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Assessment and Characterization of Leather Solid Waste from Sheba Leather Industry PLC, Wukro, Ethiopia

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ABSTRACT

Leather manufacturing processes raw hides and skins into various finished leather products, generating huge amounts of untanned and untanned leather solid wastes (LSWs). The present study investigates the LSWs generation, characterization, and management practices of the Sheba leather industry in Ethiopia. Results revealed that LSWs are categorized as non-chrome solid waste, including de-dusted salt, raw trimming, hairs, fleshing waste, pickle trimming, and splitting wastes. Chrome-based wastes include chrome shaving waste, crust leather trimming waste, buffing dust waste, finished leather trimming waste, etc. Further, solid wastes were characterized for the physico-chemical parameters viz. moisture (31.5%), ash content (7.3%), pH (5.7), carbon content (14.7%), nitrogen content (0.3%), chromium content (2%), calorific value (20,107 $kJ.kg^{-1}$), VOCs (75.1%) and carbon to nitrogen ratio (52:1). Results obtained suggested various sustainable technological options for the effective LSWs management to preserve environment.

INTRODUCTION

The leather industry plays a significant role in the present scenario's social development and global economy (Li et al. 2019). Leather solid waste (LSW) generated from the leather processing industry creates significant environmental problems due to the generation of huge amounts of solid waste and wastewater (Saira & Shanthakumar 2023). Thus, the leather processing industry is classified as a highly polluting manufacturing industry, adversely affecting the surrounding environment, i.e., soil, water, and air (Kanagaraj et al. 2006). Leather production utilizes about 85 percent chrome salts in processing raw hides or skins globally due to its low cost, easy availability, and easy use. Chromium-containing solid waste generates approximately 6,00,000 metric tons per year globally (Ocak 2012). On the other hand, one ton of hide processing in the leather industry consumes around 60 m^3 of water and generates a large quantity of wastewater (Fela et al. 2011). LSWs generated from industrial manufacturing processes contain chemicals, solvents, acids, and degraded products of the skins and hide, which are toxic. One previous work shows that processing one ton of wet salted hides or skins can generate approximately 200 kg of finished leather solid waste and 200 kg of solid waste lost in the effluents (Masilamani et al. 2016). The leather processing industry converts raw hides or skins into physically and chemically stable end products using four major stages, i.e., beamhouse operations, tanning processes, re-tanning processes, and finishing processes (Muralidharan et al. 2022). These process further includes various chemical and mechanical processes (Ozgunay et al. 2007). During the entire leather manufacturing process, huge quantities of LSWs, i.e., tanned and untanned wastes, are generated. The chrome tanning process involves the chromium sulfate chemical, the most widely used tanning agent in leather manufacturing (Famielec 2020). As a result, the chrome-containing LSWs, like chrome shaving waste generated from leather production, are categorized as toxic and hazardous due to the presence of chromium and other chemicals (Fela et al. 2011). One estimation has shown that more than 60 percent of the produced leathers are utilized for footwear manufacturing (Koppiahraj et al. 2019). Another work depicts the production of 10 kg of final leather from processing 1000 kg of raw hides, generating about 850 kg of SWs. The tannery waste proportions from various processes are fleshing (50-60%), chrome shaving, splits, and buffing dust (35-40%), skin trimming (5-7%), and hairs (2-5%), etc. (Mushahary & Mirunalini 2017).

Various researchers carry out the characterization of solid wastes (SWs) from leather processing. LSWs were characterized for the various constituents, i.e., volatile matter, pH, fats, soluble in dichloromethane, nitrogen, sodium chloride, sulfide content, and the Cr, Fe, Na, and Ca, etc. Results revealed that fleshing, shaving, and trimming waste have maximum proportions of protein and fat (Ozgunny et al. 2007). Another work highlighted the investigations on the physicochemical properties, i.e., pH, temperature (°C), alkalinity (mg.L^{-1}), moisture content (%), organic carbon (%), crude fiber (%) except chromium content from the chrome buffing dust of tannery (Emmanueul et al. 2014). Thus, it is further suggested to use fat liquoring oils and biodiesel from pre-fleshing wastes, ethane, and compost from the lime fleshings, re-tanning agents, and leather board from shaving wastes, etc. Literature suggests the various treatment methods/options for effectively managing tannery solid waste. In this connection, one report (Fela et al. 2011) suggested the thermal treatment for the huge amount of LSWs (tannery solid waste and sludge) generated from the tannery. The energy content estimated of solid wastes is equivalent to 20 MJ.kg^{-1} as dry materials, which is higher in comparison to hard coal. Ram et al. (2021) proposed sustainable solutions and technologies through biochemical and thermal energy conversion. Further, the insights are useful in preserving natural resources, public health, and the environment.

Researchers developed a technique to remove chromium from wet blue waste with the recovery of high nitrogen solid collagen waste. Nitrogen content accumulations in plants and quantifications of nitrogen in soil were tested (Lima et al. 2010). One article (Famielec 2020) reviews the treatment technologies for the LSWs containing chromium with special emphasis on incineration in an experimentally designed tunnel incinerator. Chromium was present in a higher amount, i.e., 53 % (w/w), in the form of Cr (III) oxides in residual ash and can be recycled as a Crore substitute in the metallurgical or chemical industries. Chrome-containing solid waste generated from the leather-finished trimmings (LFT) and chrome shavings (CS) from tanneries observed higher calorific values of 15.77 MJ.kg^{-1} and 19.97 MJ.kg^{-1}, respectively. Thus, these wastes could be suitably used for thermal treatment, mainly incineration and pyrolysis (Velusamy et al. 2020). Saira & Shanthakumar (2023) evaluated the existing techniques for the de-toxification of tannery wastes.

