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REUSE OF LEATHER WASTE: COLLAGEN HYDROLYZATE FOR THE TREATMENT OF TANNERIES EFFLUENTS

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Abstract: Due to the characteristics of their processes, tanneries generate liquid effluents at different acidity or alkalinity conditions, with high turbidity, suspended solids and color. These effluents must be treated to avoid environmental contamination. The objective of the present work was to study, at a laboratory scale, coagulation processes that allow the reduction of turbidity and color of tannery effluents. The work focused on the use of collagen hydrolyzate (CH) as a coagulant, obtained from the shavings that the leather process discards. Tests were made with pure CH, in combination with a commercial coagulant (aluminum sulfate) or a commercial flocculant (cationic quaternary polyamine), in order to compare the efficiency of the process. Effluents were generated with a generic tanning formula, which were treated by aeration followed by sedimentation. The results obtained show that the CH alone does not show sufficient effectiveness, but combined with both the aluminum sulphate and the cationic quaternary polyamine gives very good results, involving smaller amounts of these commercial additives. The fact that the CH is obtained from a residue of the industry itself and it can successfully replace other chemicals, lowers the costs of treating the liquid effluents while avoiding having to manage that solid waste.

Keywords: Leather shaving; tannery effluent; collagen hydrolyzate; coagulation

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INTRODUCTION

Tanneries are high impact industries in the economic, social and environmental aspects throughout the world. They mobilize 11% of the global manufacturing market. The leather industry has a consolidated value chain. It is an activity tied to two important sectors, the footwear and meat industries. For the first, it constitutes its main supplier of raw material; for the second, it is an important consumer for one of its wastes: leather (Ferreyra, 2016; Salvador, 2009a; Salvador, 2009b). Leather is a product of great international circulation - it was estimated that it mobilizes more than US $ 50,000 million per year in 2010 - whose market, according to analysts, is far from saturated. In Argentina, this industrial complex has a long historical tradition and is widely integrated into international trade, having recognized prestige for its quality and high productivity (Dirección de Oferta Exportable, 2010).

From an environmental point of view, the tannery sector has always been regarded as a net pollutant industry. While it is true that the tanning process generates highly polluting effluents, these can be controlled with the appropriate technologies (CONAMA, 1999). In addition, it should be considered that this industry takes advantage of a highly putrefiable byproduct and slow biodegradation: the skins of animals (Schneider *et al*., 2012).

When leathers are processed (average 25 kg of skin per animal), 125 kg of chrome-tanned shavings are produced for each ton of processed skin (Cantera & Bértola, 1999; Mendez *et al.*, 2007). The Argentine tanning industry has to dispose of more than 100 tons of leather shavings daily, which are discharged into sanitary landfills and / or informal dumps generating a strong impact on the ecosystem (Barucca, 2016; Tegtmeyer, 2011).

One of the initiatives designed to add value to these solid wastes is their transformation through hydrolysis (Bonilla *et al.*, 2014; Díaz *et al.*, 2006), which consists of a process of desiccation, from which two by-products are obtained with potential applications in various industries: collagen hydrolyzate and chromium hydroxide (Flores *et al.*, 2013; Schneider *et al.*, 2012). For each kg of dry leather shavings 1.7 kg of 40% m/m of collagen hydrolyzate solution (containing 73% of the nitrogen) plus 0.75 kg of chromium cake with a 70% humidity (containing 90% of the chromium) can be obtained (Bahillo *et al.*, 2004; Moreno *et al.*, 2011).

Resolving the problem of industrial effluents without previous treatment that pollute the environment, does not only go through the control, supervision and sanction to the generating industries, it also requires a research effort to develop specific, accessible and economic treatments that can be adopted by different type of industries (Alcarraz *et al.*, 2010; Ramírez *et al.*, 2000). The primary treatment of the tannery effluents consists in the removal of a substantial part of the sedimentary or floating material, which represents significant percentages of the contaminating solids. The two types of primary treatment used are coagulation and flocculation (Aguinaga, 1996; Emmer & Del Campo, 2014; Mirbagheri *et al.*, 2015).

