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Optimization of chemical cleaning of a reverse osmosis membrane from a desalination plant by means of two-step static tests

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ABSTRACT

Research in cleaning procedures of reverse osmosis membranes used in seawater desalination to minimize costs and achieve high efficiency is necessary. Multi-step cleaning can represent a useful tool, since the cleaning efficiency can be improved by means of utilization of different chemicals with complementary cleaning mechanisms. The objective of this work was the optimization of a two-step cleaning procedure to recover the membrane properties and reduce power costs. Spent Hydranautics SWC3 membranes (USA) were supplied by a desalination plant. Cleaning tests were performed in three stages: one-step static cleaning, two-step static cleaning and characterization of the membrane surface after the cleaning process. Four cleaning agents at two different concentrations were used. All possible combinations of them were considered, including sequence effect. After the cleaning process, membrane surface was characterized by field emission scanning electron microscopy coupled with energy dispersive X-ray spectroscopy and atomic force microscopy. One-step static cleaning test indicated that sodium dodecyl sulphate 1% w/v was the most efficient cleaning solution, followed by NaOH 2% w/v. Two-step cleaning tests showed that the procedure that maximized permeate flux recovery was surfactant-alkaline cleaning, whereas the one that maximized the recovery of the salt rejection index was alkaline-acid sequence. Characterization of the membrane surface after the cleaning steps confirmed that fouling deposits were significantly removed.

Keywords: RO; Multi-step cleaning; Static test; Chemical agent

1. Introduction

Costs associated with membrane cleaning in seawater reverse osmosis (RO) desalination plants can represent up to 50% of the total operation costs [1]. These costs include chemicals, heating and pumping of the solutions through the membrane module. Therefore, research in cleaning procedures that minimize costs and achieve high efficiency becomes necessary.

The efficiency of a membrane chemical cleaning procedure depends on several factors. Some of them

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are related to the nature of the fouling layer, whereas other factors are related to the characteristics of the cleaning process: hydrodynamic aspects (pressure, turbulence in the proximity of the membrane surface and cross-flow velocity), chemical factors (chemical nature of the cleaning agent, concentration and pH) and physical characteristics (temperature). The knowledge of the effect that these factors have on the efficiency of the cleaning process is fundamental to select and perform the most suitable cleaning procedure.

Membrane cleaning process can be carried out in one step or in multiple steps. In a previous work by the Garcia-Fayos et al. [2], one-step cleaning procedures were tested to clean an RO membrane used in a desalination plant. Some of the factors mentioned afore were analyzed and it was concluded that sodium dodecyl sulphate (SDS) was the most efficient cleaning agent for the conditions and membranes tested. Sodium hydroxide showed a positive behaviour as well when it was tested at 25˚C. Moreover, the membrane autopsy carried out in this previous work by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX), atomic force microscopy (AFM) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was able to confirm the efficiency of the cleaning process.

On the other hand, as a large amount of studies about membrane chemical cleaning show, multi-step cleaning can represent a useful tool for the optimization of cleaning procedures. According to Ang et al., cleaning efficiency can be improved by combining different chemicals with complementary cleaning mechanisms [3,4]. Particularly, sodium hydroxide has an exceptional ability to enhance other cleaning agent effect, due to its facility to detach the fouling layer [5].

Veza and Sadhwani investigated, in 2001, the efficiency of the chemical cleaning of RO membranes used for seawater desalination. They used acids, bases and surfactants to clean the membranes. Attending to the permeate flux criteria, the most efficient cleaning procedures were those using alkaline solutions with surfactants, acid solutions with surfactants, as well as two-step cleaning procedures using hydrochloric acid with surfactants as the first step and NaOH with surfactants as the second cleaning step. This two-step cleaning procedure was also the most efficient attending to the salt rejection criteria.

In membrane processes to treat surface water, literature recommends basic-acid cleaning sequence, whereas the inverse sequence is recommended for groundwater treatment [6]. In the case of membranes treating surface water, such as seawater, the charge of the membrane surface and foulants after the alkaline cleaning along with swelling of both the fouling layer and the membrane at high pH values enhance the fouling removal efficiency of the subsequent acid step. In the case of membranes treating groundwater, acid-basic sequence is more suitable as the acid solution removes the inorganic fouling (metallic oxides and carbonates) and prevents the inorganic compounds from precipitating at high pH in the alkaline step [6].

The objective of this work is to optimize the efficiency of the cleaning process of RO membranes that show irreversible fouling after a long time of operation in a seawater desalination plant. Two-step cleaning procedures have been investigated to maximize the recovery of membrane properties.

2. Materials and methods

2.1. Membranes

The membrane used in this work was a spiral-wound RO membrane with a diameter of 8 inches, Hydranautics SWC3 (USA), retired from a desalination plant. The characterization of the fouling layer and the cleaning tests were performed using pieces cut from the commercial RO membrane. Membrane samples of the size of 10×10 cm were used.

2.2. Membrane surface characterization

The membrane fouling characterization was carried out by SEM-EDX (Jeol JSM-6300, Japan) and AFM (Veeco Multimode, USA).

Four samples from the new membrane and four samples from the fouled membrane were gold coated and analysed by SEM. On the other hand, four samples from the new membrane and four samples from the fouled membrane were carbon coated and analysed by SEM-EDX. Thus, a quantitative chemical analysis of the membrane surface and the fouling layer deposited on the membrane surface was performed. The same amount of samples was analysed by AFM. AFM images were processed by Nanoscope software (NanoScope Services Ltd., UK) to determine different roughness parameters: R_a (average roughness), R_q (mean square roughness) and R_{max} (maximum ridge and valley height).

Field emission scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (FESEM-EDX, Zeiss Ultra55, Germany) and AFM were used to analyse the membrane surface of four samples cleaned with the best procedures in order to check the efficiency of the one-step and two-step cleaning protocols to remove the fouling layer.

2.3. One-step cleaning tests

After analysing the results obtained in a previous work by the Garcia-Fayos et al. [2], eight cleaning solutions were selected to perform the membrane cleaning. The composition of those solutions is shown in Table 1. All chemicals were supplied by Panreac (Spain).

As a first step, the efficiency of these solutions to clean the membrane was checked at 25°C following the procedure described in Fig. 1. Each cleaning solution was tested on four membrane samples and the results were averaged. Blank values of permeate flux (J_{P0}) and salt rejection index (SRI_0) were experimentally quantified using distilled water instead and were taken as a reference to determine the one-step cleaning efficiency.

