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Cleaner production and resource recovery opportunities in leather tanneries: Technological applications and perspectives

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ABSTRACT

The main aim of this review was to provide insights on the possible cleaner production (CP) options for leather manufacturing industries and propose suitable resource recovery technologies. A real case study from local tanneries in Palestine has been presented. All the processes involved in the leather tannery industry have been reviewed based on raw materials, processing parameters and effluent composition. The evaluation of the identified CP options indicates that the most practical option is manipulating the processing parameters of the tanning process for increasing its efficiency. The high contents of COD in the released streams from beam house operations and of sulfides from the unhearing step also require attention. The different technological options for resource recovery, e.g. biogas, chromium, lipids and chemicals, from leather industry wastewater and solid wastes were reviewed and discussed.

1. Introduction

Leather is one of the important materials that has been traditionally used for manufacturing clothes and footwear. The leather is conventionally produced from raw hides after being subjected to various physical and chemical-based manufacturing processes. The production process starts with a mechanical shaking step for salt removal, then, the raw hides are soaked in water with detergents for removing the dirt and salts. Thereafter, sodium sulfide and lime and are used for removing hair, through swelling and disintegration of the structure of hair proteins. After this step, deliming is performed using ammonium sulfate, where the pH is decreased. The pH is decreased further in the pickling step by using formic acid. After that, tanning is performed by adding chromium sulfate that initiates crosslinking bonds among the collagen fibers transforming the raw hide into a flexible resistant structure which is durable, stable against putrefaction, and suitable for a wide range of purposes. Eventually, dyes and other auxiliary chemicals are added to the chromium-tanned leather in order to improve its softness.

Life cycle analysis of 100 m^2 leather carried out by Joseph and Nithya (2009) showed that chemicals and energy are the dominant resource demands. The highest environmental burdens occur at the tanning and finishing stages which have high water (16 m^3) and chemical (348 kg) consumption; thus, leading to more effluent (14.7 m^3) and toxic pollutant load. According to Rao et al. (2003), end of pipe treatment options are not able to satisfy the expected regulatory standards and hence, there is a need for in-plant control measures such as the application of resource resilient technologies and the implementation of cleaner production (CP) measures. However, the characterization of wastewater (WW) from the leather manufacturing processes is a key step in developing CP strategies for the leather industry.

A recent study has investigated the physicochemical characteristics of wastewater released from leather processing and tanning in Palestine (Sawalha et al., 2019). It compared the loads of pollution released from the processing of cow and goat hides. The reported WW characteristics included: total, dissolved and suspended solids (TS, TDS, and TSS respectively), chemical oxygen demand (COD), pH, and the streams contents of chromium (Cr^{3+} and Cr^{6+}), ammonia and chlorides. As it is well known, the leather processing handles and releases large quantities of chemicals. Trivalent chromium is utilized in tanning processing, since the hexavalent chromium has no tanning effect. Occasionally, a negligeable concentration of hexavalent chromium may present in wastewater depending on the degree of treatment achieved and the process efficiency of the treatment steps. Chromium tanning WW is not classified as a hazardous waste in the draft Palestinian waste list (Al-Jabari,

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2014a), similar to the European classification. However, the Basel convention lists tanning liquor containing hexavalent chromium as hazardous, while usually it not containing hexavalent (Al-Jabari, 2014a, 2014b).

According to Sawalha et al. (2019), the released quantities of WW generated from tanneries in Palestine are less than the values reported worldwide. However, this makes the WW concentrated in pollutants, i.e. in terms of the pollutant load. The tested WW was found to contain high solid contents (TS, TDS and SS) as well as high COD and concentrations of chromium, ammonia and chloride. The discharged WW does not comply with the legal permissible limits for the investigated characteristics. The liming step was found to release the highest COD with the highest pH. No ammonia content was detected prior to deliming stage. Besides, it was also shown that the ammonia content increased when moving from tanning process to the re-tanning step (Sawalha et al., 2019).

The specific aims of this paper are summarized as follows: (i) to evaluate the different CP options for tanneries with respect to the raw materials, the production process, the operating conditions, and the tanning operations, (ii) to present a case study form local tanneries in Palestine by analyzing their present scenario and proposing practical CP options, and (iii) to propose different resource recovery options in tanneries, including water reuse, recovery and reuse of chromium, liming liquor reuse, the reuse of leather.

2. Cleaner production (CP) options in tanneries

The concept of CP is guided by the three main principles; prevention is better than reuse, reuse is better than recycling and recycling is better than disposal (Rao et al., 2003). This can cut down water, energy and chemical consumption, and minimize the generation of waste in addition to the creation of safer working conditions for workers. There are various CP options for tanneries; however, they differ in various regions across the globe as they are influenced by the socio-economic and infrastructural conditions (UNEP-MAP, 2010). The following sections highlight the potential CP options for beam house and tanning operations in a leather industry.

There are different strategies to implement CP in most of the leather manufacturing processes in order to minimize their environmental impacts. Table 1 summarizes the identified CP options based on field study and other relevant options identified/presented in existing reports and literature. They include, among others, making feasibility studies for collecting and reusing or recycling various fraction of the generated solid wastes. In addition, various changes in process sequence and protocols are also proposed. Some modifications in the inputs and operating conditions of the process are suggested to increase the operating efficiency.

2.1. Beam house operations

2.1.1. Change in raw materials

Enzymatic dehairing can substitute the conventional chemical dehairing method that contaminates the effluent with sulphide and emits hydrogen sulphide (H_2S gas). Enzyme protease extracted from *Bacillus sp* strain SB12 has a high and eco-friendly dehairing ability. It loosens the hairs which are then removed in solid form, thereby enabling the use of filtration system to separate the hairs from the float. This strategy has shown ~60% reduction of the organic pollutant load (Briki et al., 2016). Using alkaline proteases produced by diverse microbial consortia, Abraham et al. (2014) proposed an alternative solution for dehairing that can be used as a substitute for chemical dehairing. Under thermophilic circumstances, the highest protease activity was detected on the 14th day (56,270 ± 2632 activity units/g dry sample). The authors conducted studies at temperatures of 30, 50, and 70 °C, at pH values of 5.00, 8.00, and 11.00, respectively, in order to determine the enzymatic activity. As a result, when mechanically scraped with tweezers after 24 h of incubation, the cow hides demonstrated greater ease of removal of hair as compared to the control trial that did not include protease. This research also demonstrated that enzymatic dehairing of cow hides is a viable alternative method for maximizing the value of a by-product of the tannery industry, at the same time decreasing the wastewater treatment load on the facilities. Moreover, the use of enzymes during dehairing leads to swelling of the skin, thereby preparing it for the later stages (Briki et al., 2016).

Splitting at the liming stage instead of the post tanning stage reduces the amount of toxic solid waste and chemicals required for tanning operations. The Addis Ababa tannery in Ethiopia was able to save about 5500 Birr per year after switching to lime splitting (Woldeyes and Ayalew, 2008). Moreover, hide splitting was implemented as cleaner production option in Tunisia by two companies, i.e. Tannerie du Nord Utique and Société Moderne des Cuirs et Peaux. The first company saved 2100 m^3 water and 28 t of chromium per year with cost reduction benefit of 42,150 USD/year, whereas the second company managed to reduce 1850 m^3 of water and saved 26,000 USD/year (UNIDO, 2012).

The use of ammonium free deliming can reduce the emission of nitrogen into the atmosphere and wastewater. Various organic compounds such as carboxylic ether and non-swelling aromatic acids can be used (Hu et al., 2011; Rao et al., 2003). Deng et al. (2015) reviewed the carbon dioxide deliming process and reported that the method was effective as the conventional deliming method and also more economical. Carbon dioxide reacts with water forming weak carbonic acid (Eq. (1)), which reacts with lime, leading to the formation of calcium carbonate $CaCO_3$ (Eq. (2)). Calcium carbonate is further transformed into calcium hydrogen carbonate due to continuous CO_2 supply as shown in Eq. (3). However, according to Hu et al. (2011), the method is limited to thin pelt, requires special drum and proper ventilation to avoid suffocation issue due to low oxygen concentration.

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (1)$$

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O \quad (2)$$

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO)_2 \quad (3)$$

Conservation salt can be reduced through the use of environmentally acceptable antiseptics such as boric compounds. Salt free preservation can also be achieved through processing green hides which uses 25% less water compared to the conventional preservation method (Rao et al., 2003). Moreover, cold conservation of raw hides can also reduce the use of salts and also reduce the operation costs. For instance, a tannery in Tunisia (Mégisseries du Maghreb) was able to achieve a net savings of $US 50,000 per year with a payback period of one and a half years even after the incorporation of the additional electricity costs (UNEP-MAP, 2010). Salt free pickling system with non-swelling organic acid or pre-tannage prior to tanning can be used to avoid chloride contamination of the effluent (Zhang et al., 2017).

