

## Evaluation of direct osmosis high salinity (DO-HS) method by nitrate salts as draw solution in fouled RO membrane cleaning

Ali Borsalani, Seyed Mostafa Tabatabaee Ghomsheh\*, Masoumeh Mirzaei, Alireza Azimi

Department of Chemical Engineering, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

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### Abstract

In this study, cleaning of organic-fouled reverse osmosis membranes with direct osmosis high salinity (DO-HS) method by nitrate salts as draw solution was investigated. Synthetic feed water including alginate and natural organic matter were used as model organic foulants. Nitrate salts were selected as draw solution which has not been used for DO-HS cleaning until now. Physicochemical properties of these salts were investigated systematically and related to the DO-HS cleaning performance. The results revealed that the zinc nitrate (1.5 M) draw solution may generate high osmotic pressure more than NaCl. Also, the DO-HS cleaning by zinc nitrate as draw solution was found to be quite effective in cleaning reverse osmosis membranes (cleaning efficiency up to 110%) fouled by gel-forming hydrophilic organic foulants, such as alginate. The effect of physicochemical factors investigated included salt dose, salt type, organic foulants composition and cleaning contact time. It was found that the membrane needed to be cleaned for about 10 min because of the appearance of all foulants on membrane surface. Most importantly, DO-HS cleaning appeared to be an effective cleaning method, and found to be useful for membrane-based advanced wastewater reclamation, where a large fraction of the organic foulants is hydrophilic.

**Keywords:** Reverse osmosis; DO-HS cleaning; membrane; nitrate salt.

### Introduction

In reverse osmosis (RO) and nano-filtration (NF) membrane based water purification systems, fouling of all kinds—colloidal deposition and organic adhesion, formation and growth of bacterial biofilms, and precipitation of sparingly soluble minerals can limit plant performance, dominate operation, increase power consumption and maintenance concerns and increase the cost of water produced. Even with seemingly appropriate pretreatment

processes in place, full-scale NF and RO system can suffer from bio fouling and scaling, which increase applied pressure (such as energy and cost) and limit product water recovery, respectively. Therefore, fouling control at real NF and RO plants has been a decade's long battle despite exhaustive efforts to improve the membrane and module properties, optimize pretreatment processes, and improve the chemical cleaning agents [1,2].

\*Corresponding author: Seyed Mostafa Tabatabaee Ghomsheh

Tel: +98 (915) 3137897, Fax: +98 (61) 52372653

E-mail: Mostafa.tabatabaee@yahoo.com

Fouling type and accumulation rate depend strongly on feed water quality [3]. Fouling components and concentration decrease significantly when using various pretreatment methods such as microfiltration [4], sand filtration [5], activated carbon, and ultrafiltration [6]. Despite pretreatment, a fouling layer may develop on the membrane surface during the RO process. Membrane fouling can be mitigated with chemical, physical and physio-chemical. In practice, physical cleaning methods include sponge ball cleaning, forward and reverse flushing, backwashing, air flushing, ultrasonic, electrical fields and magnetic fields followed by chemical cleaning methods that are widely used in membrane applications [7,8]. However, only the chemical cleaning methods are widely applied for RO processes. In chemical cleaning, the choice of the cleaning agent is critical. The optimal selection of the cleaning agent depends mainly on the membrane material and type of foulants. Chemical method is an effective method to remove foulants, but this method, resulting in process downtime and membrane degradation, has also increased operation costs and requires stopping the RO plant operation [9]. Recently the new DO-HS technology offered a novel backwash approach for on-line membrane cleaning in RO operation without stopping the RO pump [10,11]. There was no interruption of RO operation in a new DO cleaning technology development where a high salinity solution (HS) was injected into the feed water for certain time that could induce multiple cleaning mechanisms composed of fouling lifting and sweeping as well as bio-osmotic shock and salt dissolve shock, thus could provide high cleaning efficiency [12].

There are a number of challenges that need to be overcome in order to achieve an effective DO-HS cleaning process. One of these key challenges is in developing a suitable draw solution that can generate a high osmotic pressure to produce high water flux at lower energy cost. The selection and/or development of suitable draw solution are therefore one of the big challenges to achieve the commercialization of DO-HS process, especially for cleaning RO membranes [13].

In this work, nitrate salts are explored as novel draw solutes for DO-HS applications. Compared with glucose, the nitrate salt can release ions in the aqueous solution, resulting in a superior osmotic pressure. A series of nitrate salts, e.g., potassium nitrate ( $\text{KNO}_3$ ), calcium nitrate ( $\text{Ca}(\text{NO}_3)_2$ ), sodium nitrate ( $\text{NaNO}_3$ ), zinc nitrate ( $\text{Zn}(\text{NO}_3)_2$ ), iron (II) nitrate ( $\text{Fe}(\text{NO}_3)_2$ ) and ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) are investigated as draw solutes for DO-HS cleaning. Effects of major parameters and operating conditions were systematically investigated via a RO pilot plant operation for future practical implementation.

