

Powertan: a Revolution for the Tanning Leather Sector

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Powertan is a disrupting new approach for leather tanning where the penetration inside the hide to be tanned is enhanced by the use of an externally applied electric field. Thus, the penetration is no longer controlled by the fickian diffusion mechanism by ion migration. The result is a dramatical decrease of the process time, from the almost 24 h of the traditional drum operation to few minutes. Moreover, the electric field reduces the necessity of ancillary operations like the pickling and the basification with a reduction to about one tenth of the bath/leather ratio from the about 20 L/kg. Here, the first small scale batch tests will be presented with a preliminar modeling interpretation.

1. Introduction

Leather is an extremely valuable natural product with applications across a large number of sectors, from shoes and dress fashion to automotive and furniture (Král et al., 2014). It is the tenth most traded commodity, with a total value of about USD 440 billion in 2022 (Fortune 2023). Its market is estimated to grow further with a compound annual growth rate (CAGR) of 6.2 % until 2030 (Acumen 2023). Its use by humankind dates to ancient times and it can be viewed as the first example of circular economy product because the raw material is actually a waste product from the food industry (Kesarwani et al., 2015). Accordingly, the leather market is the number one by-product market (UNIC 2023).

The fundamental step in the process of transforming the raw material into a finished product is tanning, i.e. the stable penetration into the hide of substances that fix the collagen fibres to prevent its putrefaction, (Covington, 2009). In the absence of tanning, the skin, being of natural origin, would degrade within a few days, making its further uses impossible (Muralidharan et al., 2021). The rudimental system to limit the putrefaction was primarily by drying, but it is with the introduction of the vegetal tannins treatment, that humans discovered the leather (a stabilized raw skin) (Aquad et al., 2019). Tannins, as polyphenols, interact with collagen by some weak interactions like H – bonds and improve the hydrothermal/rot resistance of it (Carçote et al., 2016). After long time, at the end of XIX century it was discovered the extraordinary stabilization effect of $Cr(III)$ salts that today is used to produce almost the 80 % of leather (ICDA, 2024).

To facilitate the diffusion of Cr , the solubility and the stability in solution, chromium basic sulphate $CrOHSO_4$ is used coupled with a previous acidic treatment (pickling) (Yang et al., 2022). The use of $CrOHSO_4$ produces the highest quality of the final product from the consumers point of view at the lower costs. $Cr(III)$ has the highest affinity to the carboxyl groups of collagen chains (the hide constituents) through the olation reaction (Covington 2009).

Tanning is preceded the pickling step where the hide is immersed in an acid solution to facilitate the $Cr(III)$ ions penetration during tanning: a $pH < 2.8$ is needed to avoid the olation reaction. After the addition of the desired amount of tanning agent, the pH value is then increased, in the so-called basification step, to about $pH = 3.3$ to stably fix the $Cr(III)$ to the collagen (Biškauskaitė et al., 2021). If these steps are not operated in the right sequence (acidification, tanning, basification) the result is a very slow penetration of $Cr(III)$ ions because diffusion has to compete with the chemical reaction, with the results of a significant increase of the time of

operation coupled with the difficulty of reaching the desired $Cr(III)$ content to stabilize all the collagen carboxylic moieties.

In summary, with reference to Figure 1 (Panduranga Rao et al., 1995; Rossi et al., 2015), the leather structure and the chemical reaction engineering phenomena related to chromium tanning are:

- Leather structure is represented as a fibre bundle of collagen originating macro pores, with a macroporosity $\varepsilon_p \approx 0.2 \div 0.3$.
- All pore channels exposed the collagen $-COOH$ groups available to react with tanning agent, $Cr(III)$.
- Cr ions move within the pores reacting (i.e., adsorption like) with the carboxyl groups. Reaction rate is function of solution pH .

Accordingly, the phenomena involved in the tanning process are:

- Soaking of the leather to reach enough humidity entrapped in the pores.
- Adsorption/desorption of the substance to/from the collagen fibres.
- Diffusion/migrations of the ions along the macropore filled with water.

