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Biofouling and scaling control of reverse osmosis membrane using one-step cleaning - potential of acidified nitrite solution as an agent

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Abstract

Biofouling is generally regarded as a major issue in reverse osmosis (RO) membrane filtration. Two-step chemical cleanings with alkaline and acidic agents are typically applied to restore the treatment capacity. In this study, the feasibility of one-step cleaning using free nitrous acid (FNA) was investigated as a novel low cost cleaning agent. The FNA cleaning solution was prepared by acidification of a sodium nitrite solution with hydrochloric acid. Seven fouled RO membranes collected from full-scale wastewater recycling and desalination plants were used to perform lab-scale cleaning trials. Membrane fouling characterisation revealed six of out of seven membranes were mainly bio-fouled, while one membrane was severely fouled by calcium carbonate. This study showed the feasibility of using FNA at pH 3.0 for biomass removal as well as for calcium carbonate scaling removal. The results from the lab-scale cleaning tests suggested that FNA can be used as a single cleaning agent for both biofouling and scaling removal. Cost analysis showed that FNA is a cost-effective solution for biofouling and scaling removal in RO filtration applications.

Keywords: Biofouling; Free nitrous acid; Membrane cleaning; Reverse osmosis.

Highlights

- Free nitrous acid (FNA) is proposed as a novel cleaning agent for RO membranes.
- FNA removes biomass and inactivates bacteria remaining after cleaning.
- FNA has potential as a cleaning agent for biofouled and scaled membranes.
- FNA-based cleaning is more cost effective than standard acid/base two-step cleaning.
- All of the above was proven with membranes fouled in full-scale plants.

1. Introduction

With the number of reverse osmosis (RO) membrane plants rapidly increasing worldwide for water recycling and seawater desalination, optimisation for sustainable operation of the membranes is essential [1]. Reverse osmosis membranes have been shown to consistently produce very high quality water independent of source water quality and can be used for a wide range of applications, including potable use. However, membrane fouling and more specifically biofouling, remains one of the major operating challenges [1, 2]. Biofouling is defined as the adhesion, growth and multiplication of bacteria present in the water on membrane surfaces, and was shown to have a negative impact on operation. The main consequences observed are decreased membrane flux, increased pollutants passage through the membranes and increased loss of pressure across the membranes train. This can eventually result in biodegradation of the membrane polymer and other components of the modules [2-4]. These effects ultimately result in increased energy and chemical costs, loss of both water production and water quality as well as reduced membrane life. Overall, membrane biofouling critically reduces the process efficiency and cost-effectiveness. The preventative measures to alleviate biofouling in the desalination industry is estimated to cost approximately 15 billion $US yearly worldwide [5].

Current strategies to control biofouling include feedwater pre-treatment to remove bacteria before they reach the RO membranes and nutrients to limit bacterial development, and dosing of biocides such as chlorine and monochloramine [6, 7]. Chlorine is a strong biocide, and has been widely used for biofouling control in membrane systems. However, its application to RO membrane is restricted as it can damage the polyamide active layer of RO membranes [8-10]. Monochloramine was found to be less detrimental to the membranes; however it has also been shown to have a limited impact on bacteria removal. Indeed, even with continuous dosing, biofouling formation has been observed [2]. In recent years, research studies

investigating membrane biofouling control have focused on optimisation of pre-treatment for the limitation of nutrients in feed water [7, 11], development of novel membrane materials (chlorine resistant [12] or anti-fouling [13]), determination of novel biocides such as DBNPA [14] or nitric oxide [15] and development of novel biological methods such as inhibition of biofilm growth by quorum sensing, biomass dispersion by cell wall hydrolase or bacteriophage and enzymatic disruption [16, 17]. Although some of these novel techniques are promising none of them have proved to dramatically improve biofouling control, and none can be implemented for full-scale plant operation in the medium term. In general, these methods do not allow complete/satisfactory removal of the microorganisms present in the feedwater and even if a process is very efficient, there is still enough cells remaining which can grow in the system [2, 18]. Over time, biofouling will develop on the RO membranes, and chemical cleaning of the RO membranes is regularly required to restore their treatment capacity.

Typically, chemical cleanings are a sequence of cleanings with alkaline (e.g. sodium hydroxide) and acidic (e.g. citric acid, hydrochloric acid) agents. Alkali cleaning is used to remove organics and biofilm present on the membranes, while acid cleaning is generally used to target scaling. However, biofilm removal using the current strategies was never found to be complete [2, 11, 19]. In addition, the commonly used cleaning agents, used in large quantities, contribute significantly to operational costs and environmental issues for their disposal.

Recent studies carried out on sewer biofilms and waste activated sludge at both laboratory and full scales, have demonstrated that free nitrous acid (FNA) is a strong biocidal agent at parts per million concentrations (0.2 – 2 mgN/L), causing deactivation of microorganisms by inducing substantial cell death and biofilm detachment [20-23]. The FNA technology is currently being applied for sulfide and methane control in sewer networks. In a recent trial of

the technology for sewer biofilm control, it has been shown that the activities of sewer biofilms were completely suppressed, accompanied by a substantial loss of biofilm after 24 hr treatment [24]. Although sewage provided ample substrates for biofilm to regrow, the recovery of sewer biofilm activities one week after treatment was less than 20%. Given the very low substrate concentration in feedwater in an RO system (in comparison to raw sewage), it is reasonable to expect that the recovery of RO membrane biofilm would be much slower in comparison to sewer biofilms.

The aim of this study was to investigate feasibility of FNA as a novel low cost cleaning agent. Its utilisation was assessed for the removal of biofouling in RO membranes for water recycling and seawater desalination. As an acid, it is anticipated that FNA will also be effective at removing inorganics from the membrane surface. Therefore, the potential of using FNA to remove RO membrane biofilm and scaling was evaluated at bench-scale without (soak cleaning tests) and with cross-flow recirculation (cross-flow cleaning tests).