Table 1
Composition of the cleaning solutions selected

Cleaning agent	Concentration (% w/v)	
Citric acid	0.01	0.2
Disodium salt of ethylenediaminetetraacetic acid (Na_2-EDTA)	0.1	4
Sodium dodecyl sulphate (SDS)	0.05	1
NaOH	0.01	2

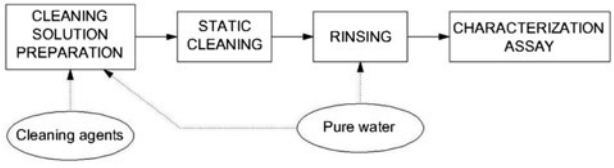

Fig. 1. Block diagram of the experimental methodology followed to carry out the cleaning tests.

Static cleaning tests were carried out according to the methodology defined by Arnal et al. [7,8]. The cleaning consisted of soaking the samples into the cleaning solution for one hour at 25°C temperature. After that, the samples were rinsed with distilled water for one hour, renewing the water every 20 min.

After the cleaning step, the characterization of the membrane permselectivity properties (permeability and SRI) was carried out to determine the process efficiency. The characterization test was performed according to the manufacturer's test conditions (55 bar, 32.000 mg/L of NaCl and 25°C). The test lasted for one hour. During the test, permeate flux (J_P) and SRI were measured every 15 min. A diagram of the pilot plant used for membrane characterization is shown in Fig. 2.

The pilot plant employed to characterize the permselective properties of the membrane was composed of a 100 L feed tank, a 25 m microfilter (Cintropur NW32, Airwatec SA, Belgium), a high pressure pump (CAT 3CP1241, USA) and three plate-and-frame membrane modules installed in series: the first two of them with capacity for eight membrane samples and the last one with capacity for four ones.

The cleaning efficiency was calculated by means of the percent of recovery of permeability and SRI with respect to the blank. One-step blank values (J_{P0} and SRI_0) were used to calculate the recovery of these parameters after the one-step cleaning procedure, according to these equations:

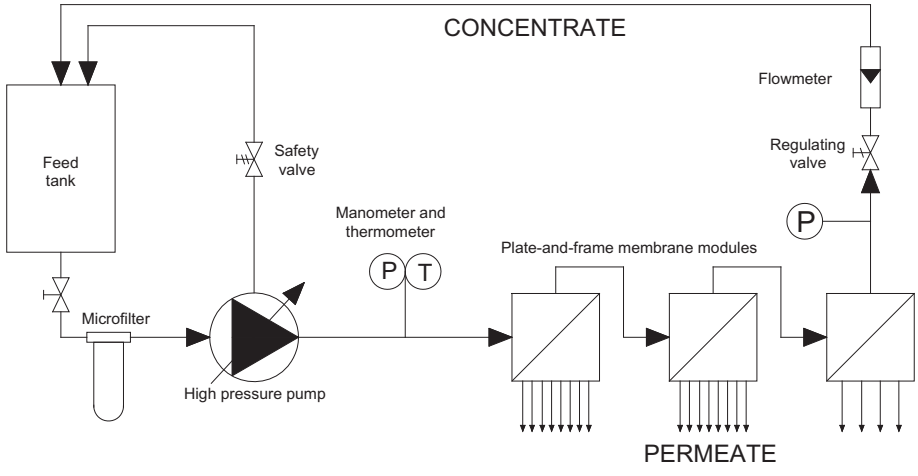

Fig. 2. Flowchart of the pilot plant used for the characterization of the membrane samples.

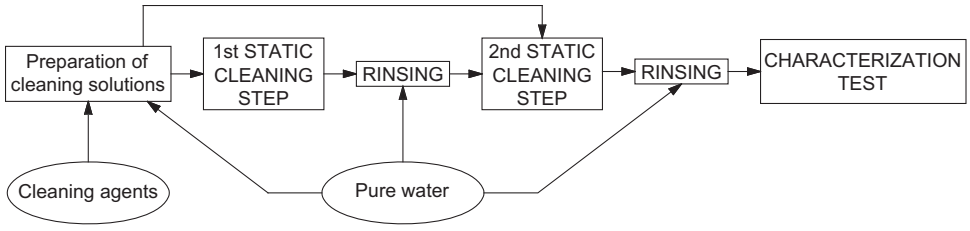

Fig. 3. Block diagram of the experimental methodology followed for the two-step cleaning tests.

$$\mathrm{Rec}(J_P)(\%) = \frac{J_P - J_{P0}}{J_{P0}} \times 100 \quad (1)$$

$$\mathrm{Rec(SRI)}\,(\%) = \mathrm{SRI} - \mathrm{SRI}_0 \quad (2)$$

2.4. Two-step cleaning tests and characterization of the permselective properties

A new protocol to perform the cleaning and to characterize the membrane properties was defined for the two-step cleaning tests. It was composed of six consecutive stages as shown in Fig. 3: preparation of the cleaning solutions, 1st static cleaning step, rinsing with pure water, 2nd static cleaning step, rinsing with pure water and characterization of the permselective properties of the membrane.

The two-step cleaning process considered all the possible combinations among the eight cleaning solutions included in Table 1. Every combination was tested on four membrane samples and the results shown are the averaged values (relative error of 3.63%). In this way, the effect of the nature of the cleaning agents, their concentration, their possible complementary cleaning mechanisms and the effect of sequence on the cleaning efficiency were studied.

Additionally, distilled water was included as a cleaning agent to determine the effect of the operating conditions on the membrane cleaning without the addition of any chemical. Averaged experimental values of permeability and SRI from 16 membrane samples cleaned by this procedure were considered as two-step blank values (J_{P02} and SRI_{02}).

The two-step static cleaning tests were carried out according to the methodology described by Arnal et al. [7,8]. Every cleaning step consisted of soaking the membrane samples into the cleaning solution at 25°C for one hour and it was followed by 30 min of rinsing with distilled water.

After the cleaning steps, permeate flux and SRI were determined to evaluate the cleaning efficiency. The characterization of the membrane permselectivity properties was performed in the pilot plant shown in Fig. 2 using the methodology previously described.

