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Multivariate comparison of reverse osmosis and nanofiltration membranes through tree cluster analysis

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ABSTRACT

Experimental trials are usually needed to integrate information reported on data sheets in order to properly drive membrane choice. It results in data-sets where each membrane is characterised by several performance descriptors. Multivariate data-mining (i.e. chemometrics) effectiveness in analysing such data-sets has been demonstrated through the comparison of seven commercial membranes. Each membrane was represented as an object described by 15 features got from trials with different single-component test solutions. Tree cluster analysis based on Ward amalgamation method was employed for multivariate data mining. The algorithm progressively grouped the membranes in clusters, adopting the Euclidean distance in the 15-dimensional feature space as a measure of similarity. Thus, a graphical output consisting into a similarity tree representing the membrane taxonomy was obtained. A restricted number of membranes, selected as representatives of each identified cluster, underwent to further experiments devoted to a systematic study on boron removal at various pH values.

Keywords: Cluster; Chemometrics; Reverse osmosis; Nanofiltration; Boron

1. Introduction

Less than 3% of water on our planet exists in a readily usable form for human activities [1]. Therefore, an impressive effort has been performed towards the development of technologies able to get freshwater from streams not exploitable as such (e.g. seawater, brackish water or even wastewater) [2,3]. In this context, energy industry could play a key role: produced water is by far the largest volume waste stream associated with exploration and production operations [4,5]. It is an aqueous mixture of numerous organic and inorganic chemical species brought to surface along with oil and gas. In order to face such complex contamination, produced water treatment entails several operations, including suspended organic removal, sweetening, heavy metal removal,

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dissolved organic removal, suspended solid removal and finally desalination [4,6].

Saline content sometimes of the order of magnitude of 100,000 mg/L further complicates produced water treatment, making its exploitation virtually unfeasible with conventional technologies [4,5,7].

Boron is a common produced water contaminant with peak content values of the order of magnitude of 100 mg/L (e.g. over 10 times higher than those of seawater) [4]. It is present mainly in the form of the weak Lewis acid $B(OH)_3$ with an intrinsic pK_A of about 9.23 at temperature of 25°C [8–11]. It accepts electrons according to Eq. (1):

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ \quad (1)$$

Anionic form is predominant at pH higher than pK_A, while at lower values the neutral form prevails [8–13].

Boron is acknowledged to be an essential micronutrient for both animals and plants with narrow range between its deficiency and excess [8]. Thus, its content in water has to be tuned according to specific user specifications or environmental restrictions. Drinking water quality guideline value of 2.4 mg/L has been recently suggested by World Health Organisation, adopting human health as leading criteria [14]. On the other hand, boron content has to be reduced till 0.3 mg/L in water streams used to irrigate sensitive crops (e.g. citrus trees) [15].

In case of saline content comparable to those of seawater (i.e. 18,000–48,000 mg/L), desalination can be effectively operated by reverse osmosis (RO) [11,16,17], frequently coupled with ultrafiltration (UF) [3] and nanofiltration (NF) as pre-treatment steps [10,18]. Boron removal can be accomplished as well, although complex desalination treatments are needed to match the most stringent specifications. Specifically, RO or NF steps operated at high pH values have to be implemented for this purpose [11,16,17,19]. An alternative route based on two RO steps, without pH value adjustment, has been also proposed for adequate boron removal [20,21].

Plenty of desalination membranes are presently available on market. Often, manufacturer data sheets only sketch membrane features, making experimental trials mandatory to properly drive users' choice. Usually, comparison is carried out through performance evaluation referred to different test solutions and operational conditions. Permeate flux (defined as the ratio between the permeate flow rate and the membrane area) and rejection (defined as R in Eq. (2), where C_F and C_P the solute concentrations, respectively, in the feed and in the permeate) are considered [16].

$$R = \left(\frac{C_F - C_P}{C_F} \right) \quad (2)$$

It results in a data-set where each membrane represents an object characterised by several performance descriptors. Interpretation of such a data-set considering one variable at a time is quite laborious. On the other hand, analysis through multivariate methods (i.e. mathematical and statistical tools able to analyse the information scattered over several descriptors) can be more straightforward. A case study is reported.

Seven commercial polyamide thin-film composite RO and NF membranes were screened as flat sheets by using a laboratory-scale unit. In particular, single-component test solutions containing, respectively, deionised water at various pH values, salts with single-charge ions and salts with double-charge ions were considered as feeds. The obtained data-set was analysed by tree cluster analysis in order to point out groups of similar membranes.

