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Characterization of Animal Leather Dust Waste from the Footwear Industry

[1]Thiago Moreira Flores, [2] Thalis de Simas Koller, [3]Sandro Heleno Auler, [4]José de Souza
[1, 2, 3 & 4]Fundação Liberato - Diretoria de Pesquisa e Produção Industrial (DPPI) - Rua Inconfidentes, 395, Bairro Primavera, Novo Hamburgo - RS - ZIP CODE 93340-140, Brazil.
Corresponding Author: José de Souza - josesouza@liberto.com.br

ABSTRACT: *Leather production is carried out on a large scale in Rio Grande do Sul, mainly by companies that have activities in the shoe industry. The production of footwear and leather accessories, the large scale production as leather dust, are usually discarded in industrial landfills. Such products are classified as hazardous because of the use of chromium in the tanning process. The most common form of disposal is the construction of landfills, the environmental legislation in force requires that the landings be impermeable so that they do not contaminate the soil or sheets of water. With this in mind, the present project carries out a characterization of the residues based on tests of moisture content and analysis of data of pH, leaching, solubilization, total organic material, total rocks, total mineral and enzymatic of existing samples to designate a function compatible. The results that can be recycled can be used as the aid material with building materials such as concrete, present suitable for the cultivation of ornamental plant species are mixed with the charred rice bark and vermiculite, are a good a source of recycling for cogeneration processes such as incineration and piracy can be used in tanning and retanning of hides, with great environmental benefit and cost reduction for tanning.*

KEYWORDS: *Stripper powder, Characterization, Chrome.*

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I. INTRODUCTION

Leather production is carried out on a large scale in the Rio Grande do Sul, mainly by companies with activities in the footwear industry. It produces leather shoes and accessories, generates large-scale waste such as leather shavings and leather dust usually discarded in industrial landfills. Such residues are classified by NBR 10004 as hazardous due to the use of chromium in the tanning process [1-2]. In the leather tanning industry, the most widely used method to ensure more excellent durability, resistance, elasticity and the thermal and hydrothermal stability properties of leather is the application of chromium 3 (Copywriting, 2008) which is a bioactive element present in the organism in small quantities [3]. However, when in high concentrations, it is potentially dangerous to health and environmental balance [4].

The disposal of this waste is often problematic, estimated that, in the tannery industry, they represent between 10 and 30% of the waste production. The most common way of eliminating them is the construction of landfills, whose environmental legislation in force requires that the dumps be impervious so that they do not contaminate the soil or groundwater. In contact with the ground, the Chromium 3 present in the waste undergoes an oxidation process and turns into chromium 6, a more toxic form of chromium and highly harmful to health [5-6].

This study aims to characterize the leather powder based on data from analysis of existing research on pH, leaching, solubilization, total organic matter, total solids, entire mineral residue, organic carbon, scanning electron microscope, caloric power, X-ray fluorescence, Granulometric Analysis, and Salinity. Further analysis is also necessary to designate a purpose that is physically and chemically compatible with the results of its characterization.

This paper presents a review of Chromium (Cr) its toxicity and the characterization of the material. In the topic, Materials and Methods, the element and the study carried out are presented. In the Results item, the authors present the effects obtained. In the Conclusions item, the authors present a summary of the conclusive aspects.

II. LITERATURE REVIEW

In general, leather is an animal skin that has undergone cleaning, stabilization (given by tanning), and finishing processes. The process of transforming hides into hides divided into three main stages in customs, tanning, and finishing. The finish, in turn, is usually divided into "wet finish," "pre-finish," and "final finish" [6 -

7]. The classification of the leathers occurs according to the leather processing stage they perform. The wet blue tannery represents the first leather processing after slaughter, when the first chrome bath happens, generating a bluish and wet tone of the leather. The semi-finished tannery uses wet blue leather as raw material and transforms it into crust (semi-finished) leather. The finishing tannery turns crust leather into finished leather, and the integrated tannery performs all processing operations, from raw leather to finished leather [7-8].

Chromium released to the environment through residues originating from industrial processing includes the tanning, textile, and metallurgy industries of iron, steel, and other metals [9-10-11]. Hexavalent chromium (Cr^{6+}) appears as toxic and mutagenic chromates and dichromates (CrO_4^{2-} and $Cr_2O_7^{2-}$) that are soluble over a wide pH range and are generally mobile in the soil / water system [12-13]. Trivalent chromium appears in the form of the Cr^{3+} cation and the CrO_2 anion, being considerably less toxic and of low mobility, due to its precipitation as oxides and hydroxides at a pH greater than 5.0 (Ray et al., 1989).

Hexavalent compounds cause an irritating and corrosive action on the human body. Exposure to hexavalent chromium can generally occur through inhalation, skin contact, and ingestion. Although the World Health Organization (WHO) establishes the limit for human consumption of 0.05 milligrams per liter, there are no scientific studies that prove which level of chromium ingested may cause the disease.

