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Management of tannery wastewaters: treatment of spent chrome tanning bath and vegetable tanning effluents

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ABSTRACT

In this work, a chain of treatment processes was proposed and described in order to reach better management of mineral and vegetable tannery wastewaters. First, chromium was precipitated from the spent chrome tanning bath by sodium hydroxide (NaOH) and then reformulated to form a complex of basic chromium sulfate which was tested successfully in mineral tanning process. On the other hand, the supernatant recovered after precipitation of chromium with NaOH was used to dilute vegetable tanning wastewaters characterized by a high concentration of polyphenols (about 2,574 mg/L). Diluted effluent was then treated by liming and tangential microfiltration using a ceramic membrane based on alumina with a nominal pore size of 100 nm and a average water permeability of 276 $L/h\,m^2$ bar. The tests revealed a very high efficiency of the combined processes dilution−liming−microfiltration. Treatment developed can work continuously and leads to a quasi-complete removal of polyphenolic compounds and turbidity from feed. The chemical oxygen demand (COD) of vegetable tanning effluent was reduced by 86−87%.

Keywords: Tannery wastewaters; Treatment; Chromium; Vegetable tannins; Liming; Microfiltration

1. Introduction

In leather industry, the transformation of the raw hide into leather requires different mechanical and chemical treatments. The tanning process can be divided into three main phases: beamhouse, tanning, and finishing. The beamhouse process normally accounts for about 40% of wastewater volume in a tannery [1]. In general, the beamhouse phase includes soaking (first process used to rehydrate and wash the hides or skins), liming (treatment with sulfides and lime milk for unhairing), washing (rinse with water and sodium bisulfide), deliming (lime removal with mineral or organic acids or acid salts), bating (enzymatic treatment to complete the removal of epiderm

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residues and more or less completely destroy the elastic fibers), and pickling (acidification in order to permit the penetration of tanning material) [2]. Chrome chemicals and vegetable extracts are the two substances currently used in tanning processes. In conventional chrome tanning processes, chromium salts are used to obtain leather which resists the boiling test [3]. Chrome tanning is currently the preferred technique being more rapid process for leather production. It is reported that 90% of all global production of tanned leathers is tanned using chromium sulfates [4]. Vegetable tanning, an older and more traditional tanning method, utilizes tannins which are natural compounds common in higher plants and brown algae. They are usually defined as water-soluble polyphenolic substances that have high molecular mass. At present, vegetable tanning is generally used for the manufacture of heavy leather [3].

Leather processing involves a series of water intensive batch processes, which are carried out in drums. A considerable portion of the offered tanning agents is neither bound nor incorporated in the hide tissue and as a result passes into the wastewater. Effluents coming from different operations of tannery contain high concentrations of organic and inorganic substances causing significant polluting phenomena. The more and more strict regulations in terms of environmental protection urge the leather industry to investigate on new strategies for the recovery and recycle of chemicals and by-products coming from the working cycle [5].

Different techniques have been proposed by several researchers to clean up tannery effluents. Refling [6] proposed a method based on a physicochemical pretreatment consisting of three phases: injection of lime and alumina combined with a step of electroflotation, followed by biological treatment. The effluents of liming process were treated by Bouzid [7] using two methods: a biological purification and treatment by electrochemical oxidation. Another method of treatment, based on the precipitation of chromium in tannery wastewater, was described by Landgrave [8]. The reduction of the toxicity of tannery effluents by coagulation flocculation was studied by Lofrano et al. [9] and Song et al. [10]. Electrochemical processes such as electrocoagulation has also been found effective and useful for tannery wastewater treatment [11]. Reuse of pickling wastewater after treating it electrochemically has been studied by Sundarapandivan et al. [12]. Pickling wastewater has been neutralized to pH 7.0 and subjected to electrooxidation using graphite electrodes. In order to comply with discharge standards, an advanced oxidation processes and activated carbon adsorption were applied by Tünay et al. [13] to the biologically treated leather tanning effluents. Treatment of tannery effluent through ozonation was investigated by Preethi et al. [14]. The influence of parameters such as influent pH, ozone flow rate, and initial effluent concentration on ozonation efficiency was examined. A maximum of COD removal efficiency of 92% has been achieved under optimum operating conditions. The removal of three most commonly used dyes in leather industry, viz. acid, direct, and metal complex dyes, by adsorption onto calcium alginate beads was studied by Aravindhan et al. [15] in dynamic batch mode. In order to minimize the pollution of tannery wastewaters, some authors propose the adoption of membrane technologies. For example, Cassano et al. [16] have experimentally studied the treatment of the unhairing, pickling, and chromium tanning effluents by membranes (UF, RO, and their combination). The use of nanofiltration for pickling and chromium tanning effluents was evaluated by Galiana-Aleixandre et al. [17] to minimize the sulfate ions concentration in the global wastewaters. For water reuse, Fababuj-Roger et al. [18] have evaluated a tannery wastewater treatment consisting of a physical–chemical process, filtration, ultrafiltration, and reverse osmosis. To reduce the city freshwater consumption by the tanners, Roig et al. [19] have studied the treatment of tannery wastewaters in order to be reutilized in tannery leather making processes. Three consecutive stages were employed: pretreatment by sand filtration, ultrafiltration, and then reverse osmosis. Catarino et al. [2] have studied the decontamination of tannery wastewaters using different unit operations to select the best treatment sequences. Textile membrane filtration, microfiltration, and ultrafiltration were complemented by screening, flocculation, or flotation operations. The use of membrane technology showed to be promising in removing organic pollutants and allowing the reuse of water and chemicals in the tannery process [2].

