Green chemicals for effective biofouling removal and preservation of reverse osmosis membranes

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Results of the short-term membrane preservation trials with Free Nitrous Acid (FNA)

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Executive summary

This deliverable, T3: "Preliminary results of the membrane preservation trials with Free Nitrous Acid (FNA)", reports on the preliminary results of Task II: Investigate the possible application of FNA and hydrogen peroxide as biocides for the preservation of RO membranes during long-term storage.

The objective of this task is to evaluate FNA for membrane storage in order to prevent microbiological growth and/or membrane degradation.

Short-term trials of one month were conducted using two unused full-scale RO membranes from Hydranautics designed for different applications (i.e. seawater desalination and wastewater recycling) and one used (fouled and cleaned) RO membrane from full-scale industrial water recycling plant in order to investigate the effectiveness of FNA as preservation solution. RO membrane coupons were stored at varying FNA concentrations as well as SBS as the reference chemical since it is already used in industrial practice. The aim is to obtain the lowest suitable concentration for preservation without biofilm development. Membrane performances (water permeability and salt rejection) were measured at bench-scale and compared to the initial conditions. The biocidal efficiency of the preservation solutions was evaluated using biomass quantification via adenosine triphosphate (ATP) measurement and scanning electron microscopy (SEM). Infrared spectroscopy (ATR-FTIR) was used to assess the integrity of each membrane sample (active layer's chemistry monitoring). The following conclusions were reached:

- ✓ No loss of performance after short-term storage was observed for the two unused membranes applied (ESPA-2 and SWC-5) in terms of permeability and salt rejection.
- ✓ After one-month storage, the hydraulic performances of the used membrane increased. However, no significant difference could be observed between the different preservation solutions tested.
- ✓ No structural damages to the active layer of the membranes occurred during short term preservation using FNA up to 10 mgN/L. All the preservation solutions tested were compatible with the RO membranes.
- ✓ Very low biomass concentration were measured in the preservation solutions, demonstrating that no significant microbial growth occurs during the short-term storage trials, whatever the preservation solution applied. However, higher ATP value was observed in the control solution with DI water only, indicating biological contamination of the preservation solution during membrane storage.
- ✓ FNA can be used as a preservation solution equivalent to SBS for short-term storage of unused and used membranes.

The further actions will be to:

- ✓ Investigate the impact of storage time, temperature, oxygen and the experimental conditions of membrane storage on the preservation solution stability,
- ✓ Carry out long-term membrane preservation trials (using 4-inch RO modules) in order to work more closely to real industrial conditions.

1. Introduction

The number of reverse osmosis plants has rapidly increased worldwide in the past decade for wastewater recycling and seawater desalination in order to increase water sources. However, these reverse osmosis plants are occasionally shut down for either short-term periods due to maintenance work or long-term periods due to low season production. RO membrane surfaces are particularly vulnerable to microbial colonization and biofilm development, resulting membrane performance decline (e.g., water permeability decrease and salt passage increase) or membrane degradation. These effects eventually result in increased energy needs, loss of water production and quality and reduced membrane life, which critically reduces the process efficiency and cost-effectiveness. When RO plants are shut down, the biofouling risk is real and biological growth in the RO system should be controlled [1].

Sodium bisulphite (SBS) solution is the current strategy to control biofilm formation during membrane storage due to its efficiency and low price (see Table 1). However SBS preservation solutions are not stable. SBS is easily oxidized into sulphate with oxygen resulting in continuous pH dropping [2-4]. Therefore, pH needs to be regularly measured and solutions replaced frequently (e.g., the pH should be monitored monthly and fresh preservation solution added if the pH drops to pH 3 or lower, in order to safeguard the membranes), leading to additional costs of maintenance and operation especially for large RO plants [3]. Furthermore, cracks might occur in the plastic of the pressure vessels when using SBS for long-term storage. Considering all the above mentioned reasons it becomes obvious that developing sustainable preservation solutions for RO membranes is important.

Table 1. Manufacturer recommendations for membrane long-term storage [2-6].

Manufacturer	**General storage procedures for composite polyamide RO membrane elements**	
	Storage time	**Chemicals (concentration)**
Hydranautics	> 30 days	Sodium bisulphite (1.0%) Formaldehyde solution (0.1 to 1.0%) Glutaraldehyde solution (0.1 to 1.0%)
Dow-Filmtec	> 48 hours	Sodium bisulphite (1.0 to 1.5%)
Toray Membrane	> 4 days	Sodium bisulphite (0.05 to 0.1%)
GE Water & Process technologies	> 20 days	Sodium bisulphite (0.5 to 1.0%) GE BetzDearborn DCL30 (3.0%)

Recent studies carried out on sewer biofilms and waste activated sludge, at both laboratory and full scales, have shown that FNA is strongly biocidal even at ppm levels, causing deactivation of microorganisms and inducing substantial cell death and biofilm detachment [7-9]. Also, it was shown that biofilm remediation was enhanced when very low doses (0.2-0.4 mgN/L) of FNA were used in combination with hydrogen peroxide (30 mg/L) [10]. The FNA technology is currently being marketed for sulfide and methane control in sewer networks. In an on-going commercial 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 hours treatment. Although sewage provided ample substrates for biofilm to regrow, the recovery of sewer biofilm activities one week after treatment was less than 20%.

The objective of this project is to investigate and demonstrate the effectiveness and benefits of FNA as a novel low cost membrane preservation agent. Its utilisation is assessed for the prevention and removal of biofouling in RO membranes for wastewater recycling and seawater desalination. For this, short-term membrane preservation trials were conducted. The main aims of this project can be defined as follows:

- Evaluate the potential of using FNA to protect RO membranes during storage and benchmark against SBS;
- Investigate the impact of storage with FNA on membrane life expectancy (i.e. membrane ageing);
- Determine the low-end dosages to preserve membrane without biofilm development.

