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Evaluation of Environmental Performance of Chrome-Free Tanning Techniques of Paiche Skins (*Arapaima gigas*)

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ABSTRACT

The leather production from paiche skins (*Arapaima gigas*) has recently grown in Peru, as this allows adding value and earnings from this Amazonian aquaculture waste. The development of this process requires that the tanning techniques could preserve environment as these are meant to take place in Amazonian zones. The present study evaluated the environmental performance of two chrome-free tanning techniques of paiche skins compared with traditional chrome tanning technique, developed at pilot scale by CITEccal Lima. The evaluation was carried out using environmental performance indicators (EPI), analyzed and compared using the grey clustering method, identifying coefficients (σ) respecting to the stablished classes in the study ($\lambda 1$ – good, $\lambda 2$ – regular, $\lambda 3$ – deficient). As result, the two chrome-free tanning techniques showed a better environmental performance than the traditional chrome tanning technique (σ – 0.54, class $\lambda 2$). The optimized tanning technique applying phenolic compounds had the best environmental performance (σ – 0.98, class $\lambda 1$), and its values for each environmental performance indicator per 1000 kg of initial processed paiche skin were: 30.0 m^3 for water consumption, 815.0 kg of chemical products applied, 2022.7 kWh for energy consumption, 105.5 kg of solid wastes; and from wastewater characterization: 2780.9 mg/L for BOD, 11682.9 mg/L for COD and non-detectable chromium. On the basis of these results, its transfer is recommended, including a wastewater treatment system and environmental management measures implementation.

Keywords: chrome-free tanning techniques, environmental performance evaluation, environmental indicators, grey clustering analysis.

INTRODUCTION

As part of productive development policies, Peru has promoted the increase of aquaculture of paiche (*Arapaima gigas*) [Chu Koo et al., 2017; Kleeberg, 2019]. This way, market projections include the increase in exportations of paiche meat, as it is, alongside trout and tilapia, the main freshwater fish species exportations in the country [Hartwich et al., 2017]. Paiche meat is exported as frozen steaks, so previously it is eviscerated and skinned, with yields between 47% and 52%. This process generates wastes such as the paiche skins, which require a properly management as they have the potential to be valorized in the production of leather [Chu Koo et al., 2017].

The leather industry transforms skins into leather through a series of processes and applying different chemical products [Covington and Wise, 2015]. Tanning is the main process, where collagen in skins is stabilized against heat, enzymatic activity and putrefaction [Beghetto et al., 2013; Zeiner et al., 2011] by a applying a tanning agent. Tanning carried out by applying basic chromium sulfate salts (BCS) is the most used tanning technique worldwide, nearly 90%, as it provides leather with desirable physical-mechanical properties such as excellent hydrothermal stability, better dying capacity and softness [Fei and Liu, 2016; Kanagaraj et al., 2008]. Nevertheless, the application of BCS leads to the generation of high concentrations of trivalent chromium Cr(III) in wastewaters and solid wastes of the process. This Cr(III) can be oxidized into Cr(VI) under certain conditions such as reaction in presence of manganese dioxide (MnO2), high temperatures and pH fluctuations in wastewaters [Apte et al., 2006; Dias da Silva et al., 2011; Zasoski and Fendorf, 1992]. Hence, the application of BCS potentially contributes to environmental pollution associated to Cr(VI), as this chromium species is specially pollutant in environment and a risk for health [China et al., 2020; Kotaś and Stasicka, 2000].

Facing this environmental challenge, several studies have presented techniques to manage chromium pollution in leather industry [China et al., 2020]. These techniques include the reduction of chromium consumption and recirculation of chromium baths in the process, high chrome exhaustion, processes of applying substances to improve chromium absorption in leather and applying alternative tanning agents in order to replace BCS [Bacardit et al., 2014; Fathima et al., 2006; Musa et al., 2011; Roig et al., 2011]. In this context, the present research aimed to evaluate the environmental performance (EP) of chrome-free tanning techniques of paiche skin developed by CITEccal Lima. These techniques are tanning with aluminum (T-Al) and with phenolic compounds (T-Ph), to determine the viability of its technological transference to the productive chain. The employed methodology consisted in evaluating the environmental performance indicators (EPI) and the analysis of indicators applying Grey Clustering Method (GCM). This method is based on grey system theory, focused on study problems that involve small samples and limited information [Liu and Lin, 2011]. It is widely applied in evaluation of environmental systems as water quality, eutrophication levels, water management and environmental conflicts analysis [Delgado and Romero, 2016; Wang et al., 2018; Zhang et al., 2014; Zhou and Xu, 2006]. It was developed to classify observation indices or observation objects in defined clusters using grey incidence matrixes or grey whitenization weight functions. The present study applied the GCM based on center point triangular whitenization weight functions (CTWF) as the tanning techniques can be treated as observation objects to evaluate its environmental performance.

METHODOLOGY

The present study applied a descriptive quantitative design, in which the environmental performance of two chrome-free tanning techniques was evaluated. These techniques are the tanning applying aluminum salts (T-Al) and phenolic compounds (T-Ph), both compared to traditional chromium salts tanning technique (T-Cr). The environmental performance of the tanning techniques was evaluated based on operation indicators such as water consumption, amount of applied chemical products, energy consumption and amount of solid wastes per skin processed, which were analyzed and compared applying the GCM to identify the technique with the best environmental performance.

Sample

The studied tanning techniques were developed in the Tanning Pilot Plant from CITEccal Lima. The paiche skins (peeled, salted and preserved) processed in the project, were provided by aquaculture companies from region Ucayali – Peru.