2. Material and Methods

2.1. Chemicals

FNA is related to the total nitrite concentration, the pH and the temperature and is calculated as follows [25]: FNA = NO_2^--N / (Ka x 10^{pH}), where Ka is the ionization constant of the nitrous acid (Ka=$e^{-2300/(T+273)}$) and T is the temperature (°C). The FNA concentration was achieved by varying the nitrite concentration and pH. The pH was adjusted with hydrochloric acid (HCl). Sodium nitrite (≥99%, Sigma Aldrich) and HCl (32%, Univar) were used to generate FNA solutions. The others cleaning solutions were prepared using sodium hydroxide (pallets, Univar), HCl solution (32%, Univar) and citric acid (99.5%, Chem-supply).

2.2. Reverse osmosis modules and fouling characterization

The cleaning trials were conducted using fouled RO modules collected from full-scale plants (Table 1). All RO membranes are commercial thin-film composite polyamide membranes.

Table 1. List of RO membranes used for the cleaning trials.

Reference No.	Source	Fouling Type	Cleaning conditions
RO1	Municipal water recycling plant	Biofouling	Soak cleaning tests*
RO2	Industrial water recycling plant	Biofouling	Cross-flow cleaning tests**
RO3			
RO4	Municipal water recycling plant	Biofouling	
RO5	Municipal water recycling plant	Biofouling	
RO6	Seawater desalination plant	Biofouling	
RO7	Coal seam gas water recycling plant	Scaling	

* Without cross-flow recirculation; ** With cross-flow recirculation

Membrane autopsies were conducted on the seven fouled membranes to characterize the fouling layer. Chemical (loss on ignition, elemental analysis, polysaccharide and protein content) and microbial (ATP) analysis were used to describe the fouling deposit. Loss of ignition (LOI) is used to determine the proportion of inorganic versus organic fraction in the fouling layer. The amount of adenosine tri-phosphate (ATP), an energy-rich biomolecule

present in all active microorganisms [26], was measured to quantify the active bacterial biomass in the fouling layer. The applicability of ATP concentration as a parameter for the assessment of active biomass present in the RO membrane fouling layer has been previously reported as a robust parameter [27]. Polysaccharides and proteins have been reported as extracellular polymeric substances (EPS) indicators [27]. EPS are abundant in biofilms and therefore protein and polysaccharide content were measured as proxy of microbial concentration. Elemental analysis via inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the metals content in the fouling deposit. Autopsy methodologies and data can be found in the Supporting Information (SI) (Table A.1&2).

2.3. Lab-scale cleaning trials

2.2.1. Protocol for chemical cleaning

Cleaning trials were carried out at lab-scale without cross-flow recirculation (soak cleaning) and with cross-flow recirculation (cross-flow cleaning). The soak cleaning tests were used for pre-screening the optimum FNA concentrations and pH for biomass removal only, while cross-flow cleaning tests were used for assessing the impact of FNA on biomass and scaling removal.

The first set of experiments was performed by soaking membrane coupons (42 cm^2) in 300 mL of cleaning solution for 24 hours. Three replicate experiments were conducted using RO1 membrane. The beakers were placed on an orbital shaker (Ratek large orbital shaker) and agitated at 120 rpm.

The second set of experiments was conducted with cross-flow recirculation using cleaning cells made of Perspex and RO2-RO7 membranes. Both membrane coupons (150 cm^2 of membrane active surface) and the respective feed spacer were placed in the cleaning cells.

Cleaning cells were designed to simulate the configuration of RO filtration system and were operated with cross-flow, without permeate production. The hydraulic performance of RO membranes were conducted in a separate cross flow filtration set-up using Sterlitech CF042 cells and described in detail in SI, Table A.1. The cleaning solutions were pumped (Cole Parmer, Masterflex L/S economy drive pump) through the cleaning cell for 24 hours according to the following protocol:

- Rinse with DI water (2 hours) to remove biomass or scaling at the external layer of biofilm.
- Recirculation of cleaning solution (22 hours)
- Rinse with DI water (15 min) to remove the chemicals.

The pump was assembled with five pump heads allowing cleaning cells to run in parallel with similar flows. In order to simulate industry cleaning practice, cross flow velocity of 0.1 m/s was applied for the cleaning trials [28].

The five cleaning solutions used for the biofouling and scaling removal are described in Table 2. Each cleaning tests were conducted with coupons from the same membrane and in replicate (RO2, n=1-3; RO3, n=1-2; RO4, n=2; RO5, n=1-3; RO6, n=2 and RO7, n=2).

Table 2. List of cleaning solutions and applied conditions used for the cleaning trials.

Cells	Type of cleaning	Chemical agent (supplier) and conditions
#1	Water (control)	DI water
#2	Alkaline (benchmark for biomass removal)	Sodium hydroxide, NaOH, pH 11.0
	Acidic (benchmark for scaling removal)	Hydrochloric acid, HCl, pH 2.0 or 3.0
		Citric acid, pH 2.0 or 3.0
#3, #4, #5	Free nitrous acid, FNA	Sodium nitrite50 mgNO_2^--N/L*, pH 2.0, 3.0 or 4.0

*Concentrations selected based on preliminary results of soak cleaning tests (data not shown).

After cleaning, membrane coupons (5.6 x 11.2 cm²) were rinsed with Milli-Q water and the recovery of the membrane performance in terms of permeability and salt rejection were assessed in a lab-scale cross-flow filtration unit. The remaining membrane coupons were used to evaluate changes in the fouling layer. Biofilm characterisation (i.e., ATP, polysaccharide and protein measurements and confocal laser scanning microscopy (CLSM)) was conducted to reveal the cleaning efficiency on biomass removal, while the presence and removal of scaling was assessed using inductively coupled plasma optical emission spectrometry (ICP-OES) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS). The results were compared to the autopsy results (i.e., initial conditions obtained before cleaning) to assess the cleaning efficiency.

2.4. Biofilm characterization methods

The biofilm was characterized before and after cleaning using ATP, Polysaccharide and protein measurements and confocal laser scanning microscopy (CLSM).

