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# Analysis And Selection Of A Tanning Alternative That Reduces The Impact Of Chromium On The Environment Using Multi-Criteria Decision Making Methods

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**ABSTRACT**

This article evaluates 15 alternatives for the reduction of the environmental impact generated by chromium salts in the manufacture of leather, it is sought that the selected alternative can allow companies to maintain or improve the quality of the product and comply with established regulations, this selection is made by means of multi-criteria decision methods (MCDM), using SAW, grey correlation and ELECTRE, which allow good results to be obtained when there are conflicts between quality, production, economic and environmental criteria. The importance of the variables is defined by hierarchical decision analysis (AHP), as a result of evaluating the costs, manufacturing conditions and pollution levels allowed in the city of Bogotá, the use of graphene oxide nanoparticles is postulated as a suitable alternative to replace traditional leather tanning as it presents properties that fully comply with the expected regulations, and yields good results in the three algorithms in which it was executed.

**Key words:** Tanning, Chromium, Leather, MCDM, Graphene oxide, Environmental impact.

## 1. INTRODUCCIÓN

In the leather industry, it is estimated that about 90% of the total production is done by traditional tanning (TC) using chromium as tanning agent (Ariram & Madhan, 2020), because it produces leathers with good handling quality, high hydrothermal stability and good physical and mechanical resistance, however, this process requires an excessive use of salts and chemicals, in addition the absorption of chromium is only 65-75% and the remaining remains in the tanning liquor making wastewater management difficult [2].

Currently Asia ranks first in leather production worldwide, followed by Latin America with a leather production for the year 2014 was 82.28 million raw hides processed, Europe ranks third among the leather producing continents, representing 16.7% of world leather production and 43.8 million bovine hides in the same year [3].

In 2014, around 4,227 million raw hides were produced in Colombia, however, for 2019 it was the sector with the highest negative growth according to DANE's industrial productivity indexes with a 22% decrease compared to the previous year (2018) [4].

Given the negative effects of the traditional process and the demands of the market, it has been sought to develop clean and chrome-free production strategies that respond to environmental challenges and keep companies in the sector competitive in both product quality and price. Some of the alternatives used involve the recycling of chromium from the tanning process wastewater [5], use of auxiliary compounds for high chrome exhaustion [6], combined tanning such as chromium sulfates and ozaxolidine, use of aluminum, vegetable tannins or nanomaterials [7], the use of ultrasound and microwaves has also been studied to improve tanning by achieving high absorption levels and shorter process time [8].

For the selection of a suitable alternative to replace or reduce the use of chromium in tanning, it is important to consider several factors such as the resulting physical and organoleptic properties of the leather, the necessary resources and the environmental impact, therefore, multi-criteria decision making methods (MCDM) appear to provide a solution to this type of problem. MCDM methods are divided into two categories: multi-objective decision making (MODM) and multi-attribute decision making (MADM) [9], the MADMs are further divided into direct scoring methods, distance-based methods, overcoming methods and methods based on utility or value functions.

The analytical hierarchical process (AHP) is carried out through the evaluation of the hierarchy by comparing in a paired way the elements of the hierarchy with respect to their dependency element, managing to evaluate the performance of the alternatives with respect to the attributes or criteria and thus allowing the selection of the alternative with the highest priority value as the best alternative [10].

SAW is characterized by its simplicity and particular ease of use, it bases its concept on the weighted sum of the criteria of each alternative analyzed, the best option is defined by the one in which the sum of the normalized weighted values is greater, the method employs only maximizing attributes and to minimize the criteria must be converted into maximizing factors before use [11].

Grey correlation is a computationally simple, robust and practical method that allows converting problems of multiple performance characteristics into a single performance characteristic, thus simplifying the optimization procedure and can effectively avoid subjective bias in the selection of a cleaner production alternative. [12], [13].

Electre is generally used in problems related to environmental management, it is a method that requires the comparison of each alternative for the calculation of an overall performance score, this was the first method of implementing the fuzzy nature in decision making through the use of indifference and preference thresholds [14].

This paper solves the problem of selection among 15 alternatives to the TC consulted in different databases such as Science Direct[1], IEEE[2], Scielo[3] y SpringerLink[4], using mathematical tools and techniques for the classification previously mentioned, in addition, an analysis of the criteria and their weighting was previously carried out using the AHP method.