## Experimental

### Materials and system

Six nitrate salts (purity  $\geq 98\%$ ) including, sodium nitrate, calcium nitrate, potassium nitrate, iron(II) nitrate, zinc nitrate, and ammonium nitrate were all purchased from Aladdin (China). Glucose (Glu,  $\geq 98\%$ ) and sodium chloride ( $\text{NaCl}$ ,  $\geq 99.5\%$ ) were supplied from Sino-pharm Chemical Reagent Co., Ltd. Cellulose triacetate (CTA) and polyamide thin film composite (TFC) flat-sheet RO membranes were employed (Zhejiang Mei Technology Co., Ltd, China). Some specifications of RO membrane is given in Table 1. Synthetic feed

solution produced in laboratory with chemistry of (20 mg/L of organic foulants (Alginate and natural organic matter), pH 6.0, 0.5 mM calcium, and 10 mm total ionic strength adjusted by

NaCl). Deionized water (DI water) was produced in laboratory using a Wuhan Pin Guan Ultrapure LAB purification system and utilized in this work.

**Table 1.** Membrane specifications

Type	Flat sheet membrane
Material	Cellulose triacetate coated with polyamide
Active area, m <sup>2</sup>	15
Feed spacer thickness (mm)	22
Permeate flow rate (Lm <sup>-2</sup> h <sup>-1</sup> )	65.2
Operation pressure	15-50
Operation pH	3-10
hydraulic resistance (m <sup>-1</sup> )	8.4×10 <sup>13</sup>
Stabilized salt rejection (%)	99.5

### RO laboratory-scale test unit

The RO system assisted by DO-cleaning in a laboratory-scale cross-flow test unit was equipped with pumps, tank (Super Duplex stainless steel) for feed, saline solution container, air regulator (R07-200-RNKA), feed temperature gauge, membrane chamber and membrane inlet and outlet gauge pressure. A HS tank (including draw solution) was added for the process of DO-HS. The feed solutions were recirculated by high pressure pump (Wanner Engineering, Inc., USA, and F20-111-2400/B) and a pulse of high concentration solution injected in to feed water after the membrane contaminated by foulants. Feed tank is capable of holding about 20 L of the solution. In order to discharge of solution after each test, the bottom of the tank is made bowl shaped and located on center. Tank outlet is equipped with a drain valve to full drain the solution from tank. Since, by pumping the fluid the tank's temperature rises, a cooling coil is placed vertically in the tank to control the feed temperature. This tank to provide pump's NPSH, have been installed at the proper height. Both permeate and retentate were

recirculated. The cross flow velocity and the operating pressure were adjusted by using a bypass valve in conjunction with a back-pressure regulator.

### Fouling and cleaning experiments

A laboratory-scale crosses flow RO membrane test unit was used for the DO-HS cleaning experiments. All the fouling experiments conducted in this study were performed using the fresh feed solution. The feed solutions were tested at their ambient pH (6± 0.45). Prior to the membrane fouling tests, baseline experiments were conducted with feed solutions lacking the foulants. This was followed by the membrane fouling experiments which were performed for three periods of ten days (30 days). This membrane orientation was chosen to ensure maximum fouling during the filtration period and also because the rough nature of the support layer allowed easy deposition of foulants particles. DO-HS cleaning efficiencies were determined at various chemical (salt concentration, salt type, and organic foulants composition) and physical (cleaning contact time) conditions. To confirm the reproducibility of the experiments,

selected fouling/cleaning runs were duplicated. The fouling rates and cleaning efficiencies obtained from the duplicate runs differed from their corresponding original experimental values by less than 5%.

Membrane cleaning followed immediately after the fouling runs. DO-HS washing is a physical membrane cleaning process where the draw solution was injected for certain time into the feed side. Permeate flux recovery after backwashing was calculated using Eq. (1) [14]:

$$\text{Flux Recovery (FR) (\%)} = J_c / J_0 \times 100 \quad (1)$$

Where  $J_c$  is the initial permeate flux after cleaning,  $J_0$  is the initial permeate flux when the clean membrane was

fouled for the first time, such that 100% flux recovery indicates total membrane permeability restoration and is 100% clean.

### Draw solution characteristics affecting DO-HS process performance

A high-efficient DO-HS cleaning process is mainly affected by several essential factors. These factors are, in general, related to the membrane performance, suitable draw solution and operating conditions. All the general draw solution characteristics and their impacts on the process performance are listed and summarized in Table 2.

