Analysis of Post-tanning Chemicals and Reduction of Pollution Load in Wastewater

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ABSTRACT:

The chemicals in post-tanning are partially retained by the leather, and the fractions remaining in the process are discharged with the wastewater. Current literature has an extensive number of studies characterizing tannery effluents. However, few studies have evaluated how groups of chemicals applied to the leather impact the quality of wastewater generated in the process. Thus, this study aims to evaluate and reduce the impact of chemicals used in the post-tanning process on the main quality parameters of the wastewater. The assessment and reduction of the pollution load of leather chemicals were carried out using a formulation from a Brazilian tannery as a case study. Results showed

that retanning agents (natural and synthetic tannins) were responsible for high inorganic pollution load in the wastewater, and the synthetic tannins were more toxic than the natural ones. The fatliquoring agents were responsible for the highest chemical oxygen demand load in the wastewater and were the chemical group that presented the highest cytotoxicity. The fixing agent and the dye contributed to the inorganic pollution load of the wastewater, and the nitrogen load of the wastewater was mainly related to the neutralizing retanner and the dye. The adjustment of the chemicals supply showed depletion in the pollution load of wastewater. The obtained leather showed quality within the required specifications of the tannery, and the formulation cost was reduced by 24%.

Keywords: leather; post-tanning; wastewater; dyes; fatliquoring agents; retanning agents; cytotoxicity.

1. Introduction

The leather industry and its products play a relevant role in the world economy, with a global trade value of approximately 80 billion dollars per year (Sivaram and Barik, 2019). This industry is especially important in the economy of developing countries (Bharagava and Mishra, 2018). According to the Center for Tanning Industries in Brazil - CICB (2020), the Brazilian tanning industry has 310 tanneries and 2,800 leather and shoe components factories. The Brazilian leather industry was responsible for exporting more than 1.1 billion dollars in 2019. Finished leather accounts for 59.6% of sales (ABQTIC, 2020).

In the post-tanning (wet-finishing) process the chemicals are not fully retained by the leather and are partially discarded in the raw wastewater of the tannery (Aquim et al., 2009; Bharagava et al., 2018; Hansen et al., 2021; Moreira et al., 2019). Some of these chemicals are difficult to remove in wastewater treatment plants, especially when they

contain salts and recalcitrant compounds (Kozik et al., 2019; De la Luz-Pedro et al., 2019; Moreira et al., 2019; Tamersit et al., 2018). Furthermore, concepts of cleaner production and pollution prevention (EPA, 1988) identify the need to reduce or eliminate waste in volume, concentration, and/or toxicity at the source, applying a preventive and integrated environmental strategy to industrial processes. Pollution prevention measures are beneficial because they reduce operating costs, reduce ecological damage resulting from the extraction and processing operations of the raw materials used, reduce employees' exposure to harmful substances and improve the company's image (El-Haggar, 2007).

Some studies have already evaluated the chemical and toxicological characteristics of post-tanning chemicals (Libralato et al., 2011; Lofrano et al., 2007, 2008; Moreira et al., 2019). However, studies relating the characteristics of leather chemicals with their impacts on raw tannery effluents and evaluating the supply of leather chemicals in processing floats are still necessary to expand knowledge in this area. Thus, this study aimed to evaluate and reduce the impact of chemicals used in the post-tanning process on the physicochemical and cytotoxic parameters of the wastewater.

2. Materials and Methods

This research used as a case study a post-tanning formulation processing wet-blue bovine leather for producing women bag. This formulation is used by a tannery located in southern Brazil. The tannery has a production capacity of 750 whole leathers per day.

2.1 Characterization of Leather Chemicals

The leather chemicals offered in the process were analyzed individually at the concentration indicated in the formulation (Table 1) and characterized for conductivity

(Hach hq40d multi-analyzer), total dissolved solids (TDS) (Hach hq40d multi-analyzer), chemical oxygen demand (COD) (SM 5220 C, 2017), biochemical oxygen demand (BOD) (SM 5210 D, 2017), total kjeldahl nitrogen (TKN) (SM 4500 Norg, 2017), ammoniacal nitrogen (NH4-N) (SM 4500 NH3 C, 2017), and cytotoxicity. Cytotoxicity assays were performed using V 79-4 cells. The cells were exposed to a culture medium that was diluted in samples containing the chemicals for 24 hours (for acute cytotoxicity) and for 96 hours (for chronic cytotoxicity). At the end of this period, two independent endpoints were performed: tetrazolium reduction assay (MTT) (Mosmann, 1983) and Sulphorhodamine B adsorption (SRB) (Skehan et al., 1990).

