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**Sodium Docusate as a Cleaning Agent for Forward Osmosis membranes Fouled by Landfill Leachate Wastewater**

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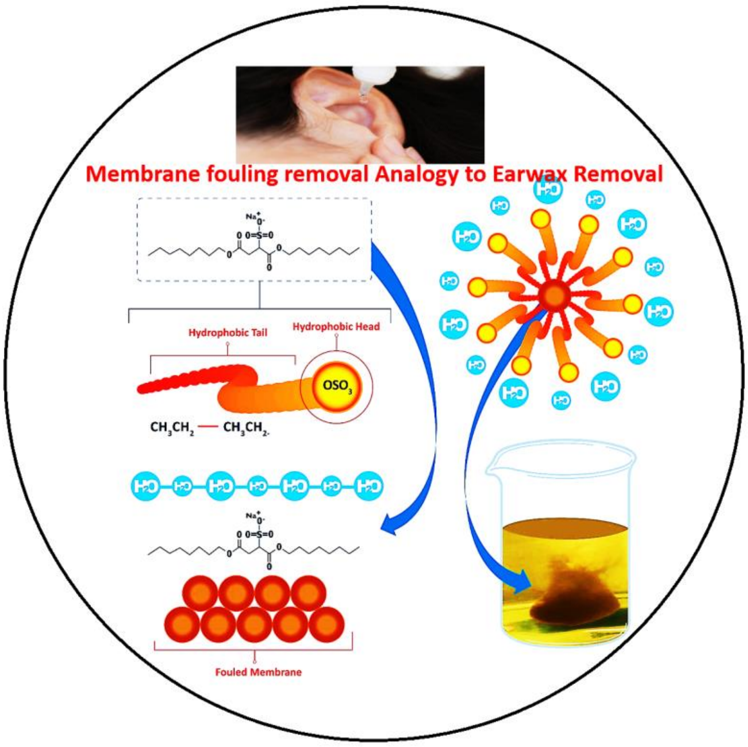


**Graphical abstract**

**Abstract**

Membrane cleaning is critical for economic and scientific reasons in wastewater treatment systems. Sodium docusate is a laxative agent and removes cerumen (ear wax). Docusate penetrates the hard ear wax, making it softer and easier to remove. The same concept could be applied to soften and remove fouling layers on the membrane surface. Once softened, the foulants can be easily flushed with water. This innovative approach can address the challenge of developing superior methods to mitigate membrane fouling and material degradation. In this study, we evaluated the efficiency of sodium docusate for cleaning fouled forward osmosis membranes with real landfill leachate wastewater. Experiments were conducted to examine the impact of dose rate, contact time, flow or static conditions, and process configuration (forward osmosis (FO) or pressure retarded osmosis (PRO) upon fouling created by landfill leachate dewatering. A remarkable (99%) flux recovery was achieved using docusate at a small concentration of only 0.1% for 30 minutes. Furthermore, docusate can also effectively restore flux with static cleaning without using pumps to circulate the cleaning solution. Furthermore, cleaning efficiency can be achieved at neutral pH compatible with most membrane materials. From an economic and energy-saving perspective, static cleaning can almost achieve the same cleaning efficiency as kinetic cleaning for fouled forward osmosis membranes without the expense of additional pumping energy compared to kinetic cleaning. Since pumping energy is a major contributor to the overall energy of the forward osmosis system, it can be minimized to a certain degree by using a static cleaning approach and can bring good energy savings when using larger membrane areas. Studies of the contact angle on the membrane surface indicated that the contact angle was decreased compared to the fouled membrane after cleaning (*e.g.* 70.3$^{o}$ to 63.2$^{o}$ or FO mode and static cleaning). Scanning Electron Microscopy revealed that the cleaning strategy was successful. Infrared Spectroscopy showed that a small amount of sodium docusate remained on the membrane surface. Docusate is more environmentally friendly than acid or alkaline solutions from an environmental perspective. Furthermore, the cleaning solution can be reused for several cycles without discarding it due to the surfactant properties of docusate.

**Keywords:** Forward Osmosis; Pressure Retarded Osmosis; Cleaning; Surfactant; Landfill Leachate

## 1. Introduction

Forward osmosis technology (FO) is generally considered a low fouling process due to the requirement of low hydraulic pressure compared to traditional pressure-driven membrane processes such as RO (reverse osmosis) and NF (nanofiltration)[1, 2]. However, membrane fouling is still one of the major issues in the FO process [3, 4]. Fouling in the FO process hinders process efficiency, deteriorates membrane performance, and increases operational costs. Although several efforts can minimize membrane fouling, it is still inevitable. To maintain continuous operation of the process, periodic cleaning employing physical or chemical cleaning of the membrane is unavoidable when concentrating wastewater with the FO process. Physical cleaning detaches weakly bonded cake layers from the membrane surface but does not remove all the fouling layers [5]. Several recent studies have proved that physical cleaning protocols are often not enough to restore the performance of the FO membrane when treating wastewater[6], and chemical cleaning may be the ultimate solution. Traditionally, acid cleaning, alkaline cleaning, cleaning with surfactants, and cleaning with oxidizing agents such as hydrogen peroxide or sodium hypochlorite have been investigated for FO membranes fouled by wastewater. The choice of appropriate chemical protocol is usually tailored to the feedwater or determined by trial and error [7], whereas sometimes chosen without any theoretical justification [8].

Drawbacks of chemical cleaning include changing membrane surface properties. This outcome may influence the separation performance of FO membranes, especially when treating hazardous wastewater such as landfill leachate [9, 10]. For instance, a caustic cleaning environment increases membrane pore size [8-10], low rejection of neutral and hydrophobic contaminants, magnesium, sodium and chloride ions, and active membrane layer swelling [11]. Caustic or acid cleaning also requires high or low pH, respectively, which sometimes exceeds the manufacturer's recommended pH range that membranes tolerate, such as cellulose triacetate membranes (CTA) with an operating pH range from 3-8 [12]. Acid cleaning also has an impact on sulphate rejections [11]. When subjected to other cleaning agents such as hypochlorite, microscopic-level chain scission of the polymer components leads to a gradual loss of mechanical strength of the membranes [13] besides the formation of hazardous and toxic halogenated by-products[14].

Furthermore, rupture of the C–S bond and changes in macroscopic membrane properties has been reported after hypochlorite cleaning. Cleaning with detergents such as Alconox is compatible only with the CTA membrane, whereas detrimental to Thin film composite (TFC) membranes [15]. Table 1 (adapted from our previous work [16]) lists the different cleaning protocols and their Impact on different types of forward osmosis membranes. In most cases, when the manufacturer recommended chemical cleaning protocol is followed, it is compatible with the membrane. Still, it may damage the other components of the system, such as feed spacers, due to the harsh environment [8, 17].

**Table 1**. Chemical cleaning protocols employed in the forward osmosis

| Cleaning agent | Mechanism of action | Impact on membrane | Reference |
|---|---|---|---|
| NaOCl | Oxidation and disinfection | Oxidative damage of TFC and CTA membranes | [18, 19] |
| Acids | Solubilization and chelation | Narrowing of pores | [15, 20] |
| Alconox (detergent) | Oxidation and disinfection | Oxidation of TFC membranes | [15] |
| Sodium hydroxide (NaOH) | Hydrolysis and solubilization | Can increase pore size leading to lower rejection of contaminants | [15] |
| Surfactant | Dispersion and emulsification | Can lead to pore-plugging | [15, 20] |
| EDTA | Chelation | Can damage TFC membrane | [15, 20] |
| Alconox+ EDTA | Oxidation, disinfection and chelation | May damage both CTA and TFC membranes | [15] |
| Hydrogen peroxide | Oxidation agent | Damage to both CTA and TFC membrane | [9, 10] |
| $Na_2EDTA$ | Chelation | May damage CTA membranes | [10] |

A substantial number of FO publications have focused on new membrane development, hybrid FO processes, novel FO draw solutions, solution recovery and modelling of the FO process[14, 21, 22]. However, the development of innovative membrane cleaning strategies for continuous FO operation is not as well advanced. A new idea is proposed to use dioctyl sodium sulfosuccinate ($C_{20}H_{37}NaO_7S$), also known as docusate sodium, as a cleaning agent for FO membranes fouled with by particularly challenging wastewater such as landfill leachate. Docusate is an anionic surfactant that acts as an excellent dispersive and wetting agent to remove cerumen (ear wax) or stool softener. It penetrates the hard symptomatic cerumen or faecal mass by making it softer, easier to break, and easier to remove [23]. With this concept, the hypothesis was that if docusate sodium can more effectively penetrate and soften the hard fouling layer, then removal from the FO membrane surface may be accomplished using conventional crossflow flushing. Supporting evidence for this hypothesis includes the fact that compared to traditional surfactants used in chemical cleaning, the critical micelle concentration (CMC) value of docusate sodium is only 0.02% (w/v) [24]. Another inherent advantage is that docusate sodium is miscible in organic and aqueous solutions because it contains both hydrophilic and hydrophobic groups. Furthermore, as a surfactant, docusate sodium produces foam and bubbles even in small concentrations. Chemical foam cleaning and bubble methods effectively and quickly clean fouled ultrafiltration membranes [25]. Docusate sodium can clean the membrane in-situ without circulation, i.e. static cleaning. Static cleaning can reduce the pumping energy cost of the system and provide some energy savings in the long run for a desalination unit. However, it cannot be generalized if the time required for cleaning in place (CIP) is the same for both cases.