**Table 2.** General draw solution characteristics affecting DO-HS cleaning process performance [15]

Draw solution characteristics	Impact on DO-HS cleaning process
Osmotic pressure	high osmotic pressure of the draw solution can generate a high driving force across the membrane in DO-HS process
Molecular weight ( $M_w$ )	The size of solutes effect on osmotic pressure. Molecules with low molecule weight produce high osmotic pressure than larger $M_w$ for equal mass of draw solution but induce higher reverse draw solute flux than larger $M_w$
Viscosity	Low viscosity is desirable for draw solution because leads to high water backwash fluxes
Water solubility	High solubility induces high osmotic pressure and therefore can achieve high water backwash

The osmotic pressure related to each draw solution is expressed in next section. Relative viscosities ( $\eta_R$ ) of draw solutions with various concentrations (1–2.5 M) against that of DI water (at the same temperature) were determined using Equation 1 [13]:

$$\eta_R = \frac{\eta_{\text{salt}}}{\eta_{\text{water}}} = \frac{t_{\text{salt}} \rho_{\text{salt}}}{t_{\text{water}} \rho_{\text{water}}} \quad (2)$$

where  $t_{\text{salt}}$  and  $t_{\text{water}}$  (s) are the respective outflow time of the draw solution and DI water, determined using a commercial Ubbelohde viscometer with temperature maintained by a water bath; their

densities, were measured by a portable density meter (DMA 35, India). In addition, the performance of DO-HS cleaning process is however affected by draw solution concentration.

Most studies have shown that higher water fluxes can be achieved by increasing the draw solution concentration. However, contrary to the theoretical solution-diffusion model, which establishes a linear relation between water fluxes and draw solution concentration, experiments have shown that this relation is non-linear. Linear relation is observed at lower concentrations, but at higher draw

solution concentration, a logarithmic relationship has been visually observed. [16–19].

Despite the general characteristics mentioned before, draw solution temperature can impact on the process performance because the properties of draw solution such as osmotic pressure, viscosity and diffusivity are affected by temperature.

Backwash fluxes in DO-HS process improved significantly at higher draw solutions temperature as observed by most studies. It is due to reduced water viscosity and therefore enhanced mass transfer with increasing temperature [20].

#### Evaluation of performance direct osmosis of high salinity (DO-HS) backwash

DO-HS membrane backwash cleaning method can be initiated by a high osmotic pressure solution injected for certain time into the feed side. This stream of draw solution moves along the membrane matrix in the pressure vessel and changes the process from reverse osmosis to forward osmosis. The DO-HS method is applicable in wastewater or seawater RO plants, because it is not dependent on raw water osmotic pressure [21].

For the DO-HS process to be most effective, the permeate pressure has to be kept high enough, and the reject flow valve has to be open to increase the shearing velocity. Practically, two pumps work simultaneously during the DO-HS process; the high pressure feed flow centrifugal pump and the osmotic pump. Power for the operation of the osmotic pump is obtained from the draw solution. The osmotic pump pushes the permeate from the low gauge pressure permeate channel to the high gauge pressure feed channel. When high osmotic pressure draw solution moves along the membrane,

fouling on the membrane become lifting.

The performance of DO process to RO membrane cleaning greatly depends on the selection of suitable draw solution as it is the main source of the driving force in this process. The primary characteristics essential for any draw solution is high osmotic pressure, much higher than the feed solution. The osmotic pressure of the ideal dilute solution is defined based on the theory proposed by Van't Hoff as shown below [22]:

$$\pi = n \left( \frac{c}{M_w} \right) RT \quad (3)$$

where  $n$  is the number of moles of species formed by the dissociation of solutes in the solution,  $c$  is the solute concentration in g/L of solution,  $M_w$  is the molecular weight of the solute,  $R$  is the gas constant ( $R = 0.0821$ ) and  $T$  is the absolute temperature of the solution.

In regard to general solutions, measuring has to be done at concentrations. Formula for osmotic pressure then comes after development into Virial order to the following form [23]:

$$\frac{\pi}{cRT} = 1 + Bc + Cc^2 + Dc^3 + \dots \quad (4)$$

where  $B$ ,  $C$ , etc. are Virial coefficients that can be determined empirically by fitting experimental osmotic pressure data, and generally the determination of  $B$  and  $C$  is sufficient to reproduce observed data.

The water passage through the RO membrane is generally described and theoretically calculated by following equation [24]:

$$j_w = A \cdot \sigma \cdot \Delta \pi \quad (5)$$

where  $j_w$  is the water flux;  $A$  is the water permeability constant of the membrane;  $\sigma$  is the reflection

coefficient and  $\Delta\pi$  is the osmotic pressure differential respectively.

On contrary, water driven under hydraulic pressure ( $\Delta P$ ) transfers through a RO membrane from the higher salt concentration side to the lower one and water flux can be calculated using Eq.6:

$$j_w = A(\Delta P - \sigma \cdot \Delta\pi) \quad (6)$$

The driving force of RO process is the pressure differential denoted in the following expression [22]:

$$\Delta P_{driving} = \Delta P - \Delta\pi = (P_F - P_p) - (\pi_F - \pi_p) \quad (7)$$

where,  $P_F$ ,  $P_p$ ,  $\pi_F$  and  $\pi_p$  are the feed pressure, permeate pressure, feed osmotic pressures and permeate osmotic pressure respectively.

