Wastes released by tanneries at Patrocínio Paulista, São Paulo State, Brazil

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Abstract

This investigation was carried out within the Paraná sedimentary basin, Brazil, and involved the sampling of sludge and residuary waters that were collected from reservoirs/decantation ponds settled in two tanneries situated at Patrocínio Paulista, São Paulo State. Two samples from each tannery were collected, stored in appropriate flasks and transported to the LABIDRO for chemical analysis. The LABIDRO (Laboratory of Isotopes and Hydrochemistry) of the Petrology Department at the Geosciences and Exacts Sciences Institute of UNESP is situated in Rio Claro city, about 240 km distant from the investigated area. The data for residuary waters were compared with guideline values established by two different legislations: (a) Rule No. 12486 (NTA60) established in 20th October 1978 by São Paulo State for defining the potable water standards and (b) Register 997 published on 31 May 1976 that defines the permissible concentration limits in effluents to be released to water bodies (coastal, fresh or ground waters) in São Paulo State. The results confirmed that leather production is an activity with high environmental impact, despite improvements that may be achieved by tanneries.

Keywords: leather, tanneries, sludge, residuary waters, São Paulo State, Brazil.

1 Introduction

São Paulo is the most populous Brazilian state, comprising ~40 million inhabitants distributed over 645 municipalities. It has the highest number of industries and economic production, reaching 31% of the Brazilian GDP-gross domestic product. Despite the vigorous industrial production that includes high

WIT Transactions on Ecology and the Environment, Vol 140, © 2010 WIT Press
www.witpress.com, ISSN 1743-3541 (on-line)
doi:10.2495/WM100321

technology goods, the state also is well developed in agriculture and cattle breeding [1]. This advanced stage of agricultural and industrial growth causes to São Paulo State a great diversity of problems related to the interaction between the society and the environment.

The cattle breeding at São Paulo State is an important economic activity, as the number reaches 12.6 million, the 5th in Brazil. However, in terms of exportation, 70% of the Brazilian meat leaves São Paulo State through Santos harbor. The state contributes with about 2 billion liters of milk per year that represents ~ 10% of the Brazilian milk production, but despite this São Paulo State is the main center consuming dairy products in the country [2, 3].

The term hide has been used to designate the skin of larger animals (*e.g.,* cowhide or horsehide), whereas "skin" refers to that of smaller animals (*e.g.,* calfskin or kidskin) [4]. The preservation process employed is a chemical treatment called tanning, which converts the otherwise perishable skin to a stable and non decaying material [4]. Although the skins of such diverse animals as ostrich, lizard, eel, and kangaroo have been used, the more common leathers come from cattle [4]. Thus, leather is a durable and flexible material created via the tanning of a putrescible animal rawhide and skin, primarily cattle hide.

The production of leather by cattle hide is an important economic activity in Brazil that is the 5th in world after USA, Russia, India and Argentine [5]. The Brazilian worldwide leather production corresponds to 10-11% and São Paulo State is the major exporter (33.1% of the national production) [5]. The number of tanneries in Brazil is about 450 and most of them (80%) employ between 20 and 99 laborers each. In the year 2006, it was processed around 45 million leather pieces, and the exportation of 34 million yielded an income of US$ 1.87 billion [5].

Leather can be produced through different manufacturing processes, ranging from cottage industry to heavy industry. In the leather industry, the skin and rawhide are bi-products of the meat industry, because the meat has greater commercial value than the rawhide and skin. The leather manufacturing process is divided into three fundamental sub-processes: preparatory stages, tanning and crusting [6].

The preparatory stages are when the hide/skin is prepared for tanning. Preparatory stages may include: preservation, soaking, liming, un-hairing, fleshing, splitting, re-liming, de-liming, bating, degreasing, frizing, bleaching, pickling and de-pickling [6].

Tanning is the process which converts the protein of the raw hide or skin into a stable material which will not putrefy and is suitable for a wide variety of end applications. The principal difference between raw hides and tanned hides is that raw hides dry out to form a hard inflexible material that when re-wetted (or wetted back) putrefy, while tanned material dries out to a flexible form that does not become putrid when wetted back [6]. There are a large number of different tanning methods and materials that can be used; the choice is ultimately dependent on the end application of the leather. The most commonly used tanning material is chromium, which leaves the leather once tanned a pale blue color (due to the chromium); this product is commonly called "wet blue" [7].