Material flow analysis

The three tanning techniques comprise the following steps: soaking, degreasing, pickling, tanning, neutralizing and fatliquoring. The material flow balance was done using the data of inputs and outputs of each step. The data considered as input were skin weight, water consumption, amount of applied chemical products and energy consumption, whereas, produced leather weight, amount of solid wastes per skin processed and wastewater volume were considered as outputs. To estimate the energy consumption of the tanning drums motors and the electric water heater used in the tanning processes, Eq. (1) was used:

$$\text{Energy consumption(kWh)} = \text{Power(kW)} \times \text{Time(h)} \quad (1)$$

The power of the tanning drums motors was 1.49 kW and the electric water heater was 1.20 kW.

Wastewater characterization

In the comparison of environmental performance of the tanning techniques, the effluent from pickling and tanning operations were sampled and characterized for each tanning technique as shown on Figure 1. Later, in the optimized phenolic tanning technique, samples were taken from pickling and tanning bath, in addition to the samples of effluents treated through the proposed system.

The wastewater sampling was done according to the criteria of standard methods for Water and Wastewater Analysis from American Water Works Association (AWWA). The samples were analyzed in a testing laboratory accredited by the requisites of the ISO 17025 standard. The studied parameters were potential of hydrogen (pH) (SMEWW-APHA-AWWA-WEF Part 4500-H+B, 23rd Ed: 2017), Biological Oxygen Demand (BOD) (SMEWW-APHA-AWWA-WEF Part 5210 B, 23rd Ed: 2017), Chemical Oxygen Demand (COD) (SMEWW-APHA-AWWA-WEF Part 5220 D, 23rd Ed: 2017), Oils and Fats (ASTM D3921-96, Reapproved 2011), Total Suspended Solids (TSS) (SMEWW-APHA-AWWA-WEF Part 2540-D, 23rd Ed: 2017), Phenols (EPA Method 420.2:1974 // EPA Method 420.4 Rev. 01:1993 Validated 2013), Total Petroleum Hydrocarbons C10-C40 (EPA Method 8015C Rev.3: 2007) and Total Chromium (EPA Method 8015C Rev.3: 2007). The results of physiochemical parameters studied on wastewater were analyzed comparing them with maximum allowable concentrations (LMP by its acronym in Spanish) for industrial tanning activities in Peru [Límites Máximos Permisibles y Valores Referenciales Para Las Actividades Industriales de Cemento, Cerveza, Curtiembre y Papel (in Spanish), 2002].

Analysis and comparison of environmental performance indicators of tanning techniques

Environmental performance indicators (EPI) were determined based on flux analysis and physiochemical characterization of effluents, the EPI selected for this study were: Water consumption per initial skin processed – WC (m^3/1000 kg), Amount of chemicals used per initial skin processed – ACP (kg/1000 kg), Energy consumption per initial skin processed – EC (kWh/1000 kg), Amount of solid waste generated per initial skin processed – SW (kg/1000 kg), as well as tannery wastewater parameters – BOD, COD and Total Chromium (mg/L).

Determination of the best environmental performance tanning technique

A whole EPI analysis applying GCM based on center-point triangular whitenization weight functions (CTWF) was carried out. This method supports on the following definition: assuming there are a set of "m" observation objects, a set of "n" criteria and a set of "s" different grey classes, according to the sample value $X_{ij\,(I = 1,2,\ldots,m;\, j = 1,2,\ldots,n)}$ of the *i-th* object (i = 1, 2,…, m), for *j-th* criteria (j = 1, 2,…, n), the *i-th* object is classified in the *k-th* grey class (k = 1, 2,…, s). The steps for grey clustering based on CTWF can be expressed as follows [Delgado and Romero, 2016; Liu and Lin, 2011; Zhang et al., 2014]:

1) Establish evaluation criteria and evaluation standards for the classes.
2) Elaborate the Whitenization Weight Functions (WF).

The WF for each indicator j and subclass k are noted as f_j^k. The center points of the grey classes are set λ_k (k = 1, 2,…, s). Functions are calculated applying the following correspondence rules [Zhang et al., 2014; Zhou and Xu, 2006], where "x" to evaluate are non-dimension data of criteria.

$$f_j^1 = \begin{cases} 1, x \in \left[0, \lambda_j^1\right] \\ \dfrac{\lambda_j^2 - x}{\lambda_j^2 - \lambda_j^1}, x \in \langle \lambda_j^1, \lambda_j^2 \rangle \\ 0, x \in \left[\lambda_j^2, \infty\right\rangle \end{cases} \quad (2)$$

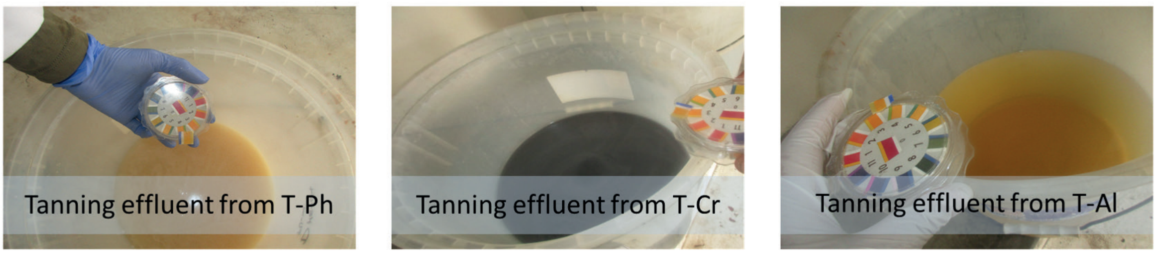

Figure 1. Tanning effluents recollected from each tanning technique

$$f_j^k = \begin{cases} \dfrac{x-\lambda_j^{k-1}}{\lambda_j^k-\lambda_j^{k-1}}, x \in \langle \lambda_j^{k-1}, \lambda_j^k \rbrack \\ \dfrac{\lambda_j^{k-1}-x}{\lambda_j^{k*1}-\lambda_j^k}, x \in \langle \lambda_j^k, \lambda_j^{k*1} \rangle \\ 0, x \in \lbrack 0, \lambda_j^{k-1} \rbrack \cup \lbrack \lambda_j^{k*1}, \infty \rangle \end{cases} \quad (3)$$

$$f_j^3 = \begin{cases} \dfrac{x-\lambda_j^2}{\lambda_j^3-\lambda_j^2}, x \in \langle \lambda_j^2, \lambda_j^3 \rangle \\ 1, x \in \langle \lambda_j^3, \infty \rangle \\ 0, x \in \lbrack 0, \lambda_j^2 \rbrack \end{cases} \quad (4)$$