In this work, the management of mineral and vegetable tanning wastewaters was studied. First, the precipitation of chromium from spent chrome tanning bath and its reformulation in order to be recycled were investigated. Secondly, we have studied the effectiveness of combined processes liming–microfiltration for the removal of turbidity and total polyphenols from vegetable tanning effluent after its dilution with supernatant of precipitation process. The effect of the suggested processes on the COD reduction was also evaluated.

2. Materials and methods

2.1. Tannery wastewaters

Spent chrome tanning bath and vegetable tanning effluent were collected from a tannery plant

(Mohammedia, Morocco). Wastewaters were collected directly from tanning drums.

2.2. Hides samples

Pickled cattle hides, prepared by soaking, liming, deliming–bating, and pickling according to the classical processes, were collected from the same tannery and stored at cold temperature in sacks of plastic before the tanning experiments. Pickled hides are used as raw material for wet-blue leather production which, in turn, is used as a raw material for crust leather production.

2.3. Apparatus and reagents

ICP-OES Optima 5300 DV Software WinLab32 from Perkin Elmer (Norwalk CT, USA) was used for analysis employing the following experimental conditions. An argon plasma power of 1,300 KW, a plasmogen gas flow of 15.0 L/min, an auxiliary gas flow of 0.2 L/min, a sample flow rate of 1.1 mL/min, and a nebulizer gas flow of 0.8 L/min, were employed to introduce the samples and made the excitation of their mineral components, using a stabilization time of 5 s and a rinse flow of 60 mL/min. Three replicates of peak area measurements were employed for each assayed solution, being used axial plasma view in all the cases except for the measurement of Ca, K, Li, Mg, Na, and Sr, for which radial view was selected. To prepare calibration standards, it was used a series of monoelemental standards for AA, of Ca, K, Mg, Na, 1,000 ppm, from Scharlau (Barcelona, Spain) which were mixed with an ICP multielemental calibration standard solution VIII, with 26 elements (Al, As, Ba, Be, Bi, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, Se, Na, Sr, Tl, Ti, V, and Zn) at a concentration of 100 ppm with 5% acid from Scharlau (Sentmenat, Spain). Nitric acid 69% trace analysis grade from Scharlau was employed to adjust pH of samples. The range of calibration was 0.05–2 ppm for trace elements and for major elements (Ca, Na, K, and Mg) from 0.05 to 75 ppm. Samples were directly analyzed with ICP-OES, without internal standard. Concentrations found was calculated from net intensity and corrected with blank of calibration and divided by the slope of calibration.

A Metrohm IC Chromatograph (Herisau, Switzerland) equipment with a Metrosep A Supp 5 (250/40 mm) column were used to analyze inorganic anions (chlorides and sulphates). The chromatographic data were processed by use of Metrohm IC Cap software operated under windows XP (32 bit). The column was operated at room temperature. The mobile phase used for IC was a 10 mM sodium carbonate–1.0 mM sodium bicarbonate. A flow rate of 1.0 mL/min, a 14.5 MPa working pressure, and an injection volume of 20 μL were employed. A suppressed conductivity detector (Metrohm 819 IC) was used for the determinations.

The other main analyzed parameters were COD, total polyphenols, turbidity, pH, and conductivity. The COD assay was performed according to the operating conditions described in the standardized experimental norm NF T 90-101 [20]. Turbidity was measured using a device (TN-100/T-100, Eutech Instruments). The pH and conductivity were measured directly by the use of a pH meter (WTW series, inolabo pH 730) and a conductivity meter model (HANNA Instruments EC 214 conductivity meter), respectively.

The Folin–Ciocalteu method was applied to determine the concentration of tannins (total polyphenols). The reagent consists of a mixture of phosphomolybdic acid and phosphotungstic acid which are reduced by phenols to their respective oxides in alkaline medium, resulting in the formation of a blue color. Calibration was carried out using gallic acid. In this work, the developed coloration was measured at 760 nm using a spectrometer (model: Visible V-1200, MAPADA). The assay protocol applied in this study is described by Marigo [21]. Being very sensitive, the dosage requires a prior dilution of samples.

All chemical reagents used were of analytical reagent grade and all solutions were prepared in distilled water. High purity water, with a resistivity of 18 Mcm, was obtained from a Milli-Q water purifier system (Bedford, USA). All laboratory material was carefully cleaned before use by first washing with a neutral detergent solution and then with distilled water.

2.4. Precipitation of chromium

The heavy metal contents of wastewaters can be effectively removed to acceptable levels by precipitating the metal in an insoluble form. Precipitation by hydroxide formation is the most common heavy metal precipitation method. The precipitation typically follows the reaction:

$$M^{n+} + n\mathrm{OH}^{-} \rightarrow M(\mathrm{OH})_n \tag{1}$$

In this work, precipitation of trivalent chromium present in spent chrome tanning bath as $Cr(OH)_3$ was carried out by adding the most common caustics used to raise the pH: sodium hydroxide NaOH and calcium hydroxide or lime $Ca(OH)_2$. The pH of the effluent was set at 9 to ensure complete precipitation of chromium. The alkaline agent (NaOH or $Ca(OH)_2$)

was added slowly and gradually with moderate stirring to homogenize the mixture. When the pH of precipitation is reached, the resulting suspension was homogenized and the decantation of formed precipitates was studied by the use of a 2 liters tall transparent cylinder. The clear fluid interface with the slurry was then measured at different times till the level falls and all particles settle at the bottom as sludge.