The positive driving force drives water from the feed side to the permeate side in a RO process ( $\Delta P_{driving} > 0$ ) while in the backwash cleaning (DO-HS) a negative driving force is required to drive water from the permeate side to the feed side ( $\Delta P_{driving} < 0$ ).

By introduction of a high saline solution to the feed side, high  $\pi_F$  can be easily gained. So, higher driving force for backwash cleaning can be achieved. Therefore, this method is called as DO backwash cleaning will continue since  $\pi_F$  dominates the backwash process.

#### Membrane surface characterization

The surface structure of membranes and roughness of the synthesized substrates and layered membranes were investigated using a KYKY EM3200 scanning electron microscope (SEM) and an atomic force microscope (AFM: DME model C-26, Switzerland) respectively. SEM images were made with an accelerating voltage of 20 Kv. The membrane was then coated with a

thin film of gold to minimize sample charging problems. To AFM image, small squares of the membrane (approximately 1 cm<sup>2</sup>) were cut and glued on glass substrate. The membrane surfaces were imaged in a scan size of 5  $\mu\text{m} \times 5 \mu\text{m}$ .

#### Results and discussion

##### Characterization of draw solution property

The physicochemical properties of six nitrate salts with sodium chloride and glucose used as draw solutes in this study are listed in Table 3, including the molecular weight, water solubility, and the pH value of the solution. They are all important properties of the draw solute to determine its final performance. Basically, higher molecular weight and higher water solubility of the draw solute are more desirable, because brings out a higher water flux in the DO-HS cleaning process. With regards to the pH value of the draw solution, it needs to be in the range of the membrane tolerance. As can be seen from Table 1 all nitrate salts have much larger molecular size than the glucose. It can also be found that the solubility of ammonium nitrate (84 M) is higher than those of other nitrate salts, sodium chloride and glucose; whereas Iron(II) Nitrate has lower solubility of 2.46 M than other salts, indicating that this draw solution may generate a negligible water back wash flux in DO-HS cleaning process. Because an ion-type draw solute with high water solubility could generate more ions than the solute with poor water solubility under the same conditions, a higher osmotic pressure may be resulted. In addition, all of solutions have neutral pH values, which are suitable for RO membranes with pH tolerant ranges of 3-10. However, iron (II) nitrate and ammonium nitrate have relative lower pH of 3.87 and 4.68 than

other salts, because Fe (II) and ammonium ions may partially hydrolyze in the aqueous solution and generate some hydrogen ions, leading to a low pH value [25].

**Table 3.** Physicochemical properties of draw solutes case study

Compound	Molecular weight(gr/mol)	Solubility (M)	Solution PH(2 M, 25°C)
Sodium nitrate	85	10.5	5.98
Calcium nitrate	164.10	7.9	4.86
Potassium nitrate	101.1	3.3	5.99
Iron(II) Nitrate	180	2.46	3.87
Zinc nitrate	189	9.78	5.2
Ammonium nitrate	80.04	84	4.68
Sodium chloride	58.5	5.4	6.98
Glucose	180.06	3.83	6.67

In addition to molecular weight, solubility and pH parameters, to consider the potential of the six nitrate salts as draw solutions, the osmotic pressure and the viscosity of their solutions should be investigated. Generally, a high osmotic pressure of the draw solution can generate a high water backwash flux in DO-HS cleaning process, whereas the high viscosity leads to high energy consumption for fluid pumping in cleaning process. Table 4 summarizes the osmotic pressure of nitrate salts, Glucose and NaCl solutions at concentration of 2 M.

The osmotic pressure was calculated using OLI Stream Analyzer 2.0 (OLI

Systems Inc., Morris Plains, NJ). As can be observed that zinc nitrate and calcium nitrate have higher osmotic pressure compared to other salts draw solution due to high solubility and dissociation ability to ions. It should be noted that osmotic pressures of six nitrate salt solutions are more than of glucose, because nitrate salts and NaCl are both electrolytes and can partially or fully dissociate into free ions in the aqueous solution, whereas the glucose (nonelectrolyte) cannot. In compared to NaCl, zinc nitrate and calcium nitrate have higher solubility, fully dissociate into free ions and produce more number of ions (each molecule produce 3ions).

**Table 4.** Osmotic pressure of six nitrate salts, glucose and sodium chloride solutions at concentration of 2M

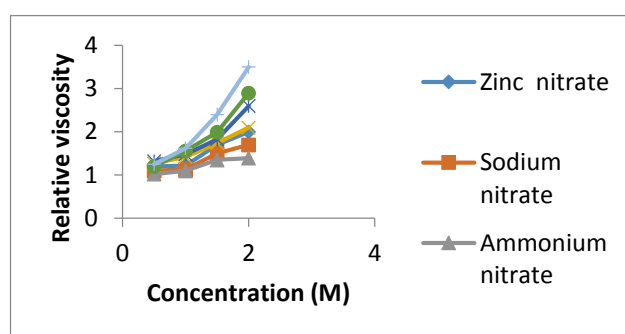
Osmotic pressure (bar)								
Concentration (M)	Sodium nitrate	Calcium nitrate	Potassium nitrate	Iron(II) nitrate	Zinc nitrate	Ammonium nitrate	Glucose	Sodium chloride
2	81	108.5	64.5	85.3	112.6	64	58.5	100.02