The biofilm was removed mechanically from the membrane surface and suspended in MilliQ water using a Braun Oral-B Vitality electrical toothbrush (Procter & Gamble, USA). The protocol is described elsewhere [27]. Total ATP was determined using the BacTiter-Glo™ reagent (Promega Corporation, USA) following a protocol adapted from Hammes et al. [29]. A set volume of the mixture (300 µL) was placed in the wells of a 96 well plate, mixed with 50 µL of the reagent and then the luminescence was measured at 38ºC after 20s orbital shaking. The luminescence response was read with a DTX 880 multiplate reader (Beckman coulter, USA), collected as relative light units (RLU) and converted to ATP concentrations (nM) using a calibration curve made with a known rATP standard (Promega Corporation, USA). The detection limit was determined at 0.01 nM ATP, upwards of which a linear correlation of R^2=0.99 was obtained.

Protein and polysaccharide contents were measured using the QuantiPro™ BCA Assay Kit (Sigma Aldrich) and the Phenol-Sulfuric acid method [30], respectively. The deposit recovered from a known membrane surface area (5x5 cm^2) was mechanically dispersed in Milli-Q water (20 mL) as described above. The samples were then mixed with reactants. These photometric methods are based on the fact that the colour of the mixture will vary with the concentration of the compound. The samples are typically analysed on an UV spectrometer (Cary 50 Bio, Varian) at set wavelengths. The signals are calibrated with bovine serum albumin (BSA) and D-Glucose (Sigma Aldrich) for the proteins and polysaccharides, respectively. Results are then reported as mg glucose or mg BSA per unit area. All measurements were done in triplicate.

Confocal laser scanning microscopy was conducted to visualise biofilm and indicate the viability of bacterial cells in biofilms. A known area of membranes (1×1 cm^2) was stained using the green fluorescent SYTO®9 nucleic acid stain and the red fluorescent propidium iodide (PI) from LIVE/DEAD® BacLight™ Bacterial Viability Kits purchased from Molecular Probes® (L-7012, Invitrogen, Australia). The SYTO®9 stain labels all bacteria in a population with intact or damaged membranes. In contrast, PI stain penetrates only those bacteria with damaged membranes, causing a reduction in the SYTO®9 stain fluorescence when both dyes are present. Thus, bacteria with intact cell membranes (viable cells) are stained green, whereas bacteria with damaged membranes (dead cells) are stained red. The stained membrane coupons were incubated in a dark place for 30 min at room temperature (20°C), allowing the staining reactions to complete and then mounted onto a glass slide for microscope observation. The stained biofilm samples were photographed using a Zeiss 510 confocal laser scanning microscopy (Australian National Fabrication Facility-QLD Node). Two excitation/emission wavelengths were used for the two florescent stains: 488 nm/500 nm for SYTO®9 and 510 nm/635 nm for PI. Twenty images were taken for randomly chosen

areas of each sample. Quantification of live and dead cells was done by determining the relative abundance of green and red pixels. The pixel area counting was conducted with DAIME (Digital image analysis in microbial ecology, by Holger Daimes). The ratio of green fluorescence to the total fluorescence (red + green fluorescence) was assumed to be equal to the ratio of viable cells to the total cells (viable + dead) in the biofilm.

3. Results

3.1. Fouling layer characterization

The analysis of organic versus inorganic fractions by LOI measurements revealed that the fouling layers of RO1 to RO6 membranes mainly consist of organic foulants (>85% of total solid content). The high amount of biopolymer-type compounds, such as polysaccharides (0.07-0.56 gGlucose/m²) and proteins (0.04-0.35 gBSA/m²), and the detection of ATP (204-4680 pgATP/cm²) confirm the presence of biofouling on the surface of these membranes. The total solid (TS) content (from LOI analysis) of membranes RO1 to RO4 (1.9±0.1 to 4.0±0.1 g/m^2) is more than double that of membranes RO5 and RO6 (0.8±0.1 and 0.5±0.2 g/m^2 respectively). This indicates the presence of a more severe fouling on RO1, RO2, RO3 and RO4. ATP concentrations are also higher for membranes RO1 to RO4 (4680±854 to 919±477 pg/cm^2) than for RO5 and RO6 (204±153 and 339±159 pg/cm^2 respectively). Protein and polysaccharide concentrations measured as indicators of microbial concentration support this hypothesis. According to these results, RO1 to RO4 could be classified as heavily fouled and RO5 and RO6 as moderately fouled.

Membrane RO7 was significantly covered with inorganic scaling. ICP-OES analyses reveal that the fouling layer contains a high quantity of calcium (21.7±3.8 gCa/m^2). Smaller concentrations of barium, potassium, magnesium and sodium were also present. SEM analysis conduct on the membrane surface indicated the presence of crystals (SI, Figure B.1), that showed high Ca, C and O signals via EDS elemental analysis (SI, Figure B.2). Signals of C (15±2 % as element weight percentage, wt%) and Ca (25±5 %) are approximatively 2 to 4 times lower than signal of O (59±3 %), based on EDS element analysis (n=18). Overall, results of SEM-EDS and ICP-OES elemental analyses performed on RO7 suggest the presence of calcium carbonate.

According to these results, RO1-RO6 are suitable for studying the effect of FNA cleaning on biofouled RO membranes, while RO7 can be used to study the effect of FNA cleaning on scaled RO membranes.