1. Establishing clustering weights

Weights are found by calculating the average of index values inverses, as follows:

$$n_j^k = \frac{\lambda_j^k}{\sum_{j=1}^m \lambda_j^k} \quad (5)$$

$$n_j^k = \frac{1/\lambda_j^k}{\sum_{j=1}^m 1/\lambda_j^k} \quad (6)$$

2. Calculating clustering coefficient σ_i^k

Clustering coefficient is calculated multiplying function values and its weights, showing the incidence grade of clustering in the grey classification.

$$\sigma_i^k = \sum_{j=1}^m f_j^k(x_{ij}).n_j^k \quad (7)$$

3. Determination and evaluation of clustering vector

Finally, the highest values of coefficients are chosen and analyze which standard evaluation classes they belong to.

$$\sigma_i^{k\cdot} = \max_{1 \le k \le s}\{\sigma_i^k\} \quad (8)$$

RESULTS AND DISCUSSION

The values of operationalized EPIs of studied tanning techniques are presented in Table 1.

Water consumption per initial processed paiche skin (WC)

According to WC indicator, T-Cr had the best performance (27.0 m^3/1000 kg), followed by T-Ph (28.0 m^3/1000 kg) and finally T-Al (30.8 m^3/1000 kg). The obtained values can be compared with water consumption connected with the tanning process activities at industrial scale that (according to Konrad et al. (2002)) is 25.85 m^3/1000 kg, similar to the value estimated by Rivela et al. (2004) at 23.0 m^3/1000 kg.

These values are in the range presented by Tünay et al. (1999) of 21.40–29.75 m^3/1000 kg [Tünay et al., 1999]. Besides, the obtained values were compared to the Environmental Reference System for Tanning Industry of Colombia (SIR-AC), benchmarking values that guide to develop the best available tanning techniques [Aragón

Table 1. Environmental performance indicators of tanning techniques in paiche skins

Indicators	Unit	T-Cr	T-Al	T- Ph
Water consumption per initial skin processed (WC)	m^3/1000 kg	27	30.8	28
Amount of chemicals used per initial skin processed (ACP)	kg/1000 kg	427	618	472.8
Energy consumption per initial skin processed (EC)	kWh/1000 kg	1053.2	1175.6	1679
Amount of solid waste generated per initial skin processed (SW)	kg/1000 kg	109.1	104	102
pH	mg/L	3.6	3.8	3.9
BOD	mg/L	4 810.0	965	4 370.0
COD	mg/L	13 137.1	3 331.2	18 197.5
Oils and fats	mg/L	15.1	45.4	147.5
Total chromium	mg/L	2888.4	N.D.	N.D.
Aluminum	mg/L	N.D.	6232.12	N.D.
Phenols	mg/L	N.D.	N.D.	8.8

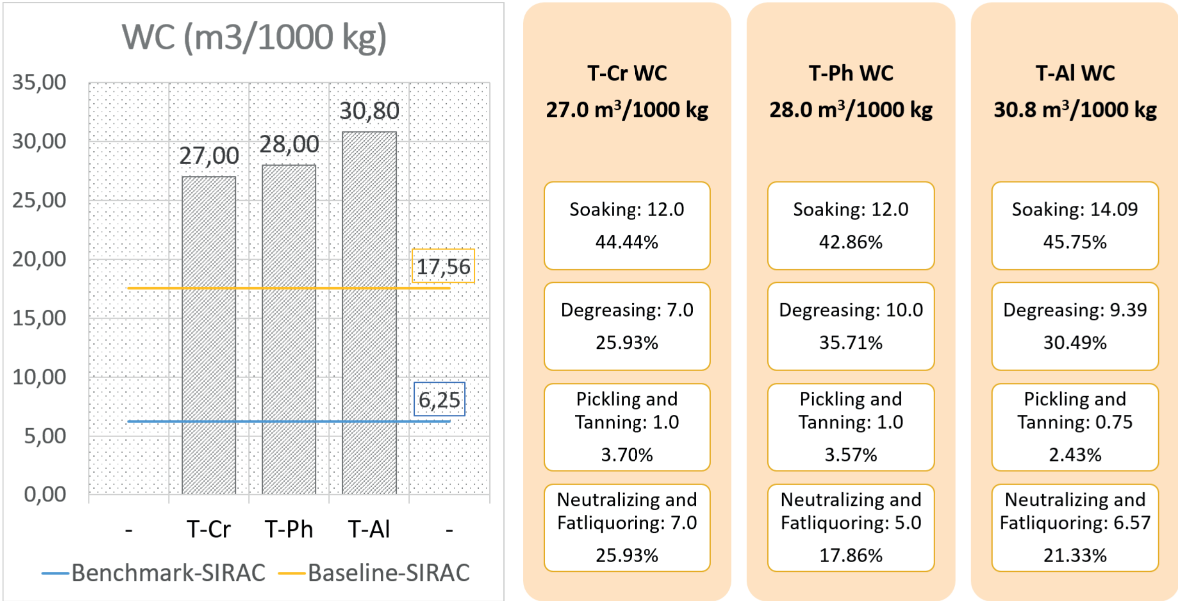

Figure 2. Comparison of water consumption per initial processed leather of tanning techniques and percentage per operation

Guzmán and Alzate Tejada, 2004]. The results are detailed in Figure 2.