2.5. Preparation of tanning chrome liquor

Reformulation of recovered chromium consists in dissolving the cake of chromium hydroxide $Cr(OH)_3$ using sulfuric acid to form chromium sulfate $Cr_2(SO_4)_3$. Basification with sodium hydroxide is then performed to produce the basic chromium sulfate $Cr_2(OH)_2(SO_4)_2$ with a basicity of 33°S.

2.6. Tanning process

Experiments were carried out to test the tanning capability of the liquor prepared from recovered chromium. Pieces of cattle hides were tanned using commercial chrome tanning agent (Chromosal B, Bayer) and recycled chrome tanning agent. Chromosal B is widely used chrome tanning salt. The underlying salt, Chromosal B, is a basic chrome sulfate with 26% Cr_2O_3 content approximately. The tanning processes were done with a certain volume of tanning float containing 2.08% (w/w) Cr_2O_3. Sodium chloride (NaCl) was added to tanning float to reach density of 6°B. NaCl salt was used in order to prevent the pelts from swelling that would otherwise be induced by the use of acids. In the absence of this salt, the differences in charges caused by acids as they penetrate the structure would cause strong osmotic pressure and this would irreversibly damage the hide or skin structure. Tests were carried out in presence of sodium formate HCOONa 0.5% (w/w). After 2 h of contact, basification was done by the use of sodium carbonate Na_2CO_3 during 3 h to form oxolation chromium (III) complexes. The basification process was stopped at pH 4. All the above percentages were based on weigh of limed hides.

After tanning, the quality of obtained leather (wet blue) was evaluated. Samples were analyzed for Cr_2O_3 [22], shrinkage temperature [22], and apparent quality tests such as penetration of chromium into skins, coloring, and firmness.

2.7. Filtration tests

Tangential filtration tests were performed on laboratory scale filtration pilot using a recycling configuration (see Fig. 1). It was equipped with an adjustable out-flow pump, a thermostatic feed tank, and a membrane module of 15 cm length. The filtration area developed by the membrane is about 32.97 cm^2. Effluent was fed into the membrane module by means of gear rotate pump. Inlet flow rate was measured by the flow meter. A valve was used to control the pressure in the system.

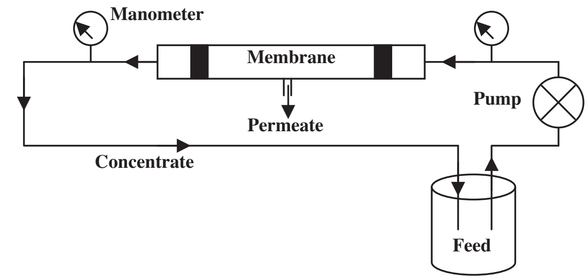

Fig. 1. Microfiltration pilot plant scheme.

A commercial ceramic membrane (Cerasiv) made from alumina was used. Its characteristics are summarized in Table 1. The membrane was conditioned by immersion in pure deionized water for a minimum of 24 h before filtration tests to obtain a stabilized flux right from the beginning of the experiment.

The permeate volume was measured during the separation process. The permeate flux J_v was calculated by dividing the permeate volume by the product of effective membrane area and the sampling time according to following equation:

$$J_{\mathrm{v}}(\mathrm{L/h\ m^2}) = \frac{\text{Permeate volume collected(L)}}{\text{Membrane area (m}^2) \times \text{Time(h)}} \tag{2}$$

The pollutants rejection R was determined by the classical relation of Eq. (3), where C_{p} is the concentration in permeate and C_{f} the concentration in the feed. The above formula was used to determine the efficiency of polyphenols and turbidity removal.

Table 1
Characteristics of ceramic membrane used through this study

Nature	Alumina-based ceramic
Pore size	100 nm
Internal diameter	7 mm
External diameter	10 mm
Filtration area	32.97 cm^2
Form	Tubular
Number of channels	1
Length	15 cm

$$R\ (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \qquad (3)$$

3. Results and discussion

3.1. Physicochemical characteristics of tannery wastewaters

The results presented in Table 2 revealed that the spent chrome tanning baths are acidic (pH = 2.8). The electrical conductivity of these baths can reach 48 ms/cm. This very high value is mainly due to the use of large amounts of salts especially sodium chloride (NaCl) which is often used to increase the density of tanning bath in order to avoid acid swelling of skin. The residual chrome tanning waste contains also high amounts of sulfate (29.40 g/L) and chloride (13.4 g/L). High levels of sulfates are due, in particular, to the use of basic chromium sulfate as a tanning agent. Chloride in tannery effluents usually originates from the large quantities of common salt (such as NaCl) used in hide and skin preservations, and the conventional acid/salt pickling process. Being both highly soluble and stable, the salt is unaffected by normal effluent treatment. Effluents of chrome tanning process have a COD of about 4,840 mg/L, and the

Table 2
Physicochemical characteristics of tannery wastewaters and supernatant of alkaline treatment