The work was divided in two parts: (1) membrane preservation trials with new, unused membranes (ESPA-2 and SWC-5) and (2) membrane preservation trials with used (fouled and cleaned) membranes from the field (industrial wastewater recycling plant).

2. Materials and Methods

2.1. Preservation solutions

Free nitrous acid (FNA). The preservation trials were conducted with FNA concentrations of 0.1, 1, 3 and 10 mgN/L. FNA is related to the total nitrite concentration, the pH and the temperature and is calculated as follows [11]:

$$FNA = NO_2^-\text{-}N / (Ka \times 10^{pH})$$

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. Sodium nitrite (≤99%) from Sigma Aldrich was used. Nitrite concentrations were analysed with a diazotization method using the TNTplus™ 840 kit (Hach, USA). The stability of FNA solution is strongly pH dependant (see technical report T1, 3.1. Stability tests). FNA solutions have shown to be stable at pH 5 over a week. This pH range was applied for membrane preservation trials. The pH was adjusted with hydrochloric acid (analytical reagent, 32%, Univar).

Sodium bisulphite (SBS). A standard SBS solution was chosen as a reference preservation solution (benchmark). Sodium bisulphite (ACS reagent grade) from MP Biomedicals was used. The preservation trials were conducted with a concentration of 10000 mg/L in order to present a typical preservation condition according to membrane manufacturer recommendations (see Table 1).

Deionised water (DI). DI water and DI water adjusted at pH 5 (adjusted with hydrochloric acid) were chosen as negative controls.

2.2. Reverse osmosis membranes

Membrane preservation trials were performed using three types of membrane samples, two unused and one used RO membranes.

- The unused membranes were commercially available TFC RO membranes from Hydranautics (USA) designed for seawater desalination and water recycling applications respectively: SWC-5 (serial #10866221) and ESPA-2 (serial #10902797).
- The used membrane (ROFNA-3) was collected from the full-scale industrial water recycling plant (Yatala Foster brewery, Australia). The membrane samples (BW30-400-FR, Filmtec membranes, serial #F3849276) were cleaned with caustic and acid consecutively as follows:
    - ✓ DI water rinsing (1h soaking)
    - ✓ Caustic cleaning (NaOH, pH 11 for 1h + 2h soaking)
    - ✓ DI water rinsing (15 min)
    - ✓ Acid cleaning (Citric acid, pH 3 for 1h + 2h soaking)
    - ✓ DI water rinsing (15 min)

Membrane coupons (63 in total) were cut out from the three RO modules (Table 2). Baseline performance measurements were taken to characterize membrane performances (water permeability and salt rejection).

Table 2. RO membrane coupons used for the short-term membrane preservation trials

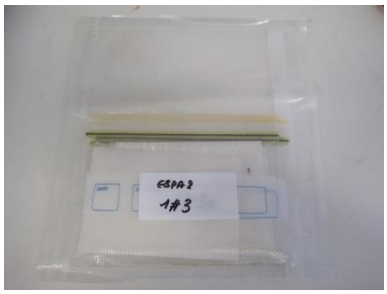
	Tested preservation solutions	ESPA-2	SWC-5	ROFNA-3
#0	Baseline (DI water)	2	2	2
#1	DI water	3	3	3
#2	DI water, pH 5	3	3	3
#3	0.1 mgN/L FNA, pH 5	3	3	3
#4	1 mgN/L FNA, pH 5	3	3	-
#5	3 mgN/L FNA, pH 5	3	3	-
#6	10 mgN/L FNA, pH 5	3	3	3
#7	SBS	3	3	3

2.3. Protocol

For each FNA preservation solution, membrane coupons were soaked in the solution for 30 min. Then the coupons were enclosed in resealable plastic bags with 20 mL of the preservation solution added to the bag. Triplicates were prepared for each preservation solution/membrane combination to assess the repeatability on the measures. The resealable bags were then enclosed in vacuum sealed bags; a vacuum pump (FoodSaver®, Australia) was used to remove the air from the plastic bags (see Figure 1). The bags were then stored in the dark and at room temperature (i.e. 20-25°C) to reproduce conditions generally used on site. As controls, parallel trials were carried out with a standard preservation solution (i.e., 1% sodium bisulphite solution), DI water and DI water at pH 5.

After one month storage time, the membranes were removed from the plastic bag and rinsed for 30 min with DI water to remove the remainder of the preservation solution. The performance of the membrane coupons was measured (permeability and salt rejection). The preservation solutions were analysed to evaluate their potential for biological growth (e.g., biomass quantification using ATP measurement). Modification of membrane structure by the solution was also being investigated using infrared spectroscopy (ATR-FTIR), while the presence of biofilm was assessed employing scanning electron microscopy (SEM).

1. The coupons were enclosed in oxygen barrier plastic bags (resealable bags) with 20 mL



2. The resealable bags were then enclosed in vacuum sealed bags

Figure 1. Protocol

2.4. Analytical methods

2.4.1. Methods for analysing the preservation solutions

Biomass quantification. Quantification of active bacterial biomass in the preservation solution was conducted by analysing the amount of adenosine tri-phosphate (ATP). Total ATP was determined using the BacTiter-Glo^{TM} reagent (Promega Corporation, USA). A set volume of the mixture (300 µL) was placed in the wells of 96 well plate forms, mixed with 50 µL of the reagent and then the luminescence was measured at 38^{o}C after 20s orbital shaking. The luminescence response was read with a DTX 880 multiplate reader (Beckman coulter, USA) and 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) (Appendix A).