Therefore, this study aimed to explore the feasibility of sodium docusate as a novel FO membrane cleaning agent for the first time. Organic fouling is a major problem in wastewater treatment by membrane processes. As a strong surfactant, sodium docusate would be suitable for organic matter removal from the FO membrane treating leachate wastewater. Research questions addressed to support the hypothesis included: (1) What is the flux recovery of fouled FO membrane after cleaning (kinetic and static) with docusate in the FO mode (when the feed solution faces the active layer and draw solution faces the support layer)? (2) How does the pressure retarded osmosis (PRO) mode (when the draw solution faces the active layer) influence cleaning performance? (3) What is the impact of sodium docusate on the membrane rejection performance? (4) Is there a possibility of energy saving by using sodium docusate as a cleaning agent?. A benchtop forward osmosis system was used to treat landfill leachate and minimize the impact on the environment. The cleaning solution was reused for the whole cycle of FO operation.

## 2. Materials and methods

### 2.1. Feed and Draw solution

The biologically treated landfill leachate wastewater was collected from Hurstville Golf Centre, Sydney, Australia and used as FS (feed solution). This landfill site was used until the early 1980s, when it was shut down, capped, and turned into a golf course. The landfill wastewater was stored in a refrigerator to avoid changing composition. Details analysis for heavy metals and contaminants of the wastewater was conducted using ICPMS (inductively coupled plasma mass spectroscopy) and presented in the **supplementary information** (**Table S.1**). The draw solution used in this study was NaCl (sodium chloride) of concentration 1 M (molar). A higher draw solution concentration was used in this study compared to 0.5M in our previous work [9, 10] to simulate harsh fouling conditions.

### 2.2. Chemical cleaning agent

Sodium docusate was procured from Sigma Aldrich, Australia and was used as a cleaning agent. Cleaning solutions prepared were of concentrations ranging from 0.1% to 0.2% by dissolving the appropriate amount in DI water and stirring with a magnetic stirrer for at least 30 minutes. **Supplementary Figure S.1** presents the chemical structure of docusate with the headgroup ion having a negative charge, thus representing an anionic surfactant. Table 2 lists the properties of sodium docusate with a surface tension of 28.7 dyne/cm for 0.1% solution and a topological Polar surface area of 118 Å², enabling it to be a great cleaning agent.

**Table 2:** Properties of sodium docusate

| | |
|---|---|
| IUPAC name | Dioctyl sodium sulfosuccinate |
| Appearance | White waxy |
| Molecular formula | $C_{20}H_{37}NaO_7S$ |
| Molecular weight (g/mol) | 444.6 |
| Surface tension (dynes/cm) | 28.7 for 0.1% solution |

| | |
|---|---|
| Common uses | Surfactant, wetting agent, and solubilizer |
| Number of Hydrogen Bond Acceptors | 7 |
| Topological Polar Surface Area | 118 Å² |

### 2.3. Membrane and experimental setup

The FO membrane made from cellulose triacetate (CTA) was procured from Sterlitech Corporation, USA. Detailed information about the intrinsic properties of this membrane can be found in our previous publication [26]. The membrane was soaked in DI water for 24 hours to ensure complete wetting and was then immersed in the FO cell (CF042D) obtained from Sterlitech Corporation. The FO lab-scale setup used in this study was similar to our previous publication [26]. The FS and DS were circulated at 1.8 Litres per minute, representing a cross-flow velocity of 33 $cmsec^{-1}$ at an ambient laboratory temperature of 25 ±2 °C. The FS was placed on a scale, and the change in the weight of the feed solution over time was converted into the water flux as given by Eq. (1).

$$J_w = \frac{(\Delta W/1000)}{A_m * t} \qquad (1)$$

Where $\Delta W$ represents the change in weight of the FS recorded with a digital computer, $A_m$ is the membrane area (0.0042 $m^2$), and t is the FO experiment time. The change in concentrations was recorded through a conductivity meter obtained from Laqua (Horiba, Australia).

### 2.4. Experimental protocol

**Supplementary Figure S.2** depicts the experimental protocol followed in this study. Experiments were conducted in the FO and PRO modes to assess the Impact of membrane orientation on flux recovery. A previously soaked CTA membrane was installed in the FO system and flushed with DI water on both sides for one hour at least. The FS and DS were then replaced with landfill leachate (500 mL) and 1M NaCl (500 mL) and circulated for 16 hours for the initial baseline performance of the membrane with the landfill leachate. After the initial baseline run, the membrane was rinsed with DI water for one minute and then cleaned with different concentrations of sodium docusate for 15 to 30 minutes, depending on the objective of each experiment. Subsequently, the membrane was washed with DI water again to remove any docusate. After each cleaning cycle, the FS and DS were replaced with fresh ones, and the experiment was repeated. Each experimental run lasted for three cycles. At the end of the third cycle, the samples were collected from the DS side for ICPMS analysis, and the membrane was cleaned with docusate to be analyzed later by FT-IR and FE-SEM. The water flux recovery was calculated using Eq. (2) for two consecutive cycles.

$$WFR = \frac{J_{wf}}{J_{wc}} * 100 \qquad (2)$$

Where $J_{wf}$ is the average water flux (LMH) of the fouled membrane for the whole 16 hours cycle, and $J_{wc}$ represents the average water flux (LMH) of the cleaned membrane for the whole cycle.

### 2.5. Procedure for static cleaning

Static cleaning was performed with the FO system filled with the sodium docusate solution on the feed solution side. A two-way close valve was used in the circulating loop of the feed solution near the FO cell to maintain the docusate interaction with the membrane. To avoid pressure build-up in the system, the flow rate was lowered to 0.1 LPM, and the cleaning solution was pumped till the system was filled with the docusate. After the desired contact time, the membrane was flushed with DI water for 5 mins to remove the excess docusate from the system.

### 2.6. Membrane characterization

The membrane morphology was studied using field emission scanning electron microscopy (FE-SEM) and Energy Dispersive x-ray spectroscopy (EDX). FE-SEM images were taken for virgin, fouled, and cleansed membranes and the same membranes were also subjected to EDX analysis. In addition, the same membranes were subjected to Fourier transformation infrared spectroscopy (FT-IR) investigation for functional group analysis.

### 2.7. Membrane rejection and wastewater analysis

ICPMS (Inductively coupled plasma spectroscopy) analysis was conducted to analyze the wastewater samples of the landfill leachate. To measure the Impact of sodium docusate on rejection, additional ICPMS tests were done for permeate samples after cleaning with docusate and compared with the baseline.

## 3. Results and Discussions

### 3.1. Influence of concentration and time of docusate on flux recovery

#### 3.1.1. FO mode with kinetic cleaning

Baseline experiments with landfill leachate feed solution and 1M NaCl draw solutions with all the pristine membranes are presented in **Fig. S.3a** for the FO mode. Due to the osmotic pressure gradient generated across the CTA membrane, the water permeation naturally occurs from the feed to the draw solution without any external hydraulic pressure. Our initial tests were conducted using landfill leachate (LFL) as the FS and 1M NaCl DS for 16 hours in the FO mode, followed by a 30-minute cleaning of the fouled membrane with DI water at a high cross-flow velocity of 0.36 $cmsec^{-1}$. The results revealed that the shear force generated by the high cross-flow velocity was insufficient to restore the permeability of the fouled membrane, with only 65 % of the average flux of the FO membrane restored (**Table S.2, supplementary information**). The lower flux recovery with DI water flushing agrees with previous studies on landfill leachate wastewater [27]. A new set of experiments was conducted for three consecutive cycles, and cleaning with sodium docusate started with a 0.1% of docusate concentration. The cleaning solution was circulated (kinetic cleaning) for only 15 minutes. **Fig.1a** presents the flux profiles for the two cycles after cleaning with reference to the baseline cycle, and **Fig. 1b** shows the flux recovery. All flux data were normalized using the same procedure as our previous work [15] and reported here to eliminate the effects of DS dilution on water flux decline. An initial water flux of 9.42 ±2 LMH and an average of 4.26 ±0.5 LMH were observed in the baseline test with LFL solution for the pristine membrane. After the first cleaning cycle, there was an excellent water flux recovery of 98% (average water flux of 4.20 ±0.5); however, it dropped to 93% after the second cleaning cycle (average water flux of 3.97±0.5) for the last cycle. Since 15 minutes of cleaning was not enough for complete flux recovery in a consecutive cycle, the cleaning time was increased to 30 minutes for the same concentration. The results are presented in **Fig.1c and Fig.1d.** Cleaning for 30 minutes restored almost 99% of water flux in the consecutive cycles. To minimize the downtime for the system, a higher concentration of 0.2 % was tested again to check whether the cleaning duration could be reduced to 15 minutes only. However, increasing the concentration to 0.2% and cleaning for 15 minutes had lower FR than the 0.1% for 15 minutes and 30 minutes **(Fig.1d and Fig.1e)**.