Two-step blank values (J_{P02} and SRI_{02}) were used to calculate the recovery of permeability and SRI after the two-step cleaning procedure, according to these equations:

$$\mathrm{Rec}(J_P)(\%) = \frac{J_P - J_{P02}}{J_{P02}} \times 100 \quad (3)$$

$$\mathrm{Rec(SRI)}\,(\%) = \mathrm{SRI} - \mathrm{SRI}_{02} \quad (4)$$

The results were also compared with the characteristics of the virgin membrane provided by the membrane manufacturer.

3. Results

3.1. Membrane fouling characterization

In Fig. 4, the SEM micrographs of the virgin and fouled membrane can be observed. Severe fouling deposition can be noticed in Fig. 4(b).

SEM-EDX analysis indicated that silica, aluminium and iron silicates were the most abundant compounds in the fouling layer and, to a lesser extent, aluminium and iron oxides and hydroxides. Inorganic and colloidal fouling were present on the membrane surface.

Fig. 5 shows the results of the AFM analysis of the virgin and fouled membrane surface. Foulants deposition provided more heterogeneity to the membrane surface, as it can be observed in Fig. 5(b). An increase in roughness parameters due to membrane fouling was observed. This increase of R_{max} was the most pronounced.

In a previous work by the authors, the ATR-FTIR spectrum of the fouling layer of the Hydranautics SWC3 membrane was performed. The results indicated that membrane foulants included silicate materials and natural organic matter (NOM) compounds, very common when treating seawater. Analogous results, obtained by other authors, were analysed by ATR-FTIR which is the fouling layer of RO membranes and used for seawater desalination.

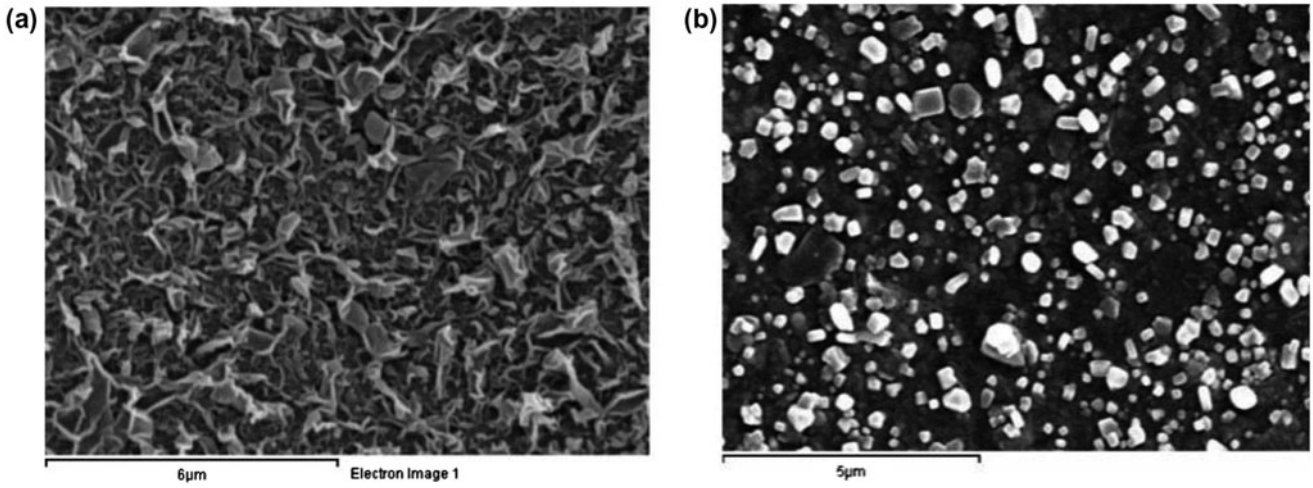

Fig. 4. SEM micrographs ×10,000 magnification: (a) virgin membrane (b) fouled membrane.

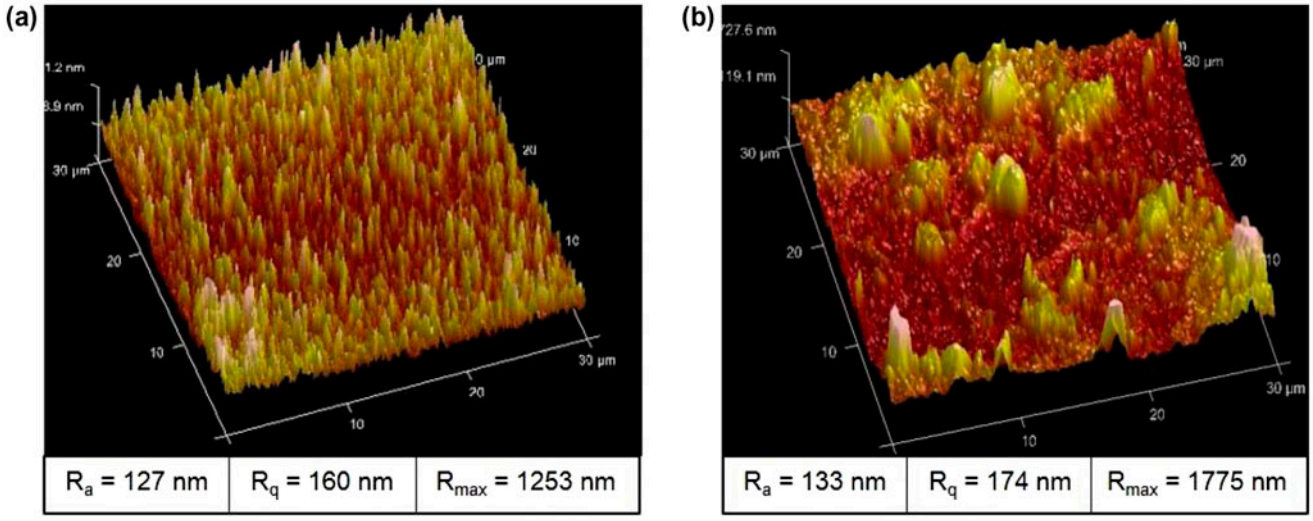

Fig. 5. AFM characterization of membrane surface roughness: (a) virgin membrane (b) fouled membrane.

They found that silicates, proteins and polysaccharide materials were part of the fouling layer [9–11].

In a previous work by the authors, the elemental analysis of the fouling layer was also performed. It revealed that around 30% of the fouling deposits were organic. The rest of the fouling materials deposited on the membrane surface (70%) were inorganic compounds, especially silicates as it was confirmed from ATR-FTIR and SEM-EDX analysis.

3.2. Cleaning tests and characterization of permselective properties

This work was divided into two blocks: one-step cleaning tests and two-step cleaning tests.

