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Application of nanofiltration for chromium concentration in the tannery wastewater

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ABSTRACT

The article presents results of investigation concerning an influence of tannery wastewater composition on chromium(III) concentration in the wastewaters during the nanofiltration process (NF). The effectiveness of this process strongly depends on mutual relation between chloride and sulfate ions concentration in tannery wastewater. For this reason, the optimum composition of the tannery wastewater should consist chloride/sulfate ions ratio close to 1. Moreover, an influence of transmembrane pressure (TMP) and the "ageing" of chromium tannery wastewater on the efficiency of the process has been investigated. Optimal range of TMP equal to 14–16 bar has been assumed for the process. It is necessary to point out that the optimum transmembrane pressure can be changed in the case of the membranes with different permeation properties. "Ageing" of the tannery wastewater reduces only a little an efficiency of the process. Experimental results demonstrated that the NF process could be successfully used for the concentration of chromium in the tannery wastewater with high permeate flux, selectivity and performance stability.

1. Introduction

Nowadays chromium tanning is widely used in tannery processes. That is why chromium, the element exhibiting mute- and cancerigenic properties, is present in the tannery wastewater. Until recently [1–3], the chromium concentration in chromium exhausted tanning bath was on the level 10–14 g/dm^3. Because of the strong environmental requirements and the rising price of chromium tan, the tanning process is leaded with high chromium exhaust from tanning bath. Just this reason the chromium concentration dropped to 1.5–4.0 g/dm^3 [1–3] but this level is still much higher than needed for the environmental requirements. The average composition of chromium tannery wastewater is presented in Table 1. It's characteristic that there are high concentration of chloride and sulfate ions in the chromium tannery wastewater.

Traditionally, precipitation method is widely used for chromium removal from tannery wastewater [4,5]. The good effectiveness of chromium(III) removal in the case of this method can be obtained for chromium concentration higher than 10 g/dm^3 [1]. That is why now, before the precipitation process the primary increase of chromium concentration in the tannery wastewaters is needed. The direct recirculation of tannery wastewater is a different method for limiting of chromium concentration in the wastewaters [6,7]. Similarly to the precipitation process also in this case the high concentration of chromium is preferred for its neutralization.

Recently, the nanofiltration process (NF) is proposed [8–11] for metal ions concentration from concentrate salt mixture solution. NF is one of middle pressure membrane process (1–3 MPa) where components separation are realized by sieving effect (pores diameter is in the order of 1 nm). Additionally the nanofiltration membranes are characterized by the surface charge. This phenomenon of NF membranes effects on low retention of monovalent ions and high retention of bi- and multivalent ions [12,13]. As a result of Donnan exclusion, in order to establish electroneutrality on both sides of the membrane, the significant increase of monovalent ions in the permeate is observed while the multivalent ions are almost totally retained by the membrane. Due to this even negative retention of monovalent ions have been obtained [14–16]. In the case of tannery wastewater (look at Table 1) such NF membrane properties can enable both effective concentration of chromium ions and separation of chromium and chloride ions in the tanning effluent.

According to [17,18] the effect of the concentration of chromium in tannery wastewater by the use of NF seemed to depend mainly on the concentration ratio of the salts and the overall ion concentration in the feed solution – the composition of the tanning wastewater.

In the present work, the effects of such operational factors as chloride and sulfate ions feed concentration, chloride/sulfate

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Table 1
Average composition of chromium tannery wastewater.

Parameter	Average composition (g/dm^3)
SS	1.4–2.8
COD	5.2–8.4
Chlorides	8.2–16.4
Sulfates	14.7–21.1
Total chromium	1.5–4.0
Org. nitrogen	0.2–0.3
Oils and fats	0.2–0.3

ions ratio, applied pressure as well as "ageing" of effluent on chromium(III) concentration in the tannery wastewater during the nanofiltration process has been investigated.