Figure 1 also gives relative viscosities of nitrate salts and NaCl solutions as a function of the solution concentration. The result displays that relative viscosity of these solutions all

increase remarkably with the concentration increase. But the difference will be greater at higher concentration. It should be noticed that all viscosities of nitrate salts and NaCl

solutions with concentration less than 1 M still remain low and those of nitrate salt solutions are slightly higher than that of NaCl solution. These value much lower than those of most other reported draw solutions [26-29]. Because a draw solution with a lower viscosity is favorable to enhance the DO-HS back wash cleaning performance, this result indicates that

zinc nitrate draw solution have better DO-HS performance (Due to its other properties) than that of other salt nitrate draw solution with the same concentration. Since this salt produces more osmotic pressure than other salts (nitrate salts, NaCl and glucose) and has good solubility, it can be a good candidate for osmosis-assisted processes.

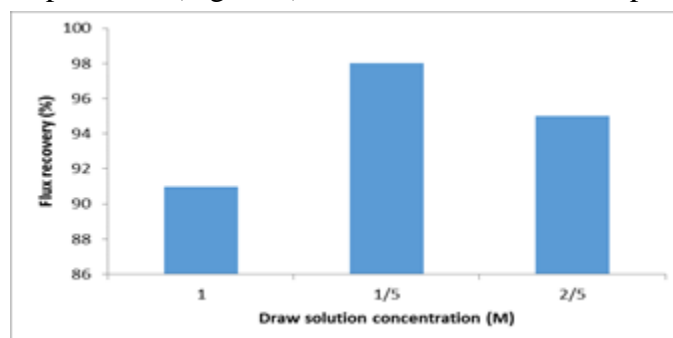


**Figure 1.** Effect of concentration on the relative viscosities of nitrate salts and NaCl draw solutions at 25 °C

#### Effect of salt concentration on cleaning of fouled RO membrane

To evaluation the effect of salt concentration (osmotic driving force) on the cleaning of fouled RO membrane, different backwash salt solution concentrations (1.0, 1.5, and 2.5 M  $Zn(NO_3)_2$ ) were used to induce water permeation. The results revealed some correlation between the increases in backwash salt solution concentration and permeate recovery. An increase in backwash salt solution concentration up to 1.5 M increased the permeate flux recovery from 91 up to 98% (Figure 2).

This might be explained by the fact that the induced backwash water permeation weakened the structure of the fouling layer leading to its removal from the membrane surface. The 1.5 M salt solution recorded higher membrane flux which corresponded to higher water permeation rate. Increasing the backwash salt concentration beyond 1.5 up to 2.5 M did not positively influence on permeate flux recovery. A slight decrease of 4% was recorded for salt concentration of 2.5 M. This result was due to the chemical aspect of the osmotic backwash process.



**Figure 2.** Effect of draw solution concentration on flux recovery (t=5 min)



### Organic foulants composition governing cleaning efficiency

The effect of fouling layer structure on its removal was evaluated using DO-HS backwash process. Fouling runs were performed with feed waters containing different mass ratios of alginate to natural organic matter (NOM), with the total foulants concentration maintained at 20 mg/L. Feed waters with different organic foulants composition will likely form organic fouling layers which are structurally different from one another, thus resulting in different cleaning efficiencies with the same cleaning solution. Following the fouling runs, each cleaning experiment was performed with 1.5M  $Zn(NO_3)_2$  solution. The cleaning efficiencies determined from the subsequent cleaning experiments are presented in Figure 3.  $Zn(NO_3)_2$  was less effective in cleaning membranes fouled by feed waters with higher NOM content. This indicates that the efficiency of DO-HS

cleaning is dependent on the type of organic foulants, and that this cleaning seems more applicable when the major foulants are polysaccharide-like substances (such as alginate) rather than Humic-like substances (such as NOM). The lower efficiency of DO-HS cleaning for the NOM-fouled membrane when compared to the alginate-fouled membranes is attributed to the hydrophobic nature of NOM. The swelling of the hydrophobic NOM fouling layer on the membrane surface during cleaning is expected to be less pronounced when compared to the hydrophilic alginate fouling layer. This likely results in less diffusion of zinc ions into the fouling layer and, hence, a limited ion-exchange reaction between zinc ions and ions bound to NOM. In fact, visual inspection after the cleaning of the alginate-fouled membrane showed the disappearance of the alginate gel layer, while NOM deposition on the membrane surface was few visible after DO-HS cleaning.

