

Electrochemical treatment of spent tan bath solution for reuse

Amel Benhadji, Mourad Taleb Ahmed, Hayet Djelal and Rachida Maachi

ABSTRACT

A spent tanning bath contains high concentration of salts, chromium and protein. The treatment system for removal of chlorides or chromium from this effluent is expensive. In this context this waste has to be reused. Our study focuses on the application of advanced oxidation processes for protein removal present in a tanning bath. To improve the quality of the chromium tanning bath, two electrochemical processes (electrooxidation and peroxi-electrocoagulation process, PEP) are investigated in a batch reactor. The effects of operational parameters such as reactor configuration, current density and electrolysis time on chemical oxygen demand (COD) and protein removal efficiency are examined. Results indicated that under the optimum operating range for process, the COD and protein removal efficiency reached 53 and 100%, respectively. The optimum values are determined for the hybrid process (PEP) under $0.13 \text{ A}\cdot\text{cm}^{-2}$ over 2 h. The treated tanning bath is used as a tanning solution in leather processing. The influence of chromium salt dose, pH solution, stirring time and contact time on the leather characteristic is evaluated. The hides tanned after the addition of 0.25% of commercial chromium salt, at pH solution, leaving them stirring for 4 h with a contact time of 2 days, and showed good hydrothermal stability and physical characteristics of leather.

Key words | electrochemical process, organic compound, recirculation, spent chromium liquor, tanning

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INTRODUCTION

Chrome tanning produces leather better suited for various applications, particularly for the upper parts of boots and shoes, and requires less processing time than traditional vegetable tanning.

For each kg of hide processed, 35–40 L of water is used. This gives rise to two major problems for the leather industry: the availability of good quality water and the treatment of such large quantities of effluent. Tannery effluent contains high levels of organic materials, heavy metals including chromium, chloride, sulfide and other pollutants (Uberoi 2000).

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Furthermore, electrolytic chromium plating baths have a high concentration of chromium as dichromate owing to the high acidity of the system. Usual chromium concentration ranges between 110 and $130 \text{ g}\cdot\text{L}^{-1}$ of chromium (Torras *et al.* 2012). The metal finishing industry and chromium plant generate substantial quantities of liquid waste containing chromium (Sozhan *et al.* 2006; Vasudevan *et al.* 2007). However, the maximum contaminant level of total chromium in the effluent is set to be 2 mg L^{-1} in Algeria.

The long-term persistence of effluent metals has put adjacent environmental areas at risk (Zeshan *et al.* 2013). It is reported that a single tannery plant is capable of groundwater pollution over a radius of 7–8 km. The release of untreated tannery effluent causes extensive damage to the ground water, land stream, surface water, and air due to its toxic procedures and the organic nature of the hide (Aravindhan *et al.*

2004; Ramteke *et al.* 2010). Bhattacharya *et al.* (2016) assessed the toxic impacts of a composite effluent from the tannery industry, evaluated using the snail, *P. globosa*, as an aquatic model. The study revealed that the protein and carbohydrate content reduced largely in the whole body tissue, gonad as well as mantle tissues and a significant genotoxicity. The literature has identified a number of health risks related to the leather industry. Occupational cancers such as cancers of the nose, hematological disorders such as aplastic anemia and leukemia, neurological impairment, dermatological disorders and musculoskeletal problems are all health risks related to the leather industry. Chromium is known to cause contact dermatitis and eczema in susceptible individuals. In addition, chronic exposure to inorganic chromium may also result in impairment of immune functions in experimental systems (Mbbs *et al.* 2010).

In this context, new technologies have been investigated for the recovery of chemicals and water in order to avoid discharging these products into the environment. Chromium recovery from tanning exhausted baths represents a significant economical and environmental advantage for the leather industry (Kiliç *et al.* 2011). The measures adopted for minimizing chromium pollution should include the chrome recovery and reuse methods; high exhaustion chrome tanning or by chrome recycling and reuse methods (Kanagaraj *et al.* 2008).

Many researchers have adopted various approaches to recover chromium from spent tanning baths. With a chemical precipitation technique the efficient removal of Cr from wastewater samples reached values higher than 99%.

An electrochemically assisted coagulation for the removal of chromium from water has been studied using zinc or magnesium as anode and galvanized iron as cathode. The results showed that the optimum Fe removal efficiency of 95% was achieved at a current density of $0.2 \text{ A}\cdot\text{dm}^{-2}$, at a pH of 7.0 (Vasudevan *et al.* 2010; Vasudevan & Lakshmi 2011). The use of Al-Zn-In as anode material allows a removal efficiency of 98.2% (Vasudevan *et al.* 2011).

In the electrocoagulation tests, the best removal efficiency of Cr is 97.76% with Al electrodes (3.0 V for 110 min), 69.91% with Cu electrodes (2.0 V for 100 min) and 90.27% with Fe electrodes (2.5 V for 100 min). In tanning tests with recovered chromium, the hides tanned with Cr recovered by chemical precipitation and by

electrocoagulation with Cu electrodes showed the minimum required amount of Cr_2O_3 for the tanning technical specifications (2.5%) (Mella *et al.* 2015).