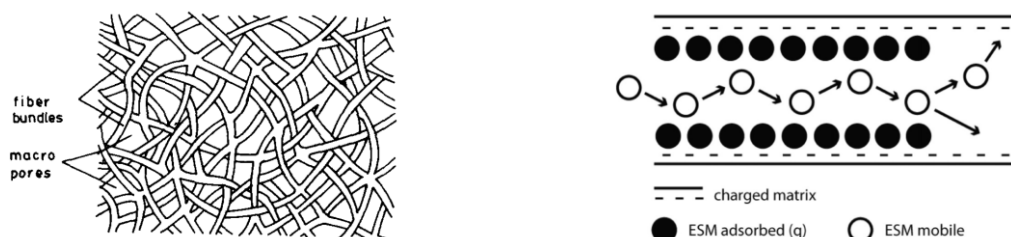


Figure 1: (left) leather structure as a bundle of fibres creating a macropore network; (right) sketch of the ion migration within the pore with chemical interaction with surface carboxyl groups of collagen fibres, with a behaviour similar to the ethosuximide (ESM) in a partitioning mode.

The idea of applying an electric field to accelerate the tanning process takes inspiration from the work done on the vitrification by immobilization in gel of nuclides (Masi et al., 2013). Being conceptually the vitreous gel and the hide similar in structure, the substantial speedup of the tanning process was expected as described by literature (Masi et al., 2019).

Overall, the aim of this work is to illustrate the experimental work done at laboratory scale as well as to give a first theoretical explanation of the process kinetics.

2. Experimental set up

A laboratory scale electrochemical cell, illustrated in Figure 2, where the hide to be tanned is placed as a porous septum separating the cathodic (-) and the anodic (+) compartments. The cell exposed a hide of $50 \times 50 \times 1.5 \text{ mm}^3$ and the tank volume is $V_L = 0.08 \text{ L}$. Two carbon felts are introduced in contact with the leather and the electrodes to better distribute the tanning solution and the electric current. From the electrochemical point of view this is a zero-gap cell.

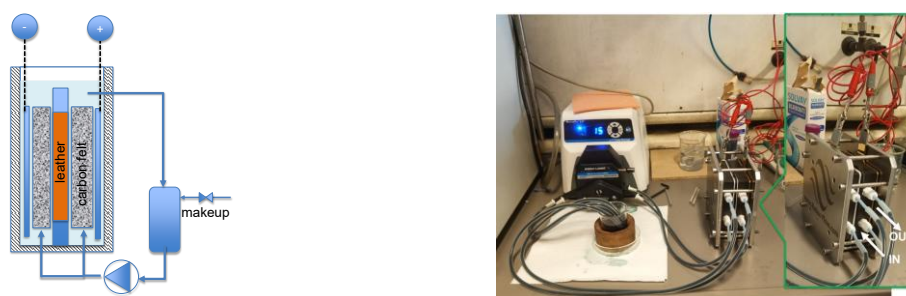


Figure 2: (left) sketch of the electrochemical cell structure with the hide to be tanned placed as the usual membrane separating the anodic and the cathodic compartments. (right) a picture of the whole system with highlighted the cell.

Continuously controlled variables were pH , temperature, applied potential ΔV and electric current I , while the cell is operated in a potentiostatic mode. Stepwise controlled variables were the tanning solution composition ($Cr(III)$ and $Cr(VI)$), leather composition ($Cr(III)$ and $Cr(VI)$) and shrinking temperature T_s after basification.

The applied voltage was always kept below $\Delta V = 2 V$, actually in operation below $\Delta V = 1.2 V$, because two main constraints: to avoid water electrolysis ($\Delta V_{H_2O} = 1.23 V$) and the oxidation of $Cr(III)$ to $Cr(VI)$ ($\Delta V_{Cr} = 1.38 V$, in acidic conditions) (Kerr, 2000). As it will be demonstrated below, the $Cr(III)$ penetration is determined by migration, thus the $Cr(III)$ flux is substantially unidirectional from the anode to the cathode. Therefore, was it not necessary to differentiate the composition in the two cell compartments with a significant simplification of the cell design.

