

# Treatment of Tannery Wastewater

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## 1 Introduction

*Manufacturing of leather, leather goods, leather boards and fur produces numerous by-products, solid wastes, high amounts of wastewater containing different loads of pollutants and emissions into the air. The uncontrolled release of tannery effluents to natural water bodies increases health risks for human beings and environmental pollution. Effluents from raw hide processing tanneries, which produce wet-blue, crust leather or finished leather contain compounds of trivalent chromium (Cr) and sulphides in most cases. Organic and other ingredients are responsible for high BOD (Biological Oxygen Demand) and COD (Chemical Oxygen Demand) values and represent an immense pollution load, causing technical problems, sophisticated technologies and high costs in concern with effluent treatment.*

## 2 Leather production

As an average of the years 1994 to 1996, globally approximately 5.5 Mio. t of raw hides on a wet salted basis were processed to yield about 0.46 Mio. t of heavy leather and about 940 Mio. m<sup>2</sup> of light leather, including split leather. In comparison, Europe produced about 0.074 Mio. t of heavy leather and about 240 Mio. m<sup>2</sup> of light leather. At the same time, world-wide 0.62 Mio. t of raw skins on a dry basis were converted into almost

385 Mio. m<sup>2</sup> of sheep and goat leather. The light leather production from goat and sheepskins yielded approximately 99 Mio. m<sup>2</sup> in Europe. [2]

80-90% of the world-wide tanneries use Cr (III) salts in their tanning processes. In some parts of the world, the Cr (III) is obtained from Cr (VI) species, which are a hundred times more toxic, but generally tannery effluents are unlikely to contain this form.

**Figure 1: Small-scale leather processing in Morocco**



## The tanning process

The production processes in a tannery can be split into four main categories:

- hide and skin storage and beamhouse operations,
- tanyard operations,
- post-tanning operations and
- finishing operations.

During the tanning process at least about 300 kg chemicals (lime, salt, etc.) are added per ton of hides [6].

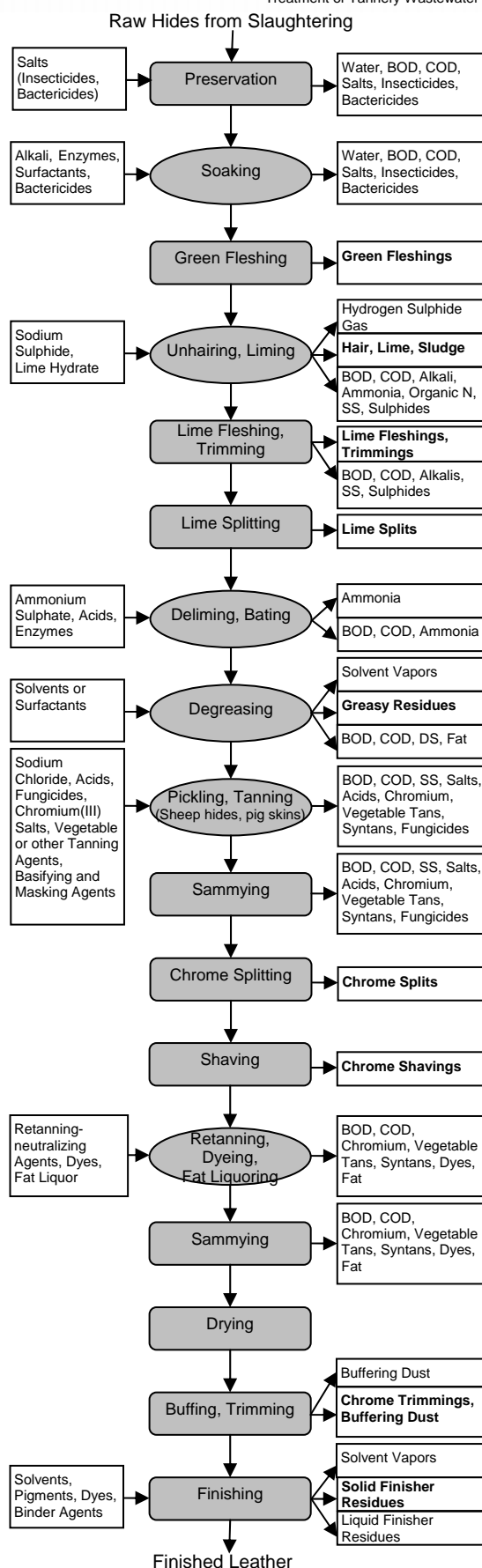
In the following the different steps of a typical tanning process and important aspects concerning the wastewater emergence are described in more detail:

The following figure provides an overview on the steps of leather processing (Source: [3]).