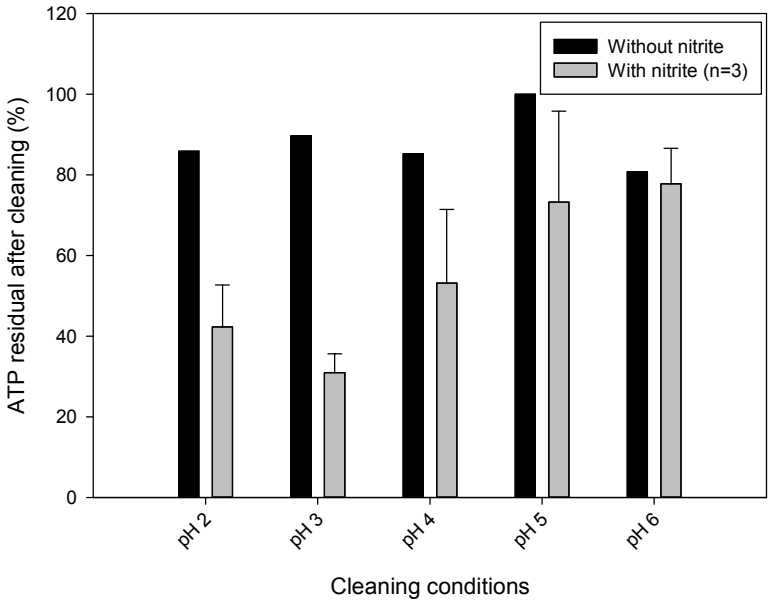
3.2. Biomass removal

The cleaning efficiency was quantified mainly in terms of total biomass or ATP removal as shown in Figure 1. Control experiments were conducted with RO1 to verify if the pH adjustment alone had an impact on biofilm removal (Figure 1a). While lower pH alone between pH 2.0 to 6.0 is not effective in biofilm removal, addition of nitrite giving rise to the formation of FNA achieves significantly higher biomass removal (*p-values* < 0.05). The ATP residual values decreased when pH decreased (i.e., higher FNA concentration). This control experiment confirms that FNA rather than nitrite is the key agent in the cleaning process. It also confirms that ATP is not removed by low pH alone, e.g. through hydrolysis processes. Based on the preliminary results of soak cleaning tests, cross-flow cleaning tests were conducted with 50 mgNO_2^--N/L as nitrite concentration. However, different pH values (pH 2.0, 3.0 and 4.0) were applied resulting in various FNA concentrations (i.e. 47, 35 and 10 mgHNO_2-N/L respectively, T=20^oC).

Figure 1b shows that FNA also significantly affects the relative ATP abundance in the fouling layer after cleaning using cross-flow recirculation. Lower ATP values are found after cleaning compared to before cleaning. The FNA cleaning agents are more effective than conventional cleaning solutions such as NaOH (pH 11.0) (*p-values* < 0.05).

For all the membranes tested, the best cleaning efficiency (>85% of biomass removal) is observed at pH 3.0. Hence, 50 mgNO_2^--N/L at pH 3.0 (corresponding to 35 mgHNO_2-N/L) are suggested as optimum conditions for biofouling removal among the conditions tested here. FNA concentration is highly sensitive to the pH level. At pH 2.0, FNA concentration

increases 10 times compared to solution at pH 3.0. However, FNA is not stable at high concentration and the lower ATP removal with FNA at pH 2.0 could be due to the faster degradation of FNA at low pH values. These results are in accordance with the disproportionation of nitrous acid in aqueous solution giving nitric acid and nitric oxide. The effectiveness of FNA is dependent of the degree of membrane fouling. FNA acts more effectively on moderately fouled membrane (94-95% total biomass removal at pH 3.0) than on heavily fouled membrane (86-96% total biomass removal at pH 3.0) (Figure 1b). Similar observations can be made for water cleaning (control) and NaOH-based cleaning (standard treatment). Even the standard treatment (NaOH, pH 11.0) did not fully recover the membrane, indicating that membranes are fouled beyond their reversibility. The results suggested that early cleaning is preferable.



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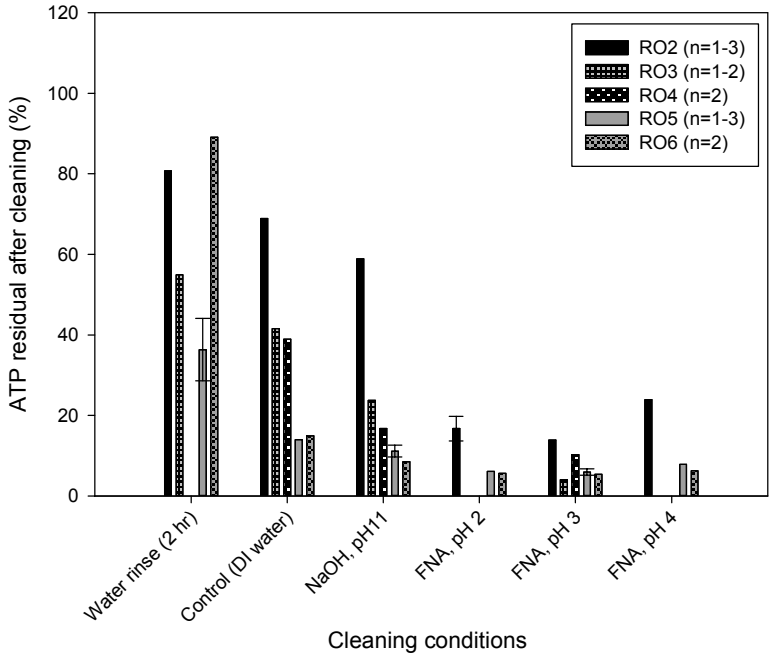


Figure 1. ATP residual after 24 hours cleaning tests performed (a) in soaking conditions (Ratek large orbital shaker, 120 rpm, RO1) with the membranes RO1, cleaning tests were conducted with FNA (grey) and without FNA (black) and pH between 2.0 and 6.0; and (b) in cross-flow conditions (cross-flow velocity 0.1 m/s) with the membranes RO2 to RO6, cleaning tests were conducted with heavily fouled (black) and moderately fouled (grey) RO membranes. Standard test conditions: FNA (50 mgNO_2^--N/L). The error bars show the standard errors of three replicate experiments. No error bars were given when less than three values were used in the calculation of the averages.

Cleaning efficiency was also quantified in terms of membrane hydraulic performances (permeability recovery and salt rejection improvement). The filtration trials on membrane coupons revealed no significant impact of different cleaning procedures on the performance of the membrane in terms of permeability and salt rejection for all cleaning conditions applied (Table C.1). All permeability changes remained non-distinguishable from the natural

variability of the membrane used. The impact of FNA cleaning on the hydraulic performance needs to be addressed at larger scales.