2.4.2. Methods applied to the membrane

Filtration trials. Hydraulic performance, i.e., pure water permeability and salt rejection tests, were carried out on laboratory scale cross-flow filtration units. The system included a 15 L tank, from which the source water is conveyed to two filtration cells in parallel with a diaphragm pump (Metering pump Z series, Tacmica). A dampener (PD36, Neptune) is fitted in the feed line after the pump to avoid flow pulsation in the system. A needle valve, to help balancing flow and pressure in the system was installed in a bypass returning the solution directly to the feed tank. A needle valve fitted in the concentrate line after the filtration cells (CF042, Sterlitech, Figure 2) was used as a backpressure valve to set the pressure and cross flow in the system. Pressure in the system was measured with a sensor (Cerabar M, Endress & Hauser) located in the feed line just before the filtration cells. Due to the type of pipes, valves and connectors a maximum pressure of 5 bar could be applied in the system. The system was operated in batch mode and consequently both permeate and concentrate were recirculated back into the feed tank. In this case, valves are fitted in the permeate line to divert the flow and determine the permeate flow rate. The membrane coupons to be tested were placed in the cells. The system was then operated at 5 bar for 15-18 hours (overnight) with DI water for compaction of the membrane coupons and stabilisation of the permeate flow. The permeability was determined from the last 3 hours of operational data. The DI water was subsequently replaced by a 1500 mg/L NaCl solution and the system was operated for another 3 hours at 5 bar during which the salt rejection was monitored using SevenEasy conductimeter (Mettler Toledo, USA).

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Figure 2. Cross flow filtration unit.

Scanning Electron Microscopy (SEM)

A Phillips XL30 scanning electron microscope (secondary electrons) was used for imaging the surface of different membrane samples dried in a desiccator for at least 24h and coated with Pt to ensure the electron drainage and to avoid sample charging. Samples of approximately 3x10 mm were cut from the coupons, placed on metal stubs, Pt coated (Centre for Microscopy and Microanalysis, UQ) and then placed in a desiccator until the measurement. The secondary electron imaging mode enables to generate high magnification images, giving information on the morphology of the surface. Typical imaging has been done at 1000x magnification rates, 10kV accelerating voltage.

Infrared spectroscopy (ATR-FTIR)

The integrity of the membrane structure of the coupons was evaluated with infrared spectroscopy on a Nicolet 5700 ATR-FTIR spectrometer. As an internal reflection element, a flat plate Germanium crystal (penetration depth of around 0.5 micron) was used to get a higher contribution of the polyamide skin top layer of the membrane to the recorded spectrum in comparison to the standard diamond crystal, where the infrared beam penetrates deeper into the sample. The membranes were placed on the ATR crystal and pressed onto the surface with a needle press. The measuring cell was covered and continuously purged with dry air to prevent interference of atmospheric moisture with the spectra.

3. Results and Discussion

3.1. Preservation trials with unused membranes

3.1.1. Hydraulic performances

The results of the trials conducted with unused membranes are shown in Figures 3 and 4, which illustrate pure water permeability and the salt rejection, respectively, for each RO membrane stored in each of the preservation solutions, as well as the control solutions. The raw data are presented in appendix B.

Before membrane storage, membrane performance were measured to establish the membrane coupons performance baselines and to further discuss the impact of the preservation solutions on the membranes. The pure water permeability baselines were 4.8±0.4 and 1.6±0.0 L/m^2.h.bar for ESPA-2 (n=2) and SWC-5 (n=2) respectively. The salt rejection baselines were 97.9±1.6 and 98.6±0.7 L/m^2.h.bar for ESPA-2 (n=2) and SWC-5 (n=2) respectively.
After one-month storage, filtration trials were performed with the stored membrane coupons (n=2) and compared with the baseline values (see Figure 3 and 4).

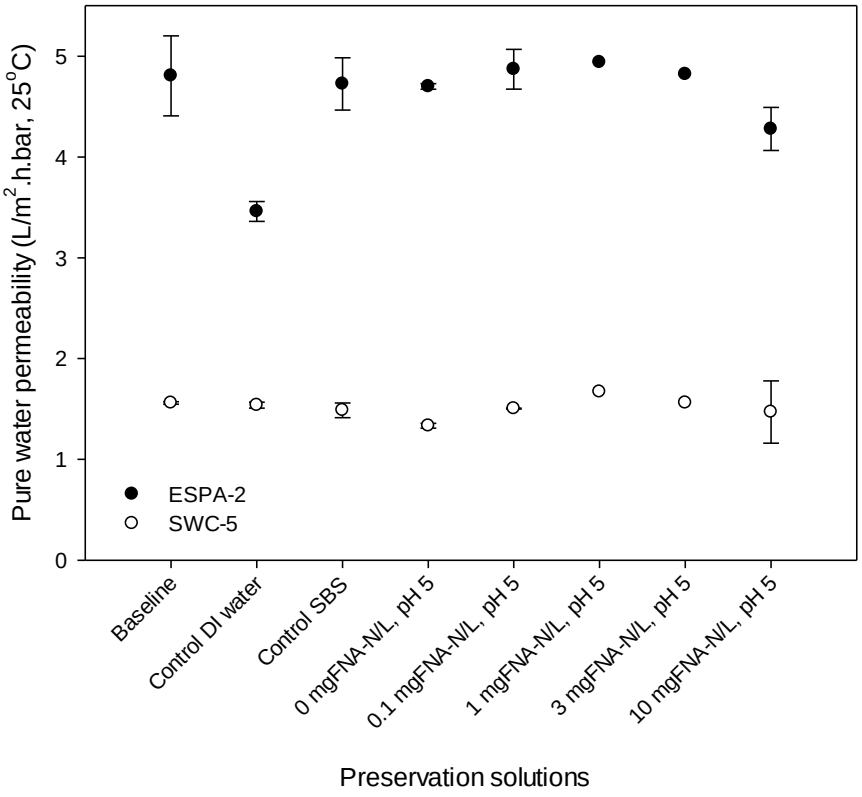


Figure 3. Pure water permeability of ESPA-2 and SWC-5 RO membranes before (baseline) and after one-month storage in different preservation solutions (n=2).