The process was invented in 1858 and involves the use of chromium sulfate or other salts of chromium. The hides once they have finished pickling will typically be between pH of 2.8-3.2 [7]. At this point the hides would be loaded in a drum and immersed in a float containing the tanning liquor [6].

Crusting is when the hide/skin is thinned, retanned and lubricated. Often, a coloring operation is included in the crusting sub-process. The chemicals added during crusting have to be fixed in place. The culmination of the crusting sub-process is the drying and softening operations [6].

Because of the various steps involved on the leather production, such an activity exhibits high environmental impact, most notably due to: the impact of livestock, the heavy use of polluting chemicals in the tanning process and the air pollution due to the transformation process (hydrogen sulfide during de-hairing and ammonia during de-liming, solvent vapors). One tonne of hide or skin generally leads to the production of 20 to 80 m^3 of turbid and foul-smelling wastewater including chromium levels of 100-400 mg/L, sulfide levels of 200-800 mg/L and high levels of fat and other solid wastes, as well as notable pathogen contamination [8]. Pesticides are also often added for hide conservation during transport. With solid wastes representing up to 70% of the wet weight of the original hides, the tanning process comes at a considerable strain on water treatment installations [8].

This paper describes the results of chemical analyses performed in effluents generated by tanneries installed at Patrocínio Paulista, São Paulo State, Brazil, where the leather production involving cattle hide has been conducted for many years. The data will be evaluated considering the possibility of the wastes utilization for increasing the soil productivity, as it has been often reported by some investigators in Brazil.

2 General features of the area studied

The study area is situated in the municipality of Patrocínio Paulista that is about 410 km distant from São Paulo city, the capital of São Paulo State. It is located at 20°37’48”S and 47°16’48”W (Fig. 1), the altitude is 800 m above sea level, the surface area of the city is ~610 km^2, the population is ~12,000 inhabitants, and the *cerrado* fields dominate the landscape of the region [10]. The major economic activities of the municipality involve the agro business, with dominance of coffee and sugarcane production [10]. There is also a large number of tanneries (about 300) settled in the municipality that are extensively involved in the leather production

The area is geologically situated at the giant Paraná sedimentary basin that extends over an area of 1.7 million km^2 (1 million km^2 in Brazilian surface) [11]. Some of these stratigraphic units of the Paraná basin (Paleozoic - Cenozoic) crop-out in it (Fig. 1): the Tubarão Group comprising the Itararé Subgroup (sandstones, conglomerates, diamictites, tillites, siltstones, shales and rythmites) and Tatuí Formation (siltstones, shales, silex and sandstones with local concretions); the Passa Dois Group comprising the Irati Formation (siltstones, mudstones, black betuminous shales and limestones) and Corumbataí Formation

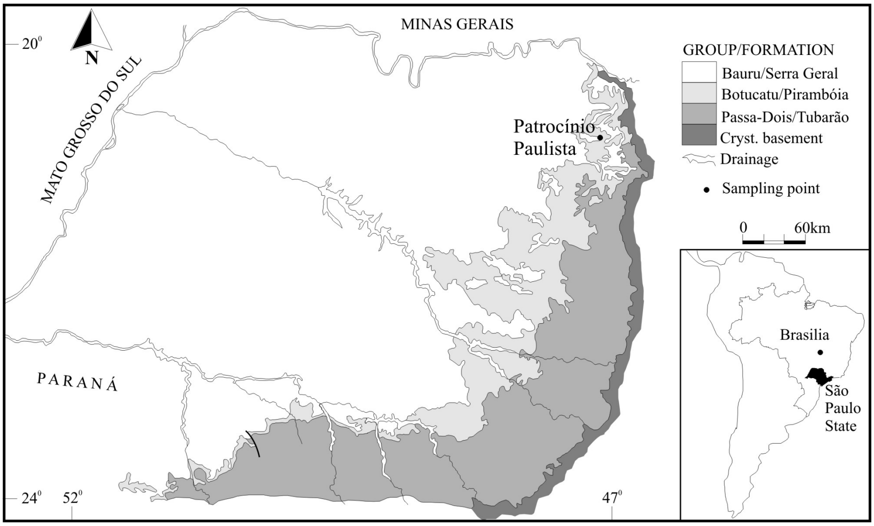

Figure 1: A simplified geological map of São Paulo State, Brazil, and location of the sampling point for chemical analyses of tannery wastes. Modified from [9].

