Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22633

128 (2018) 187–192
October

The influence of the nanofiltration method on the retentate composition after simulated chromium tannery wastewater concentration

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Received 31 March 2018; Accepted 22 June 2018

ABSTRACT

This paper compares the nanofiltration process carried out by different diafiltration modes: NF–CVD (nanofiltration carried out constant volume diafiltration), NF–VVD (nanofiltration carried out variable volume diafiltration) and NF–IVD (nanofiltration carried out intermittent volume diafiltration). Different methods of the nanofiltration process were used for the selective separation and concentration of the chromium(III) from the simulated tannery wastewater solution. The influence of the execution of the process on the degree of chromium(III) concentration, the desalination of solution, the retentate volume reduction and the permeate flux were discussed. The study allowed for the conclusion that, for the same initial conditions, methods of carrying out the nanofiltration process had effects on the final result of the study. The NF–VVD process allowed one to obtain a highest degree of washing salt out (41%), but the chromium(III) retention was on the level of 90%. In this case, the separation of the feed solution components was achieved with the smallest volume of the washing water added during diafiltration step. On the other hand, the NF–IVD process allowed for obtaining a high retention of chromium(III) of 95%, while washing out the salt was only 32%. The NF–CVD process resulted in a good degree of washing salt out of 38% and a high chromium(III) retention of 95%. Additionally, during the study, it was observed that the nanofiltration process carried out as the diafiltration CVD allowed for achieving the best retentate volume reduction compared with the NF–VVD and NF–IVD processes. Considering the results, it is evident that, in regard to the aim of the process (desalination or chromium concentration), one should use different nanofiltration method.

Keywords: Nanofiltration; Desalination; Chromium(III); Concentration; Diafiltration

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1. Introduction

Chromium is an element widely used in various industries, in particular, the tannery industry, the electroplating industry, and the metallurgy industry. The activity of these industries contributes to the large amount of wastewater containing the element [1]. Apart from chromium, these solutions also contain high concentrations of chloride salts, which disable the selection of appropriate purification methods. Although chlorides are nontoxic, deposition of their high concentrations into natural water receivers is detrimental. Currently, enabling the partial separation of chloride ions from chromium ions is used. These methods include nanofiltration (NF) [2–6]. The permeate obtained during the process contains a high concentration of chloride ions, and the retentate characterizes with a high chromium concentration. The separation of individual constituents of

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Presented at the XII Scientific Conference 'Membranes and Membrane Processes in Environmental Protection' – MEMPEP 2018
13–16 June 2018, Zakopane, Poland.

the solution is possible due to a membrane that is permeable for monovalent ions and impermeable to multivalent ions. The process mainly uses asymmetric and composite membranes.

Previous studies of the NF process allowed for the separation of chromium from the solutions containing this element. Gomes et al. [3] obtained chromium retention of 80% using a NF process with acid and a saline solution of chromium(III). In contrast, Ortega et al. [4] obtained a chromium retention of 99% during the NF process. Similar results were obtained by Religa et al. [5,6].

The discussed examples concern the chromium(III) concentration in solutions. However, they have not focused on the desalination issue. Therefore, to solve the problem of the desalination of chromium(III) solutions, the NF process carried out in a diafiltration mode is proposed. Diafiltration is a type of the filtration processes, in which a diluent is introduced to wash off low-molecular weight substances [7,8]. The diafiltration process consists of three steps: preconcentration – partial volume reduction of the feed; diafiltration – the diluent is introduced into the preconcentrated solution to wash off the low-molecular weight substances and postconcentration – relying on the concentration of the substance in the retentate [9–11]. Diafiltration may be carried out in following modes: variable volume diafiltration (VVD), constant volume diafiltration (CVD) and intermittent volume diafiltration (IVD). The VVD is a process, in which the diluent is continuously added to the retentate at specified intervals and at a fixed rate established below the permeate flow. The CVD is a process, in which a diluent is continuously added to the retentate in the amount equal to the outflow permeate [11]. The IVD is a process that comprises of the batchwise addition of a diluent to the retentate in the amount equal to the volume of permeate received.

The diafiltration process has been used for desalination purposes in the food industry (lactose in whey protein products), in pharmaceuticals, in biotechnology and in the chemical industries [7,9,10]. Using the NF process carried out in a diafiltration mode in order to reduce salt concentration in simulated solutions enables to obtain even a 97% NaCl reduction [12]. Thus, the combination of the NF process with diafiltration mode may be a preferable way of lowering the salt concentration in chromium(III) solutions.