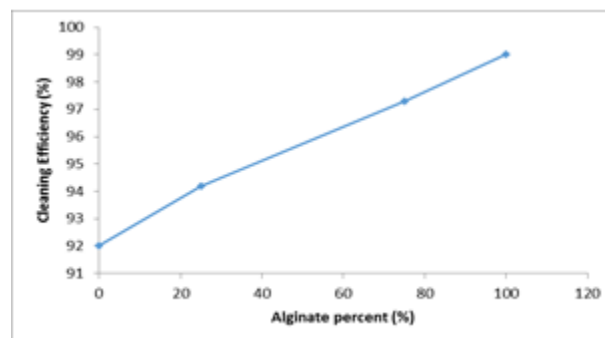


Figure 3. Influence of feed water organic composition on DO-HS cleaning of organic-fouled RO membranes (1.5M  $Zn(NO_3)_2$  as draw solution,  $T=25^\circ C$ )

### Cleaning contact time

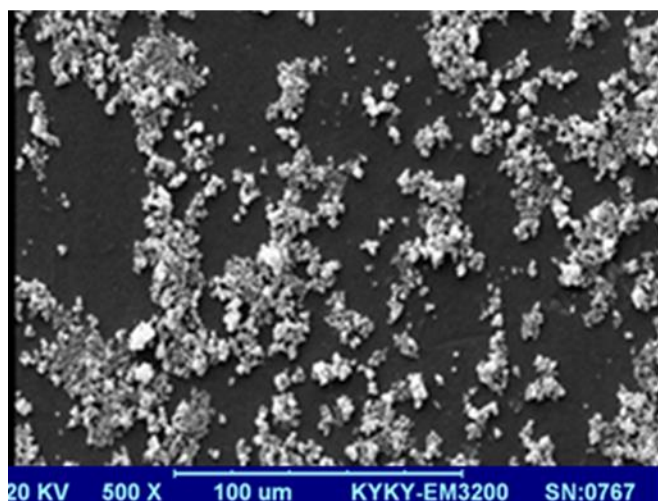
The influence of cleaning contact time on DO-HS cleaning efficiency was investigated. DO-HS cleaning was performed for 5 and 10 min with two different  $Zn(NO_3)_2$  concentrations (1 and 1.5 M). For the cleaning with 1M  $Zn(NO_3)_2$ , cleaning efficiency increased from 91% to 97% with increasing cleaning contact time from 5 to 10 min;

for 1.5M  $Zn(NO_3)_2$ , 98% and 110% cleaning efficiencies were obtained for 5 and 10 min cleaning times, respectively. These results showing that, for favorable cleaning agents in terms of chemical reaction in DO-HS process, increasing cleaning time enhances the cleaning efficiency.

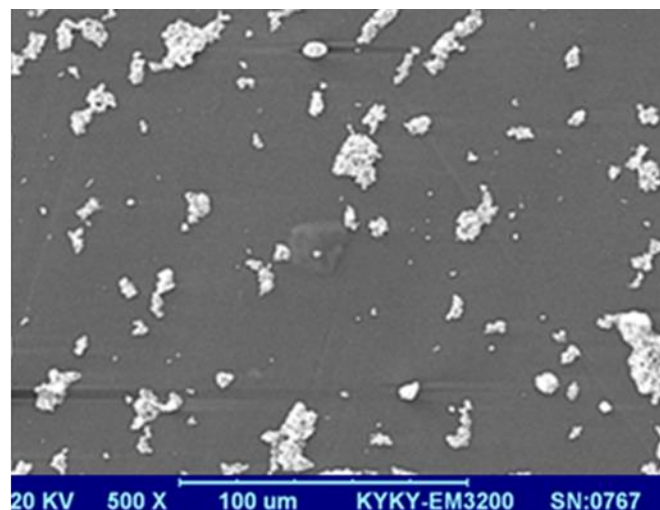
### Membrane surface analysis

The surface morphologies of the membranes were observed by SEM and AFM and the obtained results are shown in Figures 4 and 5. Analysis by SEM provides a visual and quantitative characterization of the surface of RO membrane after and before DO-HS cleaning. Fouled membranes being cleaned for different time were characterized by SEM. It can be seen by comparing the surface SEM images of membranes, the clean degrees of membrane surface after cleaning for different time increased in the sequence of 5 min < 10min. A large amount of white crystal substances disappeared in the fouling layer after 5 min cleaning, indicating that the membrane was cleaned to some extent. The SEM images of the membrane cleaned for 10 min were quite similar to that of the membrane before fouling. The foulants were cleaned with the backwash force

