Treatment and Valorization of Leather Industry Solid Wastes: A Review**

by

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Abstract

The state-of-the art of the different approaches available in the scientific literature for the treatment and valorization of solid wastes generated from the leather industry has been presented in this review. Tanning processes generate significant volumes of by-products and waste materials and, because of that, tanneries can cause serious negative environment impacts. The advancement of laws protecting the environment have prompted industrialists, environmentalists and scientists to look for the decontamination of wastes and to transform tannery solid waste materials to valuable co-products useful to be recycled or employed in other industries. Examples of the preparation of organic fertilizers, production of biomaterials, gelatins or collagens with multiple applications and production of energy by biomethanization have been proposed as solutions for untanned wastes. Several applications and treatments were proposed for tanned wastes, such as preparation of materials with multiple uses, recovery of proteins and chromium and their valorization, incineration, use of the solid tannery wastes as sorbents or adsorbents for removal of organic pollutants from wastewaters, etc. On the other hand, tannery sludges can be treated and recycled in tanning process or used for various applications in other industries. This paper has been focused on solutions and answers for researchers and concerned industry leaders who are seeking to improve the environmental quality of their activities in the tannery field.

Resumen

Lo más novedoso de la técnica en los diferentes enfoques disponibles en la literatura científica para el tratamiento y la valorización de los desechos sólidos generados por la industria del cuero se ha presentado en esta revisión. Los procesos de curtido generan volúmenes significativos de subproductos y materiales residuales, debido a ello, las curtiembres pueden causar graves impactos ambientales negativos. El avance de las leyes que protegen el medio ambiente ha llevado a industriales, ambientalistas y científicos a buscar la descontaminación de desechos y transformar los residuos sólidos de curtiembres en valiosos co-productos útiles para ser reciclados o empleados en otras industrias. Ejemplos de la preparación de abonos orgánicos, producción de biomateriales, gelatinas o colágenos con múltiples aplicaciones y la producción de energía mediante la biometanización se han propuesto como solución para los desechos no curtidos. Varias aplicaciones y tratamientos fueron propuestos para los residuos curtidos, como la preparación de materiales con múltiples usos, la recuperación de proteínas y de cromo y su valorización, incineración, el uso de los desechos sólidos de curtiembres como absorbentes o adsorbentes para la eliminación de contaminantes orgánicos de aguas, etc. Por otra parte, los barros de la curtiembre pueden ser tratados y reciclados en el proceso de curtido de pieles o utilizado para diversas aplicaciones en otras industrias. Este documento se ha centrado en las soluciones y respuestas para los investigadores y los directores de industrias que están tratando de mejorar la calidad ambiental de sus actividades en el ramo de las curtiembres.

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This is a Review category paper and was chosen for its comprehensiveness. The authors use of the word "valorization", while not commonly used in American English, was retained because some current definitions of valorization are appropriate (i.e. '..the reuse or recycling or any other action designed to obtain reusable material or energy from waste..": www.htwm.com.my/content/glossary.php) *Corresponding author: t_soufiane@yahoo.fr (S. Tahiri)

INTRODUCTION

The tannery industry is environmentally important as user of a by-product of the meat industry. However it is perceived as a consumer of resources and a producer of pollutants. Between the beginning of the tanning of the skins and the delivery of finished leather articles, there is a series of operations that produce a significant quantity of wastes. The operations involved in the transformation of hides into leather generate both liquid (wastewater) and solid (tanned and untanned solid waste) pollution loads at various processing stages (Table I).[1] The processing of one metric ton of raw hide, provides 200 kg of a leather-final product, along with 250 kg of non-tanned waste, 200 kg of tanned waste (3 kg chromium) and 50,000 kg of wastewater (5 kg chromium). Thus, only 20% of the raw material weight is converted to leather.[2] The World Bank reported that solid wastes can represent up to 70% of the wet weight of the original hides.[3] So, the lack of treatment of solid and water waste causes a serious negative environment impact.[4] Through the application of clean technologies (water saving, recycling of most pollutant baths) and solid wastes revaluation techniques, the mass balance for tanneries can be significantly improved.

Environmental concerns and escalating landfill costs have prompted industrials and scientists to look for ways to obtain valuable co-products from tannery wastes. The strategies developed try to increase the effectiveness of the industrial process by increasing the amount of products that can be sold and to reduce the amounts of wastes that require additional treatment and costs for their safe disposal in the environment.

The production of chromium-containing solid wastes (including chrome shavings and tanned splits) in a tannery has been recognized as a significant issue for many years, but, in recent years the growing environmental social conscience and the pressure made by the authorities has given the problem increasing urgency. Historically, shavings, trimmings and splits from the chrome tanning of hides and skins have been disposed of in landfills. Increased local restrictions on land disposal, recent increases in the costs of land disposal and decreases in the number of disposal sites have encouraged the research on alternative treatments for these materials.[5] The chromium in these solid wastes exists in the non-toxic +3 oxidation state, but there is growing concern that chromium could possibly be converted to a toxic +6 oxidation state. Many scientific groups have oriented their research to find a process to recycle and treat these wastes. Several applications and treatment were proposed: preparation of materials with multiple uses, recovery of proteins and the chromium itself and their valorization, incineration, use of the solid wastes as sorbents or adsorbents for organic pollutants in wastewaters, etc.

An important aspect of pollution in tannery and related industries concerns the ultimate destination of non-tanned wastes (fleshing, trimmings and splits) most often at the present time transported for disposal or at best delivered to glue factories. The chemical composition of these wastes is very interesting, and allows, industrially speaking, a technology of recovery of proteins and greases to be envisaged.[6] The principal techniques of valorization, suggested for untanned wastes, are: agronomic valorization of wastes by exploiting their high nitrogen content (preparation of organic fertilizers), production of biomaterials, gelatins or collagens with multiple applications and production of energy by biomethanization.

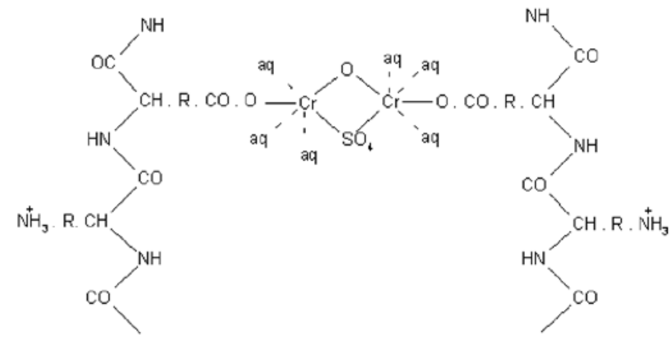

Figure 1: Molecular structure of wet blue.[8]

