate are listed in Table 1.

2.2. Chemical cleaning solutions

HCl (pH = 2), NaOH (pH = 12), EDTA-Na (pH = 11.5), 2 wt.% citric acid, 2 wt.% NaClO and 3 wt.% SDS were used as membrane cleaning agents. All the chemicals were certified analytical reagent grade and supplied by Sinopharm Chemical Reagent Co., Ltd China. The chemical cleaning solutions were prepared by dissolving the chemical in deionized water without further purification.

2.3. Membrane and membrane module

The membrane fabricated from polyvinylidene fluoride (PVDF)/N, N-Dimethylacetamide/ lithium chloride (LiCl)/ethylene glycol (12/80/5/3 wt. %) dope via phase inversion process was chosen to fabricate membrane modules. The hydrophobic hollow fibers in the number of 50 pieces were assembled into a polyester tube (diameter $d_{in}/d_{out} = 15/20$ mm/mm) with two unplasticized polyvinyl chloride (UPVC) T-tubes and two ends of the bundle of fibers were sealed with solidified epoxy resin to compose a membrane module. The effective membrane length was 100 mm for each membrane module.

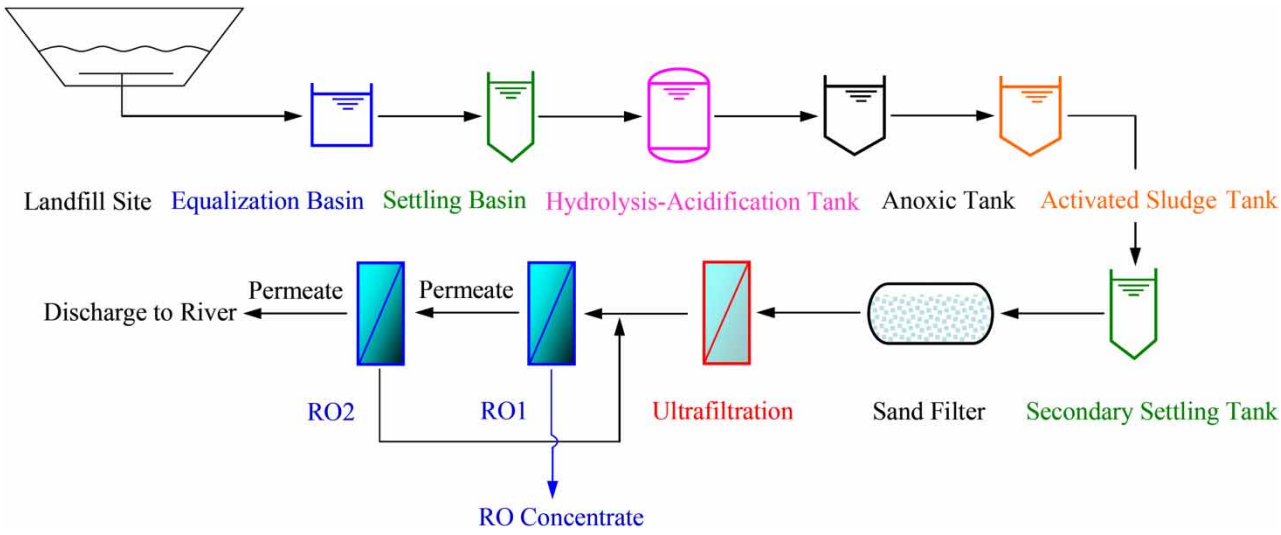


Figure 1 | Flow diagram of the landfill leachate treatment system.

Table 1 | Chemical characteristics of the LFLRO brine

Parameter	Average value	Parameter	Average value
pH	8.28	SiO_2 (dissolved, mg L^{-1})	111.83
K^+ (mg L^{-1})	437.20	Cl^- (mg L^{-1})	5,248.06
Ca^{2+} (mg L^{-1})	652.93	NO_3^--N (mg L^{-1})	399.50
Na^+ (mg L^{-1})	7,060.25	SO_4^{2-} (mg L^{-1})	515.65
Mg^{2+} (mg L^{-1})	1,734.60	HCO_3^- (mg L^{-1})	138.51
Al^{3+} (mg L^{-1})	42.23	NH_4^+-N (mg L^{-1})	404.83
Cu^{2+} (mg L^{-1})	4.20	Conductivity (mS cm^{-1})	33.46
Zn^{2+} (mg L^{-1})	22.81	TDS (mg L^{-1})	18,900.53
Mn^{2+} (mg L^{-1})	68.69	COD (mg L^{-1})	5,442.67

The effective membrane length and the total membrane area were 100 mm and 125.6 cm^2 for each membrane module, respectively. The characteristics of the membrane and membrane module are presented in Table 2.