Specifically, tree cluster analysis is a multivariate data mining (i.e. chemometric) method based on the use of distance in the multidimensional space of descriptors as a measure of similarity among objects. The algorithm provides a graphical output consisting into a similarity tree representing the object taxonomy [22].

According to that, a restricted number of membranes, selected as representatives of each indentified group, underwent further experiments devoted to a systematic study on boron removal at various pH values. The test solution compositions were defined according to a case of relevance for the energy industry (i.e. moderate salinity, high boron concentration). In particular, solutes and their respective concentrations were selected on the basis of the results obtained from real produced water samples analysed in our laboratories.

2. Methodology

Two NF membranes (i.e. NF270 and NF90), two brackish water reverse osmosis (BWRO) membranes (i.e. XLE and BW30LE) and three seawater reverse osmosis (SWRO) membranes (i.e. SW30HR, SW30ULE, and SW30XLE) were considered. All FILMTEC™ membranes were supplied by The Dow Chemical Company.

The laboratory-scale cross-flow unit reported in Fig. 1 was employed. Each flat membrane was housed into a rectangular cell (MC) with an effective membrane area of 66 cm^2 (6 cm × 11 cm) and a channel

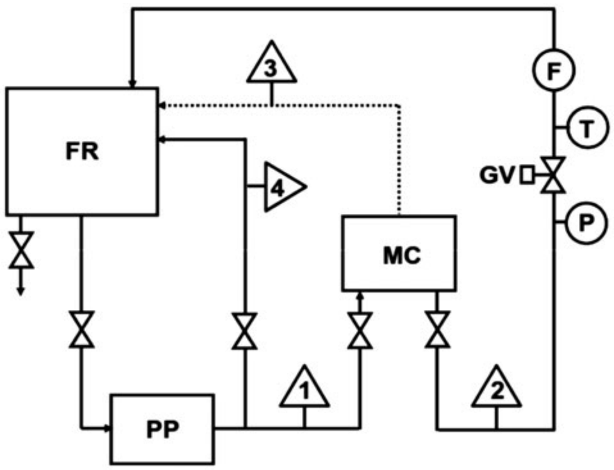

Fig. 1. Schematic of the plant used for NF and RO tests.
Notes: FR = feed reservoir; PP = piston pump; MC = membrane cell; GV = globe valve; P = bourdon gauge; T = thermometer; F = flow meter; 1 = feed inlet; 2 = retentate outlet (recycled); 3 = permeate outlet (recycled); 4 = by-pass.

height of 2 mm. The cell was fed at a constant flow rate through a piston pump (PP) equipped with a variable-frequency-drive inverter speed control. The flow rate was measured by a variable area flow meter (F). The feed temperature (T) was kept constant by a heat exchanger coil (not shown in Fig. 1) submerged in the feed reservoir (FR) and connected to a thermostatic bath. The operating pressure was set through a globe valve (GV) and measured by a bourdon gauge (P). The permeate flow rate was measured through the amount collected in a graduated cylinder after a defined time interval.

The unit was operated under recirculation mode, where both the permeate and the concentrate were recycled to the FR, except in case of permeate sample collection. This operating mode was adopted in order to maintain feed composition constant. All the relevant parts of the plant (i.e. recirculation loop piping, pump, instrumentation, valve) were made in AISI 316 stainless steel, while a flexible PVC tube was used for the permeate recirculation.

Water at different pH values (pH of 7, 9, and 11, adjusted by progressive NaOH addition) and single-component salt solutions at pH of 7 were used for the membrane screening. Specifically, the following salt solutions were considered: NaCl (6 g/L), $NaNO_3$ (1.3 g/L), Na_2SO_4 (1.3 g/L), $MgSO_4$ (1.4 g/L), and $CaCl_2$ (1.3 g/L). Deionised water and reagent grade 98–99% solutes were used for test solution preparation. Each membrane produced a data-set reporting the values of, respectively, mean water permeability and maximum conductivity rejection (both evaluated at the temperature of 25˚C, within the operating pressure range of 5–55 bar). It was processed by tree cluster analysis in order to find membranes worthy of further experimentation. Specifically, Ward amalgamation method was employed [22–25]. Euclidean distance (D) was adopted as similarity measure between the objects, according to Eq. (3) (being, X and Y two different objects defined in the i-dimensional space of respective descriptors x and y). In short, Ward amalgamation method progressively groups objects trying to form clusters characterised by the minimal distance among objects and cluster centroid (i.e. the cluster geometric centre evaluated in the i-dimensional space). The raw data were standardised before processing in order to avoid scale aberration, according to Eq. (4) (being, x' the standardised value of the descriptor i, m and s its mean and standard deviation estimated values, respectively). In practice, the descriptor values organised in Table 1 as columns were turned into the respective standardised ones.