2.1 Materials and Methods

The analyses are carried out on three batches of pickled hides, stored in a conservative pickling solution, coming from young cow. They are supplied directly by the tannery BCN Conceria S.p.A. (Santa Croce sull'Arno, Italy). Despite the different batches do not show obvious differences, it is important to consider that the various pieces of hide are taken from different parts of the animal, which can impact on the dispersion of the results.

The solvents and reactants employed in analyses are: Acetic acid (CAS: 64-19-7, Fisher Scientific, UK), Acetone (CAS: 67-64-1, Carlo Erba Reagents, France), Chromosal B (CAS: 12336-95-7, Lanxess, Deutschland), Chrome FD (CAS: 12336-95-7, River Chimica Industriale, Italy) Pickel solution (% means w/w of product under 100 g of raw hide, 40 % of water, 7-8 % NaCl, 1 % NaClO₂, 0.5 % HCOOH, 1.3 % H₂SO₄; BCN Conceria, Italy), n-hexanol (CAS: 110-54-3, Carlo Erba Reagents, France), Sulphuric acid (CAS: 7664-93-9, Carlo Erba Reagents, France), Phosphoric acid (CAS: 7664-38-2, Carlo Erba Reagents, France), Potassium dichromate (CAS: 7778-50-9, Carlo Erba Reagents, France), dipotassium hydrogenphosphate (CAS: 16788-57-1, Carlo Erba Reagents, France), 1,5-diphenylcarbazine (CAS: 205-403-7, Carlo Erba Reagents, France), Sodium bicarbonate (CAS: 144-55-8, Solvay, Italy).

The study is mainly conducted using the electrochemical cell described above.

Once the tanning process is completed, the leather samples are treated following ISO standards for sample preparation and analyses required for data collection. The major instrumentation used for the analysis and quantification of chromium in leather and in solution are: in case of the total metal analysis, ICP-OES, in case of the hexavalent one, UV-Vis following ISO 11083:1994 and ISO 17075-1:2017, while for the shrinkage temperature, a shrinkage temperature meter is used, following ISO 3380:2015, and as a cross-analysis, Differential Scanning Calorimetry (DSC) is employed. Finally, for the microscopic study of the leather, a Scanning Electron Microscope Energy-dispersive X-ray spectroscopy (SEM-EDX) is used. In the end, the calculations regarding the exhaustion of the tanning solution were carried out considering the solution before and after the tanning process, while the measurement of chromium in the leather was made after the basification process.

3. Experimental results

More than 400 experimental tests were performed so far exploring the applied potential ($\Delta V = 0 \div 2 V$), solution concentration ($C_{L,Cr}^0 = 700 \div 40,000 \text{ mg/L}$), process time ($t = 30 \div 2400 \text{ s}$), solution recirculation flow rate ($Q_L = 5 \div 40 \text{ mL/min}$). The reference recipe used a bath concentration with Chromosal B at 8 %, a recirculation flow rate $Q_L = 10 \text{ mL/min}$ and an applied potential $\Delta V = 1 V$. After, the tanned leather was basified for 1 h at $pH = 3.6$ and then let rest for 12 h before mechanically and chemically test it. The chromium content in the leather Γ_i was both directly measured on the final product and through the variation of solution composition, i.e., $V_L(C_{L,Cr}^0 - C_{L,Cr}) = m_p \Gamma_i$, being m_p the mass of the sample.

Figure 3 shows the comparison with the same exposure time and bath composition of the same leather in the absence and presence of an applied electric field. It can be easily seen the difference in aspect chromium penetrated into the hide by the different blue color. To confirm the visual appearance, the leather tanned with the application of the electric field was subjected to SEM-EDX analysis, to visualize the Cr profile along the leather thickness. It can be observed the almost uniform concentration profile within the leather thickness demonstrating the high quality of the penetration.

