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# Systems for chromium recirculation in tanneries

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**ABSTRACT**

Both hazardous chromium sludge and high salinity effluent, further biological treatment of which is technologically very difficult, are final problems in chromium wastewater treatment by the standard (precipitation) method. In this paper, the scheme of nanofiltration in a constant volume diafiltration (NF-CVD) circulation loop system that solves these problems is presented. Treatment of the model chromium tannery bath in the NF-CVD system allows obtaining the bath with 2.5 times higher chromium concentration and 3.5 times lower salt concentration than in the feed solution and the brain bath at the same time. Such baths can be actually reused in tanneries.

*Keywords:* Tannery wastewater; Nanofiltration; Chromium recirculation; Desalination

## 1. Introduction

Raw leather, a by-product and also a noxious waste of the food industry, transformed by the tanning process into the leather, forms an excellent material for the shoe industry, for the manufacture of leather goods, clothing, etc. [1]. The tanning process involves stabilization of the skin tissue by its crosslinking with the tanning agent. Actually, the chromium tanning agent is almost solely used in tanning process [2,3]. In order to enable tanning agent to react with skin, it is necessary to use an aqueous bath containing a range of excipients, which prepare the skin for the introduction of tanning agent into its structure. Thus, tannery processes entail the production of large amounts of wastewater, which contains both, organic material leached from the skin (fat, protein, etc.) and large variety of inorganic substances (Table 1) [1,2,4–6].

High concentration of chromium and high salinity are characteristic properties of tannery wastewaters [6,7]. High salt concentration in the effluent is due to the use of chemicals, such as hydrochloric acid or ammonium chloride, and salt washing out of the skin coming from conservation. The precipitation methods, which are commonly applied purification procedures of tannery effluents [8], are successful for all parameters, except for chlorides and sulfates (Fig. 1). Nowadays, the efficiency of tanning wastewaters treatment in refer to these ions is only at the level of ca. 27% [9].

Application of membrane processes, used together with the classical treatment methods, could be the solution to this problem. Researches [3,5,10] indicated a possibility of using various pressure driven membrane processes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), in tannery [11]. The driving force of all these processes is the pressure difference at both sides of the membrane. However, the different value of this pressure and transport mechanism of separated components results in significant differences in their application [12].

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Table 1
Composition of chromium tannery wastewaters [1,2,4,5]

| Parameter | The average chromium tannery wastewaters composition |
|---|---|
| pH | 3.6–3.9 |
| Total suspended solid (TSS), g $L^{-1}$ | 1.4–2.8 |
| Chemical oxygen demand (COD), g $L^{-1}$ | 5.2–8.4 |
| Chloride ($Cl^-$), g $L^{-1}$ | 9.4–13.9 |
| Sulfate ($SO_4^{2-}$), g $L^{-1}$ | 17.1–22.8 |
| Total chromium (TCr), g $L^{-1}$ | 2.5–4.0 |
| Total nitrogen (TN), g $L^{-1}$ | 0.4–0.6 |

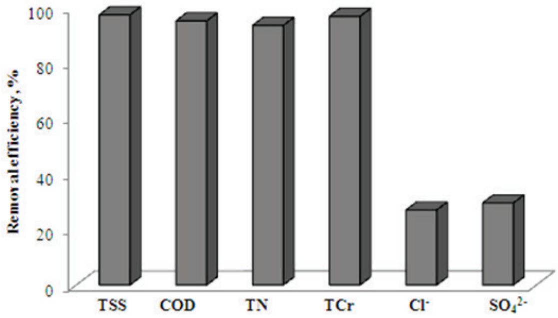


Fig. 1. The effectiveness of removal of basic pollutants from tannery effluents by the chemical-biological treatment.

NF becomes a popular technique applied to the wastewater reclamation [13–15]. NF membranes are characterized by a surface charge, density and kind of which depend on the method of the membrane preparation [12,16]. The membrane charge has crucial impact on the selectivity of these membranes. Furthermore, the pore size of the order of several-dozen nanometers results in poor retention of monovalent ions, and high rejection of multivalent ones.

Taking into account both, the composition of chromium tannery wastewater and properties of NF membranes, it can be assumed, that the use of NF process enables, on the one hand, to obtain a retentate in the form of concentrated chromium(III) solution – chromium condensate – and, on the other hand, the permeate, that is, the salt solution.