## 1.1.TRADITIONAL TANNING (CT)

The process of transformation of the skin into leather currently used in Bogota consists of four major processes called: tanning, tanning, wet finishing and dry finishing, in the first of them the raw skin (arrival from the slaughterhouse) is prepared using water, detergents, lime, sodium sulfide and other chemicals that are required to remove the hair and some layers of skin, then in the tanning process the leather is given its characteristic properties (no rotting, lightness, flexibility, etc. ) [15], then the wet drying is performed where the leather is retanned, dyed and oiled to give moisture to it and finally drying, pigmenting, lacquering and arranging the leather in aesthetic terms for sale [16].

In the tanning stage, for every 1000 kg of leather that is processed, 80 kg of basic chromium salts, 3100 lt of water are used and it is kept for four hours in the fulon so that the agent penetrates satisfactorily into the leather and it becomes leather that stands out for having a high hydrothermal stability with a shrinkage temperature (TS) of 110 °C, good

[1] http://www.sciencedirect.com/
[2] http://ieeexplore.ieee.org/Xplore/home.jsp
[3] http://www.scielo.org.co/?lng=es
[4] http://link.springer.com/

mechanical properties, a tensile strength of 25 MPa, tear strength of 45 N/mm and a percentage of elongation of 46% [17].

Leather is a material used for various consumer goods such as footwear, leather goods, furniture, among others. There are certain minimum criteria for physical parameters such as resistance and strength to ensure the durability and aesthetics of finished products. The physical properties are governed according to their final use, for example, in the case of leather goods in general, ISO TC/176 (ISO, 1979), a standard that contributes to quality assurance, and the International Union of Leather Technologists and Chemists Societies (IULTCS) establishes provisions for the measurement of physical tests, chemical analysis and solids tests. In the case of Colombia, the Colombian Technical Standards (NTC) regulate the use of this material.

### 1.2.ENVIRONMENTAL IMPACT

The pollution produced by chrome tanned leather is estimated annually at 40 million liters of wastewater [18], which contain salts that hinder biological treatment when in excess, organic material (remains of epidermis, hair and fat) in very high concentrations, sulfides, nitrogen and chromium in its oxidation state (III), which although it does not have very adverse effects, in the environment it oxidizes to chromium (VI) and is highly toxic to all forms of life, in addition to being mutagenic and carcinogenic in humans[19].

A considerable amount of liquid waste is generated in the process which contributes to biochemical oxygen demand ($BOD_5$), chemical oxygen demand (COD), total dissolved solids (TDS) and total suspended solids (TSS). In general in all unit operations each kilogram (kg) of leather being processed needs about 30-40 L of water of which 35% goes during washing and 55% is used during other unit operations and causes huge environmental damage [20].

In terms of contamination, in Bogota many of the tanneries fail to comply with the regulations allowed for wastewater disposal, according to the Bogota Secretary of Environment only 30% of the industrial sector operating there is duly legalized and 20% is in the process of processing operating licenses [21]. In table 1 shows the maximum allowable values.

**Table 1.** Maximum permissible parameters. from [22]

| Parameter | Units | Resolution 0631 of 2015 | Resolution 3956 of 2009 | Resolution 3957 of 2009 |
|---|---|---|---|---|
| Chemical Oxygen Demand (COD) | mg/L $O_2$ | 1,200.00* | - | 1,500 |
| Biochemical Oxygen Demand ($BOD_5$) | mg/L $O_2$ | 600.00* | - | 800 |

| | | | | |
|---|---|---|---|---|
| Chromium (Cr) | mg/L | - | 0.015 | 1 |

Note. The same requirements established for point discharges to surface water bodies multiplied by a factor of 1.5 apply. The above based on Chapter VIII, Article 16 of Resolution 0631 of 2015.

## 1.3.TANNING ALTERNATIVES

The best known ways of converting leather into an imputrescible material have been the use of chrome and vegetable tanning methods, however, in the last 25 years several alternatives have been proposed that seek to reduce or eliminate the use of chrome. In 1998, [5] presents a methodology that consists of recycling the wastewater from the tanning process, which reduces the residual concentration of Cr in effluents by 90.8%, reducing the supply of the agent by 15%; however, the pH obtained was too high, causing stains on the leather.