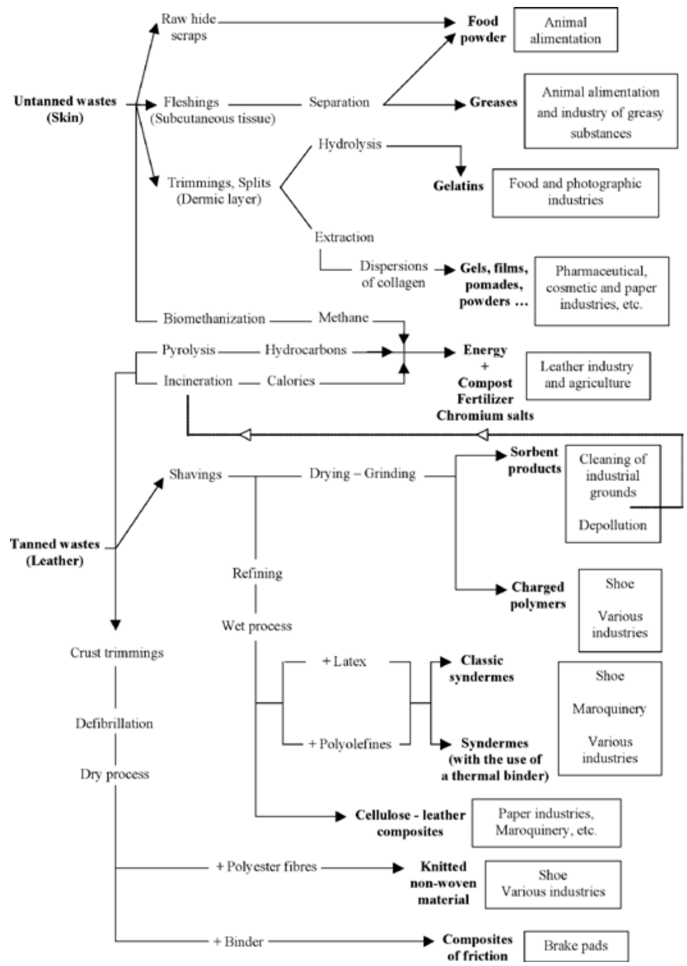

Figure 2: Valorisation of tannery and fellmongery wastes.[9]

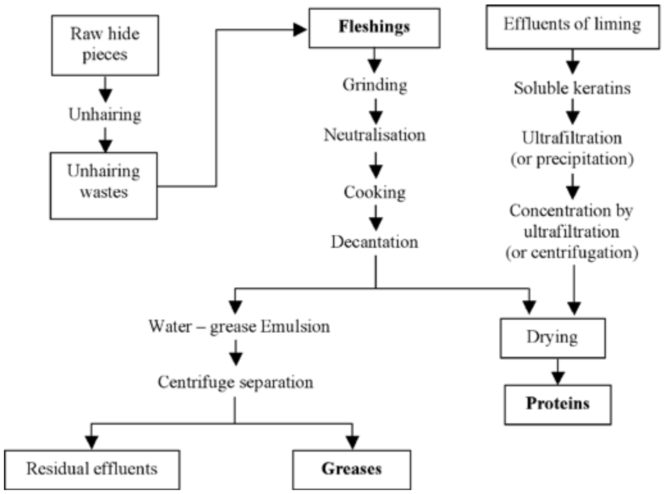

Figure 3: Recovery of proteins and greases from untanned wastes.[9]

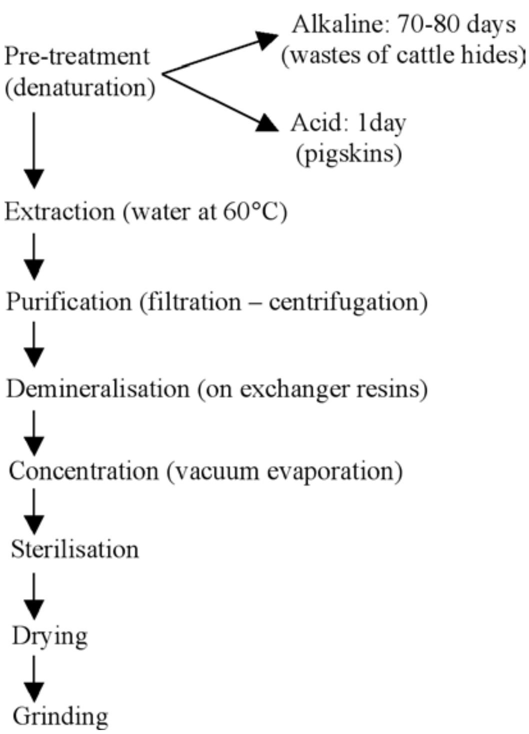

Figure 4: Manufacture of gelatin.[9]

In this paper, we will present the techniques of treatment, valorization and recycle proposed by numerous researchers for untanned and tanned solid wastes and for wastewater sludges. Theses techniques are of a great interest for improved environmental protection and economy of products by considering tannery wastes as a source of raw materials for various industries.

TANNERY SOLID WASTES

Untanned wastes

In general, untanned solid wastes are subjected to a biological degradation, which creates problems of transport and handling, and difficulties of discharge in landfill. These wastes can be an important source of bad odor with extended storage. The principal untanned wastes are the followings: [1,7]

Raw hide pieces: Untanned hide scraps without unhairing or depilation.

Fleshings: The pieces of flesh, subcutaneous and adipose tissues separated from hides or skins in the mechanical fleshing operation. Tannery fleshings are the major untanned solid wastes emanating from the beam house of a tannery.

Trimmings: The unwanted material cut away from the hide or skin at various stages to give it desired shape.

Tanned wastes

Tanned solid wastes (as chrome shavings and buffing dust) are low density and therefore occupy a large volume. It causes problems in the handling of enormous wastes generated in leather industry. The molecular structure of wet blue and consequently of tanned wastes is presented in Figure 1.[8] Wastes of chromium tanned leather primarily consist of chromium and proteins. These wastes are stables and not subject to putrefaction. The biological stability of material is the result of complexation between chromium (III) salts and the carboxyl groups of the collagen. The main tanned solid wastes are the followings: [1,7]

Chrome shavings: The small pieces of leather are shaved off when the thickness of wet blues is rendered uniform by a bladed cylinder. Wet blue is the wet chrome tanned leather which has not yet undergone the necessary further wet processes.

Tanned splits: Parts obtained by splitting the leather horizontally; the flesh splits correspond to the flesh side of the leather.

Buffing dusts: Wastes generated after treating the surface of leather by abrasion (similar to "sandpapering.")

Trimmings: Wastes resulting from the operation of geometrisation of finished leather.

Tannery sludge

Sludge is a general term referring to the residues of water or wastewater treatment which deposit as high water content silt on the bottom of settling tanks. Leather tanneries produce a large amount of sludge which contains nitrogen, calcium, magnesium, phosphorus, trivalent chromium and some sodium. The high concentration of trivalent chromium along with organic/inorganic compounds in tannery sludge may be a source of ground-water contamination in the case of land disposal. Chromium recovery from sludges is economically and environmentally interesting.

VALORIZATION OF SOLID WASTES GENERATED BY TANNERY AND FELLMONGERY INDUSTRIES

Tanneries generate considerable quantities of sludge, shavings, trimmings, hair, buffing dusts and other general wastes as a natural consequence of leather production. On a daily basis, this mass of wet solid wastes can exceed the mass of hides received and processed. The solid wastes comprising sludge, tanned and untanned wastes are inevitable by-products of the leather manufacturing process and may causes pollution.