$$D(X, Y) = \sqrt{\sum_i (x_i - y_i)^2} \tag{3}$$

$$x'_i = \frac{x_i - m_i}{s_i} \tag{4}$$

The selected membranes underwent to experiments with $B(OH)_3$ solutions (0.3 g/L corresponding to about 50 mg/L of boron), at different pH values (pH of 7, 9, and 11, adjusted by progressive NaOH addition).

The experimentation was performed by keeping constant the temperature at 25˚C and the feed flow rate at 560 L/h (corresponding to a linear velocity of the feed at the membrane surface of about 1.5 m/s). The performance of each membrane was explored in the operating pressure range of 5–55 bar, setting minimum and maximum values consistently to membrane features. Specifically, the operating pressure was increased step-by-step till its maximum value, waiting 30 min after every change for system stabilisation. For each type of membrane the permeability was evaluated by measuring the permeate flux (J) as a function of trans-membrane pressure (P). A linear relationship between J and P was found for all tested membranes and from the slope the mean values of permeability were determined. This operating procedure is exemplified in Fig. 2, regarding the runs with SW30XLE and NF270, both tested with water adjusted to pH of 11 by NaOH addition. All membranes were received in dry state and were immersed into deionised water for at least 1 h before use. The used membrane sheet was replaced with fresh ones after every change of the feed composition.

Table 1
Data-set consisting in seven commercial RO and NF membranes, each one described by fifteen performance descriptors. *A* and *R* are, respectively, the mean water permeability and the maximum conductivity rejection values. Each column heading identifies the solute used for test solution preparation: 1 = NaOH, pH of 7; 2 = NaOH, pH of 9; 3 = NaOH pH of 11; 4 = NaCl; 5 = Na_2SO_4; 6 = $MgSO_4$; 7 = $NaNO_3$; 8 = $CaCl_2$. If not specified, pH is intended to be of 7

	Mean water permeability A (L/(m^2 h bar))								Maximum conductivity rejection R (%)						
Membrane	1	2	3	4	5	6	7	8	2	3	4	5	6	6	7
NF270	12.12	12.99	12.40	11.50	12.98	11.48	9.99	13.71	59.76	56.61	28.27	84.29	89.46	19.91	33.14
NF90	5.87	5.93	5.99	3.27	5.21	6.08	5.68	5.18	76.90	81.41	92.75	99.48	99.36	85.21	99.29
XLE	5.56	5.66	6.09	3.04	5.01	4.85	6.04	4.20	89.72	87.50	97.12	99.47	99.00	90.85	97.70
BW30LE	3.91	3.89	4.16	2.54	3.95	3.51	4.33	3.24	90.77	90.65	97.70	99.59	99.10	91.18	98.95
SW30HR	0.88	0.91	0.96	0.74	0.84	0.80	0.70	0.68	91.88	97.20	99.28	99.66	99.81	98.31	99.57
SW30ULE	0.97	1.22	1.12	0.88	0.97	1.03	1.15	0.94	92.01	96.19	99.38	99.65	99.56	98.00	98.33
SW30XLE	1.22	1.09	1.09	0.85	1.10	1.07	1.12	0.94	92.77	97.03	99.55	99.87	99.57	97.50	98.07

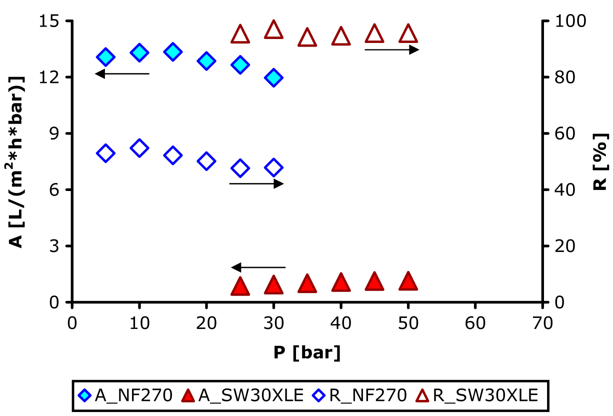

Fig. 2. Example of screening experiments. Water permeability (*A*) values and conductivity rejection (*R*) values were collected, respectively, for the SW30XLE and the NF270 membranes, both tested with water at pH of 11.