Another methodology studied has been the high chrome exhaustion where the aim is to increase the absorption of the agent through the use of auxiliary compounds to the process [6], The efficacy of several compounds has been established, such as: aromatic sulfonic acid, polymeric syntans, hyperbranched polymers, epoxy resin, nanocomposites, use of alternative solvents such as compressed carbon dioxide, ethanol, among others [23], reaching up to 98% absorption of chromium in the leather.

Also, studies and tests have been developed with the aim of replacing the use of chromium such as tanning with vegetable tannins (quebracho, mimosa, tara, etc.), with minerals (titanium, zirconium, aluminum, etc.), with aldehydes and synthetic tanning, however, none of these reach the same properties of chrome tanning[24] an additional technique is the combined tanning of the above, e.g. vegetable and mineral tanning, to produce a leather that includes important characteristics of each method.

The industry has also turned to R&D to make manufacturing processes more sustainable, with the development of nanomaterials with a particle size of about 20 μm with the aim of obtaining higher crosslinking in tanning [25], some of them are nano-TiO2, nano-SiO2, graphene oxide nanoparticles, laponite and synthesized silver, achieving leather with TS between 99°C - 107°C and mechanical properties similar to those obtained in CT, however, in some cases the use of nano-agents easily forms aggregates in aqueous media that result in the inhibition of nano-effects (Raji et al., 2019; Shi et al., 2021).

Other technologies incorporated are the use of ultrasound and microwaves that increase absorption levels and require a much shorter process time, when used in combination the chrome tanning time is reduced to 11 minutes, sufficient for good penetration and to obtain leathers with TS above 100 °C, mechanical properties comparable to the traditional method and superior tensile strength, however, as it is a recent method, more specific results have not been presented [8].

Finally, the application of supercritical fluids (SCF) has been tested whose system uses $CO_2$ and is carried out in high pressure plants controlled by PLC, even being few studies conducted on its use, it is established that it is a technology with a high investment cost that at the same time contributes to savings in chemicals and process time, in addition the $CO_2$ used can be recycled and reused in the next process cycle [28].

## 2. METHODOLOGY.

The objective of this study is to define an alternative to the TC that meets the needs of the sector, using MCDM to objectively weight and rank the evaluated alternatives, the process includes the following stages:

A. Define decision parameters.
    a. Determination of decision criteria.
    b. Ideal values.
B. Definition of alternatives.
    a. Elaboration of the decision matrix.
    b. Evaluation of criteria using AHP.
C. Results
    a. SAW.
    b. Gray correlation.
    c. ELECTRE

### 2.1.DEFINITION OF DECISION PARAMETERS.

#### 2.1.1. DETERMINATION OF THE DECISION CRITERIA.

For the definition of the criteria used to make the decision on the alternative to be selected, the most important parameters for leather tanning were consulted in the literature: the aspects of quality, production, environmental impact and economic impact, the variables and indicators to be considered for the selection of a new tanning method are established (Table 2).

**Table 2.** Aspects, variable and decision criteria.

| Dimension | Variable | Criterio | $C_i$ |
|---|---|---|---|
| Quality standards | Physical properties | Shrinkage temperature (°C) | $C_1$ |
| | | % elongation | $C_2$ |
| | | Tensile strength (Mpa) | $C_3$ |
| | | Tear strength (N/mm) | $C_4$ |
| | Organoleptic properties | Plenitude (Scalar) | $C_5$ |
| | | Smoothness (Scalar) | $C_6$ |
| | | General Appearance (Scalar) | $C_7$ |
| Economic impact | Resource consumption | Total cost ($) | $C_8$ |
| | | Commercial supplies (0=No, 1=Yes) | $C_9$ |

| | | | |
|---|---|---|---|
| Production | Production | Processing time (Hours) | $C_{10}$ |
| Environmental impact | Effluent load | COD (ml/L) | $C_{11}$ |
| | | $BOD_5$ (ml/L) | $C_{12}$ |
| | | Cr concentration (ml/L) | $C_{13}$ |

### 2.1.2. IDEAL VALUES.

For the evaluation of the criteria, ideal values are defined as shown in Table 3, considering that the physical properties must comply with the minimum values established for leather production, and the environmental parameters must comply with the maximum values allowed by current regulations, in terms of organoleptic properties, cost and processing time, the TC values are considered.