2.4. Membrane distillation setup

The DCMD experimental setup is schematically shown in Figure 2. The feed wastewater heated by heater, which was stirred continually by a magnetic stirrer, flowed through the lumen side of the hollow fibers, and the cold distillate flowed through

Table 2 | The characteristics of the membrane material and the membrane module

Membrane and module	Properties
Membrane material	PVDF
Mean pore diameter (μm)	0.16
Contact angle (°)	118.6
Porosity (%)	85.13
Inner diameter of hollow fiber (mm)	0.80
Membrane thickness (mm)	0.15
Number of hollow fibers	50
Effective membrane length (mm)	100
Effective membrane area (cm^2)	125.6

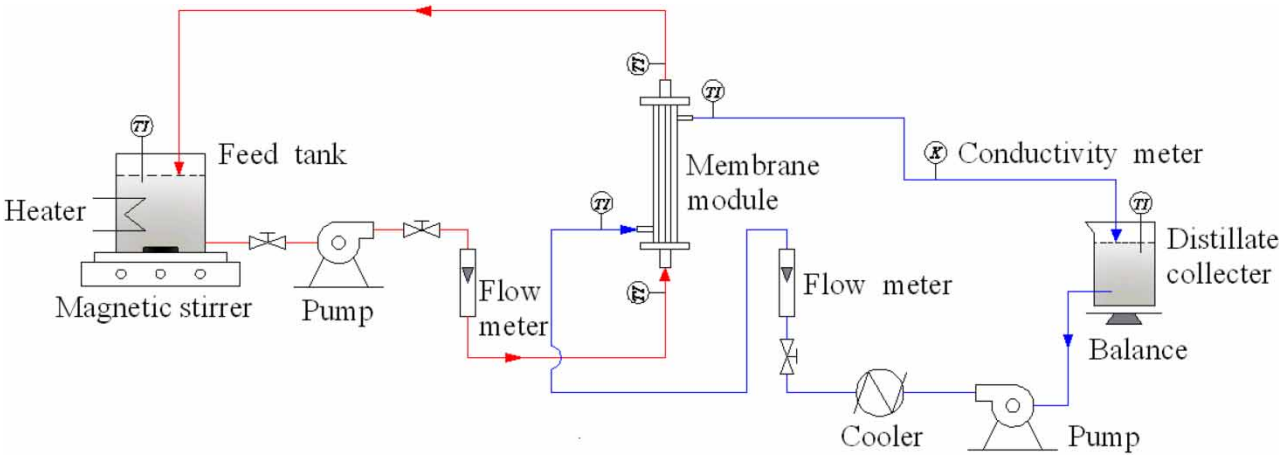


Figure 2 | Schematic diagram of the DCMD set-up.

the shell side. Both solutions were circulated in the membrane module with the help of two magnetic pumps (MP-15RN, Shanghai Seisun Pumps, China). The feed temperature was controlled by a Pt-100 sensor and a heater connected to an external thermostat (XMTD-2202, Yongshang Instruments, China). The distillate temperature was adjusted through a spiral glass heat exchanger immersed in the constant temperature trough of the cooler (SDC-6, Nanjing Xinchen Biotechnology, China). The temperature of both fluids was monitored at the inlet and outlet of the membrane module using four Pt-100 thermoresistances connected to a digital meter (Digit RTD, model XMT-808, Yuyao Changjiang Temperature Meter Instruments, China) with an accuracy of ± 0.1 °C. An electric conductivity monitor (CM-230A, Shijiazhuang Create Instrumentation Technologies, China) was used to monitor the distillate conductivity.