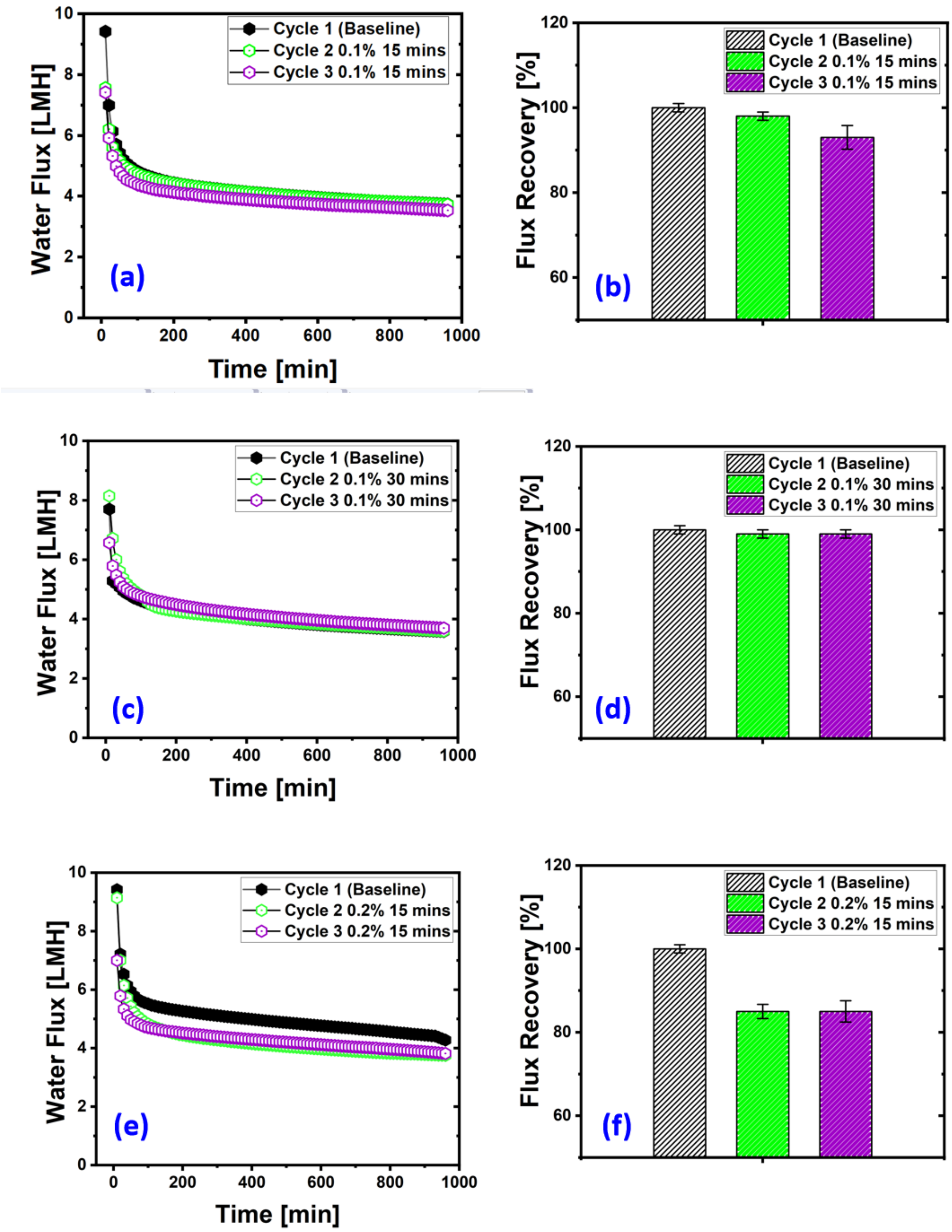


**Figure 1**: Water flux profiles and flux recovery for different concentrations and time, a) Water flux profiles in three cycles with 0.1 percent cleaning for 15 minutes, b) Flux recovery in three cycles with 0.1 percent cleaning for 15 minutes, c) Water flux profiles in three cycles with 0.1 percent cleaning for 30 minutes, d) Flux recovery in three cycles with 0.1 percent cleaning for

30 minutes, e) Water flux profiles in three cycles with 0.2 percent cleaning for 15 minutes, f) Flux recovery in three cycles with 0.2 percent cleaning for 15 minutes.

The higher concentrations of docusate probably promoted pore plugging of the FO membrane and led to lower water flux recovery. This deduction agreed with severe concentration polarisation and pore-blocking reports when higher concentrations of surfactant solutions were used to clean nanofiltration and reverse osmosis membranes [28, 29]. Higher concentrations of docusate also create more foam which can be problematic in practical applications. Therefore, a higher concentration of docusate cannot be an effective remedy, as it can enhance fouling due to micelles pore blocking.

#### 3.1.2. PRO mode with kinetic cleaning

A similar protocol to the FO mode tests was maintained for the PRO tests to investigate the influence of concentration and time on FR. Baseline experiments with landfill leachate feed solution and 1M NaCl draw solutions with all the pristine membranes are presented in **Fig. S.3b** for the PRO mode. Initial tests in the PRO mode were conducted with the LFL solution and 1M NaCl DS. Membrane cleaning was performed with DI water at high cross-flow velocity. However, this cleaning method restored 53% of the average water flux of the fouled FO membrane (**Table S.2. Supplementary information**). Subsequently, a new membrane was installed, and tests were performed for three cycles of circulating docusate at a concentration of 0.1 percent for only 15 minutes of cleaning time (**Fig. 2a**). An average water flux of 4.88 ±2 LMH was obtained for the baseline experiments in the PRO mode. This was slightly higher than the average water flux of the baseline experiments performed in the FO mode. Following the baseline experiments in the PRO mode, cleaning was performed after cycles 1 and 2, respectively, and the FR is reported in **Fig.2b.** The FR achieved was 88% after the second cycle and declined to 85% after the third filtration cycle. The initial flux in cycle 3 was lower than the previous two cycles; however, it levelled with cycle 2 flux after approximately 30 minutes. The lower initial flux may be attributed to the residual docusate in the system from the cleaning cycle. In the next set of experiments with a new membrane installed in the FO system, cleaning with docusate was conducted with the same concentration but for 30 minutes (**Fig. 2c**). The prolonged contact time of the cleaning solution exacerbated the FR for the same concentration, with 69% FR in cycle 2 and only 64% in cycle 3 (**Fig.2d**).

