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# Environmental optimization of chromium recovery from tannery sludge using a life cycle assessment approach

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#### ABSTRACT

Life cycle assessment (LCA) was used to evaluate the environmental impact of an oxidative chromium recovery method from tannery sludge, in comparison with the usual landfilling process. Three improvement options (water reduction, byproduct use and anaerobic sludge digestion) were considered. The results showed that the proposed chromium recovery process would be better environmentally than conventional landfilling in all the evaluated impact categories if the amount of chromium recovered was 43 kg per ton of sludge. This amount could be recovered if the chromium concentration was about 20 times higher than that considered in this study. Alternatively, a lower chromium concentration would produce a better result if the recovery method was optimized and implemented at industrial rather than laboratory scale, and if more accurate data were provided on environmentally beneficial when tannery sludge contains a chromium concentration of about 100,000 ppm. According to the literature, such concentrations are not unusual. The results could serve as the basis for further environmental improvements in chromium recovery and tannery sludge management and should be used in decision-making processes, especially for end-of-pipe treatments.

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#### 1. Introduction

In leather tanning processes, one of the chemicals that have the greatest environmental impact is basic chromium sulfate (BCS) [1]. BCS is a trivalent chromium salt, and the most widely used tanning agent in the leather industry.

When leather is processed by conventional tanning, only 54–57% of the chromium (Cr) applied in the form of BCS reacts with the hides and skins. The rest is discharged as liquid and solid waste [2]. Cleaner technologies, such as the high exhaustion process and chromium recycling, cannot completely eliminate chromium from wastewaters, as there is usually significant discharge from posttanning processes [3]. Therefore, it is essential to recover Cr from tannery sludge in an environmentally acceptable and economical way before the sludge can be applied safely to the land [4].

Several methods of recovering chromium from tannery sludge have been proposed, including separation of Cr(III) with sulfuric acid and recovery by oxidation to Cr(VI) [5], bioleaching using a mixture of ingenuous iron- and sulfur-oxidizing bacteria [6], and removal using a microemulsion system [7]. The main drawbacks of these methods are operational difficulties, high use of chemicals and long processing times.

Consequently, recent research has been carried out to develop a simpler chromium recovery method, based on the oxidation of Cr(III) to Cr(VI) with hydrogen peroxide [8]. The aim was to reduce the environmental impact of the tanning process by reusing the chromium recovered from sludge. This would decrease both the amount of chromium discharged to the environment and the amount of raw chromium extracted from nature.

LCA is described as a good decision-making tool. It is gaining wider acceptance in the field of environmental management as a method that enables improvement options to be quantified throughout the life cycle of a process, product or activity [9].

Although LCA has been applied to sludge management [10–13] and to the leather industry [14–19], no LCA case studies have been described for tannery sludge in particular. This sludge makes a significant contribution to the environmental impact of the tanning process [14]. Therefore, in the present study, LCA methodology was used to compare the environmental performance of an alternative chromium recovery treatment [8] and conventional landfilling.

#### 2. Methodology

LCA as defined in international standard ISO 14040 consists of four sequential steps: goal and scope definition, inventory analysis,

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Fig. 1. System boundaries of the conventional system and the sludge treatment system.

impact assessment and interpretation. Below, these four steps are described in relation to the case study.

The LCA was carried out using the GaBi 4 Software (PE International Stuttgart, Germany). The environmental impacts were obtained using factors of Centrum voor Milieukunde Leiden (CML) developed by the Leiden University Centre of Environmental Science, which were updated in 2001.

#### 2.1. Goal and scope definition

The goal of the study was to identify the environmental benefits of chromium recovery from sludge prior to landfilling, and to compare these benefits with those of direct landfilling. The scope of the study is presented in Fig. 1.

A functional unit is a measure of the function of a studied system and provides a reference to which inputs and outputs can be related. In both of the systems under study, the function is not directly related to the manufacture of a certain product, but to waste management. A certain quantity of inflow water to be treated in a wastewater treatment plant (WWTP) was considered the best choice of unit, since it is based on realistic data [20]. Therefore, 100 cubic meters of wastewater with the subsequent sludge disposal was selected as the functional unit. This amount of wastewater resulted in 362.4 kg of sludge (27.8% dry matter) in the conventional system. The composition of tannery sludge is presented in Table 1.