It is assumed that the selection of an appropriate method of the NF process operated in the diafiltration mode will reduce the chloride concentration in chromium solutions. The aim of the study was to determine the influence of the NF process arranged in different diafiltration modes (NF–CVD (nanofiltration carried out constant volume diafiltration), NF–VVD (nanofiltration carried out variable volume diafiltration) and NF–IVD (nanofiltration carried out intermittent volume diafiltration)) for the desalination of simulated chromium solutions in regard to chromium(III) concentration in the retentate and permeate flux.

2. Experimental

A NF process carried out as NF–CVD, NF–VVD and NF–IVD was performed in a laboratory installation in cross-flow cells made of stainless steel operated in batch mode with circulation, the scheme of which is presented in Fig. 1. A simulated chromium solution (4 L) was introduced to the feed/retentate tank. Next, it was pumped by a high-pressure pump (Cat Pumps – model 240) and directed to the NF module equipped with the flat sheet membrane. Two process streams, that is, the retentate-recycled to the feed/retentate tank, and the permeate, which was collected in a permeate tank, were obtained.

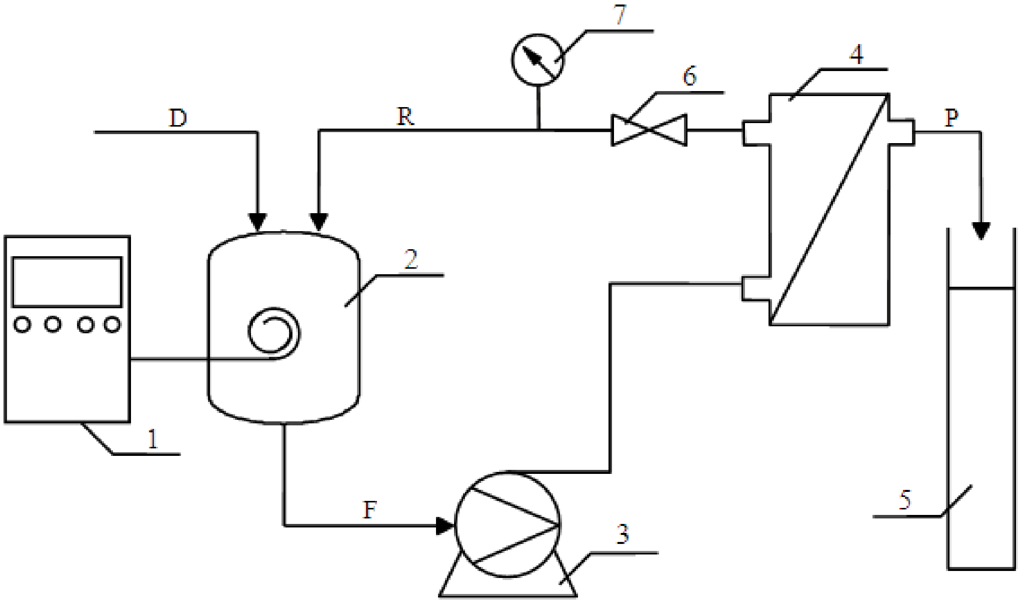

Fig. 1. The scheme of the laboratory installation for nanofiltration arranged in different diafiltration modes: 1 – thermostat, 2 – feed/retentate tank, 3 – high pressure pump, 4 – NF module, 5 – permeate tank, 6 – valve, 7 – manometer, D – washing diluent (RO water), F – feed, R – retentate and P – permeate.

The preconcentration of the NF process by diafiltration as CVD, VVD and IVD was carried out and decreased the permeate flux by about 20% compared with the initial value. In the process of NF–CVD, during the diafiltration step, a preconcentrated retentate was supplied with a diluent at a rate equal to the flow of permeate received. The diluent was introduced into the system manually by means of a measuring cylinder. One portion of the diluent added was equal to 10 cm^3. In total, 1.3 L of diluent was introduced to the system. In the NF–IVD process, 1.3 L of diluent was introduced into the preconcentrated retentate at the diafiltration step. During the process of NF–VVD, in the diafiltration step, a diluent was introduced into a preconcentrated retentate at a rate of less than about 20% compared with the rate of the permeate received. In the diafiltration step, the total volume of the introduced diluent was 1.16 L and its addition was combined with the concentration. The postconcentration step for each NF processes by diafiltration (CVD, VVD and IVD) was carried out until the decrease of the permeate flux by approximately 60%, compared with the initial value (i.e. from 35 to 15 L m^{-2} h^{-1}) was obtained.