### a) Pretanning (Beamhouse operations)

Cleaning and conditioning hides and skins produce the biggest part of the effluent load.

- Soaking:** The preserved raw hides regain their normal water contents. Dirt, manure, blood, preservatives (sodiumchloride, bactericides), etc. are removed.
- Fleshing and trimming:** Extraneous tissue is removed. Unhairing is done by chemical dissolution of the hair and epidermis with an alkaline medium of sulphide and lime. When after skinning at the slaughterhouse the hide appears to contain excessive meat, fleshing usually precedes unhairing and liming. Liming and unhairing produce the effluent stream with the highest COD value.



- *Deliming and Bating*: The unhaired, fleshed and alkaline hides are neutralised with acid ammonium salts and treated with enzymes, similar to those found in the digestive system, to remove hair remnants and to degrade proteins. During this process hair roots and pigments are removed. This results in the major part of the ammonium load in the effluents.
- *Pickling*: Pickling increases the acidity of the hide to a pH value of 3 by addition of acid liquor and salts, enabling chromium tannins to enter the hide. Salts are added to prevent the hide from swelling. For preservation purposes, 0.03-2% by weight of fungicides and bactericides are usually applied.
- *Degreasing*: Normally performed together with soaking, pickling or after tanning, degreasing is performed by organic solvents or surfactants, leading to a higher COD value in the effluent.
- *Vegetable tanning*: Vegetable tanning is usually accomplished in a series of vats (first the rocker-section vats in which the liquor is agitated and second the lay-away vats without agitation) with increasing concentrations of tanning liquor. Vegetable tannins<sup>1</sup> are polyphenolic compounds of two types: hydrolysable tannins (i.e. chestnut and myrobalan<sup>2</sup>) which are derivatives of pyrogallols<sup>3</sup> and condensed tannins (i.e. hemlock and wattle) which are derivatives from catechol<sup>4</sup>. In some cases as much as 50% by weight of tannin is incorporated into the hide.

### c) Wet Finishing (Post-Tanning):

The wet finishing processes are sometimes performed in one single float. Chromium tanned hides or Wetblue are often retanned - during that process the desirable properties of more than one tanning agent are combined - and treated with dye and fat to obtain the proper filling, smoothness and colour. Before actual drying is allowed to take place, the surplus water is removed to make the hides suitable for splitting and shaving. Splitting and shaving is done to obtain the desired thickness of the hide. The composition of pollutants in the wet finishing effluent is complex due to the presence of dyes, fat liquors and combined tanning agents, but the total amounts generated are smaller than in prior steps and often not considered as significant.

### b) Tanning (Tanyard operations):

Principally, there are two possible processes:

- *Chrome tanning*: After pickling, when the pH value is low, chromium (III) salts are added. To fixate the chromium, the pH is slowly increased through addition of a base. The process of chromium tanning is based on the cross-linkage of chromium ions with free carboxyl groups in the collagen. It makes the hide resistant to bacteria and high temperature. The chromium-tanned hide contains about 2-3% by dry weight of Cr (III). Wetblue, i.e. the raw hide after the chrome-tanning process, has about 40% of dry matter.

<sup>1</sup> The vegetable tanning agents used are typically 15-70% of commercial extract, often sulphited, then spray dried or concentrated. [2]

<sup>2</sup> myrobalan nut: fruit of *Terminalia chebuka* (Asian tree), used in medicines, for ink/dye production and for tanning leather

<sup>3</sup> pyrogallol = pyrogallic acid; weak acid, also used e.g. as developer in photography

<sup>4</sup> (catechu): astringent extract of Malayan plant *gambir* or similar vegetable extract

#### d) Finishing

The crust that results after retanning and drying, is subjected to a number of finishing operations. The purpose of these operations is to make the hide softer and to mask small mistakes. The hide is treated with an organic solvent or water based dye and varnish. The finished end product has between 66 and 85% by weight of dry matter. Environmental aspects are mainly related to the finishing chemicals which can also reach effluent water.