The valorization of tannery wastes is characterized by the extreme diversity of the techniques employed or recommended.[9,10] This diversity of the solutions rises in particular from the variety of generated waste: skin or leather, wet or dry, cheap or noble. Solid wastes generated by the leather processing industry create a major challenge for the "greening" of this industrial process. Appropriate technology has been developed for the profitable disposal of these solid wastes. Many scientific groups have oriented their research to find a process to recycle and treat these industrial residues. The solutions proposed for wastes of tannery and fellmongery industries are summarized in Figures 2, 3 and 4 and will be presented in the following paragraphs.

Untanned wastes as raw material for greases and proteins recovery

The chemical composition of untanned wastes is very interesting and allows, industrially speaking, a technology of recovery of proteins and greases to be envisaged.[6] After recovery of protein from fleshings separated from hides or skins in the mechanical fleshing operation, greasy substances usable in industry are extracted (see Figure 3).[9]

Fleshings can be obtained either before or after the liming treatment. The liming treatment alters the fat and protein content in the residual fleshings. Development of a method to re-use a vast portion of these pretanned wastes was studied by Rangel-Serrano et al (2003).[11] Untanned wastes might well constitute an important source of protein with interesting uses as biological fertilizers in agriculture or horticulture. A series of fertilization tests have been carried out in a greenhouse.[11]

Trimmings and splits from untanned wastes can undergo: (i) Hydrolysis for the preparation of gelatins usable in food and photographic industries [9] (ii) Extraction for the preparation of dispersions of collagen transformed later into gels, films, pomades, powder, etc. for cosmetic and medical applications by exploiting, respectively, regenerating properties and haemostatic and cicatrizing character of collagen.[12-15]

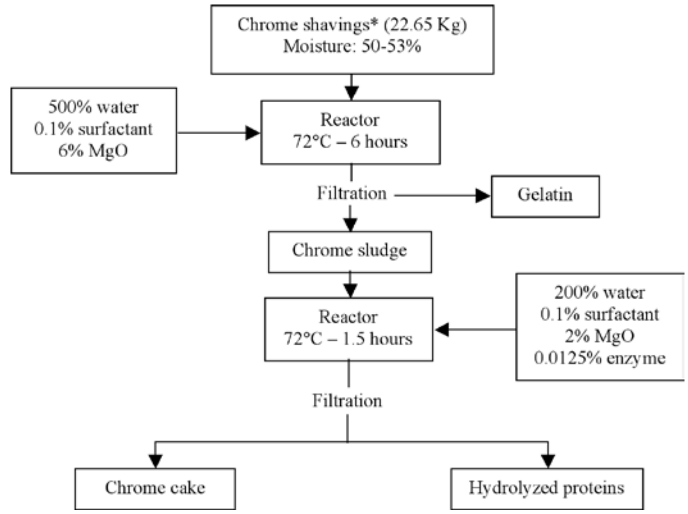

Figure 5: Treatment of chrome shavings according to M.M.Taylor.[30]
Note: % percentage based on weight of chrome shavings

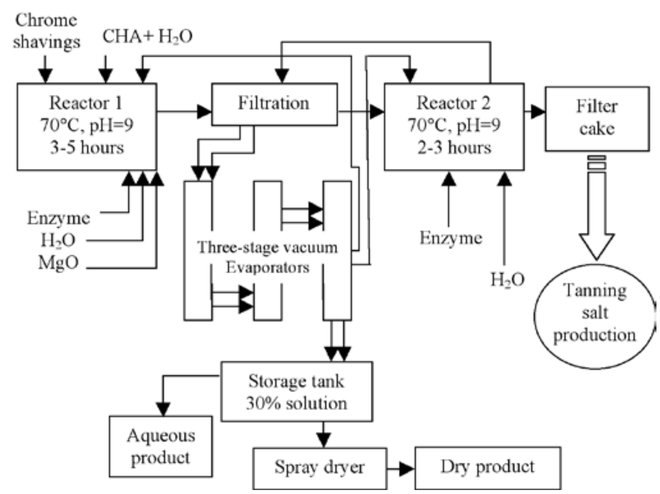

Figure 6: Treatment of chrome shavings according to K.Kolomaznik.[38] Note: CHA : Cyclohexylamine

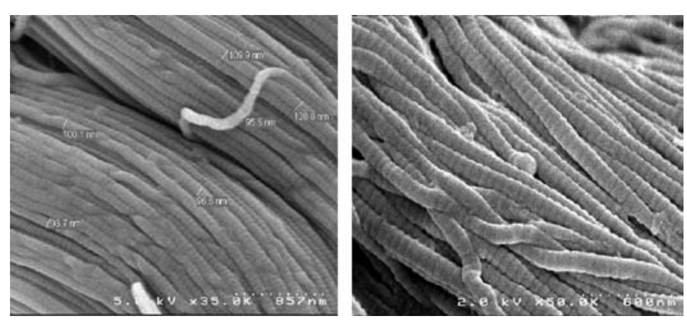

Figure 7: Scanning electron micrograph of chrome shavings.[57]

Gelatins are obtained from untanned solid wastes by controlled denaturation of the collagen which they contain.[9,16] There are two types: gelatins obtained by alkaline treatment (wastes of cattle hides) and gelatins obtained by acid treatment (pigskins). The diagram of manufacture of the gelatin is represented in Figure 4.

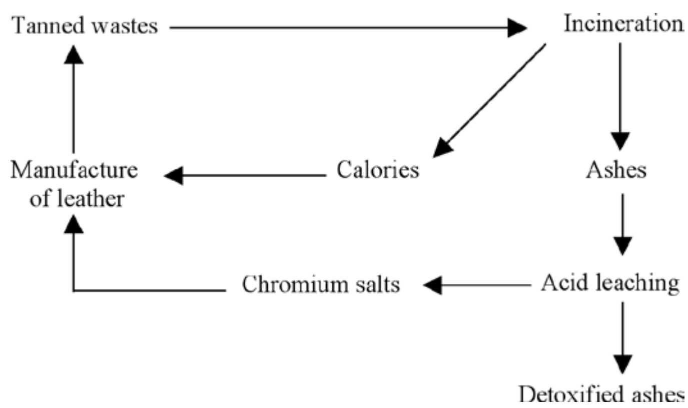

Figure 8: Potential recovery of chromium by incineration.[9]