For sake of the available space, we will here discuss mainly the effect of the electric field on the tanning at constant bath composition. Bath concentration and applied potential are the real effective process parameter. As it can be easily forecasted the influence of the recirculation flow rate is almost negligible.

As shown in Figure 4(a), the increase of the applied voltage increases the speed of the tanning process in an almost monotone manner. Tests performed by an applied electric potential showed almost the same asymptotic concentration, e.g, about $18,000 \text{ mg/kg}$, value that primarily depends on the concentration of the tanning bath. The applied voltage directly influences the time necessary to reach asymptotic value. From a macroscopic point of view, only the application of about $1 V$ leads to a full tanning in about 2 min . It is relevant to consider that a typical tanning time approaching the 24 h .

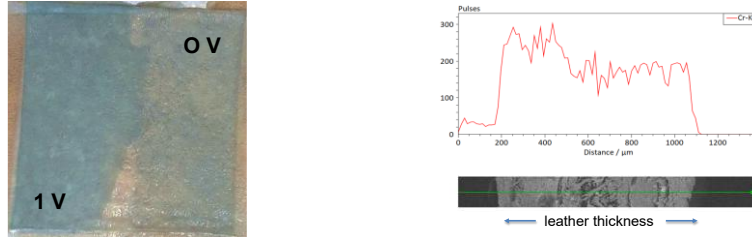


Figure 3. (left) same leather exposed and not the electric field under the reference recipes for an exposure of 300 s; (right) Cr profile within the leather thickness measure by SEM-EDX

4. Modelling

The total amount of chromium ions in leather is the sum of that contained in the macropores and that linked with collagen. Being ε_p the volumetric fraction of macropores and $\rho_p = (1 - \varepsilon_p)\rho_c$ the apparent density of leather, the total concentration (in mol/m^3) is $C_{Cr}^{tot} = \varepsilon_p C_{p,Cr} + \rho_p \Gamma_{Cr}$. The amount of the chromium linked to collagen is directly proportional to the concentration in the macropores with a behaviour similar to an adsorption isotherm with a saturation value Γ_{Cr}^∞ :

$$\Gamma_{Cr} = \Gamma_{Cr}^\infty \frac{b_{Cr} C_{p,Cr}}{1 + b_{Cr} C_{p,Cr} + b_H C_{p,H}} = \Gamma_{Cr}^\infty \frac{b_{Cr} C_{p,Cr}}{1 + b_{Cr} C_{p,Cr} + b_H 10^{-pH}} \approx K_{eq} C_{p,Cr} \approx \frac{d\Gamma}{dC_{p,Cr}} C_{p,Cr} \quad (1)$$

where Γ_{Cr} , b_{Cr} and $C_{p,Cr}$ are the adsorbed concentration (mg/kg), the adsorption constant (m^3/kg) and the concentration in the liquid phase contained in the macropores (mg/m^3), respectively. As a first approximation, to obtain analytical solutions the adsorption isotherm can be also linearized as shown in eq. (1).

The model was derived under the approximation of linear drop of electric potential V within leather (Ohm's law), with negligible decay in solutions:

$$\frac{\partial V}{\partial x} = \frac{j}{\sigma_p} \approx \frac{\Delta V_p}{L_p} \quad \text{and} \quad \frac{\partial^2 V}{\partial x^2} = 0 \quad (2)$$

