

Chromium Removal from Wastewater by Reverse Osmosis

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Abstract: - This study describes the removal of chromium from wastewater using pressure-driven membrane separation processes. It describes the rejection of trivalent chromium using a commercial membrane for reverse osmosis typed RO98pHt (Alfa Laval, Sweden). Model solutions of chromium were used for performing of separation experiments. The effects of feed pH, chromium concentration and temperature were investigated and conductivity values of all streams were observed. The results showed that pH of the feed solution and the form of occurrence have influence on the stability of dissolved particles with possible negative impact on membrane fouling. The stability of prepared solutions was managed by the diagram of area of prevailing existence. Membrane rejected almost 100% of Cr(III) at various pH values using 100 mg.L⁻¹ model solution, operating pressure 1.5 MPa and at temperature 20°C. Similar results showed separation experiments using various Cr(III) concentration from 10 till 560 mg.L⁻¹ and pH=5±0.2. Increase of operating temperature causes higher permeate flux and has no significant influence on the rejection level of Cr(III). Obtained results show differences between various feeds separations containing the same pollutant and usage possibility of reverse osmosis for wastewater treatment.

Key-Words: - chromium, tanning, pollutant, membrane separation, reverse osmosis, wastewater treatment, leather industry

1 Introduction

Wide spectrum of physical-chemical and biological treatment methods and their combination is commonly used for treatment of various wastewater. With development of new methods and with focus on higher environmental protection, some technologies no longer meet current requirements. For this purpose, membrane separation processes, especially pressure-driven membrane separation processes, have found wide use abroad in wastewater treatment, production of drinking water, process streams and chemicals recycling and other [1-3]. Membrane separation provides many advantages and versatility of usage. These processes have enforced in these areas of human activity where the other technologies dominate nowadays. We can regard them like clean, environmentally-friendly and efficient alternative to traditional processes.

Chromium wastewaters occur in various industries and there is need of their treatment or of recycling of reagents. Leather industry belongs given to its size and the amount of produced waste to these industries with large negative impact on the environment. It produces big volume of wastewaters

with different composition and some of them contain chromium. Many studies have been performed focusing on the recycling of reagents [4] and waste utilization [5, 6]. From 1 tone of wet-salted hide is manufactured approximately 200 kg of leather. Concurrently is generated more than 600 kg of solid waste during tanning process and the volume 30-35 m³ of wastewater is discharged into environment in leather industry [7]. In these wastewaters we can expect several concentrations of chromium. Basic chromium sulphate is the most popular tanning reagent in the world, because Cr(III) has positive effect on the functional properties of leather [8]. Besides high concentrations of chromium, sulphates, chlorides and organic substances wastewaters from chromium tanning are characterized by low pH value and high temperature. But according to these facts, membrane separation can find its place in treatment schema [9], for example not only to improve the quality of the recycled chromium and salts recovery. The usage of pressure-driven membrane separation processes could find the place in liming to recover lime and sulfide and in soaking and pickling for recovery and reuse salty water. Moreover, it is advantageous to replace the existing technology

with more cost effective membrane technologies [10]. Metals, lipidic substances and other impurities could presence in recovered chromium using traditional method combining alkaline precipitation of chromium and dissolution of $\text{Cr}(\text{OH})_3$ in sulphuric acid [11].

2 Membrane Separation

Membrane processes are used in general to separate homogeneous or heterogeneous liquid solutions and mixtures, gaseous mixtures, and suspensions of solid particles of microscopic dimensions (less than ca. 1×10^{-5} m) in liquids. A common feature of membrane separation is high separation efficiency. The separation selectivity depends on the particular membrane process and on the membrane type. Because membrane separations take place at ambient temperatures, there is no damage to thermolabile substances. Separated particles do not change their state during the separation process. The membrane units may be operated remotely using modern control systems that reduce the cost of labour.

Membrane processes are relatively extended abroad. The technique may be applied in low-volume batch equipment or in a continuous large capacity treatment plant.

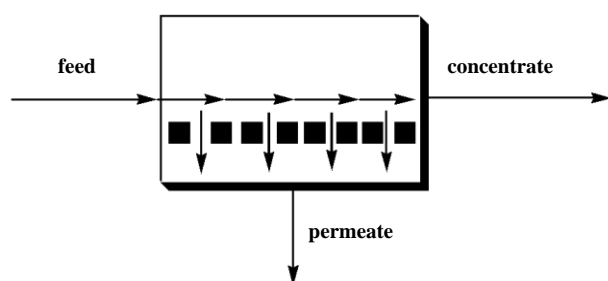


Fig. 1: Schema of membrane separation process.