2.1.2. Change of the production process

Change of pre-soaking processes can help in pollution prevention and minimization of using resources. According to UNEP-MAP (2010), fleshing should be done in the early stages upon arrival to the tannery in order to reduce unnecessary surface area, thus, less chemical and water consumption in the preceding stages. This green fleshing also produces chemical free waste(s), enabling the creation of value addition by products such as tallow. Moreover, beam house operations should proceed with the processing of fresh hides in order to reduce the storage time to avoid use of salt, pesticide or cooling conservation, leading to the saving of energy and water. A tannery in Addis Ababa, Ethiopia reduced chemical consumption after implementation of green fleshing and saved 94,164 Birr/year (Woldeyes and Ayalew, 2008). However, mechanical desalting of hides preserved using sodium chloride can also be done at the pre-soaking stage to reduce contamination of the soaking bath. Two companies in Tunisia, i.e. Tannerie du Nord Utique and Société Moderne des Cuirs et Peaux, invested 25,000 USD and 43,000 USD, respectively, in the drumming technology and managed to save 8570 USD/year and 17,000 USD/year, respectively, due to reduction of chlorides in wastewater (INEP-MAP, 2010).

Intact hair removal technique is also considered as a CP approach. According to Thanikaivelan et al. (2004), a mixture of proteolytic enzymes and small quantities of lime and sulphide can remove the hairs intact by breaking the bonding substances in the hair structure selectively. According to UNEP-MAP (2010), pre-treatment of hides with alkali such as sodium hydroxide helps to preserve the structure of the hair during sulphide dehairing enabling physical filtration; thus, it also reduces the presence of solid wastes in the effluent. Intact hair removal also allows value addition of the hair waste so that it can be applied as fertilizer in agriculture and the proteinous solid waste can also be used in treating the wastewater contaminated with dyes (Fathima et al., 2009).

The use of enzymes in beam house operations can save time and enhance product quality. Thanikaivelan et al. (2004) reported that the addition of enzymes at the soaking stage can remove solidified fats and non-collagenous proteins present in the fiber enabling easier and faster rehydration. This might create extra operation cost but save time, in addition to the production of an output with a less wrinkled grain. The recycling of spent liquor reduces water and chemical use in the tannery process (Sundar et al., 2001). The Atef El-Sayed tannery in Egypt invested in a vessel and filter worth 8333 USD to reduce salinity of pickle bath, enabling the recycling of wastewater and saved 220 m^3 of water and 23 t of chemicals per year (UNEP-MAP, 2010). Rao et al. (2003) demonstrated that recycling of wastewater in the soaking stage can be effectively done through counter soaking. The second and third soak water can be directly reused in the succeeding batches since they have low quantities of organic pollutants. This reduces the water usage by approximately 70%.

Sulphates from the unhairing stage can be reduced through recycling and nanofiltration of the spent liquor. Galiana-Aleixandre et al. (2011) conducted laboratory scale trials by testing appropriate ratios of spent unhairing liquor and fresh water that can be used in the soaking stage with an aim of exhausting the sulphates in the effluent. The authors reported that 50:50 mixing ratio was ideal and reduced 10% of sulphide input during the unhairing stage since the sulphide and hide protein reaction starts in the soaking bath. Besides, in that study, nanofiltration of unharing liquor achieved 97% retention of sulphate. Further, it was recommended that the two methods should be tested at the semi-industrial scale in order to ascertain the operational costs.

2.2. *Tanning operations*

The general evaluation of CP options reported in the literature indicated that the most feasible/urgent option would be the improvement of the tanning process for increasing process efficiency (maximizing chromium uptake by hides), as well as chromium recycling and reuse. These options are summarized in Table 1. The theoretically proposed CP strategy of replacing chromium with alternative tanning agents (e.g. aluminum oxide, zirconium and titanium compounds) is not viewed locally (i.e. in Palestine) to be technically or economically feasible. Chromium tanned leather is the best choice for the shoe making industry; it meets the required specifications for mechanical properties. Although some studies have indicated more environmental-friendly tanning agents, such as titanium that can be obtained from metal industry the wastes can be used to replace chromium and produce leather with acceptable physical and chemical characteristics (Mutlu et al., 2014). Nevertheless, combining titanium with chromium during tanning process increased chromium uptake and reduced chromium concentration in the effluent (Sivakumar et al., 2008).

The use of blended tanning, which mixes two tanning chemicals, appears to be a promising environmentally friendly alternative technology to chrome tanning, as it does not appear to have any negative effects on the qualities of the tanned leather (China et al., 2020). Some reports have revealed that betitanyl sulfate, when combined with citrate, produces leather of high quality, comparable to that produced by chromium (Castiello et al., 2011; Seggiani et al., 2014). Others have suggested the use of an environmentally friendly tanning agent based on aluminum sulfate and a composite (polyhedral oligomeric silsesquioxane-methacrylic acid) (Gao et al., 2020). The study showed that compared to chromium-tanned leather, the mechanical characteristics and thermal stability of composite-tanned leather were found to be significantly improved (Gao et al., 2020).

Table 1
Summary of CP options related to the chromium tanning process.

Cleaner production options	Example	Advantages	Disadvantages	Feasibility of local application
Tanning with alternatives tanning agents	Partial replacement of chromium oxide with titanium compounds	- Some studies have shown that it can replace chromium tanning, without affecting the leather quality. - Zero chromium discharge in the effluent.	- High leather rigidity. - More chemicals are used. - Very expensive compared to chromium compounds.	- Still not accepted by the industry.
Improving chromium uptake (exhaustion of chromium)	Optimizing the operating conditions (temperature and pH adjustment)	- Saving the chromium cost. - Reducing chromium concentration in the effluent streams. - Good leather quality.	- More energy cost may be required for some modifications - Higher operating costs and adjustment of the drum is required. - tanning process should be performed at higher temperature and longer residence time.	- Acceptable by the industry. - Local motivations for this option. - Experimental CP investigations are required.
Recovery/reuse of chromium	• Effective operation of the precipitation-regeneration treatment process (using lime and sulfuric acid).	- Saving the chromium cost. - Reducing chromium consumption. - Reducing chromium concentration in resulting WW.	- Higher treatment costs of WW. - More chemicals and extra man power are required.	- There are local constraints on the availability of the required sulfuric acid. - The option is not valid within the existing circumstances in Palestine.
Direct chromium recycling	Recycling the exhaust tanning liquor after adding chromium make up for adjusting its concertation	- Reducing the level of chromium in the waste streams. - Reducing the level of water consumption. - Simplest form of reuse.	- Some changes to tanning procedures are required. - Increasing the capital cost. - It results in changes in leather quality and color.	- This option is viewed as a theoretical option only.

In another study, it was suggested that iron could also replace chromium during tanning processing, especially for producing wet brown leather with low heat resistance. Hence, a re-tanning step with chromium or vegetable tanning agent should be applied (Sah, 2013). According to Covington (1988), combination of aluminum and titanium (IV) resulted in full and soft leather. Combination tanning of chromium and zirconium (e.g. 2% ZrO_2 and 0.5% Cr_2O_3) resulted in high exhaustion level of chromium and zirconium, yielding high leather shrinkage temperature (Sreeram et al., 2000). Using goat skin as a tanning substrate, Li et al. (2021) demonstrated that tanning with a chromium-free tanning agent based on resorcinarene and zirconium complex may boost the tear strength and tensile strength of the leather. It was also possible to increase the biodegradability of wastewater generated during the tanning process. Another study found that D-Lysine aldehyde could be utilized as a substitute for chromium in order to lessen its environmental effects. The mechanical qualities and shrinkage temperature of the resultant leather were comparable to those of chromium-tanned leather (Krishnamoorthy et al., 2013).

However, these studies are still viewed by the local industry (and in many international industrial community), as theoretical approaches. They still believe that chromium tanning is the most technically feasible approach. Thus, it is believed that the CP strategies must focus on maximizing chromium uptake in the tanning process. Higher chromium uptake could be attained during the tanning process through modifying of the tanning process and operating conditions, which can improve the process efficiency and decrease the chromium in the WW (Krishnamoorthy et al., 2013; Ludvik and Buljan, 2000).

In the traditional technology, tanning process efficiency is in the range of 60–70%. This means that the fraction of the fed chromium that is released in WW is in the range of 30–40% (Abdulla et al., 2010; Belay, 2010). In the present case study from Palestine, the uptake efficiency of chromium is about 47%. Such a low uptake efficiency explains the high chromium concentration in the WW stream. This indicates that CP measures on tanning step are essential for reducing chromium in the effluent. The advanced tanning processes have minimized chromium concentration in the effluent by enhancing chromium uptake up to 90%. A closed loop tanning system can be achieved through high chromium uptake with almost zero chromium concentration in the effluent (USAID, 2009).