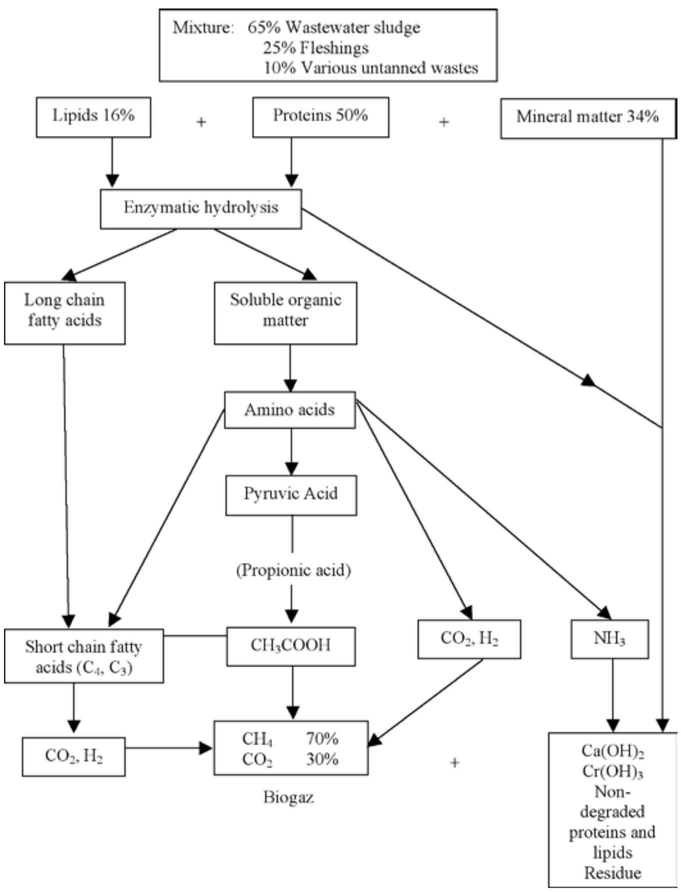

Figure 9: Biomethanization of tannery wastes.[1]

In our previous works, we have extracted gelatinous proteins from untanned solid wastes generated by tannery after elimination of hair and greases with chemical treatment. Membrane ultrafiltration was studied to concentrate the extract of soluble gelatin.[17] After lyophilization; characteristics of gelatinous products as concentration of amino acids, elemental composition, inorganic anions and nitrogen amount were determined to give a good estimation of protein quality. Results show clearly that recovered material consists mainly of proteins (~ 91.9 %) with a very interesting composition of amino acids. Using Ion Exchange Chromatography and Inductively Coupled Plasma analysis, we have evidenced that the process used in our work is very

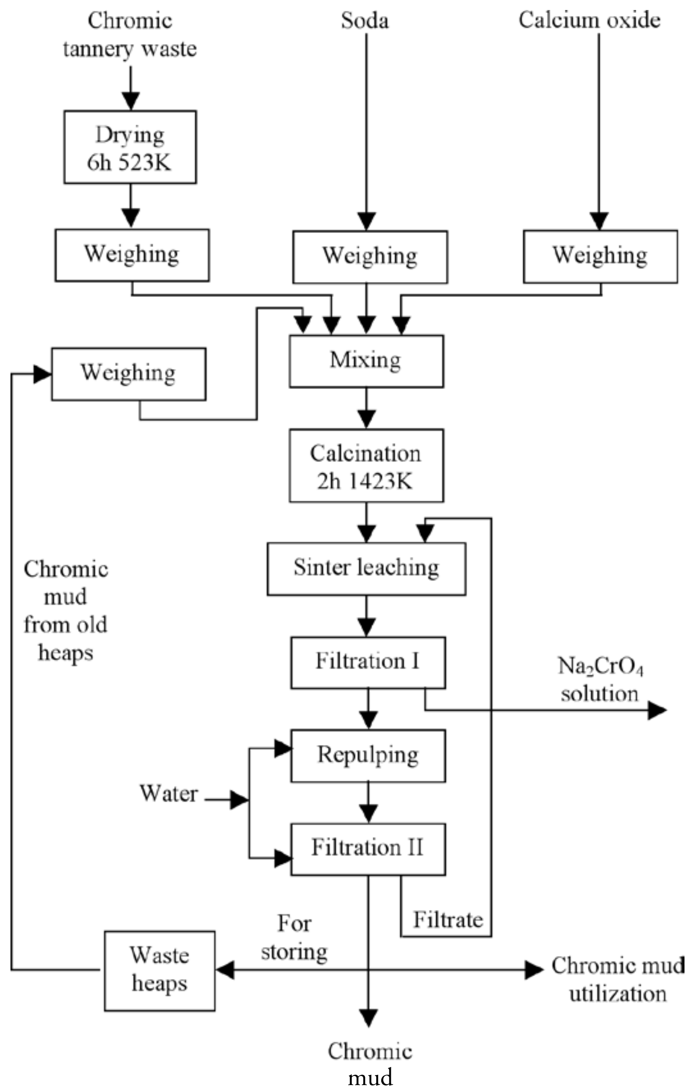

Figure 10: Utilization of tannery wastes for the production of sodium chromate (according to Z. Kowalski).[99]

efficient for recovery of gelatinous proteins with high purity. Amino acids composition determination was compared with that of some commercial proteinaceous products in order to show the feasibility of the use of recovered gelatin as raw material for industrial applications.

Recovery of proteins from tanned wastes and reuse of chromium

Alkaline hydrolysis has been used in many parts of the world for chrome recovery and for the isolation of protein fractions. Acid hydrolysis has been used to convert the wastes into a chromium-containing hydrolysate usable in the retanning or fat liquoring steps of leather finishing.[18,19] An experimental study was carried out by Bataille et al [20-23] in order to establish a process for economically transforming leather into usable proteins. The process yield is highly dependent on the granulometry of waste to be digested. M. M. Taylor and her research group [5, 24-35] have also developed two processes in which the chrome shavings are treated with alkali and enzymes to extract hydrolyzed and gelable

TABLE I
Contribution of Different Tannery Operations of Total Pollution [1]

	Liquid wastes		Solid wastes	
Operations	**Quantity**	**Composition**	**Quantity**	**Composition**
Soaking	Substantial	Salt (NaCl) Preserving agents Bacteria Defilements (blood, urine, manure, etc.)	Insignificant	
Lime liquor	Substantial	Salt (NaCl) Lime Sodium sulfide Proteins Bacteria	Insignificant	
Fleshing	Insignificant		Substantial	Fats Hide scraps with lime and sulfide
Deliming Bating	Medium	Ammonia nitrogen Enzymatic products	Insignificant	
Pickling Chrome tanning	Medium	Sodium chloride Mineral and organic acids Trivalent chromium salts	Insignificant	
Vegtable tanning	Medium	Synthetic tannins Vegetable tannins	Insignificant	
Sammying Splitting Shaving	Insignificant		Medium	Chrome tanned and wet wastes and shavings
Retanning Dyeing Fatliquoring	Medium	Synthetic tannins Dyes Fatting oils	Insignificant	
Buffing	None		Medium	Dust of tanned hide
Finishing Trimming	Low	Traces of solvents Pigments	Medium	Trimmings with finishing