The results show that the WC of the studied techniques exceeds the baseline of 17.56 m^3/1000 kg (reference value of tanning industry) and benchmark value of 6.25 m^3/1000 kg. Moreover, the soaking and degreasing stages are the more pollutant because of their high WC rates, since soaking needs significant amounts of water to rehydrate the skins and remove the chlorides used for its conservation, and long degreasing stage because of paiche skin high levels of fats [Segundo Espada et al., 2020].

The value of WC from both stages (expressed as percentage) is 70.37% for T-Cr, 70.58% for T-Ph and 76.24% for T-Al. Hence, water saving and reuse in baths of soaking and degreasing stages constitute good alternatives for water management.

Amount of chemical products applied per initial processed paiche skin (ACP)

The chemical products applied in the studied tanning techniques include bactericides, surfactants in soaking and degreasing stages, enzymes, tanning compounds (basic chromium sulphate, phenolic compounds and aluminum salts), acids in pickling and tanning stages, bases and fatliquors in neutralization and fatliquoring stage. With respect to ACP, the tanning technique with the best performance was T-Cr with 427 kg/1000 kg, followed by T-Ph with 472.8 kg/1000 kg and finally, T- Al with 618 kg/1000 kg. These results surpass the values such as average global consumption of 391 kg/1000 kg [Konrad et al., 2002], and the SIRAC value of 154.66 kg/1000 kg, presented in Figure 3.

It was found out that the most critical stages in ACP were pickling and tanning stages, as their intake percentage with respect to the whole process are 38.64% for T-Cr. 50.03% for T-Ph and 55.50% for T-Al. The values obtained for chrome-free tanning techniques are close to the value estimated of 53% in similar studies for tanning stage [Rivela et al., 2004]. The variations identified may be associated to the technology applied (tanning techniques) and working conditions (kind of processed skin) [Tünay et al., 1999]. The environmental improvement measures for this indicator are the improvement and optimization of the fleshing process, stage prior to the tanning process where connective tissue and meat residues are removed from the skin, as this stage significantly reduces the weight of the skin, so less quantity of chemical products is required in the following processes; besides, this measure also improves the quality and area of the finished leather [Konrad et al., 2002].

Energy consumption per initial processed paiche skin (EC)

T-Al with a result of 1045.03 kWh/1000 kg showed the best performance in EC, followed

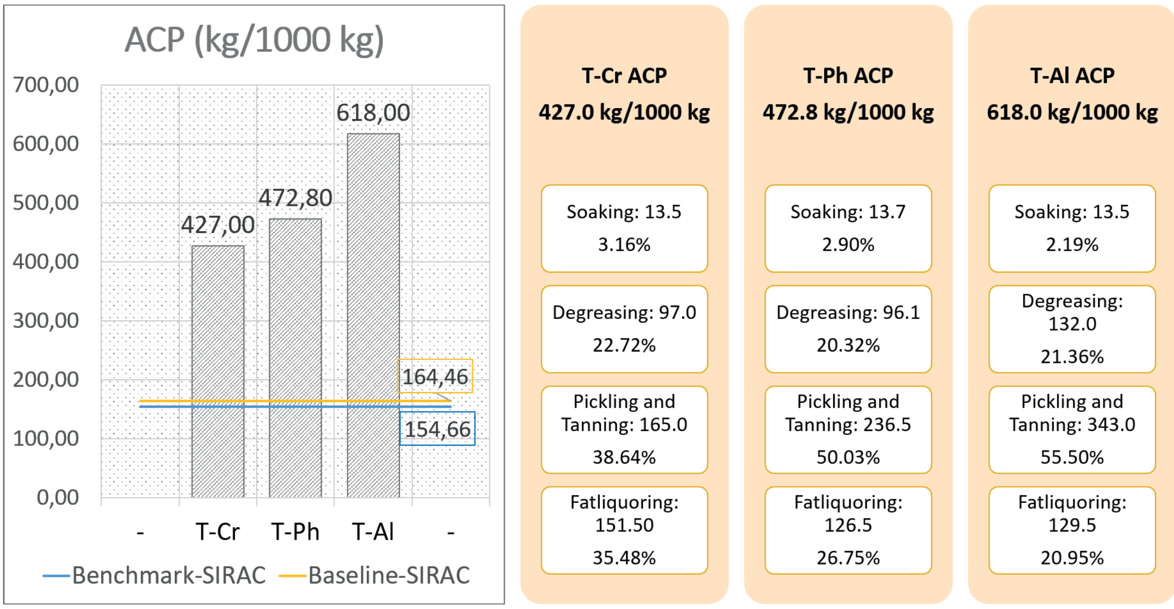

Figure 3. Comparison of the indicator amount of chemicals used per initial processed leather from tanning techniques and percentage per operation

by T-Cr with 1053.24 kWh/1000 kg and finally T-Ph with 1492.48 kWh/1000 kg. These results show high EC compared to the SIRAC values, probably due to the own characteristics of each tanning techniques that imply long working periods for the equipment and the use of water heater to increase temperature of water for degreasing and fatliquoring stages.

Figure 4 shows that fatliquoring is one of the most critical stages in EC, related to the require of water at 35 °C, heated up using a water heater, followed by pickling and tanning stages, due to processing time in the drums, that operate by the energy supplied from motors, which worked for a maximum of 10 hours, much more than other stages that work from 2.5 to 5 hours. The high values of EC require the measures to mitigate its impact, such as the use of renewable energy sources, use of more efficient equipment and control of energy efficiency.