The study was conducted for simulated chromium solutions of the following composition: 20 g Cl^- L^{-1}, 10 g SO_4^{2-} L^{-1} and 2.0 g Cr^{3+} L^{-1}. The solutions were prepared with the following reagents: NaCl (Chempur®, Poland), Na_2SO_4 (Chempur®) and $CrCl_3{\cdot}6H_2O$ (Chempur®). In the samples obtained during the process, the chromium(III) concentration was measured spectrophotometrically with 1,5-diphenylcarbazide at the wavelength λ = 540 nm on Nanocolor UV/VIS spectrophotometer. Chlorides concentration was determined by Mohr's method. The flat sheet membrane DL provided by GE Osmonics with a surface area 0.0155 m^2 and a cut-off of 150–300 Da was used. The characteristic of the DL membrane used in the experiments is presented in Table 1. The tests were carried out at 20°C ± 1°C, TMP = 1.0 MPa, and QR = 800 L h^{-1}. RO treated water with a conductivity of 41 μS cm^{-1} was used as a washing diluent.

During the process, the time of collection of the 10 cm^3 of permeate was measured to determine the permeate flux from Eq. (1) as follows:

$$J_p = \frac{V}{A \times t} \tag{1}$$

where J_p – permeate flux (L m^{-2} h^{-1}); V – volume of the received permeate (L); A – membrane area (m^2) and t – time of permeate collection (h).

Table 1
Characteristics of DL membrane [5,13–15]

Comparable feature	Membrane DL
Active layer	Polyamide
Structure of the membrane	Three layer
Surface area (m^2)	0.0155
Cut-off (Da)	150–300
Isoelectric point (pH)	3.0
Zeta potential (mV)	–13.0 [13]
pH = 4	–14.0 [14]

The chromium(III) retention ratio (R) was derived from Eq. (2) as follows:

$$R = \left(1 - \frac{C_P}{C_N}\right) \times 100\% \tag{2}$$

where C_N – concentration of chromium(III) ions in the feed (g L^{-1}) and C_P – concentration of chromium(III) ions in the permeate after time t (g L^{-1}).

The salt elution ratio (E) was determined from Eq. (3) as follows:

$$E = \left(1 - \frac{C_K}{C_O}\right) \times 100\% \tag{3}$$

where C_k – salt concentration in the concentrate during diafiltration (g L^{-1}) and C_0 – salt concentration in the feed solution after preconcentration (g L^{-1}).

3. Results and discussion

3.1. Permeate flux

In all NF processes carried out by different diafiltration methods (NF–CVD, NF–VVD and NF–IVD), decreases of permeate fluxes in time during the preconcentration step were observed (Fig. 2). This was due to the high concentration of sulphate ions and chloride ions in the retentate, which contributed to the formation of a polarization layer near the membrane surface [9–12,14]. The formation of the polarization layer had also been observed in our previous studies [16–20].

At the stage of diafiltration, depending on the process mode of the process, differences in the change of the permeate flux were observed. During the NF–CVD process, in the diafiltration step, the permeate flux was constant (Fig. 2(a)). The diluent was introduced at a rate equal to the rate of the permeate received, so the polarization layer formed on the surface of the membrane was not dissolved.

For the NF–VVD process, the diafiltration step was combined with a simultaneous concentration. Therefore, during this stage, small decreases in the permeate flux in time were observed (Fig. 2(b)). The polarization layer formed on the surface of the membrane, was responsible for the decrease of the permeate flux during the process.

In the NF–IVD process, in the diafiltration step, it was observed that the permeate flux increased when a specific portion of the diluent was introduced into the system (Fig. 2(c)). In the initial stage of diafiltration, this diluent addition caused polarization layer 'blurring.' Then, with the increased concentration of the retentate, the permeate flux began to fall again. The same phenomenon was observed in previous works [7–9,16,18].

