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Statistical analysis of data from accelerated ageing tests of PES UF membranes

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Abstract

In this research, membrane life-time was evaluated by means of accelerated ageing experiments. A pressure pulse unit was used to perform the ageing experiments in an accelerated way. An experimental design has been set up and four ageing factors were varied at two levels. The four ageing factors studied were: fouling status of the membrane, cleaning agent concentration, magnitude of the back pulse and number of applied back pulses. The integrity of the membrane modules was evaluated by means of permeability testing, pressure decay tests and bubble tests. Also tensile tests were performed to investigate the mechanical properties of the membrane modules. The collected data was used for an analysis of variance to determine which ageing factors and which combination of ageing factors influence membrane life time. The analysis showed that the fouling status in combination with the number of applied pressure pulses were significant ageing factors. Additional tensile tests confirmed these results.

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1. Introduction

Ultra filtration (UF) is increasingly used as a method for surface water purification. UF membranes have a high selectivity and are becoming economically attractive. However, one of the drawbacks of UF is that during the filtration process, the membrane is subject to fouling. Consequently, periodic cleaning is required. In the short term fouling is treated with hydraulic cleanings (back pulsing) and in the long term fouling is treated by means of chemical cleaning. The magnitude and number of back pulses, and the nature, exposure and concentration of the cleaning agent have an influence on the membrane life time.

In general failure of fibers is believed to be the result of exposure to cleaning chemicals, mechanical stress and the membrane fouling status.

Research on fiber failure was performed by Huisman and Williams [1], who analyzed the causes of membrane damage for ultra filtration membranes used to treat waste water. Autopsy results, bubble point tests and tensile strength tests revealed that the membranes were not damaged by chlorine, other halogens or cleaning agents, but merely by mechanical forces, e.g. pressure shocks. The effects of mechanical force were shown to be stronger if the membranes were fouled.

Work of Gijsbertsen-Abrahamse et al. [2], focused on the relationship between fiber failure and fiber properties. They concluded that fiber failure depends on the strength of the membrane material, the operating conditions and incidents. In this research it was found that on average fiber failure occurs annually 1–10 times on 1 million fibers.

Also Childress et al. [3] researched fiber failure with respect to fiber properties. In an evaluation of different membranes the material, the symmetry, the modulus of elasticity, diameter, thickness, potting technique and module flow pattern (inside-out, outside-in) were investigated. This research showed that stresses at the juncture of the potting is likely to lead to the formation of fractures.

In recent studies the influence of sodium hypo chlorite in a changing pH environment has been tested on PES/PS UF membranes [4–7]. It was found that in certain pH regions hypo chlorite reacts more aggressive. Other authors investigated the

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so-called ageing phenomenon for other membrane materials and applications [8–16]. Statistical analysis and modeling based on data collected by means of accelerated ageing tests was done in different fields of science and engineering [17–22]. However, little has been published on accelerated ageing tests of UF membranes. In this study, factors which influence membrane life time are systematically identified. A 4 × 2 (four factors, two levels) experimental design is constructed and each experiment is performed in threefold. With the collected data an analysis of variance (ANOVA) is performed to investigate which factors and which combinations of factors significantly influence membrane performance. Also the influence of ageing on the membrane mechanical properties is evaluated by means of tensile testing.

2. Theory

2.1. Design of experiments

In this study, four influence factors are varied at two levels. In Table 1, the factors A, B, C and D are denoted, respectively as: the fouling status, the sodium hypo chlorite concentration, the magnitude of the back pulses and the number of back pulses. Table 1 also shows the values for high- and low-experimental settings. Based on the number of applied pulses, the overall test time is for 100,000 pulses around 60–85 h and for 300,000 pulses around 170–250 h. In hypo chlorite exposure such times correspond to 60,000–85,000 ppm h and 170,000–250,000 ppm h, respectively. Assuming that in normal membrane operation a backwash is performed four times per hour, the membranes were aged after 100,000 pulses nearly 3 years, and after 300,000 pulses nearly 9 years.

A full factorial experimental design scheme is presented in Table 2. It is noted that experiments as shown in the experimental design matrix normally are executed in random order.

