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Life Cycle Assessment as a Tool for the Environmental Improvement of the Tannery Industry in Developing Countries

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A representative leather tannery industry in a Latin American developing country has been studied from an environmental point of view, including both technical and economic analysis. Life Cycle Analysis (LCA) methodology has been used for the quantification and evaluation of the impacts of the chromium tanning process as a basis to propose further improvement actions. Four main subsystems were considered: beamhouse, tanyard, retanning, and wood furnace. Damages to human health, ecosystem quality, and resources are mainly produced by the tanyard subsystem. The control and reduction of chromium and ammonia emissions are the critical points to be considered to improve the environmental performance of the process. Technologies available for improved management of chromium tanning were profoundly studied, and improvement actions related to optimized operational conditions and a high exhaustion chrome-tanning process were selected. These actions related to the implementation of internal procedures affected the economy of the process with savings ranging from US$ 8.63 to US$ 22.5 for the processing of 1 ton of wet salt hides, meanwhile the global environmental impact was reduced to 44−50%. Moreover, the treatment of wastewaters was considered in two scenarios. Primary treatment presented the largest reduction of the environmental impact of the tanning process, while no significant improvement for the evaluated impact categories was achieved when combining primary and secondary treatments.

Introduction

Tanning is the process of transforming the animal skin (a natural renewable resource) to leather (a market material used in the manufacture of a wide range of products). The increasing requirement of leather and its related products led to a global output that has risen by about 55% over the past 30 yr, with a trade value estimated to be approximately US$ 70 billion per year (*1*, *2*). Its major expansion has taken place in developing and new industrialized countries rather than in other developed economies where solid waste and wastewater treatments are not state of the art (*3*−*5*).

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The leather tanning process is composed of several batch stages associated with the consumption of large amounts of freshwater as well as the generation of liquid and solid wastes. Although tanning can be performed according to different procedures, most of the leather is obtained with chromium salts as the tanning agent. The wastewaters are characterized by significant organic load and remarkably high concentrations of inorganic compounds such as chromium, chloride, ammonia, sulfide, and sulfate (*6*−*8*). Leather processing produces chromium-bearing solid wastes in variable proportions (*9*).

The increasing consciousness for a cleaner environment demands immediate measures to control the pollution proceeding from tanneries (*1*). The main actions to reduce water consumption and solid waste generation are based on the efficient usage of raw materials and energy, optimal chemical utilization, recovery and recycling of waste, and substitution of harmful substances (*4*, *5*, *10*−*12*).

The European Community establishes an ecolabel scheme, which is intended to promote the design, production, marketing, and use of products and services with reduced environmental impact (*13*). These ecological criteria are described based on life cycle considerations (*14*). Ecolabel can promote the use of cleaner technologies in any sector that has been traditionally considered very pollutant as that of leather industry so that leather products are on the list of priority products selected for ecolabeling (*15*).

An useful tool to evaluate the environmental burdens associated with a product, process or activity is Life Cycle Analysis or Assessment (LCA). The objectives of this environmental management tool are the identification and quantification of the input and output flows of the process: energy and materials used and wastes released into the environment (*16*). The application of LCA in process selection, design, and optimization is gaining wider acceptance and methodological development (*17*−*19*).

Leather-related products such as footwear have been evaluated under LCA perspective (*20*, *21*). The tanning process turned out to be the most problematic stage, although a more profound study is necessary to quantify the associated impacts. In this work, LCA has been chosen as the methodology to study the environmental performance of the tanning process in a developing country such as Chile. The foci considered were the comprehensively quantification and evaluation of the impacts of the tanning process existing in the factory being studied as a basis to propose improvement actions. These measures were also taken under a multicriteria perspective, including both technical and economic analyses.

Methodology

LCA is compiled of several interrelated components: goal definition and scope, inventory analysis, impact assessment, and improvement assessment (Figure 1) (*22*).

Goal Definition and Scope. *Purpose.* The LCA of a tanning leather industry in Chile was performed from a "cradle to gate" perspective. The main objectives considered were the creation of a framework for quantifying the impacts of the chrome-tanning process performed in the tannery as well as the optimization of the process under a multi-criteria point of view.

Functional Unit. This unit provides a reference to which the inputs and outputs are related (*22*). The tannery under study has a process capacity of 330 ton of wet salted hides (t_{wsh}) per year for shoe production using a chrome-tanning process. (*5*). The functional unit chosen was 1 t_{wsh} input.

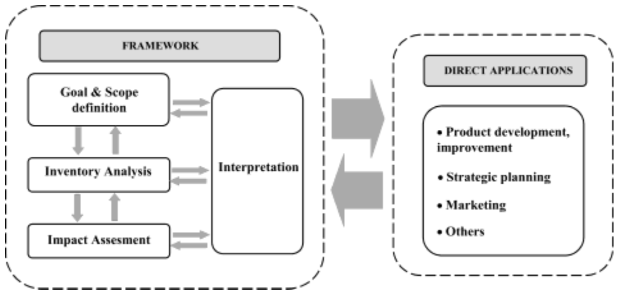

FIGURE 1. Phases of life cycle assessment.

System Boundaries. This term is defined as the interface between the product system and the environment or other product systems (*22*). The factory described in this work is representative of drum technology in beamhouse and splitting in the tanyard (*5*). The tanning process under study comprises all the steps from the raw hide to the “crust for finishing” leather using chromium as the core tanning compound (Figure 2). Three main subsystems were considered for the evaluation of the process: beamhouse, tanyard, and retanning as well as energy and chemicals supply. Pretanning and tanning processes alone are known to contribute more than 90% of the total pollution from leather processing (*23*, *24*). Dressing and finishing were not included because they strongly depend on the article produced, so it is rather difficult to obtain representative data and eventually would make a comparison of the whole life cycle impossible (*5*).

Data Quality. All the data related to the inputs and outputs of the process were obtained from the production site. The subsystems linked to chemical production were inventoried from bibliographic data: chromium and sodium salts data were collected from Milà et al. (*21*); sodium hydroxide, lime, and sulfuric acid production and wood furnace emissions data were taken from PRé Consultants Database (*25*−*29*). The electricity profile is of major importance as it broadly affects the environmental impacts assigned to energy-consuming steps. The electricity generation profile, obtained from available data from the Chilean Government (*30*), was considered. The assignment of the environmental loads associated to the different sources of electricity was made from BUWAL 250 database (*26*).