Process modification includes using of masking agents (such as dicarboxylic organic salts and acids). They enhance the penetration of the chromium complex into the leather matrix, through controlling the chromium complex size. Potassium tartrate has been demonstrated to be the most effective masking agent; as it could decrease chromium in the WW by 94.3% (Mutlu et al., 2014). Masking agents can increase chromium utilization up to 98% (Ludvik and Buljan, 2000; USAID, 2009). Various process parameters were reported to affect the tanning efficiency including pH, chromium concentration, reaction time, temperature and mechanical agitation (Technologien, 2002). For instance, better chromium fixation can be achieved through increasing the temperature. It is recommended that heating must be conducted at the beginning of the process. Slow and regular pH increase after the initial tanning step (at low pH) increases the efficiency of chromium tanning process. However, the gradual increase of pH must be controlled well because chromium precipitation problem may arise at pH values >5.0.

A high-exhaustion chrome tanning effect has been demonstrated by Zhu et al. (2020) by the employment of pH-sensitive and chromium (III)-loaded polymer nanoparticles during the tanning process. The tanned leather that was produced exhibited improved sanitary features as well as anti-adhesive capabilities against germs. In addition, some studies have discovered that submitting the hides to low-temperature plasma boosts the chromium uptake and increases the hydrophobicity of the leather that is produced (Jiang et al., 2019). In another recent study, the authors performed experiments under the influence of ultrasonic and microwave (Zhang and Chen, 2020) and a significant improvement in the penetration of chromium into leather was demonstrated and the chromium concentration in the discharged effluent was shown to be significantly reduced.

The chromium concentration in the input tanning liquor has strong effects on the tanning efficiency. Chromium penetration occurs by diffusion, and the rate increases with increasing chromium concentration. It also affects the product quality. Kanagaraj et al. (2008) reported that the leather obtained (from recovered chromium) after the tanning process had a shrinkage temperature more than 100 °C. The shrinkage temperature of the control sample also exceeded 100 °C. From their results, it is clear that the wattle extract used to recover chromium does not interfere with the tanning process. In another study, according to Prokein et al. (2017), the shrinkage temperature is the most popular method used in the leather industry to determine the heat resistance of wet blue. From the results of their study, a tanning chemical concentration of less than 4.5 (wt%) was found to be insufficient to achieve a shrinkage temperature of 100 °C. A higher temperature encourages the chemical fixing of chromium inside the skin structure, and all of the samples tested were degraded between shrinkage temperatures of 93 and 94 °C.

The technical feasibility of implementing these options must be investigated experimentally. This can be achieved utilizing a pilot scale drum. The inlet and outlet concentrations of the chromium can be determined using UV spectrophotometric analysis, then the chromium uptake efficiency can be determined through a well-established experimental technique (Jabari et al., 2009a). In that study, one of the options was experimentally investigated to demonstrate that optimization of process conditions can increase process efficiency and decrease the chromium concentration in the WW stream. The obtained leather product was then mechanically tested for its product quality. In addition to the above-mentioned CP options for improving chromium uptake, the recovery and reuse of chromium to reduce its release in the discharged waste is also feasible. A previous study by Ludvik and Buljan (2000) recommended that chromium can be directly recycled back into processing tank. The authors mentioned that recycling can reduce chromium consumption by 20%; however, recycling efficiency was only 68%, i.e. the total chromium distribution between leather during tanning and re-tanning processes with respect to direct chrome reuse by recycling. This option may result in the accumulation of other pollutants in the processing liquor. Thus, it affects the quality of the produced leather.

In Palestine, various attempts were made to treat tanning wastewater by utilizing low cost adsorbents. These include utilizing natural marl particles (Jabari et al., 2009b) and stone cutting solid waste (Al-Jabari et al., 2012). However, the industry considered the utilization of stone cutting particles. Besides, as in all adsorption-based treatments, a main question still remains unanswered: what to do with the exhausted adsorbent? The industry is still using the chemical precipitation method, i.e. with hydroxides of calcium, sodium and magnesium oxide. Previous studies have indicated that magnesium oxide resulted in the best precipitating efficiency for chromium in a pH range of 8.0–9.0, with high settling rate and reasonable sludge volume (Esmaeili and Vazirinejad, 2005). There is a chromium regeneration unit following the precipitation unit in the case study, to dissolve the precipitated chromium hydroxide in sulfuric acid, obtaining chromium sulfate solution. Thereafter, the obtained solution can be used as a tanning liquor, with a mass balance make-up adjustment. However, there are local constraints in Palestine on the availability of the required sulfuric acid for the regeneration step. The regeneration process was shut down for the past few years. Currently, high fees are being paid to discharge the obtained solid precipitate. More fees are set when the precipitate is found to be contaminated with ammonia.

According to Sawalha et al. (2019), the WW from the leather industry is concentrated and therefore, advanced processes such as an electrolytic separation or catalytic oxidation can be more efficient (Alexander and Donohue, 1990). If the WW is diluted half of its value, higher performances can be attained for both COD and chromium

Table 2
The leather manufacturing processes and the identified CP options for the case study together with other relevant options proposed in the literature.

Process	Pollution loads	The identified CP options
Mechanical Shaking	Salts	• Collect salts and send for reuse.
Fleshing	Approximately 100 kg solid waste / ton of raw cow hides (including fatty tissues and unwanted proteins)	• It is better to be performed after liming. • It is recommended to investigate protein recycling. • It is recommended to recycle the solid wastes the manufacturing of poultry feed or soaps (Dandira and Madanhire, 2013).
Soaking (1–2 days) Detergent chemicals (0.6%) Enzymes (0.5–1%) Water at 150% of the hides	≈1.5 m^3 of WW per ton of raw hides (brine solution contaminated with fats, dirt and soaps)	• Addition of detergents and disinfectants in a shorter period: 8–20 h (Dandira and Madanhire, 2013). • Implementing the concept of countercurrent soaking (Rao et al., 2003). • Use of enzymes (Rao et al., 2003; Thanikaivelan et al., 2004).
Washing (2 h) Water at 120% of the hides	≈ 1.2 m^3 of WW per ton of raw hides (contaminated with fats, dirt and soaps)	• Addition of Alkali materials (Na_2CO_3 and NaOH) to raise the pH for better effects.
Liming and unhairing (2 days for processing goat skin - 18 h for processing cow hides) 4% lime 2–3% sodium sulfide Water at 120% of the hides	≈ 1.2 m^3 of WW per ton of raw hides (contaminated with lime, hair and sulfides)	• Perform in two stages. • Use sharpening agents (HNaS and Na_2CO_3). • Intact hair removal or hair-save dehairing techniques such as alkali pretreatment dehairing (UNEP-MAP, 2010). • Use enzyme assisted unhairing to reduce COD and sulfide content in WW (UNEP-MAP, 2010; Briki et al., 2016; Alexander and Donohue, 1990). • Recycling of spent liquor (Rao et al., 2003; Galiana-Aleixandre et al., 2011).
Additional fleshing step	• solid waste 50 kg /ton of cow hide (containing flesh, tissues, hair, lime and Na_2S). • Small amount of squeezed water contaminated with soluble proteins, impurities and salts.	• Recycling the solid waste in the manufacturing of poultry feed or detergents.
Deliming (3.2 h) Stagewise additions (40, 90 then 60 min). Stages 1 & 2 at 35 °C: Detergents (0.6%) Ammonium sulfate (1%) Water at 100% of the hides Stage 3: Dekeltal (2.5%) and Orpone materials (containing NH_4Cl) (0.5%)	1 m^3 of WW per ton of raw hides from each stage	• Review performing in a single stage in other countries (Technologien, 2002). • Organic acid based deliming (Rao et al., 2003). • Carbon dioxide based deliming (Rao et al., 2003; Deng et al., 2015). • Reusing deliming liquor (Rao et al., 2003; Galiana-Aleixandre et al., 2011).
Pickling (2.7 h with drum rotating) Then, the hides are left overnight in the drum: At pH of 2.5–2.8. Additions Water at 60% of the hides 10% salt 1% formic acid 2.5% alternative acid	No WW is released	• Decrease pH value (e.g. to 2.4) for better tanning conditions. • Salt free organic acid pickling system Rao et al., 2003; Hu et al., 2011).
Tanning (8 h with drum rotating) Then, the hides are soaked for one day in the drum. Additions onto the pickling solution Water at 20% of the hides Chromium sulfate (7%) Sodium carbonate (0.2%)	0.8 m^3 of WW per ton of raw hides contaminated with chromium	• Adjust pH at lower values initially, pH = 2.4 (from pickling) then increase the pH to 4.1, by the addition of soda ash or sodium bicarbonate, to improve the chromium uptake.
Pressing	Releases about 70% of the tanning liquor from the fiber network.	
Splitting and Trimming	40–80% of the hides as solid waste	• Perform splitting at liming stage, which will reduce the amount of chromium required for tanning and will increase chromium uptake. • Make a feasibility study for using splits and trimmings as raw materials for making gelatins, glues, protein flavor …etc. (Kanagaraj et al., 2006).
Re-tanning step I (1 h) Detergent (0.5%) Other additions after 20 mins: Water at 40 °C at 100% of the hides Formic acid (0.5%)	1 m^3 of WW per ton of raw hides	
Re-tanning step II (1.5 h) Additions Water at 40 °C at 100% of the hides 1.5% sodium formate 0.1% sodium bicarbonate	1 m^3 of WW per ton of raw hides	
Re-tanning step III Dying for six hours with water at 80% of the hides 6% auxiliaries 6% enzymes 6% Limosa 0.3% Dyestuff 1% formic acid 5% oil	0.8 m^3 of WW per ton of raw hides (contaminated with dyes and oils) Emissions of VOC	• Use of non-spraying dying methods such as curtain and roller coating, use of liquid and low dust dyes (UNEP-MAP, 2010).

