

Analysis of nanofiltration parameters of removal of an anionic detergent

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Abstract

The demand for clean water is currently increasing because of the decreasing sources of drinking water the stringent environmental legislation and the rigorous quality demands. Nanofiltration may be a solution for the effective separation of anionic detergents from used water or wastewater. In this work the removal of an anionic surfactant cleaning agent by nanofiltration was investigated. The nanofiltration of aqueous solutions of the anionic surfactant was examined at detergent concentrations of 0.5, 1.0 and 5.0 g L⁻¹ at 20, 30 and 40°C and at 20, 30 and 40 bar. Statistical evaluation of the data revealed that the retention was principally affected by the temperature. The highest retention was observed at 20°C. Increase of both pressure and temperature increased the flux, but the impact of pressure was higher than that of temperature. The highest flux was measured at 40°C. There was no appreciable difference between 30 and 40 bar. The fouling index, calculated by fitting a power function to the measured data, was mainly affected by the temperature: it decreased with increasing temperature. The ideal parameters for the best retention and a reasonable flux were found to be 20°C and 30 bar and for the minimal fouling were 30°C and 30 bar.

Keywords: Membrane separation; Nanofiltration; Surfactant; Fouling index; Flux; ANOVA; Shapiro–Wilk test; Hartley test; Cochran test; Bartlett test

1. Introduction

Pressure-driven membrane separation processes, including ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), have been widely used in water and wastewater treatment

and are applied on an industrial scale worldwide. Many industrial water and wastewater effluents contain detergents in concentrations of up to 1–5 g L⁻¹, which must be largely removed prior to water recycling or discharge.

In Hungary, the recent regulations relating to effluent water limit the detergent content for biological water treatment to 0.5 g L⁻¹, and that

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of discharge water to 0.05 g L^{-1} [1]. Although membrane processes may differ greatly in their mode of operation, structures and driving forces, some advantages are common to all. They are faster, more efficient and more economical, and their operation is easier to control and maintain than other conventional separation techniques [2–4]. Further, there is only a low need for chemicals and separation is usually performed at ambient temperature, therefore allowing temperature-sensitive solutions to be treated without the constituents being damaged or chemically altered. This is important in the food industry, where temperature-sensitive products have to be processed. On the other hand, in pressure-driven membrane separation techniques, UF is becoming a viable alternative because it can operate at lower pressures and lower energy consumption than NF or RO [5,6]. Unfortunately, membrane techniques have some drawbacks too, such as a high energy consumption and especially RO or the flux decline caused by membrane fouling or concentration polarization. Membrane fouling is mainly due to the accumulation of different rejected components, such as colloidal proteins. It is possible to reduce membrane fouling by optimizing the transmembrane pressure, the cross-flow velocity or other operating parameters. Concentration polarization involves time-dependent accumulation of compounds near the membrane surface.

The basis of membrane separation processes is osmotic phenomena: diffusion of the solvent (commonly water) through a semipermeable film (membrane), and a gel layer formed on the membrane surface. Membrane permeability is expressed as the permeate flux through the membrane (J):

$$J = \frac{dV}{d\tau} \frac{1}{A} = K_M (\Delta p - \Delta \pi) \left[\text{L m}^{-2} \text{ h}^{-1} \right] \quad (1)$$

where J is the permeate flux, A is the membrane filtration area [m^2], V is the volume of the permeate [dm^3], τ is time [h], K_M is the permeability coefficient [$\text{L m}^{-2} \text{ h}^{-1} \text{ Pa}^{-1}$], Δp is the pressure

difference between the two sides of the membrane [Pa], and $\Delta \pi$ is the osmotic pressure [Pa].

For the comparison of measured data, it is useful to express the normalized water permeability (NWP):

$$\text{NWP} = \frac{J}{A \Delta p} \left[\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1} \right] \quad (2)$$

The selectivity of a membrane for a given solute and the efficiency of the NF process are expressed by the retention (R):

$$R = \left(1 - \frac{c}{c_0} \right) 100 \text{ [\%]} \quad (3)$$

where c is the concentration of the solute in the permeate phase [%] or [mg dm^{-3}], and c_0 the concentration of the solute in the bulk solution [%] or [mg dm^{-3}].