Further, they examined the possibility of solid waste management options to attain zero waste within the tannery industry. A recent review (Appala et al. 2022) highlighted the different routes of tannery solid waste conversion into biomass, a gamut of products, and energy. The primary organic resource is collagen, a natural protein in the skin hides. These are converted into useful composites such as adsorbents, adhesives, and renewable fuels such as biogas.

One recent estimation based on a global study shows that China is the leading leather exporter, followed by Italy (14.8%), Vietnam (11.6%), and Germany (5.3%) (Koppiahraj et al. 2019). The economic scenario of developing countries has also seen the contribution of leather manufacturing industries and their adverse impacts on the environment (Ministry of Agriculture and Rural Development 2009). Thus, the largest livestock population in Ethiopia has a strong input for leather manufacturing and is estimated to have about 26.5 million sheep, 55.6 million cattle, and 25 million goats. Ethiopia has 28 leather manufacturing industries, 16 large and medium-scale footwear processing, 15 garments and goods manufacturers, 3 gloves manufacturing, and 368 small and micro-scale leather products (Teklay 2018). As a result, huge amounts of tanned and untanned LSWs are generated in Ethiopian tannery industries, consequently a threat to the surrounding environment. A previous report (Framis 2018) carried out on the assessment of waste generation from the Sheba leather industry (Wukro, Ethiopia) under cooperation projects suggests utilizing the composting method for chrome-free wastes and recommended further research on solid waste generation and its effective management to protect the local environment. Therefore, we have planned a detailed study for the LSWs generation, characterization, and recommendations of technologies to reduce the challenges in waste management in an environmentally sustainable manner from the Sheba leather industry (Wukro), Ethiopia.

MATERIALS AND METHODS

Chemicals and Equipment

The present research is focused on the sample collection, sample preparation, and characterization of leather solid wastes from industrial collection to testing in the laboratory. All chemicals used are analytical grade throughout the experiments. Chemicals such as benzoic acid (for bomb calorimeter), nitric acid, sulphuric acid, perchloric acid, orthophosphoric aid (used for chromium content) and salicylic acid, sulphuric acid, and hydrogen peroxide used for the characterization of nitrogen content. The major equipment, such as the bomb calorimeter (Model IKA calorimeter C-4000) and UV-visible spectrophotometer (UV-1700, Shimadzu, Japan), are used for the calorific value and nitrogen content estimation, respectively. The oven and furnace are used for the estimation of the moisture content and volatile organic compounds, respectively.

Assessment and Generation Rate of LSWs

Assessment of the practices of leather solid waste management (LSWM) was conducted by frequent visits on-site and observations of the manufacturing processes. Auditing of the LSWM documentation, environmental policies, procedures, and waste disposal site nearby industry. The four major processes identified are i.e. beamhouse operations, tanning processes, re-tanning, and finishing processes as shown in Fig. 1. The tannery solid waste study was carried out between November 2020 to April 2021 a case study of the Sheba Leather Industry.

To determine the generation rate, a sample of ten pieces was taken, weighed before and after the unit operation of the process, and finally, calculated using the mass balance approach. The average value of waste generation in each stage is presented for ten samples. For example, in the case of de-dusted salt process generation rate (waste per tonne of raw wet salted sheep skin) was determined as follows (Framis 2018):

Mass of de-dusted salt waste (kg/ton of raw wet salted sheep skin) = $\frac{m1-m2}{m1} \times 1000$ …(1)

where m_1 is the initial mass of raw wet salted sheep skin before salt removal and m_2 is the final mass of raw wet salted sheep skin after salt removal.

The generation rate of untanned LSWs (de-dusted salt waste, raw sheep skin trimming waste, hair waste, fleshing waste, and pickle trimming waste) and tanned LSWs (chrome shaving waste, crust leather trimming waste, and finished leather trimming waste) were determined in the processing of raw wet salted sheep skin. Chrome-free SWs (raw hide