2.2. ANOVA method

This method is used to compare the magnitude of the effects of factors with the magnitude of experimental error and is called analysis of variance (ANOVA). If the magnitude of a factor effect is large in comparison to the experimental error, the changes in the selected response cannot occur by coincidence and those changes in the response are considered to be the effects of the influence factors. The factors causing a variation in the response are called significant. In this study, the so-called F-test was used in the analysis of variance and given as:

Table 1
Factors and levels

Factor	Connotation	Low (−1)	High (+1)
Fouling status	A	Clean module	Fouled module
NaClO concentration (ppm)	B	0 ppm	1000 ppm
Magnitude of the back pulse (bar)	C	0.5 bar	2.0 bar
Number of back pulses[a] (#)	D	100,000	300,000

[a] 100,000 back pulses at a frequency of around 25 pulses/min, correspond to 3 years of operation.

Table 2
Experimental design matrix

Combination	A	B	C	D
1	−1	−1	−1	−1
a	1	−1	−1	−1
b	−1	1	−1	−1
ab	1	1	−1	−1
c	−1	−1	1	−1
ac	1	−1	1	−1
bc	−1	1	1	−1
abc	1	1	1	−1
d	−1	−1	−1	1
ad	1	−1	−1	1
bd	−1	1	−1	1
abd	1	1	−1	1
cd	−1	−1	1	1
acd	1	−1	1	1
bcd	−1	1	1	1
abcd	1	1	1	1

$$F_A = \frac{S_A^2}{S_{\text{ERROR}}^2} \tag{1}$$

where S_{ERROR}^2 is the variance of the overall error and where S_A^2 is the variance with respect to factor A, estimated according to:

$$s_A^2 = \frac{K_A}{\phi_A} \tag{2}$$

ϕ_A is the degree of freedom with respect to A and K_A is the sum of squares with respect to A.

For an experimental design of 4 × 2, the sum of squares with respect to A is calculated from its contrast according to:

$$K_A = \frac{C_A^2}{2^4 n} \tag{3}$$

where n is the number of experiment repetitions and C_A is the contrast with respect to A. The contrast can be calculated using a calculation scheme proposed in [23]. If X_1 is the experimental outcome of experiment (1), and X_{a} is the outcome of experiment (a), X_{b} is the outcome experiment (b), etc., then the contrast with respect to A can be calculated as a summation of the outcomes of the experiments while the signs of the experimental values are taken from [23].

$$C_A = -X_1 + X_{\text{a}} - X_{\text{b}} + \cdots - X_{\text{bcd}} + X_{\text{abcd}} \tag{4}$$

3. Experimental

The experimental design matrix of Table 2 is quasi randomized. Each experiment is performed in threefold. After the experiment, the membrane is tested for permeability, pressure decay and defect fibers.

Tensile tests were performed to investigate the mechanical properties of the membranes. The methods used to determine these parameters are briefly discussed below. It should be noted

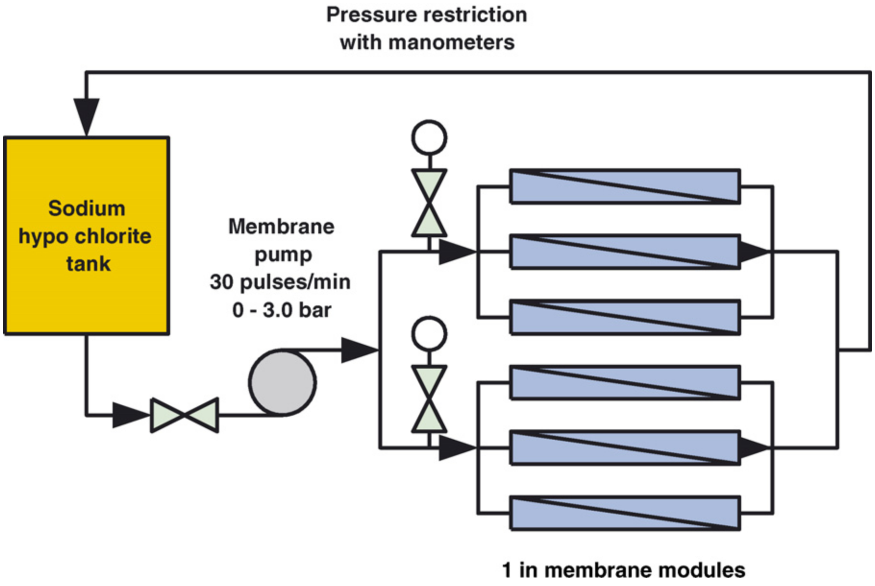

Fig. 1. Schematic representation of the pressure pulse unit.

that run (a) and (ac) could not be performed, due to the limitation of available membrane modules.