electrocoagulation treatments (Esmaeili and Vazirinejad, 2005). Nevertheless, extra attention is essential for reducing the high COD in the released streams from beam house operations, and for recovering the sulfide released from the unhearing step.

3. A Palestinian case study on possible CP opportunities in the leather tanneries

This section presents the results of a case study aimed at evaluating the CP options for leather manufacturing in Hebron, Palestine, based on the concepts and analysis of this paper. The CP Opportunities were identified after monitoring all manufacturing processes in local tanneries (Sawalha et al., 2019). The pollution sources from every process were identified, then field interviews, workshop and round table discussions with managers of local leather tanneries were facilitated.

3.1. Industrial background and wastewater

There are currently 13 tanneries in Palestine, eleven of these tanneries are located in Hebron. The manufacturing processes, the amounts of solid waste and the volumes of released wastewater from these processes are summarized in Table 2. The tanneries receive preserved salted dry hides.

3.2. CP Options in Palestine

There have been very limited research studies on adopting CP options in Palestine. For example, Shkoukani (2008) investigated the "Development of an Environmental Management System Using Cleaner Production in Palestinian Dairy Industries. The study concluded that technological changes to increase efficiency were needed, and the environmental regulations and local regulations and laws should be applied. CP options in dairy industry contributes in protecting the environment, saving resources, reducing the production cost. However, limited initiatives have been launched to control the environmental impacts of leather making in Palestine. Thus, no crystalized CP practices in tanneries could be initiated yet. Previous environmental attempts focused mainly on treating wastewater contaminated with chromium from the tanning step. Currently, the Palestine Dutch Cooperation Program (PADUCO) is gearing out new efforts to promote CP in the industrial sector in Palestine. The CP in leather industry is one of the funded projects through such an international collaborative program with researchers from the Netherlands.

Identifying CP options and implementing CP solutions are usually driven by regulative and economics motivations. The CP terminology could not be found in any of the Palestinian laws or regulations, up to the knowledge of the authors. The Palestinian legal framework is not sufficient for waste management (Al-Jabari, 2015). Recently, a Palestinian waste list was established by the Environmental Quality Authority (EQA), based on adopting the European hazardous waste system (Al-Jabari, 2014a, 2014b). Therefore, from the context of the prevailing situation in Palestine, it is recommended to review and update the current legal framework handling issues related to CP and establish an environmental database on pollution sources, loads and characteristics. In addition, auditing and modifying the existing equipment's and possibly adopting new technologies is recommended.

4. Resource recovery from liquid wastes (wastewater)

Tanning industry produces large quantities of solid wastes leading to almost non-profitable end-products. Only around 25–30% of the primary product is in the form of leather produced (Sengül and Gürel, 1993). The wwastewater from a tannery is highlight polluted, and the composition as well as the concentration of individual chemicals/pollutants vary depending upon the unit operation of a specific tanning unit. Generally, a combination of physical, chemical and biological processes can be used for the treatment of liquid and solid wastes because they can be converted to biogas and other useful products using appropriate technologies (Fig. 1).

Tannery wastewater can also be treated in a sequencing batch biofilm reactor (SBBR), i.e. by chemical oxidation in the presence of ozone (Di Iaconi et al., 2003). In that study, the treatment of tannery wastewater collected from large tannery industry from Northern Italy, in the presence and absence of ozone, was investigated. Treatment of wastewater in SBBR lead to an overall average removal of COD (96%), TKN (92%) and TSS (98%). In the presence and absence of ozone, approx. 0.1 kg VSS/kg COD was treated; this was lower than the sludge generated in a convention biological system (0.3 to 0.5 kg VSS/kg COD). The biomass density in SBBR was ~98 g VSS/L sludge and it was shown that the biomass concentration can be also maintained at values close to ~20 g VSS/L (Di Iaconi et al., 2003).

A membrane assisted hybrid bioreactor consists of a circulating bed reactor and multiple ultrafiltration membranes. This reactor type can be used for handling tannery wastewater and liquid discharge from the fish-canning industry that has high N and organic content (Fig. 2). According to Artiga et al. (2005), for this type of wastewaters, a membrane assisted hybrid bioreactor can achieve >99% COD removal at an organic loading rate (OLR) of 6.5 kg COD/m^3·d. Concerning COD and ammonia removal, their removal efficiencies were > 95% and the NH_4^+-N levels were < 10 mg/L in the effluent (Artiga et al., 2005). The advantages of this reactor type can be stated as follows: (i) ability to operate the reactor at high OLR, (ii) good settling characteristics of the sludge, (iii) high N conversion efficiencies, and (iv) steady-state operation with less reactor maintenance. The conventional sequencing batch reactor (SBR) is another potential reactor configuration that can be used for treating wastewater from tanneries (Ganesh et al., 2006). According to the authors, during the 12 h SBR cycle of operation, the removal efficiencies of COD, TKN and NH_3-N were in the range of 80–82%, 78–80% and 83–99%. In another study, the tannery waste like fleshing's, skin trimmings and wastewater sludge were treated using anaerobic digestion (Zupancic and Jemec, 2010). Tannery waste were digested for 100 days in a thermophilic anaerobic digester (AD) unit (55 °C) and approx. 0.617 m^3 kg^{-1} of volatile solids from tannery waste sludge, 0.377 m^3 kg^{-1} from tannery waste trimmings and 0.649 m^3 kg^{-1} from tannery waste fleshing's was converted to biogas.

An upflow anaerobic sludge blanket (UASB) can also be used for treating tannery wastewater. El-Sheikh et al. (2011) operated a series of UASB reactors, i.e. connected in two stages, with a holding capacity of 94 L and experiments were conducted in five different hydraulic retention times (HRT: 24, 18, 12, 8 and 5 h) for each UASB reactor. The overall proposed process showed that a 12 h HRT was the best time for treating tannery wastewater using an UASB. In another study, a continuous two-phase partitioning bioreactor was used for the treatment of synthetic leather tannery wastewater, specifically for the separation of chromium. The bioreactor was fed with synthetic tannery wastewater [4-chlorophenol and potassium dichromate] inoculated with microbial culture for the treatment of different pollutants/compounds. The organic substrate loaded was in the range of 19–94 mg h^{-1} under different HRT, ranging from 3 to 6, achieving a removal of around 89–95%. Therefore, this result clearly showed that continuous two-phase partitioning bioreactor can significantly enhance the biological treatment of tannery wastewater (Angelucci et al., 2017).