(mudstones, shales and siltstones); the São Bento Group comprising the Pirambóia Formation (sandstones, shales and muddy sandstones), Botucatu Formation (sandstones and muddy sandstones), Serra Geral Formation (basalts and diabases) and related basic intrusives; different types of Cenozoic covers like the recent deposits, terrace sediments and others formations comprising sandstones, conglomerate sandstones, muddy sandstones, etc.

3 Material and methods

This study provided chemical data for samples of sludge and residuary waters collected at reservoirs/decantation ponds settled in two tanneries situated at Patrocínio Paulista city: Finipelli and CURVASA. Two samples from each tannery were collected, stored in appropriate flasks and transported to LABIDRO for chemical analysis. LABIDRO (Laboratory of Isotopes and Hydrochemistry) of Petrology Department from Geosciences and Exacts Sciences Institute that belongs to UNESP is situated at Rio Claro city, about 240 km distant from the investigated area.

The sludge samples were dried at 60°C, one 10 g-aliquot was taken for evaluating moisture and other aliquots of variable weigh were separated for different chemical analyses. Such aliquots were inserted in distilled water or digested with different acids, depending on the requirements of the analyses. The total organic matter content was evaluated by spectrophotometry [12] held in a solution obtained after adding potassium dichromate and sulfuric acid to 1 g aliquot; organic carbon was oxidized to carbon dioxide with a parallel reduction of hexavalent chromium to trivalent chromium and an accompanying color change from orange to green read at 610 nm [12]. The organic carbon was estimated from those readings by the Walkley-Black method [13].

Several standard analytical techniques were used for obtaining others parameters analyzed in the sludge samples, for example, methyl orange end-point titration, potentiometry, ion selective electrode, and spectrophotometry. A portable meter was used for pH determination that was performed by a digital portable meter coupled to a combination glass electrode; buffer solutions equilibrated with the sample temperature were utilized to calibrate the equipment before the analyses. The bicarbonate concentration was determined by titration using a titrator with sulfuric acid standard solution to an end point evidenced by the color change of a standard indicator solution [14].

Calcium hardness (as $CaCO_3$) and magnesium hardness (as $MgCO_3$) of the samples were determined by the colorimetric method (wavelength 522 nm) after chelating calcium with EGTA and calcium and magnesium with EDTA [12], parameters that allowed to evaluate Ca and Mg contents. The analyses of sodium

Table 1: Results of the chemical analysis for sludge samples collected at Finipelli tannery in Patrocínio Paulista, São Paulo State, Brazil.

PARAMETER	UNIT	SAMPLE 1	SAMPLE 2
Date of sampling	-	October 1997	June 2000
Moisture	%	84.6	82.4
Total Solids	ppm	-	578,210
Volatile Solids	ppm	-	33,100
pH	-	7.5	8.1
Organic Matter	%	8.6	-
Organic Carbon	%	4.0	41.2
N-total	ppm	-	70,928
N-ammonium	ppm	-	14,077
N-nitrate	ppm	1,320	7,941
N-nitrite	ppm	-	107
P-total	ppm	-	2,104
Bicarbonate	ppm	56,000	-
Sulfate	ppm	12,200	-
Chloride	ppm	410	-
Fluoride	ppm	2,000	-
Sodium	ppm	116,800	72,191
Potassium	ppm	6,620	18,373
Calcium	ppm	40	361
Magnesium	ppm	-	650
Aluminum	ppm	2,880	-
Zinc	ppm	90	-
Titanium	ppm	< 1.0	-
Chromium	ppm	10,800	1,805

were done by flame photometry, whereas potassium was determined by the tetraphenylborate method that is based on the combination of K with sodium tetraphenylborate to form an insoluble white solid read at 650 nm [12].

