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Hexavalent chromium removal from chromium plating rinsing water with membrane technology

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ABSTRACT

The objective of this work is to assess the water reuse potential of aqueous streams from a metal finishing industry containing chromium using nanofiltration (NF) and reverse osmosis (RO). Process waters with hexavalent chromium were treated with NF (NF90 and MPS-34) and RO (BW30) membranes. The efficiency in terms of metal removal was very high. The NF90 membrane showed the best performance (highest flux and excellent selectivity, typically above 99%). An ultrafiltration pretreatment was required to remove the solid particles present in the process waters. NF makes possible to recycle the pure water (permeate) into the process whilst the retentate may be subjected to precipitation to recover the metal for reuse or further treatment.

Keywords: Hexavalent chromium; Nanofiltration; Reverse osmosis; Plating; Water reuse

1. Introduction

Heavy metals are known for their toxicity and non-biodegradable character, leading to bioaccumulation. Their presence in process waters and effluents is an important problem since they are hazardous for both the environment and humans and even in trace amounts represent a high risk. Therefore, efficient treatments for heavy metal-containing process waters are of priority interest.

Process waters with heavy metals are generated in a great variety of industrial activities, e.g. mining and smelting of metalliferous materials, surface finishing, metal surface treating, metallurgy, iron and steel, electroplating, electrolysis, electro-osmosis, leatherworking, photography, electric appliance manufacturing, fertilizers and pesticides, energy and fuel production, aerospace, and atomic energy installations [1]. This work focuses on metal finishing industry process waters.

Chromium is a heavy metal which has good anticorrosion properties, commonly used in the steel finishing lines to passivate the steel. The passivation process takes place in a chromium plating bath. After the bath, a rinsing step is required. Pure (demineralized) water is used for rinsing. The process water generated in this practice may contain chromium and slightly acid or neutral pH. Currently these process waters are properly treated by coagulation,

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flocculation, and precipitation in order to achieve very low levels of metals prior to discharge.

There are several techniques for removing heavy metals from process waters, such as chemical precipitation, ion exchange, adsorption, and membrane filtration [2,3]. Furthermore, there are biological methods such as biosorption [4], and others using bacteria, algae, yeasts, and fungi [5].

In this framework, membrane technology is an innovative and promising technique, which has not been widely implemented for recovering metals yet. However, the separation potential of this technology may have a high impact on the future decision-making processes as it can minimize the water consumption and give an added value to the metal finishing industry byproducts (metals).

Membrane technology is being increasingly used as a separation technique in chemical and environmental engineering, including desalination, selective separations, and process water treatment [6].

There are four different pressure-driven membrane techniques: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). The pressure required increases from MF to RO, as membrane pore size decreases. MF and UF membrane pore sizes are larger than metal ions or metal compounds, so a water soluble surfactant is added into the water to form large aggregates with the metal ions and the surfactants that may be rejected by these membranes. This process is called micellar-enhanced MF or UF [7]. NF is a membrane separation technique with pore size between RO and UF, which offers an additional separation capability as it can distinguish between charged solutes of similar size (but different net charge). RO is used in water desalination and in the production of ultrapure water as it rejects even the monovalent salts, allowing essentially only water to permeate across the membrane.

Generally, metals in solution are in form of ions. Therefore, NF and RO are suitable techniques to remove metals. One key advantage of membrane technology is that it does not require any chemical addition. Thus, it makes possible the direct recycle of the purified water stream back to the production process. Despite the above mentioned advantage, NF has been less studied for metal removal [2].

In 1980, McNulty et al. [8] evaluated several RO membranes for the treatment of real industrial rinsing water. They prepared the rinsing water by dilution of a chromic acid bath. The pH was of 1.1–1.7 and the oxidation potential of the solution made that only one of the membranes tested was stable enough. Since then, commercial membranes have improved significantly and nowadays there are acid-resistant polymeric membranes down to pH zero. Ozaki et al. [9] conducted experiments with real and synthetic process waters from the heavy metal industry at laboratory scale. They used an ultra-low-pressure RO and obtained a rejection of hexavalent chromium of 99.9% at 5 bar. Wang et al. [10] made experiments with real electroplating process water containing chromium and copper at laboratory scale with NF membranes (DL, DK, and NTR-7450), being the DL membrane the more selective one with a chromium rejection of 96.6%.