In not dimensional spatial coordinates within leather $z = x/L_p$, $z = [0,1]$ and introducing the characteristic times for migration τ_M (i.e., the transport under the effect of electric potential) and for diffusion τ_D (i.e., the transport under the effect of concentration gradient) the mass conservation equation within the leather pores takes the form:

$$\frac{\partial C_{p,Cr}}{\partial t} = \frac{1}{\tau_D} \frac{\partial^2 C_{p,Cr}}{\partial z^2} + \frac{1}{\tau_M} \frac{\partial C_{p,Cr}}{\partial z} \quad (3)$$

$$\tau_D = \frac{L_p^2 \tau_p (\varepsilon_p + \rho_p K_{eq})}{\varepsilon_p D_i} \quad (4)$$

$$\tau_M = \frac{L_p (\varepsilon_p + \rho_p K_{eq}) \sigma_p}{z F \mu_i} \frac{j}{j} = \frac{L_p (\varepsilon_p + \rho_p K_{eq}) L_p}{z F \mu_i} \frac{L_p}{\Delta V_p} \quad (5)$$

With the initial condition $C_{p,Cr}(0, z) = 0$ and the boundary conditions (constant in time as first approximation) $C_{p,Cr}(0, t) = C_{0,Cr}$, that correspond to the solution concentrations in the anodic and cathodic compartments, assumed the same by the effect of the external recirculation. About diffusivities, typical values are $D_{Cr} = 1 \cdot 10^{-9} \text{ m}^2/\text{s}$ and $D_H = 1 \cdot 10^{-7} \text{ m}^2/\text{s}$ (Sathish et al., 2019). Thus, the penetration of hydrogen is significantly faster than that of chromium. It is convenient to verify the negligible relevance of diffusion with respect migration by the comparison of the two characteristic times:

$$\frac{\tau_D}{\tau_M} = \frac{L_p^2 \tau_p \Delta V_p}{\varepsilon_p D_i L_p^2} \frac{z F \mu_i}{j} \approx \frac{\tau_p z F \mu_i}{\varepsilon_p D_i} \Delta V_p \approx \frac{\tau_p z F}{\varepsilon_p R T} \Delta V_p \approx \frac{96500 \cdot 10}{0.3 \cdot 8.313 \cdot 300} \Delta V_p \approx 1300 \Delta V_p \quad (6)$$

It clearly appears that diffusion has characteristic times 3 orders of magnitude higher than those of migration even with applied potentials of the order of 1 V. This is precisely the reference value because, as already pointed out, we must avoid the electrolysis of water and the oxidation of $Cr(III)$ to $Cr(VI)$. Accordingly, it is not necessary to differentiate the composition in the two cell compartments with a significant simplification of the cell design.

Under these approximations it is possible to obtain an analytical solution through the method of characteristics for the simplified version of eq. (3) (Polyanin, 2002):

$$\frac{\partial C_{p,Cr}}{\partial t} = \frac{1}{\tau_M} \frac{\partial C_{p,Cr}}{\partial z} \quad (7)$$

that is $C_{p,Cr} \approx C_{L,Cr}$ at $t \approx \tau_M$, where, for the process conditions adopted here:

$$\tau_M = \frac{L_p(\varepsilon_p + \rho_p K_{eq})}{zF\mu_i} \frac{L}{\Delta V_p} \approx \frac{L_p^2(\varepsilon_p + \rho_p K_{eq})}{zFD_i} \frac{RT}{\Delta V_p} \approx \frac{174}{\Delta V_p} \text{ s} \quad (8)$$

The good fit about the migration time by eq. (8) can be seen in Figure 4(b).