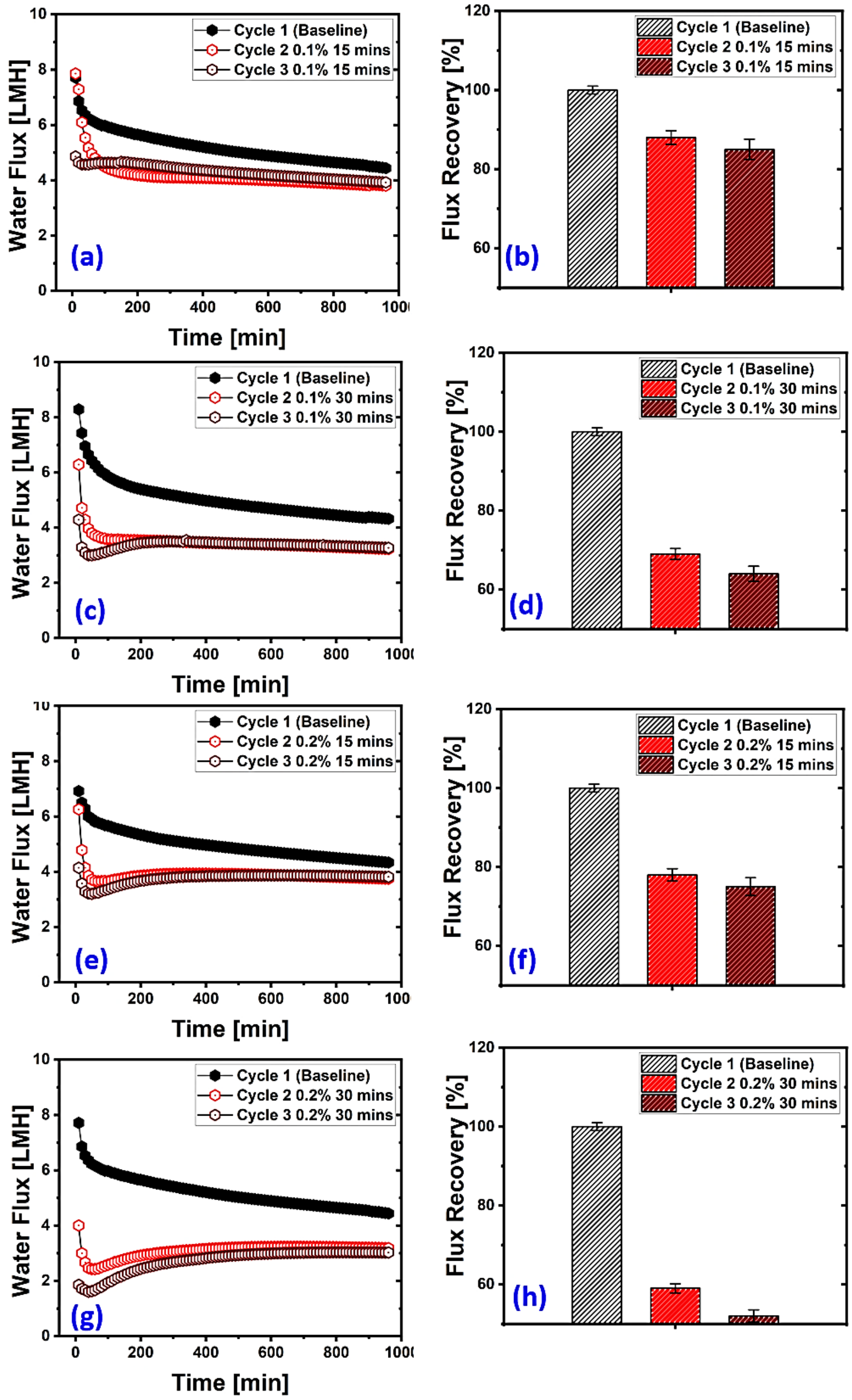


**Figure 2**: Water flux profiles and flux recovery for different concentrations and time, a) Water flux profiles in three cycles with 0.1 percent cleaning for 15 minutes, b) Water flux recovery

profiles in three cycles with 0.1 percent cleaning for 30 minutes, c) Water flux profiles in three cycles with 0.2 percent cleaning for 15 minutes. d) Water flux recovery profiles in three cycles with 0.1 percent cleaning for 30 minutes. e) Water flux profiles in three cycles with 0.2 percent cleaning for 15 minutes. f) Water flux recovery profiles in three cycles with 0.2 percent cleaning for 15 minutes. g) Water flux recovery profiles in three cycles with 0.2 percent cleaning for 30 minutes. h) Water flux recovery profiles in three cycles with 0.2 percent cleaning for 30 minutes.

The cleaning concentration was stepped up to 0.2%, and new experiments were conducted to analyze whether it could recover more water flux than the 0.1% docusate concentration. The water flux profiles are shown in **Fig.2e.** The increased concentration of 0.2% led to an FR of 78% and 75% in the second and third cycles, respectively, as presented in **Fig.2f.** Increasing the duration of the 0.2% docusate to 30 minutes had a similar effect on FR (**Fig.2g and 2h**) as 0.1%. Therefore, longer duration and higher docusate concentration are not recommended for membrane cleaning in the PRO mode. Evidently, shorter contact time and lower concentration of docusate in the PRO mode are more effective than higher concentration and prolonged contact time. Longer contact time and higher concentration can lead to pore plugging of the membrane by the surfactant and hence is not recommended.

### 3.1.3. FO mode and PRO mode with static cleaning

Previous studies on surfactant cleaning have revealed that the circulation of a cleaning solution accelerates surfactant transport to the membrane surface and facilitates micelle pore-blocking [30]. Cleaning without circulation may be beneficial in minimizing pore-blocking and reducing the pumping energy required to circulate the cleaning solution. The best concentration from the kinetic cleaning, i.e. 0.1% docusate, was chosen for static cleaning experiments in the FO and the PRO mode. The duration for static cleaning was determined through trial and error by starting from 15 minutes of contact time. The static cleaning was investigated for 15 minutes and 30 minutes for the FO and the PRO mode, respectively. Among these experimental runs, the static cleaning for 30 minutes had superior flux recovery for both the FO mode and the PRO mode, as reported here in **Fig.3.** A snapshot of the static cleaning of the FO membrane in the FO mode is presented in **Fig.3a**. The FO cell was placed sidewise with the milky docusate foam visible on the top part of the cell. The clean FO membrane in the FO mode is presented in **Fig.3b**. The water flux profiles for three cycles in the FO mode are presented in **Fig.3c,** and the FR in **Fig.3d**.

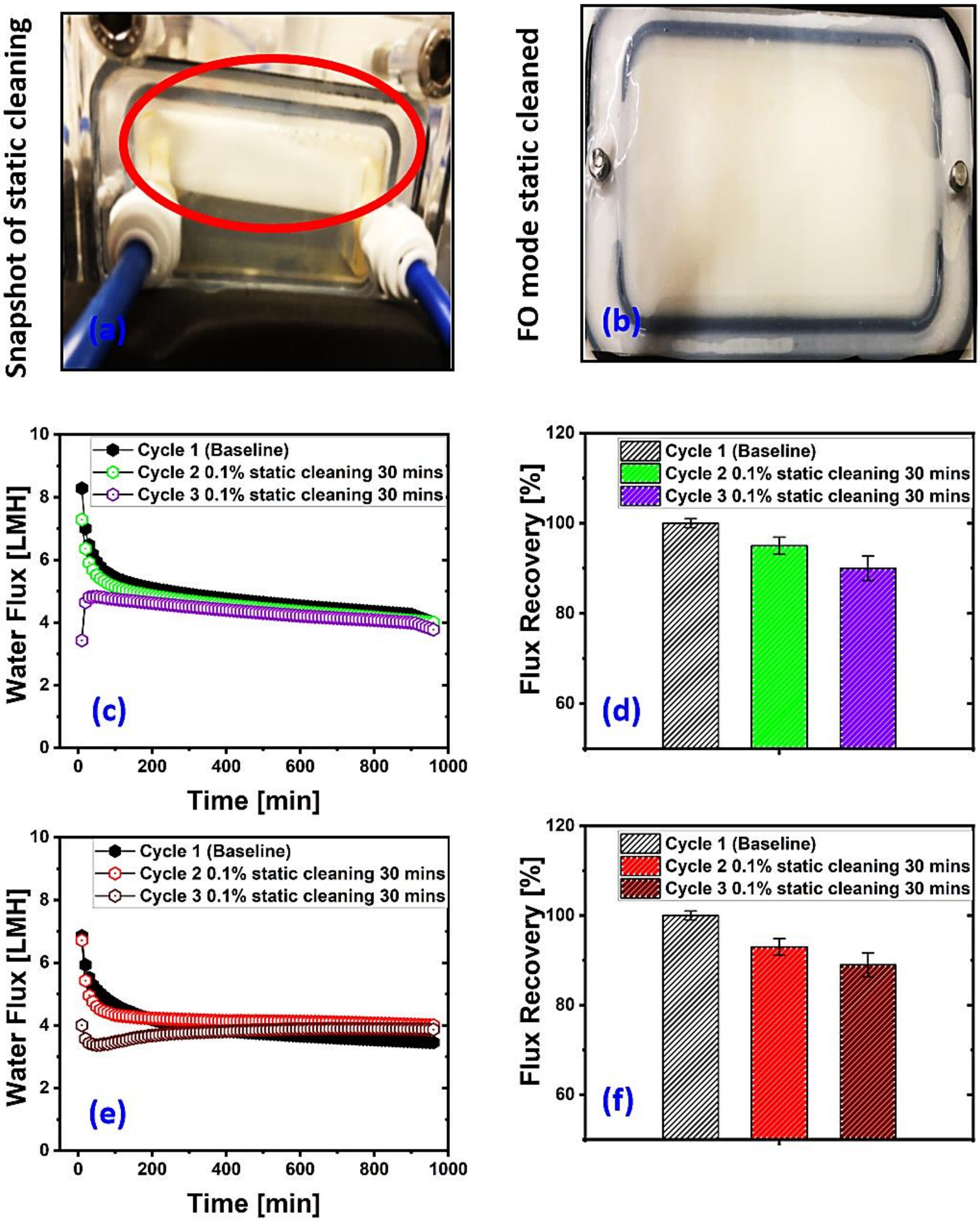


**Figure 3**: Water flux profiles and flux recovery for different concentrations and time, a) Picture of FO cell setup in the static cleaning operation, b) Cleaned membrane after static cleaning in the FO mode, c) Water flux profiles in three cycles with 0.1 percent static cleaning FO mode

d)Flux recovery for different cycles in static cleaning with the FO mode, e) Water flux profiles in three cycles with static cleaning in the PRO mode, f) Flux recovery for different cycles in static cleaning with the PRO mode

An FR of 95% and 90% was achieved for cycles 2 and 3. In contrast, static cleaning achieved FR of 92 and 91% in the PRO mode, respectively, in cycles 2 and 3 after cleaning with docusate, as depicted in **Fig.3e** and **Fig.3f**. FO membrane fouling is more difficult to mitigate in the PRO mode due to the poor mixing regime in the porous support layer [18]. It should be noted that the membrane was flushed with DI water for at least 5 minutes after static cleaning at a cross-flow velocity of 1.8 LPM to remove the excess docusate from the system.