3.1. *Pressure pulse unit*

In Figs. 1 and 2, the pressure pulse unit (PPU) is presented. The main part of the PPU is the membrane pump, which can pump sodium hypo chlorite – or water – at a pressure of 0–3 bar through membrane modules with a frequency of around 20–30 pulses/min. Pulse tests are performed, reflecting a plant's "worst case scenario", where valves open and close frequently, while generating fast pressure changes (from 0 to 2 bar in 2–3 s). Using two pressure restrictions, two sets of experiments can be simultaneously performed at two different pressures. In the experiments, industrial sodium hypo chlorite, colloquially known as caustic bleach (15 wt%, pH between 12 and 12.5) of ViVo Chemicals B.V. was used and diluted with demineralized water to a 1000 ppm solution. It is known that in the pH range 11–13, the concentration of chlorine ions in the hypo chlorite is stable. The pH of the solution used in the accelerated ageing experiments was around 11.5. This value corresponds to industrially applied pH ranges for hypo chlorite cleanings. The solution was refreshed on a daily basis. The used PES membrane modules were Norit-Xiga RX300 PSU hollow fiber UF modules with a membrane surface of 0.07 m^2. The Xiga fibers have a polysulfone housing and PES/PVP flow distributors (fibers). Every test module contains 100 fibers with a length of 30 cm. Potting procedures and materials for clean and fouled fibers were the same.

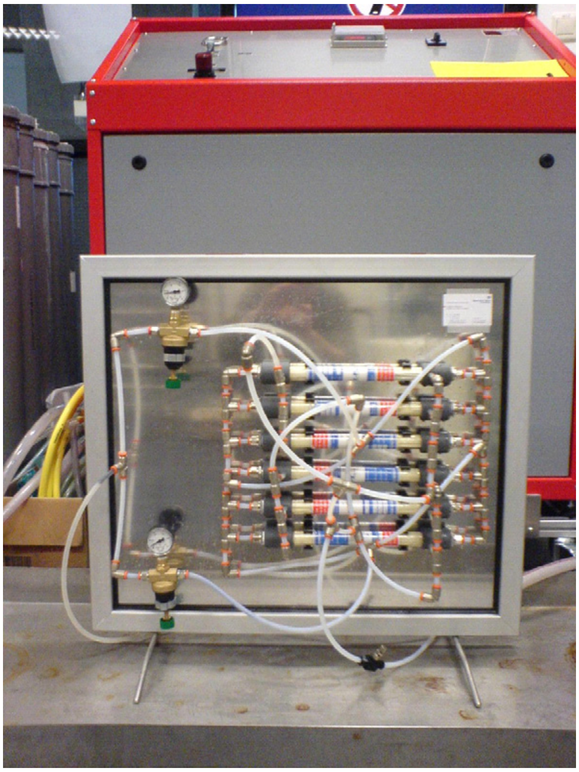

Fig. 2. Picture of the pressure pulse unit and the ageing frame.

Fouled modules were assembled from fibers that were taken from a 4-in. module that was operated in a pilot with surface water over a 6-month period. Cleaning was performed on the membrane every 24 h, only applying caustic cleaning with sodium hydroxide 0.01 M. PES fibers are known to withstand cleanings with this cleaning agent in high concentrations.

3.2. *Permeability test*

The permeability test is a commonly used measure of the overall performance of a membrane. Permeability of the membrane modules is determined at the beginning of the experiment $L_{p,0}$ (m) and is determined after 100,000 and 300,000 back pulses. To determine the permeability L_p (m), the flux ($m\,s^{-1}$) and viscosity (Pa s) are determined as a function of the transmembrane pressures (bar). In these experiments flux and viscosity were evaluated at four different transmembrane pressures in the range of 0.2–1.0 bar. The permeability of the membrane can easily be calculated from Darcy's equation:

$$\eta J = L_p \Delta P \quad (5)$$

From a graph where ηJ is plotted versus ΔP, the slope (permeability, L_p (m)) can be determined. The permeabilities of the membrane at respectively 100,000 and 300,000 back pulses are normalized with respect to the initial permeability of the membrane. The initial permeabilities of the fouled fibers was averagely four times lower as clean fibers. Fouled fibers had an average permeability of 5×10^{-13} (m) and clean fibers had an average permeability of 2×10^{-12} (m).