With the start of the postconcentration step and the increased concentration of the retentate, the concentration of the individual components of the solution increased. This led to the increase of membrane surface polarization. This phenomenon can be explained by analysing the properties of the membrane used in the process. On the surface and within the pores of the membrane, there is an electrostatic charge due to the presence of functional groups [21,22]. Most often, the NF membrane susceptibility to polarization

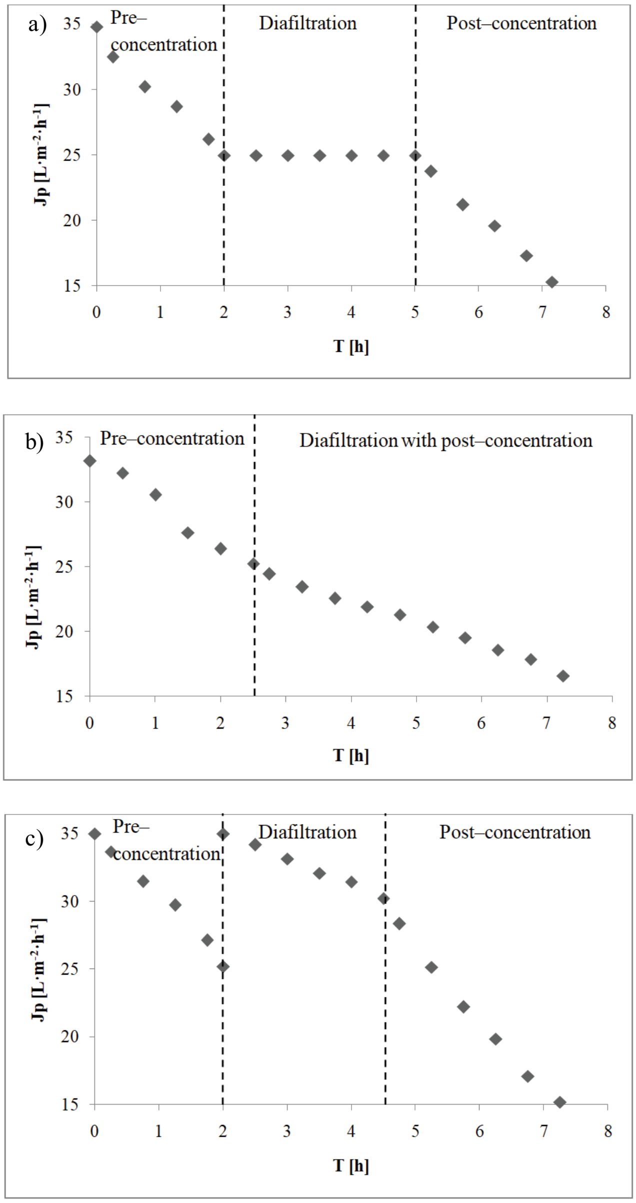

Fig. 2. Changes in the permeate flux vs. time during the (a) NF–CVD, (b) NF–VVD and (c) NF–IVD process.

is determined by the isoelectric point (IP). The IP is the pH, for which the overall charge of the membrane is equal to 0. As a rule, NF membranes have a positive charge when the pH is lower than the IP. However, when the pH is higher than the IP, the membrane has a negative charge [23]. The pH of the tested solution was 4, and it was higher than the IP of the DL membrane IP (IP = 3.0 [16,23]). Therefore, the surface of the NF membrane had a negative charge. Moreover, the increase in chromium(III) ions concentration in the retentate influenced its higher adsorption on the membrane. Consequently, this caused a decrease in the permeate flux.

3.2. Salt elution

In order to determine the degree of salt elution, a CVD diafiltration process, IVD diafiltration and VVD diafiltration at 1.0 MPa were performed. The degree of salt elution for the NF–IVD process was 32%, and for the NF–CVD process it was 38% (Fig. 3). During NF–IVD and NF–CVD processes, the same volumes of diluent (1.3 L) were introduced during the diafiltration step. So the differences in the degree of desalination in these processes were not due to the amount of diluent added (Table 2), but they were caused by the mode of the diafiltration. While carrying out the NF–CVD process, the diluent was added to the system at a rate equal to the rate of the permeate flow, and it did not dilute the retentate. The polarization layer in the diafiltration step for the NF–CVD process was constant. This caused the wash of the salt out of the system. On the other hand, in NF–IVD process, in which the diluent of volume 1.3 L was introduced into the system in a single step, the ‘blur’ of the resulting polarization layer was made and it resulted in the salt washing out of the system. However, further growth of the polarization layer prevented permeation of salt through the membrane. As a consequence, the NF–IVD process achieved a lower percentage of desalination than the NF–CVD process.