The goal of the study was to evaluate resource consumption, pollutant emissions and the consequent environmental impact in both systems. The final result of the study shows which system has better environmental performance. The specific aim was to evaluate whether the amount of chromium that was recovered was enough to environmentally justify the proposed recovery process. This study is expected to contribute to the development of alternative tannery sludge treatment strategies and to provide useful information for decision-makers. It is aimed at scientists who are developing technologies for recovering heavy metals from waste, and decision-makers in leather waste management.

# *2.2.* Description of the systems under study and the system boundaries

Two systems were defined in the study: the *Conventional System* and the *Sludge Treatment System*. Fig. 1 presents the main

Table	1		
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Composition of tannery sludge.	
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Parameters	Unit	Tannery sludge
Moisture	%	72.2
pH		7.25
Electrical conductivity	dS/m (25 °C, 1:5)	2.54
Organic material <sup>*</sup>	%	76.4
Kjeldahl Nitrogen <sup>*</sup>	%	5.51
N Ammoniacal <sup>*</sup>	%	1.07
P*	%	1.04
K*	%	0.14
Ca <sup>*</sup>	%	5.89
Na <sup>*</sup>	%	0.59
Mg <sup>*</sup>	%	0.38
Fe <sup>*</sup>	%	1.32
Zn*	%	0.13
Al*	%	0.22
Cr*	mg/kg	8041
Pb*	mg/kg	98.5
Cd <sup>*</sup>	mg/kg	18.5
Ni <sup>*</sup>	mg/kg	34.5
Cu <sup>*</sup>	mg/kg	174
Hg <sup>*</sup>	mg/kg	0.07
C/N		6.3

\* Dry matter basis.



Fig. 2. Flow chart of the conventional system.

phases included in the analysis. The systems consisted of two major groups of processes: wastewater treatment processes and sludge treatment processes. The function of the wastewater treatment processes was the same in all systems. The system boundaries were as follows: the system included the production of the main chemicals and the electrical energy. The construction of different sludge treatment facilities, including the machinery, electrical installations and transport, were excluded from the system and only the operation stage was taken into account in the analysis.

Data on the WWTP and the sludge drying plant were taken from Igualadina de Depuració i Recuperació (IDR) wastewater treatment plant and Jorba Composting Plant in Catalonia (Spain). The WWTP has a capacity of 15,000 m<sup>3</sup>/day and treats effluents from tanneries mixed with municipal wastewater in a ratio of 1:7. The average effluent volume is about  $8459 \, m^3/day$ . This WWTP has two lines: water and sludge. The sludge from the plant is sent to landfill once it has been dried in a composting plant. Data on the landfilling process was taken from the GaBi 4 database.

Data for the proposed sludge treatment to recover chromium were collected mainly from laboratory studies that will be described in Section 5 and from existing facilities, bibliographical sources and the ecoinvent database developed by the Swiss Centre for Life Cycle Inventories.

#### 2.3. Life cycle inventory analysis

The inventory is composed of the following phases: wastewater treatment, sludge drying and landfilling, and sludge treatment for chromium recovery (which includes chromium recovery, hydrogen peroxide decomposition and chromium precipitation treatments). The environmental load was calculated in relation to the functional unit for both the conventional and the sludge treatment systems. Figs. 2 and 3 present the flowcharts with the mass balance of both systems.

#### 2.3.1. Wastewater treatment

The wastewater treatment phase includes preliminary, physicochemical and biological treatment (inventory data shown in Table 2). The primary sludge from the physicochemical treatment and the secondary sludge from the biological treatment are mixed, dewatered by centrifugation and dried in a composting plant. The final sludge is then sent to landfill. The sand that is deposited in the process and the filtered materials go directly to landfill without composting. Wastewater processed in IDR is sent to another WWTP for further treatment. Consequently, the remaining contaminants are not discharged to the environment.

#### 2.3.2. Chromium recovery process

The oxidative chromium recovery process [8] was carried out with dewatered tannery sludge prior to sludge drying and the landfilling process. The main steps in the chromium recovery process include three washes followed by filtration (see Fig. 4). In order to avoid interference with other elements, hydrogen peroxide (which eliminates the potential formation of toxic byproducts) was used to oxidize Cr(III) to Cr(VI) in the first two alkaline treatments. The oxidation was performed under basic conditions, therefore the other metals in the sludge remain insoluble and chromium was separated from treated sludge in the form of chromate solution. In the last washing step, Cr(VI) was reduced to Cr(III) under acidic conditions, which enables the recovery of chromium in the form of Cr(III) solution. The treatment takes less than 4 h in total and the chromium removal efficiency is 70%.