protein products and a recyclable chrome cake. Chrome shavings were treated by magnesium oxide (MgO) in order to recover proteins, in the form of gelatin, and sludge with high content of chromium. Obtained chrome cake was then treated by MgO in the presence of an enzyme (Alcalase) to release remaining proteins and to recover them in hydrolyzed form (Figure 5).[30] The physicochemical properties of the recovered end products were studied. The recovered proteins can be applied in numerous fields: cosmetic products, fertilizers, etc. The partially hydrolyzed collagen, extracted form chromium-containing leather wastes, was chemically modified with glutaraldehyde and was used to prepare a filling product for leather processing.[36] Recently, Taylor et al (2008) [37] have proposed the application of enzymatically modified waste proteins from the leather (gelatin) and dairy (casein and whey) industries as fillers in leather production. Authors have evidenced that fillers have the potential to be economically produced from sustainable resources as an alternative to expensive and increasingly limited conventional products. To optimize the dechromation of chrome shavings, Kolomaznik et al [38] have modified the American process developed by Taylor et al [30] by using of organic volatile bases such as isopropylamine, diisopropylamine, cyclohexylamine, ammonia and others (Figure 6); this modification increases the yield of soluble protein recovered with a relatively low ash content and provides a filter cake containing more chromic oxide than that obtained with inorganic bases, thus offering an easier and cheaper processing. The potential commercial applications of end products include: i) the use of hydrolyzate as an organic nitrogenous fertilizer, ii) the use in the manufacture of biodegradable polymers for agriculture sowing tapes, iii) the production of inexpensive formaldehyde-free adhesives, iv) anti-skid agents in PVC and rubber compounds, v) their use as agents for increasing adhesion to textile backing in conveyor belt manufacture, vi) the use as heat stabilizers in PVC paste, and vii) as an additive to concrete and plaster to influence setting time, rheological properties, and the energy demands of raw material grinding. The applications proposed for recovered chromium salts involve recycle to tan hides, chromic pigments for glassmaking, manufacture of heat-resistant bricks, etc. [38]

Taylor et al (2000) [39] also demonstrated that trypsin was an effective enzyme for the isolation of protein products during the treatment of chrome shavings. The research carried out allows finding a commercial trypsin preparation efficient in solubilizing the shavings and cost effective. The influence of surfactants on the gelatin isolated from chrome shavings was studied by Cabeza et al (1999).[35] Surfactants were used during the extraction of the protein products from chrome shavings to avoid foam formation. Foam would make the manipulation of the mixtures difficult, disturbing the separation of the protein products from the residual chrome cakes, and could inactivate the enzyme. Cabeza et al (1999) [40] demonstrated the potential application, in microencapsulation, of gelatin isolated from chromium-containing solid tannery waste. As a model, an anionic semi-synthetic fatliquor, typically used in the tanning industry, was microencapsulated by complex coacervation using gelatin and acacia. The behavior of commercial gelatins (75 and 225 g Bloom) and alkali- or enzyme-extracted gelatins from chrome shavings were compared. No significant differences were found between commercial and extracted gelatins.

An *Aspergillus carbonarius* isolate, selected from an established microbial culture collection, was used by Katsifas et al (2004) [41] to study the biodegradation of chromium shavings in solid-state fermentation experiments. Approximately 97% liquefaction of the tannery waste was achieved and the liquid obtained from long-term experiments was used to recover chromium. The resulting alkaline chromium sulfate solution was useful in tanning procedures. A proteinaceous liquid was also obtained which has potential applications as a fertilizer or animal feed additive and has several other industrial uses.

In a previous study, we employed an alkaline process for the recovery of proteins in the aqueous phase of treated tanning wastes and the metallic salts in the cake.[42] After lyophilisation of the liquid; we recovered solid proteins with a high nitrogen percentage and low chrome content. We have calculated the yields of the recovered proteinaceous materials and that of the cake by weighing the isolated products throughout the process and we determined the phys-chemical characteristics of proteins and cake. Results obtained evidenced that the yields and the properties of the isolated products depend strongly on the choice of the alkaline agent. The differences of yields for protein products obtained using NaOH or Na_2CO_3 are significant as compared to those obtained using $Ca(OH)_2$ because for calcium hydroxide, the amount of cake obtained was higher than that found using sodium hydroxide or sodium carbonate and a part of the liquid and consequently of soluble proteins was sorbed by the sludges. However, the proteinic material was high in nitrogen content. The proteinaceous materials recovered with $Ca(OH)_2$ have a very low chromium amount and a less important percentage of mineral matter as compared with those recovered with NaOH and Na_2CO_3. Alkaline digestion provided a total recovery of chromium in the form of sludges. In order to revalue the chrome cakes recovered after digestion of chrome shavings and tanned splits and to avoid pollution transfer resulting in soil pollution (final disposal of sludges), we studied in our previous works the synthesis of a pigment for paint industry from cakes obtained after digestion of wastes with calcium hydroxide and the preparation of a basic chromic sulphate $[Cr_2(SO_4)_2(OH)_2,Na_2SO_4,6H_2O]$, usable in the tanning process, from sludges recovered with sodium hydroxide.[43-45]

In order to prepare anticorrosion pigments for paint industry usable in bodywork field, we have treated the chromium-lime sludge to transform the chromium, present in residual solid, into yellow pigment.[43] The solid residue was incinerated* under precise conditions of temperature with a large initial excess of oxygen in order to oxidize the trivalent chromium and to transform them to the hexavalent state. The dissolution of recovered ash by a dilute solution of nitric acid allows regeneration of a concentrated bichromate solution from which chromium was recovered in the form of solid yellow chromate by reactions of complexation and precipitation using a solution of lead (II) nitrate. The crystalline structure of the precipitate was identified by x-ray diffraction. We

TABLE II
Influence of Operating Conditions on Composition of Ashes from Tannery Wastes[1]

Chromium oxidation state desired	Temperature	pH	Excess air
Hexavalent chromium	< 600°C	Alkaline	+
Trivalent chromium	> 800°C	Neutral Acid	-

developed a paint formulation and we studied the quality of prepared pigment.[44] To evaluate the effectiveness of this product in the paint industry, standard tests were performed: visual comparison of paints color, determination of oil absorption value, assessment of dispersion characteristics from the change in fineness of grind, microscopic examination of surface films, calculation of color differences, U.V.Con exposure [tests carried out in order to evaluate the degree of degradation of panels coated with paints under specified conditions (Ultraviolet cycle 60°C, Condensate cycle 50°C). The Total time of exposure is 500 hours], outdoor exposure test, etc. It was concluded from our study that the pigment prepared could be used successfully in the paint industry because tests showed clearly that the quality of the studied pigment was as good as the commercial pigments used as references.

To protect the environment and to reuse all secondary by-products generated after alkaline treatment of tanned wastes with sodium hydroxide, we have used chemical process to purify the chrome cake for recycling. We have modified the purified chromium to basic chromic sulfates with basicity 33°S and the tanning capability of the reused product was established by tanning tests, using cattle hides and goat skins. Characteristics such as chromium oxide content and shrinkage temperature were determined. Apparent quality of obtained leather (penetration of chromium into skins, coloring and firmness of samples in wet blue stage) was also studied. Obtained results allows us to conclude that there are no significant differences in the leather tanned with either, the commercial chromium or basic chromic sulfates prepared from purified chromium.[45]

[Editor Note: Current regulations and practices in the United States do not embrace incineration and foster total elimination of hexavalent chromium on tannery sites.]