The permeate flux can be described as a function of time:

$$J = J_0 \cdot t^{-k} \left[\text{L m}^{-2} \text{ h}^{-1} \right] \quad (4)$$

where J_0 is the initial permeate flux [$\text{L m}^{-2} \text{ h}^{-1}$], t is the filtration time [h], and k is the fouling index. K can be calculated from the measured data by using a curve-fitting technique.

Surfactants, which are surface-active amphiphilic agents containing both hydrophilic and hydrophobic components, are classified into four groups depending on the charge of the hydrophilic moiety: anionic, cationic, nonionic or zwitterionic [7,8]. Anionic surfactants, predominantly used in Hungary, contain negatively charged head groups. Some of the unique properties of surfactants are low toxicity, good water solubility and high foam stability. At and above the critical micelle concentration (CMC), the surfactant monomers aggregate into micelles [9]. The CMC can be influenced by temperature, the structure of the investigated surfactant, and the quantity of organic additives in the solution [10].

In the present study, our primary aim was to reduce the surfactant content of solutions. The filterability of an anionic surfactant was investigated the optimal filtration parameters were determined.

2. Materials and methods

The anionic surfactant cleaning agent, Chemipur CL80, provided by Sole Hungaria Rt. (Szeged, Hungary), was used. Membrane filtration experiments were performed on a Uwatech 3DTA laboratory membrane filter (Uwatech GmbH., Germany) with a filtering surface area of 0.0156 m². NF was carried out with a standard DL composite membrane with a theoretical MgSO₄ retention of 96% and a high permeate flux. The surfactant concentrations of permeates and concentrate solutions were measured at 652 nm with a UV spectrophotometer (WPA Lightwave S2000) via the methylene blue active substances method [11]. Temperature and conductivity were measured with Consort C535 equipment.

The experimental data were evaluated statistically in order to obtain the parameters governing the retention and flux. The data assessment involved analysis of variance (ANOVA) or Friedman analysis, depending on the results of the Hartley, Cochran and Bartlett tests.

3. Results and discussion

3.1. Critical micelle concentration

The CMC of the detergent Chemipur CL80 was determined via conductivity measurements at three different temperatures, and from the intersection of two linear segments on a plot of conductivity versus detergent concentration. Since the anionic detergent was very alkaline, the pH was adjusted by adding 1 N HCl. The CMC of CL80 at pH 7 at 20, 30 and 40°C was 2.1, 2.65 and 2.8 g L⁻¹ respectively.

These CMC values correspond with those reported by Kowalska et al. [12], who observed

that, on increase of the temperature from 25 to 55°C, the CMC of sodium dodecylsulfate increased from 2.257 to 2.706 g L⁻¹ respectively. Our data (Fig. 1a–c) reveal that micelle formation is a very temperature-dependent process. The angles

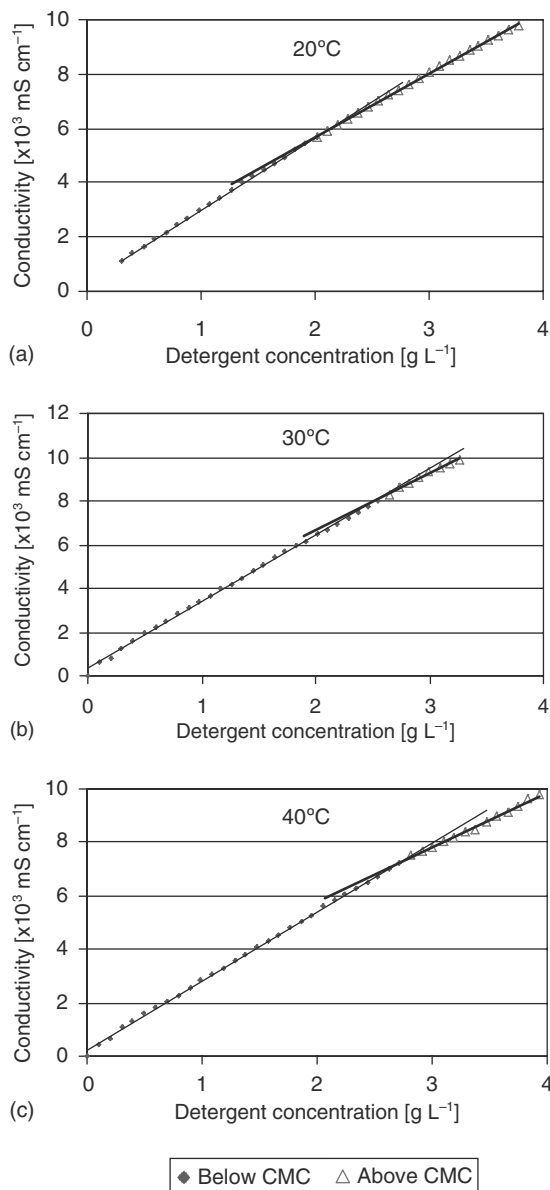


Fig. 1. Conductivity below and above CMC at pH 7 at 20°C (a), 30°C (b) and 40°C (c).