3.2.1. One-step cleaning tests

3.2.1.1. Membrane initial state. Table 2 shows the values of permeability and SRI for the virgin membrane according to the data provided by the membrane manufacturer. The values of permeability and SRI that corresponded to the one-step and two-step blanks are shown in this table as well.

As it is observed, if one-step blank and virgin membrane values are compared, membrane permeability decreased by 49% and membrane selectivity by 7.42% due to severe fouling.

3.2.1.2. Cleaning tests. The results of the one-step cleaning tests are shown in Fig. 6. The dotted lines in the graphics represent the values for the virgin membrane

Table 2
Permselective properties of the virgin membrane, one-step blank and two-step blank

	J_P (L/h m^2 bar)	SRI (%)
Virgin membrane*	0.4915	99.6
One-step blank	0.2503	92.18
Two-step blank	0.3514	88.46

*According to the technical specifications supplied by the membrane manufacturer (characterization test conditions: 55 bar, 32.000 ppm of NaCl and 25°C).

obtained from the membrane manufacturer. It can be noticed that the solution that reached the highest permeability recovery was the 1% SDS solution (136.34%). Cleaning with this solution was able to recover completely the membrane permeability, even exceeding the value of the virgin membrane. This result can be explained by the enlargement of the membrane pores and/or an increase in the porosity of the membrane skin layer due to the adsorption of surfactant to the membrane active layer [12]. However, SRI recovery did not reach the value that corresponded to the virgin membrane.

The one-step cleaning procedure using NaOH 2% also achieved great results attending to the recovery of permeability (92.04%), as it almost reached the value of the virgin membrane. Nevertheless, this procedure showed a low SRI recovery (1.77%). The rest of the solutions tested were also able to increase the membrane permeability.

On the other hand, as it can be observed in Fig. 6(b), the only solutions that achieved positive results in SRI recovery were SDS 1%, SDS 0.5%, NaOH 2% and citric acid 0.2%. The most diluted solutions (citric acid 0.01% and NaOH 0.01%) and Na_2–EDTA solutions were not efficient to recover the membrane selectivity.

These results are consistent with those obtained in a previous work [2], being SDS the best chemical agent tested followed by NaOH 2% solution, although

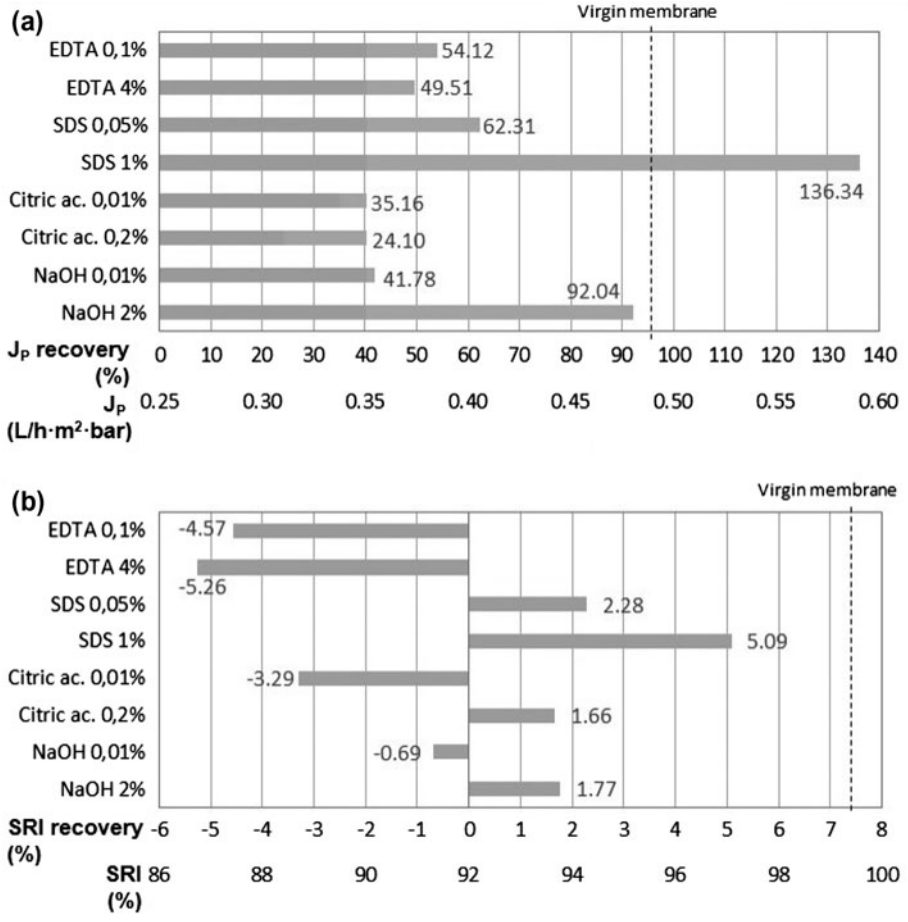

Fig. 6. Results of the one-step cleaning tests: (a) J_P recovery (b) SRI recovery.

in this case the surfactant solution SDS 1% reached better results of permeability recovery than NaOH 2% even at 25°C.

3.2.1.3 Characterization of the membrane surface after the cleaning. Fig. 7 shows FESEM micrographs of the membrane samples cleaned by the solutions that achieved the greatest cleaning efficiency. A slight decrease of the amount of fouling deposits in comparison with the fouled membrane can be observed (Fig. 4(b)). However, fouling deposits were not sufficiently removed and a significant part of them remained on the membrane surface.

FESEM-EDX was also used for analysing the elemental composition of the fouled membrane and that of the surface of the membrane samples cleaned by means of the best one-step procedures. The results are shown in Table 3.

Attending to the removal of the main elements from the membrane fouling layer (silicon, iron, aluminium, sulphur and iron), it can be observed that cleaning with SDS 1% showed higher efficiency than cleaning with NaOH 2%. The presence of oxygen increased after the cleaning process because it forms a part of the original membrane surface.

The AFM analysis of the membrane samples cleaned by the best one-step procedures is shown in Fig. 8. The surfactant solution achieved a significant decrease of all the roughness parameters in comparison with the fouled membrane (Fig. 5(b)). However, the roughness of the membrane surface increased when it was cleaned with the alkaline solution.