2.5. Membrane fouling experiments

Fouling tests were carried out using the LFLRO brine as feed. The feed and the distillate flowed co-currently through the membrane module, and the circulation feed rate was fixed at 45 L h^{-1}, while the cold side was set at 27 L h^{-1}. The feed temperature was fixed at 53 °C and the distillate temperature kept at constant 20 °C. The initial volumes of the feed and the distillate were 2.5 L and 0.25 L, respectively. During membrane fouling tests, there was no make-up water added into the feed tank, which meant that the feed was concentrated gradually. The permeate flux was calculated by the following equation:

$$J = \frac{\Delta W}{A \cdot \Delta t} \tag{1}$$

where J is the permeate flux (kg m^{-2} h^{-1}), ΔW is the mass of the permeate (kg), A is the effective area of the hollow fiber membranes (m^2) and Δt is the time interval (h). The concentration factor K can be calculated by the following equation:

$$K = \frac{Q_o}{Q_o - Q_p} \tag{2}$$

where Q_o and Q_p are the initial quantity of feed (kg) and the cumulative permeate production (kg), respectively.

2.6. Membrane cleaning experiments

The total operating time for each DCMD experiment of LFLRO brine was 30 hours. Afterwards, the membrane modules were retrieved and cleaned separately according to the following four cleaning procedures (Guillen-Burrieza *et al.* 2014; Duong *et al.* 2015):

(1) Deionized water cleaning: the membranes were rinsed with deionized water for 30 min to remove the loose deposits on the membrane surface.
(2) Chemical cleaning: the membranes were cleaned independently with different cleaning methods at ambient temperature. The cleaning solution was pumped into the membrane module and flowed through the lumen side of the hollow fibers with the circulation flow rate at 45 L h^{-1}. The chemical solutions and cleaning schemes for the five cleaning methods used in the chemical cleaning step are presented in Table 3.
(3) Deionized water flushing: the membranes were flushed with deionized water for 1.0 h at 50 °C followed by chemical cleaning. The hot deionized water flowed co-currently through the membrane module, the flow rate was 45 L h^{-1} in the lumen side of the hollow fibers. At the completion of membrane flushing, the membrane module was removed

Table 3 | Chemical solutions and cleaning schemes used for five cleaning methods

Cleaning method	Cleaning solution	Procedure
HCl-NaOH	HCl (pH = 2), NaOH (pH = 12)	HCl and NaOH flushing sequentially for 0.5 h each
EDTA-HCl	EDTA-Na (pH = 11.5), HCl (pH = 2)	EDTA and HCl flushing sequentially for 0.5 h each
Citric acid	2 wt.% citric acid	Citric acid flushing for 1.0 h
NaClO	2 wt.% NaClO	NaClO flushing for 1.0 h
SDS	3 wt.% SDS	SDS flushing for 1.0 h

from experimental setup and excess liquid on the membrane surface was allowed to drain off by gently tilting the membrane module.

(4) Dry-out: the membranes were dried in an air blowing drying cabinet for 2.0 h at 50 °C to remove the residual liquid on the membrane surface and in the membrane pores.

To evaluate the efficiencies of different cleaning methods, the DCMD experiments were carried out using the same membrane module, the 4 wt.% NaCl solution was used as the feed and operating parameters (i.e., initial volumes of feed and distillation, circulation rates and operating temperatures) were in accordance with LFLRO treatment experiment.

2.7. Membrane surface analysis

Membrane morphology was investigated with a HITACHI S-3000N scanning electron microscope (SEM) (Hitachi Ltd, Japan). Membrane samples were frozen in liquid nitrogen, fractured to obtain fragments, and sputtered with gold using a HITACHI E-1010 Ion Sputtering device for SEM observation. Membrane contact angles were tested using a contact angle measurement instrument (OCA 15EC, Dataphysics, GER). The membrane samples fouled by LFLRO brine were handled gently and without any excessive forces to ensure that the fouling layer remained intact.

2.8. Analytical methods

The total dissolved solids (TDS) (GB 11901-1989), chemical oxygen demand (COD) (HJ 828-2017) and ammonia nitrogen (NH_4^+-N) (HJ 535-2009) were measured according to the standard methods. The pH was measured using a pH meter (Five Easy, Mettler Toledo, USA). Metal ions were analyzed by ICP-AES (1200, Agilent, USA) and anions such as sulfate and chloride were measured by ion chromatograph (861, Metrohm, Switzerland). The conductivity of the LFLRO and permeate of MD process were measured using a conductivity meter (CO150, HACH, USA).