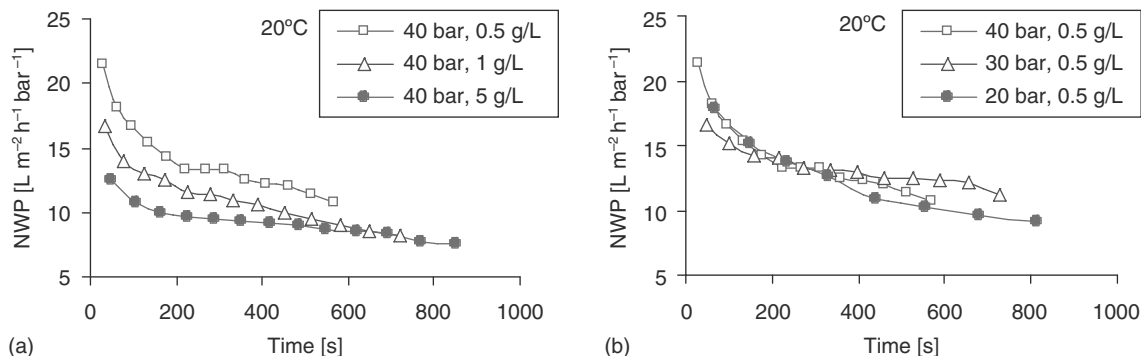


Fig. 2. Effects of surfactant concentration (a) and pressure (b) on normalized flux at 20°C.

of the intersections indicate that the effects of the size, shape and amount of the micelles are higher at 40°C than at lower temperature.

The measured fluxes similarly display a considerable temperature dependence.

3.2. Nanofiltration of anionic surfactant

The NF of aqueous solutions of CL80 (0.1, 0.5, 1 and 5 g L⁻¹) was examined at different temperatures (20, 30 and 40°C) and pressures (20, 30 and 40 bar). At 20°C NWP calculated via Eq. (2) decreased with increasing detergent concentration (Fig. 2a) and increased with increasing pressure (Fig. 2b).

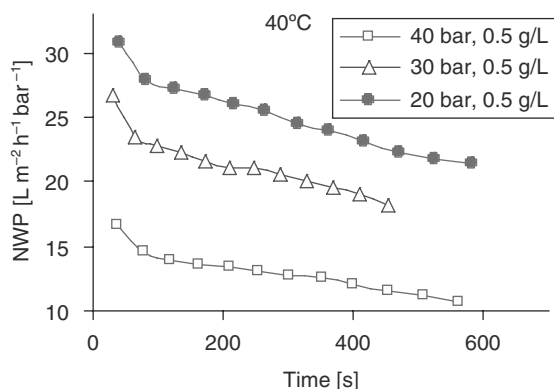


Fig. 3. Effect of pressure on normalized flux at 40°C.

At 40°C, the NWP data are different and appreciably temperature-dependent (Fig. 3). The statistical analysis (Table 5) demonstrated that the gel-layer formation is mainly determined by temperature.

At 40°C, NWP was higher at 1 g L⁻¹ than at 0.5 g L⁻¹ CL80 (Fig. 4). This phenomenon can be explained in terms of the CMC. Increasing surfactant concentration decreases the surface tension, which may lead to a decreased membrane resistance, and thus an increased flux. Further increase of the surfactant concentration causes micelle formation, which increases the surface tension and decreases the flux.

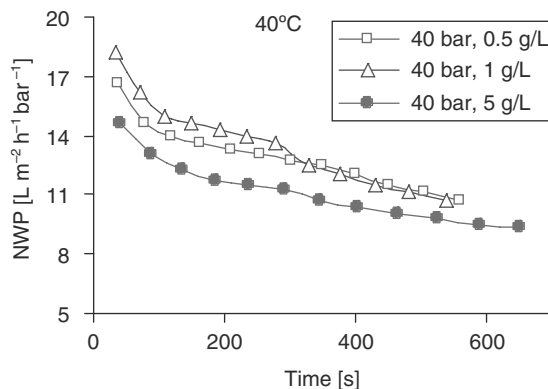


Fig. 4. Effect of surfactant concentration on permeate flux at 40°C.