The potential effects of hexavalent chromium vary, mainly, with the species and amounts absorbed into the bloodstream, the route and duration of exposure [3]. Hexavalent chromium, classified in most national and international lists of highly toxic materials, receives strict control procedures.

The characterization of material occurs due to the need for adequate selection based on performance. The characterization of the leather includes the evaluation of mechanical, electrical, bioactivity, immunogenicity, electronic, magnetic, optical, chemical and thermal properties. This characterization of properties aims mainly to estimate the performance in the "useful life" period of the material, minimizing the possibility of degradation and embarrassing failures during the use of the product [13].

The leather powder is one of the most generated solid waste in leather manufacturing industries. Like other leather residues, the leather powder obtained through manufacturing processes occurs on the finishing stage. In leather finishing, scraping occurs until reaching the thickness desired by the consumer. These residues are generated in large quantities per day, have a high concentration of heavy metals in their composition, have a low specific weight, are difficult to compact, and destined for industrial landfills [3].

III. MATERIALS AND METHODS

The initial stage of the project took place through the collection of dust from the lowering machine to gain a better understanding of the material's visual appearances. The need to obtain the content came because of the scarcity of related images found on the internet.

The grinding powder was obtained by a company in the leather sector in the Vale do Sinos region, which supplied 1 kg of waste to collaborate with the research. See figure 1 of the sample provided by the company.

Figure 1. Sample of grinder dust acquired.

Together with the results obtained in the moisture content test, already existing designs and data from experiments and analyzes carried out regarding the composition of the drawer powder were used. Reuse of tannery residues in the manufacture of concrete blocks for paving: evaluation of the characteristics of the waste, published by (NARDINO; PAIVA; NUNES, 2015) [4]. In this project, tables with ph values, total solids, total organic matter, and entire mineral residue analyzed, as well as analyzes of leaching, solubilization, and scanning electron microscopy [14].

Characterization of leather and footwear waste for recycling, published by (RIEHL et al., 2014) [2]. With this project, tables of Particle Size Analysis, X-ray Fluorescence, Elemental Analysis, and Calorific Power. Use of wet-blue leather waste as a substrate component for plants (DAUDT, GRUSZYNSKI, KÄMPF, 2007) [15], a project used to characterize the powder using the following attributes and methods of analysis: dry density, pH value, and salinity, water release curves, determining the porosity and aeration space [18].

Lowering powder: a source of organic nitrogen for agriculture, an alternative destination for a substance derived from the industrialization of leather, published by (SCHUNK, 2010) [16], a project in which the possibility of removing chrome from the lowering powder analyzed [19]. Chemical composition of chromium solution for the tanning and re-tanning of hides and bovine skins, extracted from dust and leather residues, published by (PINTO, 2009) [20]. This research used to evaluate the possible tanning of the leather and the chromium present in the grinding powder.

IV. RESULTS AND DISCUSSIONS

Through the analyzed projects and researches, the following data were considered.

Table 1. Sample of grinder dust acquired.

Analyze	Sample 1	Sample 2	Sample 3	Average	Standard deviation
pH	4.0	4.0	4.0	4.0	0.00
Total Solids (g/g)	55.0	54.5	54.3	54.6	0.29
Total Organic Matter (%)	84.4	83.4	84.6	84.6	0.53
Total Mineral Residue (%)	15.6	16.6	15.4	15.4	0.53

According to the data obtained through this table, the residue had an acidic pH value, around 4. This acidity probably comes from the type of tanning. The table also showed a high humidity value, approximately 54.6%. This result may be related to the waste collection step, collected during processing, that is, the leather that went through the drawdown was not yet dehydrated, generating a very moist residue. Regarding the total organic matter, the residues presented an average value of 84.1%; of these, the fraction of carbonaceous origin is around 46.7%. On the other hand, the total mineral residue, which indirectly represents the inorganic material present in the sample, reached an average value of 15.9%. Such results expected since the waste is of animal origin [3].

Values obtained for leachate extract and solubilized extract from the residue of the tanning process (Tables 2 and 3) show the limit concentrations of each contaminant stipulated by the ABNT NBR 10004 (2004) standard [14].

Table 2. Contaminants present in the leached extract of the waste.

Poisoning	NBR 10004/2004 limit (mg/L^{-1})	Tannery residue (mg / L^{-1})
Ba	70.0	n.d.
Cd	0.5	1.01
Pb	1.0	0.24
Cr	5.0	128.0
Ag	5.0	n.d.

Table 3. Contaminants present in the solubilized extract of the residue.