After static cleaning, the circulation of DI water to clean the excess docusate also affected the water flux recovery. Additional tests were conducted for static cleaning in the FO mode, and the membrane was soaked for an additional one hour in DI water after 30 mins docusate static cleaning. The flux recovery was slightly higher (97% in cycle 1 and 93% in cycle 2). However, additional soaking will entail extra downtime for the system, and the water flux recovery is not as high compared to the 30 mins static cleaning. Additional tests were conducted, and the membrane was soaked for one hour in DI water after static cleaning in the PRO mode. This approach improved the water flux recovery to 94% in cycle 2 after the first cleaning and 91% in cycle 3. Membrane soaking in the DI water facilitates the back diffusion of fouling materials away from the membrane surface. Therefore, it cleans the support layer pores and promotes further water flux recovery in the PRO mode.

### 3.2. FE-SEM, contact angle EDX and FT-IR Characterisation of the membranes

The fouled and cleaned membranes were further analyzed by contact angle (Table 3), and the morphological changes were observed through FE-SEM, EDX analysis and FT-IR. The contact angle for the kinetic and static cleaned membranes (Table 3) was lowered due to the docusate cleaning, implying more hydrophilicity of the FO membrane after cleaning with the docusate solution compared to the pristine membrane. The contact angle for the static cleaned was slightly lower than the kinetic cleaned, probably due to the residual docusate on the membrane surface. A similar trend was observed in the PRO mode, with the static cleaned membrane having a slightly higher contact angle than the kinetic cleaned.

**Table 3**: Contact angle for pristine, fouled and cleaned membranes

| Membrane Surface/Mode of operation | Contact angle ($^{o}$) |
| --- | --- |
| Pristine active layer | 68.15 |
| Fouled active layer | 70.23 |
| Kinetic cleaned FO mode | 64.57 |
| Static cleaned FO mode | 63.22 |
| Pristine support layer | 52.31 |
| Fouled PRO mode | 57.35 |
| Kinetic cleaned PRO mode | 53.17 |
| Static cleaned PRO mode | 55.13 |

Further analysis of the membrane morphology using SEM and SEM-EDX can provide more insights into the foulants removal by docusate. The SEM analysis (Figure 4) of the pristine, fouled and cleaned membranes can give useful qualitative information about the pristine membrane, the nature of the fouling and the efficiency of docusate cleaning. (Fig.4o). The fouled membrane in the FO mode shows a uniform cake type of fouling layer formation. The cleaned membrane in the FO mode shows great resemblance with the pristine membranes (Figure 4a to 4h), proving the efficiency of the docusate with kinetic as well as static cleaning. In the PRO mode, the SEM images of the fouled and cleaned membranes are also compared with those of pristine membranes (Fig.4i to 4o). The cleaned membrane shows a little surface conditioning, probably due to the docusate. The static cleaned membrane also shows a good resemblance to the pristine membrane. It is evident that some residual docusate is still on the membrane surface after static cleaning in the PRO mode.

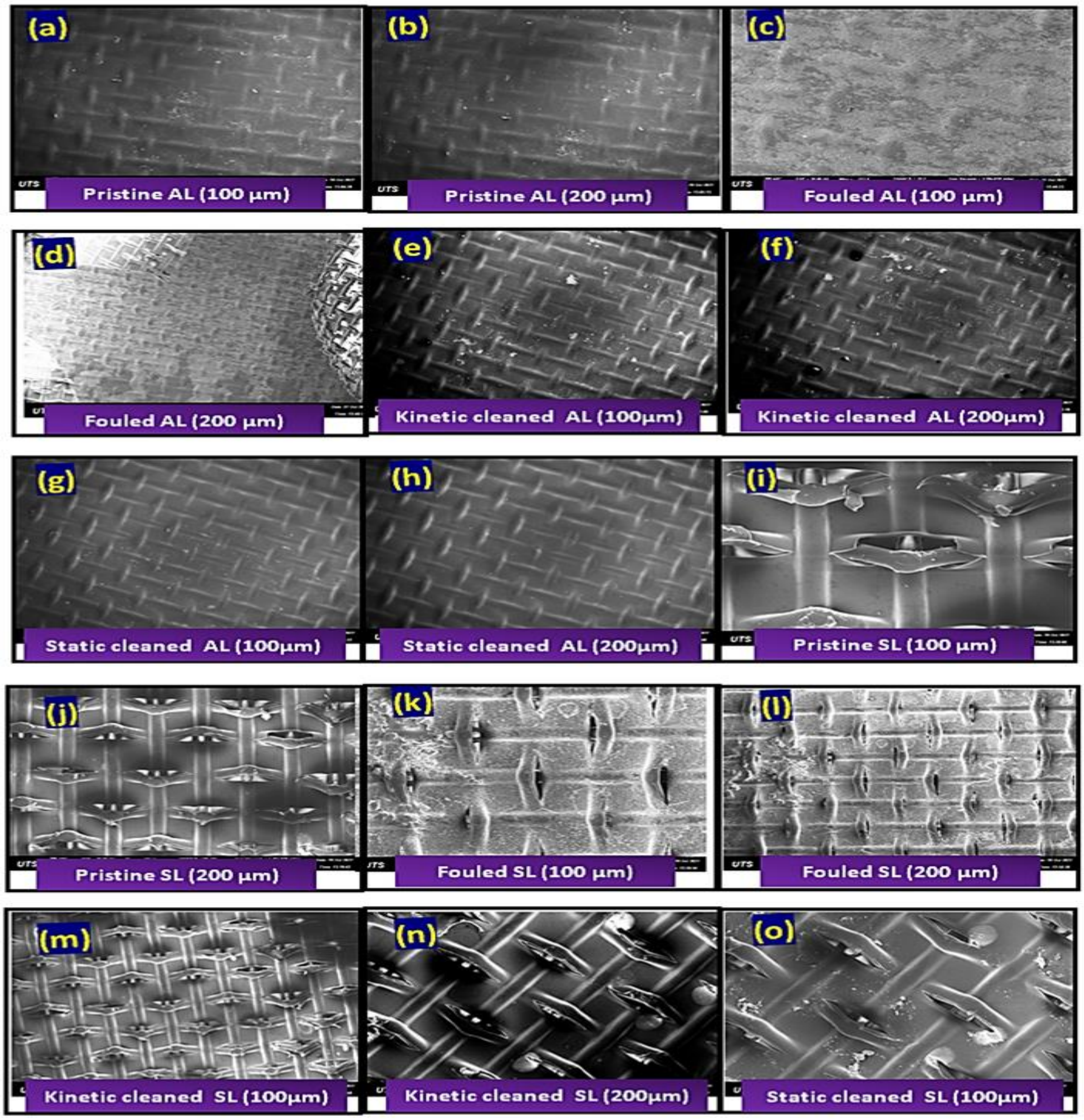


**Figure 4**: SEM images of pristine, fouled and cleaned membranes in the FO (active layer or AL side of the membrane) and the PRO mode (Support layer or SL side of membrane) a) pristine membrane in the FO mode at 100 µm, b) pristine membrane in the FO mode at 200 µm, c) fouled membrane in the FO mode at 100 µm, d) fouled membrane in the FO mode at 200 µm, e) kinetic cleaned membrane in the FO mode at 100 µm, f) kinetic cleaned membrane in the FO mode at 200 µm, g) static cleaned membrane in the FO mode at 100 µm, h) static cleaned membrane in the FO mode at 200 µm, i) pristine membrane in the PRO mode at 100 µm, j) pristine membrane in the PRO mode at 200 µm, k) fouled membrane in the PRO mode at 100

µm, l) fouled membrane in the PRO mode at 200 µm, m) kinetic cleaned membrane in the PRO mode at 100 µm, n) kinetic cleaned membrane in the PRO mode at 200 µm, o) static cleaned membrane in the PRO mode at 100 µm. All membranes were flushed with DI water after cleaning with docusate for five minutes.