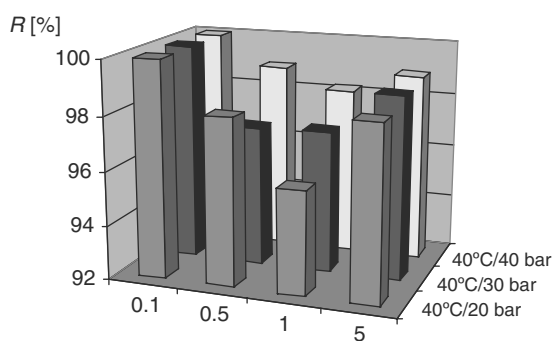
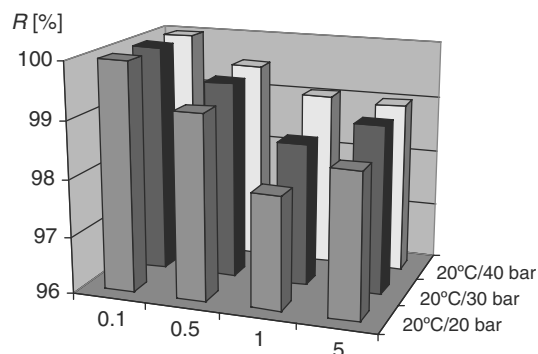
(a) Detergent concentration [g L^{-1}](b) Detergent concentration [g L^{-1}]

Fig. 5. Retentions at 40°C (a) and 20°C (b).

The highest flux, in 1 g L^{-1} solution at 40°C (Fig. 4), is related to the lowest retention in Fig. 5a, caused by the low membrane/layer resistance. At 5 g L^{-1} , the formation of large micelle particles increases the retention. The measured tendency at 40°C implies the temperature sensitivity of the surfactant.

The efficiency of removal of the surfactant from the solution was always above 94%, but at lower temperature a higher removal efficiency (>97.5%) was achieved. At 0.1 g L^{-1} surfactant concentration, no residue was detected in the permeate: the surfactant was successfully removed. Higher retention here was achieved at lower temperature. The best surfactant removal was attained at 20°C and 40 bar (Fig. 5b).

3.3. Statistical analysis of nanofiltration parameters

The Shapiro–Wilk test was used to check on the Gaussian distribution of the data. The homogeneity of variances in the different groups was checked with the Hartley, Cochran and Bartlett tests. Table 1 presents the results of the Shapiro–Wilk tests. It can be stated that the flux and fouling index values (Table 2) conformed to Gaussian distribution, whereas the retention did not. The results of the Hartley, Cochran and Bartlett tests (Table 3) demonstrate homogeneity of variances for the flux and the fouling index. Variance analysis was therefore used to evaluate the flux and fouling index data, and Friedman analysis for the retention.

Table 1
Results of Shapiro–Wilk tests

	Factor								
	Pressure (bar)			Temperature (°C)			Detergent concentration (g L^{-1})		
	20	30	40	20	30	40	0.5	1	5
Retention	0.798*	0.745*	0.703*	0.942	0.858	0.892	0.817*	0.785*	0.801*
Flux	0.925	0.899	0.902	0.912	0.984	0.951	0.911	0.926	0.936
Fouling index	0.942	0.902	0.858	0.893	0.918	0.917	0.876	0.907	0.899

Superscript * denotes statistical significance at $p = 0.05$.

Table 2
Values of fouling index (k) at different temperatures and pressures

Detergent content (g L ⁻¹)	Pressure (bar)	Temperature (°C)		
		20	30	40
0.5	20	0.2786	0.0694	0.1307
	30	0.1276	0.1946	0.1235
	40	0.2172	0.1738	0.1444
1	20	0.1360	0.0749	0.1005
	30	0.1748	0.1920	0.1674
	40	0.2245	0.1406	0.1005
5	20	0.1978	0.1146	0.1203
	30	0.1045	0.0877	0.1684
	40	0.1546	0.1168	0.1589

