Anna KOWALIK-KLIMCZAK, Paweł GIERYCZ
Warsaw University of Technology,
Faculty of Chemical and Process Engineering, Warsaw
a.kowalik@ichip.pw.edu.pl, p.gierycz@ichip.pw.edu.pl

APPLICATION OF PRESSURE MEMBRANE PROCESSES FOR THE MINIMIZATION OF THE NOXIOUSNESS OF CHROMIUM TANNERY WASTEWATER

Key words

Chromium tannery wastewater, pressure membrane processes.

Abstract

This paper presents a literature review concerning the possibility of minimizing the noxiousness of chromium tannery wastewater. Based on the comparison of different methods applied for removing chromium (III) ions from wastewater and water solutions, the special qualities of pressure membrane processes were found. The appropriate combination of pressure membrane processes enables one to obtain saline solutions that can be re-used during the tanning of skins.

1. Chromium tannery wastewater

The transformation of raw hide to leather material requires a series of actions such as soaking, dehairing, greasing, pickling, dyeing, and tanning [1, 2]. All these actions require the use of chemical reagents such as acids, lyes, tannins, sulphides, dyes, solvents, etc. As a result, highly contaminated wastewaters containing both organic substances (fats, proteins) and inorganic substances (chromium, sulphate, chloride) as well as substances having the pH in the range of 3.5 to 4.2 [1, 2] are formed. Based on literature data [3–10], Table 1 summarizes the composition of the chromium tannery effluents.

Table 1. The composition of the chromium tannery wastewater [3–10]

Parameter	Content [g/dm^3]
Total suspension solids	1.4–2.8
COD	5.2–8.4
Chloride	8.2–16.4
Sulphate	14.7–21.1
Chromium	1.5–4.0
Total nitrogen	0.2–0.3
Oils and fats	0.2–0.3

Currently, the tanning process is mainly based on chromium tannins. Approximately 80-90% of the world tanneries apply basic chromium (III) sulphate. The reason for this is the very good quality and durability of the leather obtained [11]. However, this method has a high environmental impact. During the tanning process, about 70% of the applied chromium (III) remains in the skin while the remaining part goes to wastewater [5]. The concentrations measured in the tanning exhaust baths are within the limits of 1.5–4.0 g Cr (III)/dm^3 (Table 1). Taking into account large volumes of baths, such amounts of chromium pose a considerable strain on the environment. In addition, such large losses of chromium entail substantial costs [12]. Therefore, the recovery and reuse of chromium tanning agents is important in terms of environmental protection and the process economy.

2. Methods for recovery of chromium (III) from aqueous solutions

Among the conventional methods used for recovery of chromium (III) ions from aqueous solutions, the following methods can be distinguished: precipitation, biological methods, ion exchange, adsorption, and extraction (Table 2).

Table 2. A comparison of conventional methods used for recovering of chromium (III) ions from aqueous solutions [4,12–16]

Method	Advantages	Disadvantages
precipitation	– the possibility of reducing the concentration of chromium (III) in the wastewater to the level of 20–50 g/dm^3	– satisfactory efficiency for the concentration of chromium (III) in the wastewater above 10 g/dm^3 – poor quality of the recovered chromium (III) due to the presence of impurities
biological methods	– reduction of chromium (III) up to about 94%	– the necessity to maintain the pH of the effluent within the range of 6–9 – a difficult and prolonged period of sludge inoculation

Method	Advantages	Disadvantages
ion exchange	– very good durability and ease of regeneration of the ion exchange bed	– the need for the oxidation of chromium (III) to chromium (VI) prior to the process – Bath devoted to the ion exchange column should contain no more than 0.1 g CrO_3/dm^3
carbon adsorption	– selectivity with respect to anions offering the possibility to use it for the purification of solutions containing, for example, sulphate, chloride or bicarbonate anions	– low sorption capacity of activated carbon and the need for its frequent regeneration
solvent extraction	– high efficiency	– the need for large amounts of extractable organic substances, which are often toxic and flammable