The novel approach proposed by this study is to evaluate the use of the collagen hydrolyzate obtained from the leather shavings that the tannery process discards as a coagulant in the treatment of its liquid effluents, generating a double benefit for the environment: reducing the volume of solid waste and the amount of chemicals used to treat the liquid waste.

MATERIAL AND METHODS

Preparation, collection and characterization of leather shavings

The leather shavings (after tanning, with chrome) that were used in this study came from the *Laboratorio de Curtido y Medio Ambiente*, *Instituto Nacional de Tecnología Industrial* (INTI)-*Sector Cuero*, located in Gonnet, Buenos Aires Province, Argentina. The quartering sampling method was taken into account: approximately 0.5 m^3 of shavings were homogenized, divided into 4 parts and 2 opposite parts were chosen to form another smaller sample, and thus the procedure was repeated 3 times until forming the last cluster. The final weight of the sample was 2 kg. It was stored at room temperature in a sealed plastic bag and transferred to the laboratory for the tests.

For the characterization of shavings the pH, humidity, total chromium, total proteins, oils and fats were tested. In all the determinations, the standardized methodologies indicated in **Table 2** were followed.

Obtention and characterization of collagen hydrolyzate

The production of collagen hydrolyzate was carried out using the methodology of alkaline - enzymatic hydrolysis, proceeding as follows: the shavings sample was placed in a rotating reactor with water, lime and sodium hydroxide, at 65°C, pH = 10.5, 20 rpm, during 90 min. It was neutralized to pH = 8.0, and cooled to 38°C. At this temperature, an enzymatic hydrolysis was carried out with pancreatic proteolytic enzymes during 3 hours with agitation, and 6 hours without agitation (maceration) when the temperature during which the temperature drops to 24°C. Finally, it was cooled and filtered. The "chromium cake" was retained in the filter and the collagen hydrolyzate was recovered in the filtrate.

The characterization of collagen hydrolyzate was carried out testing total solids, fats, total chromium, total proteins, nitrogen and ash. In all the determinations, the standardized methodologies indicated in **Table 3** were followed.

Obtention and characterization of effluents

Tests were carried out with effluents coming from the soaking and liming (peeling) processes. To obtain these effluents, the beamhouse processes on a goat skin in a fresh state were carried out in a reactor at laboratory scale. The general scheme of the beamhouse operations is shown in **Fig. 1**. At the end of each stage of the process, the effluents were collected in plastic containers, mixing the soaking and the liming ones, obtaining an alkaline pH effluent. Then they were stored in a refrigerator at 12°C.

The effluents were characterized by measuring total solids, suspended solids and turbidity. In all the determinations, the standardized methodologies indicated in **Table 4** were followed.

Coagulation tests

The effluents were subjected to a pre-treatment consisting of sedimentation followed by aeration. Coagulation tests were performed by triplicate using different doses of three different treatments: 1) collagen hydrolyzate alone (CH) at three different concentrations (1, 2 and 3%), 2) The three solution of collagen hydrolyzate with the addition of 2% of aluminum sulphate as commercial coagulant (CHAS), and 3) the three solutions of collagen hydrolyzate with the addition of 4% of Polifloc 5390® (cationic quaternary polyamine) as a commercial flocculant (CHPO). Aluminum sulfate and Polifloc were selected because they are widely used, economical and easy to apply.

For comparison, a usual treatment that served as control (C) and a test called blank (B) with effluent without adding any treatment were performed. The composition of each treatment and the doses that were used are listed in **Table 1**. All the tubes were shaken for 3 minutes at 150 rpm, and then the pH was adjusted and stirred for 10 minutes at 25 rpm.