3.2.2. Two-step cleaning tests

3.2.2.1 Membrane initial state. The permselective properties that corresponded to the two-step blank are shown in Table 3. Comparing with the manufacturer specifications, the values of membrane permeability and SRI were 28.5 and 11.14% lower than the nominal values, respectively. This loss of performance is due to the severe fouling gathered during the membrane's useful life. The permeability of the two-step blank is higher, whereas the SRI is lower when compared to one-step blank.

3.2.2.2 Cleaning tests. The best cleaning results in terms of recovery of the permselective properties of the membrane are shown in Fig. 9. The dotted lines in the graphics represent the values for the virgin membrane obtained from the technical specifications of the membrane manufacturer.

On one hand, as it is observed from Fig. 9(a), the cleaning procedure that reached the highest recovery of permeability composed of a first cleaning step using NaOH 2% followed by a second step with SDS 1%. This procedure achieved 76.13% recovery of the permeability. The procedure that reached the second highest recovery of permeability corresponded to the same solutions but in inverse sequence. After both cleaning processes, permeability was higher than that of the virgin membrane, which can be due to an increase in the porosity of the membrane skin layer.

If the recovery of SRI is also taken into account, two more procedures were notable: NaOH 2% followed by citric acid 0.2% (permeability recovery of

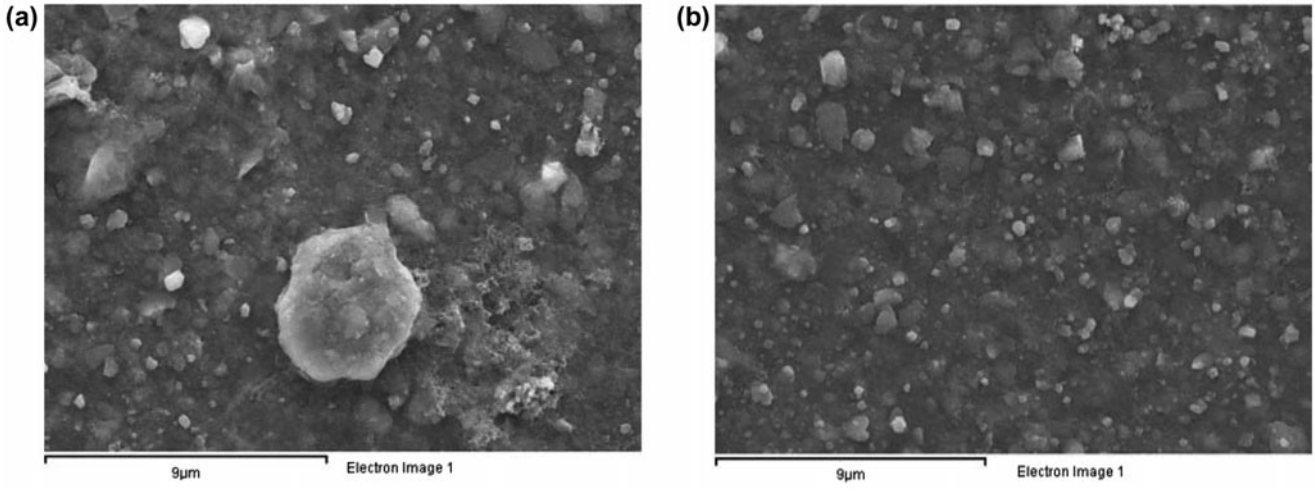

Fig. 7. FESEM micrographs of the membrane samples cleaned by: (a) SDS 1% (×6100 magnification) (b) NaOH 2% (×5900 magnification).

Table 3
Percentage distribution and variation of the elemental composition of the membrane surface when it was cleaned with the best one-step cleaning procedures: SDS 1% and NaOH 2%, in comparison with the fouled membrane, measured by FESEM-EDX

Element	Atomic % Fouled membrane	Atomic % SDS 1%	Atomic % NaOH 2%	Variation (%) SDS 1%	Variation (%) NaOH 2%
O	76.30	90.47	86.16	14.17	9.86
S	7.17	1.60	1.04	−5.57	−6.13
Si	7.01	1.14	1.26	−5.87	−5.75
Fe	3.29	2.12	2.45	−1.17	−0.84
Al	2.33	0.53	0.59	−1.80	−1.74
Na	0.94	1.81	3.72	0.87	2.79
Mg	0.88	0.19	0.25	−0.69	−0.63
P	0.67	0.00	0.00	−0.67	−0.67
Cl	0.70	1.55	2.98	0.85	2.29
K	0.29	0.12	0.11	−0.18	−0.19
Ca	0.32	0.15	0.31	−0.17	−0.01
Cr	0.11	0.00	0.00	−0.11	−0.11
N	0.00	−0.20	0.46	−0.20	0.46
Zr	0.00	0.54	0.68	0.54	0.68

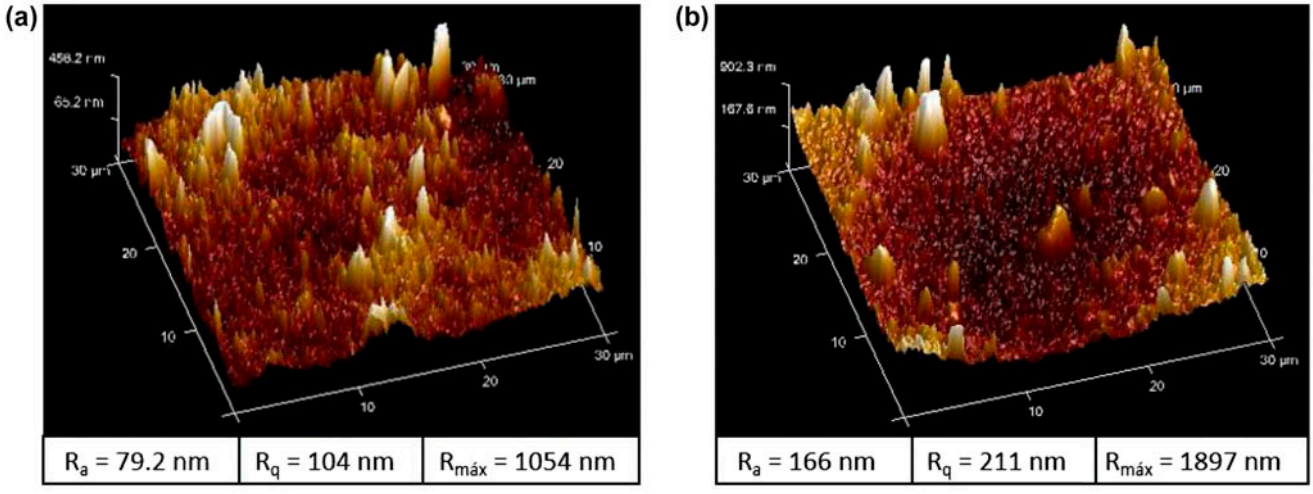

Fig. 8. AFM characterization of membrane surface roughness after cleaning by: (a) SDS 1% (b) NaOH 2%.