The objective of this work is to study the feasibility of membrane technology for removing chromium on-site from real industrial process water of a steel finishing line. The added value of applying membrane technology to this industrial waters is to have the possibility of directly recycling the permeate stream (purified water) and to recover heavy metals as a concentrate solution (the retentate stream) which could then be further processed by precipitation.

2. Materials and methods

2.1. Filtration unit

Experiments were carried out using the aqueous stream coming from a plating process plant. A small pilot filtration unit driven by a positive-displacement pump was used. Commercial NF and RO spiral membrane modules of 2.5 inch diameter were tested. Pressure transducers were placed before and after the module to monitor the pressure drop and the transmembrane pressure (TMP). A needle valve was placed after the membrane module to regulate the applied TMP. Permeate was discharged at atmospheric pressure and its flow rate was determined using a flow meter. In the retentate line, the flow was also measured with a rotameter, and a heat exchanger was used to maintain a constant temperature throughout the experiments. Temperature was monitored using a

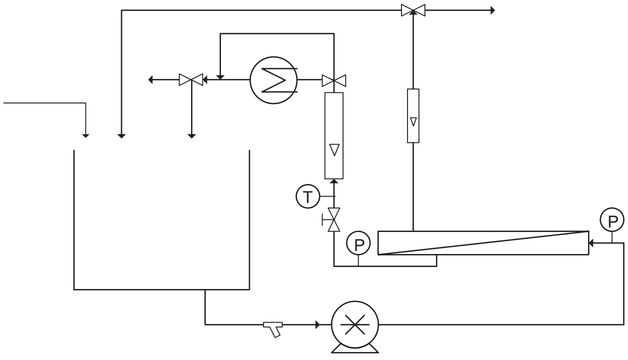

Fig. 1. Diagram of the pilot plant unit.

Pt100 probe. A diagram of the pilot plant unit is shown in Fig. 1. Two conventional cartridge filters of 50 and 5 μm were installed in the feed line to remove large particles. The feed tank had a volume of 120 L and it was fed by gravity from a 1 m^3 tank located above the filtration setup. A pump with a flexible pipeline was used to withdraw the process water and fill the overhead tank. The setup had, thus, the flexibility of conducting experiments in total recycle, batch concentration or feed and bleed mode.

2.2. Membranes

Three spiral-wound membranes of 2.5 inches diameter and 40 inches length were tested: two NF membranes (MPS-34 from Koch Membrane Systems and NF90 from Dow Filmtec) and a RO membrane (BW30 from Dow Filmtec).

Table 1 shows the information provided by the manufacturers for the three membranes. Furthermore, a ceramic UF membrane (150 kDa) from Novasep was used for the removal of sub-micron particles (<0.1 μm) as a prefiltration step.

2.3. Process water

Membrane characterization and rinsing was carried out with filtered tap water, which had a conductivity around 200 μS/cm.

The process water treated in this work is the aqueous stream resulting from the metal sheets rinsing step of a chrome plating bath. The chrome bath is made with chromic acid and dichromate. The rinsing is performed with demineralized water. The composition of the rinsing waters varied according to production criteria. The average values were 60 mg/L of Cr^{6+}, conductivity of 670 μS/cm, and pH 6. No other metals were found, as shown in Table 2.

Chromium concentration in the rinsing waters is typically below 100 pm. In order to achieve higher concentrations in this work, the actual stream was concentrated by filtration with the membranes indicated in the previous section.

Table 2
Typical process water composition

Parameter	Value
pH	7.07
Conductivity, μS/cm	490
TAC, mg/L $CaCO_3$	104
Bicarbonates, mg/L	127
Chloride, mg/L	<20
Fluoride, mg/L	<0.5
Sulfate, mg/L	60
Nitrite, mg/L	4.7
Nitrate, mg/L	37
Cadmium, mg/L	<0.05
Chromium, mg/L	84
Iron, mg/L	<0.05
Tin, mg/L	<0.05
Zinc, mg/L	<0.05

2.4. Analyses

The actual process water, and samples of the permeate and retentate streams were analyzed to determine the metal composition, pH, and conductivity, and the rest of the parameters indicated in Table 2. Metal concentration was analyzed by inductively coupled plasma-optical emission spectroscopy (Agilent ICP-OES 710-ES). pH and conductivity were measured by a Mettler-Toledo Seven Multimeter. Total alkalinity (TA and TAC) and chloride was measured by potentiometric titration. Fluorides were determined with anion selective electrode using a Metrohm 867 unit. Sulfates were analyzed by a turbidity method, using a Merck kit, based on the EPA 375.4 and APHA 4500-SO42-E standard methods; nitrites and nitrates were assessed spectrophotometrically, using a Merck kit,