In this process, electricity was used for stirring and filtering the washing solution. The energy consumption was considered to be 1.4 kWh/ton of dry sludge for stirring the sludge mixture [22] and 52 kWh/ton of dry sludge for filtering it [23]. The inventory data for the oxidative chromium recovery process (presented in Table 3) were based on a laboratory scale process. The consumption and emission figures would be optimized if the process was applied on an industrial scale. The data used here can be considered the worst case data.

#### 2.3.3. Hydrogen peroxide decomposition treatment

The hydrogen peroxide decomposition process is based on the catalytic decomposition of hydrogen peroxide in the presence of an iron catalyst [24,25]. To eliminate the residual hydrogen peroxide in the final washing solution, the first and second washing solutions were mixed and the pH of the mixture adjusted to pH 4.9-5.0 using 50% H<sub>2</sub>SO<sub>4</sub>. Then, Fe<sub>2</sub>O<sub>3</sub> (40%) was added to the solution to provide a 100 ppm concentration in the final solution. The solution was stirred for 4 h at room temperature. The H<sub>2</sub>O<sub>2</sub> and Fe(II) in the solution also function as reducing agents for Cr(VI) [26]. Most of the Cr(VI) in the chromate solution was considered to be reduced in the hydrogen peroxide decomposition process. To ensure that all Cr(VI) is reduced to Cr(III), sodium bisulfite may be added to the solution in very small amounts to remove traces of Cr(VI). In the hydrogen peroxide decomposition process, electricity was used to stir the wastewater from the chromium recovery process (taken as 0.05 kWh per metric ton of water [27]).

#### 2.3.4. Chromium precipitation process

Reduced chromate solution from the H<sub>2</sub>O<sub>2</sub> decomposition process and chromium solution from the chromium recovery treatment are considered to be precipitated with NaOH in the form of Cr(OH)<sub>3</sub>, which is dissolved with H<sub>2</sub>SO<sub>4</sub> and filtrated through diatomaceous earth to produce basic chromium sulfate (CrOHSO<sub>4</sub>) of the required concentration. The data were obtained from a real industrial plant in which BCS was obtained from tanning waste baths (the inventory data for obtaining one cubic meter of chromium liquor at 33% is presented in Table 4). The authors assumed that there is no chromium loss during the sludge treatment processes. The wastewater produced by the chromium precipitation process is considered to be recirculated and treated in the WWTP under study. The environmental impact of additional sludge produced by the treatment of recirculated wastewater was also evaluated within the boundaries of the sludge treatment system. The environmental impact of the residues from diatomaceous earth filtration was not considered, due to lack of data.





#### Table 2

Inputs and outputs of wastewater treatment.

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	Unit	Amount	Assumptions
Input			
Wastewater	kg	100,000	The antifoaming agent was taken as ethoxylated fatty alcohol-based
COD	mg/L	5030	agent
Chromium	mg/L	68	
Water	kg	758.4	
Electrical energy	MJ	457.1	
Acrylonitrile	kg	3.2	Regarding the polymer production data (for polyacrylamide), data
Antifoaming agent	kg	0.28	from acrylonitrile production was considered [21]
Iron chloride 40%	kg	11.3	
NaOH 50%	kg	9.1	
Output			
Sludge (27.8% d.m.)	kg	362.3	Electricity data were taken from the Spanish
Chromium	mg/kg (d.m.)	8041	electricity grid
Solid waste	kg	15.7	
Treated water	kg	100,405	The use of deodorization reagent in the wastewater treatment was
COD	mg/L	243	excluded, as it accounts for less than 2% of the total use of chemicals
Chromium	mg/L	0.5	

d.m.: dry matter.

#### 2.3.5. BCS production process

The chromium solution obtained from the chromium precipitation process can be used to avoid the production of virgin BCS and the extraction of raw chromium from nature. The data on chromium extraction from nature and on sodium dichromate and chromium sulfate production processes were obtained from the ecoinvent database and the literature [28], respectively. Sodium dichromate is produced by the sulfuric acid process and the electrolysis process is not included in the ecoinvent database, therefore the data is considered of poor quality. Table 4 shows the input and output data for the dichromate reduction process, in relation to the production of 20,000 L CrOHSO<sub>4</sub> at 33%. The final chromium liquor has





Fig. 4. Flow diagram of the oxidative chromium recovery process.

#### Table 3

Inventory data for chromium recovery and the H2O2 decomposition process (laboratory scale).