Table 1: Concentration of chemicals added in post-tanning processing (Hansen et al., 2020).

Leather Chemical	**Concentration (g/L)**
Sodium bicarbonate	1
Sodium formate	10
Neutralizing retanner	10
Vegetable tannin 1	30
Vegetable tannin 2	10
Synthetic tannin 1	10
Synthetic tannin 2	20
Synthetic tannin 3	15
Acrylic resin	15
Natural oil 1	15
Natural oil 2	2,5
Mixture of synthetic and natural oils 1	15
Mixture of synthetic and natural oils 2	15
Dye auxiliary	2,5
Waterproofing agent	1
Fixing agent	7
Antioxidant	0,5
Fungicide	1
Black acid dye	12,5

2.2 Reducing Pollution Load of Chemicals in Wastewater

Tests to reduce the supply of chemicals were carried out in pilot-scale and in industrial-scale drums. Since retanning and fatliquoring agents are the chemicals used in greater quantity, the reduction in the supply of leather chemicals focused on reducing the consumption of these agents. The reduction in the offer of leather chemicals was of 26%, based on tests carried out previously (Hansen et al., 2021).

The residual wastewater from the pilot scale tests were characterized before and after the reduction in the supply of chemicals, evaluating pH, conductivity, and total dissolved solids using Hach hq40d multi-analyzer. The leather produced on a pilot scale was tested for the organoleptic parameters of softness, filling, frain, and impregnation hability.

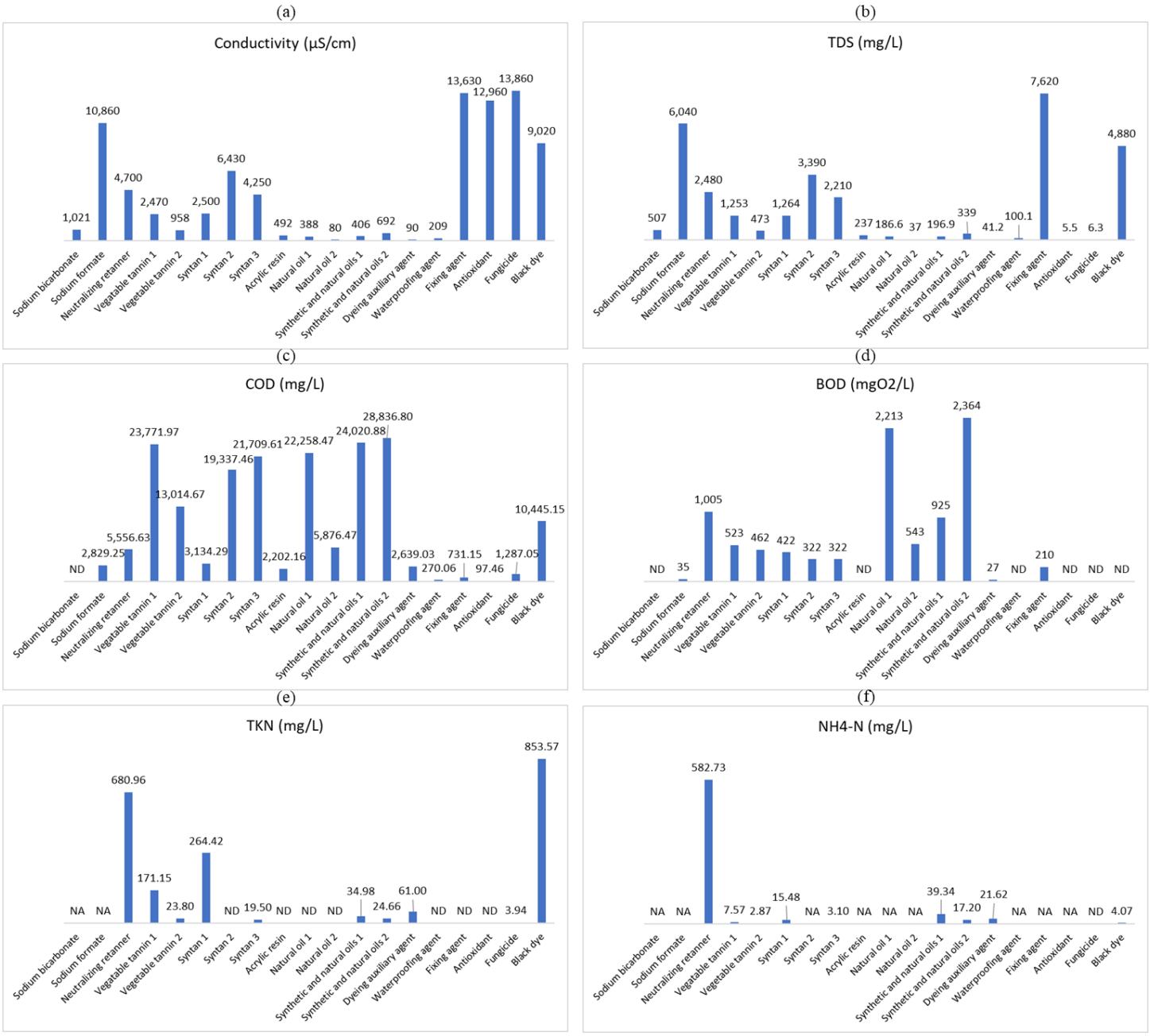
The wastewater before and after the reduction in chemical supply on the industrial scale were analyzed for pH (SM 4500 H+, 2017), conductivity (SM 2510 B, 2017), TDS (SM 2540 C, 2017), biochemical oxygen demand (BOD) (SM 5210 D, 2017), COD (SM 5220 C, 2017), and sulfate (SM 4110 B, 2017). The leather obtained was tested for tear resistance strength (ISO 3377-1, 2011), colorfastness to light ASTM D1148 (2018), colorfastness to friction (wool felt wet with water and wool felt wet with alcohol) ISO 11640 (2012).