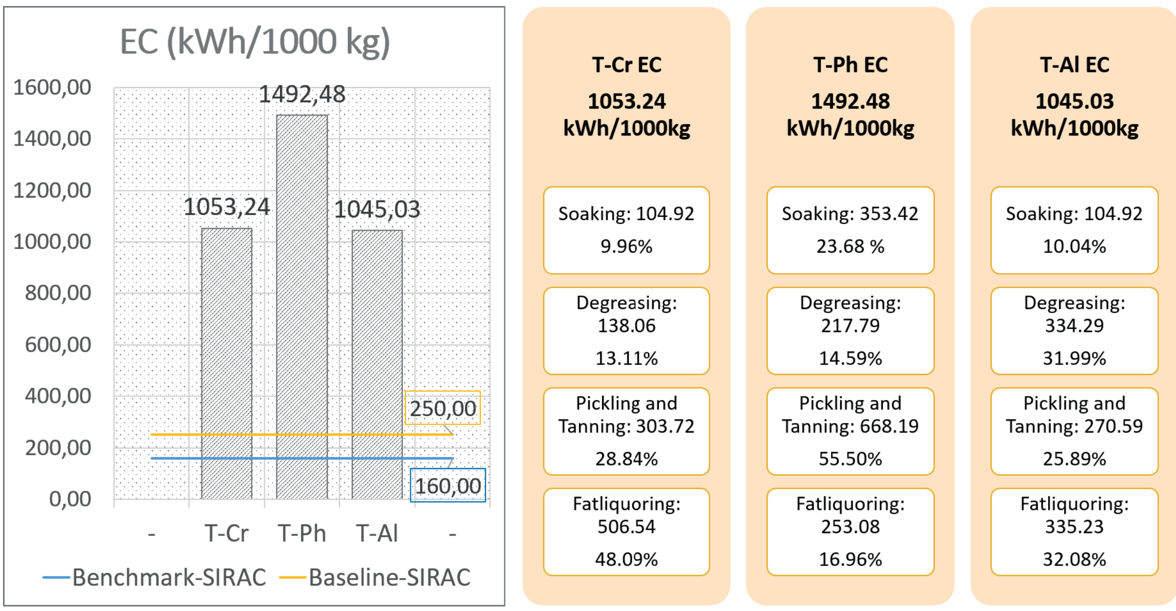

Figure 4. Comparison of the indicator energy consumption by initial processed leather of the tanning techniques and percentage per operation

Amount of solid wastes per initial processed paiche skin (SW)

The solid wastes were generated prior to the start of the tanning process, specifically in the fleshing process. In the main tanning process, no solid wastes were generated. In the next stage, crust leather production, the only waste generated was buffing dust.

It should be noted that the yields of SW were not compared, but rather the average amount of paiche skin fleshing waste was determined aiming to obtain a reference value of SW regardless of the tanning technique applied. The average value of SW generated was 105.03 kg/1000 kg; this result was analyzed in respect to the SIRAC values as shown in Figure 5.

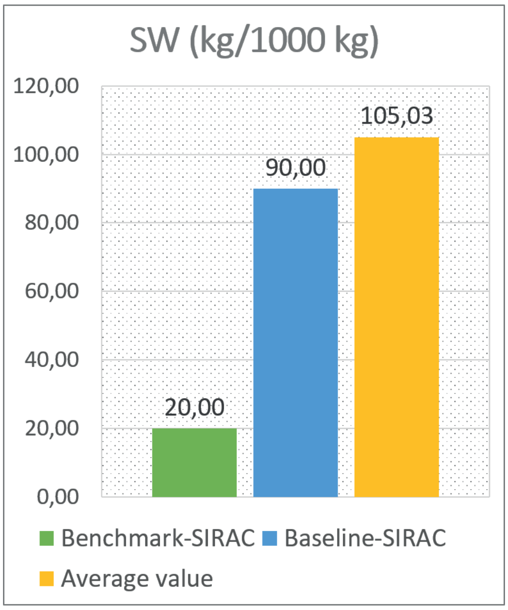

Figure 5. Value of the indicator of the amount of waste generated by the initial leather processed from the tanning techniques

Average SW did not vary significantly in respect to the SIRAC baseline value; hence, in paiche leather production, the generation of solid wastes is moderate, with 10.50% of weight of paiche skin processed, these wastes from fleshing stage have the potential to be valorized, as they are not mixed with other chemical substances or pollutants. In comparison, the estimated percentage for cow hides processing from skin to crust leather is 56.02%, according to a diagnosis study of Peruvian tanneries [CIATEC, 2006], and in other countries, the values of 27.30% were found [Rivela et al., 2004]. Fleshing wastes can be valorized as raw material for soap/surfactants industry or for the development of products for leather processing fatliquoring, another option is for feed concentrates for animals [CIATEC, 2006].

Analysis of wastewater characterization indicators

According to the results presented in Table 2, the wastewater from the 3 processes exceeds the LMP values for industrial tanning activities, due to high pollutant content in tannery wastewaters, characterized by high organic and chemical matter added by the products used in the tanning process [Konrad et al., 2002].

From the results of wastewater characterization, the more pollutant effluents correspond to T-Cr, as this presents a high concentration of total chromium (2888.37 mg/L) and organic material (13137.10 mg/L of COD). T-Al presents a high concentration of total aluminum (6232.12 mg/L) but less organic material

Table 2. Comparison of the physicochemical parameters of the tanning effluent of paiche skins with respect to the LMP of tanneries

Wastewater parameters	Tanning effluent from T-Cr	Tanning effluent from T-Al	Tanning effluent from T-Ph	LMP - sewage*	LMP - surface waters*
pH	3.6	3.86	3.91	6.0-9.0	5.0-8.5
BOD (mg/L)	4810	965	4370	500	30
COD (mg/L)	13137.1	3331.2	18197.5	1500	50
Oils and fats (mg/L)	15.1	45.4	147.5	50	20
Phenols (mg/L)**	N.D.	N.D.	8.81	0.5	
Aluminum (mg/L)	N.D.	6232.12	N.D.	---	---
Total chromium (mg/L)	2888.37	N.D.	N.D.	2	0.5

Note: * Decreto Supremo No. 003-2002-PRODUCE; ** Decreto Supremo No. 037-2008-PCM.

compared to T-Cr, evidenced by decreasing percentages of 79.9% for BOD and 74.6% for COD. These values correspond to the studies of new chrome-free tanning techniques, which apply mixes of aluminum salts, such as the tanning system based on aluminum-silicon compounds developed by Tanfor TTM with a decrease in COD of 60% [Bacardit et al., 2014] and the tanning system based con aluminum-silicon-phosphonium with a COD decrease of 41% [Fathima et al., 2006].