**Tabla 3**. Ideal values.

| Quality standards | | | | | | | Economic impact | | Production | Environmental impact | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_7$ | $C_8$ | $C_9$ | $C_{10}$ | $C_{11}$ | $C_{12}$ | $C_{13}$ |
| >80 | >40 | >12 | >=40 | 8 | 8.5 | 8 | $719,947.8 | 1 | 9.58 | 1,200 | 600 | 0.015 |

### 2.2. DEFINITION OF ALTERNATIVES

In the search for environmentally friendly processes in the tanning industry, several alternatives have been studied that, in addition to reducing the environmental impact, should be considered to meet the quality standards and be favorable for the companies in economic terms.

**Tabla 4.** Selection alternatives.

| | Autor | Descripción. | Alternativa |
|---|---|---|---|
| $A_1$ | [29] | Use of 8% Basic Chromium Salts (BCS), followed by 5% Gallic Acid (GA), following a similar process and with the same machinery as traditional tanning. | High exhaustion chromium - gallic acid. |
| $A_2$ | [29] | Use of 5% GA, and then 8% BCS | High exhaustion, gallic acid - chromium. |

| | | | |
|---|---|---|---|
| $A_3$ | [30] | No water is used, instead heptane is used which improves the level of chromium absorption, does not require a significant change in the process and the heptane can be recycled | High exhaustion with heptane. |
| $A_4$ | [31] | This tanning process is carried out with static skins with an approximate duration of 11 days, using Acacia pycnantha with a 10% offer. | Vegetable tanning without salinity with high tannin fixation. |
| $A_5$ | [32] | Application of 5% sulfonated tetraphenyl calix [4] resorcinarene and 4% zirconium, the resorcinarene must be synthesized at the application site, which requires laboratory equipment | Synthetic tanning with Agent STCR-Zr. |
| $A_6$ | [32] | Uses 12% zirconium and is a process similar to CT. | Zirconium (Zr) mineral tanning. |
| $A_7$ | [33] | Use of 3% by weight of glutaraldehyde skin and is a process similar to TC. | Glutaraldehyde tanning |
| $A_8$ | [34] | Use of 10% aluminum and a high use of formic acid. | Glutaraldehyde tanning |
| $A_9$ | [34] | Using 6% of the nanocomposite and 10% of aluminum sulfate, the use of formic acid is reduced by 60% with respect to the process that only uses aluminum, the POSS MAA must be prepared at the laboratory level. | Tanning with Nanocomposite - P(POSS-MAA). |
| $A_{10}$ | [2] | Combined tanning of 20% quebracho and 5% oxazolidine. | Combined quebracho - Oxazolidine tanning. |
| $A_{11}$ | [35] | Tanning is carried out in drums for approximately 8 hours | Combined tanning garad |

| | | | |
|---|---|---|---|
| | | using 20% garad extract and 5% oxazolidine. | extract - oxazolidine. |
| $A_{12}$ | [36] | Use of vegetable agents, 10% of tara - 10% of jathropa oil | Combined metal-free tanning with Tara and Jathropa oil. |
| $A_{13}$ | [37] | 5% glyoxal is used as a tanning agent in traditional tanning equipment. | Metal-free tanning with glyoxal |
| $A_{14}$ | [37] | Combined tannage of 5% Glyoxal and 5% Mimosa | Combined metal-free tanning with glyoxal and Mimosa. |
| $A_{15}$ | [7] | 0.04 % of nanometric graphene oxide (GO), this compound must be manufactured on site | Tanning with graphene oxide nanoparticles (GO). |

Note. % by weight in leather.

### 2.2.1. ELABORATION OF THE DECISION MATRIX

The decision matrix (Table 5) compiles the data for each of the alternatives with respect to physical and organoleptic properties, environmental impact, process time of the tanning stage which includes the pickling, tanning and basification/neutralization operations. On the other hand, the total cost reflects the consumption of electricity, water and materials needed including the tanning agent used and in the commercial supplies criterion, the availability of the main supplies in the market is evaluated, if the tanning agent has to be specially treated or processed on site, zero will be assigned, otherwise 1.