Table 3
Results of Hartley, Cochran and Bartlett tests

Factor	Hartley	Cochran	Bartlett	DF	p level
<i>Retention</i>					
Pressure	4.533	0.6821	5.834	2	0.0540
Temperature	20.566	0.7953	15.022	2	0.0005
Det. conc.	48.619	0.5071	20.264	2	0.0000
<i>Flux</i>					
Pressure	1.694	0.4451	0.612	2	0.7363
Temperature	4.916	0.6119	4.633	2	0.0984
Det. conc.	5.920	0.4611	5.587	2	0.0618
<i>Fouling index</i>					
Pressure	2.823	0.5701	2.619	2	0.2698
Temperature	4.388	0.4992	3.954	2	0.1384
Det. conc.	2.996	0.5112	2.187	2	0.3349

The ANOVA F values (Table 4) demonstrated that the flux was influenced significantly by pressure, temperature and detergent concentration. The results of detailed analysis are presented in Figs. 6–8, with the confidence interval being taken at a level of 0.95.

It can be seen that the flux increased with increasing pressure, with a significant difference between the average values at 20 and 30 bar. The flux was ~ 170 L m⁻² h⁻¹ higher at 30 bar. On temperature increase the flux progressively

Table 4
Results of ANOVA of flux values

Effect of	DF	F value	p level
Pressure	2	9.866	0.0010
Temperature	2	6.879	0.0051
Detergent concentration	2	3.404	0.0532

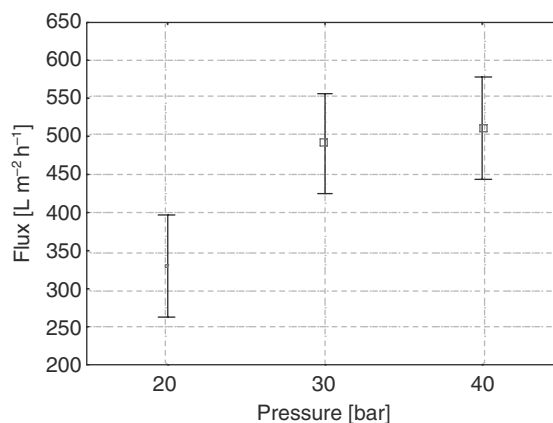


Fig. 6. Average flux with confidence interval (0.95) at various pressures.

increased. With increasing detergent concentration, the average flux decreased. The differences (~ 100 L m⁻² h⁻¹) between the averages at 0.5 and 5 g L⁻¹, and at 1 and 5 g L⁻¹ were significant.

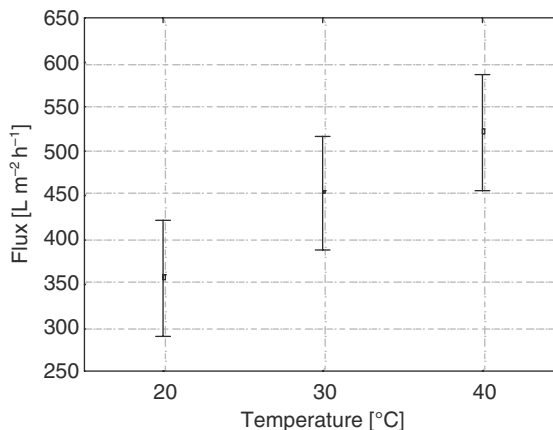


Fig. 7. Average flux with confidence interval (0.95) at various temperatures.

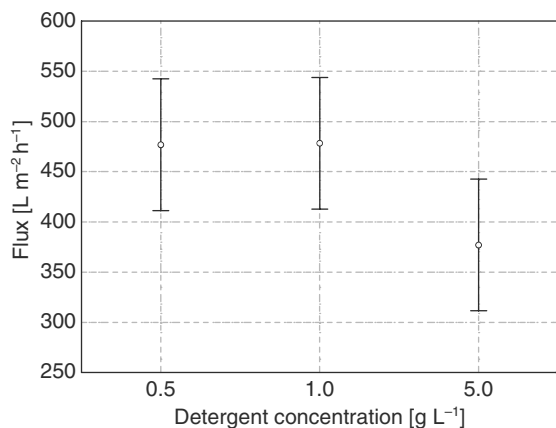


Fig. 8. Average flux with confidence interval (0.95) at various detergent concentrations.