The effluents from T-Cr and T-Al require advanced treatment for an adequate removal of the metals, as they present high concentrations of chromium and aluminum, respectively. Chromium removal can be performed by electrocoagulation (97% removal efficiency) photocatalysis (91-98% removal efficiency) and metal adsorption by agriculture and industrial material (93-99% efficiency). Aluminum removal can be performed by nanofiltration (96-98.5% efficiency) and chemical precipitation by electroplating (80–90% efficiency) [Caviedes Rubio et al., 2015]. The reference cost of wastewater treatment including advanced treatment is 0.72 US$/m^3 [Pal, 2020]. The effluents from T-Ph, present a high concentration of organic material and phenolic compounds concentration that exceeds 0.5 mg/L, the LMP value for tanning activities [Límites Máximos Permisibles de Efluentes Líquidos Para El Subsector Hidrocarburos (in Spanish), 2008; Límites Máximos Permisibles y Valores Referenciales Para Las Actividades Industriales de Cemento, Cerveza, Curtiembre y Papel (in Spanish), 2002]. The organic material from T-Ph increased with respect to T-Cr in 38.5% for COD, that can be related to the phenolic compounds applied in tanning, as these are recognized by their significantly contribution to BOD and COD in wastewaters [China et al., 2020]. The T-Ph effluents treatment can be performed by advanced oxidation with treatment costs around 0.22–0.45 US$/m^3 [Bes Monge et al., 2016].

Table 3. Ranks and standards of evaluation of the established classes

Classes / Criterias	λ1: Good performance	λ2: Regular performance	λ3: Poor performance
Water consumption per initial skin processed (m^3/1000 kg)	<27.0	27.0–30.8	>30.8
	13.5	28.9	44.3
Amount of chemicals used per initial skin processed (kg/ 1000 kg)	<427.0	427.0-618.0	>618.0
	213.5	522.5	831.5
Energy consumption per initial skin processed (kWh/1000 kg)	<1045.0	1045.0–1492.5	>1492.5
	522.5	1268.7	2014.9
BOD (mg/L)	<965.0	965.0–4810.0	>4810.0
	482.5	2887.5	5292.5
COD (mg/L)	<3331.200	331.2–18197.5	>18197.500
	1665.6	10764.4	19863.1
Total chromium (mg/L)	<3.4366	3.4– 2888.4	> 2888.4
	1.7	1445.9	2890.1

Table 4. Non-dimensional values of the evaluation standards

Criterias	Symbol	λ1: Good performance	λ2: Regular performance	λ3: Poor performance
Water consumption per initial skin processed (m^3/1000 kg)	WC	0.47	1	1.53
Amount of chemicals used per initial skin processed (kg/ 1000 kg)	ACP	0.41	1	1.59
Energy consumption per initial skin processed (kWh/1000 kg)	EC	0.41	1	1.59
BOD (mg/L)	BOD	0.17	1	1.83
COD (mg/L)	COD	0.16	1	1.85
Total chromium (mg/L)	Cr	0	1	2

Table 5. Values of the evaluated criteria and their non-dimensional values

Tanning techniques	Criterias: Environmental performance indicators					
	WC	ACP	EC	BOD	COD	Cr
T-Cr	27	427	1053.24	4810	13137.1	2888.37
T-Al	30.8	618	1045.03	965	3331.2	0
T-Ph	28	472.8	1492.48	4370	18197.5	0
Tanning techniques	Non-dimensional values of the criterias					
	WC	ACP	EC	BOD	COD	Cr
T-Cr	0.93	0.82	0.83	1.67	1.22	2
T-Al	1.07	1.18	0.82	0.33	0.31	0
T-Ph	0.97	0.91	1.18	1.51	1.69	0

Results of determination of best environmental performance tanning technique

1. Establishment of evaluation criteria and class evaluation standards

In the study, tanning techniques were established as objects of observation, the criteria were EPI, and the evaluation standards were determined based on the minimum and maximum values of each EPI [Liu and Lin, 2011]. The use of these standards are due to the lack of specific evaluation standards for the environmental performance of tanning processes of paiche skin, since standards of tanning process studies are related mostly to cow hides such as benchmarking indices of SIRAC [Aragón Guzmán and Alzate Tejada, 2004]. The evaluation standards were calculated as the midpoint ranges values, detailed in Table 3, and their non-dimensional values in Table 4. The values of the evaluated criteria and their non-dimensional values are presented in Table 5.

2. Whitenization functions

WF were elaborated for each evaluation criteria, so there are 6 set of functions for each tanning technique. The WF for WC are presented in Figure 6, the functions for other criteria have a similar structure.

$$f_j^1 = \begin{cases} 1, x \in [0, 0.47] \\ \dfrac{1-x}{1-0.47}, x \in \langle 0.47, 1 \rangle \\ 0, x \in [1, \infty\rangle \end{cases} \tag{9}$$

$$f_j^2 = \begin{cases} \dfrac{x-0.47}{1-0.47}, x \in \langle 0.47, 1] \\ \dfrac{1.53-x}{1.53-1}, x \in \langle 1, 1.53 \rangle \\ 0, x \in [0, 0.47] \cup [1.53, \infty\rangle \end{cases} \tag{10}$$