2. Materials and methods

The nanofiltration process has been performed in the laboratory installation. Model tannery wastewater stored in the termostat, 15 dm^3 feed/retentate tank was pumped (Cat Pumps - model 240) through the nanofiltration membrane. The temperature, pH, flow rate and pressure of retentate were measured.

The feed solution has been prepared using the following chemicals: $Cr(NO_3)_3 \cdot 9H_2O$ (Sigma–Aldrich, Steinheim, Germany), pure NaCl and Na_2SO_4 (Chempur®, Piekary Śląskie, Poland), and pure water (after RO system, γ = 46.1 μS/cm, pH 7.5). The characteristic of the nanofiltration membrane is reported in Table 2.

All experiments were performed in batch concentration mode, i.e. the permeate stream was collected in the permeate tank, whilst retentate stream was recycled to the feed/retentate tank. The temperature of feed solution during the process was constant and equal to 25 ± 1 °C.

The investigations have been divided into following parts:

1. In the first part, the influence of chloride (5, 10, 15 g/dm^3) and sulfate (5, 10, 15 g/dm^3) ions concentration on permeate flux, chromium(III) retention and chlorides retention as well as chromium(III) concentration has been investigated. Then nanofiltration was applied to mixtures of chromium(III) (2 g/dm^3), chloride (5, 10, 15, 20 g/dm^3) and sulfate (10 g/dm^3) ions to determine an optimal model tannery wastewater composition. During this experiment the transmembrane pressure was equal to 14 bar, temperature was kept constant on the level of 25 ± 1 °C and retentate flow was equal to 800 dm^3/h.
2. In the second part, the influence of transmembrane pressure (12, 14, 18, 24 bar) on permeate flux, chromium(III) retention and chlorides retention as well as chromium(III) concentration has been investigated. The experiment has been performed at constant temperature equal to 25 ± 1 °C, retentate flow equal to 800 dm^3/h and the feed solution consisting: 2 gCr^{3+}/dm^3, 10 gCl^-/dm^3 and 10 gSO_4^{2-}/dm^3.

Each experiment has been lasted for 3 h. Samples of permeate and retentate have been collected for determination of chromium(III) concentration in well defined time-intervals. Moreover, after the end of the experiment, samples of permeate and retentate have been collected for determination of chloride and sulfate ions concentrations.

The samples of permeate, feed and retentate have been analysed using the following methods:

- chromium(III) – spectrophotometer Semco S/E using 1,5-difenylokarbazyde method with wave length λ = 540 nm,
- chloride ions – Mohr titration method,
- sulfate ions – gravimetric method with the use of $BaCl_2$.

pH values of the feed solution varied from 3.6 to 3.9 what agreed with the real chromium tannery wastewater [19]. The pH was controlled by pH-meter (Mettler Toledo, SevenEasy model).

The retention of chromium(III) and chlorides was calculated with equation:

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

where C_P is the concentration of chromium(III) or chlorides in the permeate and C_R is the concentration of the same component in the retentate.

The influence of the "ageing" tannery wastewater (after 2, 24 and 96 h) on permeate flux, chromium(III) retention and chlorides retention as well as chromium(III) concentration has been investigated either. The experiment has been done in the same conditions as previously.

Transport properties of the tested membrane have been checked before the experiment. The membrane permeability coefficient for pure water was equal to 0.86×10^{-6} m^3/(m^2 s bar).

3. Results and discussion

3.1. The influence of co-ions (chlorides and sulfates) concentration on extent of chromium(III) concentration during the nanofiltration process

Influence of chloride ions concentration on permeate flux is shown in Fig. 1a. Increasing of chloride ions concentration in feed solution causes high decreasing of permeate flux. It decreased of about 46, 65 and 74% (referring to the base chromium solution) for chloride ions concentration equal to 5, 10 and 15 g/dm^3, respectively. The high decreasing of permeate flux is generated by increasing of osmotic pressure gradient across the membrane caused by high concentration of chloride ions. The decreasing of permeate flux results in decreasing of chromium(III) concentration in retentate consequently (Table 3).