Life Cycle Inventory. A broad analysis of the input/output flows (I/O) was carried out for a Chilean tannery. A complete physical−chemical characterization of wastewater emissions (19 streams) was performed during a 1-yr period. Chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), settled materials (SM), total solids (TS), volatile solids (VS), total suspended solids (TSS), volatile suspended solids (VSS), sulfide (S^{2-}), sulfate (SO_4^{2-}), chromium (Cr), fats, chloride (Cl^-), soluble phosphorus (P), and ammonium ($N\text{-}NH_4^+$) concentrations were determined according to Standard Methods (*31*).

Impact Assessment. Impact assessment is a technical, quantitative, and/or qualitative process to characterize and assess the effects of the environmental burdens identified in the inventory (*16*). Damage-oriented impact assessment methodology has received attention in recent years (*32*−*35*). This approach provides not only characterization (potential impacts of impact categories such as climate change) but also damage assessment for safeguard subjects such as human health (*36*). This impact assessment was performed with the Ecoindicator 99 methodology, which reflects the state of art in LCA (*37*). This study comprises different phases, which are defined next:

Classification. The inventory data are assigned to categories that represent basic environmental issues (*38*). Three conditions affecting human and environment are considered:

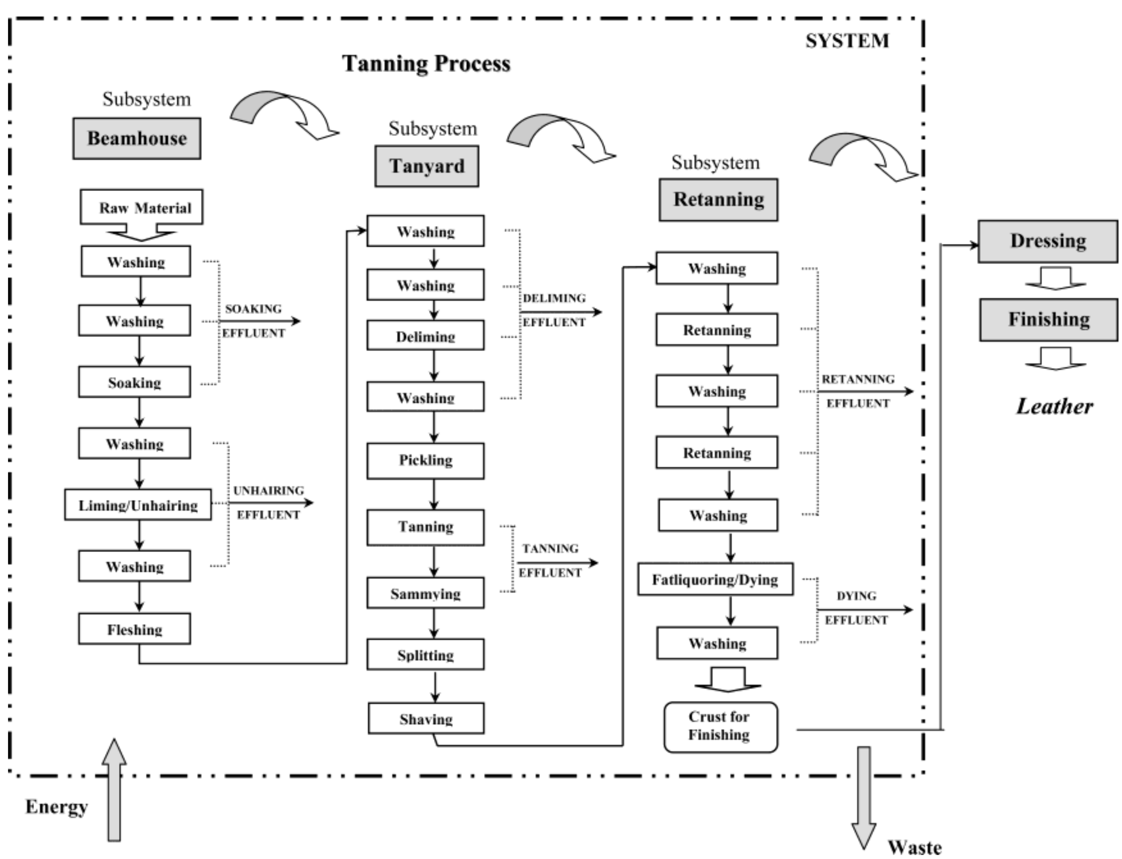

FIGURE 2. Flow sheet of leather tanning process.

TABLE 1. Beamhouse Inventory for 1 t_{wsh} Processing

Inputs

from technosphere		from environment	soaking	unhairing	total
materials and fuels (kg)		raw materials (kg)			
wet salt hide	1 000	water	4 420	6 085	10 505
NaOH	2				
biocide	4				
surfactants	9				
$Ca(OH)_2$	30				
NaHS	8				
Na_2S	8				
electricity (kWh)					
drums	14.65				
fleshing machine	23.63				

Outputs

to technosphere		to environment	soaking	unhairing	total
products and coproducts (kg)		emissions to water (kg)			
pelts	1 050	wastewater	3 245	6 280	10 065
fats	219	pH	7.1 ± 0.5	11.5 ± 1.2	10.1 ± 1.26
		COD	21.8 ± 2.7	65.3 ± 38.7	87.1 ± 38.9
		BO_5D	7.6 ± 1.9	16.6 ± 11.7	24.2 ± 11.9
		TN	1.3 ± 0.2	6.2 ± 4.0	7.5 ± 4.0
		$N\text{-}NH_4^+$	$3.0 \times 10^{-1} \pm 1.3 \times 10^{-1}$	$4.1 \times 10^{-1} \pm 1.5 \times 10^{-1}$	$7.0 \times 10^{-1} \pm 2.0 \times 10^{-1}$
		SO_4^{2-}	0.6 ± 0.1	1.1 ± 0.5	1.7 ± 0.5
		S^{2-}	$2.3 \times 10^{-3} \pm 0.3 \times 10^{-3}$	1.7 ± 1.5	1.7 ± 1.5
		fats & oil	2.6 ± 0.8	2.5 ± 1.1	5.1 ± 1.3
		Cl^-	55.2 ± 12.5	35.6 ± 20.5	90.7 ± 24.0
		Psol	$5.3 \times 10^{-2} \pm 1.1 \times 10^{-2}$	$7.6 \times 10^{-3} \pm 1.2 \times 10^{-3}$	$6.1 \times 10^{-2} \pm 1.1 \times 10^{-2}$
		TS	112.0 ± 14.3	97.1 ± 50.8	209.1 ± 52.8
		VS	11.5 ± 1.4	35.4 ± 22.4	46.9 ± 22.5
		TSS	8.0 ± 1.3	24.8 ± 16.8	32.7 ± 16.8
		VSS	5.5 ± 0.9	16.2 ± 10.7	21.8 ± 10.7
		SM	0.04 ± 0.06	0.56 ± 0.24	0.61 ± 0.25
		Cr	nd[a]	nd	nd
		CrVI	nd	nd	nd

[a] nd, not determined.