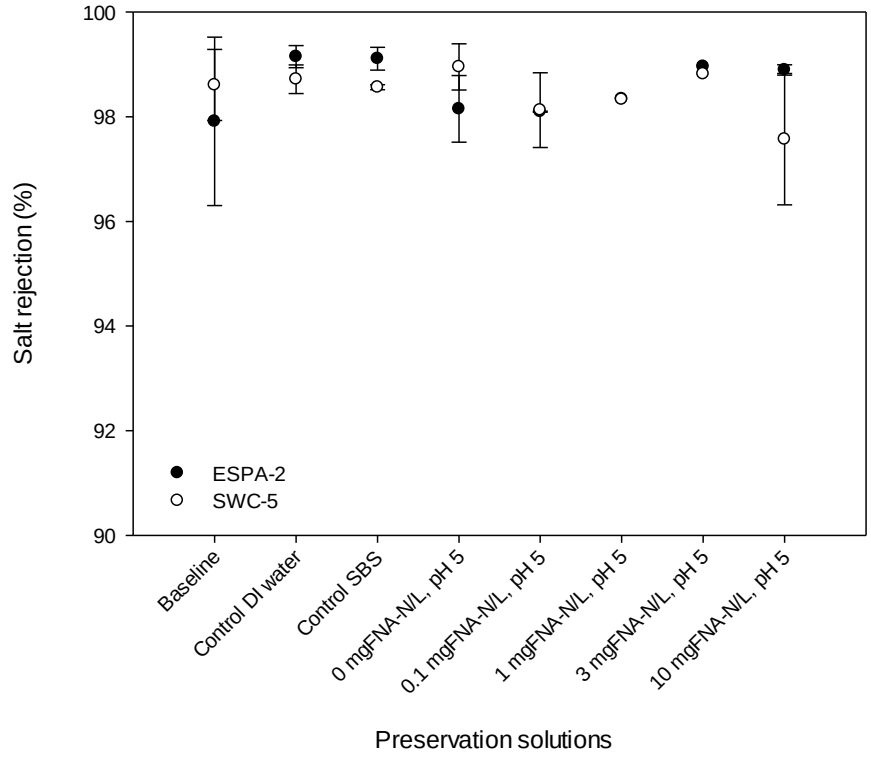


Figure 4. Salt rejection performance of ESPA-2 and SWC-5 RO membranes before (baseline) and after one-month storage in different preservation solutions (n=2).

The main results can be summarized as follows:

- Figure 3 shows that permeabilities were stable after one month storage for SWC-5 membranes. Pure water permeabilities vary between 1.3 and 1.7 L/m^2.h.bar. The permeability variation is below the 15% permeability variability acceptable due to membrane manufacturing and experimental error. Membrane producers typically specify the permeability of modules with a tolerance of ±15–20% of the nominal value [12].
- Similarly, no loss of performance after short-term storage was observed for ESPA-2 membranes, with permeabilities values between 4.3 and 4.9 L/m^2.h.bar. Only the two membrane stored in DI water (control) showed lower permeation compared to the baseline (3.5±0.1versus 4.8±0.4 L/m^2.h.bar). During the storage, the resealable bags were not closed properly resulting in leaking of preservation solutions in the vacuum sealed bag. This permeability drop after could be explained by a drying of the membrane coupons.
- In terms of salt passage, no performance difference was observed for all the membrane/preservation solution combinations tested. Salt rejections were between 98.1 and 99.2% for ESPA-2 membrane (higher than under baseline conditions) and 97.6 to 99.0% for SWC-5.

3.1.2. Biomass quantification

ATP was measured to quantify and compared the bio contamination in the different preservation solutions. Figure 5 presents the biomass concentration (ngATP/L) in the different preservation solutions after one-month storage. The following general results can be drawn:

- The highest ATP value was observed in the control solution with DI water only, indicating a higher total bacteria count compared to the other preservation solutions. This result was observed for the two unused membrane tested.
- Very low biomass concentrations were measured in the other preservation solution. However, the ATP concentration seems to decrease with FNA concentration increase (from 0 to 10 mg FNA-N/L; 27±6 to 7±0 ngATP/L).
- The lower biomass concentrations (≤10 ngATP/L) were observed for 10 mgFNA-N/L solution at pH 5 and the SBS control solution.