Table 1
Information on the membrane modules used in this work, as provided by the manufacturers

Membrane	Material	pH stability	Surface area (m^2)	Stabilized salt rejection
MPS-34	Cross-linked modified polyacrylonitrile	0–14	1.2	95–97*
NF90	Polyamide	2–11	2.6	>97**
BW30	Polyamide	2–11	2.6	99.5***

Note: Test conditions:
*3% glucose/3% sucrose or 5% NaCl, at 30 bar, and 30˚C.
**2,000 ppm $MgSO_4$, at 4.8 bar, 25˚C, and 15% recovery.
***2,000 ppm NaCl, at 15.5 bar, 25˚C, and 15% recovery.

following the DIN 38405–9 method. Carbonates and bicarbonates were calculated based on alkalinity which was in turn analyzed according to the standard method UNE-EN 9963–1.

2.5. Experimental procedures

Previously to filtration experiments, membranes were rinsed with tap water to remove any storage solution. Then they were characterized (by means of permeability and salt rejection) with tap water working at pressures from 5 to 30 bar.

Filtration experiments to determine the effect of TMP (in the range of 10–30 bar) on flux and metal rejection were conducted in total recycle mode with a feed volume of at least 120 L, in order to ensure constant feed composition. Samples of the permeate were taken at each pressure, while retentate was only sampled twice, at the beginning and the end of each run.

Concentration experiments were performed in batch mode at 30 bar by continuously removing the permeate while recirculating the retentate to the feed tank. Samples of both the permeate and retentate were taken at selected volume reduction factors. The initial volume varied from 120 L to more than 3 m^3 depending on the initial concentration of the process water.

In the usual experimental procedure, TMP-effect experiment was followed by a concentration experiment. After the concentration experiment, the system was rinsed with tap water and membrane permeability was checked to evaluate fouling. In some cases, the membrane was directly used for the next experiment, even if fouling was observed (see the experimental results for details), while in most cases, cleaning was performed in order to ensure restoration of the initial performance. Different chemicals (nitric acid, citric acid, sodium hydroxide, and Henkel Ultrasil) were used at 40°C. Concentrations and cleaning times were firstly small and if they were not efficient enough, they were increased. Thus, the cleaning time varied from 30 to 120 min. Cleaning was carried out with small cleaning solution volumes (15 L) at a retentate flow of 1,000 L/h and with the minimum TMP.

Retentate flowrate was always kept at 1,000 L/h and the temperature was manually controlled using a refrigeration loop with tap water (through the online tubular heat exchanger) which allowed maintaining the feed at 25 ± 2°C.

The selectivity of the membrane is expressed in terms of apparent rejection. It was calculated as shown in Eq. (1), where C_P and C_R are the solute concentration in the permeate and in the retentate, respectively.

$$R = 1 - \frac{C_P}{C_R} \tag{1}$$

3. Results and discussion

3.1. NF performance without UF pretreatment

In the first set of experiments, the NF90 and MPS-34 NF membranes were tested without any pretreatment or intermediate cleaning between filtrations. Each filtration run included the variable TMP section (up to 30 bar) followed by a concentration step at 30 bar. Seven process waters were tested with the NF90 membrane and five with the MPS-34 one. As expected, membrane permeability (checked with tap water after each run) decreased continuously (Fig. 2). After the series were completed, NF90 permeability had dropped to 15% of its initial value whilst in the case