Membrane processes are based on the separation of the solution into two different streams using a semipermeable membrane. Permeate contains solvent and the particles which passed through the membrane. The remaining particles which were captured by membrane form the concentrate. Fig. 1 describes schema of membrane separation processes. There is the visible difference against dead-end filtration in the setting of the process. Fluid feed stream runs tangential to the membrane in cross-flow filtration. No filtration cake is formed and caught pollutants and particles stays in concentrate. The difference across the membrane of pressure, concentration, electrical potential, or temperature serves as the driving force.

Focus of this work is usage of pressure-driven membrane separation processes for wastewater treatment. Operating conditions of these processes are mentioned in Table I. In this table we can see the large application possibility of membrane separation for many various purposes. Separation level comprises the one side suspended solid particles and monovalent ions the opposite side. In installed working stations we can meet a combination of more membrane separation processes ordinarily. Installed technology could be designed like a combination of the membrane technology and conventional technologies (coarse filtration, precipitation, coagulation and other), which serves like feed pre-treatment or concentrate post-treatment.

Table 1: Pressure-driven membrane separation processes.

separation process	particle size	operating pressure
microfiltration	$>0.1 \mu\text{m}$	$<500 \text{ kPa}$
ultrafiltration	10-100 nm	500-1000 kPa
nanofiltration	1-10 nm	1-4 MPa
reverse osmosis	0.1-1 nm	3-10 MPa

Microfiltration and ultrafiltration are most similar to the classical filtration. They are suitable for the removal of suspended particles, colloids, bacteria and viruses, high-molecular substances etc. The separation is based on the sieve-effect. These processes are commonly used like pre-treatment or main stage of treatment.

The principle of nanofiltration and reverse osmosis is the same. But the separation ability of nanofiltration is usually considerably lower. This separation technology can separate especially monovalent ions with lower efficiency than reverse osmosis, separation level of polyvalent ions is comparable. The mechanism is not based on the sieve-effect but on the diffusion.

In the case of reverse osmosis the separation proceeds on the ionic level. Mono- and polyvalent ions and low-molecular organic substances are separated. Reverse osmosis technology can be installed in industry for dissolved matter reduction, especially inorganic salts removal (chlorides, nitrates, sulphates, ammonia nitrogen). This is related to the need to use the relatively compact and non-porous membranes. The higher is the concentration of dissolved salts in feed, the higher is the osmotic pressure of feed and the higher operating pressure of device must be applied. Solvent pass through the membrane and dissolved matter is caught by membrane [12].

Nanofiltration and reverse osmosis are used like the main technologies for wastewater treatment. Pre-treatment is necessary in most installations, post-treatment could be included too, but in most cases is not needed. It depends on the type of wastewater, on the applied separation process and on the desired level permeate (actual need of operator or need of usage). Both can remove common cations and anions, organic matter and heavy metals [13] with high efficiency, but not limited to.

Osmotic pressure plays significant role in the description of reverse osmosis. It is generated by a semipermeable membrane which separates ions and solvent passes therethrough.

Osmotic pressure π is described in osmotic equilibrium. The following equation (1) is valid for electrolyte solutions.

$$\begin{aligned} \pi &= iRTc \\ i &= [1 + \alpha(v_C + v_A - 1)] \\ C_{v_C}A_{v_A} &\leftrightarrow v_C C + v_A A \end{aligned} \quad (1)$$

T is thermodynamic temperature, R is molar gas constant, c is concentration of solutes, α is the degree of dissociation, C and A mean cation and anion and v refers to quantity. So concentration of solutes and temperature have main influence on the osmotic pressure of feed solution, subsequently on the operating condition of separation process. However, that formula is only valid for very diluted and simple solutions.

Among other factors that affect reverse osmosis belong rejection R , volume reduction factor and permeate flux. Rejection indicates the separation efficiency of component or total. For calculation serve concentration values of pollutants in feed c_F and in permeate c_P . For calculation of rejection of all solutes it's possible to use conductivity values κ in feed and in permeate by equation (2).

$$R = \frac{c_F - c_P}{c_F} \cong \frac{\kappa_F - \kappa_P}{\kappa_F} \quad (2)$$

Volume reduction factor is defined like ratio between feed volume and concentrate volume. Permeate flux is hourly flux of permeate through the membrane with area 1 m². Its values are different for setup of operating conditions of separation process and can indicate membrane fouling. For final comparison of separation experiments its necessary to hold the same operating temperature

because permeate flux is increasing with temperature.