(i) Human health (HH). Categories associated to carcinogens, respiratory organics, respiratory inorganics, climate change, ozone layer, and radiation.

(ii) Ecosystem quality (EQ). Categories related to ecotoxicity, acidification/eutrophication, and land use.

(iii) Sufficient supply of resources (R). Categories related to minerals and fossil fuel supplies.

Characterization. The modeling and estimation of an environmental indicator for each category or issue are completed. Damages to HH are expressed in disability adjusted life years (DALY). Damages to EQ are expressed as potentially disappeared fraction (PDF) and potentially affected fraction (PAF) of species due to an environmental impact. The PDF and PAF values are then multiplied by the area size and the time period to obtain the damage. Damages to R are expressed as the surplus energy for the future mining of the resources.

Normalization. Normalization intends to perceive the relative magnitude for each environmental indicator under a nondimensional approach.

Valuation. Valuation permits us to weigh the contributions from the different impact categories so that they can be aggregated. HH and EQ are considered to have an equal importance, while R is considered to be half as important.

Improvement Assessment. The possibilities to upgrade the environmental performance of the system are identified and evaluated by the application of different improvement actions. The proposals will take into account the "hot spots" detected and will identify the basis of pollution-prevention opportunities. Technical and economic feasibility and treatment of the generated effluents will also be considered.

Results and Discussion

Life Cycle Inventory. A leather tannery plant using a chrome-based tanning process was evaluated (Figure 2). In the beamhouse stage, salt and dung are both eliminated from the preserved hides (soaking stage), hair is removed (unhairing stage), and hides are swollen. All these steps are carried out in drums (10 m^3 total volume), with intermediate washes between the different stages. Hides are finally fleshed in auxiliary equipment. The inventory data of the beamhouse subsystem are shown in Table 1. Thereafter, in the tanyard stage, the pelts are washed, and the remaining lime is removed (deliming stage). Afterward, pH is lowered to 4.0 to prepare the hides for the further tanning step (pickling stage). During the sammying stage, water is taken away from the tanned hide (termed as "wet blue" in the tanning industry), first by resting in trestle and later in mechanical sammying equipment. Before the shaving stage, the wet blue is immediately split to obtain material with a more uniform thickness, which will later imply lower amounts of residual shavings. The inventory data of the Tanyard subsystem are shown in Table 2. In the retanning section, the wet blue is retanned, dyed, and fat-liquored (Table 3). The energy supply used for water-heating facilities is considered as the fourth subsystem: wood furnace. The impact associated to chemical use is already included in the three main subsystems where they are used.

TABLE 2. Tanyard Inventory for 1 t_{wsh} Processing

inputs					
from technosphere		from environment			
			deliming	pickling	total
materials and fuels (kg)		raw materials (kg)			
pelts	1,050	water	6 490	450	6 930
ammonium sulfate	18.97				
sodium bisulfate	5.23				
pancreatic enzyme	3.15				
NaCl	52.3				
sodium formiate	10.46				
H_2SO_4	16				
chromium salt	63				
masking agents	15.8				
electricity (kWh)					
drums	25.42				
machine	44.94				

Outputs					
to technosphere		to environment			
			deliming (kg)	tanning (kg)	total (kg)
products and coproducts (kg)		emissions to water			
grain wet blue	355	wastewater	6 120	1 148	7 268
trimmings	37	pH	10.7 ± 0.3	3.6 ± 0.3	9.6 ± 0.4
shavings	17	COD	10.2 ± 0.7	7.5 ± 0.9	17.8 ± 1.1
split wet blue	371	BO_5D	3.5 ± 0.1	2.0 ± 1.5	5.5 ± 1.6
		TN	3.7 ± 0.1	1.0 ± 0.3	4.6 ± 0.3
		$N\text{-}NH_4^+$	2.0 ± 0.3	0.2 ± 0.01	2.2 ± 0.3
		SO_4^{2-}	12.9 ± 1.5	38.6 ± 9.3	40.5 ± 7.6
		S^{2-}	0.17 ± 0.05	$0.1 \times 10^{-3} \pm 0.1 \times 10^{-3}$	0.17 ± 0.05
		fats & oil	1.1 ± 0.3	0.1 ± 0.0	1.2 ± 0.3
		Cl^-	6.8 ± 1.1	19.1 ± 3.4	26.0 ± 3.6
		Psol	$2.2 \times 10^{-3} \pm 0.4 \times 10^{-3}$	$0.3 \times 10^{-3} \pm 0.3 \times 10^{-3}$	$2.5 \times 10^{-3} \pm 0.5 \times 10^{-3}$
		TS	32.5 ± 11.7	95.9 ± 14.3	128.3 ± 13.7
		VS	14.8 ± 4.5	17.7 ± 8.4	32.5 ± 9.0
		TSS	2.4 ± 0.1	0.8 ± 0.3	3.2 ± 0.3
		VSS	1.6 ± 0.1	0.5 ± 0.2	2.1 ± 0.2
		SM	$7.5 \times 10^{-3} \pm 8.8 \times 10^{-3}$	$4.5 \times 10^{-2} \pm 2.2 \times 10^{-2}$	$5.3 \times 10^{-2} \pm 2.4 \times 10^{-2}$
		Cr	nd[a]	$4.5 \times 10^{-3} \pm 1.1 \times 10^{-3}$	$4.5 \times 10^{-3} \pm 1.1 \times 10^{-3}$
		CrVI	nd	$2.5 \times 10^{-7} \pm 0.7 \times 10^{-7}$	$2.5 \times 10^{-7} \pm 0.7 \times 10^{-7}$
		emissions to air			
		NH_3	0.68	nd	0.68

[a] nd, not determined.

Impact Assessment. The analysis of the contribution of the different subsystems (beamhouse, tanyard, retanning, and wood furnace) to the impact categories is required to detect the hot spots. The results for the characterization step and damage assessment are shown in Table 4.

Carcinogens and ecotoxicity categories exhibit a high contribution of the tanyard and retanning subsystems (2.26×10^{-7} and 2.85×10^{-7} DALY; 7.3 and 2.59 PAF·m^2 yr, respectively). The main contribution to respiratory organics proceeds from the wood furnace subsystem (8.59×10^{-10} DALY). Respiratory inorganics and climate change categories are associated to energy consumption; both beamhouse and tanyard are the subsystems more dependent on the use of energy. Thus, they have larger impacts on the mentioned categories than retanning has. The contribution of the emissions of the wood furnace subsystem to climate change is slightly higher than the three subsystems associated with the process (0.836×10^{-7} DALY). In the acidification/eutrophication category, the ammonia airborne emission from deliming (tanyard) is the most significant aspect with the highest value (30.1×10^{-3} PDF·m^2 yr). Radiation and ozone layer categories have a minor significance. Minerals and fossil fuel categories present the largest contributions in the tanyard subsystem (1.37×10^{-4} and 0.215 MJ surplus, respectively), and the land use category is predominantly affected by the airborne emissions from the wood furnace subsystem (1.16×10^{-3} PDF·m^2 yr). Considering the damage assessment as the computation of all the individual contributions, all the damages are mainly produced by the Tanyard subsystem.