Chloride and fluoride were measured potentiometrically after adding a known amount of ionic strength adjustor to each sample, when necessary. Orion ion-selective electrodes coupled into a digital meter were used, where standards containing variable concentrations of chloride and fluoride were utilized for preparing calibration curves consisting on logarithmic straight lines involving the potential and concentration readings. Nitrate, nitrite, ammonium, phosphorus and sulfate were determined by colorimetry [12] after adding reagents to the samples that are able to produce colored complexes read by a program stored in Hach DR/2000 spectrophotometer previously calibrated in variable concentrations at different wavelengths.

The metals Al, Zn and Cr were also measured colorimetrically. The eriochrome cyanide R combines with aluminum in the sample to produce an orange-red color read at 535 nm. The zincon method [12] was utilized for measuring zinc that is read at 620 nm, whereas the 1,5-diphenylcarbohydrazide method [12] allowed determine the total chromium that is read at 540 nm.

The samples of residuary waters were analyzed by the same methods utilized for sludge, except in the case of the metals that were quantified by atomic absorption spectrophotometry and inductively-coupled plasma spectrometry rather than colorimetry.

Table 2: Results of the chemical analysis for samples of residuary waters collected at CURVASA tannery in Patrocínio Paulista, São Paulo State, Brazil.

PARAMETER	UNIT	SAMPLE 1	SAMPLE 2
Date of sampling	-	February 1996	April 1996
pH	-	7.7	7.7
Organic Matter	%	5.7	n.m.*
Organic Carbon	%	3.3	n.m.*
Sodium	mg/L	2,000	187
Potassium	mg/L	100	10.8
Calcium	mg/L	1,300	211
Magnesium	mg/L	100	27.5
Chloride	mg/L	3,640	1,559
Bicarbonate	mg/L	420	15.5
Nitrate	mg/L	0.40	3.52
Sulfate	mg/L	3,200	700
Fluoride	mg/L	21.9	0.19
Aluminum	mg/L	800	1.3
Zinc	mg/L	10	0.2
Titanium	mg/L	10	< 0.002
Chromium	mg/L	200	12.1

*n.m. = not measured.

Table 3: Parameters established by Rule No. 12486 (NTA60) published on 20th October 1978 by São Paulo State.

PARAMETER	UNIT	VALUE
Color	Pt-Co	10 – 20 mg/L
Odor	-	Absent
Turbidity	NTU	2 - 5
Dry Residue	mg/L	< 500
pH	-	from 5 to 9
Aspect	-	Limpid
Consumed Oxygen	mg/L	< 2.5
Residual Chlorine	mg/L	< 0.3
Nitrate	mg/L	< 10
Chloride	mg/L	< 250
Fluoride	mg/L	< 1
Sulfate	mg/L	< 250
Arsenic	mg/L	< 0.05
Barium	mg/L	< 1
Cadmium	mg/L	< 0.01
Lead	mg/L	< 0.05
Cyanide	mg/L	< 0.2
Copper	mg/L	< 1
Hexavalent chromium	mg/L	< 0.05
Mercury	mg/L	-
Total iron	mg/L	< 0.3
Manganese	mg/L	< 0.05
Selenium	mg/L	< 0.01
Zinc	mg/L	< 5
Total Coliforms	n/100mL	Absent
Total Solids	mg/L	< 500

4 Results and discussion

The results for the analyses of sludge samples are reported in Table 1. Sample 1 is enriched in several compounds inclusive chromium, as expected. Because such waste has high levels of potassium and organic matter in its chemical composition, as well as moderate amounts of nitrogen, it could represent an alternative to supply these nutrients in crop production, as have been reported by some research works, for instance, documenting an increase on the corn productivity in Acre State, Brazil [15].

However, some soils don't respond positively to the application of this sludge and there is risk on soil salinization due to the high sodium content (Table 1).

The disposal problem is aggravated because of the high content of chromium in the waste and efforts were made by the tannery for reducing it, which involved some modifications on the steps for leather production. Sample 2 was collected

Table 4: Permissible concentration limits in effluents established by São Paulo State Register 997 published on 31 May 1976.