In any case, the residual tan bath cannot be reused directly, because its characteristics (e.g. higher amount of neutral salts and organic components) are not appropriate to begin the tanning process because the leather obtained would present a poor appearance and would not meet the required physical properties.

One available treatment technology of these processes widely used in recent years is advanced oxidation processes (AOPs) (Selvabharathi *et al.* 2016). It is said that the electrochemical oxidation could be applied as a process treatment in order to remove organic compounds (Ferrag-Siagh *et al.* 2013) (Figure 1).

Da Costa *et al.* (2016) have reported the treatment of fuel station effluent. The results showed that dissolved organic carbon and chemical oxygen demand (COD) abatements of 55.2 and 61.5% were achieved, using Ti/Pt anode adding K_2SO_4 as supporting electrolyte.

Fenton's oxidation process is influenced by the advantages of both oxidation and coagulation processes. In this advanced oxidation process, the organic substances are reacted with hydrogen peroxide in the presence of inexpensive ferrous sulfate to reduce toxicity and COD. Research

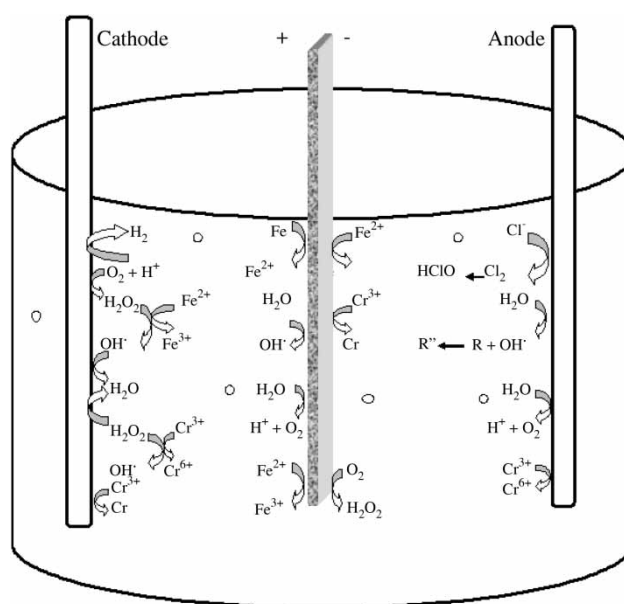


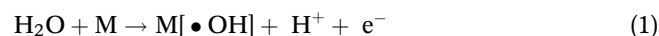
Figure 1 | Mechanisms of different compounds on combined electrochemical processes.

has demonstrated that the oxidation mechanism by Fenton's reagent is due to the reactive hydroxyl radical generated in an acidic solution by the catalytic decomposition of hydrogen peroxide. Hence the process presents some disadvantages such as potential risk in transportation of H₂O₂, and sludge production. The electro-Fenton method has the advantage of allowing a better control of hydroxyl radical (•OH) production and ensures the production, *in situ*, of H₂O₂ by O₂ cathodic reduction in acidic medium, thus avoiding acquisition, shipment and storage of H₂O₂. Moreover, there is no production of iron sludge during this process, and consequently, no subsequent disposal problem has been found unlike the Fenton reaction (Särkkä *et al.* 2015a).

Treatability of bilge water was investigated by electrochemical processes: electrocoagulation/electroflotation process and also the electro-Fenton process as an indirect electrooxidation process is studied by Ulucan & Kurt (2015). The results showed that the aluminum electrodes are more efficient than iron electrodes for 10 minutes of treatment. COD and oil-grease removal values obtained are 64.8 and 57% and 36.2 and 12.5% for electrodes of Al and Fe, respectively. On the other hand, by the electro-Fenton process, it is seen that higher removal efficiencies are obtained in comparison to the electrocoagulation method, with the COD and oil-grease removal being equal to 71 and 69%, respectively. Brillas & Casado (2002) evaluated the efficiency of electro-Fenton process in treating tannery effluent, where they reported that the COD removal obtained at pH 3 and at neutral pH is 70 and 60%, respectively. The electro-Fenton process and electrochemical oxidation processes are studied by Kurt *et al.* (2007), where they reported a 60–70% reduction in COD within 10 min. Zhang *et al.* (2016) assessed the degradation of perfluorinated compounds in wastewater treatment plant effluents by electrochemical oxidation with Nano-ZnO coated electrodes.

Recently the applications of the peroxi-electrocoagulation process (PEP) as an electrochemical method in the Fenton process have been reported. The technique generates less sludge than chemical coagulation. This method is based on the generation of hydroxyl radical (•OH), which attacks the organic substrates present in the wastewater and then degrades them. In this method H₂O₂ is externally applied into the electrocoagulation system while a sacrificial Fe anode is used as Fe²⁺ source and Fenton reactive is formed

in the process (Yazdanbakhsh *et al.* 2015). The PEP is proposed to improve H₂O₂, chloride oxidation, •OH production and several other radicals, *in situ*, during electrooxidation treatment. These intermediates increased mineralization efficiency of the process (Canizares *et al.* 2009). Organic pollutant can be anodically destroyed by direct electrooxidation, where the pollutants are adsorbed on the anode surface and destroyed by the electron transfer reaction:



where M, R and RO represent the anode surface, organic matter and oxidized organic matter respectively.