A specific analytical test was adopted for the boron rejection evaluation. In particular, the boron concentration was determined by the spectroscopic method based on the absorbance in the wavelength interval of 410–420 nm of the yellow complex formed with azomethine-H [11]. A Merck Spectroquant Pharo 300 spectrophotometer coupled with a Merck Spectroquant reactor and the relevant Merck boron kit was employed.

Conversely, rejection evaluation based on electrical conductivity that has been verified, to be directly correlated with solute concentration, in the range under study (according to the literature [26]), was adopted for the other test solutions.

3. Results and discussion

Features obtained from the screening experiments are resumed in the data-set reported in Table 1. For the same type of RO and NF membrane, the variation of water permeability between tests carried out with pure water or salt solutions are within the range of flux variability reported in the literature for polyamide-thin-film composite membranes [27]. In general, the SWRO membranes are characterised both by the highest rejection values and by the lowest water permeability values, calculated from the ratio between the permeate flux and the operating pressure. They differ slightly from the BWRO membranes, being the latter ones characterised by lower rejection capacity and higher water permeability. The two NF membranes behave very differently one to each other. Surprisingly, NF90 shows rejection and water permeability values comparable to those of brackish water RO membranes. Conversely, NF270 shows appreciable rejection values only in case of feed containing the bulkier double-charge anions (i.e. Na_2SO_4 and $MgSO_4$) according to Table 2 [28] and water permeability values about twice NF90 ones.

These differences can be explained according to membrane polyamide-thin-film textural properties, recalling that size sieving is always an underlying separation mechanism for NF membranes. In particular,

Table 2
Hydrated radii *r* of the ions in test solutions used for the membrane screening [28]

Ion	*r* (nm)
Cl^-	0.33
NO_3^-	0.33
SO_4^{2-}	0.38
Na^+	0.36
Ca^{2+}	0.41
Mg^{2+}	0.43

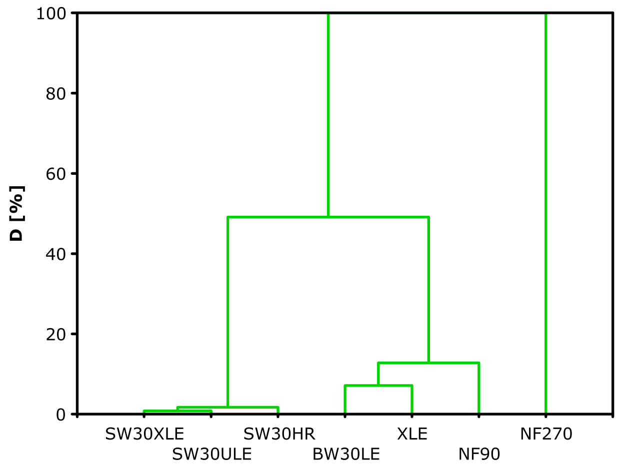

Fig. 3. Similarity tree from tree cluster analysis. Distance (*D*) is expressed as percentage referred to the maximum distance measure between considered objects.

NF270 is by far looser than NF90 (0.84 and 0.68 nm are their respective mean pore sizes), while both brackish water and seawater RO membranes are virtually non-porous [13,16,18].

NF270 peculiarity is well evidenced in the similarity tree sketched in Fig. 3. The latter one is the output coming from the application of tree cluster analysis to the data-set reported in Table 1. Tree cluster analysis identifies also NF90 as a singleton, although with an appreciable level of similarity with the BWRO membranes.

The similarity tree points to a higher level of similarity between the BWRO membranes and most of all, among the seawater ones.

According to this taxonomy, four membranes (i.e. NF270, NF90, BW30LE, and SW30XLE) were chosen to cover the widest RO and NF membrane spectrum during further experiments devoted to a systematic study on boron removal at pH of 7, 9, and 11. Specifically, NF90 was selected according to its peculiar performances. In fact, under the operating conditions adopted for screening, NF90 behave close to BWRO membranes, although it is a NF one. Indeed, the four membranes behave differently also in this context.

Fig. 4 shows a substantial constancy of water permeability (*A*) values within the studied pH interval for each of the four selected membranes. As expected, the highest water permeability values were obtained for the NF membranes with NF270 value over 10-fold SW30XLE one.