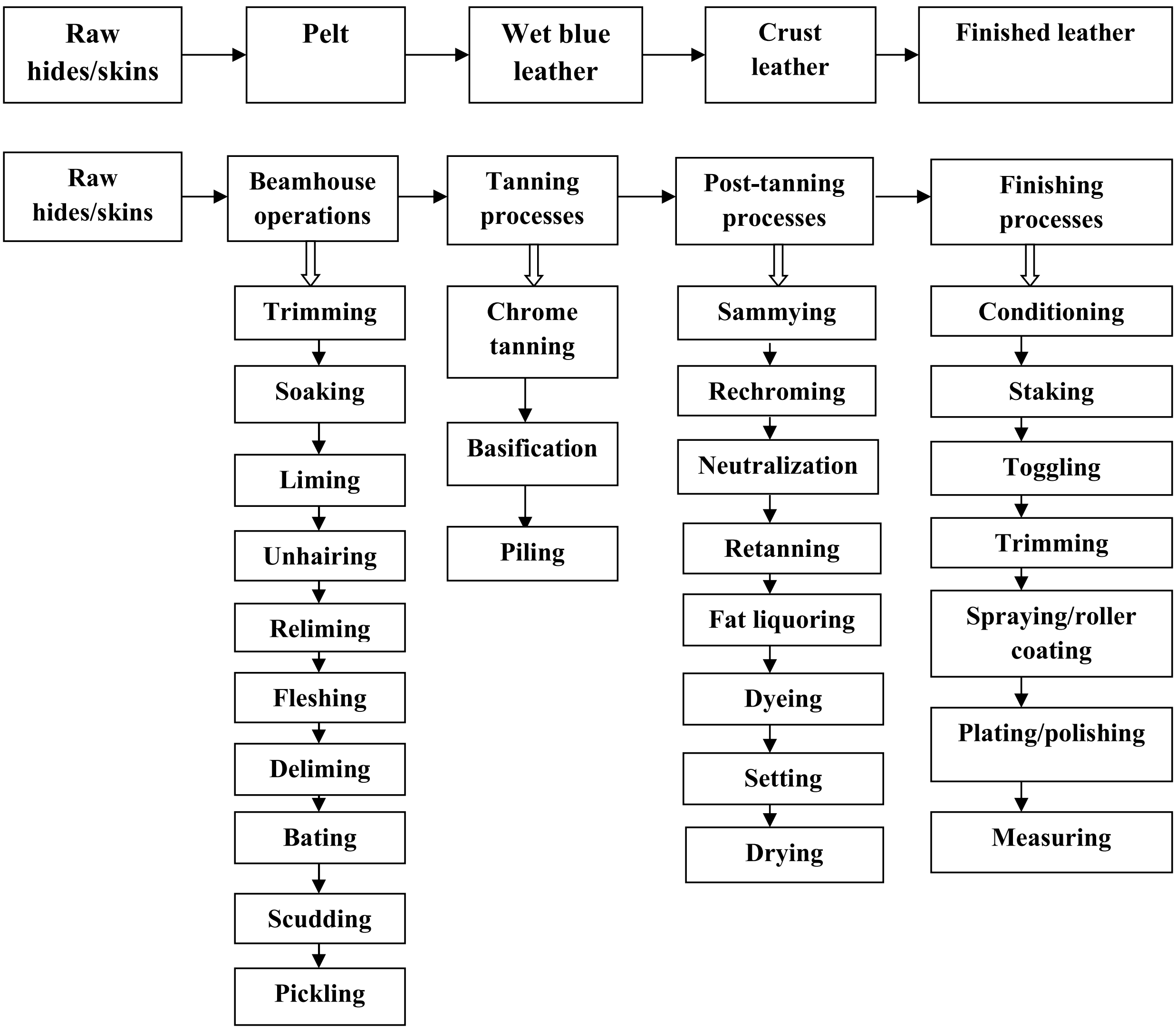

Fig. 1: Flow diagram of the leather production process in the Sheba leather industry.

trimming waste, fleshing waste, and splitting waste) and chrome-containing LSWs (chrome shaving waste, crust leather trimming waste, and finished leather trimming waste) were generated and estimated accordingly. Raw hide processing generates solid waste i.e. trimming waste, fleshing waste, splitting waste, chrome shaving waste, crust leather trimming waste, and finished leather trimming waste (Fig. 1).

Chrome shaving waste is generated by shaving the tanned sheep skins when the tanning process is over and the waste depends upon the required shaving thickness of the wet blue leather. The Beamhouse process is a major source of solid waste generation in the leather industry (Paul et al. 2015) and includes several sub-processes i.e. de-dusted salt, skin trimming, skin unhair, fleshing and pickle trimming, etc. (Hashem et al. 2014).

Sources of Leather Solid Wastes

Leather processing involves four main stages viz. beamhouse operations (trimming, unhairing, fleshing, pickling, and splitting processes), tanning processes (shaving process), re-tanning processes (trimming and buffing processes), and finishing processes (trimming process). Various sources have been identified from the entire processing of the Sheba leather industry, which are the non-chrome containing LSWs viz. de-dusted salt waste, raw trimming waste, hair waste, fleshing waste, pickle trimming waste and splitting waste, and chrome containing wastes viz. chrome shaving waste, crust leather trimming waste, buffing dust waste and finished leather trimming waste. Thus, types and sources of LSWs were evaluated for the physical composition and nature of the wastes depending upon the unit operations. This will further help in the management of LSWs generated from the entire process. Table 1 shows the types of waste and their sources of samples collected from various processes in the industry.

Characterization of LSWs

Physico-chemical parameters i.e. calorific value, ash content, volatile organic compounds content, moisture content, pH value, chromium content, carbon content, and nitrogen content were determined after collection from wastes. pH value was measured by a digital pH meter. To check the calorific value, 0.5 grams of waste sample was transferred into the sample holder which was placed in the bomb and the sample was burned using oxygen gas as activation energy. The following equations (2 and 3) were used to measure the (Onukak et al. 2017; Singh et al. 2022) calorific value on the dry basis.

$$\text{Calorific value (Kcal/kg)} = \frac{\Delta T * C - Qf}{m} \times \text{F or} \quad \ldots(2)$$

$$\text{Calorific value (kJ/kg)} = \frac{\Delta T * C - Qf}{m} \times \text{F} \times 4.184 \quad \ldots(3)$$

Where ΔT represents the difference between the initial and final temperature measured (K), 'C' is the heat value of the water equivalent, 2183 calorie/Kelvin, 'Q_f' is the heat value of nickel-chrome thread and the cotton thread, 19.1 calorie per Kelvin, 'm' is the mass of LSWs sample in gram and 'F' is the correction factor which is 1.033.