**Tabla 5.** Decision matrix.

| | Quality standards | | | | | | | Economic impact | | Production | Environmental impact | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alter. | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_7$ | $C_8$ | $C_9$ | $C_{10}$ | $C_{11}$ | $C_{12}$ | $C_{13}$ |
| Unidad | °C | % | Mpa | N/mm | | | | COP | 0/1 | Horas | ml/l | ml/l | ml/l |
| $A_1$ | 102 | 66 | 19 | 57.88 | 9 | 9 | 8 | $ 911,763.80 | 1 | 8.9 | 2,100 | 850 | 375 |
| $A_2$ | 105 | 67 | 19 | 58.86 | 10 | 9 | 9 | $ 911,763.80 | 1 | 8.9 | 2,000 | 825 | 475 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $A_3$ | 109 | 55.7 | 17.8 | 43.9 | 7 | 7 | 7 | $ 2,082,949.14 | 1 | 5.2 | 14,150 | 4,550 | 18.42 |
| $A_4$ | 81 | 28 | 24 | 35 | 7.5 | 7.5 | 7.5 | $ 1,234,304.49 | 1 | 266 | 11,600 | 7,500 | 0 |
| $A_5$ | 88.9 | 58 | 80.6 | 100.5 | 8 | 8 | 8 | $ 918,913.64 | 0 | 11 | 1,640 | 530 | 0 |
| $A_6$ | 91.2 | 54 | 33.4 | 56.8 | 8.5 | 7 | 7.5 | $ 744,004.72 | 1 | 8.7 | 2,780 | 450 | 0 |
| $A_7$ | 87 | 38 | 20.69 | 61.74 | 8.5 | 8 | 8 | $ 965,584.06 | 1 | 5.6 | 2,100 | 700 | 0 |
| $A_8$ | 62.1 | 55 | 19 | 44 | 8 | 8 | 8 | $ 617,265.34 | 1 | 9.2 | 2,250 | 550 | 0 |
| $A_9$ | 73.5 | 56.9 | 18.1 | 67.9 | 7.9 | 8.5 | 8 | $ 1,273,717.77 | 0 | 13 | 2,535 | 780 | 0 |
| $A_{10}$ | 102 | 59 | 25 | 66.71 | 8 | 9 | 8 | $ 2,920,548.67 | 1 | 7.9 | 97,800 | 29,000 | 0 |
| $A_{11}$ | 103 | 75 | 19.41 | 64.68 | 8 | 8.5 | 8 | $ 2,545,638.71 | 1 | 7.9 | 108,420 | 14,000 | 0 |
| $A_{12}$ | 88 | 73 | 21.96 | 28.45 | 7 | 7.5 | 8 | $ 1,645,454.31 | 1 | 6.3 | 4,900 | 1,700 | 0 |
| $A_{13}$ | 72 | 58 | 20.29 | 49.05 | 8.6 | 9 | 8.5 | $ 641,053.40 | 1 | 7.2 | 11,460 | 4,980 | 0 |
| $A_{14}$ | 92 | 59 | 21.57 | 51.012 | 9 | 7.8 | 7.8 | $ 1,211,622.80 | 1 | 7.2 | 40,310 | 13,990 | 0 |
| $A_{15}$ | 96.8 | 62.5 | 26.2 | 54.3 | 8 | 9 | 8.5 | $ 926,011.94 | 0 | 6.2 | 605 | 345 | 0 |

### 2.2.2. EVALUATION OF CRITERIA

For the application of the MCDM methods, the first step was to assign weights to each of the criteria mentioned in Table 1, for which the AHP algorithm was run three times, evaluating the weights of the dimensions, variables and criteria.

Table 6 shows the relative importance scale used to determine the weights.

**Table 6.** Saaty's scale

| Scale | Definition |
|---|---|
| 1 | Equally importance |
| 3 | Moderately importance |
| 5 | Strongly importance |
| 7 | Very strongly importance |
| 9 | Extremely importance |

| | |
|---|---|
| 2, 4, 6, 8 | Intermediate values |

For each run of the algorithm, the consistency ratio (CR) was validated, which must be in the range (-0.1 to 0.1) and was found with equations 1, 2 and 3.