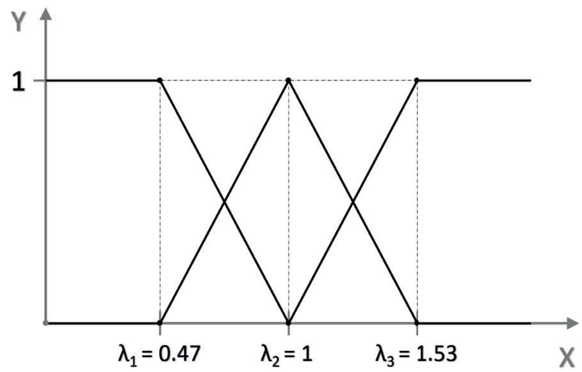

Figure 6. Whitenization functions

Table 6. Whitenization functions values for T-Cr, T-Al and T-Ph

Tanning technique	WF	WC	ACP	EC	BOD	COD	Cr
T-Cr	f1	0.12	0.31	0.29	0.00	0.00	0.00
	f2	0.88	0.69	0.71	0.20	0.74	0.00
	f3	0.00	0.00	0.00	0.80	0.26	1.00
T-Al	f1	0.00	0.00	0.30	0.80	0.82	1.00
	f2	0.88	0.69	0.70	0.20	0.18	0.00
	f3	0.12	0.31	0.00	0.00	0.00	0.00
T-Ph	f1	0.06	0.16	0.00	0.00	0.00	1.00
	f2	0.94	0.84	0.70	0.38	0.18	0.00
	f3	0.00	0.00	0.30	0.62	0.82	0.00

$$f_j^3 = \begin{cases} \frac{x-1}{1.53-1}, x \in \langle 1, 1.53 \rangle \\ 1, x \in \langle 1.53, \infty \rangle \\ 0, x \in [0,1] \end{cases} \quad (11)$$

Values of WF calculated for each tanning technique are presented in Table 6.

3. Clustering weight

Weights were calculated for each indicator based on the data evaluation standards, and results are detailed in Table 7.

4. Clustering coefficient σ

Coefficients were calculated by applying equation 8, and its results are presented in Table 8.

5. Determination and evaluation of the clustering vector

The highest values obtained from coefficients were chosen, and their belonging to an evaluation clustering was verified, the results are highlighted in Table 8. The highest values of clustering coefficients from chrome-free tanning techniques belong to class λ1: Good performance, where T-Al obtained 0.990 while T-Ph obtained 0.978. In comparison, T-Cr obtained 0.536, which belongs to class λ2: Regular performance. Applying fundamentals of the Grey Clustering method, the tanning technique with the best environmental performance was determined, where higher values of a class shown more correspondence. As a result of comparing the environmental performance from tanning techniques:

Table 7. Clustering weight

Criteria	λ1	λ2	λ3
WC	0.002	0.167	0.186
ACP	0.003	0.167	0.18
EC	0.003	0.167	0.18
BOD	0.007	0.167	0.156
COD	0.008	0.167	0.155
Cr	0.977	0.167	0.143

Table 8. Clustering coefficient

Tanning techniques	*λ1*: Good performance	*λ2*: Regular performance	*λ3*: Poor performance
T-Cr	0.002	0.536	0.308
T-Al	0.99	0.442	0.079
T-Ph	0.978	0.508	0.277

T-Cr (0.536, class λ2) < T-Ph (0.978, class λ1) < T-Al (0.990, class λ1)

Hence, the studied chrome-free tanning techniques showed better environmental performance compared to T-Cr, where T-Al presents the best environmental performance, followed by T-Ph.

The evaluation of the environmental performance of the tanning techniques on paiche skins was carried out on the techniques applied on a pilot scale to identify the technique to be transferred to production scale. Thus, the T-Al could have been recommended, as this technique allowed the production of leather that accomplished the Peruvian Technical Standards (NTP) for quality in leather and footwear. However, as the project was in execution, the leather produced by this technique suddenly gave off a fishy smell and started yellowing. This related to the insufficient removal of fats from paiche skin, consequently, the T-Ph was selected for the transference to production scale.

When the causes were investigated, using the characterization analysis of degreasing effluents, it was concluded that this operation had not been efficient enough-, thus, it was optimized in order to reduce the probability of compromising the properties of the leather. Furthermore, according to skin degradation studies on fish skin, it is normal in the processing of fish skin, and is related to the generation of lactic acid from glycogen or oxidation of remaining fats in skin [Barrenechea Cisneros, 2019; Huss, 1998]. Hence, the degreasing process was improved, by increasing the concentration of hydrocarbons, enzymes and degreasing surfactants, and degreasing was applied before and after pickling [Segundo Espada et al., 2020].

Evaluation of the environmental performance of the optimized tanning technique

The process for the optimized tanning technique (T-OPh) is detailed in Figure 7, which shows inputs and outputs per stage. It is necessary to point out that the solid wastes from fleshing stage amounted to approximately 105 kg/1000 kg.

In Table 9, environmental performance indicators for T-Ph and T-OPh are compared. Where WC increased in 2.0 m^3/1000kg, ACP increased in 342.2 kg/1000 kg and EC increased in 530.20 kWh/1000 kg. BOD and COD indicators decreased, probably related to the degreasing optimization and the dilution of chemical products in effluents, as more water was consumed.