	Chromium recovery process	H <sub>2</sub> O <sub>2</sub> decomposition process	Assumptions
Input			
Sludge (27.8% d.m.)	373.4 kg	-	Regarding Fe <sub>2</sub> O <sub>3</sub> , which is the iron catalyst used in the hydrogen
Chromium	8041 mg/kg (d.m.)		peroxide decomposition, data from Fe(III)chloride production were used
Water	2767.5 kg	_	
Electrical energy	19.9 MJ	27.3 MJ	
H <sub>2</sub> O <sub>2</sub> (50%)	37 kg	-	
Na <sub>2</sub> CO <sub>3</sub>	150.5 kg	-	
H <sub>2</sub> SO <sub>4</sub> (96%)	95.8 kg	3.8 kg	
Chromate Solution	-	1960.8	
Chromium		123.7 mg/L	
Iron (III) chloride (40%)	-	0.5 kg	
Output			
Sludge (23.5% d.m.)	357.8 kg	-	The impact of sodium bisulfite production has been excluded, as only
Chromium	2951.9 mg/kg (d.m.)		very small quantities are used (less than 1%)
Chromate solution	1960.8 kg	-	
Chromium	123.7 mg/L		
Chromium solution	1049.3 kg	1964.5 kg	
Chromium	346 mg/L	123.4 mg/L	
Evaporated water	56.8 kg	-	

d.m.: dry matter.

a concentration of 34.62 g Cr/L. The molasses production process was not included, due to a lack of data and the very low amounts that are used.

#### 2.3.6. Sludge drying and landfilling

The function of the sludge drying processes is the same in both conventional and sludge treatment systems. However, as chromium is recovered in the sludge treatment process, less sludge is produced with lower chromium content (as seen in Figs. 2 and 3).

Dewatered sludge is dried by aerobic digestion with waste wood in the Jorba Composting Plant. A total of 25% of the waste wood that is used for the composting is put into landfill with the compost. The remaining 75% of the wood can be reused in the composting process. The amount of wood that is lost is recovered with the new input of waste wood. During the sludge drying procedure, which generally lasts 4 weeks, sludge and wood lose half of their water content. Temperatures over 70 °C are reached during the process.

The rain water and leachate from composted piles are collected and reused to increase the moisture content of the piles. European Union data were used on the diesel fuel for transport.

For the impact assessment of the landfilling phase, the process structure and data were taken from the GaBi database. The landfilling process described in the GaBi database is a municipal waste

#### Table 4

Inventory data for chromium precipitation and BCS production processes (data from a real industrial plant).

	Chromium precipitation process	BCS production process
Input		
Chromium solution	17,000 kg	-
Chromium	2.05 g/L	
Water	-	17,838.2 kg
Electrical energy	46.9 MJ	43.92 MJ
H <sub>2</sub> SO <sub>4</sub> aq. (96%)	130.5 kg	5271.46 kg
NaOH (30%)	355.1 kg	-
Sodium dichromate	-	5331.07 kg
solution (32%)		
Methanol	-	533.1 kg
Molasses	-	25 kg
Output		
CrOHSO <sub>4</sub>	1270 kg	26,660 kg
Chromium	34.62 g/L	34.62 g/L
Wastewater for recirculation	16,190 kg	-
Evaporated water	-	2325.81 kg

landfilling process that considers different values for chromium emission to air, water and soil. However, in our case, additional chromium is disposed in the landfill with tannery sludge. This amount of chromium was assigned as emissions to air water and soil, according to the calculated ratios (see the inventory data in Table 5).

Landfilling data from GaBi also includes energy recovery. However, this factor was not considered, as the organic content of sludge is converted to  $CO_2$  under aerobic conditions during the sludge drying process [29]. Consequently, it is not degraded to methane in the landfill. For the same reason,  $CH_4$  and  $N_2O$  emissions in the conventional landfilling process (obtained from GaBi) should be reduced or eliminated, and only  $CO_2$  and NOx emissions should be taken into account. However, due to a lack of specific and accurate data, these emissions were considered as they are included in the database. This assumption was not significant in the results of the two-system comparison.

#### 3. Results and interpretation

The impact assessment was carried out up to the characterization step. There was no normalization or weighting of the impacts.

#### Table 5

Inventory data for the sludge drying phase in a conventional system.