In wastewater treatment high value of volume reduction factor is usually required. Because amount of concentrate isn't negligible and other techniques are needed for its removal. But last permeate parts are characterized by worse composition than first permeate usually. It could affect negatively the quality of mixed permeate which influences its usage.

3 Chromium and its Occurrence

The anthropogenic sources of chromium are wastewaters from metallurgy, metal coatings, leather industry and textile industry. Wastewater from chromium tanning can contain up to 4100 mg.L⁻¹ of Cr(III) [11].

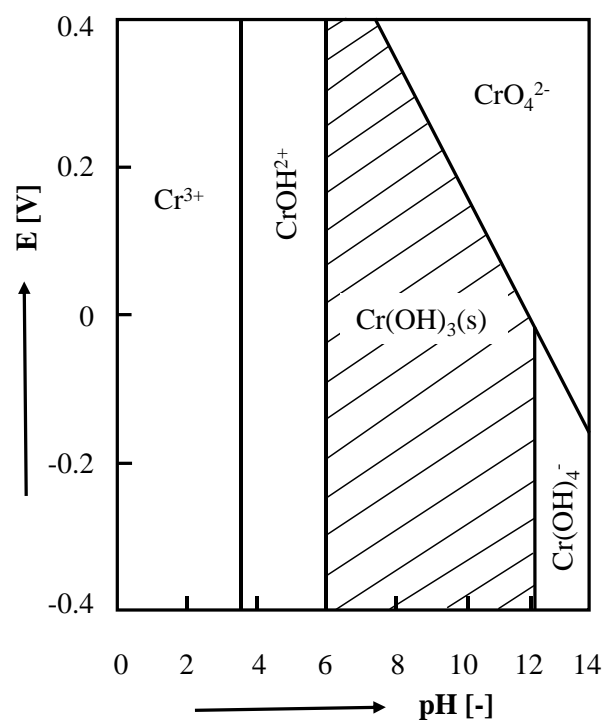


Fig. 2: E-pH diagram of area of prevailing existence of Cr(III)-Cr(VI) system, $c(\text{Cr}_{\text{total}})=0,52 \text{ mg.L}^{-1}$, $t=25^\circ\text{C}$.

Chromium occurs in waters most often in two oxidation states Cr(III) and Cr(VI). Chromium can be bonded to organic matter. The most stable form of occurrence is Cr(III); Cr(VI) compounds are strong oxidative reagents. Under normal conditions is hexavalent chromium simply reduced into trivalent chromium. But under some conditions opposite reaction occurs and toxic hexavalent chromium is formed [14]. From this purpose for

example chrome-tanned wastes represent long-time threat for the population health and for the environment. Cr(III) could be oxidized to Cr(VI) by oxidants like for example peroxides. But there exist the possibility of Cr(III) oxidation into Cr(VI) in gentle conditions by air in large pH range [15]. Occurrence of both form in waters is described in Fig. 2, which shows the dependence of oxidation/reduction potential E on pH [16].

Hexavalent chromium is classified as a carcinogen. Technical legislation of chromium wastewater treatment is strict from this purpose and is based on the probability of presence hexavalent chromium. With this problem is connected the need of sensitive method for chromium determination. The overview of usable methods for various purposes is described in [17].

4 Materials and Methods

Behavior simulation of Cr(III) solution on membrane was performed under various conditions. The influence of pH, concentration and temperature was studied. For this experiments the membrane typed RO98pHt (Alfa Laval, Sweden) for reverse osmosis was chosen. The rejection of NaCl solution of this composite membrane is higher than 97% (NaCl 2 g.L⁻¹, 1.6 MPa, 25°C). Operation conditions: pH range 2-11, typical operating pressure range: 1.5-4.2 MPa, maximum operating pressure: 55 MPa, temperature 5-60°C [18]. Hexavalent chromium is oxidation reagent and can destroy the membrane, so this solution wasn't used.

For this purpose the feed solution was prepared using CrCl₃·6H₂O (Lach-Ner) and distilled water. Solution of NaOH (Roana) was used for the pH adjustment of feed.