Materials containing leather fibers

Tanned wastes are mainly used for the production of new materials because their intrinsic phys-mechanical properties (absorption capacity, mechanical resistance). Synthetic leathers or "Syndermes," an invention toward the end of the 19th century, have been industrially manufactured since the Second World War. They are obtained by paper technique using chrome shavings which constitute one of the most important sources of tanned wastes. Syndermes are used in shoe industry and maroquinery.[6,9] In addition to classic Syndermes, Dermatene® is another material containing leather fibers which was obtained by the use of a thermal binder (polyethylene). The main advantages of Dermatene® compared to traditional Syndermes are the following: high water absorption capacity, best dimensional stability and aptitude of thermoforming and thermal welding. Dermatene is used in shoe and handbag industries. It is also used in automobile seat covering constructions, side panels and other trim..[9] Another type of material containing leather scraps is Dermomat®, which is synthetic leather constituted of leather fibers, polyester (40 at 50%) and a binder (8 at 10%). This material has good mechanical and hygienic properties (resistance to moisture and to mold), it can be used in the industry of the seat (office, community, automobile), for lining shoe manufacture and in the elaboration of impregnated fabrics for sport articles.[9,46] Leather scraps are also used in the form of polymer-waste composite for manufacturing wear soles. These composite materials contain from 65 to 75% of leather scraps and 25 to 35% of binder containing PVC.[9]

The leather fibers were used for obtaining composites of improved friction properties and an interesting cost.[9] For example; leather scraps have been used for manufacturing composites for brake pads. Wastes were dried using fluidized-bed drier and then grounded. Leather scraps, metal and thermosetting resins were mixed. Then, a molding by compression - polymerization was carried out.

The insulating properties of collagenic fibers were exploited for the preparation of a collagen - polyisocyanate composite resistant to fire and a collagen - synthetic rubber composite usable as phonic insulator.[47-49]

The possibility of addition of leather residues to the composition of the ceramic pastes for the manufacture of construction materials was studied. This research was focused on the preparation of performance materials containing cement and waste leather scraps. Bricks of construction or facing were also manufactured by adding small quantities of leather wastes (2, 5 and 10% in weight) to pastes of clay extracted from Oua Jrine quarry in Fez,Morocco. The physical characteristics of prepared bricks are interesting. These bricks have good refractory and mechanical quality and have a decorative aspect inherent to their content of leather wastes.[50,51]

In addition to synthetic leather and above mentioned materials, various uses of fibers resulting from the leather wastes can be made,[52-55] in particular: i) molded products containing leather scrap and a binder (i.e. ethylene - acrylic acid copolymer) for the manufacture of bottles stoppers, plates, goblets, etc, ii) thermoplastic hardener material, consisted of leather scrap and elastomer or plastic binder, iii) rope for a tennis racket, iv) additives for rubber, and v) thermoformable material containing fibers of leather wastes, binder and cross-linking agent, etc.

Many other formulations of copolymers integrating collagen resulting from leather wastes have been proposed, mainly by the countries of Eastern Europe;[52-54] such as i) collagen (45%) + cellulose or cotton (35%) + polyethylene (20%), ii) collagen + PVC + various additives, iii) collagen (30%) + fibers of polyester (40%) + fibers of polypropylene (30%), iv) copolymer containing collagen (35 to 50%) and polyester impregnated by latex and acrylic resin, the whole is coated with a layer of polyurethane, v) collagen + polyurethane + elastomer [poly(ethyleneterephtalate) + polystyrene], and vi) collagen + elastomer + plasticizer, etc.

Absorbing product for cleaning soiled industrial grounds

The water absorbing properties of leather are better known than its ability to absorb organic compounds, such as solvents and hydrocarbons. The operations of degreasing and fat-liquoring well illustrate the affinity of leather for these types of materials.

The Technical Center of Leather, Lyon, France, in collaboration with the French Petroleum Institute, undertook a study which led to the development of a product (Dermopol®) usable for the cleaning of the industrial grounds soiled by oils or hydrocarbons.[56] Various tests of cleaning were carried out with a product elaborated from dried and crushed chrome shavings of bovine leather. These tests were carried out with various types of pollutants: oils, hydrocarbons, solvents, etc, and on various types of floor surfaces: rough concrete, painted concrete, tiles, plastic flooring, etc

The manufacture of a sorbent product from wet chrome shavings (wet-blue of bovines) comprises the following phases:[56] after drying continuously in a hot air drier, chrome shavings with a water content lower than 10% were crushed to graduals smaller than 5 mm. A mixture containing granulated leather and a fine powder of rubber, in a proportion 70-30 was prepared to avoid the development of cohesive and adhesive properties of the product in the presence of oil, under the effect of the trampling or the passage of vehicles, leading to the formation of a not easily eliminable product. The manufactured sorbent was then conditioned in bags and pallets.

Because the lower heat value (> 5000 Kcal/Kg dry) of chrome shavings, the destruction of the product by incineration after use can allows the recuperation of energy as well as chromium oxide from ashes which can be recycled.[56]

Decontamination of polluted water through the use of tanned solid wastes

In previous studies, the ability of chrome shavings and buffing dusts to remove methylene blue and organic textile dyes from aqueous solutions was studied by us in a static batch reactor and using column technique.[57,58] It was evidenced that buffing dusts proved to be a much better adsorbent than chrome shavings for cationic dyes. On the other hand, the adsorption of anionic dyes was very important on the two studied wastes. The pH was an obvious influence on the adsorption of dyes. Adsorption of cationic dyes is less favorable under acidic conditions (pH <3.5) and at high pH values (pH >10.5). The adsorption of anionic dyes on both considered adsorbents was more favorable under acidic conditions (pH <3). The adsorption on chrome shavings was improved by the use of fine particles. The kinetic adsorption was also studied. Adsorption isotherms, at the optimum operating conditions, were determined and the isotherm parameters were calculated. Adsorption of dyes on tannery wastes follows the Langmuir model. The column technique could be applied to treat significant volumes of solutions. In another study,[59] we demonstrated that an acidic pH medium and a temperature of 50ºC were the best conditions for "direct dyes" removal by using chrome shavings and we have evidenced the feasibility of decontamination of dye polluted waters from a textile factory, being found a removal yield higher than 90% under precise conditions of pH and temperature.