	Unit	Amount
Input		
Sludge (27.8% d.m.)	kg	362.4
Chromium	mg/kg (d.m.)	8041
Rain water	kg	1.8
Electrical energy	MJ	2.8
Iron sulfate	kg	1.6
Wood residue	kg	642.1
Diesel	kg	0.8
Output		
Evaporated water (emissions to air)	kg	261.5
Grey compost (40% d.m.)	kg	261.5
Chromium	mg/kg (d.m.)	4400
Wooden residue (waste for recovery)	kg	481.6
Chromium (heavy metals to landfill)	kg	2.59E-05
Chromium (+III) (heavy metals to fresh water)	kg	1.57E-08
Chromium (heavy metals to sea water)	kg	7.01E-08
Chromium (heavy metals to fresh water)	kg	7.71E–07
Chromium (heavy metals to air)	kg	5.93E-08
Chromium (heavy metals to industrial soil)	kg	2.50E-05

d.m.: dry matter.



Fig. 5. Relative contribution of each sludge treatment stage to different impact categories.

GaBi 4 with CML 2001 impact assessment methodology was used to calculate the potential environmental impacts. Energy consumption and some of the environmental impact categories devised by Guineé et al. were included in the study [30]. These categories include abiotic depletion potential (ADP), acidification potential (AP), eutrophication potential (EP), freshwater aquatic ecotoxicity potential (FAETP), global warming potential (GWP), human toxicity potential (HTP), marine aquatic ecotoxicity potential (MAETP), ozone layer depletion potential (ODP), photochemical ozone creation potential (POCP) and terrestrial ecotoxicity potential (TETP).

The influences of different improvement options (a reduction in water consumption, the use of byproducts in the chromium recovery process instead of commercial chemicals, and the anaerobic digestion of sludge prior to the chromium recovery treatment) were also analyzed.

#### 3.1. Environmental evaluation of sludge treatment

The proposed sludge treatment system can be used to recover chromium and to produce BCS. As a result, less chromium goes to landfill and fewer virgin raw materials are needed in BCS production.

In this section, the potential environmental impact of each process in the sludge treatment system, were evaluated to identify any associated hot spots. The relative contribution of each stage to the overall environmental load is presented in Fig. 5.

In the sludge treatment system, WWTP, chromium recovery, sludge drying and landfilling were the most adversely affected phases, while other processes were less significant. The environmental benefits of avoiding BCS production were especially significant in the FAETP category, in which about 60% of the impact was eliminated.

The chromium precipitation process appeared to be the least polluting operation, as it contributed no more than 5% to most of the impact categories. The most significant burdens in all the evaluated impact categories were due to the use of chemicals (sulfuric acid, soda and hydrogen peroxide) in the chromium recovery process and consequently to the production of these compounds. If the amount of sulfuric acid, soda and hydrogen peroxide used in the process could be reduced, then the environmental impact would diminish accordingly.

## 3.2. Environmental comparison between sludge treatment and conventional treatment

Two major processes, wastewater treatment and sludge drying and landfilling are found in both systems. Additionally, the sludge treatment system includes a chromium recovery process. Fig. 6 illustrates the calculation of values for each impact assessment category in relation to the processes involved in both systems.

The contribution of WWTP, sludge drying and landfilling phases to most of the impact categories was similar in both systems. One exception was the category of TETP, in which the impact of sludge drying and landfilling was higher in the conventional system, due to chromium disposal in the landfill [14]. As mentioned above, the use of chemicals such as sulfuric acid, soda and hydrogen peroxide in the sludge treatment system made an additional contribution to most of the impact categories when compared with the conventional system. EC, ADP and AP were the impact categories that were most affected by this contribution, with 605%, 332% and 212% increases in overall impact, respectively. The production of chemicals used in chromium recovery doubled the impact of sludge treatment in the GWP, POCP and ODP categories, but affected MAETP and HTP to a lesser extent, with an increase of 42% and 46%, respectively.

However, sludge treatment performed significantly better in the FAETP category, due to BCS production. In this category, the overall environmental impact was 156% lower in the sludge treatment than in the conventional system.

#### 3.3. Process improvement assessment

#### 3.3.1. Reduction of water consumption

A sensitivity analysis was conducted to assess the optimization of water consumption when the chromium recovery stage process is applied on an industrial, rather than a laboratory, scale.



Fig. 6. Impact assessment of sludge treatment (ST) and conventional (C) systems with contributions of the different processes.

Reduction in water consumption by 20%, 40% and 60% were evaluated.

As expected, scaling down the water consumption improved the environmental performance of the sludge treatment system, as fewer chemicals were used. A 60% reduction in water usage provided better environmental benefits, particularly in FAETP, with a 22% reduction in overall impact. AP, ADP and HTP were the next most affected categories after FAETP, with an environmental improvement of 18%, 15% and 14% respectively. However this reduction in water consumption only produced a small variation of no more than 7% in EP, GWP and ODP impact categories.