Parameter	Spent chrome tanning bath	Vegetable tanning effluent	Supernatant (NaOH)	Supernatant Ca $(OH)_2$
pH	2.8	3.5	9	9
Conductivity (ms/cm)	47.8	53.4	82.9	56.5
Turbidity (NTU)	269	446	7.03	3.13
COD (mg/L)	4,840	60,016	2,400	1,452
Total polyphenols (mg/L)	–	2,574.26	–	–
Sulfates (g/L)	29.40	14.60	26.70	27.00
Chlorides (g/L)	13.40	22.50	13.14	13.80
Al (mg/L)	1.35	5.63	0.04	0.05
B (mg/L)	2.53	0.83	nd[a]	0.01
Ba (mg/L)	0.04	0.06	nd[a]	nd[a]
Be (mg/L)	nd[a]	nd[a]	nd[a]	nd[a]
Bi (mg/L)	8.67	nd[a]	0.01	0.01
Ca (mg/L)	344.06	758.39	10.43	68.70
Cd (mg/L)	nd[a]	nd[a]	nd[a]	nd[a]
Co (mg/L)	2.14	0.05	nd[a]	nd[a]
Cr (mg/L)	6176.97	4.95	0.03	0.15
Cu (mg/L)	nd[a]	nd[a]	nd[a]	nd[a]
Fe (mg/L)	1.77	30.20	nd[a]	nd[a]
K (mg/L)	43.50	1,600.76	4.64	4.78
Li (mg/L)	0.04	0.14	0.01	0.01
Mg (mg/L)	150.54	622.85	1.80	0.33
Mn (mg/L)	0.15	11.89	nd[a]	nd[a]
Mo (mg/L)	nd[a]	nd[a]	nd[a]	nd[a]
Na (mg/L)	25,356.62	15,574.71	34,967.85	25,387.12
Ni (mg/L)	nd[a]	2.55	nd[a]	nd[a]
Pb (mg/L)	0.89	0.21	nd[a]	nd[a]
Se (mg/L)	nd[a]	nd[a]	nd[a]	nd[a]
Sr (mg/L)	3.22	4.58	0.06	0.19
Ti (mg/L)	nd[a]	nd[a]	nd[a]	nd[a]
Tl (mg/L)	2.36	nd[a]	0.01	0.01
V (mg/L)	1.92	nd[a]	nd[a]	nd[a]
Zn (mg/L)	0.86	2.85	nd[a]	nd[a]

[a]Not detected.

turbidity was measured to be up to 269 NTU. The most striking feature of this spent bath is its high chromium content, which is approximately 6,177 mg/L. The chromium content in the effluent will be transmitted in the environment where it can undergo oxidation reactions and consequently be converted to hexavalent chromium Cr(VI) which is the most toxic form. The physicochemical characterization shows that the values of several parameters analyzed exceed generally the limit values of industrial discharges [23]. Therefore, the composition of the spent tanning bath acknowledges the urgent need for proper treatment of these wastewaters.

In the case of vegetable tanning effluent, the results of physicochemical analysis show that the average pH is also acidic (pH = 3.5). The recorded value of the turbidity of this effluent (446 NTU) is greater than that observed in the case of wastewater of mineral tanning. Electrical conductivity that reflects the concentration of ionic medium is about 53.4 ms/cm, this value is due to the presence of soluble salts such as sodium chloride in water. The important value of the COD (60 016 mg/L) is due to the presence of a very high amount of vegetable tannins. The total polyphenols content is 2574.26 mg/L. The sulfate and chloride contents are 14.6 g/L and 22.5 g/L, respectively (see Table 2). As with the release of chrome tanning effluent, the values of the parameters analyzed exceed the discharge limit values [23].

3.2. Separation of chromium and characterization of supernatants

Decantation of chromium hydroxide, formed at pH 9, was carried out in a 2 liters tall transparent cylinder. Figs. 2 and 3 show the evolution of the clear fluid interface with the slurry at different times. As it can be seen, the precipitates start settling at a uniform velocity which is normally a function of the local solids concentration. The velocity of settling is about 96.96×10^{-3} m/h and 1.296×10^{-3} m/h in the case of precipitates obtained with lime and caustic soda, respectively. The important settling velocity measured in the case of lime can be explained by its action as coagulating during the precipitation/settling process. In the case of chromium hydroxide sludge obtained during the precipitation of chromium with NaOH, the use of a filter press after decantation is highly recommended to ensure maximal removal of water trapped in formed sludge.

The comparative study between the physicochemical characteristics of the supernatants, obtained by the use of caustic soda and lime, shows a difference in the conductivity which is about 83 ms/cm and 57 ms/cm, respectively. The conductivity is high when sodium hydroxide is used as a chemical reagent precipitation because sodium remains in the supernatant after precipitation of chromium hydroxide. Table 2 reflects the effect of alkaline precipitation with NaOH and $Ca(OH)_2$ on the composition of chemical elements in supernatants recovered after sludge settling. The ICP-OES analysis shows a very significant reduction of the concentration of most metals especially chromium. The concentration of this element decreases from 6,177 mg/L to 0.03 mg/L and to 0.15 mg/L when the precipitation is made, respectively, with sodium

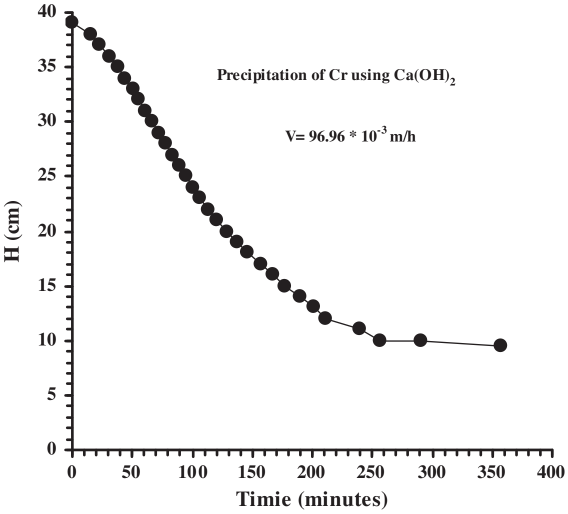

Fig. 2. Decantation as a function of time of the precipitate obtained by the use of lime.