The EDX analysis revealed further information regarding the efficiency of docusate cleaning (Table 4 and Figure 5). Table 4 lists the elemental composition of the virgin, fouled, kinetic and static cleaned membranes in both the membrane orientation. The EDX analysis of the fouled membrane indicates the presence of Ca, Fe, Na, Al, Si and Mg, and the dominant foulants are Fe, Al and Si. The presence of clay in the landfill leachate wastewater can lead to Aluminium silicate fouling, hence the higher percentage of these elements. The EDX spectra of the cleaned membranes in the FO mode with kinetic cleaning resemble the virgin membrane; however, some foulants are visible in the SEM-EDX images of the static cleaned membrane in the FO mode. This may be attributed to the absence of turbulence due to the static cleaning mechanism. These foulants can be easily flushed away with DI water, and thus flushing with DI water after cleaning with docusate is recommended for static cleaning.

**Table 4**: EDX analysis of virgin, fouled and cleaned membranes.

| Elemental composition | Virgin membrane | Fouled AL-FS | Kinetic Cleaned AL-FS | Static cleaned AL-FS | Fouled AL-DS | Kinetic Cleaned AL-DS | Static cleaned AL-DS |
|---|---|---|---|---|---|---|---|
| C | 56.2 ±2.6 | 41.3±1.9 | 58.3±2.7 | 55.2±1.2 | 35.4±2.2 | 42.77±7 | 66.8±4.7 |
| O | 37.9 ±1.8 | 34.9±1.6 | 36.5±1.8 | 38.2±0.9 | 33.0±2.0 | 48.95±9 | 29.1±2.2 |
| Ca | 5.1 ±4.1 | 2.7±3.9 | 4.2±4.2 | 0.0±4.6 | 9.1±4.8 | 0.55±4 | 1.6±6.6 |
| Fe | 0.6 ±1.3 | 6.9±1.3 | 0.3±1.3 | 5.0±1.5 | 5.7±1.6 | 3.33±1.3 | 1.8±1.9 |
| Na | 0.2 ±0.2 | 2.9±0.3 | 0.4±0.2 | 0.0±0.3 | 3.6±0.4 | 1.28±0.2 | 0.1±0.4 |
| Al | 0.0± 0.3 | 3.6±0.4 | 0.0±0.3 | 0.4±0.5 | 4.0+0.5 | 0.26±0.3 | 0.0±0.5 |
| Si | 0.0±0.4 | 6.9±0.6 | 0.0±0.3 | 0.4±0.5 | 8.3±0.8 | 0.94±0.4 | 0.0±0.6 |
| S | 0.2±1.0 | 0.0±1.0 | 0.0±1.0 | 0.0±1.1 | 0.0±1.2 | 1.63±1 | 0.0±1.6 |
| Mg | 0.0±0.3 | 0.8±0.3 | 0.3±0.3 | 0.7±0.3 | 0.8±1.2 | 0.28±0.3 | 0.6±0.4 |

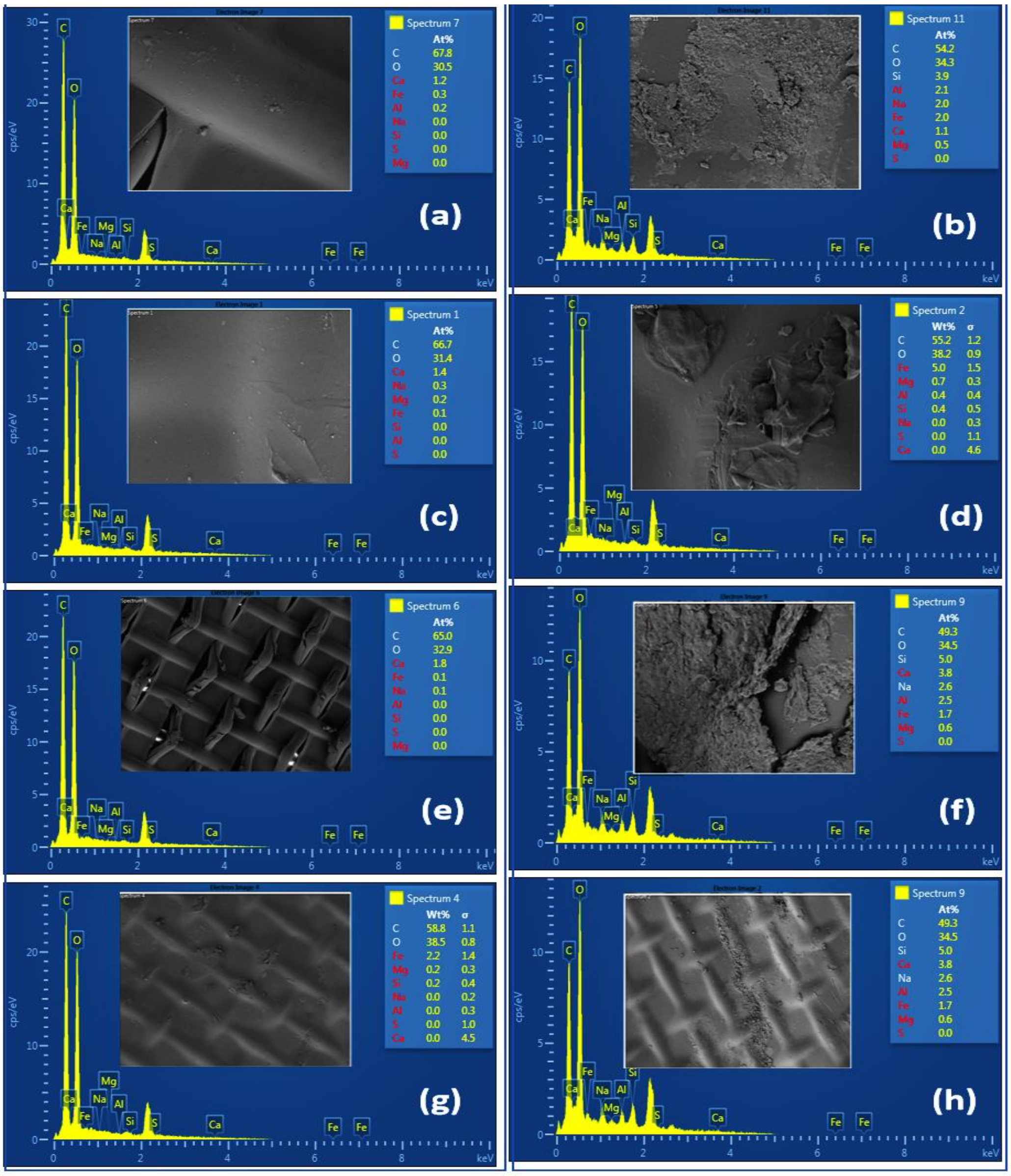


Figure 5, EDX spectra of membranes a) EDX spectra of the virgin membrane in the FO mode, b) EDX spectra of the fouled membrane in the FO mode, c) EDX spectra of the kinetic cleaned membrane in the FO mode, d) EDX spectra of the static cleaned membrane in the FO mode

The cleaning efficacy of the docusate cleaning was evaluated using FTIR analysis, which compared the characterization of cleaned and fouled membranes to that of the virgin membrane. The cleaned membrane with 0.1% for 30 mins static and kinetic cleaning in the FO mode and 0.1 % for 15 mins and 30 mins with kinetic and static cleaning in the PRO mode were reported only since these concentrations and durations had exhibited the best performance. The FT-IR spectrum of the docusate is also presented to assess whether any docusate was adsorbed onto the cleaned membrane. **Fig.6a** and **Fig.6b** present the FT-IR of docusate, pristine, fouled and cleaned membranes for the FO and the PRO mode, respectively. The majority of the bands in the FT-IR of the fouled membrane in the FO and the PRO mode may be attributed to organic foulants showing that organic fouling is the primary issue when treating landfill leachate wastewater. The FT-IR of the fouled membrane in the FO and PRO modes shows a visible diminishing of the peak at 1735, usually attributed to the fatty acids fouling [31]. The band stretching at wavenumber 1643 in the FO and the PRO mode may indicate protein fouling [32].