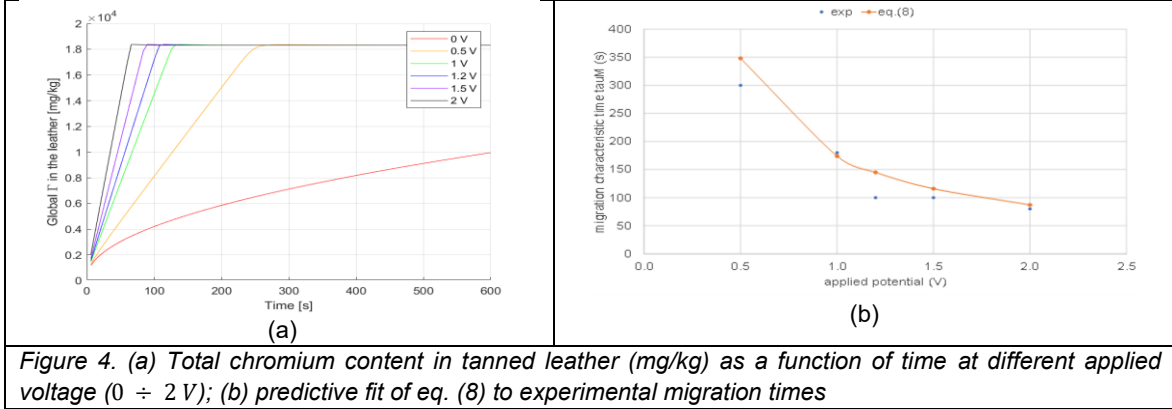


Figure 4. (a) Total chromium content in tanned leather (mg/kg) as a function of time at different applied voltage (0 ÷ 2 V); (b) predictive fit of eq. (8) to experimental migration times

5. Conclusions

This work demonstrated the great innovation of a tanning process sustained by the application of an electric field. The main conclusions that can be drawn from the experimental point of view are:

- it is confirmed the possibility to run a very fast tanning process, in the order of about 500 times lower, leading to a tanned leather with a chromium content even greater than that of conventional processes;
- the process is intrinsically safe because the lower voltages and consequently no risk of H_2 development and no oxidation to toxic $Cr(VI)$;
- it is confirmed the unidirectional ion penetrations from anode to cathode

All these aspects are confirmed by the preliminary process modelling:

- Short time process, below 2 min;
- Asymptotic $Cr(III)$ in leather controlled by $Cr(III)$ in tanning bath;
- Tanning time controlled by $\Delta V/L_p$
- Negligible influence of Q_L

Accordingly, these results are the basis to start the design of an industrial tanning cell where the leather is continuously fed to the machine and with a residence time in the order of 2 min.

Considering the necessary specific power obtained in the laboratory $P_W^s = 0.02 \div 1.20 \text{ W/m}^2$, the continuous cell must be powered by a power between $P_W = BL_{el}P_W^s$ and $P_W^s = 0.01 \div 0.6 \text{ W}$, confirming the negligible electrical consumption, in the maximum order of one hundredth of a kWh per single skin.

Nomenclature

b_{Cr} – Cr adsorption constant in leather, [m^3/kg]	Γ – Cr adsorbed in leather, [mg/kg]
$C_{p,Cr}$ – $[Cr]$ in the liquid phase contained in the macropores, [mg/L]	t – process time for the experiment, s
$C_{L,Cr}^0$ – $[Cr]$ in solution at time 0, [mg/L]	m_p – hide weight, [kg]
ρ_c – collagen apparent density, [kg/m^3]	ρ_p – hide apparent density, [kg/m^3]
Q_L – recirculation flow rate of tanning solution, [mL/min]	$C_{p,Cr}^{tot}$ – final $[Cr]$ in leather, [mg/m^3]
Γ^∞ – saturation of Cr adsorbed in leather, [mg/kg]	ΔV – standard potential, [V]
V_L – tanning solution volume, [L]	ε_p – macroporosity, []
$C_{L,Cr}$ – $[Cr]$ in tanning solution at the end of the process, [mg/L]	V – electric potential, [V]
b_H – H adsorption constant in leather, [m^3/kg]	x – cross-sectional dimension, [mm]

$C_{p,H}$ – [H] in the liquid phase contained in the macropores, [mol/L]	j – current density, [A/m ²]
K_{eq} – adsorption equilibrium constant, [m ³ /kg]	σ_p – leather electric conductivity, [S/m]
ΔV_p – potential difference measured on leather [V]	L_p – leather length [mm]
z – not dimensional coordinate, [0,1]	τ_M – migration time [s]
τ_p – tortuosity, []	τ_D – diffusion time [s]
D_i – diffusivity, [m ² /s]	μ_i – diffusion time [s]

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