#### 3.3.2. Using byproducts instead of virgin chemicals

The use of byproducts in the chromium recovery process instead of commercial sodium carbonate and sulfuric acid was evaluated. It was assumed that sodium carbonate could be replaced with the waste product of a hydrogen producing reaction, and sulfuric acid could be replaced by a byproduct of the nonferrous metal sector. Due to credits in the chemical production, the replacement of commercial products significantly reduces the contribution of the chromium recovery process to some impact categories. The greatest reductions were found in the ADP and AP categories (52% and 56%, respectively).

In combined scenarios, which consist of both byproduct use and a 50% reduction in process water, the environmental results for the FAETP impact category were better for the sludge treatment system than for the conventional system. In most of the other categories (except for ODP and ADP), impact values that were similar to those of the conventional treatment were found (see Fig. 7).

#### 3.3.3. Anaerobic digestion of tannery sludge

An alternative scenario that considered the anaerobic digestion of tannery sludge prior to the chromium recovery process was investigated. Data on anaerobic sludge digestion were obtained from the literature [12,21] and found to agree with data from a real plant (Estació Depuradora d'Aigües Residuals de Manresa [EDAR], located in Catalonia, Spain).

In this biological decomposition process, dewatered sludge (27.8% dry solid content) is anaerobically degraded by the action of microorganisms in a closed digestion tank. The average weight percentage of volatile matter in the dry sludge is 72%. Approximately 48% of this volatile matter degrades into gases during digestion. The gases that are produced are generally composed of two thirds methane and one third  $CO_2$  in volume ratio, with a density of 1.13 kg/Nm<sup>3</sup>. One third of the total biogas production is consumed to maintain the digester at a constant temperature of 35 °C [21]. The excess gas can be employed to produce electricity and heat with yields of 36% and 50%, respectively [31]. The mineral part of the dry sludge was assumed to stay constant during the entire digestion period [32].

The corresponding  $CO_2$  emissions were considered in the sludge landfilling process, rather than in the anaerobic digestion.

Fig. 7 shows the comparative results of sludge treatment with and without anaerobic digestion. Anaerobic digestion has energy advantages, due to the biogas production, and lessens the energy consumption of sludge treatment by 38%. In addition, it considerably reduces the environmental contribution of sludge treatment to all impact categories, especially to ADP (34%), GWP (30%) and POCP (30%), as less sludge is produced and fewer chemicals are used. E. Kiliç et al. / Journal of Hazardous Materials 192 (2011) 393-401



Fig. 7. Impact assessment results of the conventional system and the sludge treatment system using different scenarios (50% reduction of water consumption, use of by-products instead of virgin chemicals in the chromium recovery process, and sludge treatment with anaerobic digestion).

The anaerobic digestion scenario combined with the reduction of water consumption and the use of by-products would considerably improve the environmental performance of the sludge treatment system. The results of this combined scenario are similar or even better than those of the conventional system, except perhaps in two of the impact categories (ADP and ODP).

#### 4. Discussion

The sludge treatment enables recovery of 70% of the chromium. However, in these conditions and with data from a laboratory scale process, sludge treatment turned out to be environmentally worse than conventional treatment, mainly due to the use of chemicals and the low quantity of BCS produced. Such a result is not surprising if it is considered that the sludge has a low concentration of chromium, which needs high quantities of water and chemicals to be recovered. The environmental credits obtained from the avoidance of virgin chromium sulfate production would compensate for the burden of the recovery treatment if the amount of chromium recovered by this method was 43 kg of Cr per ton of sludge. This value is obtained by calculating the necessary amount of chromium solution that enables the proposed system to have equal or lower contribution to all impact categories, compared to the actual system of sludge disposal. To attain this level of recovery, the concentration of chromium would have to be 20-fold higher than that considered in this study (one of the lowest concentrations described in the literature). A high concentration of chromium in sludge can be found in other tannery industry areas, as described in the literature [5–7,33] with values ranging mainly from 17,000 to 150,000 ppm. Concentrations could be less than this if more accurate data on dichromate production from chromium ore were available and if the recovery process was optimized when implemented on an industrial, rather than a laboratory, scale.