44.61%) and NaOH 0.01% followed by citric acid 0.2% (permeability recovery of 38.40%). Both are alkaline-acid sequences and achieved a permeability value similar to that of the virgin membrane.

On the other hand, looking at the graph shown in Fig. 9(b), the two-step cleaning procedure that obtained the highest SRI recovery corresponded to NaOH 2% followed by citric acid 0.01%, reaching an SRI of 96.43% (7.97% recovery).

Two more cleaning procedures were able to recover more than 7.5 points of SRI: SDS 1% followed by Na_2–EDTA 4% (SRI value of 96.33%) and NaOH 2% followed by citric acid 0.2% (SRI value of 96.26%). The fact that three of the four best procedures attending to SRI recovery were alkaline-acid sequences are worth mentioning, since that sequence is the most recommended for membranes treating surface water in the literature [6].

Considering J_P and SRI recovery as a whole, two cleaning procedures were selected as the best ones. If permeability recovery is decided as the main criteria, cleaning with SDS 1% followed by NaOH 2% was the best procedure, achieving a permeability of 0.6128 L/h m^2 bar (J_P recovery of 74.39%) and an SRI

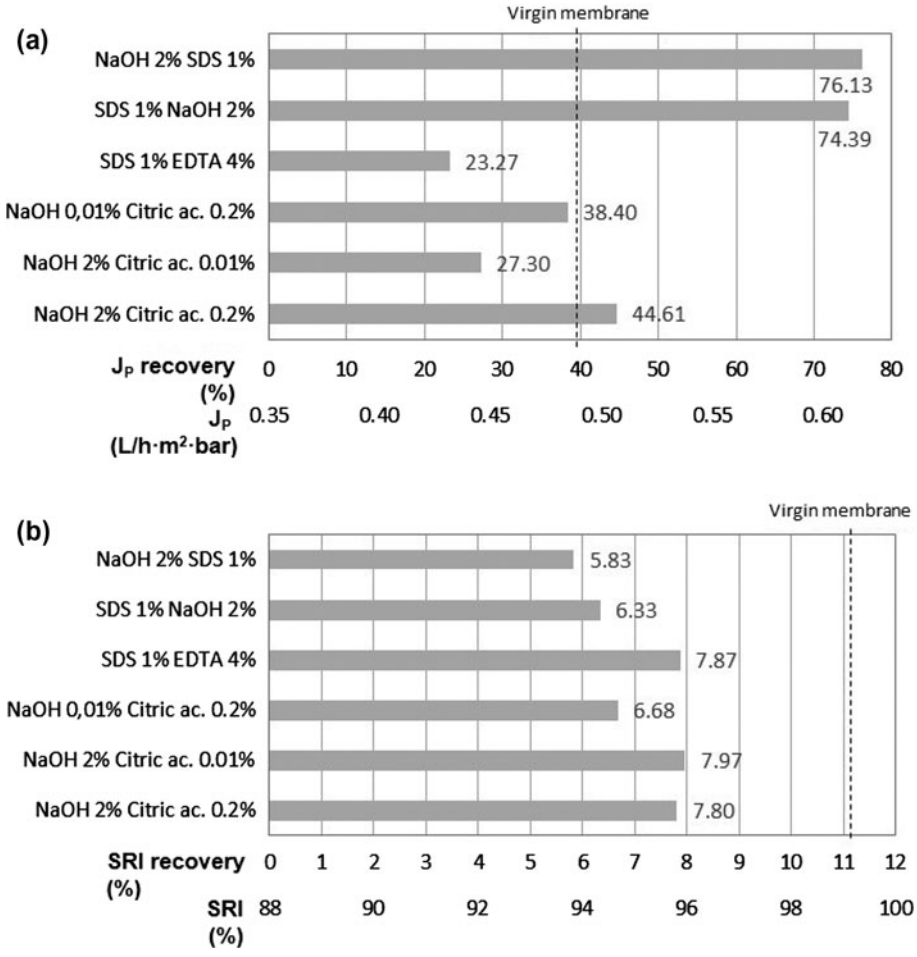

Fig. 9. Best results of the two-step cleaning procedures: (a) permeability recovery (b) SRI recovery.

of 94.79%. From now on, this cleaning procedure will be referred to as procedure (1). Conversely, if SRI recovery is decided as the main criteria, NaOH 2% cleaning followed by citric acid 0.2% was the most suitable procedure, achieving an SRI of 96.26% and a permeability of 0.5082 L/h m^2 bar, slightly higher than that of the virgin membrane. This alkaline-acid procedure will be referred to as procedure (2) from now on.

After an analysis of the results from the one-step cleaning and the two-step cleaning, complementary cleaning mechanisms between NaOH and citric acid were observed, since combination of both in the two-step procedures produced higher cleaning efficiency than when they were used alone in one-step cleaning. In addition, slightly better results in terms of cleaning efficiency were noticed when alkaline-acid sequence was applied than when the inverse sequence was considered. According to the literature, alkaline-acid sequence becomes more efficient when a significant part of the foulants is of organic nature, as it usually occurs in seawater desalination processes [6]. The cleaning efficiency did not improve when Na_2–EDTA was considered in any of the steps.

For the highest values of permeability achieved, the addition of an alkaline step either after or before the surfactant step supposed a slight improvement. However, by means of the two-step cleaning procedures it was not possible to obtain SRI values greater than that obtained by SDS 1%, although the recovery of SRI was higher.

3.2.2.3. Characterization of the membrane surface after the chemical cleaning. Besides the recovery of the permselective properties of the membrane, the characterization of the membrane surface after the cleaning process by microscopy techniques such as FESEM and AFM becomes useful to confirm the efficiency of the cleaning procedures tested.