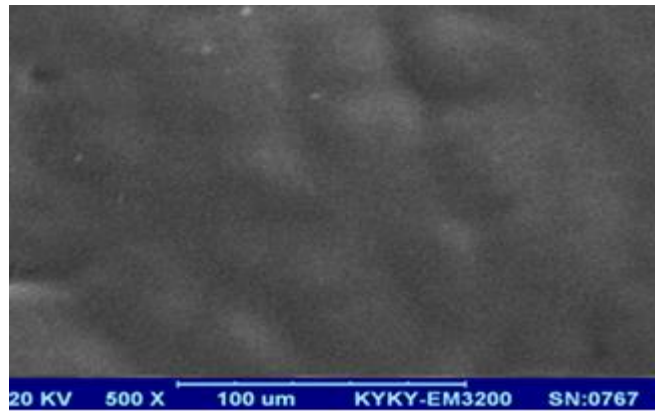
by two steps: foulants lifting and sweeping. The thickness of fouling layer on membrane surface was different. Inevitably, it would take different time to loosen up the foulants. So the membrane surface became increasingly cleaner during the 10 min and then leveled off. This confirmed that the best cleaning time for the membrane was 10 min. AFM images of the fouled membrane and fouled membranes being cleaned for different time were shown in Fig. 5. These images confirm that the cleaned membrane has smoother structure than the fouled membrane. The surface roughness parameters of membranes in scan areas of 5  $\mu\text{m} \times 5 \mu\text{m}$  were calculated by DME SPM software and are presented in Table 5. As shown in Table 5, the surface roughness of RO membrane with 5 min cleaning time is higher than 10 min.



(a)

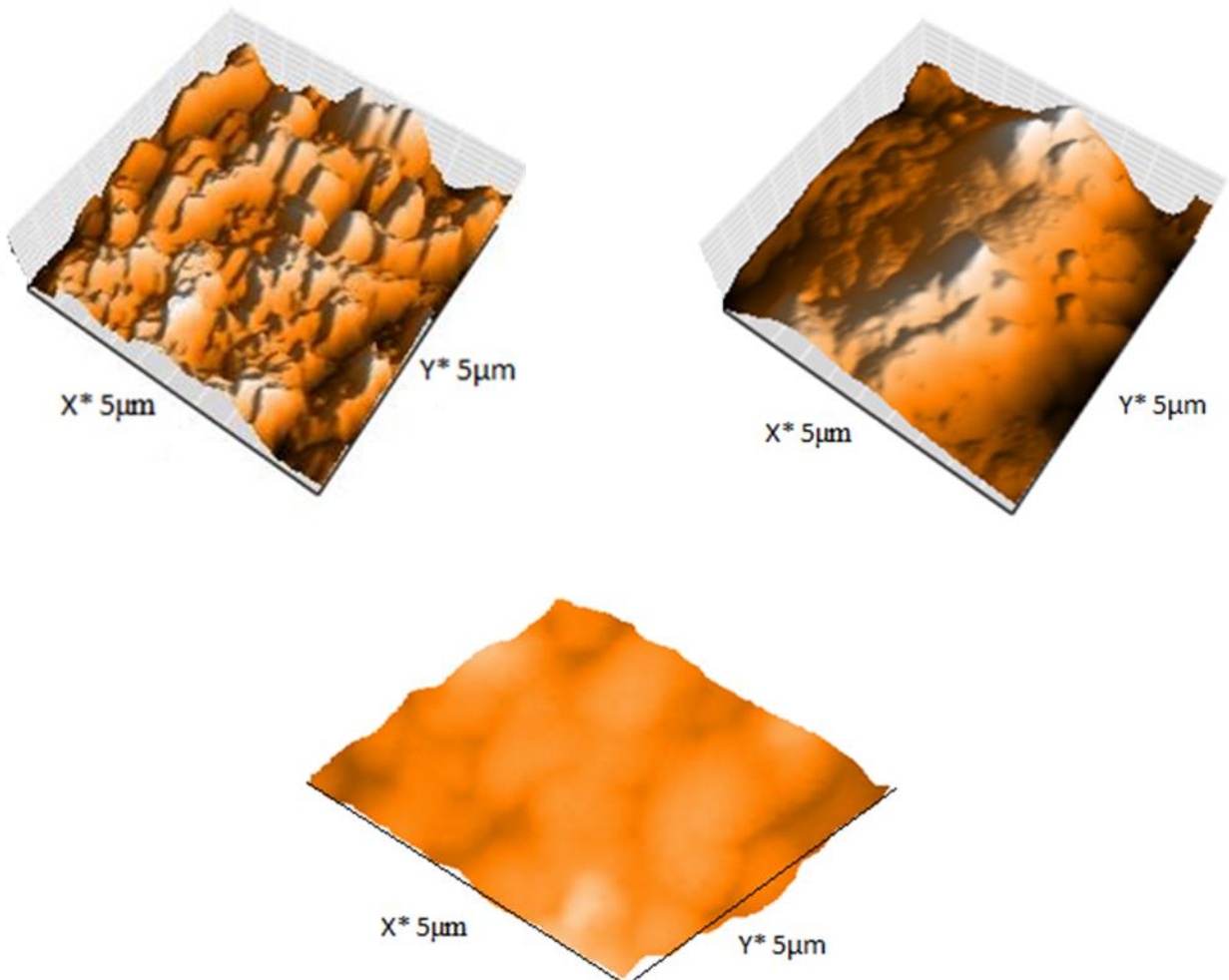


(b)



(c)

**Figure 4.** SEM images of the fouled and cleaned RO membrane samples. (a) Fouled RO membrane sample. (b) Membrane cleaned for 5 min (c) membrane cleaned for 10 min.μ