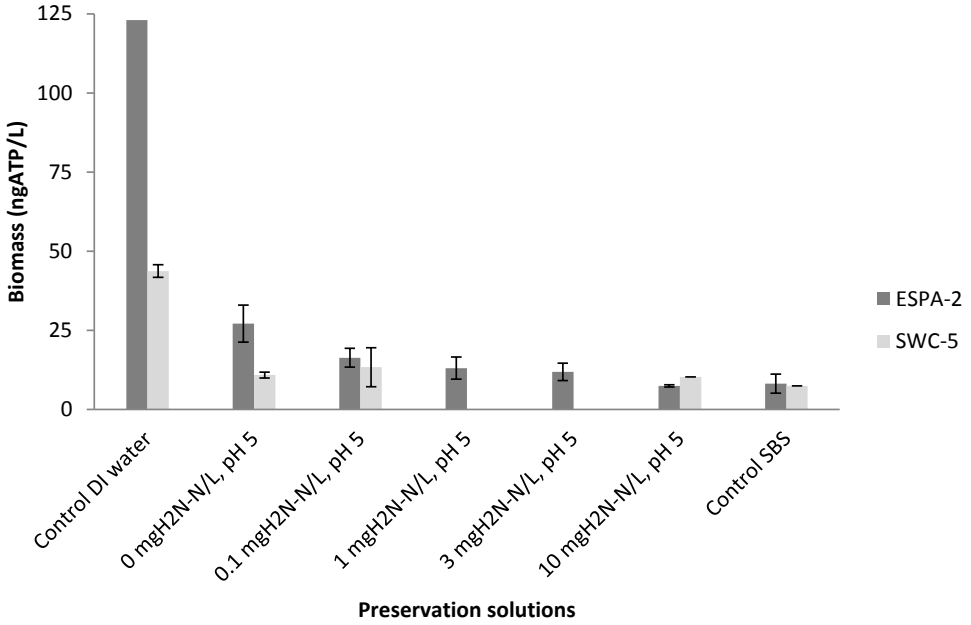
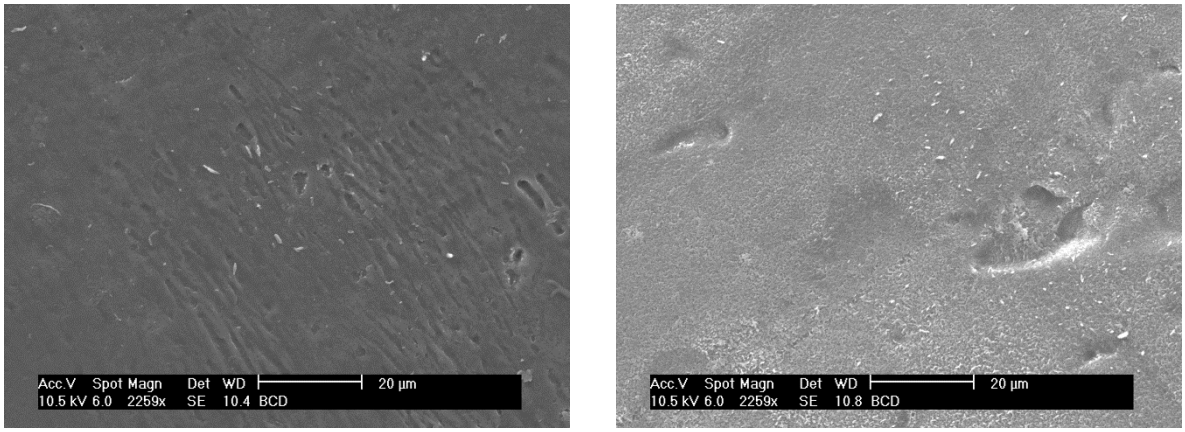


Figure 5. ATP content in different preservation solutions after one-month storage. All ATP measurements were measured 3 times (for 3 triplicates).

SEM images were conducted on the SWC-5 membrane coupons to identify the adherence of bacteria on the membrane surface (see Figure 6). The presence of bacteria could be observed only on two membrane samples, i.e., membranes stored with 0.1 mgN/L of FNA, pH 5 and SBS solution, and only on low proportion. These results support the ATP results: no/low bacterial growth/contamination could be observed after one-month storage, whatever the preservation solution applied.

During storage in full-scale application, it is difficult to isolate the RO system from air, resulting in SBS oxidation resulting in continuous pH dropping. Once SBS is oxidized it can act as nutrient for anaerobic bacteria, resulting in formation of heavy film of anaerobic bacteria [1]. However, in this study, unused membrane were used limiting the bacteria contamination compared to used membranes and one-month storage was likely too short to observe biofouling development. These results suggest the limitation of short-term trials versus long-term trials.



a b

Figure 6. SEM (Pt coating) analysis of the membranes (feed side) after one-month storage in (a) 0.1 mgFNA-N/L, pH 5 solution and (b) SBS solution.

3.1.3. Attenuated total reflection-Fourier transform infrared (ATR-FTIR)

Although no hydraulic performance decline were observed, ATR-FTIR spectroscopy was applied to investigate if membrane modifications occurred during the storage, i.e., to study the compatibility of the preservation solutions and the membranes. The wavenumber of interest are 1541 cm^{-1} and 1609 cm^{-1} which are the wavelengths of N-H bonding of amide and C=C (double) bonds of aromatic amide respectively. These double bonds are occurring in polyamide structures.

The spectra measured for the membrane coupons after one-month storage are presented in Appendix C. No variations in absorbance intensity were observed between the different samples. No clear chemical conversion of the membrane active layer could be observed on the samples tested. The ATR-FTIR peak intensity collected for these two peaks were similar to the ones obtained for the baseline membrane. These results suggested that no structural damages to the active layer of the membranes occurred during short term preservation using FNA up to 10 mgN/L.

3.2. Preservation trials with used membranes

3.2.1. Hydraulic performances

The results of the trials conducted with used membranes are shown in Figures 7 and 8, which illustrate pure water permeability and the salt rejection, respectively for each of the preservation solutions tested, as well as the control solutions. The raw data are presented in appendix B.

The pure water permeability and salt rejection baselines were 4.1±0.6 L/m^2.h.bar and 95.5±1.8% respectively, based on n=2 measurements. After one-month storage, permeability increased, indicating an improvement of the hydraulic performances of the membranes, while no clear trend could be observed for salt rejection. The performance could not be measured for the control with DI water at pH 5.