The FESEM analysis of the samples cleaned by means of the two selected protocols revealed a

considerable decrease in the amount of fouling deposits. In Fig. 10, micrographs of the membrane samples cleaned with the best two-step cleaning procedures are shown. In both of them, the original form of the membrane surface can be clearly observed if they are compared to the micrograph of the virgin membrane (Fig. 4(a)). Therefore, these two cleaning procedures were able to remove the fouling layer from some membrane areas, until reaching the original state of the surface. However, some deposits still remained on some areas of the membrane surface after the cleaning process.

It was not possible to clearly observe the original surface or the membrane when it was cleaned by the one-step protocols, as it can be observed from Fig. 7.

The elemental composition of the deposits remaining on the membrane was determined by FESEM-EDX. As it was also observed in a previous work by the authors, the deposits were mainly composed of silica, aluminium silicates and iron silicates, which indicate that the fouling phenomenon was mainly of inorganic and colloidal nature [2]. Fig. 11 shows the microanalysis spectrum of a deposit composed chiefly of aluminium silicate, analysed from a sample cleaned by means of procedure (1).

In order to quantify the elemental composition of the membrane surface after cleaning with procedures (1) and (2), FESEM-EDX analysis was carried out. Averaged values of the elemental composition of the cleaned samples and the variation from the fouled membrane are shown in Table 4.

From Table 4, a considerable decrease in the presence of the main elements that are part of the fouling deposits on the membrane can be observed. The removal reached with procedure (2) was slightly greater than that achieved by means of procedure (1). Silicon, sulphur, iron and aluminium were the most removed elements, in this order. The lessening of the amount of these elements indicated a good removal of silica, iron and aluminium silicates, and sulphates. The increase in the presence of oxygen in the elemental distribution after the cleaning step can be explained by the fact that this element is part of the composition of the original membrane surface. Therefore, the cleaning efficiency of these two procedures was confirmed.

Both two-step cleaning procedures obtained greater removal of foulants than the one-step cleaning procedures. Consequently, attending to the variation of the elemental composition of the membrane surface after the cleaning process, the best results were achieved by the alkaline-acid two-step procedure (2) followed by the SDS 1%–NaOH 2% cleaning (1), and after that the one-step SDS 1% cleaning and, finally, the one-step NaOH 2% cleaning. These results are consistent with the nature of the membrane fouling layer, which was determined in a previous work by the authors by means of SEM-EDX, ATR-FTIR and elemental analysis [2]. The fouling layer was composed of 70% inorganic compounds, mainly colloidal foulants such as silicates and 30% organic materials such as NOM. Alkaline-acid cleaning sequence is recommended for surface water processes, where membrane organic fouling is very common [6], while anionic surfactants such as SDS are proved to be very efficient removing organic and colloidal foulants due to their emulsifying power that facilitates the fouling layer detachment [13–15].

Lastly, the roughness of the samples cleaned by the best two-step cleaning procedures was also

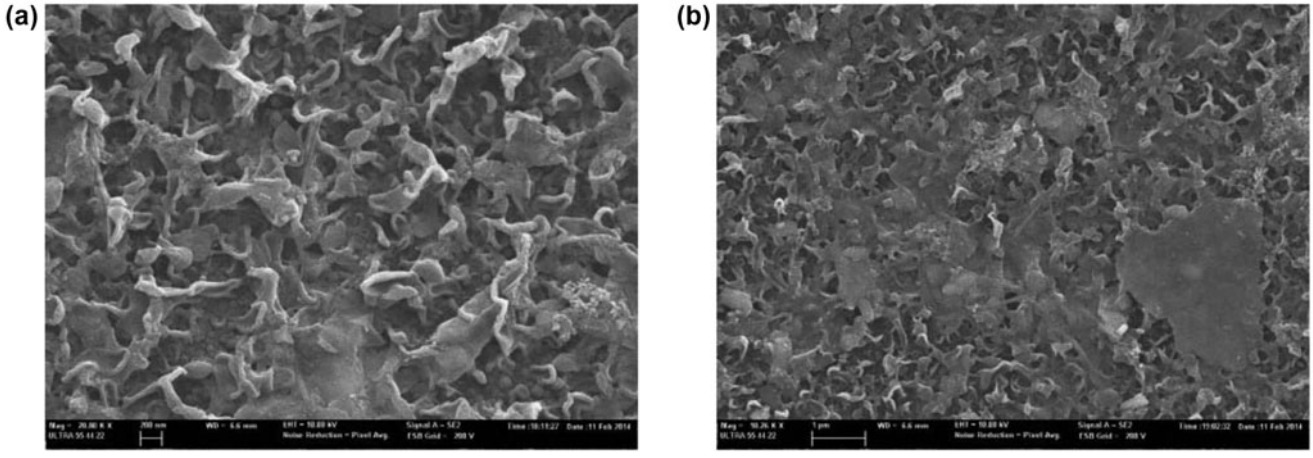

Fig. 10. FESEM micrographs of the membrane samples cleaned by: (a) SDS 1%-NaOH 2% (×21000 magnification); (b) NaOH 2%-citric acid 0.2% (×10500 magnification).

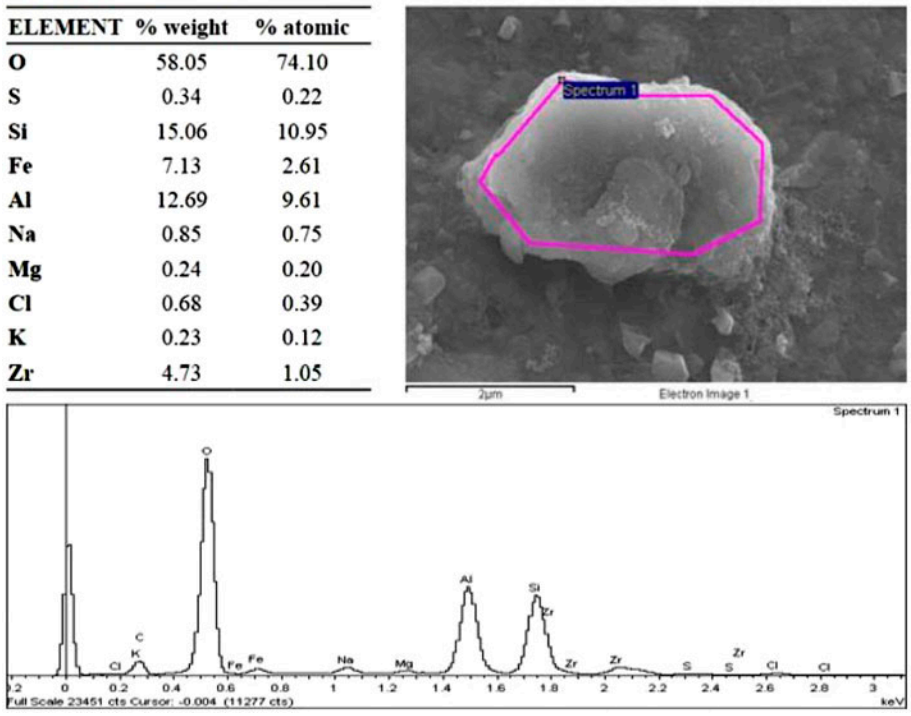

Fig. 11. FESEM-EDX microanalysis spectrum of an aluminium silicate deposit found on the surface of a membrane sample.