In this paper, a desalination effect of the simulated, exemplary chromium tannery wastewater treated by NF in a constant volume diafiltration (NF-CVD) mode was studied. Influence of the diluent volume on salt removal was especially analyzed. On the basis of the obtained results, a concept of treatment of chromium tannery wastewater with NF-CVD circulation loop was presented. Its advantages and disadvantages were indicated. Moreover, it was shown, that the classical treatment technology, assisted by membrane processes, could be successfully used to solve the problem of chromium tannery wastewater utilization.

## 2. Experimental

NF process, conducted in the diafiltration mode, was carried out with the use of the membrane laboratory installation described in [17]. The process was performed at the pressure of 1.0 MPa and at constant temperature of 20°C. The thin film, polyamide NF membrane, with DL trade sign, of an effective surface area of 0.0155 $m^2$ and cut-off 150–300 Da, provided by GE Osmonics, was used in the process.

Experiments were performed with the use of simulated solution of chromium tannery wastewater, which contained 2 g $Cr^{3+}$ $L^{-1}$, 10 g $SO_4^{2-}$ $L^{-1}$ and 20 g $Cl^-$ $L^{-1}$. The solution was prepared using following chemicals: $CrCl_3 \cdot 6H_2O$ (Chempur®), pure NaCl (Chempur®), pure $Na_2SO_4$ (Chempur®). Samples of retentate and permeate, collected during the process, were analyzed in terms of concentration of chromium with the spectrophotometric method with 1.5-diphenylcarbazide on Nanocolor UV/VIS at the wavelength $\lambda$ = 540 nm. The chloride concentration was analyzed by Mohr method.

Initial volume of the feed was equal to 4 L. NF process, conducted in the diafiltration mode, included three steps: pre-concentration, diafiltration – the salt is being washed out from the retentate by a washing diluent added with the rate equal to the rate of the permeate collection – and post-concentration. During the pre-concentration step, the volume of the feed solution was reduced. In each experiment, a collected volume of the permeate during the pre-concentration step was the same and equal to 1.3 L. Such feed volume reduction ensured high permeate flux during the diafiltration step. During the diafiltration step, the different volume of a washing diluent (1.3; 2.7; 3.5 L) into a pre-concentrated model chromium solution was added. RO water with conductivity equal to 41 μS $cm^{-1}$ was used as the washing diluent. The last step was post-concentration, which was carried out until permeate flux reduction by ca. 60% of its initial value.

The change of the permeate flux during the processes was determined by the measurement of time required to receive 10 ml of permeate.

## 3. Results

NF process, conducted in the diafiltration mode, was carried out for three different volumes of a washing diluent added during the diafiltration step. In the first variant, 1.3 L of the washing diluent was added. It was a lower volume than the volume of the retentate after the pre-concentration. In the second variant, the washing diluent volume added was equal to the volume of the retentate after the pre-concentration. In the third variant, more the washing diluent (3.5 L) than a volume of retentate after the pre-concentration was added. In the proposed variants the pre-concentration step was carried out until the permeate flux decreased by ca. 20% (amount of retentate equal to 2.7 L). The changes of permeate flux during for all variants of experiments are presented in Fig. 2.

During the pre-concentration step, the changes of the permeate flux in time were observed for all variants. These changes were the same for each variant. The permeate flux was stabilized in the diafiltration step by the washing diluent addition. For each variant, a change of the permeate flux in this step of process had a similar course (Fig. 2). Decrease of the permeate flux in time was observed in the post-concentration for each variant, but a rate of this change depended on the variant. In the first variant, the change of the permeate flux was the fastest. In the second and third variant, the change of the permeate flux was significantly slower. It is necessary to point out that the change of the permeate flux was related to the salt washing out level (Table 2).

During the pre-concentration step, the permeate was removed and at the same time a concentration of salt in retentate was constant. Whereas, according to the low permeability of the membrane towards chromium and sulfate ions, their concentration in the solution increased. This led to an increase of membrane polarization [17] and consequently the decrease in the permeate flux during the pre-concentration step was observed.

In the diafiltration step, the permeate flux was stabilized by addition of the washing diluent, but it increased slightly at the end of the diafiltration step. This increase could be related to the washing out of salt during this step. After the diafiltration step, the washing diluent addition was stopped.