3. RESULTS AND DISCUSSIONS

3.1. Membrane fouling experiment

As shown in Figure 3, during the first 18 hours of operation, the feed was concentrated gradually, with significant permeate flux decline and conductivity increase, indicating the accumulation of membrane fouling. Over this period, the permeate flux declined by about 55.5% and the permeate conductivity increased from 36 to 118 μS cm^{-1}. In addition to the membrane fouling, the permeate conductivity increase in the concentration stage could also be attributed to the migration of NH_3 and volatile organic compounds through the membrane pores (Ding *et al.* 2006a, 2006b; Lin *et al.* 2018; He *et al.* 2019).

When the concentration factor reached 5.0, the permeate was fed back to the feed tank every half an hour to keep the concentration factor constant in the last 12 hours. The permeate flux slightly declined and stabilized at about 4.70 kg m^{-2} h^{-1} as

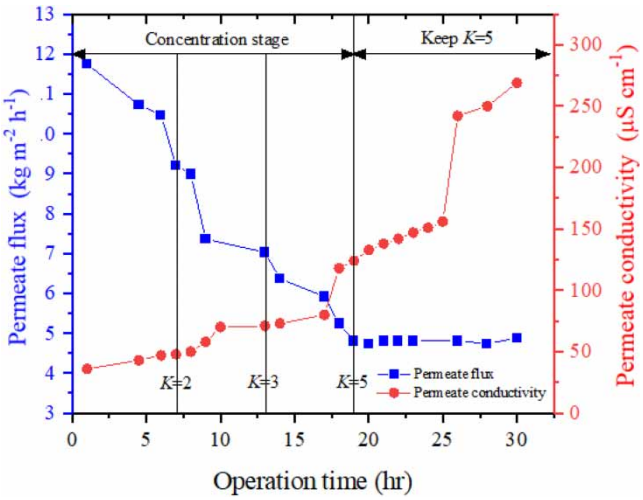


Figure 3 | Variation of permeate flux and permeate conductivity as functions of the feed concentration factor throughout the DCMD process treating LFLRO brine.

the experiment terminated, which was only 39% of the initial permeate flux. Besides, the permeate conductivity rose to 269 μS cm^{-1}, suggesting that the permeate quality deteriorated continuously.

Physical photos of the membrane before and after the DCMD experiment are shown in Figure 4. Compared with a virgin membrane module (Figure 4(a)), the membrane module after treating LFLRO brine showed visual signs of fouling where brownish deposits covered and clogged some hollow fibers (Figure 4(b)), which would lead to the decline of the feed flow rate and caused the permeate flux decrease.

The SEM images of the fouled membranes and element distribution corresponding to these images are shown in Figure 5. At low magnification, a relatively even distribution of a fouling layer and apparent salt crystals can be seen on the inner surface of the fouled membrane (Figure 5(b)). Figure 5(c) shows a closer image of the fouling layer where three different deposit morphologies are revealed: a porous underlying deposit which was composed of organic scaling and inorganic elements identified by energy dispersive spectroscopy (EDS) (Figure 5(f)), a small number of relatively pure salt crystals on the fouling layer was identified as NaCl by EDS (Figure 5(d)), and some lumpy scaling with a rough surface was identified by EDS as a mixture of inorganic salts primarily consisting of O, S, K, Na, Mg, Ca (Figure 5(e)). Furthermore, the cross-sectional image (Figure 5(a)) showed the presence of internal crystals and organic scaling, suggesting that scaling not only occurred on the surface, but also within the pores and internal structure of the membrane. With deposits inside membrane pores, membrane

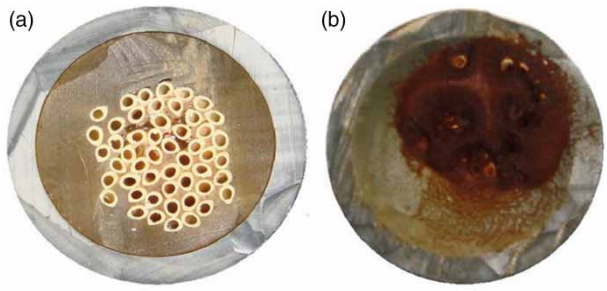


Figure 4 | Photos of the hollow fiber inlets: (a) before membrane fouling experiment (b) after membrane fouling experiment.