Sorption by natural organic substrates, inorganic materials or synthetic fibers is one of the most popular methods used for the separation of oily wastes from contaminated water. Previously, we studied the ability of chrome shavings (CS) and of buffing dusts of crust leather (BDCL) to remove motor oils and oily wastes from demineralised water and natural seawater.[60] Tannery solid wastes are composed mainly by proteins and have a highly organized structure in the form of fibers (ϕ : 100 nm) which are parallel and very tight to each other (see Figure 7).[57] This structure is favorable to use tanned wastes as sorbents. We have evidenced that these wastes have a high oil sorption capacity which depends strongly of sorbent nature. Tanned solid wastes are capable of absorbing many times their weight in oil (6.5-7.6 and 12.8-14.5 g/g dry substrate respectively for ground CS and BDCL). The low density porous tanned waste granules float on the surface of water and can remove hydrocarbons and oil films. The removal of oils from water surface is a quasi-instantaneous process. After use, the saturated waste floats and can be removed in an efficient and easy way. The results look fairly promising as an alternative to remove oils from industrial effluents and from contaminated coastal areas. Additionally to these works, we have shown that chrome shavings saturated with organic dyes have also a high capacity for oil sorption (5-6.5 g/g) and can remove quantitatively oil spots on water surfaces in a fast way.[59] The capacity of raw and dyed chrome shavings to remove oils from water is higher than 96%. A simple foaming allows us the evacuation of the sorbed pollutant without waiting. After treatment, the surface of water becomes practically clean.[59]

We have also studied the ability of chrome shavings to remove hydrocarbons (n-hexane, isooctane, and toluene) from water.[61] Wastes fibers from tannery industry are capable of absorbing many times their weight in hydrocarbons (6.3 g of hydrocarbons per gram of chrome shavings). We have verified that the removal efficiency of the pollutants from water is complete and that the sorption is a quasi-instantaneous process. We have developed a new procedure for the determination of hydrocarbons retained in solid tanned wastes from polluted waters.[62] The method uses near-infrared (NIR) transmission spectra obtained from leachates of the hydrocarbons with CCl_4 using a partial least-squares (PLS) calibration model based on the use of mixtures of n-hexane, isooctane, and toluene diluted with CCl_4.

Wastewater generated from the semi-chrome process presents a problem of separating chromium from vegetable tannins by conventional precipitation. Saravanabhavan et al

(2004) [63] have described a viable solution for the disposal of solid wastes; such as chrome shavings. Theses authors have reported the removal of tannins and recovery of chromium using chrome shavings as adsorbent. They have reported a tannin removal efficiency of about 96%. The tannin-free chromium bearing liquor after the adsorption process was subjected to conventional chromium recovery and was then used for tanning as a 40% replacement of commercial basic chromium sulphate. The tannin containing chrome shavings were used as a reducer for the preparation of basic chromium sulphate and this was also used for tanning trials.[63] The possibilities of using shavings to absorb some compounds as vegetable tannins contained in tannery wastewater were also studied by Manzo et al (1989).[64]

Incineration

The energy valorization of tannery waste by incineration has advantages as allowing the interior processing of waste at the manufacturing site, thus removing the need for a collection while generating appreciable economy of energy. Many investigators have recovered chromium by incineration at a variety of temperatures.[65] Under precise conditions, i.e., a temperature between 450 and 600 °C, an alkaline pH ensured by the addition of lime or sodium carbonate, and in the presence of a constant oxygen surplus, it is possible to transform all of the chromium present in tanned wastes into hexavalent chromium. Concentrated solutions of sodium bichromate are regenerated by simple leaching with acidified water. The residual ashes are completely white, which is the sign of a total absence of hexavalent or trivalent chromium. Another possibility consists of the use of a high temperature (850–1000 °C) limiting to the maximum extent the conversion of trivalent chromium into hexavalent chromium.[1]

The majority of wastes resulting from the manufacture of leather and mainly those obtained subsequently to the operation of tanning have a considerable lower heat value. The LHV is between 4000 and 5000 Kcal per kg of raw waste. Moreover, while operating under determined conditions, it is possible to recover the chromium contained in ashes.[1,9]

Various incineration equipments can be used according to the capacity and the type of waste to be treated: fixed-grating incinerators for quantities lower than five tons of waste per day, fluidized-bed incinerators for wastes in larger amounts (especially if sludges are added) and rotary incinerators for relatively wet wastes. For all these equipments, it is essential to envisage a post-combustion at 800°C in order to eliminate any risk of odor.

The thermal behavior of chrome shavings and of sludge recovered after digestion of tanned wastes with $Ca(OH)_2$ was studied in our previous work.[66] Ashes obtained after incineration of wastes at various temperatures were analyzed by X-ray diffraction and EDX method. We evidenced that the main crystalline phases present in the ash obtained at 600°C are Cr_2O_3 and NaCl. The diffractograms revealed an increase in the intensities of the chromium oxide peaks and a very notable decrease of the amount of sodium chloride at 1100°C. EDX analysis revealed a total disappearance of the chlorine peak at this temperature. Scanning electron micrographs showed that the waste lost its fibrous aspect when the temperature increases. Formation of aggregates was noted after 550 °C. Combustion of organic matter and decarbonation phenomena are the main steps observed on GTA and DTA curves of sludge. These phenomena are, respectively, exothermic and endothermic. The diffractogram of sludge recorded at 550°C, in the presence of a constant oxygen surplus, indicated the presence of $CaCrO_4$ and $CaCO_3$.

Some researchers have recovered chromium by hydromineralorgic way. Treatments by incineration give generally ashes with significant amount of chromium. Many American patents[67] show technologies which could be integrated in tanneries and lead to industrial applications. The recovery of chromium from ashes by simple leaching with acidified water allows the regeneration of concentrated solutions of bichromate at 20% (Figure 8).

To obtain a high yield of Cr leaching requires carefully controlled conditions of incineration: a temperature between 450 and 600°C, an alkaline pH ensured by the addition of lime or sodium carbonate, and the presence of a constant oxygen surplus.[1] After reduction, a chromium sulphate correctly basified can be used in tannery. Table II presents the optimum conditions for obtaining trivalent or hexavalent chromium.

The possibility of valorization of ashes produced after incineration of tannery wastes for cement industry application was studied by Yatribi et al (2001).[68] The effect of adding ashes at different percentages (ranging from 0 to 45%) on physical and mechanical parameters of cement was reported (compressive strength, bending strength, expansion, etc).

Aerobic composting

Tanneries produce substantial amounts of sludge and untanned wastes susceptible to fermenting under aerobic conditions. The sludge contains nitrogen, calcium, magnesium, phosphorus, trivalent chromium and some sodium. Given careful management these sludges can be used as soil amendments, either directly or after composting.[69] Various composting techniques can be used depending on the amounts of sludge and wastes to be treated: natural, accelerated and mechanical composting. Composting is readily possible with a mixture of sludge and untanned wastes having an average thermal value of 4500 kcal/kg of dry matter (DM). A material containing 70% dry matter, usable in agriculture, may thereby obtained.[1]

Amir et al (2008) [70] have tested composting as a cost-effective method for tannery solid waste management to overcome many of the environmental hazards and produce a stable, rich material for soil fertilization. Two composting trials were conducted after neutralization by ammonia or lime. The aim of the neutralization was to avoid the antimicrobial effects of the acidity in the tannery waste, thus ensuring correct composting. Structural characterization of humic acids isolated from raw and composted materials was carried out.

Anaerobic digestion: Biomethanization

Biomethanization, which is environment friendly, is one of the most benevolent technologies as it leads the generation of energy from wastes while rendering them suitable for application as a rich source of organic fertilizer. Biogas is relatively odor-free, and the biosolids residue obtained after anaerobic digestion is rich in nutrients and finds application as an organic fertilizer in agriculture.[71]

Biomethanization allows anaerobic stabilization of solid wastes and sludge. This mesophilic digestion requires twenty days of contact and produces 0.75 to 1.15 liters of gas per liter of digester and per day having a content of methane ranging between 70 and 78%.[9] Biomethanization scheme in tannery, as applied to a mixture of wastewater sludge, fleshing, trimmings and splits, is summarized in diagram of Figure 9.[1]

Tannery fleshings could be subjected to biomethanization. The fleshing from industries and bio-sludge consists mainly of carbohydrates, lipids, proteins and inorganic materials. Microbes have the ability to transform polymers into simple soluble molecules such as amino acids, fatty acids and simple sugars.[71] Vasudevan and Ravindran (2007) [71] have reported an investigation with the aim to accelerate the fleshing digestion process by inoculation of sludges with efficient proteolytic bacteria, after which it could be subjected to biomethanization.