$CI = \frac{\lambda_{max} - n}{n-1}$ (Equation 1)

$IA = \frac{1{,}98(n-2)}{n}$ (Equation 2)

$CR = \frac{CI}{IA}$ (Equation 3)

Where
n: Number of selection criteria.
IA: Random index.
CI: Consistency index
CR: Consistency index.
λmax: Average of weighted weights.

In the first instance, the AHP algorithm was used to determine the weight of each dimension, the results of which were: quality standards with 29.4%, economic impact with 24.9%, environmental impact with 37% and production with 8.7%, The environmental impact is rated with greater importance due to the search for a sustainable alternative that reduces or eliminates the use of chromium; in second place is the quality of the leather that determines the competitiveness of the companies; finally, there are the raw material acquisition costs, its availability on the market and the production time.

After this, the algorithm was run for each of the following dimensions to evaluate its performance for tanning 1000 kg of raw hide:

- Quality standards: organoleptic properties (25%) and physical properties (75%), because it is considered important for the manufacture of footwear and jackets that the leather has characteristics that provide durability and resistance.
- Economic impact: (100%) In this dimension, only the consumption of resources during the tanning stage is considered.
- Environmental impact: (100%) In this section, only the discharge that each alternative generated on the effluents was taken into account.
- Production: (100%) The time taken for the tanning process is considered.

For the third AHP, the following variables were evaluated:

- Physical properties: In this variable, the algorithm was run with 4 indicators and the results were as follows: shrinkage temperature (48.9%), % elongation (23.5%), tensile strength (13.8%) and tear strength (13.8%), the shrinkage temperature is higher since part of the leather produced is used for footwear manufacturing where the process subjects the leather to high temperatures (generally in vulcanization), then there is the elongation percentage that establishes how flexible the processed leather can be and finally there is the tear and tensile strength.

- Organoleptic properties: The 3 criteria were scored and gave the following results: fullness (26%), general appearance (63.4%) and softness (10.6%), while the softness and fullness of the leather are important in the manufacture of luxury goods, in this case the overall appearance prevails as the manufacturing percentage of this type of goods is lower. [38]

- Effluent load: In this variable, 3 criteria were rated, which yielded the following results: COD (29.7%), $BOD_5$ (16.4%) and concentration of chromium in effluents (53.9%), these results are given since the objective of the proposal is to reduce the impact of chromium in effluents, in second place this COD that establishes the amount of oxygen required in the effluent so that it is achieved to exhaust the pollutant and then the BOD, also these parameters are important in the measurement of pollution.

- Resource consumption: In this variable, two indicators were rated: total cost of the tanning process (75%) and availability of materials (25%). These results are given because the cost of the process is important to evaluate the competitiveness of tanning and then there is the availability and ease of acquisition of these materials.

The table 7 shows the results obtained by multiplying the percentage weights of the indicators, variables and dimensions.

**Table 7.** Percentage priority of each dimension, variable and indicator.

| Dimension | Initial Weight | Variable | Second AHP | Indicator | Third AHP | % weight criterion. |
|---|---|---|---|---|---|---|
| Quality standards | 29.4% | Physical properties | 75% | Shrinkage temperature | 48.9% | 10.78% |
| | | | | % elongation | 23.5% | 5.18% |
| | | | | Tensile strength | 13.8% | 3.04% |
| | | | | Tear resistance | 13.8% | 3.04% |
| | | Organoleptic properties | 25% | Plenitude | 26.0% | 1.91% |
| | | | | Smoothness | 10.6% | 0.78% |
| | | | | General Appearance | 63.4% | 4.66% |

| | | | | | | |
|---|---|---|---|---|---|---|
| Economic impact | 24.9% | Resource consumption | 100% | Total cost | 75.0% | 18.68% |
| | | | | Commercial inputs | 25.0% | 6.23% |
| Production | 8.7% | Production | 100% | Processing time | 100.0% | 8.70% |
| Environmental impact | 37.0% | Effluent load | 100% | COD | 29.7% | 10.99% |
| | | | | $BOD_5$ | 16.4% | 6.07% |
| | | | | Cr concentration | 53.9% | 19.94% |

## 3. RESULTS

### 3.1. SAW

For the execution of the method, initially the decision matrix was standardized (Table 3), so that the ideal result of each item was given the total percentage obtained through the AHP method (Table 8) and the worst obtained zero, performing an interpolation to know the weight of the criteria of each alternative, the next step was to add the values obtained from the criteria to obtain the total score of the alternative in a range of 0 to 1, where alternative $A_{15}$ obtained the best value with 0.77.