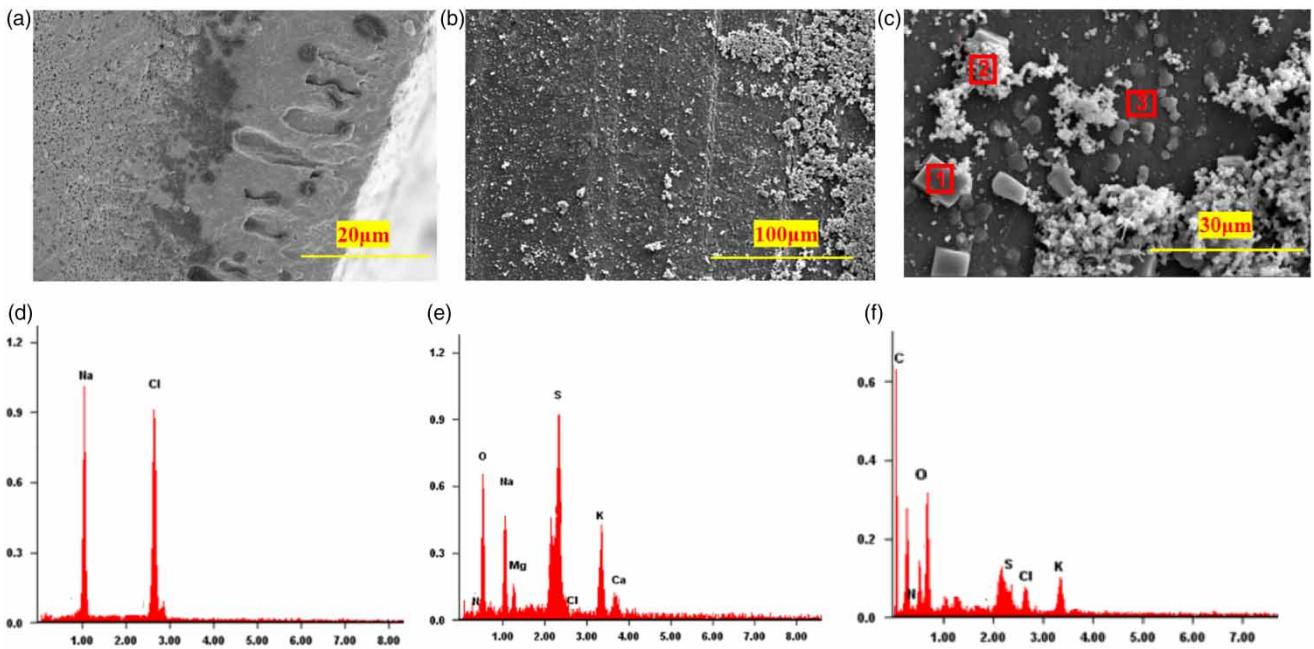


Figure 5 | SEM micrographs of the fouled membrane: (a) cross-section, (b) and (c) surface with different magnification, and EDS spectra of the deposits: (d), (e) and (f) are corresponding to three positions marked 1, 2, 3 in the picture c, respectively.

wetting would occur, and as a result, the permeate conductivity increased as shown in Figure 3. Besides, the decline of the permeate flux shown in Figure 3 was also associated with the pore clogging by scale deposits formed on the membrane surface and the pore narrowing or blocking by the adsorption of foulants to pore walls.

3.2. Chemical cleaning assessment

Five cleaning methods, 2 wt.% NaClO, 3 wt.% SDS, HCl (pH = 2)-NaOH (pH = 12), EDTA (pH = 11.5)-HCl (pH = 2) and 2 wt.% citric acid cleaning, were tested in this study. To evaluate the performance of membranes cleaned by five different cleaning methods, DCMD experiments were performed using 4 wt.% NaCl as feed solution, and the variations of permeate flux and permeate conductivity were analyzed. For comparison, the performance of pristine membrane was also tested via MD experiment.