In a study by Alighardashi et al. (2017), a membrane bioreactor (MBR) was combined with an adsorption unit containing walnut shell granular activated carbon as the packing material for the treatment of tannery wastewater. More than 98% of COD was removed at a C:N ratio of 13:6.5. The overall ammonium removal was 99% and 70% at pH values <6.0. During the breakthrough time of 15 and 25 min, the nitrate removal was >95%. Berhe and Leta (2018) tested an anaerobic sequencing batch reactor for the co-digestion of tannery wastewater and solid waste in different mixing ratios, under mesophilic temperature conditions. The study revealed that, methanogenic reactor having a

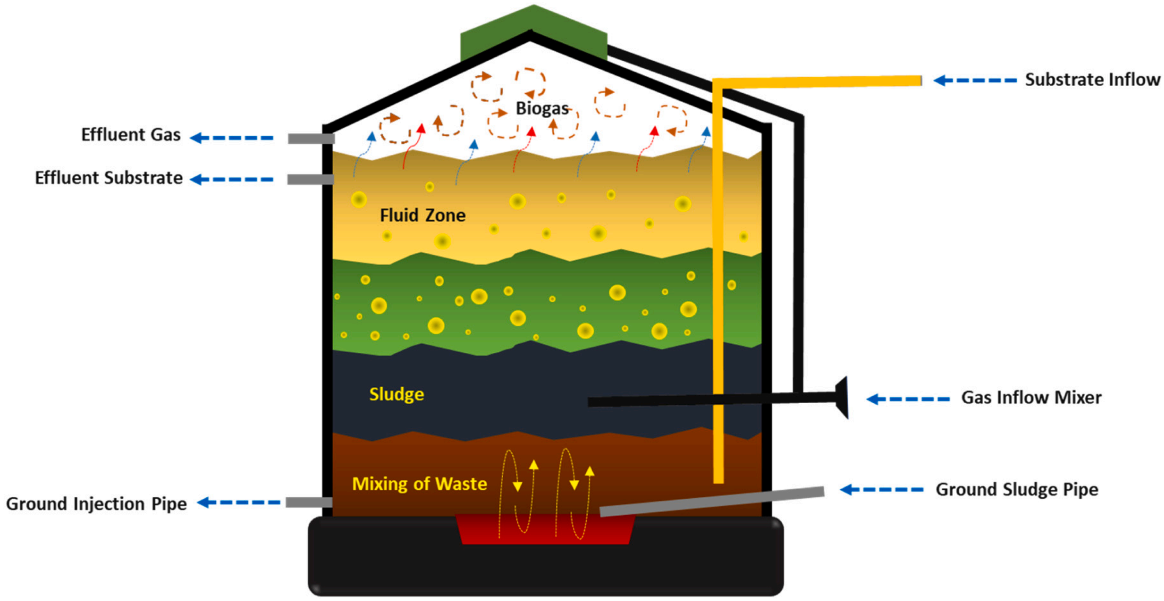

Fig. 1. Anaerobic digestion of tannery effluent to produce biogas.

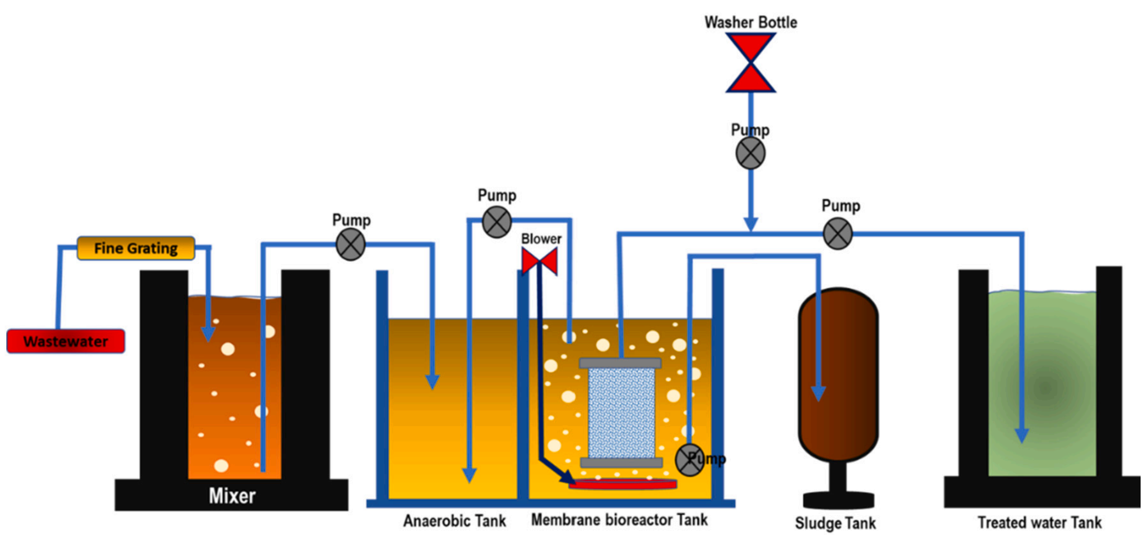

Fig. 2. Membrane bioreactor for the treatment of tannery wastewater and sludge.

50:50 ratio of liquid and solid waste was able to achieve: biogas production = 415 mL/d; amount of methane: 251 mL/d; methane content: 60.5% and COD removal: 75%. Thus, the authors proposed that co-digestion techniques provide better treatment efficiency and generates more biogas than mono-digestion of tannery waste. Hydrodynamic cavitation (HC) was also used for the treatment of tannery waste effluent (TWE) before anaerobic digestion using a slit venturi cavitating (SVC) unit. The SVC was operated at a pressure of 5 bars for approx. 2 h. The production of biogas and COD removal was 2 times higher in the raw TWE than those achieved in the HC treated TWE. Around 68 mL biogas/g volatile solids and 43% COD was removed from the HC treated TWE. After adding food waste to HC treated TWE showed an increase in the biogas production, by up to 7.8 and 11.8-fold, respectively (Saxena et al., 2019). Thus, an anaerobic digester can be combined with other reactor configurations and/or modified for the treatment of COD rich wastewaters and convert them into biogas and liquid digestate (Fig. 3).

5. Resource recovery from solid wastes

The digestion of solid sludge can be performed in different type of bioreactor configurations. In a preliminary study by Akyol et al. (2015), the highest yield of biogas was 0.172 L biogas/g VS_{added} at an inoculum ratio of 1:10 and the solids content was 10.6%. Thus, 0.089 L CH_4/g VS_{added} of methane yield was achieved within an I:S ratio of 1:2. This study provided an idea to increase the yield of biogas by varying the substrate and solid ratio (Akyol et al., 2015). In another recent study (Agustini et al., 2020), AD was used for the digestion of tannery solid waste to produce biogas of 1.9 ± 0.3 mL/VSS. Umaiyakunjaram and Shanmugam (2016) used a flat sheet submerged anaerobic membrane bioreactor (SAMBR) for the recovery of biogas from high suspended solids containing raw tannery wastewater sludge. The SAMBR showed 90% COD removal with a biogas yield of 0.160 $L.g^{-1}$ $COD_{removed}$.

6. Chromium recovery from tannery wastes

The tannery industry produces tons of heavy metals during

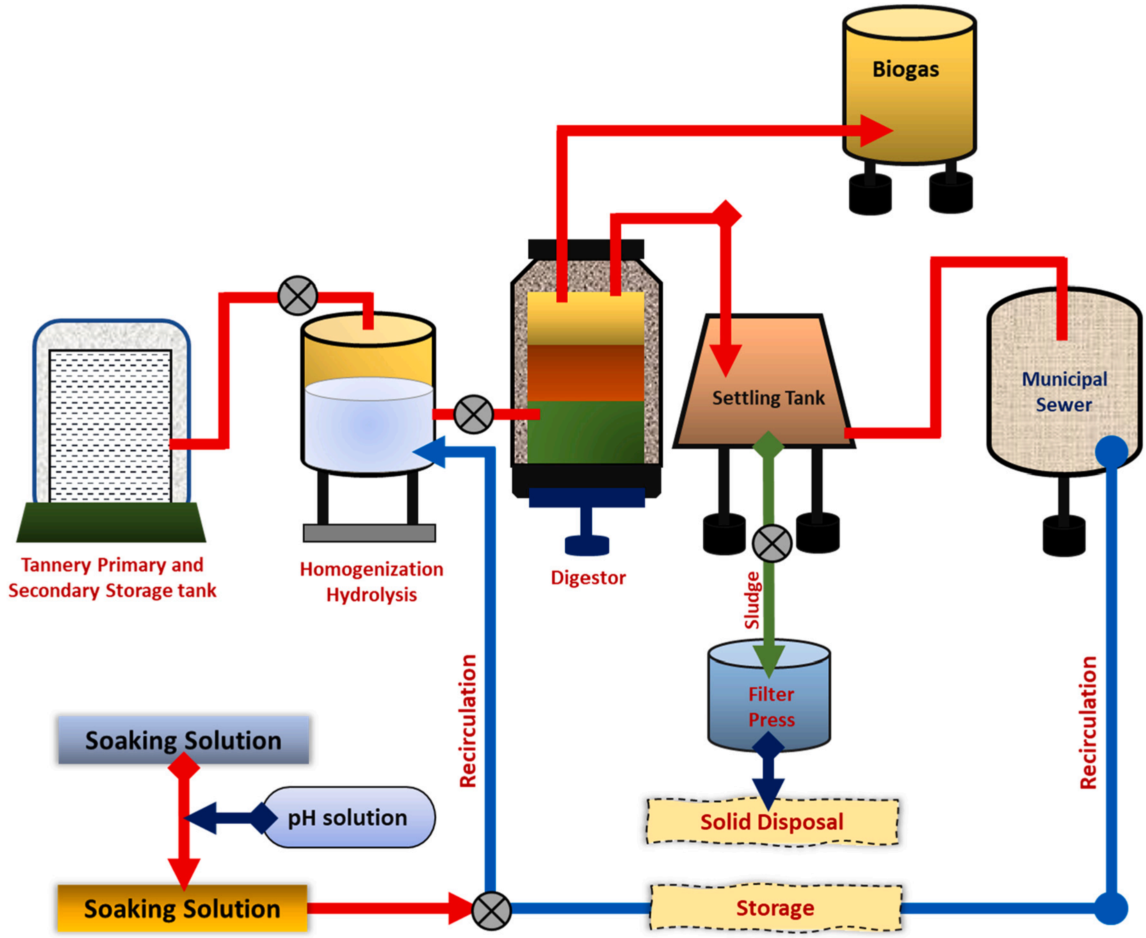

Fig. 3. Schematic for the co-digestion of tannery waste for biogas production.