Feed solution 100 mg.L⁻¹ of Cr(III) was prepared under various pH values within 3-6. After that membrane separation was applied. Separation experiments were performed under these parameters: operation pressure 1.5 MPa, temperature 20°C and value of achieved volume reduction factor 4. After this group of experiments one pH value was chosen and other separation experiments were performed under the same operating conditions using feed solutions 10, 100 and 560 mg.L⁻¹ of Cr(III). Finally, the influence of temperature on the separation of Cr(III) was investigated. Stability of membrane process, Cr(III) rejection, pH values of streams and permeate flux were measured during every experiment.

After every separation experiment analysis of all streams were performed. Chromium concentration

was measured on AAS SensAA (GBC Scientific Equipment, Australia), conductivity on conductivity-meter GMH3430 and pH values on pH-meter GMH3530 (Greisinger Electronic, Germany).

All separation experiments were performed on membrane separation unit LAB-M20 (Alfa Laval, Sweden) in laboratory scale. The equipment was customized for batch processing. The volume of the feed tank was ca. 12 L. The actual separation takes place on a plate-and-frame module DSS equipped with 36 membranes with total membrane area 0.63 m². A Rannie piston pump with maximum operating pressure of 6.0 MPa was used. A separate water supply was used to maintain the pistons of the pump moist. A flow liquid-liquid heat exchanger cooled the membrane module. Water from the faucet served as the cooling agent.

5 Results and Discussion

5.1 Influence of pH

pH of solution is important factor influencing the stability of prepared Cr(III) solution. Solutions with pH values within 3-6 were stable; increasing pH over 6 flocculation occurred and floccules fallen to the bottom of the vessel. For the membrane separation only Cr(III) solutions with pH values 3.3 (RUN1), 5 (RUN2) and 5.5 (RUN3) were used.

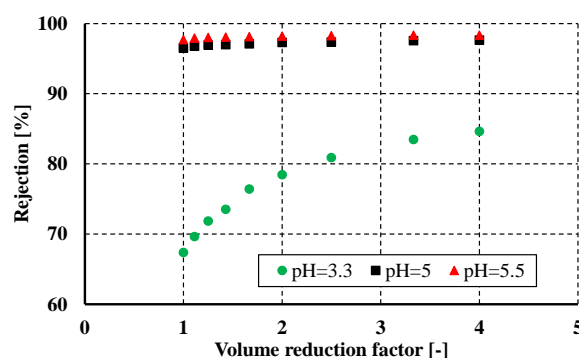


Fig. 3: Dependence of rejection on volume reduction factor under different pH values [100 mg.L⁻¹ Cr(III)].

Fig. 3 describes rejection during the separation experiment based on streams conductivity measurement. According to obtained results - rejection and stability of separation process - pH=5 was chosen for experimental continuing. Not every wastewater is characterized by so low pH value. Separation at pH=3.3 (natural pH of CrCl₃ solution) brings extra cost with use of acid in higher amount

in the case of "standard" wastewater treatment. For example carbonates decompose already at pH=4.5 completely.

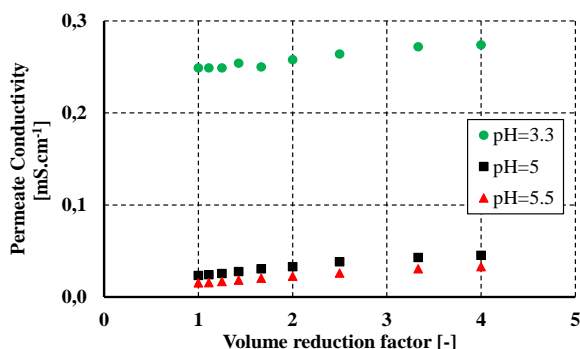


Fig. 4: Dependence of permeate conductivity on volume reduction factor under different pH values.

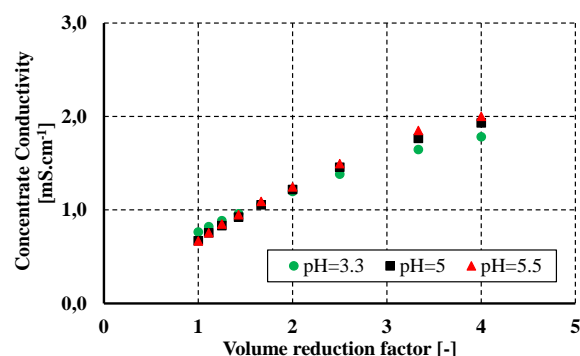


Fig. 5: Dependence of concentrate conductivity on volume reduction factor under different pH values.