Figure 6 showed the permeate flux recovery rates after membrane cleaning, and the variations of permeate flux and permeate conductivity during the DCMD experiments with 4 wt.% NaCl solution are shown in Figure 7. The initial permeate flux was 12.5 kg m^{-2} h^{-1} and kept stable throughout the MD process when using pristine membrane; besides, the permeate conductivity stayed lower than 10 μS cm^{-1}, indicating nearly 100% salt rejection. Among all five cleaning methods investigated, SDS cleaning showed the best cleaning efficiency. Following SDS cleaning, nearly 100% of the initial flux was restored and the permeate flux remained stable above 12 kg m^{-2} h^{-1} during the MD process; it was noteworthy that no significant salt leakage was observed, and the permeate conductivity kept stable below 20 μS cm^{-1}. A similar result was found in the initial flux recovery for the NaClO cleaning method. Although 97.9% initial permeate flux recovery was achieved and the permeate flux remained above 10 kg m^{-2} h^{-1}, the permeate conductivity rose rapidly throughout the MD process, indicating serious salt leakage and the occurrence of membrane wetting. For acid-base solution cleaning, only 62.8% initial permeate flux recovery was achieved after the HCl-NaOH cleaning, and slightly higher rates were gained after EDTA-HCl cleaning and citric acid cleaning at 71.3% and 77.7%, respectively. Besides, a similar variation trend of permeate flux and permeate conductivity was shown after acid-base solution cleaning. The permeate flux gradually decreased, along with the rapid increase of permeate conductivity, indicating pore clogging by scale deposits formed on the membrane surface and membrane wetting caused by foulants inside the membrane pores.

The SEM images and contact angles of fouled membranes after five cleaning methods and pristine membrane are shown in Figure 8. After SDS cleaning, there was no obvious fouling layer on the membrane surface, and membrane pores can be clearly seen in the SEM image, suggesting the effective removal of foulants by SDS, which was consistent with others' findings (Li & Elimelech 2004; Ang *et al.* 2006, 2011). It is noteworthy that EDTA, which was confirmed to be effective for removing organic-Ca^{2+} composite pollutants in the results of Ang *et al.*, was found to be inefficient in our study (Ang *et al.* 2006, 2011). Considering the pollutants Ang *et al.* used were a mixture of sodium alginate, humic acid and Ca^{2+}, there were other organic and divalent cation pollutants (e.g., Mg^{2+}) in the LFLRO brine that would form organic-inorganic complexes, thus, we

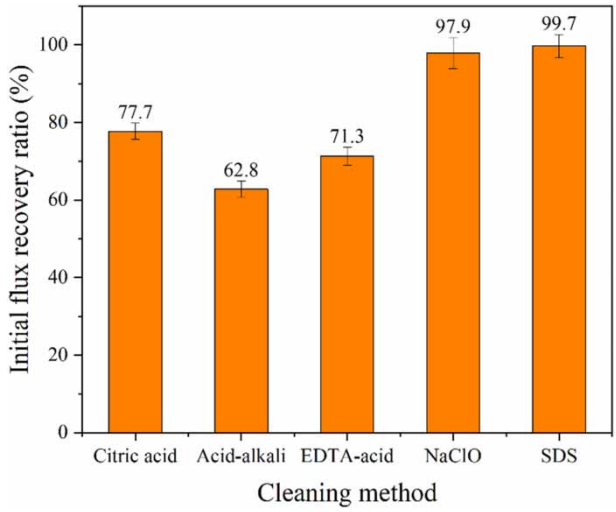


Figure 6 | Comparison of the initial flux recovery rates achieved by the five cleaning methods.