treatment, but chromium remains the major concern due to its high toxicity and difficulty in recovery. Several strategies have been followed by researchers to remove chromium from tannery waste. Numerous attempts have been made to recover heavy metals from liquid waste, obtain raw materials from tannery sludge that can be used for preparing clay products and produce biogas from the anaerobic digestion of liquid waste from tannery industry (Basegio et al., 2002; Berhe and Leta, 2018). Chromium is the most dominating tanning agent, i.e. approximately 85% of the leather industry uses chromium (Sundar et al., 2001). Chromium is conventionally treated using different physical and chemical techniques such as adsorption, sedimentation, electrochemical process, biological operations, cementation, coagulation/flocculation, filtration, membrane process, chemical precipitation and solvent extraction (Angelucci et al., 2017; Borra et al., 2017; Ha et al., 2018; Jin et al., 2016; Johnson et al., 2017; Koushkbaghi et al., 2018; Mella et al., 2015; Michalski et al., 2016; Neoh et al., 2016; Zhao and Chen, 2019).

In a field scale investigation, the tannery waste sludge collected from different tanneries namely Jajmau tannery waste treatment plant (ITW), Jajmau municipal waste treatment (IMW) and Unnao distillery (IDW) were treated in batch reactors (Singh et al., 2010). The inoculum was prepared by mixing the sludge of a full-scale anaerobic bioreactor and cow dung slurry and the maximum methane content in the biogas varied between 60 and 65% depending upon the operational conditions and the type of sludge digested from the different tanneries (Singh et al., 2010). In another study, a flat sheet submerged anaerobic membrane bioreactor (SAMBR) acclimatized with hypersaline anaerobic seed sludge was tested for biogas production. The SAMBR showed high yielder COD removal (> 90%) and biogas yield (0.160 $L.g^{-1}$ $COD_{removed}$), and good correlation was observed between the permeate flux and TSS (0.95) and biogas and $COD_{removed}$ (0.96), respectively (Umaiyakunjaram and Shanmugam, 2016). In another study, anaerobic digestion of tannery waste rich with chromium in chromium leather shavings was performed to produce biogas (Priebe et al., 2016). Increasing the concentration of chromium in waste significantly reduced the production of methane and biogas. The highest production of biogas was achieved between 3 and 36 days, up to 162.2 mL g^{-1} with a methane content of 73.7%. According to the authors, a significant increase in biogas production (74–181%) was obtained by treating or mixing the leather substrate with readily degradable materials prior to its use as a substrate for anaerobic digestion (Priebe et al., 2016). Thus, bioreactor with different modification and combination of different chromium rich tannery sludge can give higher rates of biogas production.

7. Recovery of chemicals from tannery wastes (e.g. lipids, elastin)

Tannery industry generates large volume of tannery fleshing from dehairing of animal hides, skins, shavings and trimming. Generally, fleshing is rich in fats, proteins, blood, water, salt and other wastes which are dumped or less utilized and become a serious concern of environmental pollution (Dayanandan et al., 2013). About 50–60% of waste is generated from the hide fleshing collected from the tannery (Colak et al., 2005). Steapsin is used for the co-digestion of fleshing (primary substrate) and different sludge fractions generated from tannery wastewater (Kameswari et al., 2011). It was shown that, the addition of steapsin (0.25 and 1.0 g) to 7.5 g of volatile solids enhanced the hydrolysis step during the anaerobic co-digestion of tannery fleshing (Kameswari et al., 2011). The by-products obtained from the fleshing of tannery industry can be used as a biofertilizer and poultry feed after recovering the fat using lipase. Studies by Dayanandan et al. (2013) on the production of lipase using *Aspergillus tamarii* MTCC 5152 were influenced by the oil cakes composed of wheat bran and gingili oil cake. Solid state fermentation oil cake with fungus produced approximately 758 u/g of lipase after 5 days of incubation. While oil cake supplemented with glucose and peptone increased the enzyme production up to 793 u/g. Lipase enzyme produced through this fermentation shows 92% of fat solubility from tannery fleshing (Dayanandan et al., 2013). The results of these studies have clearly demonstrated that the wastewater and solid waste fractions from tanneries offer good potential for converting "waste to wealth", and by implementation the best available technologies, the concept of "circular biorefineries" can be promoted in developing countries.

8. Recommendations

The following recommendations can be made based on the review of existing literatures and by considering the case-study from Palestine: (i) reviewing and updating the current legal framework related to the implementation of CP measures, (ii) initiating awareness campaigns regarding the usefulness of CP in tanneries, (iii) establishing an environmental database on pollution sources, loads and characteristics, (iv) auditing and modifying the existing equipment's and possibly adopting new technologies, (v) substituting toxic chemicals with green and natural ones, (vi) segregation of wastewater from the tanning process from other wastewater streams, and (vii) mixing alkaline wastewater streams with acidic streams in an equalization tank to level out the pH of the wastewater streams.

After a thorough evaluation of the identified cleaner production (CP) options, it was determined that the most practical and urgent options would be to improve the operating conditions of the tanning process in order to increase the efficiency, i.e., better exhaustion and uptake of chromium, rather than to use alternative technologies. It is advised that an experimental research be conducted to determine the technical viability of the process as well as the effects of process alterations on the quality of the leather produced. Aside from that, pilot and semi-industrial scale tests should be carried out to identify environmentally friendly and long-term strategies for recovering biogas and other value-added products from the high COD content present in discharges from beam house operations.

9. Conclusions

There are now 13 tanneries in Palestine, all using traditional tanning procedures and regulated by their material use characteristics. A variety of CP options were revealed based on an analysis of manufacturing process performance, solid waste generation, and wastewater released by these tanneries. Process modification (e.g. fleshing after liming, counter-current soak), use of new materials (e.g. enzymes for unhairing and carbon dioxide and/or organic acid for deliming and pickling), waste recycling (e.g. protein recycling from fleshing, salt collection and reuse for temporary preservation of hide) and waste recycling were identified as the important CP options.

Declaration of competing interest

The authors whose names are listed immediately below certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

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References

Abdulla, H.M., Kamal, E.M., Mohamed, A.H., El-Bassuony, A.D., 2010. Chromium removal from tannery wastewater using chemical and biological techniques aiming zero discharge of pollution. In: Proceeding of Fifth Scientific Environmental Conference, pp. 171–183.

Abraham, J., Gea, T., Sánchez, A., 2014. Substitution of chemical dehairing by proteases from solid-state fermentation of hair wastes. J. Clean. Prod. 74, 191–198. https://doi.org/10.1016/j.jclepro.2014.03.035.

Agustini, C.B., da Costa, M., Gutterres, M., 2020. Tannery wastewater as nutrient supply in production of biogas from solid tannery wastes mixed through anaerobic co-digestion. Process Saf. Environ. Prot. 135, 38–45. https://doi.org/10.1016/j.psep.2019.11.037.

Akyol, Ç., Demirel, B., Onay, T.T., 2015. Recovery of methane from tannery sludge: the effect of inoculum to substrate ratio and solids content. J. Mater. Cycles Waste Manag. 17 (4), 808–815. https://doi.org/10.1007/s10163-014-0306-2.

Alexander, K., Donohue, V., 1990. Cleaner Technologies In The Tanning Industry. British Leather Confederation, Northampton, England.

Alighardashi, A., et al., 2017. Performance evaluation of membrane bioreactor (MBR) coupled with activated carbon on tannery wastewater treatment. Membr. Water Treat. 8 (6), 517–528 (https://doi.org/10.12989/mwt.2017.8.6.517).

Al-Jabari, M., 2014a. Establishing hazardous waste list for a developing country: Palestinian case study. J. Eng. Archit. 2, 187–196 (https://doi.org/10.15640/jea.v2n2a13).

Al-Jabari, M., 2014b. Comparative study of international and regional systems for the hazardous waste classification and listing. Int. J. Environ. Glob. Clim. Chang. 2 (4).