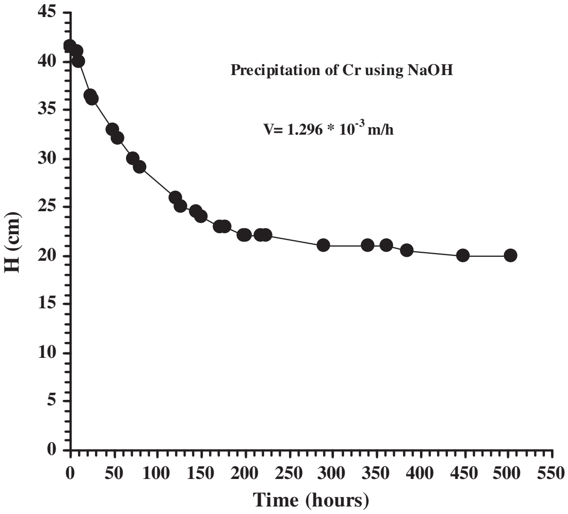

Fig. 3. Decantation as a function of time of the precipitate obtained by the use of caustic soda.

hydroxide and lime. There is, therefore, a quasi-complete elimination of the amount of chromium present in spent tanning chrome baths. On the other hand, the decline in chemical elements concentration can be explained by the formation of metal hydroxides according to the reaction of Equation 1. Analysis of supernatants by ICP-OES shows that residual concentrations of Al, Ba, Cd, Co, Cr, Cu, Pb, Mn, Ni, Se, Zn, and Fe are below those recommended for discharges. In the case of sodium (Na), the content of this element increases from 25 357 to 34 968 mg/L, after treatment of the effluent with sodium hydroxide, because sodium which is very soluble stills in the supernatant after settling.

3.3. Preparation of chrome tanning liquor

Chromium recovered as metal hydroxide $Cr(OH)_3$ has no tanning character. It should be reformulated to give a tanning product in the form of basic chromium sulfate $Cr_2(OH)_2(SO_4)_2$. To achieve this goal, the chrome cake obtained by alkaline precipitation using sodium hydroxide is dissolved by adding a well calculated amount of sulfuric acid. Then, a basification of the obtained chromium liquor is carried out by means of sodium hydroxide. The reformulation was performed taking into account the stoichiometry of the following reactions:

$$2Cr(OH)_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 6H_2O \quad (4)$$

$$Cr_2(SO_4)_3 + 2NaOH + 6H_2O \rightarrow Cr_2(OH)_2(SO_4)_2 + Na_2SO_4 + 6H_2O \quad (5)$$

Calculations show that 0.427 kg of sulfuric acid (H_2SO_4) and 0.116 kg of NaOH should be added to one kilogram of dry sludge containing 22.1% Cr_2O_3 (0.221 kg of chromium oxide). The liquor then obtained is stocked, its chrome content and basicity were adjusted before reuse in leather manufacture. The desired basicity is about 33°S.

3.4. Evaluation of recycled chrome tanning process

Pieces of cattle hides were chemically treated using two tanning liquors: the first is synthesized from precipitated chromium as described previously, and the second was prepared from Chromosal B according to the conventional method. The tanning capability of recycled chrome liquor was evaluated and compared to that of standard tanning agent. In order to show the effect of tanning operation on thermal stability of skins, we have studied the evolution of the retraction of the samples as a function of temperature. Retraction of leather (tanned skin) gradually heated in an aqueous medium was established by placing the leather for a minute at several temperatures ranging from ambient to 100°C. Fig. 4 shows that both recycled and commercial chrome tanning processes increase considerably the thermal resistance of skins in boiling water. Curves of Fig. 4 show that contraction of tanned leather is very low by comparing it to that of untanned hides. The shrinkage temperature is about 100°C in the case of two tanning chrome agents.

Results show that leathers obtained with reformulated chromium have a chromium oxide content of about 3.678%. This content is very similar to that determined in leathers obtained with the commercial tanning agent (3.565%). Apparent quality tests (see Table 3) revealed that the penetration of chromium into skins is good. The color of tanned skins is blue and the coloring is similar to that of the wet blue prepared using commercial chromium (Chromosal B). The tanned samples are also relatively firms than the limed hides. These results allow concluding that the quality of tanning with reformulated chromium is very satisfying. Therefore, the developed process would not only reduce toxic in tanning effluents but also provide quality leather and higher economic return.