PARAMETER	UNIT	VALUE
pH	-	between 5 and 9
Temperature	°C	< 40
Settleable solids	mL/L	< 1
Oil and grease	mg/L	< 100
BOD[1]	mg/L	< 60
Arsenic	mg/L	< 0.2
Barium	mg/L	< 5
Boron	mg/L	< 5
Cadmium	mg/L	< 0.2
Lead	mg/L	< 0.5
Cyanide	mg/L	< 0.2
Copper	mg/L	< 1
Hexavalent chromium	mg/L	< 0.1
Total chromium	mg/L	< 5
Phenols	mg/L	< 0.5
Tin	mg/L	< 4
Soluble Iron (Fe^{2+})	mg/L	< 15
Fluoride	mg/L	< 10
Soluble Manganese (Mn^{2+})	mg/L	< 1
Mercury	mg/L	< 0.01
Nickel	mg/L	< 2
Silver	mg/L	< 0.02
Selenium	mg/L	< 0.02
Zinc	mg/L	< 5

[1]BOD=Biochemical Oxygen Demand (5 days, 20°C).

after the changes were introduced and the results indicate that despite some compounds like sodium and chromium had concentrations reduced in the sludge, this was not the case for others constituents like organic carbon, nitrate and potassium.

The results for the analyses of residuary waters utilized during the leather production by CURVASA tannery are given in Table 2. The data for Sample 1 were initially compared with guideline values established by two different legislations: Rule No. 12486 (NTA60) established in 20th October 1978 by São Paulo State for defining the potable water standards (Table 3); Register 997 published on 31 May 1976 that defines the permissible concentration limits in effluents to be released to water bodies (coastal, fresh or ground waters) in São Paulo State (Table 4). It is possible verify that for some constituents in Sample 1 like sulfate, chloride, fluoride, zinc and chromium the guidelines values are exceeded. With the purpose of reducing their presence in the residuary waters, the tannery suspended the application of carbonates in the process and started the utilization of calcium oxide. Sample 2 was collected after the changes were introduced and the results indicated that the initiative caused reduction in all those constituents and others like sodium, potassium, calcium, magnesium, aluminum, titanium and bicarbonate. However, the nitrate concentration increased and the reduction was not enough to cause a chromium decrease up to a concentration level below 5 mg/L, as allowed by São Paulo State Register 997 (Table 4).

Thus, the presence of several salts and metals in the residuary waters is not favorable for their direct disposal into the ground due to the possibility of groundwater contamination. This may be illustrated by the results of a study carried out inside the area of the *Couro do Norte* industry, located in the Icoaraci Industrial District (Belém-PA) [16]. The investigation covered the shallow subsurface and was performed in order to investigate the possibility of underground contamination by liquids used in the industrial processing of dead animal skin to produce tanned hide. The used geophysical methodology was: resistivity (imaging and vertical electric soundings), spontaneous potential, electromagnetic (slingram) and ground penetrating radar (GPR). The integrated geophysical interpretation of data indicated the underground flow direction and a shallow plume of contamination, caused probably by the disposal of effluents by the *Couro do Norte* industry.

In conclusion, the leather production is an activity with high environmental impact, but improvements may be achieved by tanneries, mainly in countries where the environmental legislation is not lax. To give an example of an efficient pollution prevention system, chromium loads per produced ton are generally abated from 8 kg to 1.5 kg [17]. VOC emissions are typically reduced from 30 kg/t to 2 kg/t in a properly managed facility [17]. Thus, the process remains highly polluting all the same. A review of the total pollution load decrease achievable according to the UNIDO [17] posts precise data on the abatement achievable through industrially proven low-waste advanced methods. It has been pointed out that [16] "even though the chrome pollution load can be decreased by 94% on introducing advanced technologies, the minimum residual load 0.15 kg/t raw hide can still cause difficulties when using landfills and composting sludge from wastewater treatment on account of the regulations currently in force in some countries."

Acknowledgement

CNPq (National Council for Scientific and Technologic Development) in Brazil is thanked for partial financial support of this investigation.

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