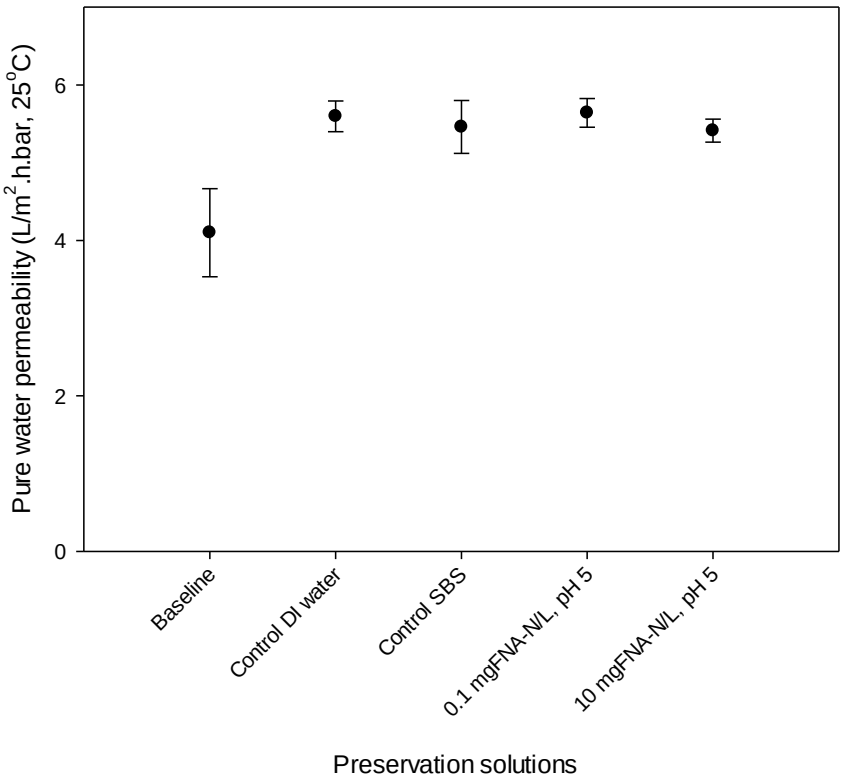


Figure 7. Pure water permeability of fouled membranes (ROFNA-3) before (baseline) and after one-month storage in different preservation solutions.

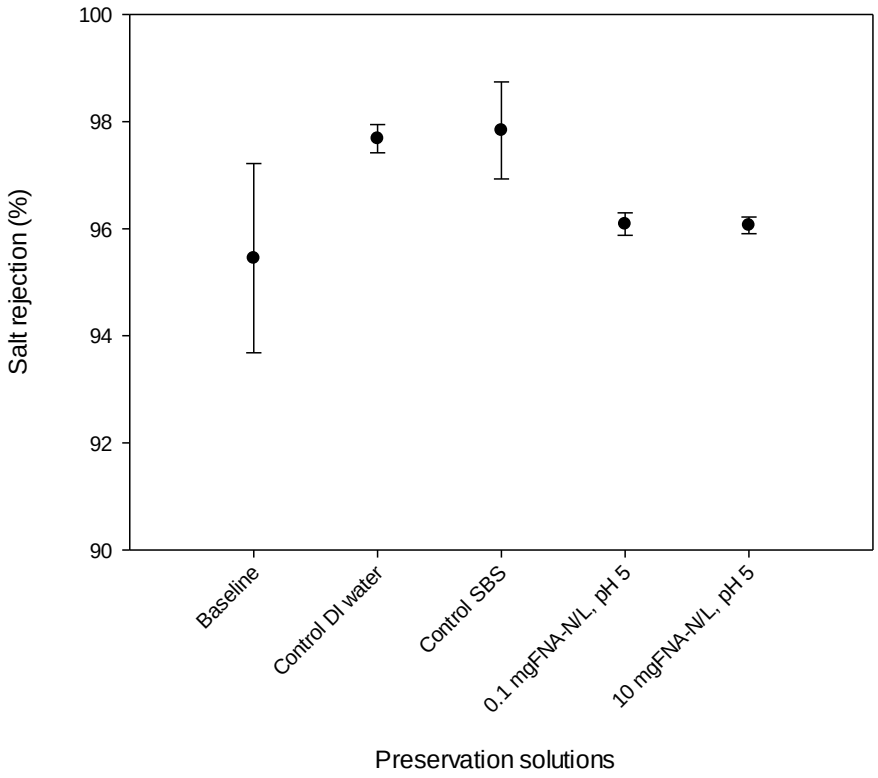


Figure 8. Salt rejection of fouled membranes (ROFNA-3) before (baseline) and after one-month storage in different preservation solutions.

However, no significant difference could be observed between the different preservation solutions tested in terms of hydraulic performances. Pure water permeabilities vary between 5.4 and 5.6 L/m^2.h.bar and the salt rejections vary between 96.1 and 99.8%. The increase of pure water permeability observed is likely due to a positive cleaning effect of the one-month soaking.

3.2.2. Biomass quantification

Figure 9 presents the biomass concentration (ngATP/L) in the different preservation solutions after one-month storage. ATP values showed higher biomass concentration compared to the ones conducted for the unused membranes. This is likely due to a detachment of foulant from the used membranes during storage. However similar trends were observed compared to the short-term membrane preservation trials performed with unused membranes:

- The highest ATP value was observed in the control solution with DI water only (1022±830 ngATP/L), indicating a larger bio-contamination/bacterial growth.
- The lowest biomass concentration (≤220 ngATP/L) were observed for 10 mgFNA-N/L solution at pH 5 (219±134 ngATP/L) and the SBS control solution (105±35 ngATP/L).