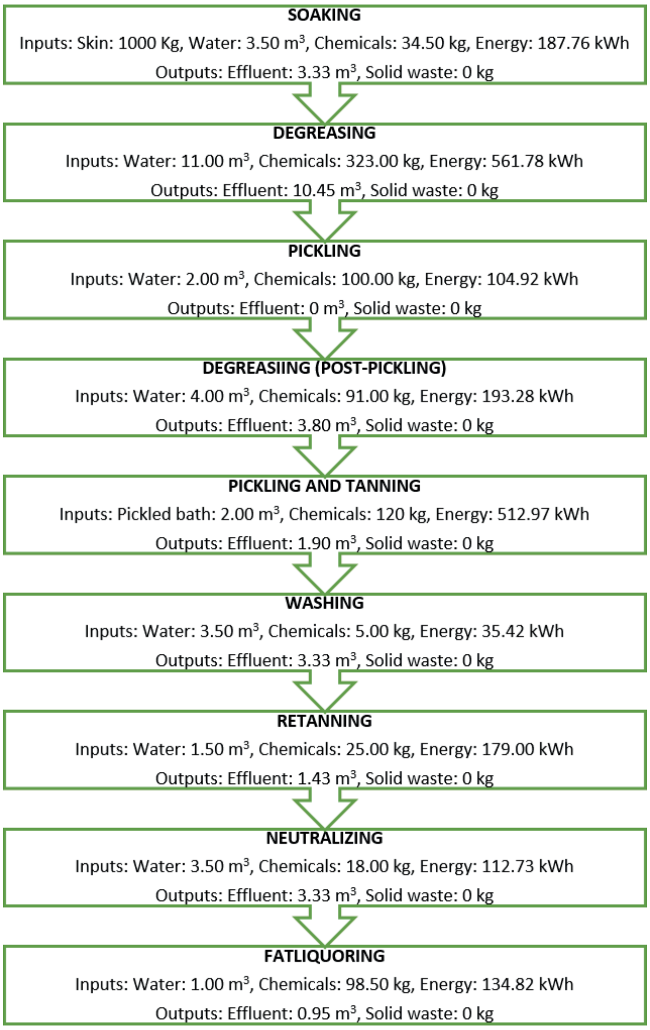

Figure 7. Inputs and outputs of the T-OPh

Nevertheless, there is still high concentration of organic material that requires treatment to be discharged. For environmental performance applying Grey Clustering, a decrease was observed compared to T-Ph (0.978, class $\lambda 1$: Good performance), as its results were slightly lower with a maximum clustering coefficient of 0.977, class $\lambda 1$: Good performance, but it does not affect the class.

Regarding the characterization of the composite effluent (proportional mixture of effluents from each operation), high organic material and concentration of oils and fats was determined, with values of 9120.00 mg/L for BOD, 27365.90 mg/L for COD, 8318.20 mg/L for fats and 2698.80 mg/L for total petroleum hydrocarbons, 5.02 mg/L for phenols, 2500.00 mg/L for TSS and pH of 4.19. The high fats concentration is due to the fat content in paiche skins, approximately 45% [Segundo Espada et al., 2020], which is higher than traditional skins used for tanning, such as cow hides (2–4%), goat skins (12–15%) or sheep skins (30–40%) [Afsar and Cetinkaya, 2008; Choudhary et al., 2004].

Table 9. Comparison of operational environmental performance indicators of T-Ph and T-OPh

Indicators	T-Ph	T-OPh
Water consumption per initial skin processed (m^3/1000 kg)	28	30
Amount of chemicals used per initial skin processed (kg/1000 kg)	472.8	815
Energy consumption per initial skin processed (kWh/1000 kg)	1492.48	2022.68
BOD (mg/L)	4370	2870
COD (mg/L)	18197.5	11682
Total chromium (mg/L)	N.D.	N.D.

Table 10. Comparison of the parameters of the treated effluent with respect to the LMP

Evaluated parameters	LMP – sewage	LMP – surface water	Treated effluent
pH	6.0-9.0	5.0 – 8.5	4.72
TSS (mg/l)	500	35	12
Oils and fats (mg/L)	50	30	19.6
BOD (mg/L)	500	20	68.6
COD (mg/L)	1500	30	682.7
Phenols (mg/L)	0.5		0.15
Hydrocarbons (mg/L)	20		8.76

Wastewater treatment system for optimized tanning technique

Aiming to make technological transfer of optimized tanning technique viable, a wastewater treatment pilot scale system was proposed, that includes the processes of sedimentation, sifting, flotation and coagulation-flocculation, which reduced the pollutant charge from effluents. The results from characterization show that the treated effluent accomplishes the standards established by LMP for sewage discharges for all evaluated parameters except for pH, since the effluent is too acidic (pH=4.72), value out of the range established by LMP (pH 6–9); therefore, in order to ensure that the treatment complies with all the values of the LMP, the addition of a neutralization process would be suitable.

Regarding the values of LMP on water bodies, these values are stricter on its quality parameters, and were accomplished on the parameters of TSS, oils and fats, phenols and hydrocarbons. The parameters of BOD and COD exceed the standards. The results are presented in Table 10.

The comparison showed the feasibility of the wastewater treatment system for the effluents generated, since the results mostly accomplished the standards of LMP and with a treatment cost of 0.33 US$/m^3 [Hani Rodriguez, 2009]. Furthermore, the studies to improve the removal of high concentration of organic material must be carried out, through the techniques like advanced oxidation that achieve better removal ratios.

CONCLUSIONS

The present study identified the application of phenolic compounds as the tanning technique with the best environmental performance for transfer at scale production; the optimized technique (T-OPh) is the most suitable for this purpose. On the basis of its results for environmental performance indicators that surpass the benchmarking values for tanneries, it is recommended to apply the measures of environmental management, such as water saving and reuse, as well as optimization of the fleshing process as this allows the saving of chemical products, the use of energy from renewable sources, in addition to more energy efficient equipment and machines as well as implement a wastewater treatment system for their effluents, as high concentration of organic material and oils and fats was identified after wastewater characterization. The wastewater treatment system could include sedimentation, sifting, flotation and coagulation-flocculation, as it demonstrates efficacy in the removal of BOD, COD, TSS, oils and fats, phenols, hydrocarbons, in the case of pH, neutralization would be necessary to accomplish the standards of LMP, and it is recommended to conduct further studies about the treatment of this kind of effluents.

Finally, as a recommendation, the evaluation of environmental performance of alternative tanning techniques is necessary to assure that the tanning processes lead to sustainability. The replication of this study helps that process, applying the methodology, and improving it by new analysis such as life-cycle assessment, cost-benefit analysis, which will allow extending the scope of the indicators from local scale or production to a global scale.

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