A different time of the post-concentration step was observed for each variant of experiments. In variant 1, where volume of added water was the lowest, a post-concentration was short (Fig. 2(a)). A small amount of the washing diluent addition in the diafiltration step resulted in the decrease of salt concentration from 20.0 g $L^{-1}$ to about 12.5 g $L^{-1}$ (Table 2). The progressive concentration polarization of the membrane was caused both by a still large amount of salt and the large concentration of multivalent ions in the retentate. Additionally, the mineral deposition on the membrane surface after a process was observed, which resulted in the membrane scaling. In this variant, the volume of the permeate collected during the post-concentration was only 1.1 L. Both the low level of the feed volume reduction and the scaling of the membrane caused the low finish chromium concentration equal to 3.81 g $L^{-1}$.

In the variant 2, the washing diluent volume addition was two times higher than the variant 1. As a result, the salt concentration in the concentrate was equal to 7.65 g $L^{-1}$. The high reduction of salt concentration in the diafiltration step allowed extending the duration of the post-concentration step. Consequently, the permeate volume collected in variant 2 was equal to 1.3 L. The volume of the feed was reduced almost three times and chromium concentration in the concentrate was equal to 4.93 g $L^{-1}$.

In variant 3, 3.5 L of a washing diluent was added to the retentate during the diafiltration step. Chlorides concentration in the concentrate was equal to 5.81 g $L^{-1}$. During the post-concentration step, 1.4 L of the permeate was collected. This allowed for 3.3 times reduction of the feed volume. In this variant, the final concentration of chromium in the concentrate was equal to 5.48 g $L^{-1}$.

The process of NF, carried out in CVD mode, enabled both, threefold increase in the chromium concentration and four times decrease of salt concentration into the condensate with high efficiency of the process maintained.

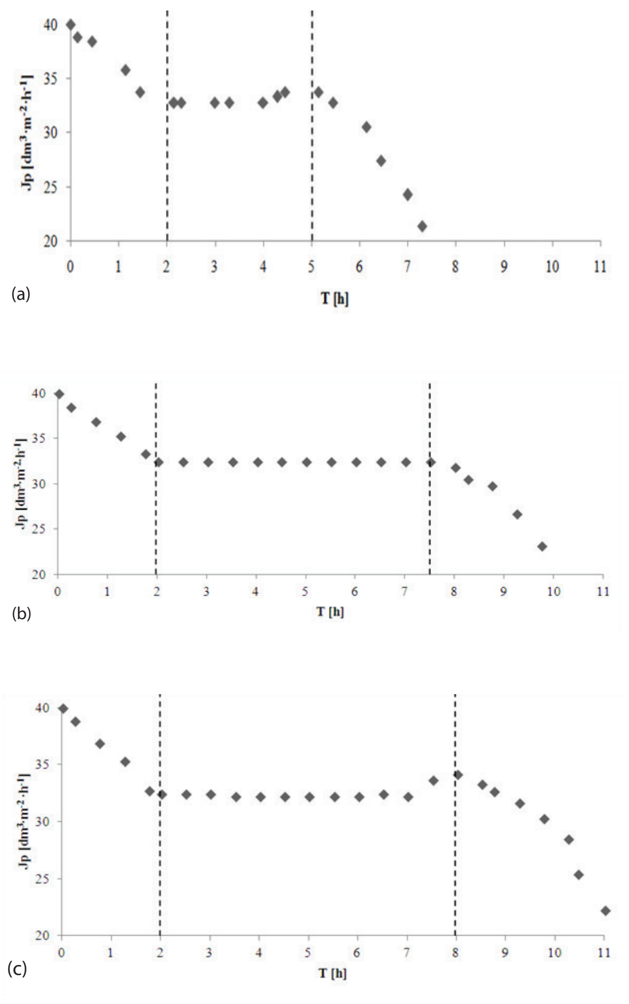


Fig. 2. The changes of the permeate flux in time for the NF-CVD process by addition of a different volume of washing diluent during diafiltration step: (a) the volume of the washing diluent equal to 1.3 L; (b) the volume of the washing diluent equal to 2.7 L; (c) the volume of the washing diluent equal to 3.5 L.