### 3.2. GRAY CORRELATION

Due to the criteria have different dimensions and quantity, they cannot be directly compared and we proceed to normalize the decision matrix (Table 3), taking into account that the positive criteria, are those that indicate that the performance of an alternative improves with a higher value, such as, the shrinkage temperature, % elongation, tensile strength, tear strength, fullness, softness, general appearance, supplies and the negative criteria indicate that the performance improves with a lower criterion value such as total cost, process time, $BOD_5$, COD and chromium discharge concentration. Once the normalized matrix and the reference data that are the best value of each criterion are determined, the calculation of the relational coefficients that represent the relationship between the reference data matrix and the compared data matrix is performed and finally the global correlation coefficient of each alternative is defined (Table 8), resulting in the alternative that presents a higher performance is the Tanning with graphene oxide nanoparticles (GO) since it obtained a gray correlation coefficient of 0.70 and the least favorable alternative is vegetable tanning without salinity with high tannin fixation.

### 3.3. ELECTRE.

In the Electre method, the concordance matrix reflects the extent to which a given number of attributes of the alternative $a_i$ is preferred to the alternative $a_k$, by summing the weights associated with the criteria in which alternative i is better than alternative k, in case of a tie, half the weight is assigned to each of the alternatives, the discordance matrix measures the extent to which there is no attribute in which the alternative $a_k$ is better than the alternative $a_i$ by adding the weights associated with the criteria and considering the maximum degree of disagreement that can exist between the alternatives, Table 8 shows the results using ELECTRE.

As this selection method refers to the definition of overcoming relationships, the result is that alternative $A_{15}$ is equal or better in the criteria evaluated than 13 other alternatives, taking into account the weights given to each criterion in general terms; however, alternative $A_2$ has a concordance value greater than the threshold set at 0.5, when the discordance matrix is performed, the maximum degree of disagreement does not exceed the threshold for this matrix, so it is not possible to speak of a complete superiority of $A_{15}$ over $A_2$.

**Table 8.** Results of MDCM methods.

| Alternative $A_i$ | Gray correlation | SAW | ELECTRE |
|---|---|---|---|
| | $r_i$ | $r_i$ | Overqualify |
| $A_1$ | 0.61 | 0.48 | 1 |
| $A_2$ | 0.69 | 0.53 | 2 |
| $A_3$ | 0.50 | 0.35 | 0 |
| $A_4$ | 0.48 | 0.42 | 1 |
| $A_5$ | 0.63 | 0.62 | 2 |
| $A_6$ | 0.59 | 0.66 | 9 |
| $A_7$ | 0.57 | 0.58 | 5 |
| $A_8$ | 0.58 | 0.61 | 7 |
| $A_9$ | 0.52 | 0.49 | 1 |
| $A_{10}$ | 0.61 | 0.51 | 1 |
| $A_{11}$ | 0.62 | 0.56 | 4 |
| $A_{12}$ | 0.57 | 0.56 | 5 |
| $A_{13}$ | 0.64 | 0.62 | 9 |
| $A_{14}$ | 0.58 | 0.60 | 6 |
| $A_{15}$ | **0.70** | **0.77** | **13** |

The result of each of the decision methods executed, agrees that GO nanoparticle tanning is the best option to implement as an alternative to CT, because it does not use chromium and the levels of COD and BOD5 remain below those established by regulations, in addition to which the wastewater generated has a good biodegradability index. It is a method that requires a very low dosage of tanning agent (0.04 %) and its utilization rate is very high (99.7%); as for the product, the physical properties are superior to CT and visually it obtains similar qualification.

The leather treated with GO nano particles obtains a high shrinkage temperature, surpassed only by the processes with high chrome exhaustion and in which a combination of oxazolidine and vegetable agents are used; however, the wastewater from the latter present high levels of COD and BOD5, putting them at a disadvantage since it is the environmental criteria that have the greatest weight for the evaluation of the alternatives.