3.3. Pressure decay test

The pressure decay test (PDT) can be used to check the integrity of a membrane unit. The main principle is based on measurement of the pressure drop on the feed side after draining and pressurizing. In general, the applied pressure is approximately 1 bar. Acceptable pressure drops are around 1.5 mbar min^{-1}.

3.4. Bubble test

The bubble test can be used to locate damaged membrane fibers. The principle is based on the pressurization of the membrane below bubble point pressure in a water filled basin. Bubble tests are performed with test pressures around 0.3–0.5 bar. After location of the damaged fiber, the fiber is repaired with use of special repair equipment.

3.5. Tensile tests

One of the most fundamental tests to determine the mechanical properties of a material is the tensile test. In this study, a tensile test apparatus of Zwick is used to determine the modulus of elasticity and the rupture point. A 10-N load cell is used to strain the test fibers.

4. Results

Figs. 3–5 show the results for the 14 performed experimental runs. Especially for runs (ad), (abd), (acd) and (abcd) the increase in permeability, PDT values and number of defect fibers is striking. Those experiments encompass fouled modules. Another striking result that can immediately be derived from the data is that clean modules can be operated under high pressures (2.0 bar) with high cleaning agent dosings (1000 ppm) for a high number of pressure pulses (300,000) without major change in permeability and without detectable fiber leakage. It should be further noted that the variation in experimental outcomes of the PDT for tests (abd) and (acd) and (abcd) may be caused by difference in qualities of the modules, based on their initial permeabilities.

The analysis of variance for the different membrane performance measurements yield the results graphically presented in Figs. 6–8 . The critical F-values are denoted by the dotted line (95% significant) and the dashed line (99% significant). The factors A (fouling status), D (number of back pulses) and the combination AD, yield F-values that exceed the critical F-values for all three integrity methods. If $F > 4.49$, the effect of the influence factor is 95% significant, and if $F > 8.53$, the effect of the influence factor is 99% significant. It is further noted that the calculated F-value is proportional to the square of its contrast. The contrast is directly calculated from the experimental values. However, the calculation scheme used to calculate the contrasts, influences the outcomes by the positive of negative sign added in the summation. For example, from Fig. 3, it can be seen that the experiments ad, abd and acd have the highest changes in

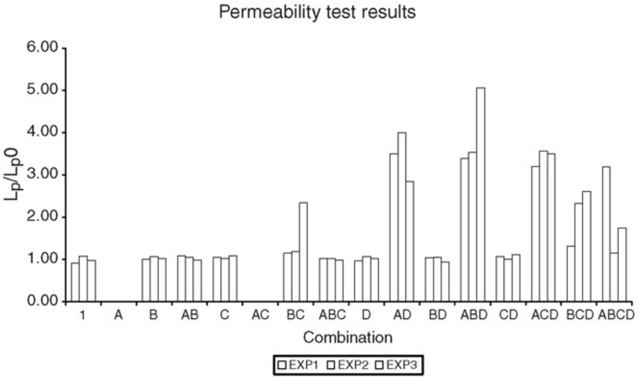

Fig. 3. Experimental values for the permeability tests.

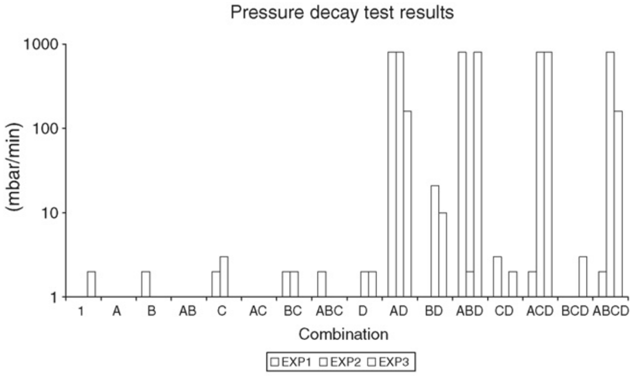

Fig. 4. Experimental values for the pressure decay tests.