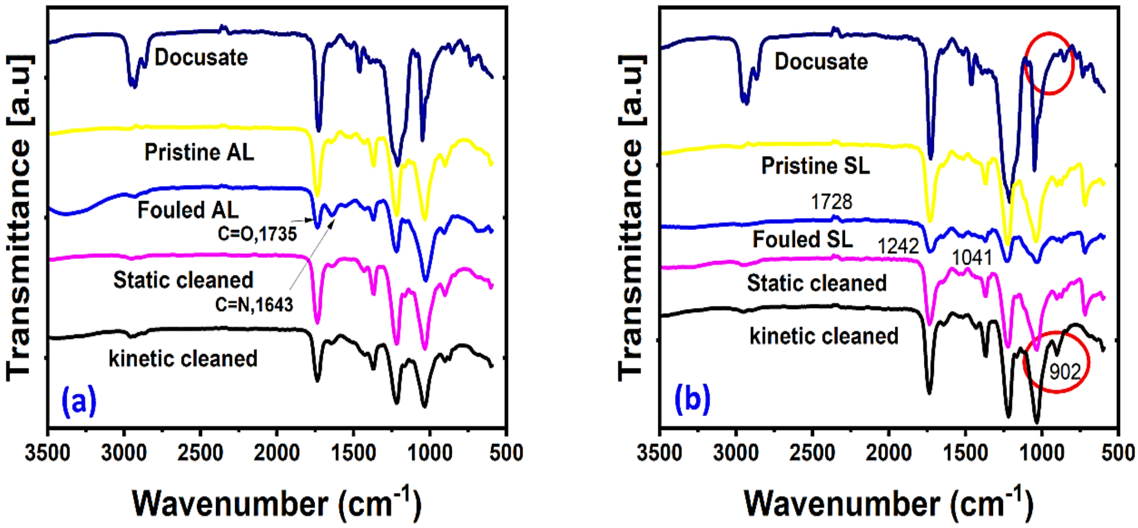


**Figure 6**, a) FT-IR spectra of membranes for docusate and pristine, fouled and cleaned membranes in the FO mode, b) FT-IR spectra for docusate and membranes for pristine fouled and cleaned membranes in the PRO mode.

The FT-IR of the cleaned membranes in both modes, i.e. the FO and the PRO, shows remarkable resemblance with the pristine membrane, implying cleaning with docusate was effective. The docusate adsorption to the membrane is visible for the wavenumber 902 $cm^{-1}$ in the PRO mode with kinetic cleaning. This band is absent in the pristine membrane and indicates that docusate might cause some pore plugging in the PRO mode. Similarly, the static cleaned membrane resembles the pristine membrane for the FO mode more than the kinetic cleaned.

## 3.3. Impact of cleaning on the rejection performance

The rejection performance of the cleaned docusate membrane was compared with the pristine membrane to assess the impact of chemical cleaning on the selectivity performance of the FO membrane. The samples were collected after the end of the first cycle for the pristine membrane and at the end of the third cycle for cleaned membranes with the docusate solution in the FO and the PRO mode. As presented in **Fig.7**, the pristine FO CTA membrane rejected 94% ±5 of the divalent magnesium ions. The membrane cleaned with docusate in the FO mode for 15 mins and 30 mins duration maintained almost the same rejection as the pristine membrane. Similar results were obtained in the PRO mode to reject divalent magnesium ions. Hence, cleaning the FO membrane with docusate has no impact on the retention of Mg ions compared to other cleaning protocols, such as hydrogen peroxide and acid cleaning with HCl, which leads to a decrease in the retention of divalent Mg ions [26]. Almost no differences are observed in rejecting docusate cleaned and pristine membranes for calcium, potassium, barium, and lead. Again this observation was superior to a previous study which indicated cleaning with HCl resulted in a slight decrease in the retention of Ba ions when treating landfill leachate wastewater [9].

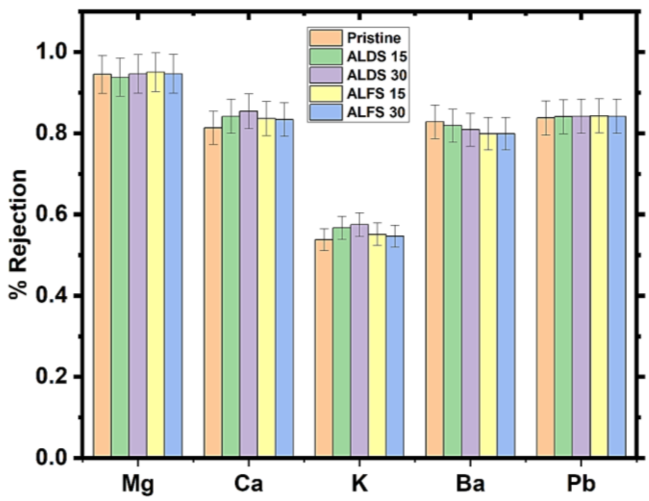


**Figure 7**, Impact of docusate cleaning on the rejection of contaminants in the landfill leachate wastewater, ALDS 15 and ALDS 30 refers to membrane cleaned in the AL-DS for 15 and 30 mins respectively, ALFS 15 and ALFS 30 refers to membrane cleaned in the ALFS mode for 15 mins and 30 mins respectively.

## 3.4. Energy consumption of static cleaning

Fouling and energy consumption are directly connected to each other. A higher degree of membrane fouling may lead to higher energy consumption by cleaning the FO membrane at high cross-flow rates or pumping chemical cleaning solutions. A major proportion of FO energy is consumed in the reconcentration of the draw solution for reuse, and the rest of the energy is consumed in pumping the feed and the draw solutions. The use of the FO process in this study for dewatering landfill leachate does not involve DS regeneration. The majority of energy utilized is pumping the feed solution and the draw solution, and the additional pumping energy for the chemical cleaning during the cleaning of the fouled membrane. Though it is claimed that physical cleaning protocols recover most of the FO water flux with low energy input, it is not supported by a systematic investigation [33]. In contrast, chemical cleaning consumes more energy than physical cleaning, particularly landfill leachate treatment [27]. The pumping energy of the FO system for the landfill leachate wastewater in this study can be estimated using Equation (3).

$$E = \frac{P_{FS} Q_{FS} + P_p Q_p}{\eta Q_P} \qquad (3)$$

where $P_{FS}$ and $P_p$ represents the hydraulic pressure of the landfill leachate wastewater (bars) and permeate water, $Q_{FS}$ and $Q_p$ indicates the flow rate of the FS and the permeate, and $\eta$ represents the pump efficiency, assumed to be 0.85. The baseline tests in the FO mode consumed an average of 0.024 ±0.01 kWh/m$^3$. The kinetic cleaning in the FO process consumed an average of 0.0011 ±0.001 kWh/m$^3$ per cleaning cycle. The kinetic cleaning was conducted at the same cross-flow velocity as the baseline tests, as higher cross-flow velocities would require more energy. Since excellent FR was achieved with a static cleaning in the FO mode, static cleaning would help save energy during the cleaning procedure (a saving of 0.0011 kWh/m$^3$) for each chemical cleaning cycle. It should be noted that flushing with DI water after static cleaning was for a very small duration (negligible energy consumption) and not considered in the energy consumption for static cleaning.

## 3.5. Mechanism of Action of sodium docusate

Sodium docusate is a laxative and medication to clear the ear canal blockage by cerumen (ear wax). Docusate penetrates the hardened stool, softens it and then dispersion it. This concept could be applied to membrane cleaning. As anionic surfactant, docusate has a hydrophobic tail and hydrophilic head, as shown in **Fig.8a.** Initially, sodium docusate cleaning involves the formation of micelles around the foulants in the wastewater (**Fig.8b and Fig.8c**), followed by the transfer of the foulants from the membrane surface to the bulk feed solution (**Fig.8d**). The transfer of foulants from the membrane surface is also evident from the experimental results as shown in **Fig.8d**. When docusate is applied for membrane cleaning, the micelles are formed then they break down partially to bind the foulants and cover the membrane surface [30]. In the next step, the binding of the micelles to the foulants causes displacement of the foulants from the membrane. Eventually, the surfactant occupies the membrane surface, including spots liberated by the foulants. Once the surfactant occupies the membrane surface, the membrane becomes more hydrophilic. After cleaning, anionic surfactant molecules on the membrane surface may also lead to an increased repulsion between the membrane surface and negatively charged organic foulants in the landfill leachate wastewater [34]. However, care should be taken because if the cleaning time and concentration of docusate are not optimized, the occupation of the membrane surface by docusate can act as an adsorption site for micelles leading to fouling. Fig. 8 depicts the flocs of foulant after cleaning with docusate.