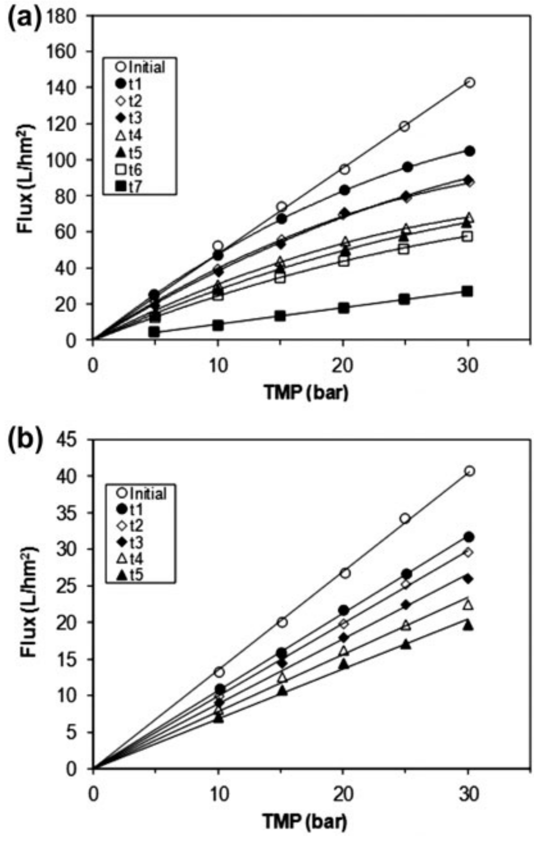

Fig. 2. (Tap) water permeability (at 25°C) decreased with each process water filtration test cycle including pressure and concentration experiments for the (a) NF90 and (b) MPS-34 membranes. Tap water conductivity was around 200 μS/cm.

of the MPS-34, this drop was about 50%, although, this membrane was much less permeable already from the beginning.

Process water filtration rate also decreased steadily (Fig. 3) while the pressure drop was found to increase. Nevertheless, the chromium rejection stayed relatively constant for the NF90 membrane and decreased for the MPS-34, being in both cases around 95%.

In order to restore the initial permeability of the membranes, several cleaning cycles were performed at the end of the runs. NF90 membrane was subjected to Ultrasil (0.2 to 0.5 wt. %) and nitric acid (1 wt. %) solutions at 40°C. MPS-34 was also cleaned with Ultrasil (0.5 wt. %) and nitric acid (1–2 wt. %) solutions at 40°C. Tap water flux was measured after each cleaning step. Fig. 4 summarizes these results. The water permeability improvement was clearly insufficient. Visual inspection of the membrane modules showed particle deposition. The average particle size analyzed by light scattering was 0.12 μm. Those submicron particles, not removed with the coarse prefiltration cartridges used, were the main cause of flux decline. Therefore, a tighter pretreatment was necessary. For that purpose, ceramic MF (0.2 μm) and UF (150 kDa) membranes were tested, but only the latter was able to remove the particles. The pretreatment filtration was carried out with a cross velocity of 4 m/s, a TMP of 11.3 bar and a water recovery close to 90%. The initial flux was of 780 L/hm^2 and declined roughly 15% over the whole run. However, rinsing the equipment with tap water was enough to restore initial conditions, indicating negligible fouling.

Once the pretreatment was installed, a new NF90 membrane was tested and its performance was compared with that of the same membrane type without pretreatment (Fig. 5) during several weeks. The flux did show a more stable value over time. Furthermore, after each filtration run, the water permeability was checked to evaluate fouling. When the water

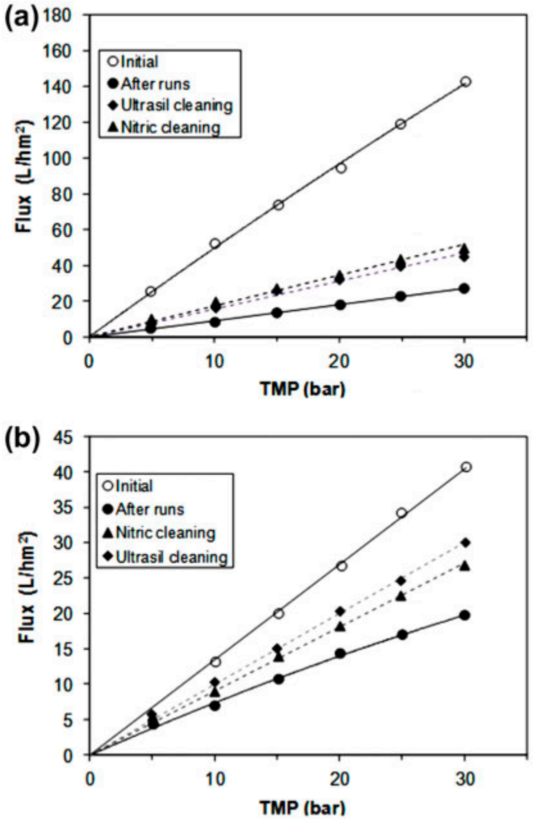

Fig. 4. Fouling and cleaning efficiency (measured as water flux) after the first set of experiments (see the text for details) using NF90 (a) and MPS-34 (b) membranes.