Fig. 4 and Fig. 5 describe conductivity change for permeates and for concentrates during the separation experiments. By permeates conductivity values remained at the same level, so produced permeate was similar quality at every moment of separation experiment. The growth of conductivity achieved minimum values. There is visible difference between separation at pH=3.3 and pH>5. Hydrated form (Fig. 2) is rejected with higher efficiency. Conductivity of concentrates increased during separation experiments and values at all pH were comparable.

5.2 Influence of Concentration

Experiments using three different concentration of Cr(III) in wide range have been performed to evaluate the influence of concentration. They were concentrations 10, 100 and 560 mg.L⁻¹; corresponding marking RUN4, RUN2 and RUN5. Feed pH value was adjusted in every separation experiment to 5. During separation experiments no significant change in rejection values was observed.

Only in the case of experiment RUN4 it took a while to reach constant rejection similar to others. The course of separation experiments is described in Fig. 6 and Fig. 7.

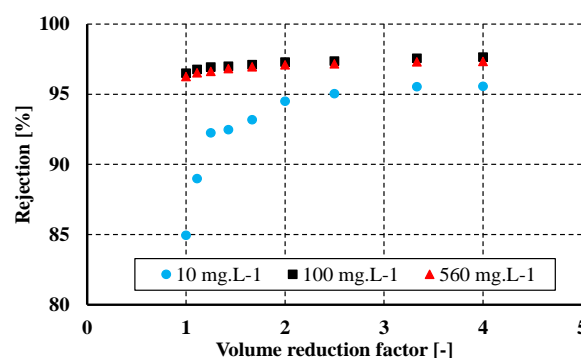


Fig. 6: Dependence of rejection on volume reduction factor under different Cr(III) concentrations and pH=5.

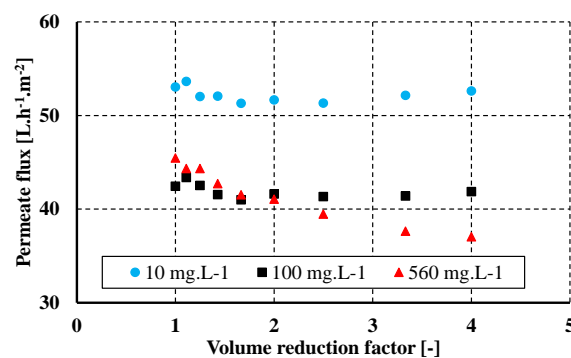


Fig. 7: Dependence of permeate flux on volume reduction factor under different Cr(III) concentrations and pH=5.

Using operating pressure 1.5 MPa we can observe changes of permeate flux comprising different feed concentrations. Permeate flux is the highest in experiment RUN4. Values for experiments RUN2 and RUN5 are comparable. There is no significant decrease of permeate flux in time but it could differ using real wastewater sample. Only in the case of experiment RUN5 we can see a slight decrease of permeate flux because Cr(III) concentration of feed water was considerably higher.

Fig. 8 and Fig. 9 describe conductivity change for permeates and for concentrates during the separation experiments. The comparison showed that the higher is the Cr(III) concentration in feed, the higher is Cr(III) concentration in permeate. This is a logical conclusion. But while experiments RUN4 and RUN2 gave similar quality permeate at every moment of separation experiment, conductivity of permeate by RUN5 increased more

rapidly. Conductivity of concentrates increased during separation experiments depending on the feed Cr(III) concentration.

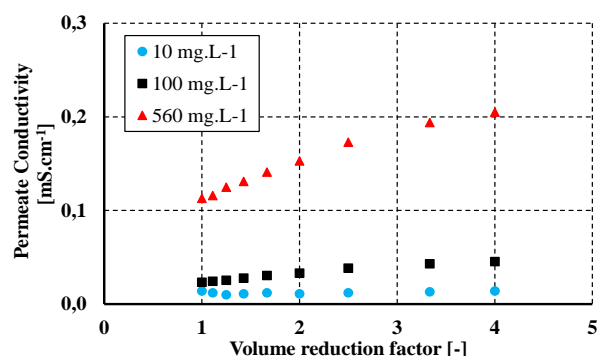


Fig. 8: Dependence of permeate conductivity on volume reduction factor under different Cr(III) concentrations and pH=5.