Ash content was determined by igniting 1 gram of sample in a furnace at 950^{o} C for 3 hours and ash was cooled in a desiccator for 1 hour and weighed and was determined (D2617 ASTM, 2001). Moisture content was estimated by the hot air oven method (D3790 ASTM, 2001) while pH by using a digital pH meter. Further, volatile organic compounds (D2617 ASTM, 2001) and chromium content were measured using a furnace (at temperature 950° C) and wet oxidation method (ASTM D2807) using titration, respectively. Fixed carbon content was estimated from its ash content, volatile organic compounds content, and moisture content (Onukak et al. 2017). Nitrogen presence was measured by using the three steps viz. digestion, filtration, and determination.

Table 1: The sources and types of leather solid waste generated by the Sheba leather industry.

S. No.	Types of leather solid waste	Sources	Leather processing stage
1.	De-dusted salt waste	Hand-shaking salt removal process from raw hides/skins	Preparation stage
2.	Raw trimming waste	Raw skin/hide trimming process	
3.	Hair waste	Sheep skin unhairing process	Beam house operation
4.	Fleshing waste	Fleshing process	
5.	Pickle trimming waste	Pickle trimming process	
6.	Splitting waste	Hide splitting process	
7.	Chrome shaving waste	Shaving process	Tanning process
8.	Crust leather trimming waste	Crust leather trimming process	Re-tanning process
9.	Buffing dust waste	Crust leather buffing process	
10.	Finished leather trimming waste	Finished leather trimming process	Finishing process

Finally, the sample was determined by using a UV-visible spectrophotometer at 570 nm wavelength as described elsewhere (Kruis 2014). Sample preparation was carried out using different operations viz. drying (oven drying), shredding (size reduction), crushing (using crusher) and milling (grinding mill), and the resulting powder samples were used for the laboratory analysis before chemical parameters (calorific value, ash content, volatile organic compounds, chromium content, and nitrogen content).

RESULTS AND DISCUSSION

Generation Rate of Leather Solid Wastes

Samples were collected to quantify the LSWs generated from different processes employed in the industry (Fig. 2). They used mass balance analysis techniques to estimate the processing of raw hides and sheep skins.

Generation Rate from the Processing of Raw Sheep Skin

Beamhouse operations: Among all processes pickle trimming process generates minimum waste (13.6 $kg.ton^{-1}$), whereas the sheep skin hair process generates maximum waste (117.7 $kg.ton^{-1}$). This is mainly attributed to removing unwanted parts of raw sheep skin. After soaking operations, unhairing or liming by using chemicals such as lime $Ca(OH)_2$, sodium hydrosulfide (NaHS), and sodium sulfide (Na_2S) on sheep skins generates a large amount of waste (Ranjithkumar et al. 2017). Further, the fleshing process removes excess flesh and fats through a mechanical process. In the pickling process, skin is treated in a solution composed of salts and acids to lower the pH of 2.8-3.0.

Chrome shaving, crust, and finished leather trimming waste: The results obtained after estimation show an average of 39.7 kg of chrome shaving waste was generated per tonne of raw sheep skin processed. Crust leather is trimmed to obtain a uniform structure and remove the unnecessary parts of the leather by trimming. In addition, this type of solid waste is produced after the post-tanning process. Finished leather is trimmed to achieve uniform surface effects and improve the general appearance per the desired purpose of leather. Generation rates are calculated accordingly after the trimming process.

Therefore, LSWs from the Sheba leather industry during the entire processing of raw sheep skin. One tonne processing of raw sheep skin waste generation from four main processes, mainly i.e. beamhouse operations (de-dusted salt waste, raw sheep skin trimming waste, hair waste, fleshing waste and pickle trimming waste) is 188 $kg.ton^{-1}$ (73.52%), tanning process (chrome shaving waste) is 39.6 $kg.ton^{-1}$ (15.50%), re-tanning process (crust leather trimming waste) is 15.5 $kg.ton^{-1}$ (6.1%) and finishing process (finishing leather trimming waste) is 12. $kg.ton^{-1}$ (4.9%).

A study from Ethiopia's leather industry indicated that the total LSWs generated were 664.5 $kg.ton^{-1}$ of wet salted sheep skin (Teklay 2018). The present study shows the maximum percentage (73.5%) of LSWs are generated from the beamhouse operations (e. g. non-chrome based), whereas the minimum percentage (4.9%) of LSWs are generated from the finishing process (e.g., chrome-containing waste) (Fig. 3). The chrome based solid waste and its disposal are the biggest problems due to chromium a heavy metal in higher concentrations (Pati et al. 2014). On the other hand, a comparison between the individual processes indicates