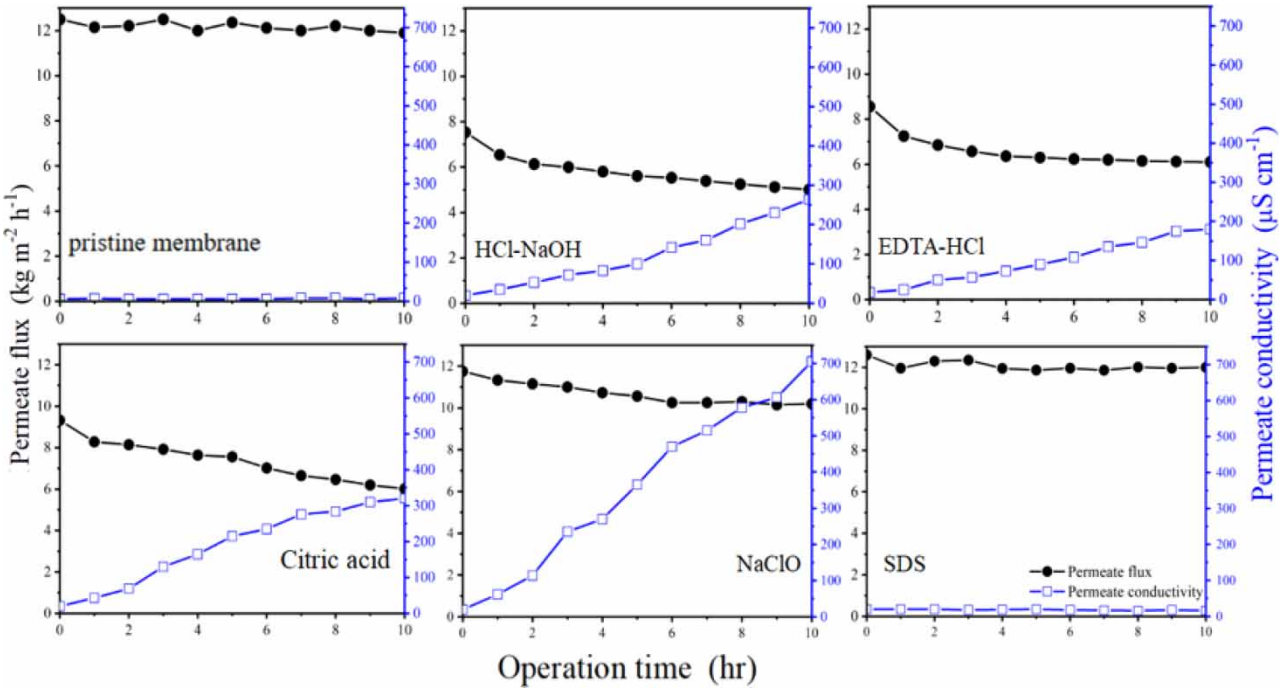


Figure 7 | Permeate flux and permeate conductivity in 10-hour continuous DCMD experiments with 4 wt.% NaCl solution using pristine membrane and fouled membranes that cleaned by HCl-NaOH, EDTA-HCl, 2 wt.% citric acid, 2 wt.% NaClO and 3 wt.% SDS, respectively.