3.5. Determination of membrane permeability

The measurement of the pure water permeability is conducted employing the permeability method using pure water as the medium. The pure water

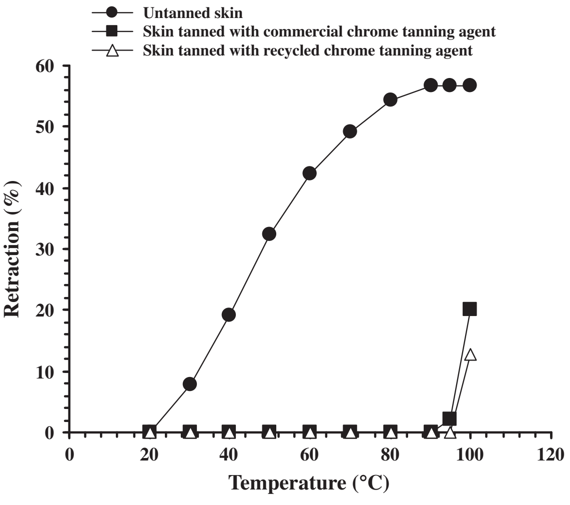

Fig. 4. Retraction of untanned and tanned skin vs. temperature.

Table 3
Characteristics and apparent quality of tanned skin

Parameter	Skin tanned with commercial chrome agent	Skin tanned with recycled chrome agent
Cr_2O_3 (%)	3.565	3.678
Shrinkage temperature (°C)	100	100
Penetration of tanning agent	Good	Good
Color	Blue	Blue
Firmness and consistency	+	+
General aspect	Correct	Correct

permeability is defined as the volume of water that passes through a membrane per unit time, per unit area, and per unit of transmembrane pressure. Permeability is obtained by measuring the flux at increasing pressures. This property indicates the effort required to generate permeate for a membrane and is an easy way to compare the working effectiveness of an employed membrane with its initial performance.

Alumina microfiltration membrane was first characterized by its water permeability. Fluxes are measured at different transmembrane pressures ranging from 0.3 to 1.8 bar. The effect of pressure on the flux for water is shown in Fig. 5. It can be observed that the stabilization of the water flux through the membrane takes approximately 20 min. Experiments show also that the water flux through the membrane depends on the applied pressure. As it can be seen, stabilized flux increases from 90.6 to 472.7 L/h.m^2 with an increase in working pressure from 0.3 to 1.8 bar (see Fig. 5). Flux can generally be described as a function of transmembrane pressure according to Darcy's law ($J_v = L_p \times \Delta P$), where J_v is volumetric flux (L/h m^2), L_p is hydraulic permeability of a membrane (L/h m^2 bar), and ΔP is transmembrane pressure (bar). The permeability constant L_p can easily be determined experimentally as the slope of a flux–pressure plot. As shown in Fig. 6, the pure water flux is a linear function of the pressure. The average membrane permeability determined using pure distilled water is 276 L/h m^2 bar (see Fig. 6). The alumina membrane is subsequently tested for the treatment of vegetable tanning effluents after dilution and liming. Dilution was carried out by the use of the supernatant obtained after precipitation of spent chrome tanning with caustic soda. All microfiltration experiments presented below were carried out at pressure 1 bar.

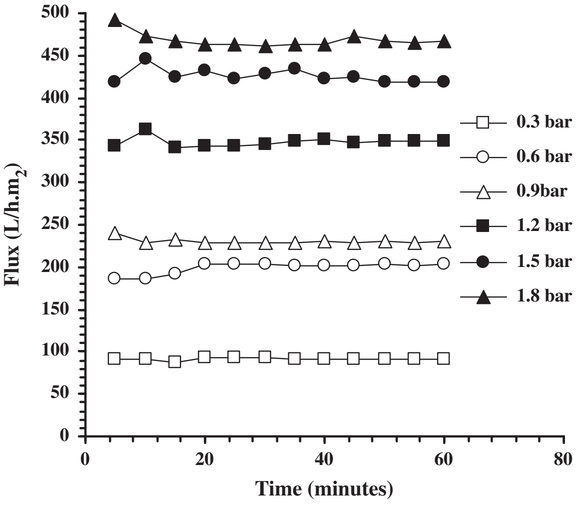

Fig. 5. Water flux vs. operating time.

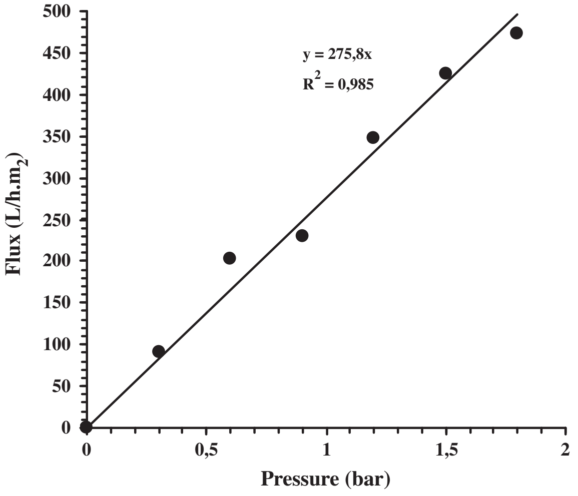

Fig. 6. Variation of water flux as a function of pressure.

3.6. *Coupling liming–crossflow microfiltration*

Vegetable tanning effluents have a high organic pollution load due to the presence of vegetable tannins. It is very difficult to treat vegetable tanning wastewater directly "without dilution" by the combined processes liming–microfiltration. The high concentration of organic pollutants in effluent requires high amount of lime and, therefore, the suspension becomes very difficult to be filtered. To facilitate their processing, the residual baths were diluted 10 times with the supernatant obtained from the precipitation of chromium with NaOH. This seems very feasible because the chrome tanning is currently the most practiced process, this leaves suggest that the used baths of mineral tanning are more abundant than vegetable tanning effluents.