In terms of absolute value, one contribution to a certain impact category may appear to be very significant; however, when considering the total impact, this consideration could have a minor relevance. The normalization and weighting among the different categories may permit a more accurate evaluation. Results from the weighting among the damage assessment are briefly presented in Table 5. The damage to ecosystem quality (EQ) is the most relevant damage identified, with a percentual contribution to the global impact of 73%. Damage to resource (R) represents only the 9.2% of the global impact. Taking into account the weighting results, the relative contribution of the different substances in terms of percentage of the global environmental impact of the process can be calculated (Table 6). The chromium content of wastewater from tanyard and retanning subsystems accounts for significant toxicological impacts, so the contribution of chromium to ecosystem damage is noticeable (69.4%). In addition, Cr (VI) detected in these wastewaters provides a contribution of 6.76% to the overall impact. Ammonia air emissions from the deliming step are also significant (3.86%). Other pollutants

TABLE 3. Retanning and Dying Inventory for 1 t_{wsh} Processing

Inputs

from technosphere		from environment	deliming	pickling	total
materials and fuels (kg)		raw materials (kg)			
grain wet blue	355	water	3 545	1 990	5 535
surfactants	7.51				
sodium formiate	5.38				
fats	20.9				
chromium salt	14.2				
tanning extracts	39.6				
formic acid	3.6				
dye	1.4				
electricity (kWh)					
drums	13.95				

Outputs

to technosphere		to environment	retanning	dying	total
products and coproducts (kg)		emissions to water (kg)			
crust	420.9	wastewater	3 480	2 040	5 520
		pH	3.8 ± 0.5	3.7 ± 0.4	3.8 ± 0.7
		COD	19.1 ± 4.5	9.5 ± 7.3	28.6 ± 8.5
		BO_5D	3.0 ± 0.2	1.8 ± 0.1	4.7 ± 1.2
		TN	0.8 ± 0.1	0.14 ± 0.04	1.0 ± 0.2
		$N\text{-}NH_4^+$	0.28 ± 0.14	0.05 ± 0.01	0.33 ± 0.15
		SO_4^{2-}	18.2 ± 1.2	3.0 ± 2.9	21.24 ± 2.9
		S^{2-}	$1.0 \times 10^{-3} \pm 0.1 \times 10^{-3}$	$0.36 \times 10^{-3} \pm 0.01 \times 10^{-3}$	$1.4 \times 10^{-3} \pm 0.5 \times 10^{-3}$
		fats & oil	0.2 ± 0.1	0.30 ± 0.02	0.5 ± 0.1
		Cl^-	3.9 ± 0.2	0.8 ± 0.4	4.7 ± 1.1
		Psol	$2.5 \times 10^{-3} \pm 0.2 \times 10^{-3}$	$0.2 \times 10^{-3} \pm 0.1 \times 10^{-3}$	$2.7 \times 10^{-3} \pm 2.5 \times 10^{-3}$
		TS	48.7 ± 3.0	8.9 ± 1.8	57.6 ± 8.3
		VS	12.1 ± 1.9	4.2 ± 1.2	16.3 ± 4.1
		TSS	2.6 ± 0.2	0.5 ± 0.1	3.1 ± 0.8
		VSS	1.9 ± 0.1	0.49 ± 0.03	2.4 ± 1.0
		SM	0.07 ± 0.03	$3.0 \times 10^{-3} \pm 3.2 \times 10^{-3}$	0.07 ± 0.03
		Cr	$1.52 \times 10^{-3} \pm 0.35 \times 10^{-3}$	$0.09 \times 10^{-3} \pm 0.01 \times 10^{-3}$	$1.61 \times 10^{-3} \pm 0.35 \times 10^{-3}$
		CrVI	$1.1 \times 10^{-7} \pm 0.2 \times 10^{-7}$	$2.4 \times 10^{-7} \pm 0.6 \times 10^{-7}$	$3.5 \times 10^{-7} \pm 0.6 \times 10^{-7}$

TABLE 4. Characterization and Damage Assessment/Ecoindicator 99 (Average Value)

category	unit	beamhouse	tanyard	retanning	wood furnace	total
Characterization Step						
carcinogens	$DALY{\cdot}10^7$	0.182	2.26	2.85	0.0447	5.34
respiratory organics	$DALY{\cdot}10^{10}$	0.952	3.69	0.0345	8.59	13.27
respiratory inorganics	$DALY{\cdot}10^7$	1.73	2.38	0.0773	1.78	5.97
climate change	$DALY{\cdot}10^7$	0.284	0.367	0.035	0.836	1.52
radiation	$DALY{\cdot}10^{11}$	1.22	5.10			6.32
ozone layer	$DALY{\cdot}10^{11}$	1.44	1.34	0.0281	0.555	3.36
ecotoxicity	$PAF{\cdot}m^2\,yr$	0.0189	7.30	2.59	0.00346	9.91
acidification/ eutrophication	$PDF{\cdot}m^2\,yr{\cdot}10^3$	3.99	30.1	0.256	5.37	39.72
land use	$PDF{\cdot}m^2\,yr{\cdot}10^3$	0.231	0.659		1.16	2.05
minerals	MJ surplus$\cdot 10^4$	0.516	1.37		0.634	2.52
fossil fuels	MJ surplus$\cdot 10^1$	0.815	2.15	0.142	0.739	3.85
Damage Assessment						
human health	$DALY{\cdot}10^7$	2.20	5.01	2.96	2.67	12.84
ecosystem quality	$PDF{\cdot}m^2\,yr{\cdot}10$	0.0611	7.60	2.59	0.0688	10.32
resources	MJ surplus$\cdot$10	0.815	2.16	0.142	0.74	3.86

linked to energy consumption in the four subsystems have a secondary input to the environmental impacts of the process (less than 15%). The control and reduction of chromium and ammonia emissions will be the critical points to be considered for the improvement options.