Boron rejection (*R*) values for each membrane are reported in Fig. 5. At pH of 7, where boron is mostly present as $B(OH)_3$, SWRO membranes and BWRO ones are by far the most efficient. Difference among membrane features decreases at pH of 9 and almost

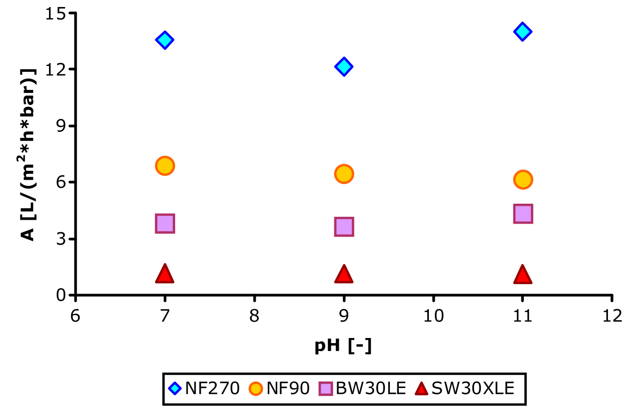

Fig. 4. Mean water permeability (*A*) values gathered on selected membranes at various pH values, feeding a test solution containing about 50 mg/L of boron.

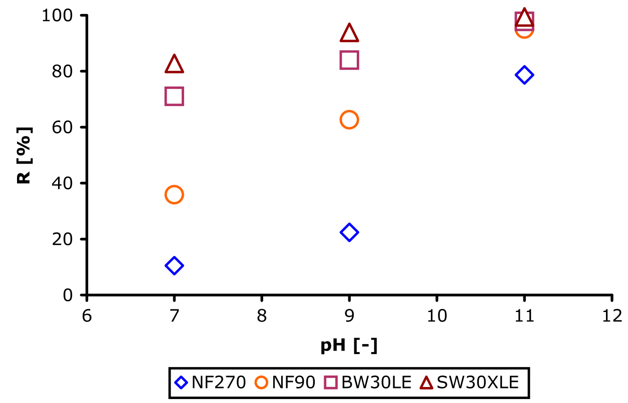

Fig. 5. Maximum boron rejection (*R*) values gathered on selected membranes at various pH values, feeding a test solution containing about 50 mg/L of boron.

disappears at pH of 11, where $B(OH)_4^-$ prevails over $B(OH)_3$. The increase in boron rejection is particularly impressive for NF membranes with NF270 passing from 10.53% at pH of 7 to 78.71% at pH of 11. The latter value is only 20% lower than the one measured for SW30XLE under the same pH conditions. This behaviour can be interpreted recalling that $B(OH)_3$ is expected to have a smaller hydrated radius than $B(OH)_4^-$. Furthermore, surface negative charge of polyamide thin-film composite membrane increases with pH, due to progressive ionisation of polyamide carboxylic moieties [29]. According to that, both size sieving and electrostatic repulsion cooperate for boron rejection at pH higher than pK_A of $B(OH)_3$, where the anionic form $B(OH)_4^-$ prevails [8–13]. Noteworthy, maximum boron rejection values were obtained at the operating pressures of 15, 25, 30, and 45 bar, using, respectively, NF270, NF90, BW30LE, and SW30XLE.

Globally, the obtained results indicate that loose polyamide thin-film composite NF membranes can be a valid alternative to RO ones for the rejection of boron at pH higher than pK_A of $B(OH)_3$. In particular, NF membranes show slightly lower boron rejection values and markedly higher water permeability values. Nevertheless, the proper membrane choice and process configuration depend on the maximum admissible boron concentration in permeate, according to final water destination. Lower operating pressures have to be considered a further advantage of NF membranes.

These results are consistent with the ones previously reported for experiments performed in similar operating conditions, although using solutions with a boron content 10-fold lower [13].

4. Conclusion

Tree cluster analysis has been effectively used for rational membrane comparison and selection. This multivariate analysis method has been applied to a data-set consisting in seven commercial RO and NF membranes, each one described by 15 performance descriptors, coming from screening experimentation. A systematic study on boron removal at various pH values has been then performed on membranes selected to cover the widest RO and NF membrane spectrum. It has been evidenced that NF membranes can be considered alternative to RO membranes for the removal of boron at high pH values. Under such operating conditions, NF membranes have shown water permeability values markedly higher and boron rejection values slightly lower than RO ones.

The future activity has to consider the extension of the data-set used for initial screening by introducing additional membranes and performance descriptors (e.g. resistance to fouling, to cleaning and to disinfection). The selection among redundant descriptors has to be also considered in order to limit the experimental effort.

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