Higher concentration of chloride ions in feed solution causes its higher concentration in membrane pores and finally higher concentration in permeate. According to Donnan equilibrium between two water phases separated by the membrane increase of the anions stream causes increase of the cations stream [12]. In the case of high concentration of negative charged chloride ions it's possible that the chromium ions acts as active ions covering of membrane charges. As the result decreasing of chromium(III) retention in the investigated systems (Table 3) was observed. That is why for most effective chromium(III) concentration the low chloride ions concentration is more preferred.

Influence of sulfate ions concentration on extend of chromium(III) concentration in retentate is shown in Fig. 1b. Increasing of sulfate ions concentration in feed solution causes decreasing of permeate flux. It decreased of about 26, 38 and 47% (referring to the base chromium solution) for sulfate ions concentration equal to 5, 10 and 15 g/dm^3, respectively. It means that in the investigated systems polarization phenomena is

Table 2
Characteristic of NF membrane used in the experiments.

Manufacturer	GE Osmonics
Type	CK
Configuration	Flat sheet
Membrane polymer	Cellulose acetate
Rejection size	92% Na_2SO_4
Membrane active area	0.0155 m^2
pH operating range	2–8
Max. pressure operating	31 bar
Max. temperature operating	50 °C

Table 3
The influence of chlorides/sulfates ions on chromium(III) retention and concentration. Feed phase: pH 3.6; $T = 25 \pm 1\,^{\circ}C$. TMP = 14 bar. Retentate flow, $V_R = 800\,dm^3/h$.

Composition of feed			Chromium(III) retention (%)	Chromium(III) concentration (%)
Chromium(III) (g/dm^3)	Chlorides (g/dm^3)	Sulfates (g/dm^3)		
2	–	–	100	113
2	5	–	96	104
2	10	–	95	100
2	15	–	93	94
2	–	5	96	110
2	–	10	96	104
2	–	15	94	101

much lower than in the case of chloride ions. Only the smaller decreasing of permeate flux, caused by grow of sulfate ions, is profitable for increasing of chromium(III) concentration in feed solution (Table 3), which remained on the level above 100% in the investigated range of sulfate ions concentration. Properties of the NF membrane as well as specific kind of ions presented in the investigated systems cause high retention of chromium(III) what additionally supported increase of chromium(III) concentration.

Influence of chloride/sulfate ions ratio on permeate flux is shown in Fig. 2. Increasing of chloride/sulfate ions ratio in feed solution causes decreasing of permeate flux.