Indirect electrooxidation using electro-generated oxidizing agents, such as chlorine, hypochlorite and oxygen peroxide, ozone and hydroxyl radicals formed as intermediates from water oxidation to O₂ at the surface of the anode (Rajkumar *et al.* 2007; Oh *et al.* 2010; Särkkä *et al.* 2015b).

Aziz *et al.* (2016) reported that peroxi-electrocoagulation process yielded 88.36% COD removal from distillery industrial effluents within the reaction time of 240 min.

Consequently, this process may be used to treat tannery wastewater containing organic compounds. The presence of salt and chromium in the tanning bath are serious environmental concerns of leather making. The treatment system for removal of chlorides or chromium from this liquor seriously affects the viability of the tanning industry (Sundar *et al.* 2013). So, it is necessary to reuse this chromium liquor after a decrease of organic compound concentration.

The objective of the present work is to study the electrochemical processes application on the treatment of chromium bath wastewater using a graphite anode, stainless steel cathode and steel electrode placed between them. The electrochemical process is used to improve the quality of the chromium tanning bath by reducing organic pollution for a possible recirculation of this effluent in the tanning process. Unlike PEP that uses an iron sacrificial anode, we have used a graphite one to improve organic compound oxidation. The steel sacrificial electrode is connected on bipolar configuration to generate Fenton reactions without the addition of oxygen peroxide.

In this study, the effects of several process conditions such as current density and electrolysis time on the protein and COD removal efficiency are studied. The reuse of a treated chromium bath in the tanning process is investigated. The influences of commercial salt chromium amount, pH solution, time of stirring and time contact are studied. Leather's mechanical characteristics are examined.

MATERIALS AND METHODS

Tanning bath

The chromium tanning bath is collected directly from the tanning drum of an Algerian leather plant processing 1,500 hides/day and generating a total average effluent flow of 180 m³/day.

Electrochemical treatment of tanning bath

A batch electrochemical reactor is used for the treatment of tanning wastewater with a net volume of 1 L. A magnetic stirring (MINI MR D7813 Staufen) is used to maintain the homogenization of the water during the electrochemical run. The current is applied by a constant voltage/current controlled DC power source (Dazheng DC power supply PS-305D).

A comparison study between electrooxidation process and hybrid treatment PEP (Figure 2) is conducted at a current density of 0.06 A·cm⁻² during 1 h. Different kinds of electrodes are used: stainless steel electrode used as a cathode, the anode is in graphite (8 cm²). In the case of PEP, a steel electrode (0.63 cm²) is placed between the anode and the cathode in hybrid configuration with an inter-electrode distance of 3.5 cm.

The reaction started with the application of the specified current density (0.06, 0.13, and 0.19 A·cm⁻²) and electrolysis time is studied (1, 2, 3, 4 and 5 h).

At appropriate time intervals, samples were taken from the reactor to determine the COD and protein values.

Analysis techniques

The physical and chemical parameters of the tanning bath were determined. The pH and the electrical conductivity of the raw and treated wastewater were determined using

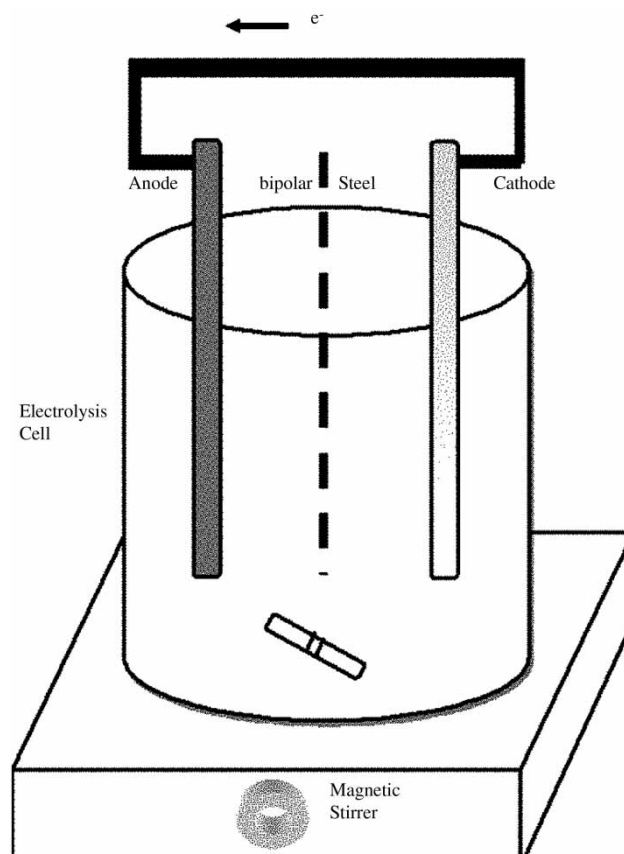


Figure 2 | Schema of electrochemical process.

pH 210 HANNA and HI 2314 HANNA respectively. The analyses of biological oxidation demand (BOD) was carried out by Thermostat schrank Aqua Lytic.