3.3. Viability of bacteria remaining on membrane surfaces

Microscopic assessment of LIVE/DEAD-stained bacterial cells was used to investigate whether FNA and other cleaning solutions influenced bacteria viability in the fouling layer (Figure 2). This method was only applied to the moderately fouled membranes (RO5&6), due to lower biofilm density resulting in better quality of images. The CLSM images of RO5&6 before and after cleaning are presented in SI (Figure C.2&3). After 24 hours cleaning, the proportion of viable cells on the membrane surface decreased for all cleaning solutions tested (Figure 2). These results are in accordance with the biomass removal measured as ATP and presented in Figure 1b.

The percentage of viable cells in the biofilm on RO5 membrane in the presence of FNA, pH 3.0 (32%) is significantly lower than that in the presence of NaOH (58%) (*p-values* < 0.05). These ratios are higher than previously reported in the literature for anaerobic sewer biofilm (FNA at 0.255 mgN/L for 6 h can induce about 80% of microbial inactivation) [21] but this could be explained by the more compact biofilm in RO application due to the applied pressure. The cleaning trials conducted with the RO6 membrane from a desalination plant show better bacteria killing efficiency. The proportions of live cells for the membrane RO6 are as follows: before cleaning (60%) > water rinse for 2 hours (52%) > water rinse for 24 hours (41%) > NaOH (38%) > FNA (6-7%). Examination of the confocal images (Figure C.2&3) reveals that the biofilm on membrane RO5 is more dense than on membrane RO6 and might be more challenging to disrupt. However, CLSM analysis performed for the two membranes show that the biocidal effect of FNA is higher than that of NaOH. A higher-level of inactivation of bacteria remaining on the membrane is expected to delay their regrowth.

Furthermore, this staining protocol only show the ratio of cells with an intact versus a damaged cell membrane, which means that that the determined percentage of viable cells is a conservative estimate, but more cells may actually be dead.

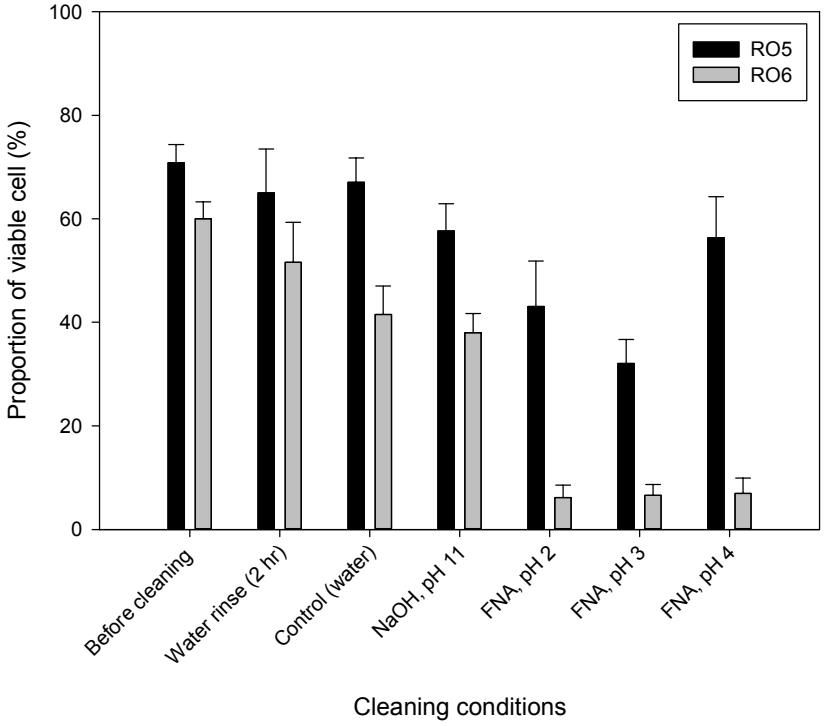


Figure 2. Proportion of viable cells in membrane biofilm before and after 24 hours cleaning tests for the membranes RO5 and RO6. Standard test conditions: FNA (50 mgNO_2^--N/L), cross-flow velocity 0.1 m/s. The error bars show the standard errors of 15 to 60 CLSM images.

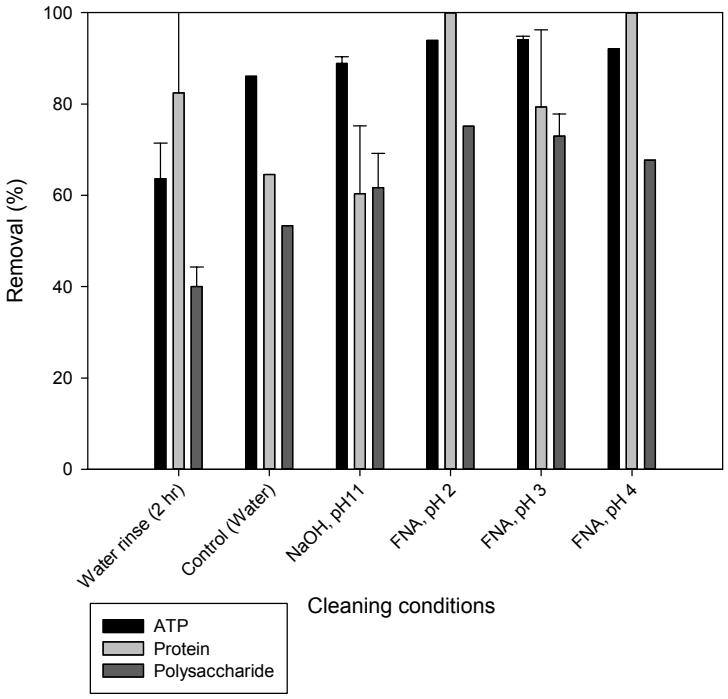
3.4. Polysaccharide and protein removal

In addition to ATP measurement, protein and polysaccharide content was measured for the moderately fouled membranes (RO5&6) to investigate the impact of FNA and other cleaning solutions on organics (Figure 3). Although polysaccharides and proteins are components of both bacteria and EPS matrix, they are usually measured as proxy of EPS.