**Figure 5.** AFM images of (a) fouled RO membrane, (b) fouled membrane cleaning for 5 min, (c) fouled membrane cleaning for 10 min

**Table 5.** Roughness parameters of membrane surface calculated with DME SPM software

Membrane	S <sub>a</sub>	S <sub>q</sub>	S <sub>z</sub>
Fouled RO membrane sample	30.4	13	42.6
Membrane cleaned for 5 min	7.7	5	15.3
Membrane cleaned for 10 min	3.3	4	9.4

### Mechanisms of DO-HS cleaning

A cross-linked fouling layer is formed on the membrane surface in the presence of calcium ions, which bind to organic foulants and form bridges between adjacent foulants molecules. During filtration and draw solution injection, the alginate gel layer swells and, thus, results in the lessening of the structural integrity of the gel network. Following the weakening of the structural integrity of the gel network, an actual breakup of the gel network takes place as a result of an ion-exchange between Zn<sup>2+</sup> and Ca<sup>2+</sup>, which results in the freeing of Ca<sup>2+</sup> ions and alginate molecules from the cross-linked gel network. A layer-by-layer removal of these reaction products from the fouling layer to the bulk solution takes place through the hydrodynamics/mass transfer.

In this way, by the salt penetration to the layer, the structure of it becomes loose. On the other hand, osmotic pressure induced by salt draw solution causes high flow backwash water which faces the membrane and consequently the weakened gel layer attracts water prompted by the higher osmotic gradient; it then expands in thickness weakening its attachment onto the membrane surface. In the process the permeating water forms a barrier between the loosened gel layer and the membrane. The weakened layer is then lifted off the membrane surface by the tangential shear force induced by the cross-flow velocity of the draw solution. So, the membrane surface cleared from foulants.

### Evaluation of DO-HS cleaning performance

The effectiveness of DO-HS cleaning process is showed by measuring the relative permeability (which is the ratio of permeability at the time over that on Day 1), of RO membranes as a function of passing time of the pilot plant operation. The capacity of osmotic backwash in restoring good operational flux was evaluate. The membrane was fouled and cleaned repeatedly over three period of time (per ten days) .We therefore compared the initial permeate flux decline rates after cleaning cycles to those when the membrane was initially used and the obtained rates are listed in Table 6. According to the values presented in Table 6, the initial permeate flux decline rate increased with the number of backwashing cycles; from 0.0338 to 0.065 h<sup>-1</sup> by the end of the 2nd cycle. Although, it became lower again after the 3rd backwash cycle. The total volume of accumulated permeate over the backwash cycles suggests that the membrane had a similar performance even after three backwash cycles. In addition to measurement of the initial permeate flux decline rates, the volume of permeate over the backwash cycles was collected. These volumes illustrated that the membrane had a similar performance even after three backwash cycles. The total amounts of 2714mL and 2723 mL were collected as permeate volumes after 10 and 20 days of filtration and were close to the 2782mL collected when the membrane was used for the first time. After the 3rd cleaning cycle the permeate volume declined by only 3.12% when

compared to that of the initial experiment. Therefore, it can be concluded that osmotic backwash was

successful in restoring membrane permeate flux as well as maintaining operational flux.

**Table 6.** Initial permeate flux decline rates ( $\text{h}^{-1}$ ) and corresponding accumulated permeate volumes for three DO-HS cleaning cycles

Membrane	Initial permeate flux decline rate ( $\text{h}^{-1}$ )	Collected volume of permeate (mL)
Initial fouling run	0.031	2782
After 10 days (first)	0.0338	2714
After 20 days (second)	0.065	2723
After 30 days (third)	0.043	2695

### Conclusion

In this research study, suitability of nitrate salts as novel draw solutes in the DO-HS cleaning process was demonstrated using a series of lab-scale experiments. The physicochemical (solubility, molecular size) and solution properties (osmotic pressure, viscosity, and pH value) were demonstrated systematically. Among the six draw solutions, zinc nitrate draw solution with desirable big molecule size, highest water solubility, and neutral pH value, low relative viscosity, and highest osmotic pressure exhibits a comparable water flux to that of NaCl draw solution, which is superior to most other nitrate salt draw solutions. Based on the results from the fouling/cleaning experiments and the AFM force measurements, it was proposed that lifting and sweeping of gel layer that weakened by osmotic back wash are the major mechanisms involved during the DO-HS cleaning. Fouling layer removal was found to be a function of both cleaning water permeation rate and shear forces induced by the cross-flow velocity sweeping across the membrane surface. This was achieved by the concentration of 1.5 M zinc nitrate draw solution and cleaning time of 10 min. Also the DO-HS process was found to be effective not only in restoring the permeate flux of fouled RO membranes, but in

maintaining operational flux as well. Results showed that zinc nitrate as draw solution was quite effective in cleaning reverse osmosis membranes (cleaning efficiency up to 110%).

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