The influence of the different experimental parameters was studied by following the change of COD and protein concentration. COD was analyzed following standard procedures (ISO 6060, 1989) using the ECO[®] Thermoreactor Closed Reflux Titrimetric Method. Protein was analyzed using a spectrophotometer at 595 nm in the presence of Bradford reagent; and the total amount of Cr in the wastewater was determined by using an atomic absorption spectrometer (AAS Varian AA240). The titration method was used to determine chloride concentration (Mohr method).

Tanning tests with treated tanning bath

The tanning tests were conducted in a tanning drum with a pickled hide sample (1 p² of surface) in the presence of

different commercial chromium salt concentrations: 0, 0.125, 0.25, 0.375 and 0.5%. Initial conditions to reach optimum conditions were fixed at pH 3.2 (standard process) and at pH of treated water (pH = 3.8). The stirring was continued for a period of 1–4 h. Then the liquor was allowed to settle for a period of 1, 2 and 4 days. To assure the fixation of tanning metal, the pH was controlled (pH = 4) by adding calcium bicarbonate.

A control sample using standard tanning processes, was carried out to compare the experiments.

In order to check the tanning performance, the samples of leather were analyzed through the determination of the shrinkage temperature (Tg) at 80 ± 2 °C.

The wet blue leathers were further processed to upper leathers employing a standard process. Physical properties such as bending, wet and dry friction tests were examined in the leather factory.

RESULTS AND DISCUSSION

Spent tan liquor characterization

Typical characteristics of sample from chromium tanning are presented in Table 1. The low pH value of the tanning wastewater was due to the presence of acids in the tanning bath.

At the pickling step, sodium chloride (NaCl) was also added to prevent acid swelling of the hide; therefore, the conductivity of the tanning wastewater was high. The presence of organic materials in tanning liquor, such as dissolved proteins, were detected by measurement of

Table 1 | Analysis of spent tan liquor

Parameter	Measure
pH	3.70
Conductivity (mS cm ⁻¹)	41
Turbidity (FNU)	25.20
Protein (g·L ⁻¹)	1.41
Total chromium (mg·L ⁻¹)	4,040
COD (mg O ₂ ·L ⁻¹)	1,776
BOD ₅ (mg O ₂ ·L ⁻¹)	5
Chloride (g·L ⁻¹)	16

COD, BOD₅ and protein concentration. The spent waste showed a COD value of 1,776 mg O₂·L⁻¹ higher compared to the Algerian regulation (1,000 mg O₂·L⁻¹) and we noted that wastewater contains an amount of protein (1.41 g·L⁻¹).

The BOD₅/COD ratio represents the proportion of biodegradable organics matter in the effluent. If this ratio is less than 0.4, the sample has a low biodegradability. In this study, the BOD₅/COD = 0.0028 < 0.4 which means that the biodegradability of sample is certainly very low. However, the presence of chromium and Cl⁻ contribute to increase the value of COD.

The effluent from tanning showed a strong blue color due to the presence of chromium (4,040 mg·L⁻¹) which is higher than the regulation (4 mg·L⁻¹). Therefore, it may be concluded that it is more valid to recover chromium from the spent liquor. After appropriate treatment for removing organic compound, the tanning bath can be reused in the leather factor.

Treatment of tanning bath by electrooxidation and hybrid processes

A performance comparison of PEP and the electrooxidation reactor for the treatment of tanning wastewater was conducted at constant current density.

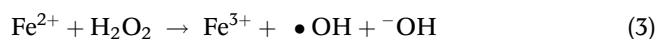
The COD and protein concentration of treated water are shown in Table 2. In these experiments, the current density was kept constant at 0.06 A·cm⁻² and electrolysis time was 1 h. As expected, the COD and protein concentrations were much lower in wastewater treated by PEP than that treated in the electrooxidation reactor. COD was reduced to 1,664 and 1,248 mg O₂·L⁻¹ with the electrochemical process and hybrid process respectively. Protein attenuation was increased significantly when using the hybrid electrochemical process in the presence of steel electrode; the protein concentration was reduced to 0.02 g·L⁻¹. These

Table 2 | Comparison between electrooxidation and PEP treatment (current density: 0.06 A cm⁻²; electrolysis time: 1 h; initial pH: 3.70)

Parameter	Electrooxidation	PEP
COD (mg O ₂ ·L ⁻¹)	1,664	1,248
Protein (g·L ⁻¹)	1.21	0.02

results indicate a decrease of organic compounds, especially in the presence of steel anode.

The organic compounds removal could be attributed to the fact that the system suffered from both electrooxidation and Fenton process simultaneously. These results can be explained by the generation, *in situ*, of iron ions produced by electrolyze oxidation of the steel electrode. According to the literature, at $\text{pH} < 3.0$ soluble ionic iron is the dominant species and hydroxide iron flocs are quite poorly produced (Fernandes *et al.* 2015). The Fe^{2+} catalyzed hydrogen peroxide (Fenton reagent produced *in situ*) to produce hydroxyl radicals by reaction (3) which oxidizes organic matter and therefore reduces the COD and protein concentration (Yazdanbakhsh *et al.* 2015):



The fastest protein removal under hybrid processes could be ascribed, in principle, to the higher production of $\bullet\text{OH}$ by the continuous generation of Fe^{2+} from steel electrode (Vasudevan 2014).