Table 5
Results of ANOVA on fouling index

Effect of	DF	F value	p level
Pressure	2	2.077	0.3540
Temperature	2	9.198	0.0101
Detergent concentration	2	3.857	0.1454

The ANOVA *F* values (Table 5) revealed that the fouling index was influenced significantly by temperature, but not by pressure and detergent concentration. The effects of temperature on the

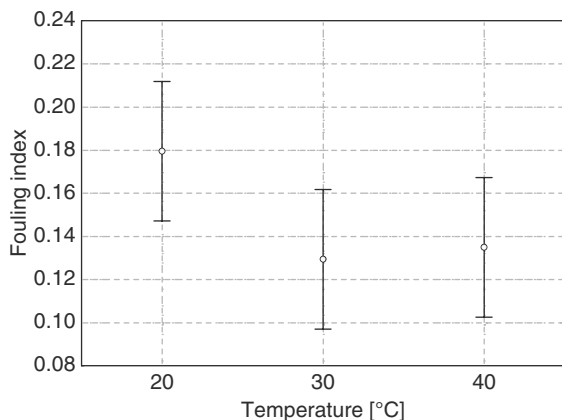


Fig. 9. Average fouling index with confidence interval (0.95) at various temperatures.

Table 6
Results of Friedman analysis on retention

Effect of	DF	Chi-square value	p level
Pressure	2	2.076	0.3540
Temperature	2	9.197	0.0101
Detergent concentration	2	3.857	0.1454

average fouling index are illustrated in Fig. 9, with the confidence interval being taken at a level of 0.95.

On temperature increase from 20 to 30°C or to 40°C, the average fouling index decreased significant (by ~0.03 unit). Friedman analysis (Table 6) indicated that the retention was influenced significantly by temperature (*p* = 0.0101), but not by pressure or detergent concentration increase.

The medians, quartiles (25th and 75th percentiles), and maximum and minimum values of retention calculated for samples at various temperatures are presented in Fig. 10.

On temperature increase from 20 to 30°C, the median retention decreased by 1.2%. The difference between the averages at 30 and 40°C was not significant. The medians, quartiles

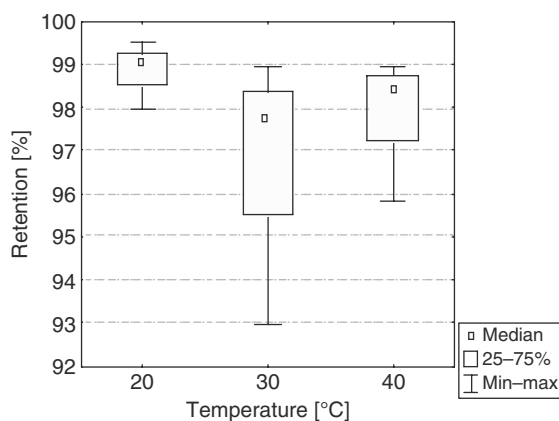


Fig. 10. Median, quartiles, and maximum and minimum retention values calculated for samples at various temperatures.

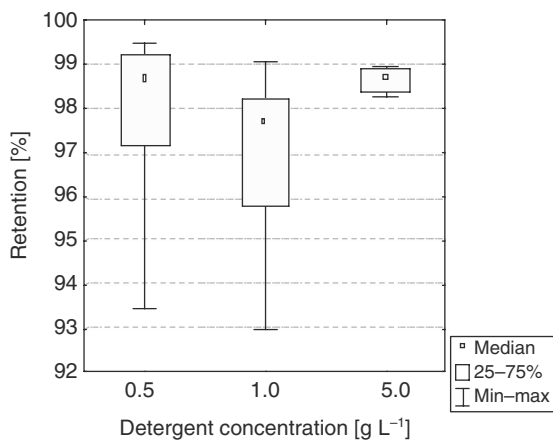


Fig. 11. Median, quartiles, and maximum and minimum retention values calculated for samples with various detergent concentrations.

(25th and 75th percentiles), and maximum and minimum retention values calculated for samples with various detergent concentrations are presented in Fig. 11.

The median retention was lowest at a detergent concentration of 1 g L⁻¹.

4. Conclusions

The retention was principally affected by the temperature, the highest retention being observed at the lowest temperature. The highest flux was measured at the highest temperature. The fouling index was mainly affected by the temperature, decreasing with increasing temperature. The ideal parameters for the best retention and a reasonable flux, and for minimal fouling were 30°C and 30 bar or and 40 bar. Increasing pressure was associated with an increasing flux, but this phenomenon was overshadowed by influence of the changes in gel-layer formation with increasing detergent concentration.

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