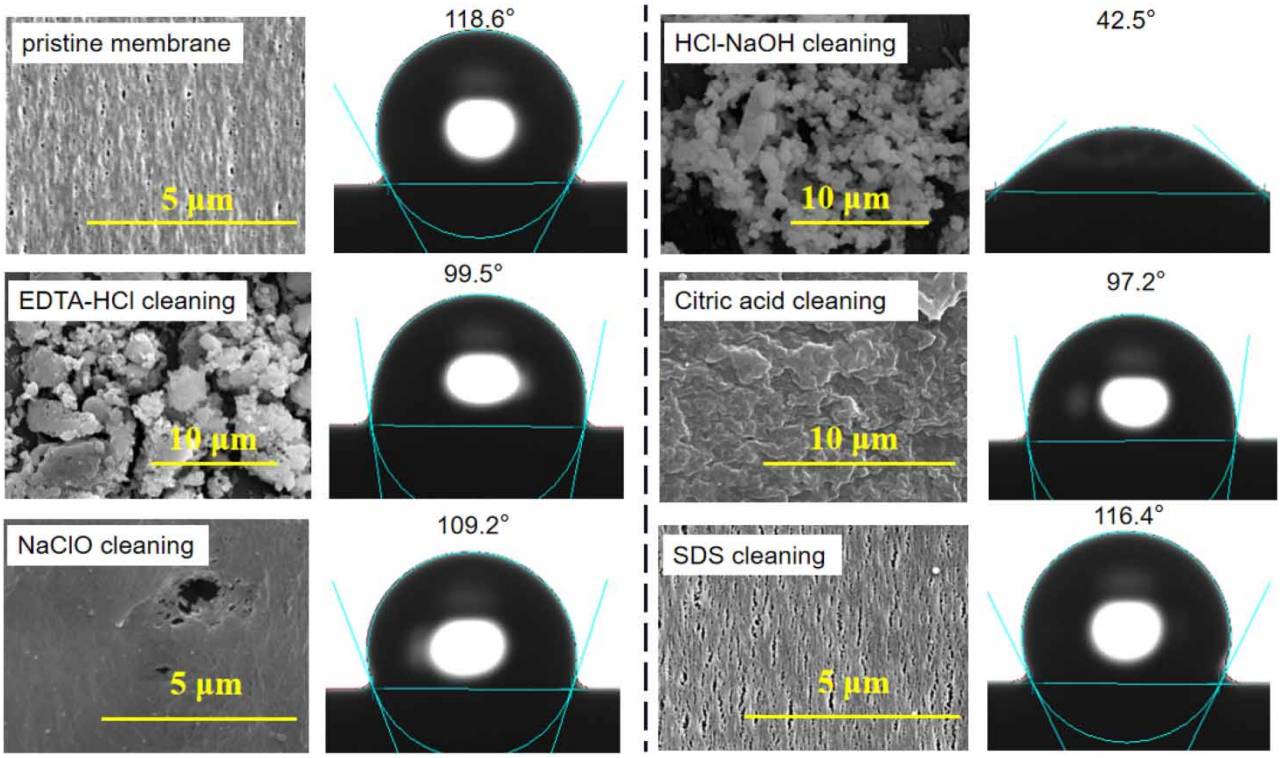


Figure 8 | SEM micrographs and contact angles of membrane surface: pristine membrane and membranes after cleaning.

thought that under the experimental conditions of this study, SDS may be more effective in breaking up organic-metal ion bindings than EDTA due to its hydrophilic and hydrophobic structures (Wang *et al.* 2015). Besides, SDS can enter the membrane pores and remove absorbed foulants (Liikanen *et al.* 2002), thus obtained better cleaning efficiency.

As observed by Mo *et al.* and Yu *et al.*, NaOH and acid cleaning were inefficient and removed only part of organic-inorganic composite pollutants (Mo *et al.* 2010; Yu *et al.* 2013). After HCl-NaOH and citric acid cleaning methods, a notable amount of scaling was observed on the membrane surface.

Though only relatively few precipitations can be seen on the membrane surface after NaClO cleaning, the fuzzy membrane pores in the SEM image indicated that there were still pollutants inside or around membrane pores. Besides, the obvious signs of membrane damage were shown on the membrane surface, which may be due to the strong oxidizability of NaClO (Wang *et al.* 2018).

Contact angle measurements of membranes also demonstrated the variations in the efficiency of the five cleaning methods (Figure 8). The virgin membrane showed good hydrophobicity with high contact angle of 118.6°. After DCMD treatment of LFLRO brine, the membrane surface became completely hydrophilic, and the contact angle decreased to 0°. The strong reduction of contact angle suggested the occurrence of serious membrane fouling, which was consistent with the results in section 3.1. Nearly 100% of contact angle was restored (116.4°) after SDS cleaning. In contrast, NaClO, EDTA-HCl, citric acid and HCl-NaOH cleaning restored the contact angle to 109.2°, 99.5°, 97.2° and 42.5°, respectively.

Collectively, the results reported here suggest that the membrane fouling during DCMD treatment of LFLRO can be controlled by effective cleaning methods. We took both inorganic and organic foulant on the membrane surface into account and found that the cleaning efficiency of cleaning methods investigated in this study followed an order of SDS > NaClO > citric acid > EDTA-HCl > HCl-NaOH.

4. CONCLUSIONS

DCMD was effective in concentrating LFLRO brine with high concentration of organic and inorganic contaminants. Although the water recovery can reach as high as 80%, the organic and inorganic contaminants caused severe membrane fouling both on the membrane surface and inside membrane pores.

The fouled MD membranes were cleaned with different cleaning methods, acid-base and citric acid solutions cleaning was ineffective in restoring the permeate flux and the salt rejecting ability of membrane. 2 wt.% NaClO cleaning achieved higher permeate flux recovery rate, but poor cleaning efficiency in removing the foulants inside the membrane pores. Besides, the NaClO cleaning method may cause damage to the membrane. The 3 wt.% SDS cleaning method gained nearly 100% permeate flux recovery rate and no significant salt leakage was observed during the MD process. These results showed that the SDS can be used to restore the membrane performance after MD processing LFLRO brine, thus achieve long stable MD operation.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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