The main reason for combining on-site, steel and graphite anodes is to improve the oxidation capacities of the two individual processes creating a synergetic system.

Effect of current density and electrolysis time

The efficiency of the hybrid electrochemical processes for COD and protein removal is tested under different operational conditions of current density and electrolysis time. Current density has a significant influence because it is the driving force in electromigration of charge. The experiments were carried out varying the current density from 0.06 to 0.19 A cm^{-2} over 5 h. In these experiments, the pH of wastewater was not adjusted.

Figure 3 shows the effect of the current density on the COD removal efficiency in the electrochemical process. COD attenuation was increased significantly when the current density increased. That is, COD was reduced by 49.2, 53.5 and 65.25% at 0.06, 0.13 and 0.19 A cm^{-2} respectively after 5 h electrolysis. This is explained by increased production of oxidants such as hydroxyl radicals, peroxy radicals or ozone from electrodes at higher current densities

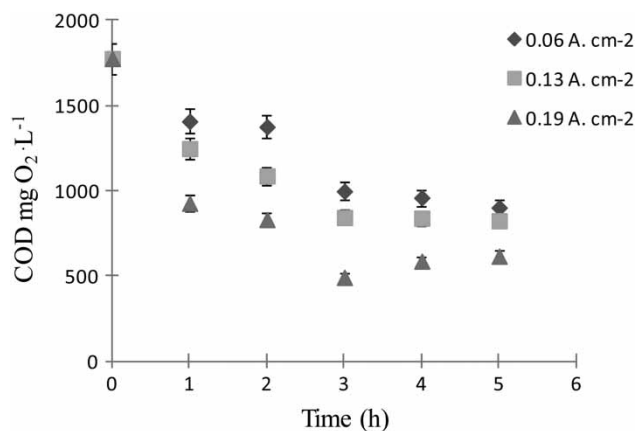


Figure 3 | COD evolution under different current densities (initial COD: 1,776 $\text{mg O}_2 \text{L}^{-1}$; initial pH: 3.7; distance between electrodes: 3.5 cm).

(Wu *et al.* 2012). At the same time, an extent of steel electrode dissolution of iron increases, according to Faraday's formula, which will help the electrochemical oxidation of organic compounds (Yazdanbakhsh *et al.* 2015). Therefore, the dissolution rate of iron electrodes increases with current density and consequently more ferrous ions are produced.

As can be seen, the initial reaction rate decreased slightly with time. The increase of the electrolysis time up to 3 h did not significantly affect the removal of COD. This may be due to the fact that the hydroxyl radicals produced may be consumed by the organics present in the effluent (Sekaran *et al.* 2013). The result is in agreement with the observation made by Sekaran *et al.* (2013) for the oxidation of refractory organics by Fenton reaction to reduce organic load in tannery wastewater.

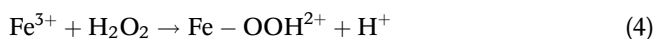
The application of the highest current density can be suggested in order to obtain maximum degradation of the organic content after 3 h electrolysis.

It is noticed that the pH is decreased during the treatment (from 3.5 to 2) (Table 3) corresponding to the decrease in the efficiency of COD removal. The same results

Table 3 | pH value of treated liquor chromium (initial pH: 3.70; electrolysis time: 5 h)

Current density (A cm^{-2})	pH value
0.06	2.72
0.13	2.03
0.19	2.3

were observed by Karthikeyan *et al.* (2012) on oxidation of organics present in tannery effluent. This can be explained by the inhibition of the generation of hydroxyl and perhydroxyl radicals in the presence of H^+ (Yazdanbakhsh *et al.* 2015). Cruz-Rizo *et al.* (2017) reported the generation of acidic derivatives such as carboxylic acids during the electrochemical oxidation of organic compound. Moreover, it was reported that at very low pH 2, the surplus hydrogen ions favor the backward reaction leading to an increase in Fe^{3+} concentration as shown in the following equation:



Alternately, the conversion of Fe^{3+} to Fe^{2+} was inhibited, and thus, the concentration of Fe^{2+} available for generation of hydroxyl radical decreased substantially, and the removal of COD was impaired (Karthikeyan *et al.* 2012).

Kang & Hwang (2000) have observed that the overall COD removal efficiency is shown to be a maximum around a reaction of pH 3.5 for the treatment of non-biodegradable landfill leachate by Fenton's oxidation. Yazdanbakhsh *et al.* (2015) studied COD removal of azithromycin from synthetic wastewater by peroxi-electrocoagulation process. The results showed that the optimum removal efficiency of 95.6% is achieved at a current density of $20 \text{ mA}\cdot\text{cm}^{-2}$ at pH 3.