While analysing the methods summarized in Table 2, it was found that, due to the heterogeneous composition of the chromium tannery wastewater (Table 1), the most suitable method for extracting the chromium is precipitation. With the use of sodium hydroxide, the chromium is precipitated as a chromium (III) hydroxide sludge, which is then filtered on a filter press. The obtained chromium hydroxide is dissolved in sulphuric acid. After measuring the pH and adding the appropriate amount of fresh chromium, this product can be re-used for tanning leather. However, the chromium tannin recovered by this method contains so much protein substances, fats and other contaminants (mainly from the hide) that it cannot be used to produce high-quality leather [3, 12, 15]. Consequently, this method leads to the disposal of large amounts of chromium solid waste that can contaminate soil and groundwater.

3. Pressure membrane processes

In order to improve the quality of the recovered chromium sulphate bath and to test alternatives to chemical processes, research has been carried out using pressure membrane processes. The pressure membrane processes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). In all these processes, the driving force is the pressure, which is different on each side of the membrane. The value of this pressure and the mechanism of transporting the particles being separated can be different, and this can complicate the scope of the particular process. The comparative characteristics of the pressure membrane processes are presented in Table 3.

Table 3. The characteristics of the pressure membrane processes [17]

Microfiltration	Ultrafiltration	Nanofiltration	Reverse osmosis
Low transmembrane pressure (<2 bar)	Low transmembrane pressure (1–10 bar)	Transmembrane pressure (5–30 bar)	Transmembrane pressure (10–100 bar)
Osmotic pressure (can be omitted)	Osmotic pressure (can be omitted)	Osmotic pressure (plays a role)	High osmotic pressure (5–25 bar)
Symmetric, porous membrane	Symmetric or asymmetric, porous membrane	Nano–porous, asymmetric membrane – integral or composite	Solid, asymmetric membrane – integral or composite
Pore size approx. 0.1–10 µm	Pore size approx. 0.001–10 µm	Pore size approx. 2 nm	Pore size < 2 nm
The mechanism of separation – sieving	The mechanism of separation – sieving	The mechanism of separation based on dissolution and diffusion	The mechanism of separation based on dissolution and diffusion

Pressure membrane processes have a number of significant advantages over conventional methods of recovering chromium (III) from aqueous solutions (Table 2). First of all, they do not require the use of additional chemicals, and they are characterized by low power consumption, They also allow for separation in a continuous manner, which can easily be combined with other unit processes [1, 17]. For the purpose of chromium (III) recovery from aqueous solutions, the processes of ultrafiltration, nanofiltration, and reverse osmosis can be applied (Table 4).

Table 4. The comparison of the applicability of the pressure membrane processes for the removal of chromium (III) from aqueous solutions [9, 18, 19]

Process	Characteristics
ultrafiltration	– due to the pore size of ultrafiltration membranes, they are not retained by them – the addition of complex substances (e.g., polyethylene imine) enables an increase of the size of the chromium (III), and even twenty times reduction in its concentration in the solution
nanofiltration	– allows for the separation of monovalent ions (permeate) and multivalent ions (retentate) – operates at a lower pressure than reverse osmosis
reverse osmosis	– high osmotic pressure due to the presence of high concentrations of chloride and sulphate ions – the necessity to apply high pressure – satisfactory efficiency of solutions containing not more than 5 gCl^{-}/dm^3 and 1 gCr^{3+}/dm^3

In the case of ultrafiltration, a direct recovery of chromium (III) from aqueous solutions is not possible. In recent years, the method that is increasingly used for extracting chromium (III) from aqueous solutions is polymer-enhanced ultrafiltration [19–21] or micellar-enhanced ultrafiltration processes [22–24]. Korus [21] demonstrated that, in the polymer enhanced ultrafiltration, the highest retention of chromium (III) is obtained by using polyethylene imine. In turn, Konopczyńska et al. [24] found that, in the case of micellar solution ultrafiltration, the most efficient removal of chromium (III) is obtained by using a mixture of two surfactants that is anionic and nonionic.