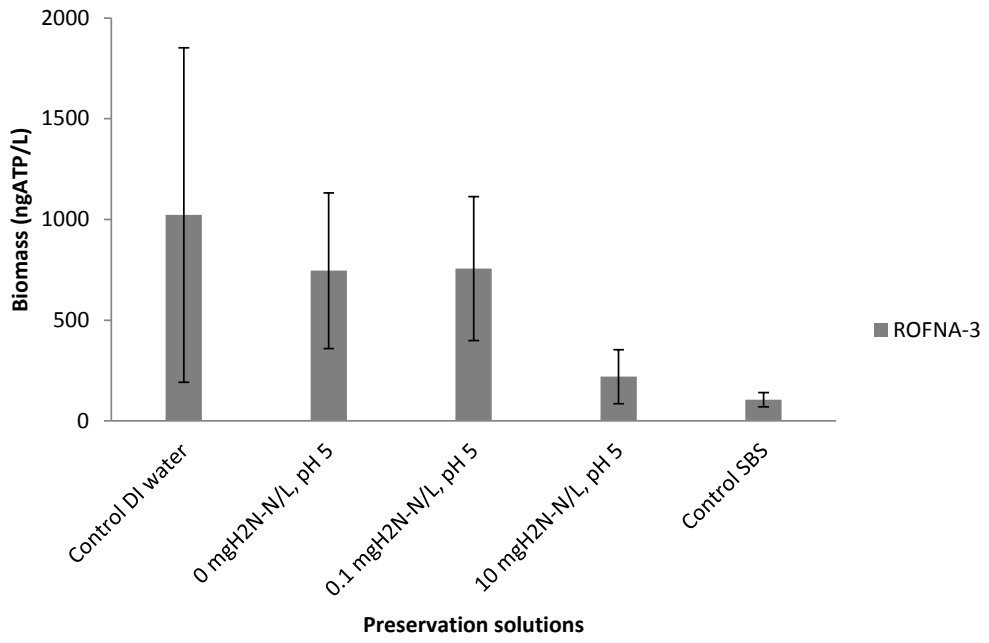


Figure 9. ATP content in different preservation solutions after one-month storage. All ATP measurements were measured 3 times in triplicates.

4. Conclusion and Perspectives

For this project the efficiency of free nitrous acid for membrane storage in order to prevent microbiological growth and/or membrane degradation was investigated and was benchmark against sodium bisulphite.

Short-term preservation trials performed with unused and used RO membrane coupons stored in different FNA solutions for one month revealed the suitability of FNA for this application.

No membrane degradation (loss of hydraulic performance and integrity) could be observed for the different chemicals. The permeability and salt rejection were stable after one month storage and infrared spectroscopy analysis demonstrated that no chemical changes occurred on the polyamide layer of the membranes. The results show that FNA can be an equivalent preservation solution to SBS (reference) for short-term storage of unused membranes. Both chemicals maintained a low level of bacteria on the membrane (SEM analysis) and in the preservation solution (ATP analysis). The short term preservation trials conducted confirmed the stability of the membrane performance when stored in FNA. However no significant differences were observed compared to the controls: solution with DI water and DI water, pH 5 (no biological contamination or membrane degradation). One-month of storage was likely too short to observe biofilm development. It was not possible to determine the low-end dosages to preserve membrane without biofilm development. Furthermore, the performance variation of the membranes observed were not significant considering experimental errors and natural variation of the membrane.

These results suggest the limitation of short-term trials (no biofilm development) and the use of membrane coupons instead of full-scale plant RO elements (large performance variation and time consumption for filtration trials). Therefore, the long-term preservation trials will be conducted with 4-inch RO modules to conduct trials in closer realistic plant conditions. However, due to the price of RO module and as membrane showed to be compatible with the preservation solutions/chemicals applied, a better investigation of preservation solution stability will be conducted. Secondary effluents could for example be used to simulate the presence of foulants on the membrane and study the biological growth risk during long-term storage.

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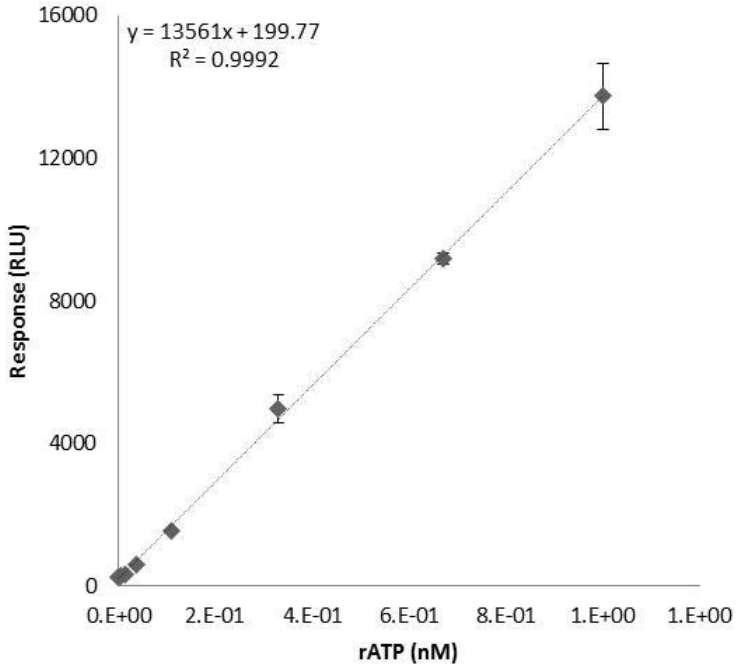
Appendix

A. ATP calibration curve with the optimised protocol and a pure ATP standard in sterile water. Error bars show the standard deviation on 3 measurements.