Figure 3 shows slow efficiency in removal of COD ($<1,000 \text{ mg O}_2\cdot\text{L}^{-1}$) from tanning wastewater. As is presented in Table 1, the used water contained a considerable amount of Cl^- ($16 \text{ g}\cdot\text{L}^{-1}$).

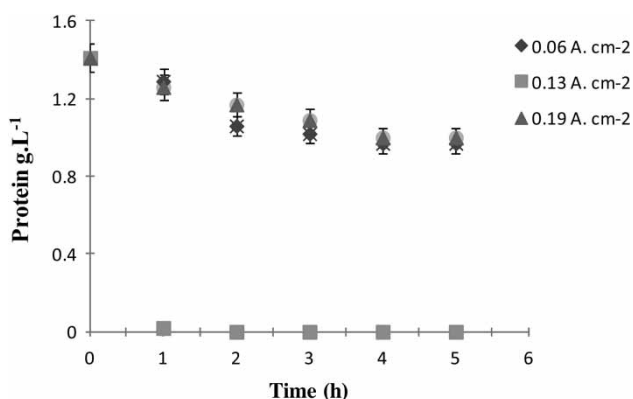


Figure 4 | Protein concentration evolution under different current densities (initial protein concentration; $1.41 \text{ g}\cdot\text{L}^{-1}$; initial pH: 3.7; distance between electrodes: 3.5 cm).

Figure 4 shows the effect of current density on the removal of protein with different electrolysis times. The removal efficiency is independent of the current densities. For example, the maximum removal efficiency of 100% was observed with a current density of $0.13 \text{ A}\cdot\text{cm}^{-2}$; and the efficiency decreased to 12 and 15% at current densities of 0.19 and $0.06 \text{ A}\cdot\text{cm}^{-2}$ respectively.

In addition, it can be seen that the protein removal efficiency was nearly 100% when the electrolysis time was 2 h, however it remained constant afterwards. So, increasing the detention time did not have a considerable impact. The result may be attributed to the chemical oxidation of the dissolved organic matter in the wastewater. In other words, the PEP system allows an indirect oxidation of organic compounds by the action of the homogeneous oxidants: hydroxyl radicals generated in the Fenton reaction, active chlorine species and hydrogen peroxide (Un *et al.* 2008). According to Fernandes *et al.* (2015) the presence of Cl^- promotes the indirect electro-oxidation, mediated by electrogenerated active chlorine, which increases EO efficacy. It has been reported that Cl^- acts as a scavenger for $\cdot OH$ radicals generated in solution and decreases the concentration of these radicals (Kiwi & Nadtochenko 2000).

To clarify the oxidation effect of active chlorine in oxidation treatment of the tanning bath, the changes in the concentration of chloride were monitored. As shown in Figure 5, the chloride concentration decreased from 16 to $12 \text{ g}\cdot\text{L}^{-1}$. This result revealed that chloride was consumed during the electrochemical process.

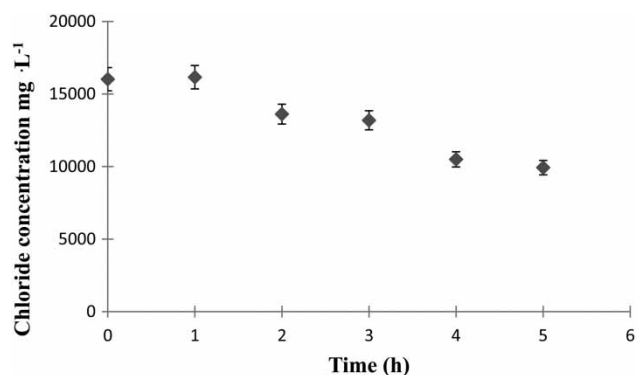
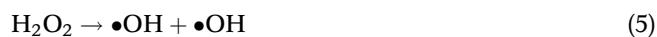


Figure 5 | Chloride concentration evolution with different electrolysis times (initial chloride concentration: $16 \text{ g}\cdot\text{L}^{-1}$; initial pH: 3.7; distance between electrodes: 3.5 cm; current density: $0.13 \text{ A}\cdot\text{cm}^{-2}$).

Similar results were observed by Souza *et al.* (2015) for organic pesticide in the presence of chlorides. It was suggested that when NaCl is present in wastewater as an electrolyte, Cl⁻ ions are transformed into HOCl (Guenfoud *et al.* 2014). The higher production of oxidants in the solution accelerates the degradation of organic compounds.

Figure 6 shows the evolution of hydrogen peroxide concentration. The concentration increased with time which confirms electrolysis generation of this compound produced by the bi-electron reduction of O₂ gas, mainly at the cathode (Brillas & Martínez-Huitle 2015). We observed a retarded rate of decomposition of COD at higher H₂O₂ concentration. The observation was found to be consistent with the results reported by Karthikeyan *et al.* (2012) on oxidation of tannery wastewater. At higher H₂O₂ concentration, the hydroxyl radicals generated were converted into hydroxyl ions (Equations (5) and (6)) (Karthikeyan *et al.* 2012):



Reuse of tanning treated bath

In these experiments, we used the chromium tanning liquor treated by PEP in the appropriate conditions parameters.