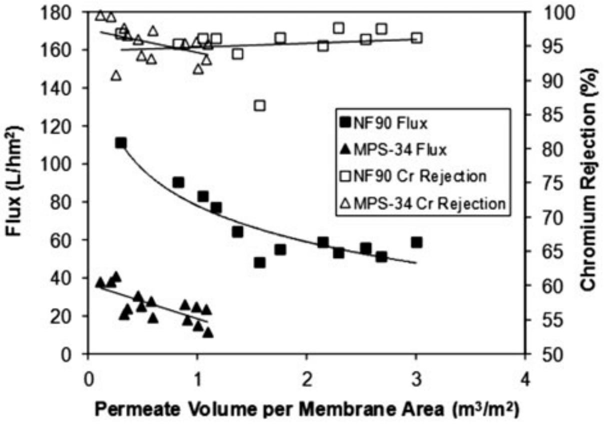

Fig. 3. Evolution of flux and chromium rejection for NF90 and MPS-34 membranes with filtered volume without UF pretreatment at 30 bar and 25°C.

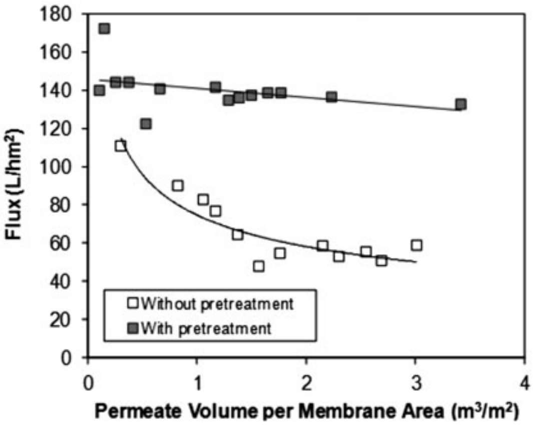

Fig. 5. Evolution of flux with filtered volume for NF90 with and without UF pretreatment at 30 bar and 25°C.

permeability had decreased more than 10%, a cleaning step using 0.3 wt. % nitric acid at 40˚C was carried out. This procedure proved to be successful in restoring membrane performance.

3.2. Filtrations with UF pretreatment

3.2.1. Membrane selection

Once the UF pretreatment was installed, new spiral wound modules (the two NF ones already reported and a RO membrane: BW30) were also fitted and characterized with tap water. The initial water permeability (Fig. 6) was higher for the NF90 membrane (5.7 L/m^{2}h bar), and lowest for the MPS-34 (1.3 L/m^{2}h bar), while the BW30 gave an intermediate value (2.6 L/m^{2}h bar). MPS-34, being a pH stable NF membrane, with a thicker active layer, is the least permeable. The same filtration rate order was found with the process waters, though concentration polarization (and fouling, to a lower extent) resulted in flux values below those of tap water.

In the range of concentrations tested (variable due to daily fluctuations), the flux was not significantly affected by the initial chromium concentration. Chromium rejection, experimentally determined from the permeate and retentate concentrations was very high. Both for the NF90 and BW30 membranes were above 99% while MPS-34 showed a rejection around 97%.

The (relative) high rejection of the NF90 membrane (compared with the BW30 one) can be explained if the solute flux for both membranes is considered, as shown in Fig. 7. Both membranes behave according to the solution-diffusion transport mechanism, and clearly the RO membrane (BW30) has a lower chromium permeability coefficient (as indicated by the slope), which indicates that BW30 is tighter than NF90. The higher chromium rejection observed for NF90 in Fig. 6 is, therefore, just a result of the differences in feed concentration.

Based on the experimental results, the MPS-34 membrane was excluded from further experimental tests. Both the BW30 and NF90 were considered worth a deeper study, since the former gave an outstanding rejection (but lower flux) and the latter had the best flux and also high metal rejection.