Table 2
Characteristic of process parameters

| Parameter | NF-CVD | | |
|---|---|---|---|
| | Variant 1 | Variant 2 | Variant 3 |
| Final volume of the retentate, L | 1.6 | 1.4 | 1.2 |
| Final chromium concentration in the retentate, g $L^{-1}$ | 3.81 | 4.93 | 5.48 |
| Final chloride concentration in the retentate, g $L^{-1}$ | 12.48 | 7.65 | 5.81 |
| Water consumption, L | 1.3 | 2.7 | 3.5 |
| Average, final chromium concentration in the permeate, g $L^{-1}$ | 0.10 | 0.14 | 0.14 |
| Average, final chloride concentration in the permeate, g $L^{-1}$ | 14.46 | 12.76 | 11.42 |
| Process time, min | 450 | 585 | 660 |

The results indicate that for the efficient salt washing out in the diafiltration step, the addition of a washing diluent in the amount at least equal to the volume of the retentate after pre-concentration step is required.

The addition of a different volume of the washing diluent in the diafiltration step influenced not only the effect on desalination and concentration of chromium but also on the process duration. In variant 1, where the added volume of the washing diluent was equal to the permeate volume collected in the pre-concentration, the process time was the shortest. In next variants, where a high washing diluent volume was added, the process time elongated. This increase was due to an extent of the diafiltration step. Therefore, the shortening of the process time can be achieved by limiting of the washing diluent amount added in the diafiltration step. Reduction of the washing diluent volume, with simultaneous maintenance of high salinity rate and high chromium concentration in the concentrate, is possible by providing of the higher pre-concentration of the feed solution.

## 4. Discussion

### *4.1. Intermediate recirculation – the classical precipitation method*

Currently, the precipitation method is mainly used to chromium removal from tannery wastewaters [18,19]. The scheme of the treatment of chromium tannery wastewater by the precipitation method is shown in Fig. 3.

Chromium is most often precipitated with sodium hydroxide. The sludge obtained is then filtered off. Occasionally, the filtered sludge after dissolution in sulfuric acid can be reused for tanning process as a regenerate of the chromium tannin [3]. In addition, the effluent characterized by high salinity and chromium concentration of 20–100 mg $L^{-1}$ is obtained. The effectiveness of chromium removal by this method depends on its concentration in the wastewater. Satisfactory results are obtained at chromium concentrations above 10 g $dm^{-3}$ [10]. Currently, tanning is commonly carried out with high chromium depletion, which reduces its concentration to a level of about 2–4 g $L^{-1}$. Thus, in order to achieve a high efficiency of the precipitation, the pre-concentration of chromium in tannery wastewater before the process is recommended [15].

Generally, the precipitation method allows reducing chromium in the wastewater to a level that does not disturb its further treatment. This method is also simple in terms of process and apparatus.

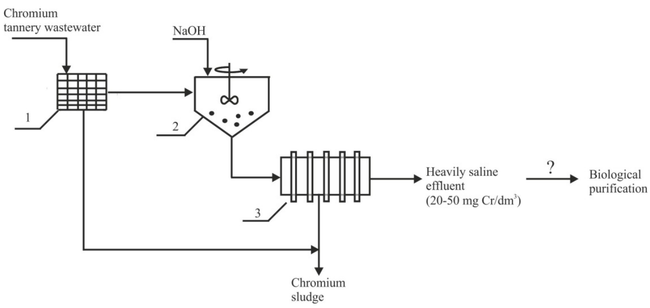


Fig. 3. Treatment of chromium tannery wastewater by precipitation method: 1 – pre-treatment module, 2 – precipitation of $Cr(OH)_3$ tank, 3 – filter press module.

The disadvantage of the precipitation method is connected with weak quality of the chromium tannin regenerate, which apart from chromium, contains high load of proteins and fats [3,20,21]. Contaminants included in the chromium tannin regenerate adversely affect the leather, impairing its quality. Consequently, the lack of interest in its use by tanneries is observed. In addition, high salt concentration remains in the filtrate generated from the dewatering of the chromium sludge hinders the performance of its further biological treatment.

### *4.2. Immediate recirculation – NF-CVD circulation loop*

Taking into account limits of conventional tannery wastewater treatment method, NF process with constant volume diafiltration mode is proposed to achieve an effective salt removal from the chromium wastewater – the salt is washed out from the wastewater by a washing diluent addition with the rate equal to the rate of the permeate collection. The scheme of chromium tannery wastewater regeneration by NF-CVD circulation loop is presented in Fig. 4.