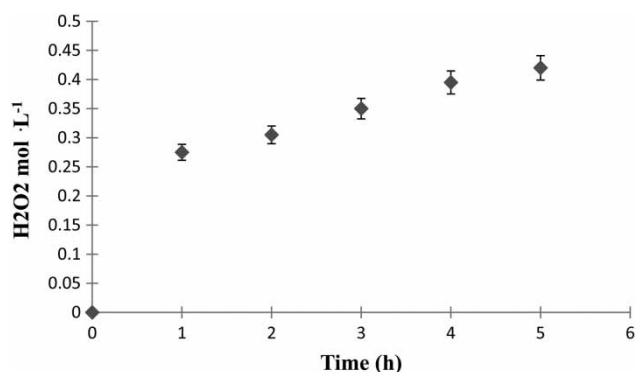


Figure 6 | Hydrogen peroxide concentration evolution with different electrolysis times (initial pH: 3.7; distance between electrodes: 3.5 cm; current density: 0.13 A cm⁻²).

Pickled hide was used for tanning studies. Chrome tanning was followed for all the experiments. Two hundred mL of treated tanning bath with different amounts of fresh BCS (basic chromium sulfate, the trivalent form of chromium) were used for the tanning process. Also, the effects of operational parameters such as pH liquor, time stirring in the drum and contact time of hide and chromium liquor was studied. The final basification was adjusted to pH 4.0.

The procedure followed for tanning was the same for both experimental and control processes. The wet blue leathers were further processed for upper leather by employing standard processes.

Some representative experiments are given in Table 4. The chromium salt used influences the behavior of the leather. The dose rate plays an important role: at high dose, wet blue leather presents a good hydrothermal stability. On the other hand, a decrease of the stirring time decreases the quality of the leather. However, the decrease of contact time at higher chromium doses stabilizes the obtained leather.

As shown in Figure 7, the hide tanned with a spent liquor bath (sample control) at pH 3.2 over 4 h of stirring time in the drum and 2 days of contact time (sample a) is sensitive to high temperatures. However, when using the treated chromium bath at pH 3.8 over 4 h of stirring time in the drum and 2 days of contact time, the obtained leather showed low hydrothermal stability (sample b). Also, when this liquor, obtained from PEP, is pre-acidified at 3.2 and reused for tanning in the drum over 2 days in 4 h of mechanical stirring, the leather has low hydrothermal stability (sample c).

The experimental results show that the efficiency for tanning hide was obtained when using 0.25% of chromium salt at pH 3.8 with a stirring time of 4 h during 2 days of contact time (sample e). The obtained samples present a brown color due to the presence of the metals chromium and oxidized Fe (Mella *et al.* 2015). In fact, iron has been considered as an effective mineral-tanning agent. Wenzel *et al.* (2010) proposed a process for preparation of chromium-iron complex which was used in the leather industry.

When the contact time is higher (4 days), we observed the swelling phenomenon. This could be possibly due to

Table 4 | A collection of representative experiments for reuse of treated spent liquor chromium in tanning process

Dose of chromium salt (g/pi ² of hide)	Liquor pH	Stirring time (h)	Contact time (day)	General observations
0	3.8	4	2	Bad hydrothermal stability Wet blue
0	3.2	4	2	Bad hydrothermal stability Brown color of leather
0	3.2	4	4	Good hydrothermal stability Swelling of wet blue
0.25	3.2	4	4	Good hydrothermal stability Swelling of wet blue
0.5	3.2	4	4	Good hydrothermal stability Swelling of wet blue
0.5	3.2	4	2	Good hydrothermal stability Wet blue
0.5	3.2	2	2	Bad hydrothermal stability Brown color of leather
0.5	3.8	4	2	Good hydrothermal stability Wet blue
0.25	3.8	4	2	Good hydrothermal stability Wet blue

the fact that chrome compounds of the treated liquor forms an aqua hydrocomplex during hydration and undergoes hydrolysis liberating acid. This acid binding to skin protein causes swelling (Sundar *et al.* 2013), however, when the contact time was 2 days, the swelling phenomenon was not observed.

From the results we have observed a high hydrothermal stability of leather when BCS was introduced on tanning solution. That is because of the crosslinking capability of metals (chromium and iron) with that of collagen carboxylic groups with a covalent coordinate bond (Rao *et al.* 2002). The tanning process, by inducing cross-linking, stabilizes the crystalline of collagen (Wang *et al.* 2010). As a consequence of crosslinking, a hydrothermal stability is conferred. However, when the chromium complex does not bind to different side chain carboxyl sites of collagen, which depend on the amount of chrome on the liquor, hydrogen bonds in the triple helix are broken by rising temperature which is observed as shrinking (El Boushy & van der Poel 1994).

According to the technicians from the tannery, the visual and physical properties of the leather after reusing the treatment tanning bath of the tanning operation are

excellent and identical to those obtained when the standard process is followed. The flex testing leather (up to the standard value of 50,000 rpm), and dry and wet friction tests were not altered by using recovered chromium in the tanning experiment.