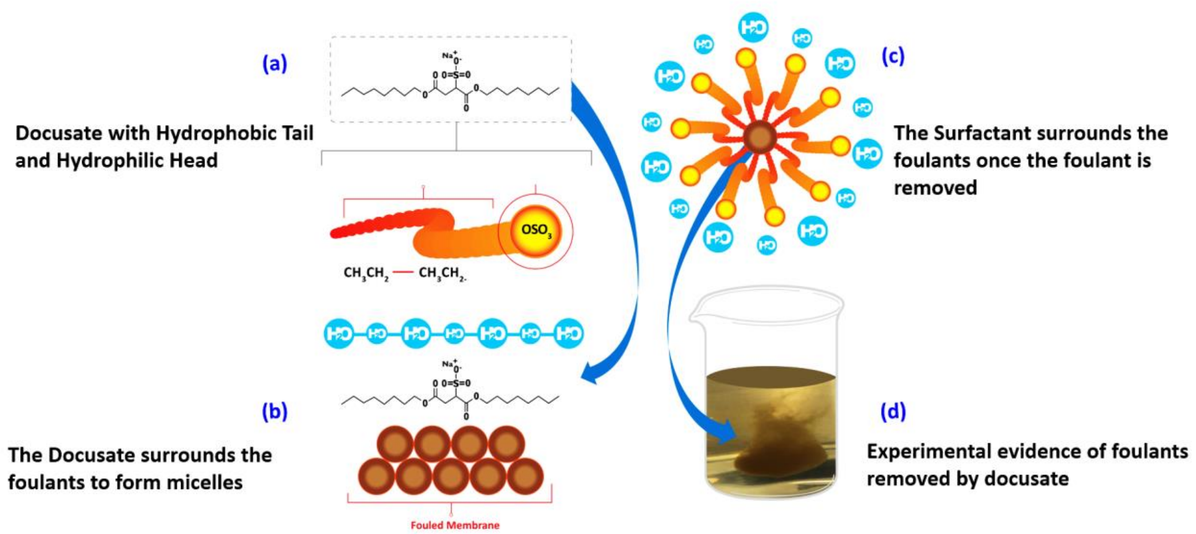


**Figure 8**, Flocs of foulants in the cleaning solution after membrane cleaning with sodium docusate

### 3.6. Cleaning efficiency and advantages compared to other surfactants

Compared to other surfactants such as SDS (sodium dodecyl sulphate), sodium docusate is an environmentally friendly chemical that is not harmful to humans as it is used in medical treatments. In contrast, SDS (sodium dodecyl sulphate) surfactant was reported to have adverse human and environmental impacts (https://doi.org/10.1016/j.yrtph.2021.105022). Many researchers have reported the negative impact of SDS on marine organisms [35]. Docusate is a strong foaming agent that provides more cleaning action than conventional surfactants. Furthermore, Docusate concentration for cleaning is 1 to 2% (circa 10 to 20 ppm), while SDS concentration for cleaning is between 0.1 to 0.3M (29 to 87 ppm). In terms of cost, sodium docusate is cheaper than SDS, making it an attractive cleaning agent. The cost of sodium docusate is 32% cheaper than SDS (Sigma Aldrich, Australia).

## 4. Conclusions

Sodium docusate was evaluated as a novel cleaning agent for fouled forward osmosis membranes. Although forward osmosis is considered a low fouling process compared to reverse osmosis, the process is still subjected to irreversible fouling, particularly when treating real wastewater with high organic content, such as landfill leachate, for longer durations. Although beneficial, traditional cleaning agents such as alkaline and acid cleaning cannot be suitable for all types of membranes or compatible with the types of wastewater. High water flux recovery was achieved in the FO mode with kinetic as well as static cleaning. In the PRO mode, the performance of the docusate was also satisfactory; however, care might be taken as the docusate can enhance pore-plugging in the PRO mode if circulated for a long time. A proportion of pumping energy can be saved with static cleaning, bringing long-term benefits for commercial projects using docusate as a cleaning agent.


## Acknowledgements

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# Supplementary information

## Sodium Docusate as a Cleaning Agent for Forward Osmosis membranes Fouled by Landfill Leachate Wastewater

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Table S.1. Charectaristics of wastewater analyzed through ICP-MS

| Parameter | Value | Unit |
|---|---|---|
| Turbidity | 32±2 NTU | NTU |
| Colour and appearance | Light to dark brown with visible particles | |
| pH | 7.1±2 | - |
| Total dissolved solids (TDS) | 2500 | mg/L |
| Mg | 80±3 | mg/L |
| Ca | 65±3 | mg/L |
| K | 421±3 | mg/L |
| $Ba^{2+}$ | 0.31±3 | mg/L |
| Pb | 0.0053±3 | mg/L |

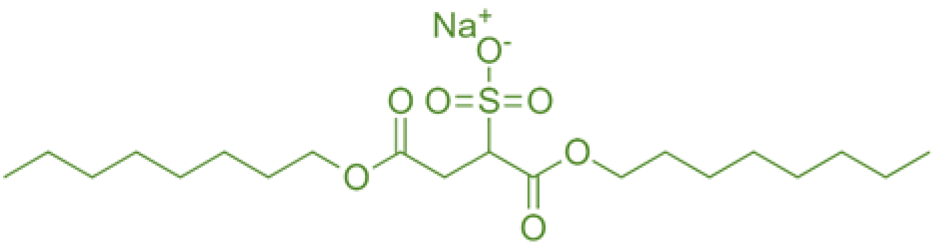

Figure S.1. chemical structure of sodium docusate

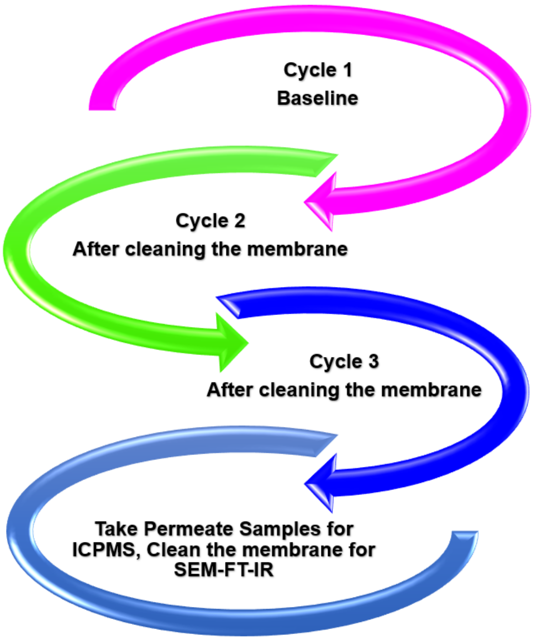


Figure S.2. Experimental protocol followed in this study.

**3.1. Membrane baseline performance with landfill leachate**

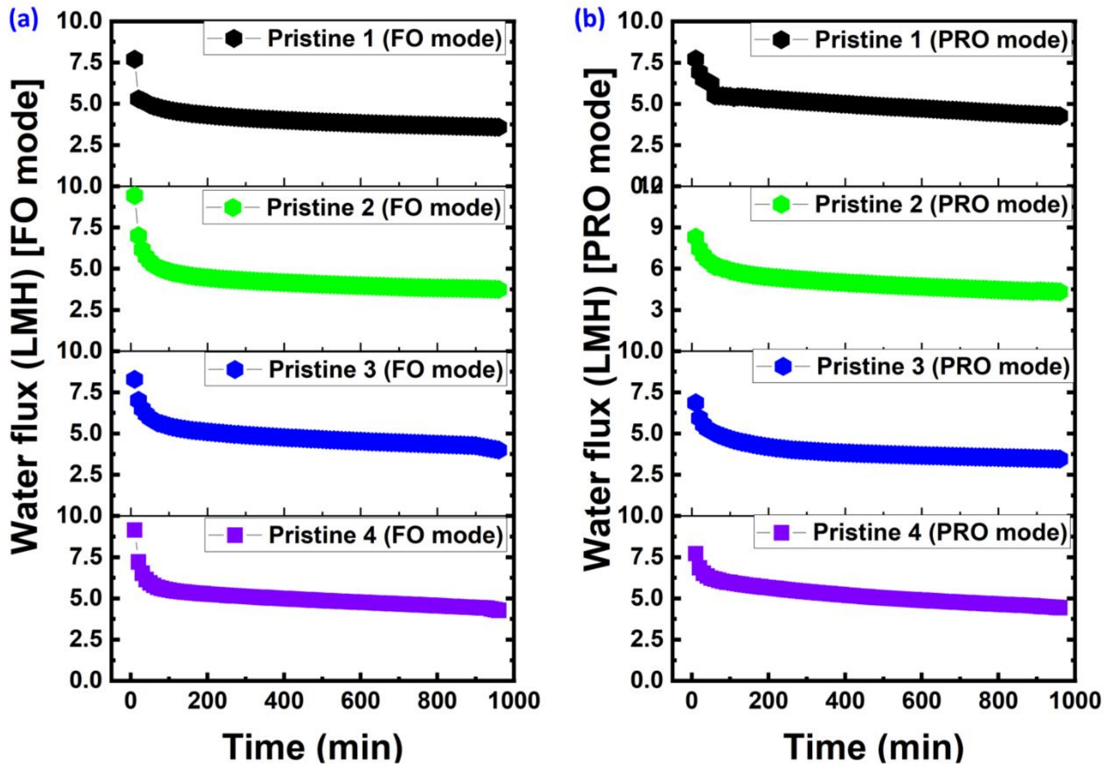


Fig.S.3. Baseline performance of Pristine membranes, a) FO mode, b)PRO mode

Table.S.2. Cleaning with DI water at 2 LPM

| Membrane mode | Baseline cycle flux (average) | Cycle 1 (average) | Cycle 2 (average) |
|---|---|---|---|
| FO | 4.3±2 LMH | 3.3 LMH | 2.8 LMH |
| PRO | 4.8 ±1 LMH | 3.1 LMH | 2.4 LMH |