The salt elution rate for the NF–VVD process was 41% (Fig. 3). During this process, 1.16 L of water was introduced in the diafiltration step. This was a lower volume than in the case of the NF–IVD and NF–CVD processes. Introducing a smaller volume of diluent resulted in a 9% higher rate of desalination than in NF–IVD and a 3% higher rate of desalination than in NF–CVD. The differences could be explained

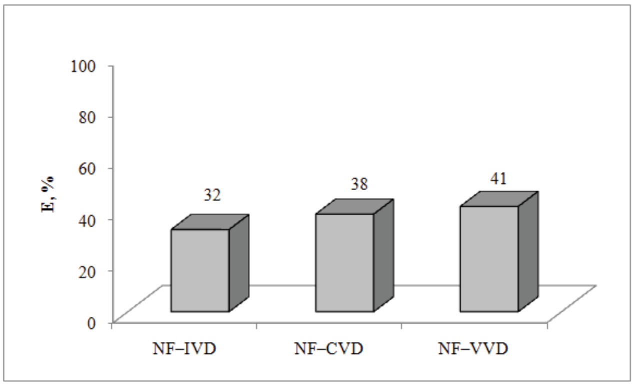

Fig. 3. The degree of salt elution: NF–IVD, NF–CVD and NF–VVD.

Table 2
Characteristics of the processes, process time (min) should be written with every process 435 min

Parameter	NF–IVD	NF–CVD	NF–VVD
Feed volume (L)	4.0	4.0	4.0
Final retentate volume (L)	1.8	1.6	2.6
Water consumption (L)	1.3	1.3	1.16
Final chloride concentration in the retentate (g L^{-1})	13.5	12.5	11.9
Final chromium(III) concentration in the retentate (g L^{-1})	3.5	3.8	2.7
Process time (min)	435	435	435

considering two aspects [10,16,22]. First, they were due to the NF process arrangement regarding the applied diafiltration mode. Simultaneous, slow concentration influenced on salts elution from the system, but it also allowed them to maintain at a high concentration in the retentate throughout the process. Secondly, the introduction of the diluent in the amount slightly below the volume of permeate received caused a much slower increase in the polarizing layer on the membrane surface. Therefore, the entire process could intensify the permeation of salt. NF processes carried out by different diafiltration modes allowed for the reduction of the salt concentration from 20.0 to 13.5 g L^{-1} (NF–IVD), to 12.5 g L^{-1} (NF–CVD) and to 11.9 g L^{-1} (NF–VVD) (Table 2).

3.3. Chromium(III) retention

Of the performance of NF in different diafiltration modes (NF–CVD, NF–VVD and NF–IVD) allowed for obtaining favourable desalination of solutions of chromium(III), while maintaining a high retention of chromium(III) itself (Fig. 4). In the NF–IVD process, the obtained retention of chromium was 95%. The same chromium(III) retention was obtained for the NF–CVD process. In the case of the NF–VVD process, the retention of chromium was 90%. The slight decrease in the degree of the retention of chromium(III) was caused by the method of introducing the diluent during the step of diafiltration.

Both, the high chromium(III) retention and the volume reduction of the feed allowed for high chromium concentration in the retentate (Table 2). During the study conducted for each system, nearly double the concentration of chromium was obtained in comparison with the initial value. The highest concentration of chromium was obtained in the NF–CVD process, and the lowest was obtained in the NF–VVD process (Table 2).

3.4. Water balance

Based on the results obtained for the tested systems, a water balance was performed (Fig. 5). In both, the NF–IVD process and the NF–CVD processes, the final total volumes were the same. However, in the NF–VVD process, the final total volume was different as compared with NF–IVD process and NF–CVD process and this difference was 0.14 L.

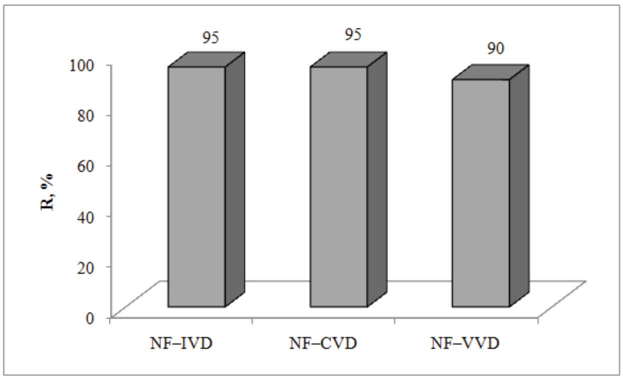

Fig. 4. Chromium retention: NF–IVD, NF–CVD and NF–VVD.