The removal rate of polysaccharide correlates with biomass removal rate (based on ATP values) after 24 hours cleaning tests. This suggests that FNA has an effect on both bacteria and EPS matrix. It is noticeable that similar ATP and polysaccharide removals were reached for both membranes. However, FNA was more efficient in removing protein for the RO membrane from the municipal wastewater recycling plant (RO5) than the one from the seawater desalination plant (RO6). Again, by combining with the results presented in Figure 1b, pH 3.0 appears to be a preferable option.

However, each FNA cleaning solution shows a higher ATP removal (92-95%) compared to the polysaccharides removal (68-90%), implying that FNA is more efficient for bacteria than for organics removal. The resistance of the EPS matrix against chemical cleaning was demonstrated by Hijnen et al. [27].

NaOH is known to be efficient for colloidal, organic and biofouling removal and would be expected to show high polysaccharide and protein removal. However the standard cleaning solution in the trials shows average organic removals of only 59-60% and 62-79% of proteins and polysaccharides respectively, which is similar or lower than organic removal observed after FNA cleaning.



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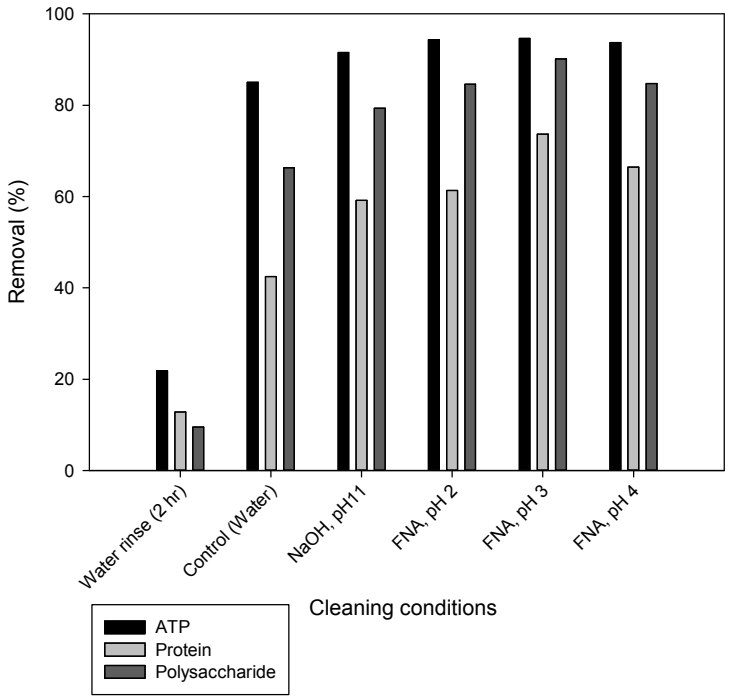

b.

Figure 3. Biomass removal (%, based on ATP values) and protein and polysaccharide removal (%) after 24 hours cleaning tests for the membranes (a) RO5 (n=1-3) and (b) RO6 (n=2). Standard test conditions: FNA (50 mgNO_2^--N/L), cross-flow velocity 0.1 m/s. The

error bars show the standard errors of three replicate experiments. No error bars were given when less than three values were used in the calculation of the averages.

3.5. Scaling removal

Cleaning at low pH is useful to control calcium carbonate scaling ($CaCO_3$) and possibly iron fouling (i.e., iron oxide/hydroxide) [28]. As an acid, it is anticipated that FNA will also be effective for removing inorganics from the membrane surface via hydronium ion activity. Tests were carried out to establish the efficacy of FNA to remove scaling, i.e., to verify that the addition of nitrite does not alter the efficiency of commonly used cleaning solutions in scaling mitigation. A severely fouled membrane module from a full-scale coal seam gas water treatment plant (RO7) was used for this study. Based on the autopsy results, the fouling layer is mainly composed of calcium carbonate (as presented in Section 3.1). According to the standard manufacturers' cleaning procedures, HCl and citric acid at low pH are recommended for cleaning RO membranes with severe $CaCO_3$ fouling [28, 31]. Therefore, the efficiency of FNA for scaling removal was compared with these two alternative cleaning solutions (i.e., HCl (pH 2.0-3.0) and citric acid (pH 2.0-3.0)). Along with these cleaning agents, DI water and 10 v/v % of nitric acid (HNO_3) were applied as controls. A solution of 10 v/v% HNO_3 at pH 0.5 was used for ICP-OES analysis to dissolve/digest the fouling material, and it is reasonable to assume that $CaCO_3$ scaling would be completely removed from the membrane at this extreme pH level.

Figure 4 presents the dissolved calcium content (based on ICP-OES results) removed from the membrane surface after the 24 hour cleaning tests. SEM-EDS analyses were also conducted on the membrane before and after cleaning for all cleaning solutions at pH 3.0 (HCl, FNA and citric acid), which is also the pH selected for biofouling removal. SEM images and element wt% distribution are available in the SI (Figures B.1&2).

The results shows that FNA at pH 2.0 and 3.0 are as effective as commonly used descaling agents (HCl and citric acid), implying that addition of nitrite in the acid cleaning solutions does not modify its efficiency to remove scaling. Water removed only 4.4±0.1 g/m^2 of calcium from the membrane surface, while the other control (10 v/v % HNO_3 at pH 0.5) successfully removed 32.4±1.7 g/m^2. Higher calcium removal is observed compared to the autopsy results (32.4±1.7 versus 21.7±3.8 g/m^2), likely due to the introduction of shear rate at the membrane surface, improving the solubility of the fouling layer. All cleaning solutions show similar calcium removal ranging between 34.3±1.4 and 28.5±4.6 g/m^2. These values are comparable to the calcium removed by the control (HNO_3), which suggests that maximum calcium removal is reached with all the cleaning solutions. This conclusion is supported by the SEM-EDS results (as SEM images and element weight percentage (wt %)) presented in SI (Figures B.1&2). The element wt% reveals that only 1% of calcium element is present on the membrane after cleaning with HCl, FNA and citric acid adjusted at pH 3.0 versus 24% before cleaning.