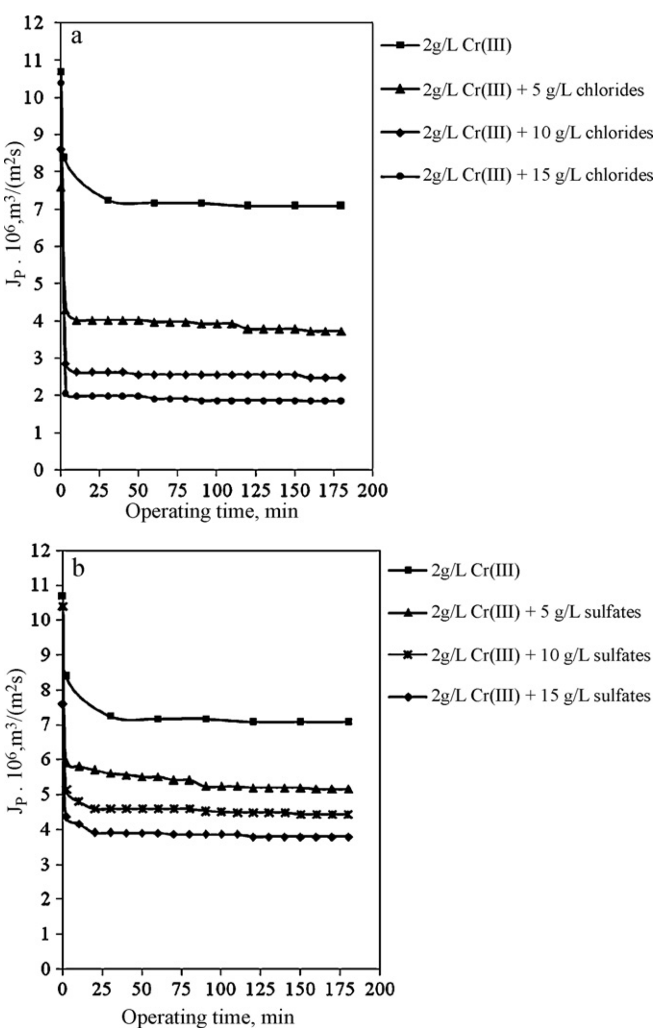

Fig. 1. Permeate flux (J_P) vs. operating time for different (a) chlorides and (b) sulfates concentration. Feed phase: pH 3.6; $T = 25 \pm 1\,^{\circ}C$. TMP = 14 bar. Retentate flow, $V_R = 800\,dm^3/h$.

Presence of chloride and sulfate ions in the mixture changes the equilibrium of the system and leads to decrease of chromium(III) retention compared to the systems with only one kind (chloride or sulfate) ions. The level of chromium(III) retention dropped below 80% as a consequence of increasing of chloride/sulfate ratio (Fig. 3). For chromium concentration the low chloride/sulfate ions ratio in feed is favorable.

Influence of the chloride/sulfate ions ratio on retention of chloride ions is shown in Fig. 3. It is evident that increase of the chloride/sulfate ions ratio causes decreasing the retention of chloride ions. Comparable experimental results were stated by several researchers [14–16,18]. Therefore, the highest chloride/sulfate ions ratio in feed is the most important factor for the highest concentration of chloride ions in permeate stream.

Taking into account the chromium(III) concentration in the real tannery wastewater equal to $2\,gCr^{3+}/dm^3$ and the chloride ions concentration equal to $10\,gCl^-/dm^3$ as well as our previous results the following composition of chromium "model" tannery wastewater: $2\,gCr^{3+}/dm^3$, $10\,gCl^-/dm^3$ and $10\,gSO_4{}^{2-}/dm^3$, was assumed for further investigations. The selected sulfates ions concentration ensures chloride/sulfate ions ratio close to 1 and, as a consequence, the optimum efficiency for chromium(III) concentration during the NF process. Because of mono-stage of tanning process there are some possibilities of real chromium tannery wastewater modification.

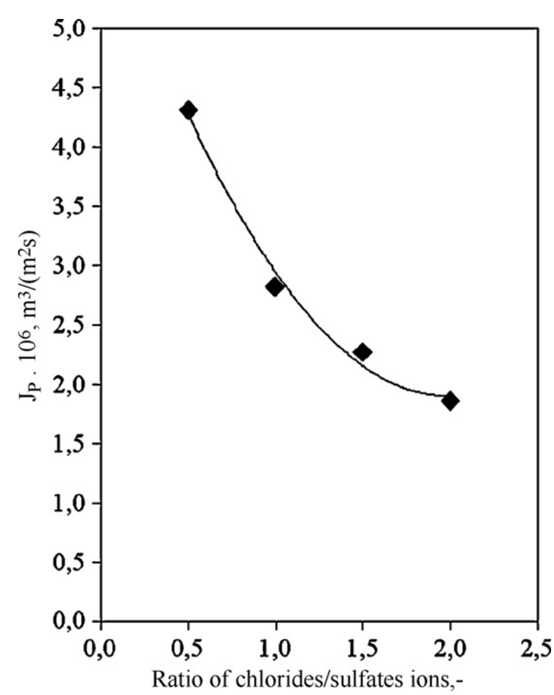

Fig. 2. Permeate flux (J_P) vs. chlorides/sulfates ions ratio. Feed phase: pH 3.6; $T = 25 \pm 1\,^{\circ}C$. TMP = 14 bar. Retentate flow, $V_R = 800\,dm^3/h$.