Improvement Assessment. *Pollution Prevention Actions.* Technologies available for improved management of chromium tanning were profoundly studied (*23, 24, 39–42*). The proposed improvement actions were studied to combine environmental performance and economic viability (Figure 3). Chrome recovery is, from a chemical point of view, a simple process with excellent environmental results, but it needs careful analytical control and requires special equipment. However, the tanners in the present case study did not support this option, even though it has been successfully implemented in other tanneries. Other possibilities such as closed-loop systems and process innovations (i.e., an enzyme-assisted dehairing process and the biocatalyzed three-step tanning technique) had a similar acceptance. It is expected that the increasing concern for the environment would lead

TABLE 5. Weighting Step of Damage Assessment/Ecoindicator 99 (Average Value)[a]

damage	beamhouse	tanyard	retanning	wood furnace	total
human health	4.27	9.73	5.74	5.17	24.91
ecosystem quality	0.596	74.1	25.3	0.671	100.67
resources	2.74	7.24	0.476	2.49	12.95
total	7.61	91.07	31.52	8.33	138.53

[a] All values are multiplied by 10^3.

TABLE 6. Main Pollutants and Their Percentual Contribution to the Overall Environmental Impact

	beamhouse	tanyard	retanning	wood furnace	total
Cr		51.20	18.20		69.40
CrVI		2.84	3.92		6.76
NH_3		3.86			3.86
SO_x	2.0	0.45	0.04		2.49
CO_2	0.39	0.48	0.04	1.11	2.02
coal	0.84	1.12	0.21	0.22	2.39
natural gas	0.63	3.73	0.13	0.11	4.60
crude oil	0.35	0.30	0.008	1.33	1.99
total	4.21	63.98	22.55	2.77	93.51

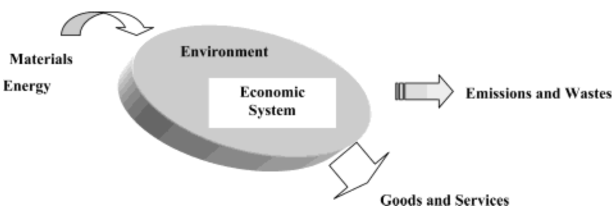

FIGURE 3. Environmental system analysis.

to a global challenge, these practices and would become widespread.

The specific actions selected were as follows:

Action A1: Optimized operational conditions of the chrome-tanning process. The most conventional tanning agent corresponds to water-soluble Cr(III) in the form of chromium sulfate. While this salt presents acute toxicity to aquatic species (*43*), once it is absorbed by the hides during the tanning process, Cr(III) becomes substantially fixed into the leather matrix, which prevents its lixiviation, and no measurable toxicity is apparent. The “classic” chromium tanning carried out in long floats is characterized by poor exhaustion; 30−50% of the chromium being lost with the wastewater. Data obtained from a mass balance show a chromium exhaustion of 65% for the case study. This value can be raised to 90% Cr uptake by altering effortless operational parameters (*39*, *44*−*46*): temperature set to 50 °C, pH adjusted to 4.5, and float level controlled.

Action A2: Optimized operational conditions of the chrome-tanning process (action A1) and auditing lime and $(NH_4)_2SO_4$ addition. An excess of lime is added during the unhairing stage to obtain a saturated solution since only dissolved slaked lime is active for the unhairing process. Residual lime is removed by $(NH_4)_2SO_4$ in the deliming process. When using ammonium salts for deliming, the ammonium reacts with the alkaline liquors to form ammonia gas, which is released to air. Auditing of lime and $(NH_4)_2SO_4$ additions provide savings in both chemical products and release of ammonia (*12, 44*).

Action B1: High exhaustion chrome-tanning process. A new chrome-tanning step with a combination of Alutan (an aluminum-based compound, accounting for 12% Al_2O_3) and basic chromium sulfate is proposed (*39*, *47*). With this action, the chrome absorption achieved is around 90% during the tanning, and the spent solution can be reused in pickling (*4*).

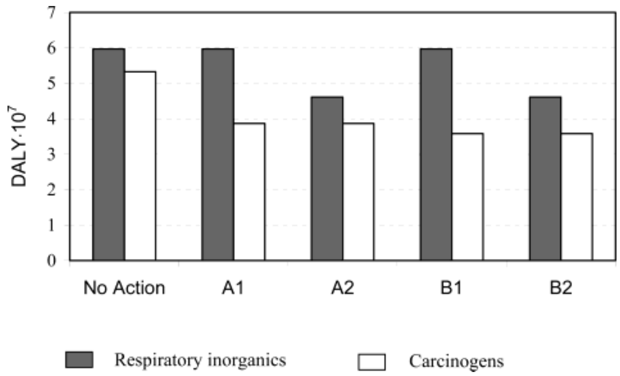

FIGURE 4. Main categories of damage to human health: characterization of the actions.

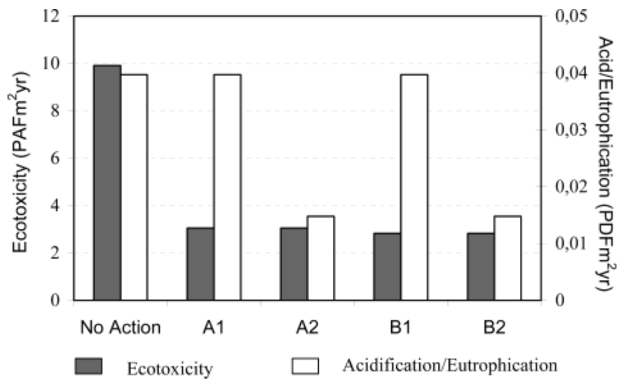

FIGURE 5. Main categories of damage to ecosystem quality: characterization of the actions.

Action B2: High exhaustion chrome-tanning process (action B1) combined with auditing of lime and $(NH_4)_2SO_4$ addition.

The environmental effects associated to the proposals permit us to detect the possibilities of improvement. In terms of HH damage, the main categories were respiratory inorganics and carcinogens. Results from the characterization of the actions are summarized in Figure 4. Action A1 clearly diminishes the carcinogens category value (once chromium wastewater content is reduced, the contribution of tanyard to human toxicity decreases considerably), while respiratory inorganics are unaffected. Action B1 also decreases the impact of the carcinogens category. Ammonia emission from the deliming has the most important effect in relation to the respiratory inorganics category. Actions A2 or B2 considerably reduce the impact in terms of this category.

In relation to EQ, two categories are studied in detail because they represent nearly total damage: ecotoxicity and acidification/eutrophication (Figure 5). Regarding the ecotoxicity category, all the actions proposed show a great effect since chromium discharge was reduced. Actions A2 or B2 also effectively reduce the impact of the acidification/eutrophication category by avoiding ammonia emission from deliming. Therefore, considering the reduction of chromium and ammonia emissions, Action B2 appears to be the best of the proposed practices.