The main products of the alkali-enzymatic hydrolytic reaction of chrome shavings are gelable protein hydrolysate, enzymatic hydrolysate, and chrome sludge. In chrome sludge, the rest of the biomaterial is collagen protein. Approximately 20-40 % (on free moisture basis) is strongly bound as co-ordinate complex with chromium, which creates serious problems for further treatment of it to recover tanning salt. Saha et al (2003) [72] have found a possible solution of this problem by decreasing the content of collagen protein using anaerobic digestion. These authors have reported that during anaerobic digestion, the content of biomaterial associated with the chrome sludge decreased while the quantity of free chromium increased. These observations were confirmed by attenuated total reflectance (ATR) using FTIR spectrophotometry and scanning electron microscopy (SEM) analysis.

Valorization of chrome sludge generated by wastewater treatment

Sludges could be used in agriculture (compost, soil amendment). The fertilizing qualities of sludge have been demonstrated for truck-farm, cereal and fodder corps,[73] for fescue, corn and pea corps.[74] Mazur and Koc [75,76] have reported a comparison of three tannery sludges with natural manure, with and without the addition of mineral fertilizing elements. Description of this agricultural application of sludges was detailed by M.C. Carré, A. Vulliermet and B. Vulliermet [1] in their book entitled "Tannery and environment". Farm use of sludges involves hazards due to the presence of *a priori* unfavorable constituents. Some elements will be directly toxic for the soil's vegetable, animal and microbial organisms. Others will accumulate in plants or soil, depending on whether they are assimilatable or no, or end up in surface or ground waters trough run-off or leaching the major hazards are caused by heavy metals.[1] The use of tannery sludge in agriculture presents a limiting factor due to the presence of chromium which prevents their commercialization. Indeed, the use of this sludge can cause environmental problems such as for example the contamination of groundwater. The AFNOR (Association Française de Normalisation) standard advises against the agricultural use of sludges containing more than 200 mg of chromium per kg.[9,77]

Another application of chrome sludges is the incorporation of these wastes in concretes in the form of aggregates. Sludges are generally added with clay and are thermally treated (1000 - 1200°C). To have an economic process, expansive treatments which allow the manufacture of expanded aggregates with low density are used. In the case of the expanded aggregates, the formation of a reticule structure blocks the migration of heavy metals. Moreover it is possible to recover the heat released by combustion for drying. In the case of the ceramic type aggregates, there is no absorption of water by capillary suction. There is immobilization of the alkaline ions and heavy metals, in the form of minerals.[9]

Metalliferous wastes from the leather industry are used in the synthesis of a green glass stain using a pyromineralurgical process. A dye was synthesized by M.S. Bacou (1997) [78] using flocculated tannery wastes with high chromium content, to which silica was added previously to calcination. Mineralogical evolution is described as a function of silica content, of given granulometry, and an optimization of mineralogical composition and operating conditions is performed in order to obtain an inert product (no hexavalent chromium) and to fulfill requirements of end-users (glass industry) in terms of color and fusibility.[78]

Swarnalatha et al (2006) have studied the solidification/stabilization of thermally-treated toxic tannery sludge.[79] Tannery sludge was subjected to starved-air combustion at 800°C, which prevented the conversion of Cr(III) to Cr(VI). Authors have confirmed the efficiency of starved-air combustion using differential thermo-gravimetric analysis; electron spin resonance and Fourier transform infrared analysis. The calcinated sludge was solidified/ stabilized using fly ash, clay, lime and Portland cement as mixture constituents. The solidified specimens were tested for compressive strength and heavy metal fixation. The stabilization of chromium (III) in the cement gel matrix was confirmed with scanning electron microscopy.

To avoid landfilling and to produce recyclable tanning liquor, chromium tannery sludges are generally solubilized by sulfuric acid.[80] On the other hand; several techniques were used to separate chromium from tannery sludge. Shen et al (2001) [81] have studied the isolation of chromium (III) from acid extract. These authors proposed a three-step process for the separation of Cr(III) from interfering metal elements (Al, Fe, Ca, Mg and Zn) present in the acid leachate. Others authors have studied the bioleaching of chromium from tannery sludge. Wang et al (2007) [82] have shown the ability of an indigenous sulfur-oxidizing *A. thiooxidans* to leach chromium from these wastes. This process is efficient and allows the solubilization of up to 99% of chromium.

Chromium recovery from tannery sludge's based on thermal oxidation followed by chromate acid extraction was proposed, in analogy with the pyrometallurgical process of chromate production from chromite: Beccari et al [83-86] have studied the recovery of chromium from high calcium tannery sludge by incineration. Cr(III) oxidation in large amount is obtained without any additive reagent and with a little oxygen excess. No chromium was found in the fumes. Authors have revealed that temperatures over 400°C do not significantly affect the oxidation percentage and that 90% of the Cr contained in the sludge can be recovered from the ashes by a two-step extraction treatment. Cr(VI) extracted solution is suitable for recycling in the tanning process after usual reduction with sugar and sulphuric acid.

Other possible valorization strategies

Additional applications proposed for tannery wastes include the following fields: i) traditional use of gelatins in the manufacture of the adhesives,[87] ii) use of aqueous collagen dispersions in paper industry to increase the mechanical resistance of papers,[88] iii) preparation of filling and finishing products of the skins containing acrylic polymer and collagen hydrolysats,[12] iv) use of collagen for the preparation of supports of enzymes,[89-91] v) use of collagen in human and animal alimentation,[20,92-96] vi) manufacture of surfactants,[97,98] vii) substitution of chromium ores by chromium-containing solid waste in order to prepare sodium chromate (see Figure 10),[99] and viii) use of hydrolysate from chrome-tanned wastes for producing biodegradable plastics particularly applicable in agriculture,[100] etc.

CONCLUSIONS

As can be seen from the work and references cited throughout this manuscript, many researchers' and scientific groups have oriented their research to find sustainable processes to recycle and treat solid wastes of leather industry; wastes which are rich in proteins and/or chromium. These wastes are available in great quantities and at low costs. Conversion of solid waste into by-products reduces pollution load and can also be commercially beneficial. The marketability of products prepared from wastes with these potential applications should encourage the industry to recycle tannery wastes instead of paying to dispose of them in landfills.

In fact, it is very probable that many other ideas will be studied and developed in order to find sustainable applications for these industrial residues. It is also likely that other interesting works have been carried out but have not been published. We hope that this review provides guidance for committed industrial and governmental environmental leaders and facilitates ideas for further studies by researchers' seeking to improve the environmental quality for leather industry.

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