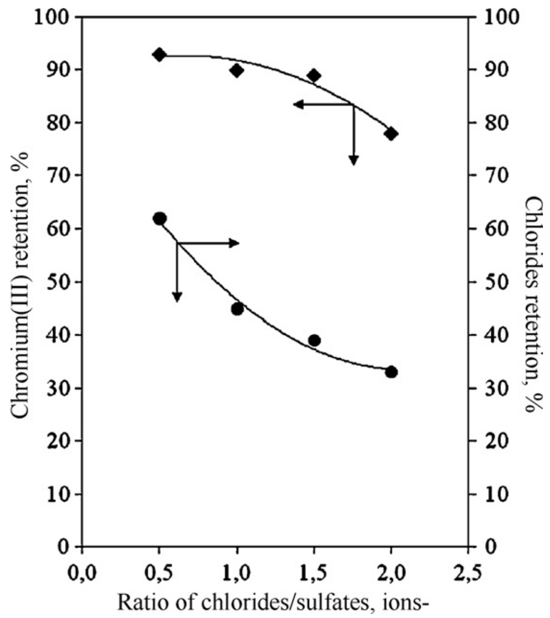

Fig. 3. Influence of chlorides/sulfates ratio on chromium(III) retention (♦) and chlorides retention (●). Composition of feed: 2 gCr^{3+}/dm^3, 10 gCl^-/dm^3, 10 gSO_4^{2-}/dm^3, pH 3.6; $T = 25 \pm 1$ °C. TMP = 14 bar.

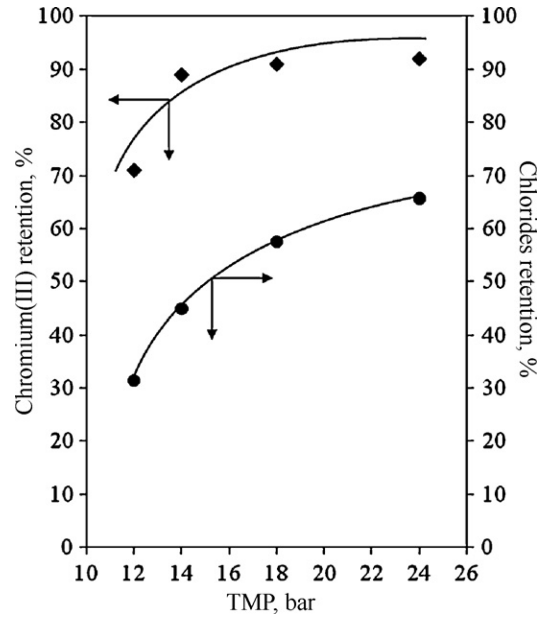

Fig. 4. Influence of transmembrane pressure on chromium(III) retention (♦) and chlorides retention (●). Composition of feed: 2 gCr^{3+}/dm^3, 10 gCl^-/dm^3, 10 gSO_4^{2-}/dm^3, pH 3.6; $T = 25 \pm 1$ °C.

3.2. The influence of transmembrane pressure on extent of chromium(III) concentration and composition of permeate

Effect of transmembrane pressure in range of 12–24 bar on permeate flux during the nanofiltration of chromium "model" tannery wastewater can be expressed by linear equation:

$$J_P = 1.6 \times 10^{-7} \cdot \Delta p$$

where J_P is the permeate flux (m^3/(m^2 s)) and Δp is the transmembrane pressure (bar).

The obtained results show that increase of the transmembrane pressure causes significant increase of permeate flux as well as makes low positive influence on chromium(III) concentration and its retention (look at Fig. 4). For proposed feed composition the only a little polarization effect was notice ($R^2 = 0.983$).