Wastewater Treatment. Wastewater and solid waste treatments are not state of art in most developing countries. The factory evaluated is an example of this deficiency since it discharges wastewater directly into a nearby river. The treatment requirements for the wastewaters characteristic of this type of industry are high, and setting the applicable

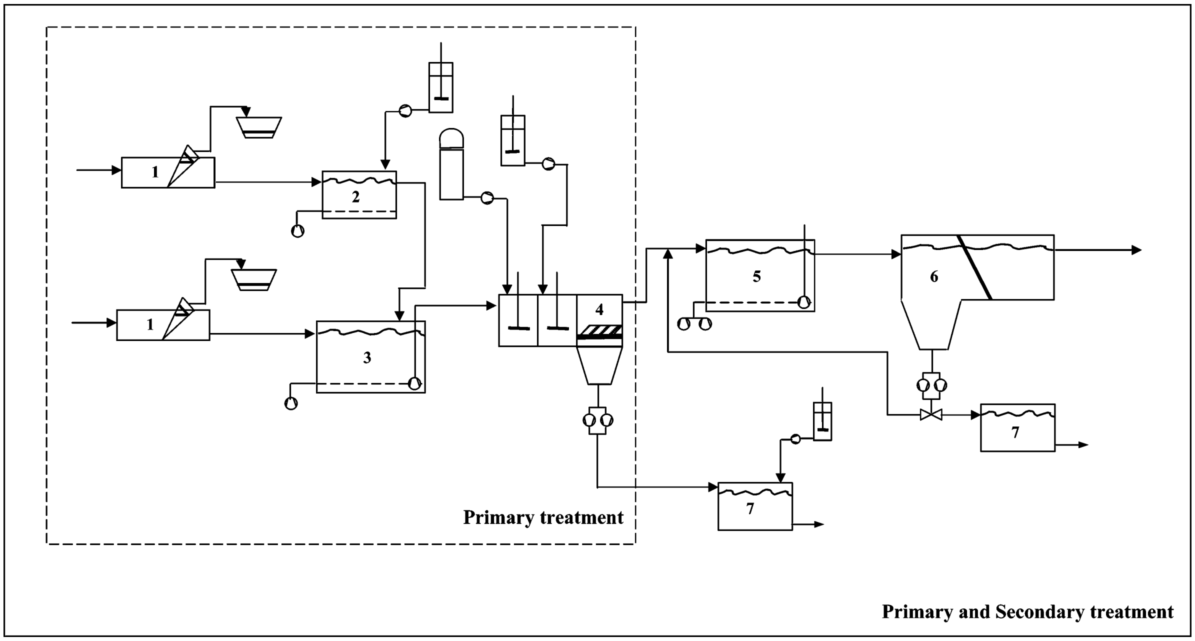

FIGURE 6. Flow sheet of the proposed wastewater treatment plant. 1, trash racks; 2, sulfide oxidation; 3, homogenization; 4, chemical setting; 5, biological reactor; 6, secondary setting; 7, sludge thickeners.

discharge standards is quite difficult and calls for a systematic evaluation (*6*). The actions proposed can effectively reduce the environmental impact of the tanning process; however, regulatory emission discharges must be reflected and respected. Thus, the implementation of a wastewater treatment plant has to be considered to satisfy legal requirements. To evaluate the impact of the wastewater treatment system, a Galician tannery facility (with effluent characteristics being very similar to the Chilean one) was inventoried and analyzed.

Figure 6 shows the flow diagram of the proposed wastewater treatment plant. The wastewater from the unhairing step must be segregated and pretreated in order to remove large solids. The sulfide contents of the unhairing effluent can be reduced by means of aeration in the presence of a catalyst such as a manganese salt. Other effluents, after the pretreatment, are to be discharged to the equalization tank. Homogenization often functions as a non-recyclable biological reactor and provides sizable COD removal (*8*). This argument is supported by the data obtained from the wastewater treatment plant of the Galician tannery. The pretreatment step provides a percentage of SS removal of 85%, which accounts for a parallel COD and chromium removal. Chemical settling with $FeCl_3$ and a cationic polyelectrolyte (see inventory data in Table 7) generates an ideal effluent with a COD around 1000 mg/L and virtually no SS or Cr. Active sludge can remove between 84 and 92% of the BOD at a hydraulic retention time of 6 h and mean cell residence time of 3−10 d, conditions that will be set depending upon the temperature ranging from 10 to 17 °C (*1*). Sludge thickeners are used to reduce the total volume of sludge for disposal.

LCA has been used by several authors to estimate the environmental loads from wastewater systems (*48*−*55*). Two scenarios of wastewater treatment were considered to evaluate their cost and environmental performance (see Figure 6):

(i) Removal of solids by trash racks, sulfide oxidation, homogenization, and chemical setting (primary treatment).

(ii) Primary system with a further biological treatment.

Chemicals consumption, electricity demand, and outputs to the technosphere were obtained from analysis of the Galician tannery. Selected parameters of the inventory results are shown in Table 7. Regarding to the primary treatment, the total amounts discharged associated to the effluent concentrations (i.e., COD) exceed the Chilean and European legal requirements. After the biological treatment (primary and secondary treatments), the effluent could be legally discharged under the European point of view. Note that the main electricity consumption is related to biological treatment (53 kWh).

Economical versus Environmental Assessment. A sustainable tanning process is defined as a socially acceptable and cost-effective method. Since LCA only includes environmental aspects, it needs to be complemented with the evaluation of the costs associated to the implementation of the proposed improvement actions (*56*). The action costs estimated in this analysis were restricted to internal direct costs. Direct costs include expenses related to capital expenditures for building, equipment, renewals, etc. and operating costs (such as operating labor, materials, utilities, maintenance, and waste disposal). External costs, such as the cost of landfill use to dispose of the waste (i.e., alternative uses are precluded) were not included in the analysis.

The environmental consequences related to the costs of the different actions proposed (procedures in tannery and wastewater treatment) are drawn in Figure 7, which may provide valuable information for decision-making. All the actions toward the objective of the cleaner production (actions A1, A2, B1, and B2) offer savings on the costs of the process. The fixed assets necessary to be acquired do not have a significant depreciation quote, and the energy consumption of the measures considered is irrelevant. The technological implementation reduces chemical consumption and enhances the economy of the process for both conventional optimized leather processing (actions A1 and A2) and advanced leather tanning process (actions B1 and B2). Environmental global impact is effectively reduced by actions A1, A2, B1, and B2 to values ranging from 44 to 50% of the overall environmental impact of the existing process. The actions also provide cost saving of US$ ranging from 8.63 (action A2) to 22.5 (action B1) for the processing of 1 t of wet salt hides (t_{wsh}).