Lime is commonly used in treatment to facilitate the settling of pollutants in urban and industrial effluents. In this work, we treated the intermediate effluent (residual vegetable tanning liquor diluted 10 times by the use of supernatant recovered after precipitation of chromium) by lime (2 g/liter of effluent). Lime reacts rapidly with soluble polyphenolic compounds and forms suspension which can be removed easily by microfiltration. The effluent was then filtered at a pressure of 1 bar through an alumina membrane microfiltration using the system previously described. The variation of permeate fluxes of water and effluent as a function of time is shown in Fig. 7. Permeate fluxes are low in comparison with those obtained with distilled water. This can be explained by the effect of contaminants which changes the dynamic proprieties of water as viscosity for example. Normally, the flux behavior through a membrane is totally different in the case of a pure solvent as in the case of a solution (solvent + solute). Generally, during the filtration of a solution through a membrane, an accumulation of solute in the vicinity of the membrane surface usually occurs under the effect of the pressure gradient.

The effectiveness of the proposed treatment was evaluated by determining the turbidity reduction rate and the total polyphenols removal efficiency. The results, presented in Figs. 8 and 9, demonstrate the capability of the combined treatments in removing pollutants from effluent. In fact, we found a complete disappearance of turbidity; this is due to the removal of colloids and color. By reporting the yields of treatment to raw and intermediate effluents, we have revealed that the removal rate of total polyphenols can reach 98% and 82%, respectively, hence the effectiveness of the proposed process of treatment which allows to purify continuously the effluents and to achieve very high levels of purification at a less ideal time.

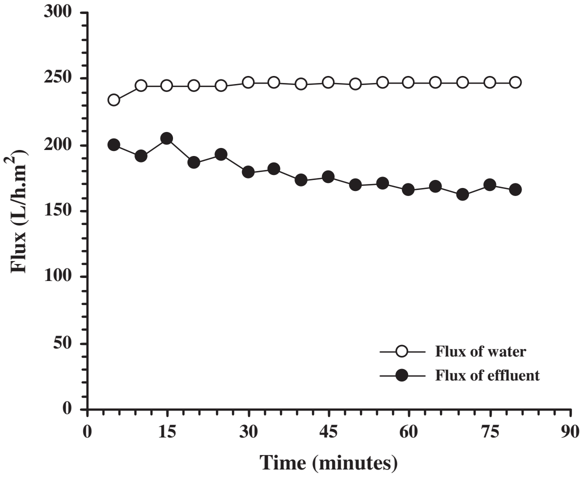

Fig. 7. Permeate flux of water and effluent as a function of operating time (pressure = 1 bar).

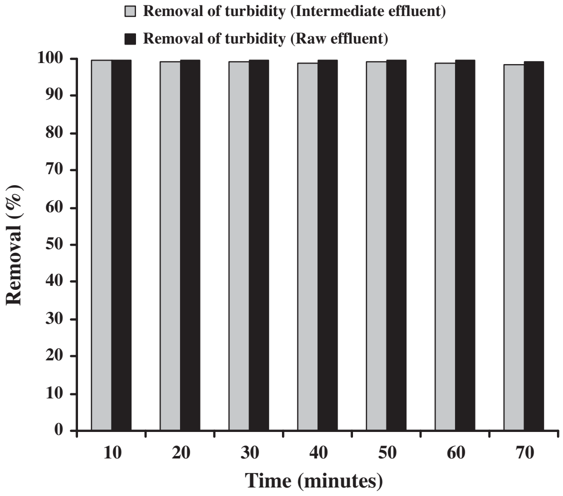

Fig. 8. Removal of turbidity as a function of operating time (pressure = 1 bar).

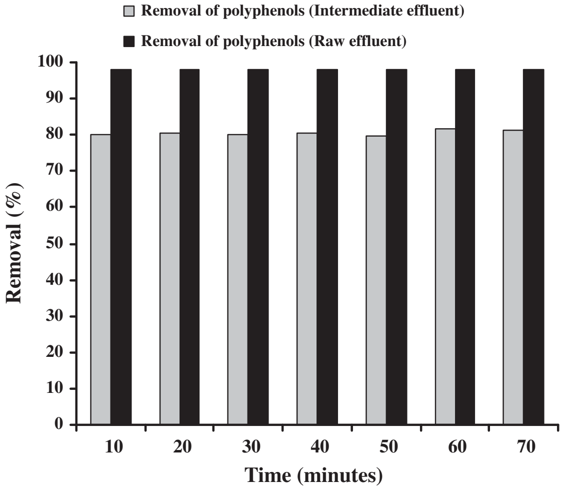

Fig. 9. Removal of polyphenols as a function of operating time (pressure = 1 bar).

In order to show the effect of the combined processes dilution–liming–microfiltration on reduction of pollutants in vegetable tanning wastewaters, permeates were collected and its COD was then analyzed. According to the obtained results, the treatment developed decreases considerably the COD concentration. The reduction of COD content can reach 86−87%.