The results show either that the chlorides retention increases with increasing of the transmembrane pressure. It's consequence of the decreasing of diffusive transport of those ions with simultaneous domination of their convection transport caused by the water flux increase [20]. Thus, obtaining of permeate flux containing high concentration of chloride ions needs application of the low transmembrane pressure. As Meihong et al. [21] indicated decrease of operating pressure is possible because of that decreasing of chloride retention would minimized the osmotic pressure difference between the feed and permeate. On the other hand, decreasing of the pressure causes reduction of the permeate flux what results in decreasing of chromium(III) concentration in retentate. That is why the optimum transmembrane pressure, in this case, is in range of 14–16 bar. It is necessary to point out that the optimum transmembrane pressure can be changed in the case of the membranes with different permeation properties.

Table 4 shows the results for application of NF to chromium "model" tannery wastewater for TMP equal to 14 bar.

The NF membrane rejected 90.2% of the chromium and 98.7% of the sulfates, whereas the chlorides retention was 44.9%. These results justify the use of the NF process to obtain and reuse of the permeate stream in the pickling step and the retentate stream in the tanning step.

Table 4
Analytical determinations of samples from NF of chromium "model" tannery wastewater (2 gCr^{3+}/dm^3, 10 gCl^-/dm^3, 10 gSO_4^{2-}/dm^3, pH 3.6; $T = 25 \pm 1$ °C). TMP = 14 bar.

Parameter	Feed	Permeate	Retentate	Retention (%)
pH	3.7	3.8	3.8	–
Total chromium (g/dm^3)	2.0	0.198	2.015	90.2
Chlorides (g/dm^3)	10.0	5.540	10.050	44.9
Sulfates (g/dm^3)	10.0	1.350	10.140	98.7

3.3. The influence of the "ageing" of chromium tannery wastewater on efficiency of chromium(III) concentration during the nanofiltration process

One of the most important properties of the tannery wastewater is its "ageing". The "ageing" phenomenon is characterized by some complex reactions between components of tanning exhausted bath passed during the time. It changes, sometimes drastically, the physico-chemical properties of the tannery wastewater.

Obtained results show that the permeate flux for "ageing" wastewater was a little low then one for "fresh" wastewater but it was independent of the age of the chromium tannery wastewater. Decreasing of permeate flux has positive influence on the permeate composition. The retention of chloride ions decreased about 4–5% for "ageing" chromium tannery wastewater. However the sufficient drop of chromium(III) retention which for the "ageing" wastewaters amounted even below 80% was noticed. The concentration of chromium(III) decreased to the level of 97% as consequence.

On the basis of this results its evident that "ageing" creates a new ion equilibrium in the system what influences on the efficiency of the process.

4. Conclusions

Due to decreasing of chromium concentration in tannery wastewater its re-concentration is necessary for effective chromium recirculation. The aim of the work done was concerned on the investigations of influence of composition of tannery wastewater on extent of chromium(III) concentration during the nanofiltration process. Especially important for chromium concentration is chloride/sulfate ions ratio in the chromium tannery wastewater. It was shown that high efficiency of the process is obtained for the chloride/sulfate ions ratio close to 1. Because of mono-stage of tanning process there are some possibilities of real chromium tannery wastewater modification. Such wastewater composition guarantees obtaining of retentate being high concentrated chromium(III) solution and permeate containing the highest amount of chloride ions. As a consequence the recirculation of the streams (retentate and permeate) leaving the nanofiltration module can be possible. Such process both limits the use of chromium tanning and reduces the chloride ions concentration in the wastewater. Additionally it allows for high reduction of the water used in the tanning process.

It was stated also that the best transmembrane pressure for the tested membrane with permeability factor equal to $0.86 \times 10^{-6}\,m^3/(m^2\,s\,bar)$ should be on the level of 14–16 bar. Unfortunately, because "ageing" of tannery wastewater affected efficiency of the process (look at the obtained results) the chromium(III) retention level even below 80% can be expected for real tannery wastewater.

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