#### 5. Conclusion

In this study, a tannery sludge treatment to recover chromium was environmentally evaluated by means of LCA and compared with a conventional treatment system. The results revealed that end-of-pipe treatments usually increase the environmental impact, due to the quantity of chemicals and energy used, unless the treatment is simple and recovers a significant amount of waste. Therefore, the recovery method is of interest when tannery sludge contains a high chromium concentration. Compensation of process burdens occurs when the chromium concentration is 20 times higher than that considered in this study. The environmental performance of the chromium recovery process improves when it is applied on an industrial scale. In this respect, three improvement options were evaluated: the reduction of water consumption, the use of byproducts instead of virgin chemicals, and the anaerobic digestion of tannery sludge prior to chromium recovery. In the 50% water reduction and byproduct use scenario for the sludge treatment, a significant improvement and better environmental performance that was comparable to the conventional treatment was found. Aerobic or anaerobic digestion of tannery sludge prior to the chromium recovery treatment considerably improved the environmental profile of the sludge treatment system and would probably also increase the percentage of chromium recovery (to more than the 70% described [8]), due to the lower content of organic matter that binds the chromium. This point should be further investigated at laboratory and pilot plant scale.

The results obtained from this LCA study highlight the opportunities for improving the chromium recovery process. The information can be used to make further environmental improvements in this process. These results could serve as the basis for improving tannery sludge management options and for decisionmaking processes, especially for end-of-pipe treatments.

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#### References

- R. Puig, B. Notarnicola, A. Raggi, LCA of Italian and Spanish bovine leather production systems in an industrial ecology perspective, in: R. Puig, B. Notarnicola, A. Raggi (Eds.), Industrial Ecology in the Cattle-To-Leather Supply Chain, Franco Angeli Publishing, Milano, 2007, pp. 32–68.
- [2] J. Ludvik, Chrome balance in leather processing, Regional programme for pollution control in the tanning industry in south-east Asia, United Nations Industrial Development Organization Report, 2000, pp. 1–18.
- [3] IULTCS, IUE-4 Assessment for chromium containing waste from the leather industry, in: International Union of Environment IUE, 2004, pp. 1–4.
- [4] S. Avudainayagam, M. Megharaj, G. Owens, R.S. Kookana, D. Chittleborough, R. Naidu, Chemistry of chromium in soils with emphasis on tannery waste sites, in: G.W. Ware (Ed.), Reviews of Environmental Contamination and Toxicology, vol. 178, Springer, New York, 2003, pp. 53–91.
- [5] G. Macchi, M. Pagano, M. Pettine, M. Santori, G. Tiravanti, A bench study on chromium recovery from tannery sludge, Wat. Res. 25 (1991) 1019– 1026.
- [6] S. Zhou, L.X. Zhou, S.M. Wang, D. Fang, Removal of Cr from tannery sludge by bioleaching method, J. Environ. Sci. 18 (2006) 885–890.
- [7] T.N. Castro Dantas, K.R. Oliveira, A.A. Dantas Neto, M.C.P.A. Moura, The use of microemulsions to remove chromium from industrial sludge, Water Res. 43 (2009) 1464–1470.
- [8] E. Kılıç, J. Font, R. Puig, S. Çolak, D. Çelik, Chromium recovery from tannery sludge with saponin and oxidative remediation, J. Hazard. Mater. 185 (2011) 456–462.
- [9] F. Consoli, D. Allen, I. Boustead, J. Fava, W. Franklin, A. Jensen, N. Oude, R. Parrish, R. Perriman, D. Postlethwaite, B. Quay, J. Seguin, B. Vigon, Guidelines for life-cycle assessment: A 'Code of Practice' SETAC-Society of Environmental Toxicology and Chemistry, Brussels and Pensacola, 1993.
- [10] K.I. Strauss, M. Wiedemann, An LCA Study on sludge retreatment processes in Japan, Int. J. Life Cycle Assess. 5 (2000) 291–294.
- [11] J. Hong, J. Hong, M. Otaki, O. Jolliet, Environmental and economic life cycle assessment for sewage sludge treatment processes in Japan, Waste Manage. 29 (2009) 696–703.
- [12] Y.J. Suh, P. Rousseaux, An LCA of alternative wastewater sludge treatment scenarios, Resour. Conserv. Recycl. 35 (2002) 191–200.
- [13] G. Houillon, O. Jolliet, Life cycle assessment of processes for the treatment of wastewater urban sludge: energy and global warming analysis, J. Cleaner Prod. 13 (2005) 336–345.
- [14] L. Milà, X. Domènech, J. Rieradevall, R. Puig, P. Fullana, Use of life cycle assessment in the procedure for the establishment of environmental criteria in the Catalan eco-label of leather, Int. J. Life Cycle Assess. 7 (2002) 39–46.
- [15] B. Rivela, M.T. Moreira, Life cycle assessment as a tool for the environmental improvement of the tannery industry in developing countries, Environ. Sci. Technol. 38 (2004) 1901–1909.
- [16] K. Joseph, N. Nithya, Material flows in the life cycle of leather, J. Cleaner Prod. 17 (2009) 676–682.
- [17] L. Milà, X. Domènech, J. Rieradevall, P. Fullana, R. Puig, Application of life cycle assessment to footwear, Int. J. Life Cycle Assess. 3 (1998) 203–208.