Poisoning	NBR 10004/2004 limit (mg/L^{-1})	Tannery residue (mg / L^{-1})
Cd	0.005	0.02
Pb	0.01	0.38
Cu	2.00	0.01
Cr	0.05	309.43
Fe	0.30	3.31
Mn	0.10	0.14
Ag	0.05	n.d.
Na	200.00	2597.14

Through the results presented in table 3, it was possible to verify that the concentration of the chromium metal (Cr) present in the leached extract of the residue showed a concentration higher than that stipulated by the norm NBR 10004 (2004) [18]. Thus, the tannery residue classified as Class I - Hazardous solid waste [4]. Table 3 shows the concentration values of contaminants present in the residue solubilized. The metals

Cd, Pb, Cr, Fe, Mn, and Na exceeded the limit values, with emphasis on the concentration of Cr and Na which presented, respectively, rates of six thousand times and thirteen times higher than the limits legislation [4].

Using existing micrographs using a scanning electron microscope (SEM), the fibers that make up the leather are analyzed, as well as the pores or voids present in the residue. The microstructure presented by the waste can favor its intimate contact with concrete or other materials.

Table 4. Values of pH, salinity and dry density (ρs) of the treatments.

Treatments	RR fraction	Natural pH	Corrected pH	Salinity at the beginning of cultivation	Salinity at the end of cultivation	ρs
	(%)	H_2O	H_2O	(g/L^{-1})	(g/L^{-1})	(g/L^{-1})
CACV	0.0	7.8	6.8	1.1	0.5	157.0
1RR: 3CACV	25.0	5.6	5.6	2.4	1.6	157.0
1RR: 1CACV	50.0	4.9	5.2	3.9	2.4	146.0
3RR: 1CACV	70.0	4.1	4.9	5.1	3.0	139.0
RR	100.0	3.7	5.0	7.5	3.3	130.0

Table 5. Volume of substrates occupied by macro, meso and micropores.

Treatments	RR fraction	Solids	Macroporous	Mesopores	Micropores
	(%)	(%)	(%)	(%)	(%)
CACV	0.0	15.0	51.0	17.0	17.0
1RR: 3CACV	25.0	10.0	53.0	15.0	22.0
1RR: 1CACV	50.0	8.0	57.0	13.0	22.0
3RR: 1CACV	70.0	9.0	53.0	15.0	23.0
RR	100.0	7.0	53.0	14.0	27.0

Tables 4 and 5 show that, with the addition of RR, the density of mixtures reduced more, in a linear fashion between such limits. Such values are in the density range considered suitable for cultivation in containers of a few centimeters in height [15-16]. High volumes of aeration space were found in the five mixtures (between 51 and 57%), while the amounts of Agua Mesoporos were below the range of 24 to 40%, but within the range considered to be of excellent performance for cultivation with frequent irrigation.

As a conditioner in mixtures, RR promoted a reduction in density and an increase in porosity, in particular increasing the volumes of macro and micropores. Its high salinity, however, proved to be limiting to plant growth. Therefore, the suggested use restricted to a maximum of 50% of the volume in mixtures.

In X-ray Fluorescence, found that the material analyzed has Cr as the significant element, with more than 50%. In a smaller quantity, S has more than 5%, and the remaining elements present are Ti, Si, Fe, Ca, Al and K, representing less than 5% of the elements present in the grinding powder. In the elementary analysis carried out by the International Solid Waste Forum, the carbon content had value of 48%. This factor is the main responsible for the waste combustion process, which allows verifying the potential use of these residues for the production of heat energy through the incineration process. The results obtained in this same research to determine the ash content of the leather machine powder was 6.23%.

The project "Chemical composition of a chromium solution for tanning and re-tanning of bovine hides and skins, extracted from dust and leather residues" points to the possible process of transforming "leather powder" into a rich acid solution in collagen proteins and with a considerable amount of chromium oxide, to be used in the tannery to tan skins. In addition to the tests and analyzes carried out, the Federal University of Lavras, Brazil, developed a process to remove the chromium from the residue of leather industrialization. Cleaning the slurry dust from the slurry is an interesting alternative to the special landfills.

V. CONCLUSION

The scanning electron microscopy analysis showed that due to the intertwining of the leather fibers and the pores presented in its matrix, there might be a favoring of the interaction of the residue with materials such as concrete. The raw material is suitable for reuse/treatment using the technique of stabilization/solidification with matrices of materials such as cement.

In general, the porosity in the treatments provides to be adequate for the cultivation of ornamental and forest species, which have resistance to salinity and affinity to substrates with low density and high porosity in little height containers using a 50% mixture of bark. Carbonized rice and vermiculite, considering that, in such vessels, it reduces free drainage, thus providing higher water retention. In addition to the possibility of removing the chromium element with the regeneration of the substantial part, the material rich in organic nitrogen surpasses commercial nitrogen fertilizers concerning the absorption of micronutrients.

Results such as low moisture content, high calorific value, and low carbon content indicate that these residues are a good source of recycling for cogeneration processes, such as incineration and pyrolysis. The low ash content suggests a significant reduction in the volume of the post-burning residue. The residues also presented a substantial presence of chemical substances, which form a chemical process, can be used in the tanning and retanning of leathers, with great benefit to the environment and cost reduction for the tannery.

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