Table 4
Percentage distribution and variation of the elemental composition of the membrane surface when it was cleaned with (1): SDS 1%–NaOH 2% (2): NaOH 2%–citric acid 0.2%, in comparison with the fouled membrane, measured by FESEM-EDX

Element	Atomic % fouled membrane	Atomic % procedure (1)	Atomic % procedure (2)	Variation (%) (1)	Variation (%) (2)
O	76.30	90.24	94.76	13.94	18.46
S	7.17	1.47	1.29	−5.70	−5.88
Si	7.01	0.89	0.54	−6.12	−6.47
Fe	3.29	1.34	1.07	−1.95	−2.22
Al	2.33	0.36	0.25	−1.97	−2.08
Na	0.94	2.68	0.51	1.75	−0.42
Mg	0.88	0.11	0.06	−0.77	−0.83
P	0.67	0.00	0.00	−0.67	−0.67
Cl	0.70	2.19	0.42	1.50	−0.27
K	0.29	0.06	0.04	−0.23	−0.26
Ca	0.32	0.14	0.06	−0.19	−0.26
Cr	0.11	0.00	0.00	−0.11	−0.11
N	0.00	0.03	0.56	0.03	0.56
Zr	0.00	0.50	0.44	0.50	0.44

analysed by AFM, as Fig. 12 shows. The maximum ridge and valley height (R_{max}) was considerably reduced from 1,775 (Fig. 5(b)) to 1,239 nm by cleaning with SDS 1% followed by NaOH 2%. The alkaline-acid procedure caused a smaller reduction of R_{max}. A more homogeneous surface was observed after the cleaning process in comparison with the fouled membrane. However, two-step cleaning procedures could not reach the decrease in the roughness parameters achieved by SDS 1%.

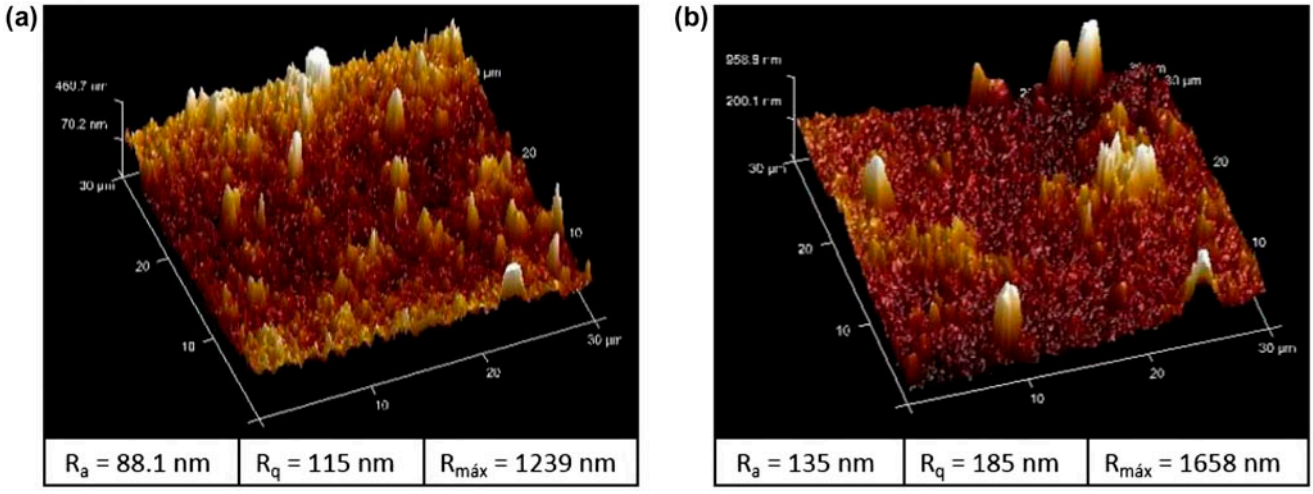

Fig. 12. AFM characterization of membrane surface roughness after cleaning by: (a) SDS 1%–NaOH 2% (b) NaOH 2%–citric acid 0.2%.

4. Conclusions

The one-step cleaning experiments indicated that the surfactant SDS was the best cleaning agent tested. The two cleaning solutions that obtained the best results in terms of permeability and SRI recovery were SDS 1% and NaOH 2%.

Regarding the two-step cleaning tests, two procedures were selected taking into account the results of permeability and SRI recovery. SDS 1% cleaning followed by NaOH 2% was the two-step cleaning procedure that achieved the greatest recovery of the membrane permeability. By means of this procedure, membrane permeability reached a value of 0.6128 L/h m^2 bar (J_P recovery of 74.39%) and an SRI value of 94.79% (SRI recovery of 6.33%). Attending to the criteria of SRI recovery, an alkaline-acid procedure showed the best results. Cleaning with NaOH 2% as a first step and with citric acid 0.2% as the second step increased the SRI up to a value of 96.26% (7.8% recovery) and the permeability up to 0.5082 L/h m^2 bar (44.61% recovery).

Complementary cleaning mechanisms between NaOH and citric acid were noticed, and higher cleaning efficiency was obtained when alkaline-acid sequence was used instead of the inverse sequence.

The addition of a second cleaning step improved the efficiency of the cleaning process. Slightly higher recovery of the membrane permeability was observed. Moreover, the characterization of the membrane surface by FESEM-EDX revealed that a significantly greater amount of the deposits were removed by means of the two-step protocols that were selected, in comparison with the best one-step cleaning protocol. By means of both, the characterization of the permselective properties of the membrane and FESEM-EDX analysis, it was confirmed that the efficiency of the cleaning processes was selected to remove the fouling deposits.

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