3.2.2. RO BW30 membrane performance

A set of experiments were conducted with the BW30 membrane in order to test its performance as a function of process variables: feed concentration (variable as expected from an actual production site) and TMP (see Fig. 8). In this set of experiments, there was one of the process waters with an acidic pH (3.5)

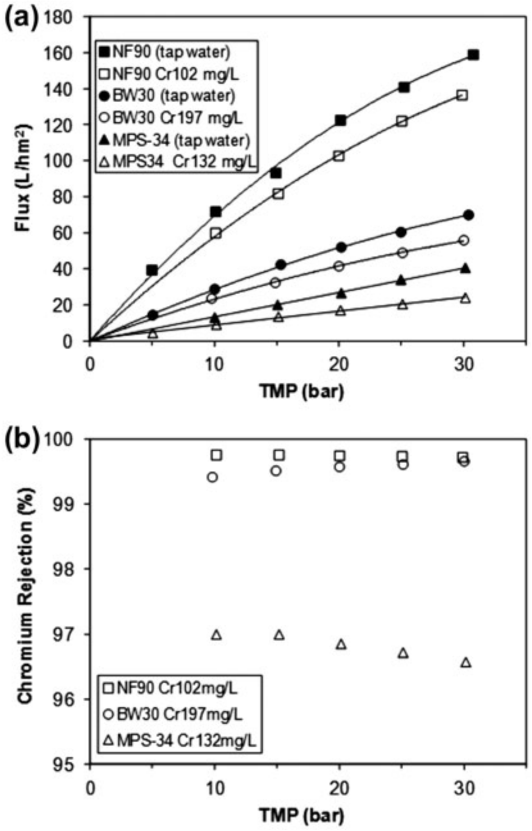

Fig. 6. Effect of TMP on the flux of tap water and process waters (a) and on the chromium rejection (b) at 25˚C for NF90, BW30, and MPS-34 membranes. Actual feed concentration for each run is indicated in the legend.

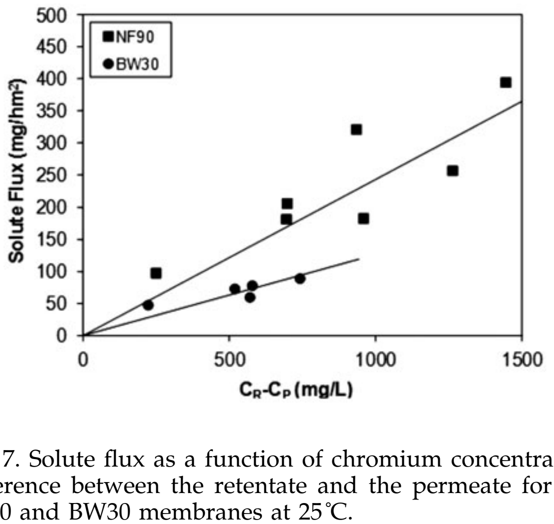

Fig. 7. Solute flux as a function of chromium concentration difference between the retentate and the permeate for the NF90 and BW30 membranes at 25˚C.

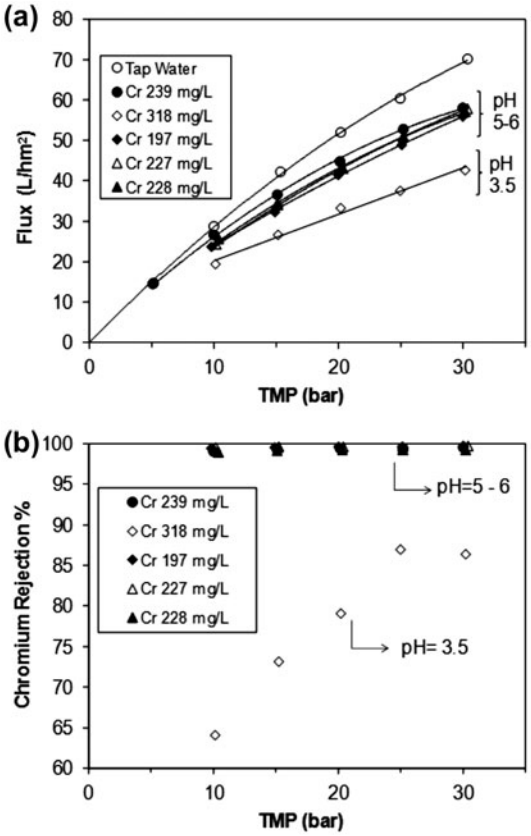

Fig. 8. TMP effect on the flux (a) and the rejection (b) observed for the BW30 membrane at 25˚C when treating process waters with different feed concentration and pH. Experiments are ordered by time in the legend.