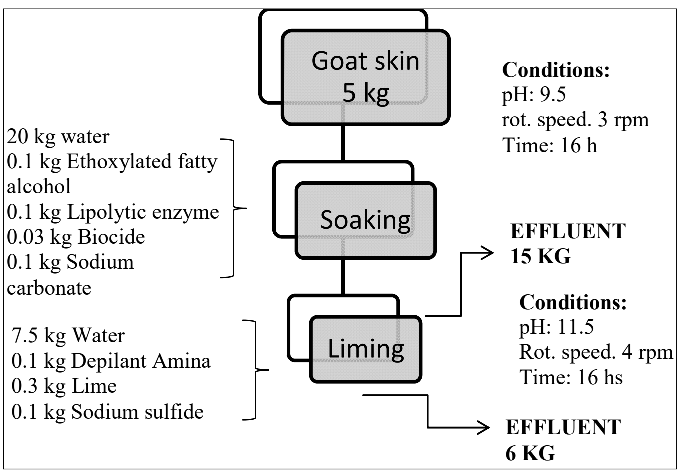

Fig.1 Schema of the beamhouse processes at laboratory scale carried out to obtain the effluents.

Table 1. Proportion of reagents used in the treatments

Treatment	Hydrolizate (%)	Aluminum Sulfate (%)	Polifloc 5390 (%)
Blank	-	-	-
1CH	1	-	-
2CH	2	-	-
3CH	3	-	-
1CHAS	1	2	-
2CHAS	2	2	-
3CHAS	3	2	-
1CHPO	1	-	4
2CHPO	2	-	4
3CHPO	3	-	4
Control	-	2	4

CH: Collagen hydrolizate; AS: Aluminum sulfate; PO: Polifloc 5390®

In the evaluation of the process efficiency, turbidity and color were measured following a standardized methodology (IRAM-8539, 1989).

RESULTS AND DISCUSION

Characterization tests

The characterization of the leather shavings, generated after the buffing operation to a chrome-tanned cowhide (wet blue), are presented in **Table 2**. The samples used in this work had a higher concentration of protein than other published previously by other authors, this allowed to recover a higher content of collagen hydrolyzate (Jordán Nuñez, 2011; Moreno *et al.*, 2011; Reyes, 2016).

The results obtained from the characterization of the collagen hydrolyzate samples are shown in **Table 3**. The percentage of proteins and total solids are below the values obtained in other works. The content of chromium and ash found are similar to those studied in some studies (Bonilla *et al.*, 2014; Cantera & Bértola, 1999), and superior to those obtained by other authors (Moreno et al., 2011). This is an indicator of the level of contaminant residues contained in the hydrolyzed collagen.

Table 2. Characterization of leather shavings

	Dry base	Wet base	Methodology
pH	-	4.10	IRAM-8508, 2000
Humidity (%)	-	35.7	IRAM-8502, 1988
Chrome (mg/L)	3.03	1.95	IRAM-8510, 1992
Fat (%)	0.90	0.58	IRAM-8503, 1988
Protein (%)	86.5	55.6	IRAM-8506, 1989
Nitrogen (%)	13.8	8.90	IRAM-8506, 1989
Ash (%)	15.2	9.80	IRAM-8504, 1989

Table 3. Characterization of collagen hydrolyzated

		Methodology
Total solids (%)	31.2	APHA-2540B, 2012
Chrome (mg/L)	2.50	IRAM-8510, 1992
Fats (%)	0.51	IRAM-8503, 1988
Proteins (%)	69.5	IRAM-8506, 1989
Nitrogen (%)	10.5	IRAM-8506, 1989
Ash (%)	15.2	IRAM-8504, 1989

Table 4. Characterization of effluents

		Methodology
pH	10.0	IRAM-8508, 2000
Total Solids (mg/L)	28000	APHA-2540B, 2012
Suspended Solids (mg/L)	1600	APHA-2540B, 2012
Turbidity (NTU)	790	APHA-2130B, 2012

The characterization of the effluents used is shown in **Table 4**. It can be observed the alkaline pH of the mixture obtained, with a large amount of total solids, a minority of suspended solids and an average turbidity.

Coagulation tests

Influence of pH

The pH is an important factor for proper coagulation, since each coagulant effectively operates at a specific pH to which it exhibits maximum removal (Chowdhury *et al.*, 2013; Lasindrang *et al.*, 2015). The extension of the efficient pH range depends on the type of coagulant used and the characteristics of the effluent (Bajza *et al.*, 2004; Song *et al.*, 2004).