Al-Jabari, M., 2015. Analysis of the palestinian laws and systems within the context of preparing the palestinian hazardous waste list. Arabic. Int. J. Environ. Glob. Clim. Chang. 93–108.

Al-Jabari, M., Abualfailat, M., Shaheen, S., 2012. Treating leather tanning wastewater with stone cutting solid waste. Clean-Soil Air Water 40, 206–210. https://doi.org/10.1002/clen.201000431.

Angelucci, D.M., Stazi, V., Daugulis, A.J., Tomei, M.C., 2017. Treatment of synthetic tannery wastewater in a continuous two-phase partitioning bioreactor: biodegradation of the organic fraction and chromium separation. J. Clean. Prod. 152, 321–329. https://doi.org/10.1016/j.jclepro.2017.03.135.

Artiga, P., Oyanedel, V., Garrido, J., Mendez, R., 2005. An innovative biofilm-suspended biomass hybrid membrane bioreactor for wastewater treatment. Desalination 179 (1–3), 171–179. https://doi.org/10.1016/j.desal.2004.11.065.

Basegio, T., Berutti, F., Bernardes, A., Bergmann, C.P., 2002. Environmental and technical aspects of the utilisation of tannery sludge as a raw material for clay products. J. Eur. Ceram. Soc. 22 (13), 2251–2259. https://doi.org/10.1016/S0955-2219(02)00024-9.

Belay, A.A., 2010. Impacts of chromium from tannery effluent and evaluation of alternative treatment options. J. Environ. Prot. 1, 53–58. https://doi.org/10.4236/jep.2010.11007.

Berhe, S., Leta, S., 2018. Anaerobic co-digestion of tannery waste water and tannery solid waste using two-stage anaerobic sequencing batch reactor: focus on performances of methanogenic step. J. Mater. Cycles Waste Manag. 20 (3), 1468–1482. https://doi.org/10.1007/s10163-018-0706-9.

Borra, C.R., Blanpain, B., Pontikes, Y., Binnemans, K., Van Gerven, T., 2017. Recovery of rare earths and major metals from bauxite residue (red mud) by alkali roasting, smelting, and leaching. J. Sustain. Metall. 3, 393–404. https://doi.org/10.1007/s40831-016-0103-3.

Briki, S., Hamdi, O., Landoulsi, A., 2016. Enzymatic dehairing of goat skins using alkaline protease from *Bacillus sp. SB12*. Protein Expr. Purif. 121, 9–16. https://doi.org/10.1016/j.pep.2015.12.021.

Castiello, D., Calvanese, G., Puccini, M., Salvadori, M., Vitolo, S., Seggiani, M., 2011. A technical feasibility study on titanium tanning to obtain upper quality versatile leather. In: XXXI IULTCS Congress (International Union of Leather Technologists and Chemists Societies).

China, C.R., Maguta, M.M., Nyandoro, S.S., Hilonga, A., Kanth, S.V., Njau, K.N., 2020. Alternative tanning technologies and their suitability in curbing environmental pollution from the leather industry: a comprehensive review. Chemosphere 254, 126804. https://doi.org/10.1016/j.chemosphere.2020.126804.

Colak, S., Zengin, G., Ozgunay, H., Sarikahya, H., Sari, O., Yuceer, L., 2005. Utilization of leather industry prefleshings in biodiesel production. J. Am. Leather Chem. Assoc. 100 (4), 137–141.

A.D. Covington 1988. Leather tanning process using aluminium (III) and titanium (IV) complexes, Google Patents.

Dandira, V., Madanhire, I., 2013. Design of a Cleaner Production Framework to Enhance Productivity: Case Study of Leather Company. International Journal of Science and Research (IJSR), India.

Dayanandan, A., Rani, S., Shanmugavel, M., Gnanamani, A., Rajakumar, G.S., 2013. Enhanced production of *Aspergillus tamarii* lipase for recovery of fat from tannery fleshings. Braz. J. Microbiol. 44 (4), 1089–1095. https://doi.org/10.1590/S1517-83822013000400010.

Deng, W., Chen, D., Huang, M., Hu, J., Chen, L., 2015. Carbon dioxide deliming in leather production: a literature review. J. Clean. Prod. 87, 26–38. https://doi.org/10.1016/j.jclepro.2014.09.066.

Di Iaconi, C., Lopez, A., Ramadori, R., Passino, R., 2003. Tannery wastewater treatment by sequencing batch biofilm reactor. Environ. Sci. Technol. 37 (14), 3199–3205. https://doi.org/10.1021/es030002u.

El-Sheikh, M.A., Saleh, H.I., Flora, J.R., AbdEl-Ghany, M.R., 2011. Biological tannery wastewater treatment using two stage UASB reactors. Desalination 276 (1–3), 253–259. https://doi.org/10.1016/j.desal.2011.03.060.

Esmaeili, A., Vazirinejad, R., 2005. Chromium (III) Removal and Recovery From Tannery Wastewater by Precipitation Process. Science Publications.

Fathima, N.N., Aravindhan, R., Rao, J.R., Nair, B.U., 2009. Utilization of organically stabilized proteinous solid waste for the treatment of coloured waste-water. J. Chem. Technol. Biotechnol. 84, 1338–1343. https://doi.org/10.1002/jctb.2186.

Galiana-Aleixandre, M.-V., Mendoza-Roca, J.-A., Bes-Piá, A., 2011. Reducing sulfates concentration in the tannery effluent by applying pollution prevention techniques and nanofiltration. J. Clean. Prod. 19, 91–98. https://doi.org/10.1016/j.jclepro.2010.09.006.

Ganesh, R., Balaji, G., Ramanujam, R., 2006. Biodegradation of tannery wastewater using sequencing batch reactor—respirometric assessment. Bioresour. Technol. 97 (15), 1815–1821. https://doi.org/10.1016/j.biortech.2005.09.003.

Gao, D., Cheng, Y., Wang, P., Li, F., Wu, Y., Lyu, B., Ma, J., Qin, J., 2020. An eco-friendly approach for leather manufacture based on P (POSS-MAA)-aluminum tanning agent combination tannage. J. Clean. Prod. 257, 120546 https://doi.org/10.1016/j.jclepro.2020.120546.

Ha, T.T., Quan, V.A., Hop, N.Q., Thuy, T.M., Ngoc, N.T., Que, L.X., 2018. Studying on the adsorption of chromium (VI) on polyaniline modified with activated tea residue. Vietnam J. Chem. 56 (5), 559–563. https://doi.org/10.1002/vjch.201800047.

Hu, J., Xiao, Z., Zhou, R., Deng, W., Wang, M., Ma, S., 2011. Ecological utilization of leather tannery waste with circular economy model. J. Clean. Prod. 19 (2–3), 221–228. https://doi.org/10.1016/j.jclepro.2010.09.018.

Jabari, M., Aqra, F., Shahin, S., Khatib, A., 2009a. Monitoring chromium content in tannery wastewater. J. Argent. Chem. Soc. 97 (2), 77–87.

Jabari, M., Aqra, F., Shahin, S., Khatib, A., 2009b. The treatment of chromium tanning wastewater using natural marl. Chem. Speciat. Bioavailab. 21 (3), 185–191. https://doi.org/10.3184/095422909X12473263943097.

Jiang, Y., Li, J., Liu, F., Zhang, Z., Li, Z., Yang, M., Li, L., 2019. The effects of surface modification using O_2 low temperature plasma on chrome tanning properties of natural leather. J. Ind. Text. 49 (4), 534–547. https://doi.org/10.1177/1528083718804205.

Jin, W., Du, H., Zheng, S., Zhang, Y., 2016. Electrochemical processes for the environmental remediation of toxic Cr (VI): a review. Electrochim. Acta 191, 1044–1055. https://doi.org/10.1016/j.electacta.2016.01.130.

Johnson, C.R., Shindgikar, N.D., Beurel, M.M., 2017. Overcoming environmental and technical challenges for well cementing: a global perspective. SPE Prod. Oper. 32 (01), 12–27. https://doi.org/10.2118/172792-PA.

Joseph, K., Nithya, N., 2009. Material flows in the life cycle of leather. J. Clean. Prod. 17 (7), 676–682. https://doi.org/10.1016/j.jclepro.2008.11.018.

Kameswari, K.S.B., Chitra, K., Subramanian, P., Kumarasami, T., 2011. Enhancement of biogas generation by addition of lipase in the co-digestion of tannery solid wastes. CLEAN-Soil Air Water 39 (8), 781–786. https://doi.org/10.1002/clen.201000408.

Kanagaraj, J., Velappan, K., Babu, N., Sadulla, S., 2006. Solid wastes generation in the leather industry and its utilization for cleaner environment-a review. J. Sci. Ind. Res. 65, 541–548.