The wastewater treatment of the process with action B2 has been also considered and evaluated. The weighting step shows that the total environmental impact of action D (primary and secondary treatments) has a similar significance

TABLE 7. Inventory Results (Selected Parameters) for the Treatment Systems

Primary Treatment

inputs from technosphere		outputs to environment	
materials and fuels (kg)		emissions to water (kg)	
MnO_2	0.6	wastewater	13 000
NaOH 10%	17	pH	7.5
$FeCl_3$	1.5	COD	13.00
polyelectrolyte	9.2×10^{-3}	BOD	6.89
wastewater[a]	13 000	TSS	2.04
pH	8.28	TN	5.81
COD	133.5	Cr	0.08
BOD	34.42	solid waste (kg)	
TSS	39.07	non-chromium containing	15
TN	13.11	chromium containing	35
Cr	1.86		
electricity (kWh)			
equipment	20		

Primary and Secondary Treatments

inputs from technosphere		outputs to environment	
materials and fuels (kg)		emissions to water (kg)	
MnO_2	0.6	wastewater	13 000
NaOH 10%	17	pH	7.5
$FeCl_3$	1,5	COD	1.69
polyelectrolyte	$9.2{\cdot}10^{-3}$	BOD	0.90
wastewater[a]	13,000	TSS	2.00
pH	8.28	TN	1.74
COD	133.5	Cr	0.08
BOD	34.42	solid waste (kg)	
TSS	39.07	non-chromium containing	30
TN	13.11	chromium containing	75
Cr	1.86		
electricity (kWh)			
equipment	73		

[a] Minimization of water consumption by washes optimization has been considered (*4*, *25*).

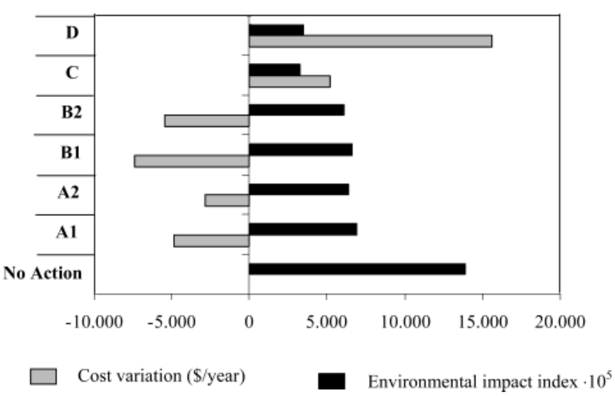

FIGURE 7. Environmental and cost indexes of the actions. Action A1, improved operational conditions of the chrome-tanning process. Action A2, action A1 and auditing lime and $(NH_4)_2SO_4$ addition. Action B1, high exhaustion chrome-tanning process. Action B2, action B1 and auditing lime and $(NH_4)_2SO_4$ addition. Action C, action B2 and primary treatment. Action D, action B2 and primary and secondary treatments.

to the value obtained when only action C (primary treatment) is considered. Despite the fact that no improvement on the environmental index is achieved by the application of the biological treatment, a significant increase of costs is associated to its implementation.

The major objective of LCA has to be the development of criteria for promoting sustainable management, production, and treatment systems especially within small- and medium-sized enterprises so that it can be the tool for identifying ecoproducts and promoting the use of cleaner technologies.

The accomplishment of cleaner technologies by tanneries depends on the demonstrated reduction of the emission loads with quantifiable economical benefits referred to product quality improvement, material, or cost reduction. The options proposed, which present ease of application with the minimum additional investments, provide not only a large reduction of the environmental impacts but also a reduction of operational costs and low cost of implementation, which makes their realization more viable. Further research must be done to demonstrate improved environmental performance and economy of process innovations.

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Literature Cited

(1) Ram, B.; Bajpai, P. K.; Parwana, H. K. *Process Biochem.* **1999**, *35*, 255−265.

(2) Ramasami, T.; Sreeram, K. J.; Gayatri, R. *Sources of pollution in tanneries, mitigation and case studies in Unit 1: Legal requirements. Manual on design, operation and maintenance of tannery effluent treatment plants*; RePO-UNIDO: Chenai, India, 1999.

(3) Sykes, R. *Leather* **1995**, *197*, 17−22.

(4) Rao, J. R.; Chandrababu, N. K.; Muralidharan, C.; Balachandran, U. N.; Rao, P. G.; Ramasami, T. *J. Cleaner Prod.* **2003**, *11*, 591−599.

(5) Konrad C.; Lorber, K. E.; Méndez, R.; López, J.; Muñoz, M.; Hidalgo, D.; Bornhardt, C.; Torres, M.; Rivela, B. *J. Soc. Leather Technol. Chem.* **2002**, *86*, 18−25.

(6) Tünay, O.; Kabdasli, Y.; Orhon, D.; Ates, E. *Water Sci. Technol.* **1995**, *32*, 1−9.

(7) Jochimsen, J. C.; Jekel, M. R. *Water Sci. Technol.* **1997**, *35*, 337−345.