3. Results and Discussion

3.1 Characterization of Leather Chemicals

The characterization of each leather chemical of the post-tanning formulation is shown in Figure 1.

Figure 1: Conductivity (a), TDS (b), COD (c), BOD (d), TKN (e), and NH4-N (f) of post-tanning chemicals.



NA - not analyzed.
ND - not detected.

The analysis of the leather chemicals provided information on how each group of chemicals used in the formulation contributes to the pollution load of the effluents:

- Deacidulants showed high conductivity and TDS, and the neutralizing retanner showed the highest ammoniacal nitrogen pollution load in the formulation. The safety data sheet for this chemical indicates that it is an aromatic sulfone, which possibly has amine groups attached to its chemical structure, given the result of nitrogen.
- Retanning agents were responsible for high inorganic pollution load (conductivity and TDS).
- Fatliquoring agents were the chemical group responsible for the highest COD load.
- The fixing agent and the acid dye showed high conductivity and TDS and the acid dye also showed high total nitrogen pollution load.

Cytotoxicity results of the chemicals are shown in Table 2. The results are presented as cell viability compared to the negative control (control test without the presence of chemicals). Thus, the higher the cell viability percentage, the lower the toxicity of the chemical. Synthetic tannins were more toxic than vegetable tannins. Fatliquoring agents were the chemical group with the highest cytotoxicity, which was related in this study to the use of surfactants to obtain these chemicals, since oils are applied in floats as aqueous emulsions. The cytotoxicity of surfactants occurs due to the lysis of the cell membrane (Hansen et al., 2020). Fungicide also showed acute and chronic cytotoxicity, which was expected due to the presence of substances such as chlorobenzene in its composition.

Table 2: Cytotoxicity assays of chemicals.

	MTT 24h		MTT 96h		SRB 24h		SRB 96h	
Chemical	Average	Desvpad	Average	Desvpad	Average	Desvpad	Average	Desvpad
Sodium bicarbonate	99,3	8,3	75,2	3,2	102,0	1,3	89,5	9,8
Sodium formate	39,6	5,2	47,0	3,9	56,4	7,9	27,7	4,3
Neutralizing retanner	72,5	5,7	4,4	0,2	76,7	3,4	4,9	1,0
Vegetable tannin 1	40,3	2,3	51,3	8,0	87,7	3,1	42,9	0,9
Vegetable tannin 2	85,7	6,5	30,8	2,7	90,0	1,4	48,2	2,5
Synthetic tannin 1	43,7	5,0	5,3	0,5	41,2	4,6	1,7	0,4
Synthetic tannin 2	3,2	1,0	4,5	0,6	1,0	1,4	1,1	0,3
Synthetic tannin 3	4,5	4,5	4,7	0,9	0,6	0,4	0,4	0,2
Acrylic resin	18,8	5,2	5,4	1,2	23,1	5,9	1,7	0,6
Natural oil 1	3,3	1,1	0,0	0,1	4,7	1,2	3,4	0,6
Natural oil 2	8,6	6,4	3,2	1,1	4,2	0,6	1,1	0,1
Mixture of synthetic and natural oils 1	2,4	0,5	3,0	0,3	6,1	11,1	1,0	0,2
Mixture of synthetic and natural oils 2	0,7	1,3	5,8	0,8	4,2	3,4	2,4	0,1
Dyeing auxiliary agent	2,7	0,7	4,8	0,4	5,6	1,3	2,7	0,3
Waterproofing agent	121,6	7,2	11,4	2,8	87,9	3,3	12,6	4,9
Fixing agent	109,1	16,0	68,3	6,1	100,9	2,1	97,7	1,2
Antioxidant	111,3	5,5	78,2	2,1	105,3	0,6	99,1	1,7
Fungicide	3,3	0,7	4,5	0,5	4,5	1,7	4,8	1,1