Kanagaraj, J., Babu, N.C., Mandal, A., 2008. Recovery and reuse of chromium from chrome tanning waste water aiming towards zero discharge of pollution. J. Clean. Prod. 16 (16), 1807–1813. https://doi.org/10.1016/j.jclepro.2007.12.005.

Koushkbaghi, S., Zakialamdari, A., Pishnamazi, M., Ramandi, H.F., Aliabadi, M., Irani, M., 2018. Aminated-Fe_3O_4 nanoparticles filled chitosan/PVA/PES dual layers nanofibrous membrane for the removal of Cr (VI) and Pb (II) ions from aqueous solutions in adsorption and membrane processes. Chem. Eng. J. 337, 169–182. https://doi.org/10.1016/j.cej.2017.12.075.

Krishnamoorthy, G., Sadulla, S., Sehgal, P.K., Mandal, A.B., 2013. Greener approach to leather tanning process: d-Lysine aldehyde as novel tanning agent for chrome-free tanning. J. Clean. Prod. 42, 277–286. https://doi.org/10.1016/j.jclepro.2012.11.004.

Li, W., Ma, J., Zhou, Y., Sun, X., Gao, D., 2021. The application of sulfonated tetraphenyl calix[4] resorcinarene as a novel, multi-functional and eco-friendly ligand in zirconium tanning system. J. Clean. Prod. 280, 124337 https://doi.org/10.1016/j.jclepro.2020.124337.

Ludvik, J., Buljan, J., 2000. Chrome Management in the Tanyard. United Nations Industrial Development Organization.

Mella, B., Glanert, A.C., Gutterres, M., 2015. Removal of chromium from tanning wastewater and its reuse. Process Saf. Environ. Prot. 95, 195–201. https://doi.org/10.1016/j.psep.2015.03.007.

Michalski, R., Jablonska-Czapla, M., Szopa, S., Lyko, A., Grygoyc, K., 2016. Variability in different antimony, arsenic and chromium species in waters and bottom sediments of three water reservoirs in Upper Silesia (Poland): a comparative study. Int. J. Environ. Anal. Chem. 96 (7), 682–693. https://doi.org/10.1080/03067319.2016.1180382.

Mutlu, M.M., Crudu, M., Maier, S.S., Deselnicu, D., Albu, L., Gulumser, G., Bitlisli, B.O., Basaran, B., Tosun, C.C., Adiguzel Zengin, A.C., 2014. Eco-leather: properties of chromium-free leathers produced with titanium tanning materials obtained from the wastes of the metal industry. Ekoloji 23 (91), 83–90. https://doi.org/10.5053/ekoloji.2014.9110.

Neoh, C.H., Noor, Z.Z., Mutamim, N.S.A., Lim, C.K., 2016. Green technology in wastewater treatment technologies: integration of membrane bioreactor with various wastewater treatment systems. Chem. Eng. J. 283, 582–594. https://doi.org/10.1016/j.cej.2015.07.060.

Priebe, G., Kipper, E., Gusmão, A., Marcilio, N., Gutterres, M., 2016. Anaerobic digestion of chrome-tanned leather waste for biogas production. J. Clean. Prod. 129, 410–416. https://doi.org/10.1016/j.jclepro.2016.04.038.

Prokein, M., Renner, M., Weidner, E., Heinen, T., 2017. Low-chromium- and low-sulphate emission leather tanning intensified by compressed carbon dioxide. Clean Technol. Environ. Policy 19 (10), 2455–2465. https://doi.org/10.1007/s10098-017-1442-x.

Rao, J.R., Chandrababu, N., Muralidharan, C., Nair, B.U., Rao, P., Ramasami, T., 2003. Recouping the wastewater: a way forward for cleaner leather processing. J. Clean. Prod. 11 (5), 591–599. https://doi.org/10.1016/S0959-6526(02)00095-1.

Sah, N., 2013. Greener Approach to Leather Techniques. Centria University of Applied Sciences.

Sawalha, H., Alsharabaty, R., Sarsour, S., Al-Jabari, M., 2019. Wastewater from leather tanning and processing in Palestine: characterization and management aspects. J. Environ. Manag. 251, 109596 https://doi.org/10.1016/j.jenvman.2019.109596.

Saxena, S., Saharan, V.K., George, S., 2019. Modeling & simulation studies on batch anaerobic digestion of hydrodynamically cavitated tannery waste effluent for higher biogas yield. Ultrason. Sonochem. 58, 104692 https://doi.org/10.1016/j.ultsonch.2019.104692.

Seggiani, M., Puccini, M., Vitolo, S., Chiappe, C., Pomelli, C., Castiello, D., 2014. Eco-friendly titanium tanning for the manufacture of bovine upper leathers: pilot-scale studies. Clean Technol. Environ. Policy 16 (8), 1795–1803. https://doi.org/10.1007/s10098-014-0722-y.

Sengül, F., Gürel, O., 1993. Pollution profile of leather industries; waste characterization and pretreatment of pollutants. Water Sci. Technol. 28 (2), 87–96. https://doi.org/10.2166/wst.1993.0083.

Shkoukani, M.F., 2008. Development of an Environmental Management System Using Cleaner Production in Palestinian Dairy Industries. Birzeit University.

Singh, R., Mandal, S., Jain, V., 2010. Development of mixed inoculum for methane enriched biogas production. Indian J. Microbiol. 50 (1), 26–33. https://doi.org/10.1007/s12088-010-0060-7.

Sivakumar, V., Jeyaraj, K., Chandrasekar, R., Swaminathan, G., 2008. Tanning Alternatives. Leather International. https://www.leathermag.com/features/featuretanning-alternatives/ (Accessed in March 2021).

Sreeram, K.J., Kanthimathi, M., Rao, J.R., Sundaran, R., 2000. Development of an organo-zirconium complex - organozir as possible alternative to chromium. J. Am. Leather Chem. Assoc. 95, 324–332.

Sundar, V.J., Ramesh, R., Rao, P.S., Saravanan, P., Sridharnath, B., Muralidharan, C., 2001. Water management in leather industry. J. Sci. Ind. Res. 60, 443–450.

Technologien, N., 2002. Treatment of tannery wastewater infogate. https://energypedia.info/images/6/62/Treatment_of_Tannery_Wastewater.pdf (Accessed in August, 2021).

Thanikaivelan, P., Rao, J.R., Nair, B.U., Ramasami, T., 2004. Progress and recent trends in biotechnological methods for leather processing. Trends Biotechnol. 22 (4), 181–188. https://doi.org/10.1016/j.tibtech.2004.02.008.

Umaiyakunjaram, R., Shanmugam, P., 2016. Study on submerged anaerobic membrane bioreactor (SAMBR) treating high suspended solids raw tannery wastewater for biogas production. Bioresour. Technol. 216, 785–792. https://doi.org/10.1016/j.biortech.2016.06.017.

UNEP-MAP, 2010. Towards a More Sustainable Tannery Sector in the Mediterranean (PDF accessed in February 2018).

UNIDO, 2012. Transfer of Environmental Sound Technology in the South Mediterranean Region - (MED TEST): MED TEST Case Study Leather Sector -TUNISIA. United Nations Industrial Development Organization, Vienna, Austria.

USAID, 2009. Environmental Guidelines Part III: Micro- and Small Enterprises. Chapter 4.3 - Leather Processing: Cleaner Production Fact Sheet and Resource Guide, 4.1-4.8, 26.

Woldeyes, B., Ayalew, A., 2008. Cleaner production for solid waste management in leather industry. Zede J. 25, 1–7.

Zhang, J., Chen, W., 2020. A rapid and cleaner chrome tanning technology based on ultrasound and microwave. J. Clean. Prod. 247, 119452 https://doi.org/10.1016/j.jclepro.2019.119452.

Zhang, H., Chen, X., Wang, X., Qiang, X., Li, X., Li, M., 2017. A salt-free pickling chrome tanning approach using a novel sulphonic aromatic acid structure. J. Clean. Prod. 142 (Part 4), 1741–1748. https://doi.org/10.1016/j.jclepro.2016.11.113.

Zhao, C., Chen, W., 2019. A review for tannery wastewater treatment: some thoughts under stricter discharge requirements. Environ. Sci. Pollut. Res. 26, 26102–26111. https://doi.org/10.1007/s11356-019-05699-6.

Zhu, R., Yang, C., Li, K., Yu, R., Liu, G., Peng, B., 2020. A smart high chrome exhaustion and chrome-less tanning system based on chromium (III)-loaded nanoparticles for cleaner leather processing. J. Clean. Prod. 277, 123278 https://doi.org/10.1016/j.jclepro.2020.123278.

Zupancic, G.D., Jemec, A., 2010. Anaerobic digestion of tannery waste: semi-continuous and anaerobic sequencing batch reactor processes. Bioresour. Technol. 101, 26–33. https://doi.org/10.1016/j.biortech.2009.07.028.