As a result of such conception, two solutions might be obtained: the permeate, which can be used in the pickling stage of the tanning process (the process preparing the skin to the introduction of a tanning agent) and the retentate, which can be used, after tannin supplementation and pH correction, as a regenerated tanning bath. As we indicated previously [22], the leather tanned with the regenerated by membrane processes chromium baths have the same properties as the leather tanned with a fresh tannin agent.

Proposed chromium tannery wastewater regeneration concept allows for both, chromium and salt recirculation. In order to this concept implementation, two conditions must be satisfied: (1) some additional washing diluent volume should be added and (2) a significant reduction of the load of the organic pollution during the chromium wastewater pre-treatment should be ensured.

Results presented in this work (Table 2) indicate that the volume of the washing diluent equals the volume of the retentate after the pre-concentration step enables the salt content

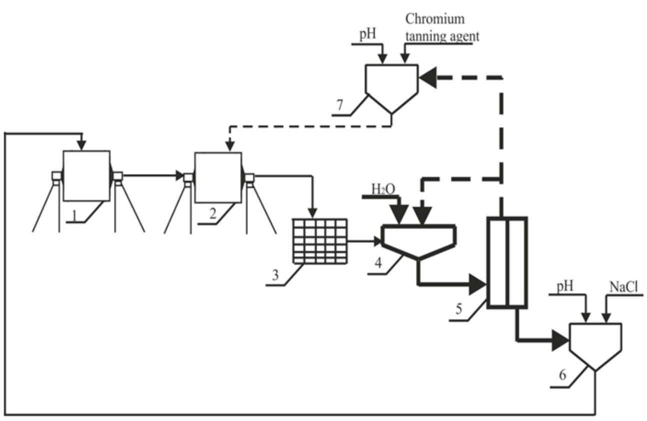


Fig. 4. Recirculation of chromium tannery wastewaters by NF-CVD circulation loop: 1 – pickling stage; 2 – tanning stage, 3 – pre-treatment module, 4 – equalization tank, 5 – NF membrane module; 6 – regenerated pickling bath, 7 – regenerated chromium bath, ——► – recirculation of the pickling bath, - - -► – recirculation of the chromium bath, —— – NF-CVD circulation loop.

decrease to the satisfactory level. Further experiment should be focused on both possibilities of a more effective pre-concentration of the chromium recirculate bath and partial recirculation of the washing diluent during diafiltration step.

Actually, there is no complex solution of the tannery wastewater pre-treatment, which allows obtaining high quality recirculated chromium bath. After desalination and chromium concentration, such recirculate can be directly turned back to the process (Fig. 3). The other solution is always possible. It seems that the chromium precipitation from such "dipper" pre-treatment bath should be effective and very high quality chromium regenerate should be obtained. It should be also noted that, in this case, the filtrate after dewatering of the chromium sludge, will contain chlorides concentration at a level, which does not affect its further biological treatment.

## 5. Conclusion

Now, due to the increasing quality requirements for environment and the leather, the classical method of recirculation of chromium tanning wastewaters does not satisfactory work. The regenerate of the chromium tannin obtained during precipitation process becomes troublesome waste. The solution based on the membrane processes may be an alternative. The proposed solution, that is, NF of chromium tannery wastewater at constant volume diafiltration mode, enables effective recirculation of chromium, and allows significant reduction of chloride ions concentration in the wastewater directed to further biological treatment.

The obtained results indicate that the membrane processes, in spite of the improving of technological requirements and environmental issues, gives the opportunity of the elimination of restrictions, which are characteristic for the classical treatment method used for chromium tannery wastewaters recovery. The proposed solution eliminates not only toxic chromium from the wastewater but also solves the problem of appearing salt. The permeate and the retentate streams, which leave the NF module, can be reused in the process as regenerated baths. Such a solution also allows for substantially complete closure of the process water cycle.

The disadvantage of the proposed solution, at this moment, is small number of results concerned the tanning wastewater pre-treatment ensuring further effective recirculation of nanoparticles. It is necessary to continue works focused on the increase of efficiency of NF process used for the tannery wastewater treatment. The studies should be led in both the laboratory and the pilot scale.

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