(8) Ates, E.; Orthon, D.; Tünay, O. *Water Sci. Technol.* **1997**, *36*, 217−223.
(9) Rao, J. R.; Thanikaivelan, P.; Sreeram, K. J.; Nair, B. U. *Environ. Sci. Technol.* **2002**, *36*, 1372−1376.
(10) Kabdasli, I.; Tünay, O.; Orhon, D. *Water Sci. Technol.* **1999**, *40*, 261−267.
(11) Tünay, O.; Kabdasli, I.; Orhon, D.; Cansever, G. *Water Sci. Technol.* **1999**, *40*, 237−244.
(12) Integrated Pollution Prevention and Control (IPPC). *Reference Document on Best Available Techniques for the Tanning of Hides and Skins*; Institute for Prospective Technological Studies, Technologies for Sustainable Development, European IPPC Bureau: 2001; accessed at http://eippcb.jrc.es/pages/FActivities.htm.
(13) Regulation (EC) 1980/2000 of the European Parliament and of the Council of 17 July 2000 on a revised community ecolabel award scheme.
(14) Environment 2010. *Our Future, Our Choice*; The Sixth Environment Action Programme of the European Community 2001−2010; Decision 1600/2002/EC of the European Parliament and of the Council of 22 July 2002.
(15) The EU Ecolabel. *Prioritisation of New Eco-label Product Groups. A discussion paper—November 2002*; Interim report of the European Commission; accessed at europa.eu.int/ecolabel.
(16) Consoli, F. *Guidelines for Life Cycle Assessment: A code of practice*; SETAC: Sesimbra, 1993.
(17) Clift, R. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 347−350.
(18) Clift, R. *Process Saf. Environ.* **1998**, *76* (B2), 151−160.
(19) Azapagic, A. *Chem. Eng. J.* **1999**, *73*, 1−21.
(20) Milà, Ll.; Domènech, X.; Rieradevall, J.; Fullana, P.; Puig, R. *Int. J. Life Cycle Assess.* **1998**, *3* (4), 203−208.
(21) Milà, Ll.; Domènech, X.; Rieradevall, J.; Fullana, P.; Puig, R. *Int. J. Life Cycle Assess.* **2002**, *7* (1), 39−46.
(22) International Standard. ISO 14040, 1997.
(23) Thanikaivelan, P.; Rao, J. R.; Nair, B. U.; Ramasami, T. *Environ. Sci. Technol.* **2003**, *37*, 2609−2617.
(24) Thanikaivelan, P.; Rao, J. R.; Nair, B. U.; Ramasami, T. *Environ. Sci. Technol.* **2002**, *36*, 4187−4194.
(25) BUWAL 132. Oekobilanz von Packstoffen, Stand 1990; Schriftenreihe Umwelt 132; BUWAL 3003: Bern, 1990.
(26) BUWAL 250. Ökoinventare für Verpackungen; Schriftenreihe Umwelt 250; Bern, 1996.
(27) PWMI Report 6 PVC APME. Ecoprofiles of the European plastics industry, report 6, Polyvinyl chloride, April 1994.
(28) PWMI Report 5, Allocation APME. Ecoprofiles of the European plastics industry, report 5, Coproduct allocation in chlorine plants, April 1994.
(29) ETH-ESU. *Öko-inventare von Energiesystemen*, 3rd ed.; Frischknecht, et al., Eds.; 1996 (German language only); accessed at www.energieforschung.ch.
(30) Accessed at www.economia.cl.
(31) APHA-AWWA-WPCF. *Standard Methods for Examination of Water and Wastewater*, 17th ed.; APHA: Washington, 1989.
(32) Erlandsson, M.; Lindfors, L. *Int. J. Life Cycle Assess.* **2003**, *8* (2), 65−73.
(33) Hertwich, E. G.; Hammitt, J. *Int. J. Life Cycle Assess.* **2001**, *6* (5), 265−272.
(34) Seppälä, J.; Hämäläinen, R. P. *Int. J. Life Cycle Assess.* **2001**, *6* (4), 221−218.
(35) Goedkoop, M.; Hofsteletter, P.; Müller-Wenk, R.; Spriemsma, R. *Int. J. Life Cycle Assess.* **1998**, *3* (6), 352−360.
(36) Itsubo, N. *Int. J. Life Cycle Assess.* **200**2, *7* (3), 178.
(37) Goedkoop, M.; Spriensma, R. *The eco-indicator 99 -A damage oriented method for life cycle impact assessment*; Methodology Report; Pré Consultants B.V., 2000.
(38) *Life-Cycle Impact Assessment: The State-of-the-Art*; Report of the SETAC Life Cycle Assessment (LCA) Impact Assessment Workgroup, SETAC LCA Advisory Group; Society of Environmental Toxicology and Chemistry (SETAC) and SETAC Foundation for Environmental Education: Pensacola, FL, 1998.
(39) Sreeram, K. J.; Ramasami, T. *Resour. Conserv. Recycl.* **2003**, *38*, 185−212.
(40) Thanikaivelan, P.; Rao, J. R.; Nair, B. U.; Ramasami, T. *J. Am. Leather Chem. Assoc.* **2003**, *11*, 79−90.
(41) Thanikaivelan, P.; Rao, J. R.; Nair, B. U.; Ramasami, T. *J. Am. Leather Chem. Assoc.* **2003**, *98*, 173−184.
(42) Madhan, B.; Fathima, N. N.; Rao, J. R.; Subramanian, V.; Nair, B. U.; Ramasami, T. *J. Am. Leather Chem. Assoc.* **2003**, *98*, 263−272.
(43) Cooman, K.; Gajardo, M.; Nieto, J.; Bornhardt, C.; Vidal, G. *Environ. Toxicol.* **2003**, *18*, 45−51.
(44) CONAMA (Environmental National Commission). *Guía para el control y prevención de la contaminación industrial*: *Curtiembre* (*Guide for control and prevention of industrial pollution*: *Tannery*); Santiago, Chile, 1999; accessed at http://www.conama.cl/portal/1255/articles-26240_pdf_curtiembres.pdf.
(45) Covington, A. D. *J. Am. Leather Chem. Assoc.* **1991**, *86*, 376−405.
(46) Covington, A. D. *Chem. Soc. Rev.* **1997**, *26*, 111−26.
(47) Ramasami, T.; Rao, J. R.; Chandrababu, N. K.; Parthasarathi, K.; Rao, P. G.; Saravanan, P.; Gayatri, R.; Sreeram, K. J. *J. Soc. Leather Technol. Chem.* **1999**, *83*, 39−45.
(48) Lundin, M.; Bengtsson, M.; Molander, S. *Environ Sci Technol* **2000**, *34*, 180−186.
(49) Roeleved, P. J.; Klapwijk, A.; Eggels, P. G.; Rulkens, W. H.; Starkenburg, W. *Water Sci. Technol.* **1997**, *35*, 221.
(50) Emmerson, R. H. C.; Morse, G. K.; Lester, J. N.; Edge, D. R. *J. Inst. Water Environ. Manage.* **1995**, *9*, 317.
(51) Matsuhashi, R.; Sudoh, O.; Nakane, K.; Hidenari, Y.; Nakayarna, S.; Ishitani, H. Life cycle assessment of sewage treatment technologies. Presented at IAWQ conference on “Sludge—Waste or Resource?”, Czestochowa, Poland, June 26−28, 1997.
(52) Neumayr, R.; Dietrich, R.; Steinmüller, H. Life cycle assessment of sewage sludge treatment. *Proceedings of the 5th SETAC Annual Conference*, Brussels, December 1997.
(53) Mels, A. R.; Nieuwenhuijzen, A. F.; van der Graaf, J. H. J. M.; Klapwijk, B.; de Koning, J.; Rulkens, W. H. *Suistainability criteria as a tool in the development of new sewage treatment methods. Options for closed water systems: sustainable water management*; Wageningen, March 1998.
(54) Ødegaard, H. *Vatten* **1995**, *51*, 291.
(55) Dennison, F. J.; Azapagic, A.; Clift, R.; Colbourne, J. S. Assessing management options for sewage treatment works in the context of life cycle assessment. *Proceedings of the 5th SETAC Annual Conference*, Brussels, December 1997.
(56) Lundin, M.; Morrison, G. M. *Urban Water* **2002**, *4*, 145−152.

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