- [18] D.W. Nazer, R.M. Al-sa'ed, M.A. Siebel, Reducing the environmental impact of the unhairing–liming process in the leather tanning industry, J. Cleaner Prod. 14 (2006) 65–74.
- [19] D. Castiello, M. Puccini, M. Seggiani, S. Vitolo, F. Zammori, Life cycle assessment (LCA) of the oxidative unhairing process by hydrogen peroxide, J. Am. Leather Chem. Assoc. 103 (2008) 1–6.
- [20] F. McDougall, P. White, M. Franke, P. Hindle, Integrated Solid Waste Management: A Life Cycle Inventory, Blackwell Science, Oxford, UK, 2001.
- [21] A. Hospido, M.T. Moreira, M. Martín, M. Rigola, G. Feijoo, Environmental evaluation of different treatment processes for sludge from urban wastewater treatments: anaerobic digestion versus thermal processes, Int. J. Life Cycle Assess. 10 (2005) 336–345.
- [22] K. Johansson, M. Perzon, M. Fröling, A. Mossakowska, M. Svanström, Sewage sludge handling with phosphorus utilization—life cycle assessment of four alternatives, J. Cleaner Prod. 16 (2008) 135–151.
- [23] E. Gasafi, L. Meyer, L. Schebek, Using life cycle assessment in process design, J. Ind. Ecol. 7 (2003) 75–91.
- [24] R. Watts, S. Kong, M. Dippre, W.T. Barnes, Oxidation of sorbed hexachlorobenzene in soils using catalyzed hydrogen peroxide, J. Hazard. Mater. 39 (1994) 33-47.
- [25] S. Lin, M.D. Gurol, Catalytic decomposition of hydrogen peroxide on iron oxide: kinetics, mechanism and implications, Environ. Sci. Technol. 32 (1998) 1417–1423.
- [26] J. Guertin, A., J.A. Jacobs, C.P. Avakian, Chromium(VI) Waste Stream Processing, Reducing Agents for Cr(VI) Chromium(VI) Handbook, CRC Press, USA, 2005, 371–482.
- [27] C. Remy, A. Ruhland, Ecological assessment of alternative sanitation concepts with life cycle assessment, Final report for subtask 5 of the demonstration project "Sanitation Concepts for Separate Treatment of Urine, Faeces and Greywater" (SCST), 2006, pp. 1–196.
- [28] J.M. Canela Ros, Anàlisis del cicle de vida de pell adobada al crom, Escola Universitària Enginyeria Tècnica, Escola Superior d'Adoberia, 1997, pp. 1–181.
- [29] K. Spanos, G. Skodras, P. Koukos, Composting of organic residues, Cost action E9 – Life cycle assessment of forestry and forest products (WG1-4), in: End of Life – Recycling, Disposal and Energy Production, 1998, pp. 1–6.
- [30] J.B. Guinèe, M. Gorreé, R. Heijungs, G. Huppes, R. Kleijn, A. de Koning, L. van Oers, A. Weneger, S. Suh, H.A. Udo de Haes, H. de Bruijn, R. van Duin, M. Huijbregts, Life cycle assessment. An operational guide to the ISO standards, CML, Leiden University, Leiden, 2001.
- [31] A. Arlt, L. Leible, H. Seifert, E. Nieke, B. Fürniss, Processing of sewage sludge for energetic purposes—a challenge for process technology, Bioprocess Solid Waste Sludge 2 (2002) 19–29.
- [32] L. Appels, J. Baeyens, J. Degreve, R. Dewil, Principles and potential of the anaerobic digestion of waste-activated sludge, Prog. Energy Combust. Sci. 34 (2008) 755–781.
- [33] R. Naidu, I.R. Willet, S. Mahimairaja, R. Kookana, K. Ramasamy (Eds.), Towards Better Management of Soils Contaminated with Tannery Waste, Australian Center for International Agricultural Research, Canberra, Australia, 2000, pp. 1–174.