CONCLUSIONS

The main objective of this study was to reuse a chromium tanning bath in the tannery after appropriate electrochemical treatment of the wastewater.

We evaluated the performance of a hybrid electrochemical reactor for the removal of organic pollutants, especially protein, from the tanning bath. According to the results of the present study, we found that PEP using steel and graphite anodes helped to improve the removal of protein and COD by direct and indirect processes. Increasing the current density had positive impacts on the performance of the reactor. In addition, it was found that electrolysis time has no effect on electrochemical performance. The hybrid electrochemical process degraded

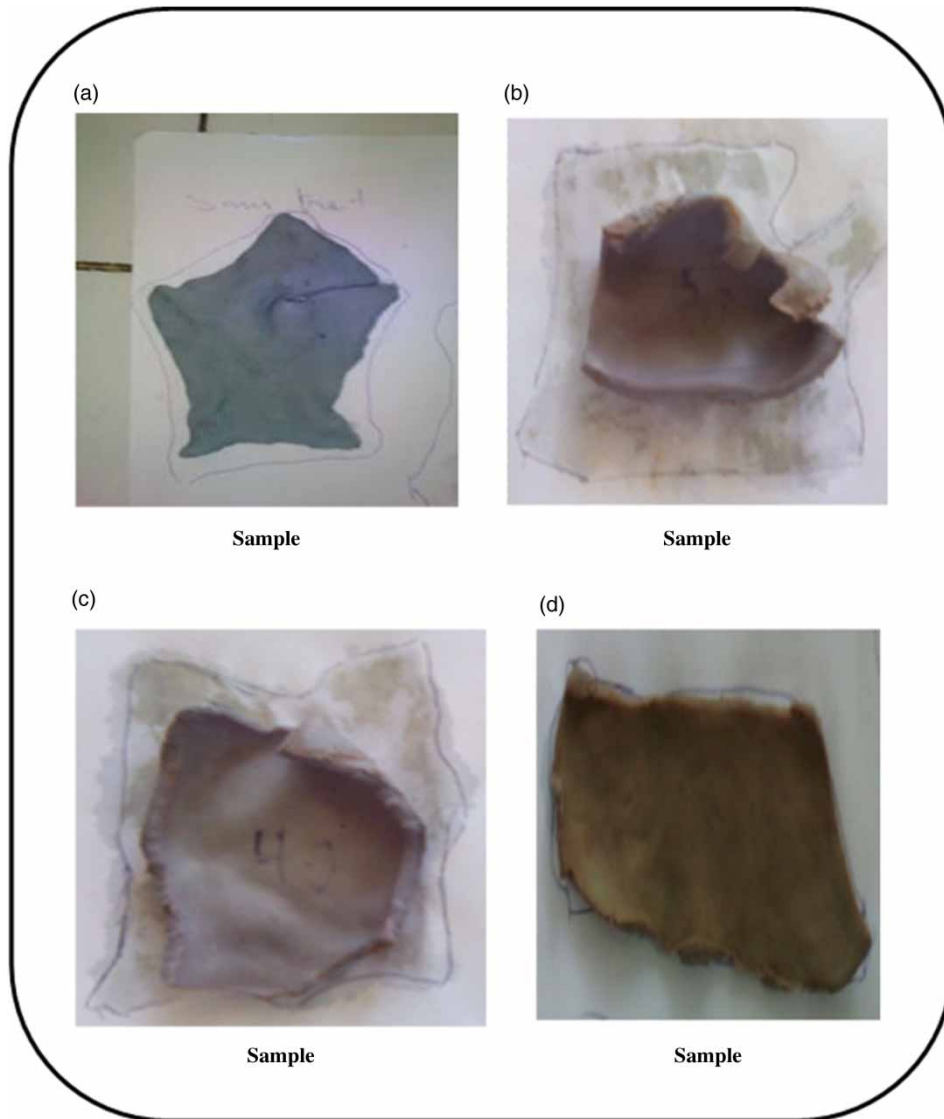


Figure 7 | Tanning with treated chromium bath: (a) spent liquor bath (sample control) at pH 3.2 during 4 h of stirring time in the drum and 2 days of contact time; (b) treated chromium bath at pH 3.8 in 4 h of stirring time in the drum and 2 days of contact time; (c) treated chromium bath at pH 3.2 and reused for tanning in the drum during 2 days in 4 h of mechanical stirring; (d) 0.25% of chromium salt at pH 3.8 with stirring time of 4 h over 2 days of contact time.

100% of protein and 53% of COD under a current density of $0.13 \text{ A}\cdot\text{cm}^{-2}$ over 2 h.

Finally, tanning tests with a treated chromium bath showed good hydrothermal stability with a minimum required amount of commercial chromium salt (0.25%) at the pH solution during 4 h of stirring and 2 days of contact hide-treated bath.

The physical properties of the experimental leathers, including flex testing, dry and wet friction tests, were carried

out for the control and experimental leather. We observed that leather tanned with treated spent chromium liquor was comparable to chrome tanned control leathers.

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