To evaluate the influence of pH on the removal efficiency of total solids, we worked at 2 pH values: the original sample (pH = 10) and a neutral value (pH = 7). Doses of 2% hydrolyzed collagen (2CH), 2% hydrolyzed collagen with 4% Polifloc (2CHPO), and 2% hydrolyzed collagen with 2% aluminum sulfate (2CHAS) were used. The removal of total solids was taken as a relevant parameter. The best results, as shown in **Fig. 2**, were found at pH 7, for all cases.

Influence of dosage

The dose of coagulants is a factor that has a major role in determining the efficiency of the coagulant (Ahmad *et al.*, 2008; Bakar & Halim, 2013; Chowdhury *et al.*, 2013; Song *et al.*, 2000). In the treatments carried out in this work, different doses of collagen hydrolyzate obtained from chrome-tanned leather shavings and with additions of a commercial coagulant or flocculant were used.

Table 5 shows the results obtained from the experiments for each case tested. The selected parameters were the removal of turbidity and the removal of color.

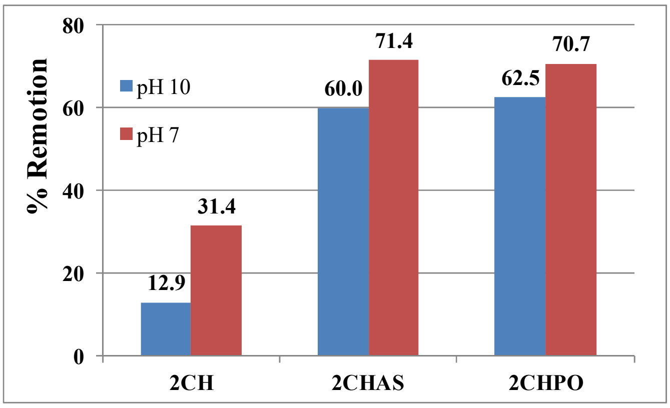

Fig. 2 Removal of total solids obtained with three treatments at different pH conditions.

Table 5. Removal of turbidity and color with each treatment

Treatment	**Effluent**	
	Turbidity Remotion (%)	Color Remotion (%)
1CH	20.1	48.5
2CH	18.2	27.2
3CH	16.2	8.6
1CHSA	93.8	92.0
2CHSA	91.1	89.8
3CHSA	90.0	86.7
1CHPO	89.7	91.1
2CHPO	92.8	89.2
3CHPO	93.1	87.3
Control	99.1	99.0

In the case of treatments with hydrolyzate alone, the removal of turbidity and color reaches low values compared to the control. The mixture with either aluminum sulphate or polyelectrolyte gives greater removal efficiencies.

It is concluded that the joint work of a coagulant and a flocculant is synergistic and leads to a high removal efficiency. The removals achieved with these combinations, using a collagen hydrolyzate obtained from the residual chrome shavings, are similar to those obtained by other authors using collagen hydrolyzate from different origins (Teh *et al.*, 2016; Lee *et al.*, 2014; Haydar & Aziz, 2009b; Song *et al.*, 2004; Bajza *et al.*, 2004).

CONCLUSIONS

This research focused on the use of collagen hydrolyzate obtained from chrome-tanned leather shavings, a residue of the leather industry, as a coagulating agent and the influence of the dose and pH applied in the treatment.

It has been established that it is convenient to use a neutral pH to obtain better removal efficiencies.

Regarding the use of the collagen hydrolyzate only as a coagulant, it is observed that the decrease of turbidity and color are very low in comparison with the control. These results lead to using this hydrolyzate together with a coagulant or a flocculant. It can be said that the obtained hydrolyzate exerts a synergistic work with these additives. The results obtained indicate that CH can be used in both situations.

It is interesting to note that this work provides the basis for the use of mixtures of residues rich in proteolytic enzymes from other industries to obtain collagen hydrolyzate with this purpose of coadjuvant in the coagulation and flocculation of industrial effluents, thus better reuse would be available of waste giving a lower environmental cost.

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