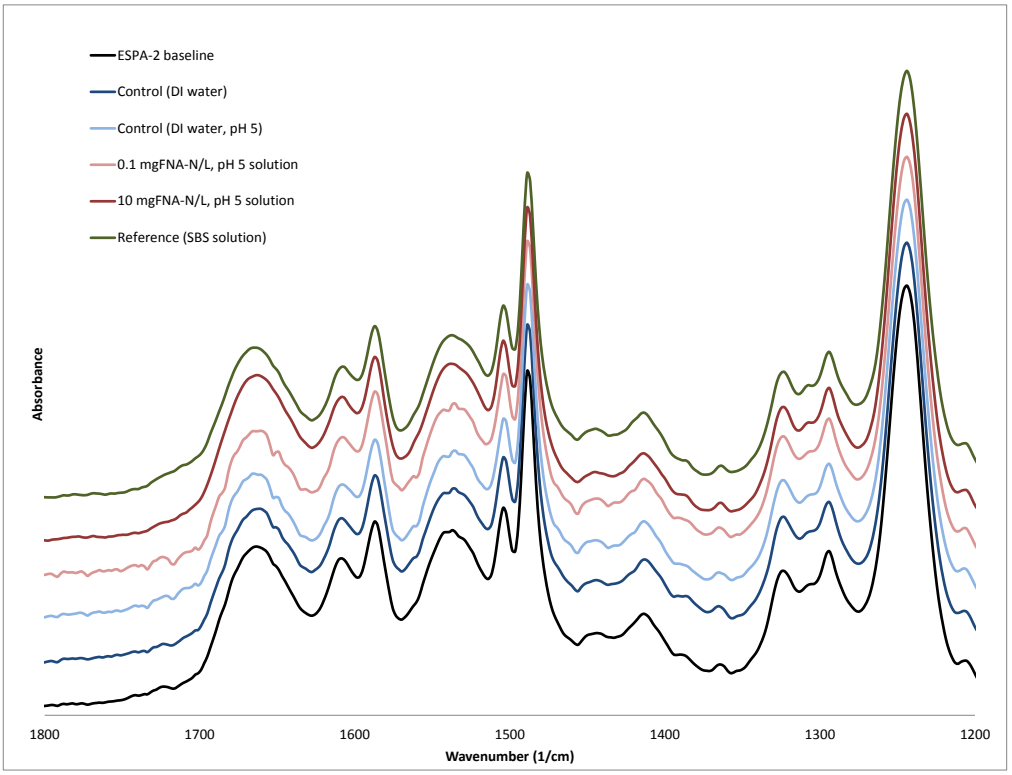


B. Permeability and salt rejection results (Permeability (L/m^2.h.bar, 25^{o}C)/ Salt rejection (%)) of the short-term membrane preservation trials.

	ESPA-2			SWC-5			ROFNA-3		
	Pure water permeability (L/m^2.h.bar, 25^{o}C)	Salt solution permeability (L/m^2.h.bar, 25^{o}C)	Salt rejection (%)	Pure water permeability (L/m^2.h.bar, 25^{o}C)	Salt solution permeability (L/m^2.h.bar, 25^{o}C)	Salt rejection (%)	Pure water permeability (L/m^2.h.bar, 25^{o}C)	Salt solution permeability (L/m^2.h.bar, 25^{o}C)	Salt rejection (%)
1#0a	5.0±0.1	3.2±0.1	96.8±0.4	1.6±0.0	1.3±0.0	99.1±0.1	4.5±0.1	2.8±0.1	94.2±1.6
1#0b	4.4±0.1	3.1±0.1	99.1±0.0	1.6±0.0	1.2±0.1	98.1±0.8	3.7±0.1	n.a	96.7±1.4
1#1a	3.4±0.1	2.7±0.1	99.3±0.1	1.6±0.1	1.1±0.1	98.5±0.5	-	-	-
1#1b	3.5±0.1	2.7±0.1	99.0±0.1	1.5±0.1	1.1±0.0	98.9±0.1	5.6±0.2	3.4±0.0	97.7±0.3
1#2a	4.7±0.1	3.4±0.3	98.6±0.1	1.3±0.1	1.1±0.1	98.6±1.0	n.a	n.a	n.a
1#2b	4.7±0.2	3.4±0.3	97.7±0.0	1.3±0.1	1.1±0.1	99.3±0.4	n.a	n.a	n.a
1#3a	5.0±0.1	2.9±0.0	98.1±0.2	1.5±0.4	1.0±0.1	97.6±0.4	n.a	n.a	n.a
1#3b	4.7±0.2	3.5±0.2	98.1±0.0	1.5±0.0	1.3±0.1	98.6±0.4	5.6±0.2	3.8±0.1	96.1±0.2
1#4a	4.9±0.1	2.8±0.1	98.3±0.2	1.7±0.1	1.2±0.0	98.3±0.5	-	-	-
1#5a	4.8±0.3	3.7±0.5	99.0±0.1	1.6±0.1	1.2±0.0	98.8±0.4	-	-	-
1#6a	4.1±0.1	2.8±0.2	98.8±0.1	1.5±0.5	1.1±0.1	98.5±1.0	5.4±0.1	3.4±0.2	96.1±0.2
1#6b	4.4±0.1	3.2±0.2	99.0±0.0	1.7±0.0	1.4±0.1	96.7±0.6	n.a	n.a	n.a
1#7a	4.9±0.4	2.8±0.2	99.3±0.0	1.5±0.0	1.1±0.0	98.6±0.1	5.7±0.1	3.4±0.1	97.2±0.1
1#7b	4.5±0.1	3.7±0.5	99.0±0.1	1.4±0.0	1.0±0.0	98.5±0.2	5.2±0.2	3.2±0.1	98.5±0.2

C. FTIR spectrum of (a) ESPA-2 and (b) SWC-5 membrane stored one month in different preservation solutions.

a.



b.