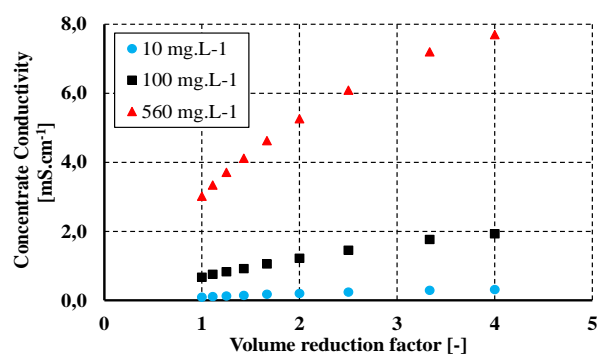


Fig. 9: Dependence of concentrate conductivity on volume reduction factor under different Cr(III) concentrations and pH=5.

5.3 Influence of Temperature

Temperature influences the following parameters of separation process - osmotic pressure and permeate flux. Feed solution was prepared under the same conditions like in the case of experiment RUN2. The operating temperature was increased in range 15-26°C and the influence of temperature on permeate flux and rejection was observed.

In Fig. 10 we can see strictly linear trend of experimental values of permeate flux. Increasing the temperature by 1°C will increase the permeate flux of 3.6%. The effect of the chromium concentration in permeate is negligible. Chromium concentrations in permeate by various temperature values are showed in Fig. 11. Concentration of chromium may be affected by small measurement error or by operator error. These values are essentially comparable.

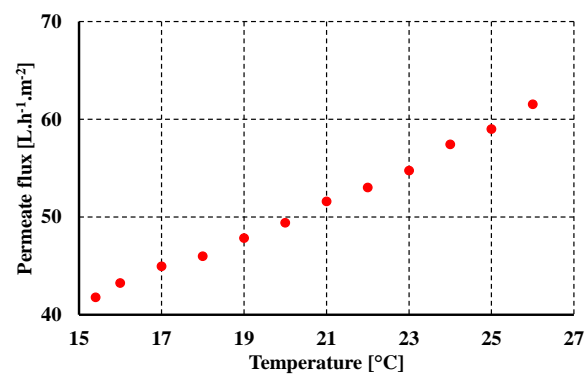


Fig. 10: Dependence of permeate flux on temperature.

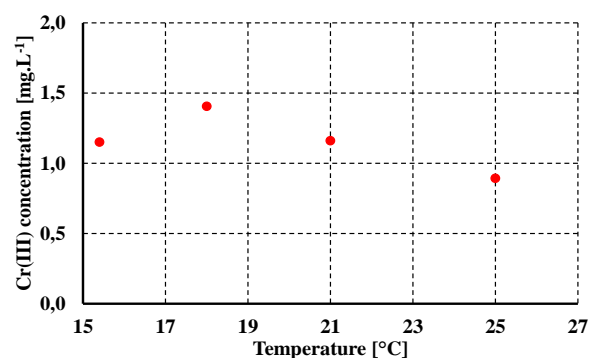


Fig. 11: Dependence of Cr(III) concentration in permeate on temperature.

Table 2 comprises composition of the feed and permeate in all separation experiments. Rejection of Cr(III) achieves in all case high values near 100%. Due to the size of Cr³⁺ reverse osmosis provides sufficient reserve in rejection. Nanofiltration in general separates these ions with similar efficiency but rejection of monovalent ions could not be sufficient.

Table 2: Feed and permeate composition in separation experiments.

experiment		RUN1	RUN2	RUN3	RUN4	RUN5
pH [-]	feed	3.2	5	5.5	5.2	4.9
	permeate	1.6	0.62	0.07	0.13	3.3
Cr(III) [mg.L ⁻¹]						
rejection [%]		98.5	99.4	99.9	98.7	99.4

6 Conclusion

In this study membrane separation of chromium by reverse osmosis using various operating conditions was performed. Separation experiments with Cr(III) solutions provided very good results given to high rejection values. The results showed that pH of feed solution has influence on the stability of dissolved particles with possible negative impact on membrane fouling. Prepared feed solutions were

stable till pH=6, over this value floccules sedimentation occurred. RO98pHt rejected almost 100% Cr(III) at various pH values using 100 mg.L⁻¹ concentration level, operating pressure 1.5 MPa, volume reduction factor 4 and at temperature 20°C. Similar results showed separation experiments using various Cr(III) concentration from 10 till 560 mg.L⁻¹ and pH=5±0.2. Increase of operating temperature causes higher permeate flux and has no significant influence on the rejection.

These results have positive impact on the application of membrane separation processes in wastewater treatment for rough setting of working conditions in the case of real wastewater from chromium tanning treatment or other wastewater containing chromium.

However, taking in mind that complete laboratory and pilot-plant experiments including appropriately pre-treatment for separation process optimization must be preceded by final treating technology installation every time.

7 Acknowledgement

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