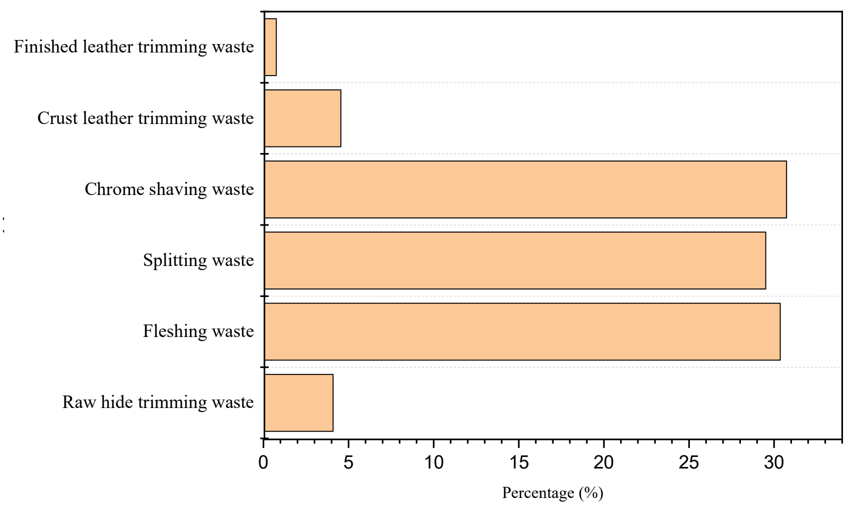

Fig. 2: Generation rate of leather solid wastes during the processing of raw hides involving various processes from finished leather trimming waste to raw hide trimming wastes.

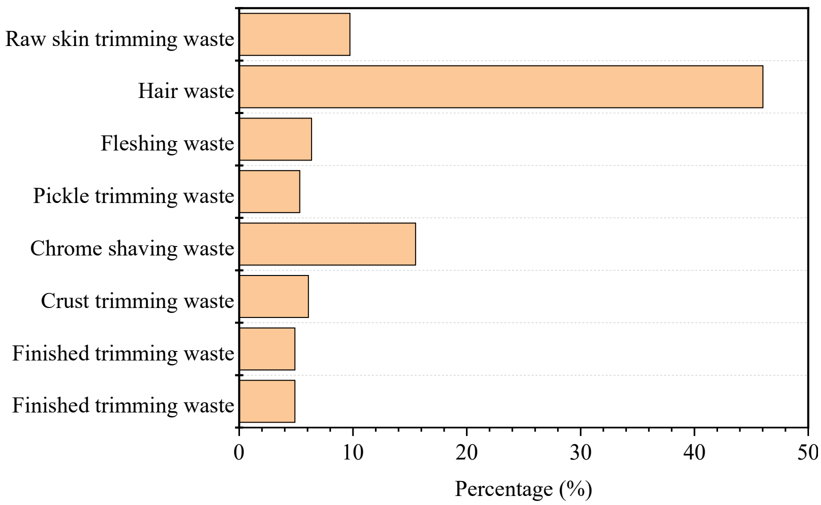

Fig. 3: Solid waste generation during the processing of raw sheep skin from skin trimming, hair, fleshing, pickle trimming, chrome saving, crust trimming, and finished wastes.

Fig. 4: Leather solid waste (%) generation rate from the four major production stages, such as beam house operations, tanning, re-tanning, and finishing processes.

the largest quantity (46%) of waste as hair waste and the lowest amount (4.9%) as finished leather trimming waste (Fig. 4). One report shows that one ton of wet salted sheep skin generates 262 kg of wastes which is around 26.2% of the total weight of sheep skin processed (Kanagaraj et al. 2006). Another observation for the Sheba leather industry, the daily maximum soaking capacity of raw sheep skins is 9000 kg, and the maximum raw sheep skin soaking capacity is 2700 tons per year.

Generation of Solid Waste from Raw Hides Processing

Trimming waste is generated by cutting the unnecessary parts of the hide by the trimming process, and 28.4 $kg.ton^{-1}$ of average waste is generated. Trimmed hides are subjected to cleaning (fleshing process), generating the fleshing waste of around 211 $kg.ton^{-1}$ of hides processed. Further, hides are split into two or three layers by splitting process, and waste (205 $kg.ton^{-1}$) is generated by removing the hides' unnecessary layers as per the hide's intended use. Chrome shaving waste is generated by shaving the tanned hides; waste generation depends on the shaving thickness of the wet blue leather, which further depends on the end use of the finished leather (213.5 $kg.ton^{-1}$). Crust leather is trimmed to obtain a uniform structure and remove the leather's unnecessary parts by trimming.

Moreover, this type of solid waste is generated after the re-tanning process. Hence, an average of 31.6 kg.ton^{-1} of crust-trimming waste of raw hides is processed. Finished leather is the final step in leather manufacturing and is trimmed to achieve a uniform finished surface as per the required quality of the final product. This process generates about 5.2 kg.ton^{-1} of waste.

Table 2 systematically presents the waste generation from various processes involved in leather manufacturing. However, the generation rate of LSWs depends on the type and quality of raw material and operational technologies used during the manufacturing process of leather (Coară et al. 2016). Among all processes, the minimum quantity (5.2 kg.ton^{-1}) of waste is generated from finished leather trimming, whereas the maximum waste generated is 213.4 kg.ton^{-1} from chrome shaving waste. In addition, beam house operations (rawhide trimming waste, fleshing waste, and splitting waste) generate waste of around 444 kg.ton^{-1} (63.9%), tanning process (chrome shaving waste) is 213.4 kg.ton^{-1} (30.7%), re-tanning process (crust leather trimming waste) is 31.6 kg.ton^{-1} (4.5%). The finishing process (finishing leather trimming waste) is 5.2 kg.ton^{-1} (0.7%). An earlier study shows that 75-80% of input raw wet salted hides or skins are generated as LSWs in the leather manufacturing industry (Oruko et al. 2014).