while the others had a pH between 5 and 6. All the experiments with the typical process waters had a flux around 83% of the initial tap water and a chromium rejection above 99%. The experiment conducted at pH of 3.5 gave a flux around 63% of the initial water flux and a lower rejection. The lower flux has been explained in terms of shrinking of the skin layer [11]. In all cases, rejection increased with TMP, which is better seen at low pH: at 10 bar the rejection was 62% and at 30 bar, 85%. This lower rejection at low pH values can be related with the net charge of the membrane. Its isoelectric point is 4.1 [12]. When the pH is lower than the isoelectric point, the membrane surface becomes positively charged and therefore the anions that the hexavalent chromium forms ($Cr_2O_7^{2-}$, $HCrO_4^-$ and CrO_4^{2-}) can permeate more easily through the membrane and the observed rejection decreases.

Five concentration experiments were also performed right after each of the TMP-effect experiments, at 30 bar. They all produce similar results, like those reproduced in Fig. 9 as a function of water recovery.

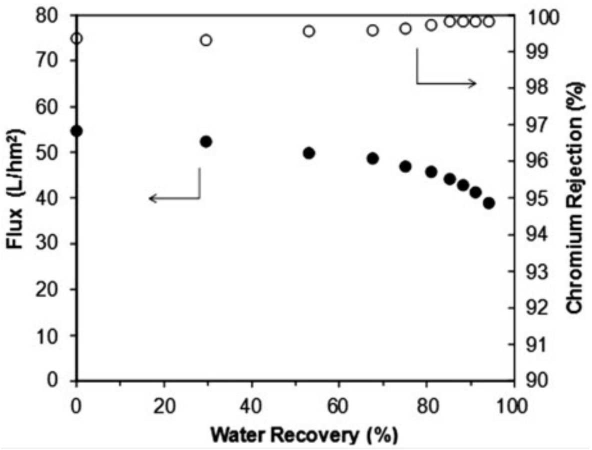

Fig. 9. Effect of water recovery on the flux and on the chromium rejection observed at 30 bar and 25˚C with the BW30 membrane. Initial chromium concentration was 228 mg/L.

Water recovery gives an indication of the extent of water (permeate) recovery which is possible (at a non-zero flux), owing to the limitations related to the concentration of the solutes (chromium ions, in this case) in the feed stream.

The initial chromium concentration was of 228 mg/L, and as water recovery increases, since the rejection was close to 100%, the concentration in the feed increases leading to a gradual flux decrease (the final flux was 29% lower than the initial one). The experiment was run until 95% water recovery was reached. A slight increase on rejection was also observed. This could be due to the displacement of the equilibrium associated chromic anions form, favoring the formation of $Cr_2O_7^{2-}$, which is better rejected than the other related species. For a pH of 7 and the initial chromium concentration of 228 mg/L, hexavalent chromium was in the form of CrO_4^{2-} and $Cr_2O_7^{2-}$. As the concentration of chromium increases, more of the $Cr_2O_7^{2}$ species is formed [13] and it could be better rejected because of their larger size.

3.2.3. NF90 membrane performance

As presented for the BW30 membrane, a set of experiments was conducted with the NF90 one in order to test its performance (flux and chromium rejection) as a function of process variables: feed concentration and TMP (Fig. 10). The process water had concentrations ranging from 29 to 107 mg/L. The flux increased with TMP pressure as expected and was close to 90% of the water flux. There was not significant effect of concentration on flux. The chromium