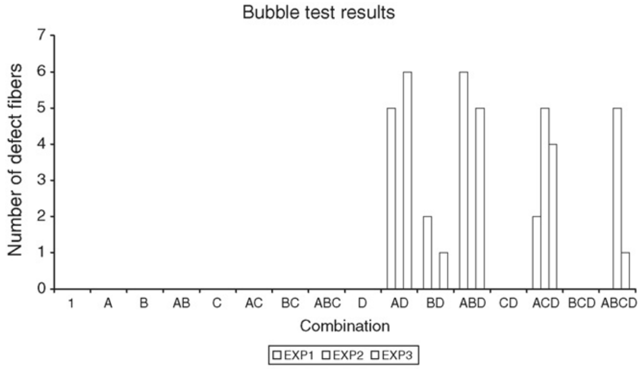

Fig. 5. Experimental values for the bubble tests.

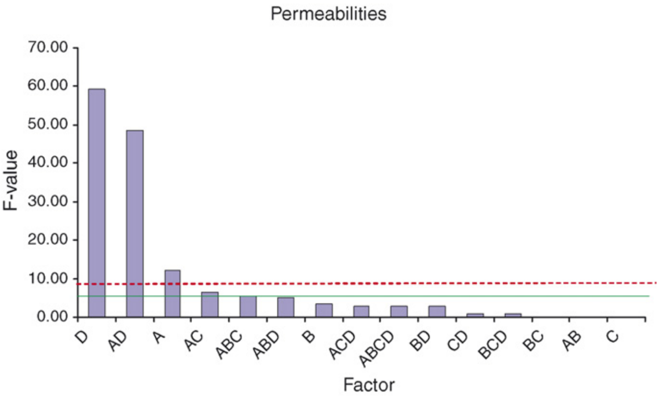

Fig. 6. *F*-values for the permeability tests.

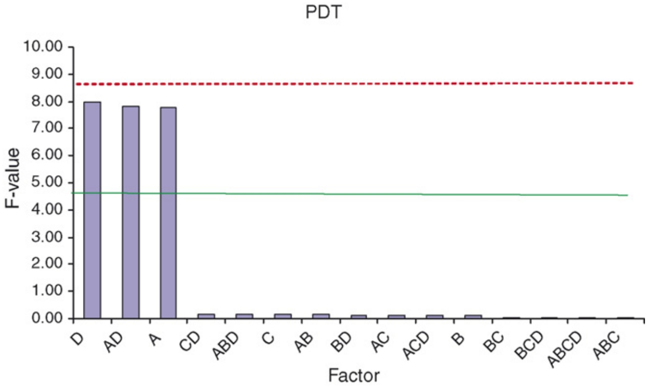

Fig. 7. *F*-values for the pressure decay tests.

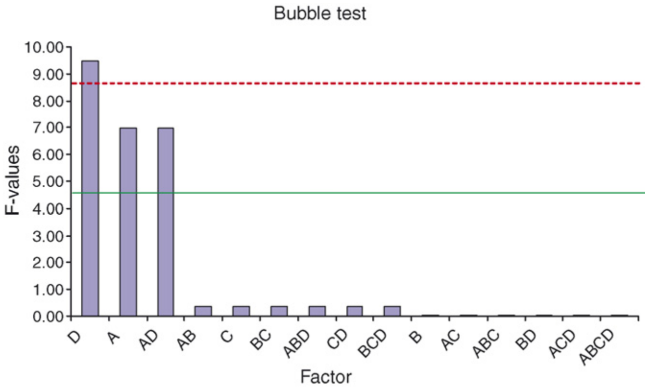

Fig. 8. *F*-values for the bubble tests.

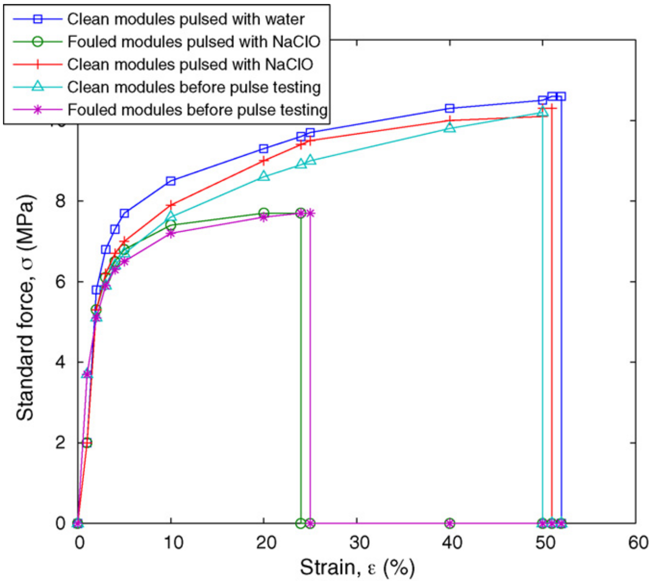

Fig. 9. Tensile test values.