Another work cites the total solid waste generation of around 730 kg from the processing of one tonne of raw wet salted hides, which is further correlated to the major processes such as raw trimming, fleshing, chrome shaving, and buffing dust (Fela et al. 2011). The data depicted that the highest percentage (63.96%) of LSWs generation from the beamhouse operations and the lowest percentage (0.76%) from the finishing process (Fig. 5). Further, this shows that the largest quantity (30.7%) of LSWs generated as chrome shaving waste and the lowest quantity (0.76%) as finished leather trimming waste. Furthermore, the Sheba leather industry in the current scenario generates about 694 kg of waste from the processing of 1 tonne of raw hides, and it accounts for 69.4% of the LSWs from the raw wet salted hides. Besides these, the Sheba leather industry has the maximum daily soaking capacity of raw hides is 8,600 kg, and total waste generation is about 2,580 tonnes per year, taking 300 working days annually. Thus, the total waste generated from the processing of raw hides is 1,792 tons per year of LSW.

Assessment of Current Practices of Leather Solid Waste Management

The assessment conducted on the leather solid waste management practices of the Sheba leather industry indicated that all the leather solid wastes generated during the entire leather manufacturing process are disposed of in the open dumping area nearby to the manufacturing compound. It was observed that the untanned leather solid wastes (de-dusted salt waste, raw trimming waste, hair waste, fleshing waste, pickle trimming waste, and splitting waste) and tanned leather solid wastes (chrome shaving waste, crust leather trimming waste, buffing dust waste and finished leather trimming waste) are disposed into the same dumping area without any proper segregation and treatment. Moreover, the Sheba leather industry has no leather solid waste management mechanism. However, the tanned leather solid wastes are chrome-based solid wastes categorized as toxic and hazardous that affect public health and create environmental pollution, viz. agricultural soil pollution, surface water pollution, groundwater pollution, and air pollution. Therefore, the chrome-free leather solid wastes and chromed-based leather solid wastes should be segregated, collected, treated, and dumped separately. In addition, the Sheba leather industry should construct its suitable landfill site per the type, quantity, characteristics, and environmental impact of the LSWs generated.

Characterization of Leather Solid Waste

To check the characterization of LSW, various tests such as calorific value, ash content, volatile organic compounds, moisture content, pH, chromium content, fixed carbon content, nitrogen content, and carbon-to-nitrogen ratio were performed.

Table 2: Leather solid wastes generation rate during the processing of raw hides.

S. No.	Types of leather solid wastes	Waste generation kg per kg of hide processed	Waste generation kg.ton^{-1} of hides processed	Total solid waste generated (kg. ton^{-1} of raw hides processed)
1.	Raw hide trimming waste	0.03	28.4	694.7
2.	Fleshing waste	0.20	210	
3.	Splitting waste	0.20	205	
4.	Chrome shaving waste	0.21	213.5	
5.	Crust leather trimming waste	0.03	31.6	
6.	Finished leather trimming waste	0.005	5.2	

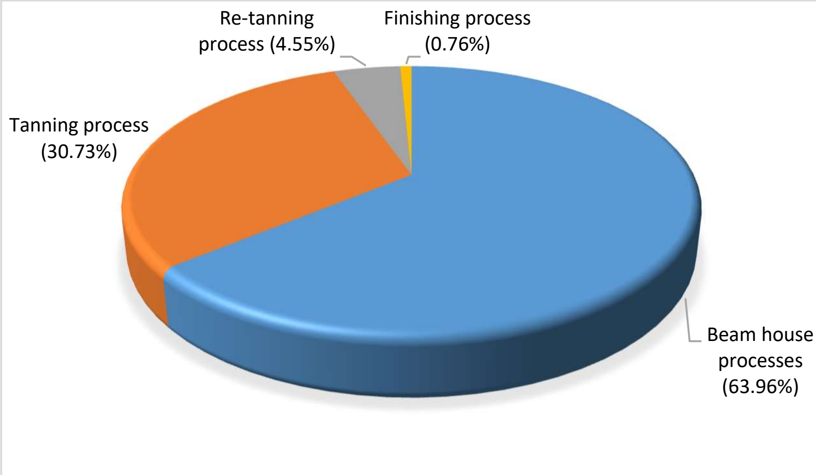

Fig. 5: Solid waste generation (%) from the four main of manufacturing leather from raw hides (Beamhouse operations, tanning, re-tanning, and finishing processes).

Table 3: Physico-chemical characterization of leather solid wastes from the Sheba leather industry.

S. No.	Types of leather solid waste	Physico-chemical parameters								
		Calorific value [kJ.kg^{-1}]	Ash content %	VOC [%]	Moisture content [%]	pH	Cr [%]	C [%]	N [%]	C: N
1.	Fleshing waste	20,314	5.30	82	76.5	12.5	NA	12.4	0.26	47.7:1
2.	Chrome shaving waste	16,899	13.3	7	42.0	3.9	1.6	14	0.26	54:1
3.	Crust leather trimming waste	21,380	5.5	74.8	13.7	4.0	1.6	17.5	0.30	58.4:1
4.	Buffing dust waste	21,575	6.5	77.7	7.8	4.0	1.6	12.8	0.27	47.5:1
5.	Finished leather trimming waste	20,368	5.8	70	17.7	4.1	1.5	16.8	0.32	52.5:1

Calorific value: The calorific value represents the maximum amount of energy present in the LSWs and is affected by solid waste's ash and moisture content. Higher ash and moisture content of LSWs decreases the calorific value. Thus, the calorific value is the most important parameter to determine the suitability for energy recovery utilization (Onukak et al. 2017). Table 3 indicates the average calorific value of 20,107 kJ.kg^{-1} ranges from a minimum value of 16,898 kJ.kg^{-1} for chrome shaving waste up to a maximum value of 21,574 kJ.kg^{-1} for buffing dust waste. The results obtained have a higher calorific value than the minimum required value of 5020 kJ.kg^{-1} with MC greater than 45%. They agree with using solid waste for thermal applications (Alrikabi & Khaleefah 2005).