The cleaning tests conducted with the scaled membrane RO7 (no organic fouling) showed no additional benefit of using FNA rather than HCl or citric acid for scaling removal. However, in the presence of combined scaling/organic fouling the presence of FNA can lead to a better organic fouling/scale removal compared to low pH alone.

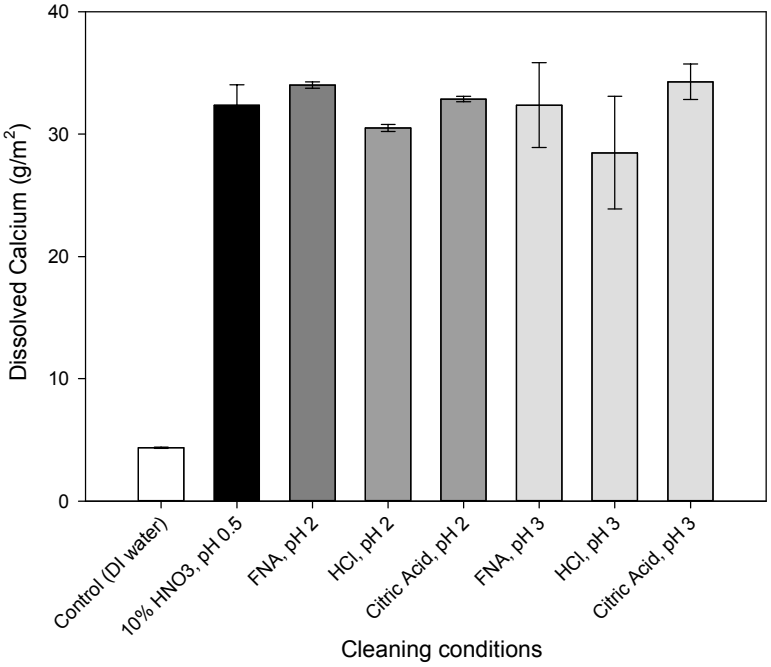

Figure 4. Dissolved calcium content removed from the membrane surface after 24 hours cleaning tests with membrane RO7. Standard test conditions: FNA (50 mgNO_2^--N/L), cross-flow velocity 0.1 m/s. The error bars show the standard errors of four measurements from two replicate experiments.

4. Discussion

4.1. Benefits of using FNA as a new cleaning agent

A new cleaning solution containing FNA was applied to control membrane biofouling, and compared with NaOH as a conventional cleaning agent. For all the membranes tested, the FNA cleaning agents were more efficient than NaOH (pH 11.0). While the effect of FNA is shown to be positive for all the different membrane tested, the extend of cleaning appeared to be dependent in the degree of membrane fouling, as is in the case with NaOH as the cleaning solution. According to Hijnen et al., biofilms develop chemical and mechanical stress resistances and their removal efficiency will vary with biofilm strength, age/maturity and history (e.g., exposure to cleaning) [27]. In this study, FNA acted more effectively on moderately fouled membranes than heavily fouled membranes, suggesting that early cleaning is preferable, or more extensive cleaning may be required for heavily fouled membranes. Cleaning efficiency was reported to involve both chemical reaction (between the cleaning agents and the foulant) and mass transfer (from bulk phase to fouling layer) mechanisms [32]. It is possible that heavily fouled membranes have a compacted biofilm layer resulting in a lower mass transfer reducing the permeation of the cleaning agent into the fouling layer [33]. Inversely, biofilms on the moderately fouled membranes were easily disrupted as the transfer of the cleaning solution in the fouling layer was enhanced.

Another key finding of this study is the high bactericidal efficiency of FNA. CLSM analysis performed for the two membranes demonstrated the biocidal effect of FNA is higher than that of NaOH. Bacteria were effectively killed and removed by FNA, which is an important criterion for selecting a cleaning strategy. Quick biofilm regrowth results in a repetition of the biofouling-related system failure. Although, it is difficult to avoid bacteria regrowth, the use of a biocide can slow down/minimise this phenomenon. Other techniques such as nutrient availability and limitation have also been investigated [7, 11].

Previous research on biofouling removal has mostly been conducted with laboratory-prepared biofilms using non chlorinated tap water supplied with additional nutrients (e.g., sodium acetate, nitrogen and/or phosphorus source) [19, 27], RO feedwater from full-scale water treatment plant [34] or pure culture of model bacteria such as *Pseudomonas aeruginosa* [15, 35]. The structure and composition of the fouling layer can affect the cleaning efficiency [33]. In addition, hydraulic stress during biofilm growth has been reported to have an impact on its resistance to the detachment during cleaning [36]. In this study, the chemical cleaning of RO membranes was investigated with fouled membranes collected from full-scale plants including: industrial (RO2&3) and municipal (RO4&5) water recycling plants and a seawater desalination plant (RO6) in order to develop a better understanding of the applicability of FNA on various fouling matrix. Based on the autopsy results, the RO5 and RO6 membranes present similar fouling (in terms of ATP, LOI and ICP results), although the two membranes are from different origins (Municipal water recycling plant versus seawater desalination plant, respectively) and quite different fouling removal results. FNA showed better protein removal for RO5 compared to RO6, while similar ATP and polysaccharide removals were observed for both membranes. This result clearly supports that the cleaning efficiency is affected by the nature and structure of the fouling layer.

Finally, the FNA-based cleaning is also effective for the removal of calcium carbonate scaling. No significant difference was observed between the commonly used cleaning agents (HCl and citric acid) and the FNA cleaning solution (*p-values* > 0.05), indicating that the scaling removal capacity was maintained when nitrite was added to an acid solution (to form FNA).

This demonstrated that FNA can simultaneously achieve biofouling and scaling removal. Consequently, FNA could be used as a single cleaning agent for both biofouling and scaling removal in order to reduce costs associated with two-step cleaning. In the presence of

combined inorganic/organic fouling, such as calcium-organic complexes, the benefit of tackling all types of fouling in one step can be highly valuable.