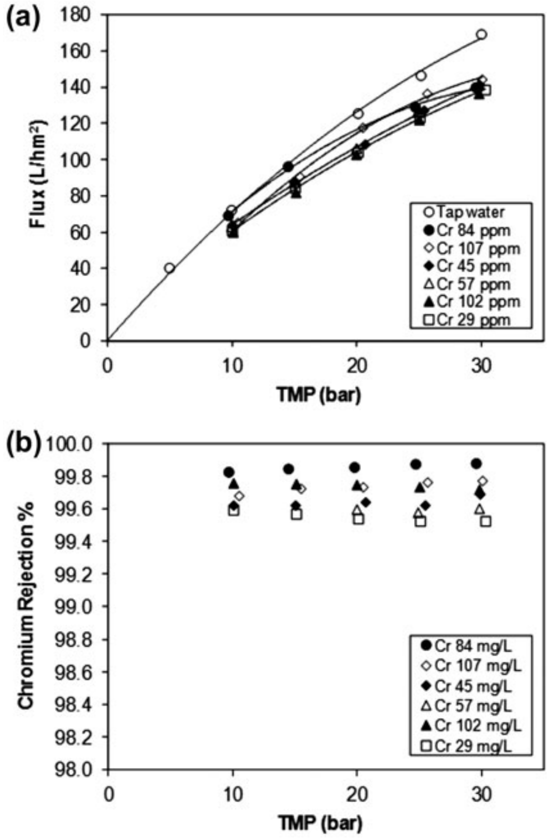

Fig. 10. Effect of the TMP on (a) the flux for the initial tap water and for the process waters and (b) on the rejection for different feed concentrations at 25˚C using NF90 membrane. The chromium feed concentration is showed in the legend. Experiments are ordered by time in the legend.

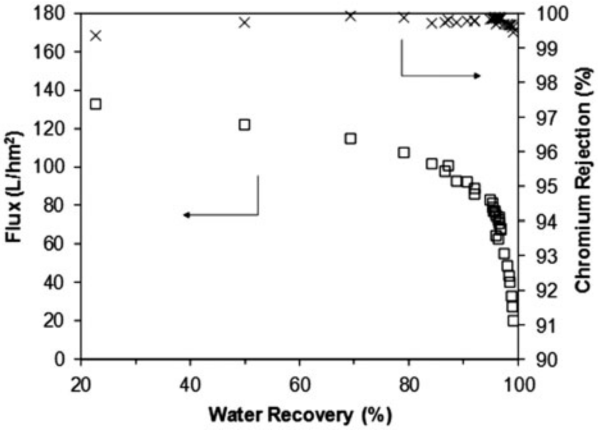

Fig. 11. Effect of the water recovery on the flux and on chromium rejection at 30 bar and 25˚C for NF90 membrane. The initial chromium concentration was 180 mg/L.

rejection was always higher than 99.5%.This membrane showed a stable and reproducible performance over time.

The effect of water recovery was also assessed in concentration experiments. Fig. 11 shows a typical result, for a feed containing 180 mg/L of chromium (initial flux was 140 L/m^{2}h). Feed concentration increased with water recovery up to 19.5 g/L (at the expense of a sharp flux decrease for high recovery values, down to 20 L/m^{2}h). A reduction of 15% in the flux is observed at 80% water recovery, and at 90% recovery it reached 30%. After 90% recovery, the flux drop is steep, which has to be taken into account when designing the full-scale plant based on this technology as it will be uneconomical to reach such high values.

Despite the flux drop, rejection was always higher than 99.5%, as shown in Fig. 11, which is a clear indication that NF is a robust technology which offers a dependable permeate quality even with the feed concentration variations. Moreover, comparing the performance of the RO and the NF membrane, the latter is the best choice as for a similar reclaimed water quality it offers a higher productivity (flux) at the same operating conditions.

For the NF90 membrane a good compromise between productivity (flux) and the permeate quality was found at 80% water recovery (operating at 30 bar and room temperature) where permeate conductivity was still lower than 15 µS/cm with chromium concentration below 1 mg/L. With the appropriate pretreatment and a good cleaning protocol, as those used in this work, it is possible to reach the desired water quality for reuse and at the same time recover chromic ions in a reduced volume which can then be to subjected further treatment or recycle back to the plating bath.

4. Conclusions

NF and RO membranes are feasible techniques to remove hexavalent chromium from electroplating rinsing water. All the membranes tested showed a chromium rejection above 97%. The highest flux was given by NF90, followed by BW30 and MPS-34, respectively. NF90 was overall the best performing membrane with the highest flux and observed rejection higher than 99.5%.

Solid particle fouling (clogging) was irreversible, which made pretreatment essential. Two cartridge filters of 50 and 5 µm for coarse particles and one 150 kDa UF membrane were effective in removing the submicron particles and ensuring stable long term performance of the NF spiral wound module.

It is possible to achieve 80–90% water recovery (depending on feed concentration) and produce a permeate quality (with chromium concentration below 1 mg/L and less than 15 μS/cm conductivity) sufficient for direct reuse in the rinsing step of the chromic plating bath.

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