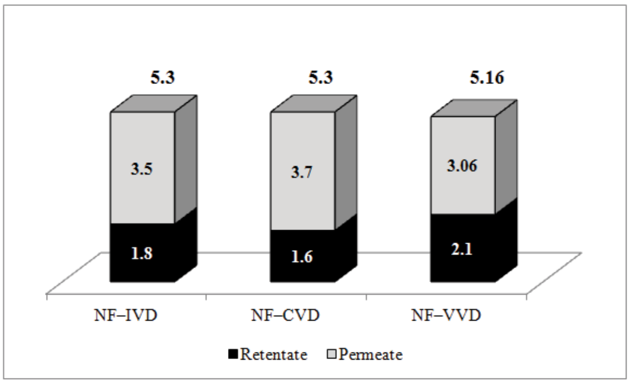

Fig. 5. Water balance for NF–IVD, NF–CVD and NF–VVD.

The final retentate and permeate values for each tested system were different. During the NF–CVD process, a lower retentate volume was obtained compared with the NF–IVD and the NF–IVD process. In addition to the NF–CVD process, a higher final permeate volume was obtained compared with the NF–IVD process. In both processes, the same volume of diluent (1.3 L) was introduced. Compared with the NF–VVD process, the final retentate volume was nearly 1.5 times higher than the one obtained during the NF–CVD process. Higher feed volume reduction results influenced on the high chromium(III) concentrations in the concentrate (Table 2). For the NF–CVD process, a higher volume of permeate was also obtained compared with the NF–VVD process. The NF–CVD process revealed a better degree of salt washing from the retentate than the NF–IVD process, despite the introduction of the same diluent volumes (Table 2), but the desalination was much lower than in the NF–VVD process, in which lower diluent amount was introduced. It is evident that the amount of diluent added and the method of NF process arrangement in regard to diafiltration, both influence on the degree of the salt washout and chromium(III) concentration rate.

4. Conclusions

The aim of this work was to compare the influence of NF processes arranged in different diafiltration modes on the degree of the desalination of simulated chromium(III) solutions, the concentration of chromium(III) and the permeate flux. The NF process was carried out using three different diafiltration modes (NF–CVD, NF–VVD and NF–IVD). The mode of the diafiltration was found to have an influence on the final results of the study.

In order to obtain a high degree of salt washout, the NF–VVD process is proposed. The combination of the diafiltration step of simultaneous concentrations results in the following: (1) higher salt elution (41%) at the addition of smaller volumes of diluent (1.16 L), (2) maintenance retention of chromium(III) at 90% and (3) significantly slower growth of the polarization layer on the surface of the membrane enabling the permeation of salt.

To achieve a good degree of salt washing, while maintaining a high retention of chromium(III), the NF–CVD process is proposed and it allows for the following: (1) a good degree of salt washout (38%) obtained by introducing a diluent system at a volume equal to the volume of permeate collected in the preconcentration (1.3 L), (2) high chromium(III) retention of 95% and (3) maintaining a constant polarization layer in the diafiltration step enabling salts permeation.

In order to achieve a high degree of chromium(III) retention, the NF–IVD process is proposed. This process results in the following: (1) high chromium retention of 95% and (2) a salt wash degree of 32% when introducing a single portion of the diluent into the system equal to a volume of permeate after preconcentration (1.3 L).

Symbols

NF–CVD — Nanofiltration carried out constant volume diafiltration
NF–VVD — Nanofiltration carried out variable volume diafiltration
NF–IVD — Nanofiltration carried out intermittent volume diafiltration
CVD — Constant volume diafiltration
VVD — Variable volume diafiltration
IVD — Intermittent volume diafiltration
QR — Retentate flow, L h^{-1}
TMP — Transmembrane pressure, MPa
RO — Reverse osmosis
J_p — Permeate flux, L m^{-2} h^{-1}
R — Chromium(III) retention ratio, %
E — Salt elution ratio, %
V — Volume of the received permeate, L
A — Membrane area, m^2
t — Time of permeate collection, h
C_N — Concentration of chromium(III) ions in the feed, g L^{-1}
C_P — Concentration of chromium(III) ions in the permeate after time t, g L^{-1}
C_k — Salt concentration in the concentrate during diafiltration, g L^{-1}
C_0 — Salt concentration in the feed solution after preconcentration, g L^{-1}

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