3.2 Reducing Pollution Load of Chemicals in Wastewater

The adjustment in chemicals supply on a pilot scale resulted in reduction in conductivity and total dissolved solids in the wastewater (Table 3). The results of the analysis of the wastewater in industrial scale tests also showed a reduction in the

concentrations of conductivity, TDS, BOD, and COD (Table 4). There was high exhaustion of the chemicals due to the absorption on the wet-blue leather, reaching up to 89.8% reduction of BOD, which is related to an improvement in the diffusion of oils, since the various post-tanning chemicals are less concentrated together in the float.

Table 3: Wastewater analysis on a pilot scale.

Residual float	pH	Condutivity (µS/cm)	TDS (mg/L)
Residual float I* (Original Process)	3.90	1,994	11,580
Residual float I (Chemical reduction)	3.75	1,789	9,440
Residual float II** (Original Process)	3.72	689	3.62
Residual float II (Chemical reduction)	3.62	586	3.10

*Residual Float I: retanning, fatliquoring, and dyeing wastewater
**Residual Float II: fatliquoring and fixing wastewater

Table 4: Wastewater analysis on an industrial scale.

	pH	Conductivity (µS/cm)	TDS (mg/L)	BOD (mg/L)	COD (mg/L)	Sulfate (mg/L)
Residual float I (Original process)	3,4	>5000	27,716.5	1,610	9,295.03	11,599.65
Residual float I (Chemical reduction)	3,4	>5000	23,633.0	1,258	6,710.13	10,033.96
Residual float II (Original process)	3,2	>5000	7,846.5	2,012	13,725.26	2,352.13
Residual float II (Chemical reduction)	3,2	>5000	6,211.0	205	7,292.37	1,885.61

The organoleptic evaluation of the leather showed that softness, filling and grain had equal mean results before and after chemical reduction on a pilot scale (Table 5), and the visual analysis of impregnation showed superior results after the reduction in the supply of chemicals, which may be related to the lower concentration of other chemicals, which would compete in the diffusion of the resin into the leather.

Table 5: Organoleptic evaluation of the leather.

	Original formulation		Chemical reduction	
	Average*	Desvpad	Average*	Desvpad
Softness	3	0	3	0
Filling	4	0	4	0
Grain	2.33	0.47	2.33	0.47
Impregnation	3	0	5	0

*scale from 1 (worst result) to 5 (best result)

The Physical-mechanical quality requirements were met on the leather produced on the industrial scale for all the tested parameters (Table 6). In addition to the reduction in the pollution load of the raw wastewater, there was a reduction of at least 24% in the process costs, considering only costs related to chemicals used in the formulation.

Table 6: Physical-mechanical tests on finished leather produced with chemical reduction (Hansen et al., 2021).

Physical-mechanical test	Result	Requirement
Tear resistance strenth (N)	107.91	60 for large handbag (ISO 3377-1:2011, 2011)
Colorfastness to light	5	≥ 3* (Basf, 2005)
Colorfastness to friction - water	5	≥ 3* (Basf, 2005)
Colorfastness to friction - alcohol	4 a 5	≥ 3* (Basf, 2005)

Conclusions

This study showed that the leather chemicals used in the formulation represent a relevant contribution to the organic and inorganic pollution load of raw wastewater. The results, both on pilot and industrial scale, showed that it was possible to reduce the pollution load of the raw wastewater, maintaining the organoleptic properties of the leather and meeting the established physical-mechanical requirements. In addition, formulation costs were reduced by 24%.

These results motivate more efforts to reduce the environmental impacts of tanneries, as the extrapolation of the use of this technique in other tanneries can reduce the mass of leather chemicals used and the pollution load of this industry's wastewater.

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