Overall LSWs generated having calorific values from chrome shaving waste (16,898 kJ.kg^{-1}), crust leather trimming waste (CT) (21,380 kJ.kg^{-1}), buffing dust waste (21,574 kJ.kg^{-1}), finished leather trimming waste (F) (20,367 kJ.kg^{-1}). Moreover, chrome shaving, crust leather trimming, buffing dust, and finished leather trimming waste should be segregated and collected in separate areas to prevent mixing with other leather solid wastes with higher moisture content. Previous work (Onukak et al. 2017) investigated the tannery solid wastes (TSWs) in six briquettes, i.e., comprising varying ratios of chrome shavings (CS), flesh (FS), hair (HR), and buffing dust (BD) were characterized from Nigerian industry. The briquettes having calorific values from 18.6 to 24 MJ per kg were comparable to other fuel sources such as sub-bituminous coal (20-24.7 MJ.kg^{-1}). Author (Oyelaran et al. 2017b) assessed the energy and combustion efficiency of briquettes prepared from the TSWs for heating purposes. Among different types of TSWs, i.e., BD, CS, FS, and HR samples, their calorific values observed were between 18 and 21.8 MJ.kg^{-1}, where fleshing has better quality than the other three tannery wastes.

Ash content: Ash is an inorganic residue obtained after exposing LSWs to a particular temperature, and observance of higher ash content reduces the combustion efficiency and heating value (Onukak et al. 2017). Results (Table 3) show that the minimum value of ash content was 5.3% from fleshing waste, whereas the maximum value was 13.3% from chrome shaving waste. The average value of ash content was found to be 7.3%, which indicates that more than 92% of LSWs are organic. The author performed a proximate analysis of various prepared briquettes, indicating 3.2% ash content in the HR briquette, whereas 4.2% ash content was observed in the BD briquettes (Oyelaran et al. 2017a). The permissible level of ash content from the LSWs was suggested to be around 35% in earlier work (Singh et al. 2011).

Volatile organic compounds: The flame's length estimates volatile organic compounds (VOCs) while burning LSWs and higher VOC content generates a longer and shorter flame that contains fewer VOCs. The observation shows a minimum value of 70% for finished leather trimming waste and a maximum value of 82% for fleshing waste. Results were further corroborated that the BD briquettes have the least volatile matter, an average of 1.6%, followed by CS briquettes, with an average of 1.7%. In comparison, HR briquettes have the highest value of an average of 4.5%, followed by FS with an average of 2%. This implies that more energy will be required to burn off the volatile matter in HR briquettes before releasing heat energy (Oyelaran et al. 2017b). One report indicated that VOC's presence is more than 40% suitable for solid waste's various thermal and biological treatments (Singh et al. 2011).

Moisture content: Moisture content (MC) is the weight loss measurement by drying at 100° C of the LSWs. MC is an important parameter to estimate the suitability of LSW options for various treatments and disposal. The result is shown (Table 3) that the MC in BD waste is 7.8%, while the maximum in the case of FW is 76.5%. The finding shows that the MC of FS is much higher than the other process due to the generation from the beam-house processing stage involving wet processing. Further, CT, BD, and F wastes have relatively low MC, 13.7%, 7.8%, and 17.6%, respectively, because of generation from tanning and re-tanning leather processing dry stages.

pH value: LSWs' pH greatly influences the surrounding environment if disposed of in open land unsafely. Besides, more alkaline or acidic wastes reduce soil fertility, water palatability, and crop productivity. It can be seen from Table 3. CS waste shows a minimum pH of 3.9. FS has a maximum pH of 12.5 and an average value of 5.7.

Further, FS waste is alkaline due to the unhairing and liming process performed before this stage. The remaining processes, i.e., CS, CL, BD, and F, pH in the acidic range (4-4.2), attributed mainly to tanning and re-tanning processes carried out in acidic media. Thus, it was recommended to segregate the wastes having higher alkalinity from the acidic media, and treatment is done accordingly.

Chromium content: Chrome tanning is used as a tanning material to provide unique features such as high thermal stability, flexibility, and high resistance for the finished leather. Chromium is applied in the tanning and re-tanning process with different percentages as chromium sulfate. Chromium has the potential to contaminate the surrounding environment (agricultural soil, surface water, and groundwater) and have negative impacts (Nigam et al. 2015). It was observed that LSWs range from the minimum value of 1.5% for F waste to the maximum value of 1.6% for CS waste, and thereby, average chromium was around 1.6%. It is further corroborated by the tanned LSWs, e.g., CS, CL, BD, and F, which have higher chromium content beyond the permissible limits in water (WHO 2011) and soil (Rahaman et al. 2016). The variation in chromium concentrations also depends upon the types of waste generated, and the tanning process used about 5.5 to 7.0% of chromium sulfate.