In addition, GO nano-particles must be prepared in-situ because they are not commercially available, implying an increase in the cost of tanning due to the need to acquire equipment and trained personnel for the preparation of the agent, but this is offset by the reduction of the environmental impact generated.

The ELECTRE and SAW results place the Zr tanning alternative ($A_6$) in the second position, its advantage is that it reduces the environmental impact, the cost is increased by 3% compared to CT and the leather meets the established mechanical properties, although the softness and general appearance is inferior, this alternative stands out since the importance of the environmental and economic impact criteria represent a weight of 62% in the decision, in contrast, in gray correlation the position is occupied by the use of gallic acid – chromium ($A_2$), a high exhaustion method that allows a greater penetration of Cr in the skin reducing its concentration in wastewater by 90%, has a favorable biodegradability and the levels of COD and BOD5 decrease by 70%, it should be taken into account that in gray correlation the importance of the criteria is not applied, which is why this alternative surpasses the Zr tanning, since it presents better mechanical properties and better visual appearance, which favors the overall qualification of the high exhaustion process.

On the other hand, one of the important properties to be considered is the shrinkage temperature which is reflected in the % of importance given by AHP, however, the alternative with the highest TS which is high depletion with heptane is in the last position in the ELECTRE and SAW rankings and the penultimate in gray correlation, although it has mechanical properties that meet the quality standards, the tanning process time is the shortest compared to the other alternatives and the Cr, it does not stand out because it presents poor organoleptic properties, the cost almost triples and the levels of COD and BOD5 increase compared to the TC, reflecting that it does not dominate or surpass any of the other alternatives.

## 4. DISCUSSION

In general terms, the studied alternatives are more environmentally sustainable as they reduce the concentration of chromium in the wastewater between 90% and 100%, hence the importance of using decision making tools that allow the evaluation of multiple criteria for the selection of the most beneficial method, given that the contamination caused by any tanning agent is an important factor for the selection of the alternative but it must be assessed that it generates a tanning with desirable characteristics for the product to be marketable and profitable.

The process that is postulated as the best alternative to TC is tanning with GO nanoparticles, which despite showing lower tear strength, meets the requirements set out in table 3 and is rated by the authors as having excellent softness and elasticity properties, in addition other nanoparticles such as Nano-SIO2 have larger particle sizes and therefore give poor results.

For the use of GO nanoparticles, an on-site manufacturing process must be carried out, which requires laboratory equipment and specialized personnel; however, these characteristics were not widely evaluated in the decision-making process and may represent a limitation for companies in the sector if they do not have the capacity to produce them, outsource the process or find them easily on the market.

The top 3 is completed by the use of zirconium and glyoxal agents, which also eliminate the use of chromium, but the use of zirconium at 12% by weight in leather gives a better shrinkage temperature and according to the authors achieves leathers with good dyeing properties, excellent filling and physical properties, although it has disadvantages in the organoleptic properties, due to its weak binding capacity with collagen, which produces an uneven distribution in the leather.

On the other hand, the use of glyoxal, although it does not achieve leathers with a high shrinkage temperature, it does present good organoleptic properties superior to the requirement of table 3. Furthermore, the author has tested the tanning of glyoxal assisted with mimosa to increase the shrinkage temperature, without affecting other leather parameters, however, although it increases the TS it decreases its overall performance since due to the higher presence of phenolic compounds it increases between 70 and 71% the COD and $BOD_5$ parameters respectively

## 5. CONCLUSIONES

In this study a cleaner tanning method is proposed, based on the analysis of 15 alternatives and their subsequent selection using multi-criteria decision making tools, the methods used were ELECTRE, SAW, gray correlation and the use of AHP for the designation of percentage weights per evaluated criterion, the results are presented in terms of the overqualification of the alternatives or the $r_i$ coefficient depending on the method used. According to the results, tanning using graphene oxide nanoparticles allows the resulting leather to have physical and organoleptic properties similar to those of conventionally tanned leather, but with a minimal environmental impact that complies with regulations. However, to take the step to full implementation of graphene oxide, a thorough analysis of the risks, opportunities and economic implications of large-scale implementation of this alternative should be made.

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