permeability. Those values contribute mostly to the calculation of its contrast:

$$C_A = \cdots + X_{\mathrm{ad}} \cdots + X_{\mathrm{abd}} \cdots + X_{\mathrm{acd}} \cdots = 4.95$$

$$C_B = \cdots - X_{\mathrm{ad}} \cdots + X_{\mathrm{abd}} \cdots - X_{\mathrm{acd}} \cdots = 1.43$$

$$C_{AB} = \cdots - X_{\mathrm{ad}} \cdots + X_{\mathrm{abd}} \cdots - X_{\mathrm{acd}} \cdots = 0.02$$

For this reason, the factor A can be significant, but a combination which includes this factor, such as AB is not.

Fig. 5 shows the number of defected fibers for the different experiments. For membrane modules that were pulsed 300,000 times (all combinations with D), 300,000 pulses correspond to approximately 9 years of operation. During this test period, on average no more than 6 fibers defected, which corresponds to 0.6 breacher per year.

Also integrity data from a full scale plant, with multiple modules, was collected. Every 24 h an airflow test was conducted for the duration of a 2-year period. During this period, on average no more than 1–3 breaches defected, which corresponds to 0.5–1.5 breaches per year. These numbers correspond to results presented in this research.

Tensile tests have also been performed with non-defected membrane fibers from experiment (cd) (clean modules, back pulsed with water), (bcd) (clean modules, back pulsed with NaClO), (abcd) (fouled modules back pulsed with NaClO) and with clean and fouled fibers that were not used in the pulse tests. During the tensile tests, fibers broke in the middle and not at the

Table 3
Tensile test curves

Type	E (MPa)	ε_r (%)	σ_{m} (N)
Clean (initial)	226.69 (s=17.50)	50.80 (s=5.23)	2.70 (s=0.18)
Fouled (initial)	230.95 (s=10.34)	23.87 (s=4.12)	2.19 (s=0.07)
Clean (pulsed with water)	243.92 (s=19.21)	51.83 (s=4.73)	2.80 (s=0.16)
Fouled (pulsed with NaClO)	228.15 (s= 9.42)	22.70 (s=3.87)	2.16 (s=0.08)
Clean (pulsed with NaClO)	227.24 (s= 5.28)	50.23 (s=1.58)	2.94 (s=0.06)

grip. The tensile tests were performed in sixfold and the average results are plotted in Fig. 9. Fig. 9 shows the standard force or stress, σ (MPa) as a function of the strain ε (%). Striking is the difference in elongation ε_r (the rupture point or strain at break) for clean modules and fouled modules. The mechanical properties of clean and fouled fibers after pulse testing were similar to the clean and fouled fibers before testing: Mechanical properties do not seem to change much after intense exposure to NaClO, but drastically change if the fibers are fouled. In Table 3, the elastic modulus, E, the elongation, ε_r and the maximal force, σ_{m} are shown with the calculated standard deviations.

5. Conclusions

A systematic study of factors that influence membrane life time was performed. An experimental design was developed and executed and the results were analyzed by means of ANOVA (Analysis of variance). The study revealed that the fouling status of a membrane, the number of applied back pulses and the combination of those two factors influence membrane integrity significantly. It also showed that the effect of sodium hypo chlorite (at pH conditions of approximately 11.5) and the magnitude of the applied pressure pulse, did not significantly influence membrane performance. Additional tensile tests were performed and showed that the rupture point of fouled modules is almost half of the value for clean modules. Mechanical properties of clean modules back pulsed with water and sodium hypo chlorite were similar.

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Nomenclature

C	contrast
E	elastic modulus (MPa)
F	value of F-test
J	flux (m s^{-1})
K	sum of squares
L_p	permeability (m)
n	number of experiment repetitions
ΔP	transmembrane pressure (Pa)
s	standard deviation
S	variance
X	experimental value
Greek letters	
ε_r	elongation (%)
η	viscosity (Pa s)
σ	standard force (MPa)
σ_{m}	maximal force (N)
ϕ	degree of freedom

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