Fig. 10 illustrates the overall stages of treatment proposed in this study. The main steps of the process are as follows:

(i) separation of chromium from spent tanning bath by insolubilization and precipitation as chromium hydroxide,
(ii) pumping chromium sludge to a filter press after settling,
(iii) reformulation of precipitated chromium by redissolution of the cake with sulfuric acid and adjustment of the basicity by adding sodium hydroxide,
(iv) recycling of reformulated chrome liquor in the tanning process,
(v) routing of the supernatant obtained to a storage tank to be recycled in the beamhouse section of tannery or for use in dilution of vegetable tanning effluent,
(vi) treatment of diluted vegetable tanning effluent by liming and crossflow microfiltration, and
(vii) recycling of permeates in the beamhouse section of tannery.

4. Conclusion

In this study, an integrated treatment scheme for better management of both spent chrome tanning bath and vegetable tanning effluent has been thoroughly investigated. Chromium was recovered in the form of metal hydroxide and was then reformulated to produce basic chromium sulfate which is a tanning agent. Its tanning capability was compared with that of commercial tanning agent. Obtained results allow us to conclude that there were no differences in the leather that had been tanned with either the commercial chromium or basic chromic sulfates prepared from precipitated chromium. On the other hand, the large volume

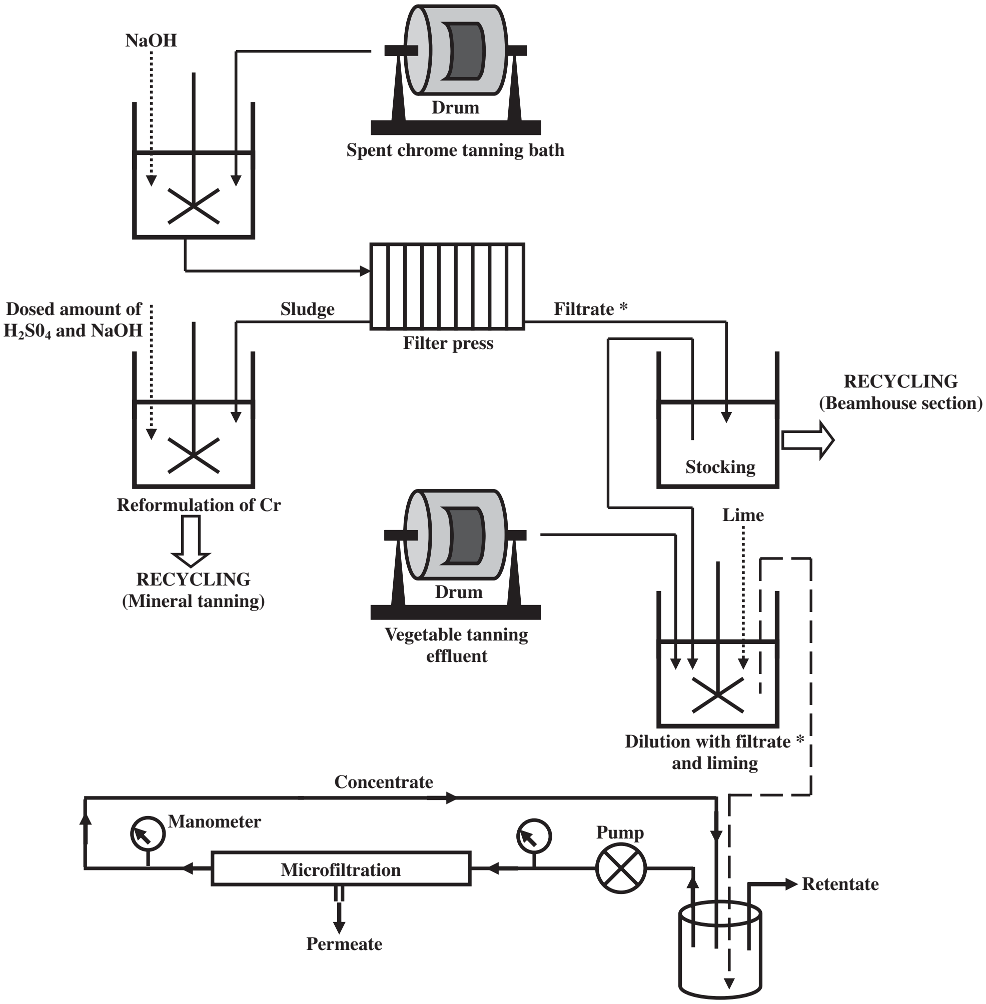

Fig. 10. Scheme of the proposed treatment processes.

of supernatant produced after alkaline precipitation of chromium and separation of cake was used to dilute vegetable tanning wastewaters.

Liming combined with crossflow microfiltration was successfully applied for the purification of vegetable tanning effluents after their dilution with the clear supernatant recovered after precipitation of chromium. The results showed the effectiveness of the treatment being studied and its usefulness for the cleanup of vegetable tanning wastewater. Tangential microfiltration process, operated at lower pressure (1 bar), was seen to remove turbidity from the feed completely. The elimination of total polyphenols from diluted tanning effluent is quasi-complete. The removal rate of polyphenolic compounds can reach 98%. Combined processes dilution–liming–microfiltration decreases considerably the COD concentration. The reduction of COD content can reach 86−87%.

This integrated treatment strategy has proven to be an effective treatment for highly polluted tanning wastewater. The main objectives of our later works are the recycling of supernatants of the alkaline precipitation and permeate of microfiltration in beamhouse operations, the treatment and valorization of microfiltration retentate, and the development of new treatment processes for the purification of other effluents of the tanning industry.

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