Therefore, the chrome-containing LSWs, viz. chrome shaving waste, crust leather trimming waste, buffing dust waste, and finished leather trimming waste, should be segregated, collected, treated, and disposed of separately from the non-chrome LSWs like fleshing waste. In addition, significant environmental problems (surrounding agricultural soil, surface, and groundwater pollution) are created due to the improper management of chrome-containing LSWs. Thus, to minimize environmental risks, tanned LSWs should be managed in a sustainable manner using waste-to-energy options, viz. thermal treatment technologies (incineration, pyrolysis, gasification, and plasma technology), anaerobic digestion and composting process after pre-treatment for chromium presence. Further manufacturing of various valuable products and end products or ash must be safely disposed of in a secured landfill area.

Carbon content: Carbon content is an important parameter to determine the suitability of LSWs to implement waste-to-energy technological options for solid waste management (Singh et al. 2011). The carbon content of LSWs generated ranges from the minimum value of 12.4% for fleshing waste up to the maximum value of 17.5% for crust leather trimming waste. The average carbon content of LSWs was found to be approximately 14.7%. A carbon content of less than 15 percent is considered to implement the thermal treatment methods (Alrikabi & Khaleefah 2005). Fleshing waste, chrome shaving, and buffing dust wastes contain carbon content of 12.4%, 14%, and 12.8%, respectively, which is less than 15%. Therefore, these wastes could be utilized for the waste to energy production in the industry. However, fleshing waste contains higher moisture content (76.5%), and thermal treatment is not economically feasible due to high-temperature requirements.

In addition, crust and finished leather trimming waste containing carbon content of 17.5% and 16.8%, respectively, can be utilized for energy recovery applications by mixing with the other LSWs with low carbon.

Nitrogen content: Nitrogen content is a crucial parameter to know the carbon to nitrogen ratio of LSWs to evaluate their suitability to implement anaerobic digestion and composting process (waste to energy). Nitrogen is an important nutrient responsible for the growth of microorganisms, which is required for the effectiveness and productivity of the biological treatment system of LSWs (Kaosol & Wandee 2009). Table 3 presents the minimum nitrogen of 0.2% for fleshing waste up to the maximum value of 0.3% for finished leather trimming waste.

Carbon to nitrogen ratio (C: N): Carbon to nitrogen ratio is a key parameter to determine the suitability of solid waste to implement the waste-to-energy options, e.g., anaerobic digestion and composting processes. Carbon serves primarily as an energy source for microorganisms, and nitrogen is critical for microbial population growth. If nitrogen is limited, microbial populations will remain small and take longer to decompose the leather solid waste. Excess nitrogen, beyond the microbial requirements, is often lost from the system and can cause odor problems in the surrounding environment (Kaosol & Wandee 2009). Table 3 indicates that the carbon-to-nitrogen ratio of the leather solid wastes generated from the Sheba leather industry ranges from the minimum ratio of 47.4:1 for buffing dust waste up to the maximum ratio of 58.4:1 for crust process waste and the average carbon-to-nitrogen ratio of the solid waste was found to be 52:1. The carbon to nitrogen ratio requirement of the solid wastes to implement the anaerobic digestion and composting processes is 20-50:1 (Rastogi et al. 2020). The carbon to nitrogen ratio of fleshing waste and buffing dust waste was found as 47.7:1 and 47.4:1, respectively, which is within the range of the required value of 20-50:1. The laboratory result assures that fleshing waste and buffing dust waste are suitable to implement the anaerobic digestion and composting processes. On the other hand, the carbon to nitrogen ratio of chrome shaving waste, crust leather trimming waste, and finished leather trimming waste was 53.9:1, 58.4:1, and 52.4:1, respectively, which is above the range of required value 20-50:1. However, carbon to nitrogen ratio of solid waste can be adjusted to achieve the requirement 20-50:1 with additional nitrogen sources wastes such as manure, sewage sludge (biosolids), septic and urea. Therefore, the untanned and tanned LSWs (fleshing waste, chrome shaving waste, buffing dust waste, crust leather trimming waste, and finished leather trimming waste) generated from the Sheba leather industry are suitable to implement the biological treatment options, e.g., anaerobic digestion and composting processes.

CONCLUSIONS

The present research assessed and characterized leather solid waste (LSW) in the Sheba leather industry. Type of leather solid wastes generated from the unit operations of the four main leather processing stages (beamhouse operations, tanning processes, re-tanning processes, and finishing processes) are classified as chrome-free solid wastes, viz. de-dusted salt waste, raw trimming waste, hair waste, fleshing waste, pickle trimming waste and splitting waste and chrome containing solid wastes viz. chrome shaving waste, crust leather trimming waste, buffing dust waste and finished leather trimming waste. The annual generation amount of leather solid wastes during sheep skins and hides processing is 690 tonnes and 1,792 tonnes, respectively. As a result, the Sheba leather industry generates 2,482 tonnes of leather solid wastes per year while processing 5,280 tons of raw wet salted sheep skins and hides. Furthermore, the physico-chemical characterization results indicated that the average inorganic residue or ash content of the leather solid wastes is 7.3 %, ensuring that more than 90% of the leather solid wastes generated from the Sheba leather industry are organic. Average results obtained from the physico-chemical characterization of LSW were calorific value (20,107 kJ.kg kg.ton^{-1}), ash content (7.3%), volatile organic compounds content (75.1%), moisture content (31.5%), pH value (5.7), chromium content (1.6%), carbon content (14.7%), nitrogen content (0.3%) and carbon to nitrogen ratio (52:1).

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