In contrast, nanofiltration and reverse osmosis may be practically applied to the chromium (III) ions from aqueous solutions in a direct way [5–9, 17, 18]. In the case of recovering of chromium (III) ions from aqueous solutions by reverse osmosis, it is necessary to apply a high transmembrane pressure, which is associated with high costs of processing [18]. Therefore, the chromium (III) ion recovery from aqueous solutions by nanofiltration is more economically advantageous. The applicability of nanofiltration for chromium recovery from tannery effluents was described in detail by Cassano et al. [5–9]. The study was conducted on a pilot scale where two types of spiral wound polyamide modules were examined (cut off 150–300 kD). The nanofiltration was carried out at a transmembrane pressure of 14 bars at the two feed flow rates of 450 and 2200 dm^3/h. Regardless of the type of the membrane module and the feed flow rate, a very high retention of chromium (III), amounting to 97% [9] and 99% [5-8], was obtained.

In addition, a relationship between the degree of the concentration of the chromium (III) solution and the content of organic matter in the effluent is observed [9]. It shows that, the larger the ratio of chromium to the COD concentration in the tannery wastewater (i.e., the less it contains organic substances), the more concentrated is solution of chromium that can be obtained in the nanofiltration process. This means it is necessary to reduce the concentration of organic substances, prior to the introduction of tannery wastewater into the nanofiltration process. Fabiani, et al. [10] proposes the use of microfiltration and/or ultrafiltration to remove the suspension, COD, organic nitrogen, and fats from tannery effluents. The ultrafiltration was performed on polysulfone membrane modules (cut off 60 kD), while a ceramic module (10 nm) was used for microfiltration. The results summarized in Table 5 confirm the possibility of using microfiltration and/or ultrafiltration for the purpose of preparing tannery wastewater prior to nanofiltration. Similar results were obtained in the framework of our own work [25].

Table 5. The results of microfiltration and/or ultrafiltration of tannery wastewater [10]

Parameter	Retention, %		
	MF	UF	MF and UF
Total suspended solids	93.3	99.6	70.0
COD	41.3	33.0	32.4
Organic nitrogen	64.0	51.0	20.0
Fats	61.7	91.8	92.0

As a result of a combination of micro-, ultrafiltration and nanofiltration processes, two streams are obtained: the first one containing a high salt concentration of monovalent ions and the second one being a concentrated solution of chromium sulphate, which could be reused in the tanning technology [5–9]. However, considering the properties of the nanofiltration membranes, the effect of variation in the concentrations of chlorides and sulphates in tannery wastewater on the possibility of the retention of chromium appears to be of particular interest. Our laboratory study [26] confirms that, from the perspective of separation of wastewater into two baths, which can be reused in the tanning of hides, the most favourable option is to lead the process of nanofiltration at a ratio of ion concentration Cl^-/SO_4^{2-} at the first level. Additionally, an important part of the process is the selection of the nanofiltration membrane possessing the appropriate load surface of the skin layer [27, 28].

Summary

Pressure membrane processes offer technical possibilities of the introduction of a closed circuit of process streams in tannery factories. The important practical issues that researchers still need to face include the selection of appropriate membranes for various processes and optimizing the parameters of the process taking into account the variability of the composition of chromium tannery effluents.

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Zastosowanie ciśnieniowych procesów membranowych w celu minimalizacji uciążliwości chromowych ścieków garbarskich

Słowa kluczowe

Chromowe ścieki garbarskie, ciśnieniowe procesy membranowe.

Streszczenie

W pracy dokonano przeglądu literaturowego dotyczącego możliwości minimalizacji uciążliwości chromowych ścieków garbarskich. Na podstawie porównania różnych metod stosowanych do usuwania jonów chromu(III) ze ścieków i roztworów wodnych stwierdzono szczególne możliwości ciśnieniowych procesów membranowych. Polegają one na tym, że odpowiednie połączenie ciśnieniowych procesów membranowych umożliwia uzyskanie kąpieli soli, które mogą być ponownie użyte podczas garbowania skór.