The FNA cleaning solution can be prepared by simultaneous addition of sodium nitrite and HCl. According to the experimental results, 50 mgNO_2^--N/L at pH 3.0 is the optimum condition for RO biofouling removal among the conditions applied in this study. A biofouling removal efficiency of up to 96% was obtained, and the scaling removal efficiency was comparable to the conventional acid cleaning solution. Therefore these conditions were used for cost calculation. As similar cleaning conditions were used for the different cleaning solutions, such as volume, cross-flow velocity, duration and temperature, the economic study was based on the chemical cost only with the results presented in Table D.4. The chemical costs of the FNA cleaning solution (Strategy A) was compared with the benchmarks used in this study (i.e., Strategy B: NaOH treatment at pH 11.0 followed by HCl treatment at pH 2.0). The acid consumption to maintain low pH for scaling removal is dependent on the amount of calcium carbonate present on the membrane surface. Hence, the total acid required to maintain a pH of 2.0 (Strategy B) and 3.0 (Strategy A) was calculated from the cleaning solution titration using the scaled membrane RO7 and presented in Figure D.1-3 in SI. The chemical cost associated with the two-step cleaning strategy to control biofouling and scaling appears to be significantly higher than using FNA alone (2.3\$/m^3 versus 1.7\$/m^3). Membrane manufactures recommend 0.04-0.08 m^3 of cleaning solution per 8-inch RO element depending on the severity of the fouling [31]. In addition to cost effectiveness, the one-step cleaning strategies simplify the cleaning operation compared with the two-step strategies and lower the risk of irreversible fouling and membrane damage. Furthermore, the FNA cleaning solution is readily biodegradable (to N_2) through denitrification after dilution with other wastewater streams. Therefore its disposal after use will not cause environmental problems such as increased salt load and can be simply discharged after dilution. FNA is readily

available at low costs as it can be formed from the commonly available sodium nitrite and HCl, or even produced from ammonium containing wastewater as recently demonstrated for wastewater recycling applications [37]. However, it should be highlighted that a full economic assessment must be done on a case by case basis considering the specific conditions of the systems and also the chemical supplier, delivery and waste disposal options.

4.2. Proposed mechanisms

FNA has an effect on active bacteria cells and organics as evidenced by ATP and polysaccharide & protein removal, respectively, and also descales. NaOH at pH 11.0 removes organics by hydrolysis and solubilisation of the fouling layer [33], while the FNA cleaning mechanism remains unknown.

CLSM analysis showed the inactivation of cells on the membrane after FNA application. The biocidal effect of FNA has already been demonstrated on anaerobic sewer biofilm and waste activated sludge applications [20, 38]. Jiang *et al.* suggested the role of reactive derivatives, such as dinitrogen trioxide (N_2O_3), nitrogen dioxide (NO_2) and nitric oxide (NO), which can be generated when FNA is formed from nitrite under acidic conditions [20]. While N_2O_3 and NO_2 can disrupt the function of proteins or induce cell damage, respectively [39], NO is known to be a highly toxic compound for bacteria [40]. It has been reported that NO is also able to induce the dispersion of biofilms (e.g., *Pseudomonas aeruginosa* biofilms and multi-species biofilms from water distribution and treatment systems) [41, 42].

In addition to the biocidal effect, acidified nitrite (FNA) can remove organics such as proteins and polysaccharides, which can be mainly associated to EPS. EPS acts as a matrix holding microbial cells together and protecting them from external aggression/stress. Consequently it is important for a cleaning agent to remove EPS and not only inactivated bacteria cells.

Biofilms are a combination of organic, inorganic and biological species. Membrane autopsies reveal the presence of multivalent ions (e.g., Ca, Fe, Mg) in biofilm, which can bind with organic molecules. As an acid, FNA was shown to dissolve this inorganic matrix (e.g., divalent cations) embedded in the biofilm thereby helping to break down the structural integrity of the fouling layer and to disperse/weaken the biofilm making it easier to remove. The metal content results (via elemental analysis using ICP-OES) before and after cleaning were low (close to the limit of detection) and no difference could be noticed to support this hypothesis. However, previous research conducted on toxic metal removal from acidified sludge and the breakdown of EPS in waste activated sludge using FNA suggested that FNA likely reacts with EPS leading to its breakdown [43, 44]. Zhang *et al*. suggested that FNA may change the chemical structure of EPS and has an impact on UV absorbing substances [43, 44], while Du *et al.* verified that FNA efficiency resulted from the release of organically bound metals [43, 44].

Ultimately, the effect of FNA on fouling removal is likely to be a combination of all these factors and consequently makes FNA a suitable cleaning agent for the removal of biofouling and scaling in one step. However, biofouling is dependent on feed water characteristics and processes, consequently no unique cleaning strategy can be applied. Cleaning conditions, such as cross-flow velocity, duration or temperature need to be optimised for each individual plant, depending on feed/plant conditions. A long-term pilot-scale study would be needed to further investigate the economic potential and practical application of FNA as a new RO cleaning agent.

5. Conclusions

The impact of FNA on biofouling and scaling removal was investigated at different pH levels using fouled RO membranes from full-scale plants including industrial and municipal water recycling plants and also a seawater desalination plant. The following conclusions can be drawn:

- FNA cleaning is effective in removing bacteria and organics from membrane surfaces; it also causes substantial inactivation of bacterial cells remaining on the membrane surface after cleaning. FNA cleaning has a superior performance in bacteria and organics removal than the current method of NaOH cleaning at pH 11.
- A nitrite concentration of 50 mgNO_2^--N/L and a pH level of 3.0 are suitable conditions for biofouling removal.
- For scale removal, FNA at pH 2.0 and 3.0 is as efficient as the commonly used descaling agent (HCl and citric acid). This effect, along with the effect of FNA on biofouling removal, implies that the use of FNA as a cleaning solution can simultaneously achieve both biofouling removal and descaling.
- FNA cleaning is a cost-effective method for biofouling and scaling removal in RO filtration applications.

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Biofouling and scaling control of reverse osmosis membrane using one-step cleaning - potential of acidified nitrite solution as an agent

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