### 3 Wastewater production and treatment

Table 1 provides an overview on water consumption in individual processing operations during the tanning process. Depending on the type of applied technology (conventional or advanced) the water consumption varies extremely. Technologies that can be regarded as advanced in comparison to conventional methods involve processes usually termed low-waste or cleaner technologies (high exhaustion, chrome fixing). Mainly in dry regions, where water supply is limited, this factor plays an important role.

**Table 1: Water consumption in individual processing operations (C-conventional technology, A-advanced technology [1])**

Operation	Discharge (m <sup>3</sup> /t raw hide)	
	C	A
Soaking	7-9	2.0
Liming	9-15	4.5
Deliming, Bating	7-11	2.0
Tanning	3-5	0.5
Post-tanning	7-13	3.0
Finishing	1-3	0
Total	34-56	12

In addition to the water required for individual processing operations, a certain amount of water is used in pasting/vacuum dryers, for cleaning, or sanitary and similar purposes. The minimum volume required is 2-3 m<sup>3</sup>/t raw hide under conditions of very good housekeeping.

Table 2 summarizes the pollution loads discharged in effluents from individual processing operations during the tanning process.

#### 3.1 Wastewater treatment

Tanning industry is one of the oldest industries of the world and the problem of treatment and disposal of these wastes is probably as old as the industry itself.

Tanneries wastewater effluent is treated in many different ways. There are situations in which an individual tannery applies all the below-described wastewater treatment steps on site. In other situations an individual tannery may apply (on site) only pre-treatment or a part pre-treatment or no treatment at all, sending the effluent to a centralised effluent treatment plant. Nevertheless, a treatment is necessary due to the wide range of toxic effects on the environment caused by untreated tannery effluents and sludges.

The following treatment steps are necessary and will be described in more detail afterwards:

- Mechanical treatment
- Effluent treatment
- Post-purification, sedimentation and sludge handling

##### 3.1.1 Mechanical treatment

Usually the first treatment of the raw effluent is the mechanical treatment that includes screening to remove coarse material. Up to 30-40% of gross suspended solids in the raw waste stream



can be removed by properly designed screens. Mechanical treatment may also include skimming of fats, grease, oils and gravity settling. After mechanical treatment, physico-chemical treatment is

usually carried out, which involves the chrome precipitation and sulphide treatment described in chapter 3.1.2 and 4.

**Table 2: Summary of pollution loads discharged in effluents from individual processing operations (C-conventional technology, A-advanced technology [1])**

Operation	Technology	Pollution load (kg/t raw hide)								
		SS	COD	BOD <sub>5</sub>	Cr	S <sup>2-</sup>	NH <sub>3</sub> -N	TKN	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Soaking	C	11-17	22-33	7-11	-	-	0.1-0.2	1-2	85-113	1-2
	A	11-17	20-25	7-9	-	-	0.1-0.2	1-2	5-10	1-2
Liming	C	53-97	79-122	28-45	-	3.9-8.7	0.4-0.5	6-8	5-15	1-2
	A	14-26	46-65	16-24	-	0.4-0.7	0.1-0.2	3-4	1-2	1-2
Deliming, Bating	C	8-12	13-20	5-9	-	0.1-0.3	2.6-3.9	3-5	2-4	10-26
	A	8-12	13-20	5-9	-	0-0.1	0.2-0.4	0.6-1.5	1-2	1-2
Tanning	C	5-10	7-11	2-4	2-5	-	0.6-0.9	0.6-0.9	40-60	30-55
	A	1-2	7-11	2-4	0.05-0.1	-	0.1-0.2	0.1-0.2	20-35	10-22
Post-Tanning	C	6-11	24-40	8-15	1-2	-	0.3-0.5	1-2	5-10	10-25
	A	1-2	10-12	3-5	0.1-0.4	-	0.1-0.2	0.2-0.5	3-6	4-9
Finishing	C	0-2	0-5	0-2	-	-	-	-	-	-
	A	0-2	0	0	-	-	-	-	-	-
Total	C	83-149	145-231	50-86	3-7	4-9	4-6	12-18	137-202	52-110
	A	35-61	96-133	33-51	0.15-0.5	0.4-0.8	0.6-1.2	5-8	30-55	17-37

COD Chemical Oxygen Demand, BOD<sub>5</sub> Biological Oxygen Demand (in five days), SS Suspended Solids, TKN Total Kjeldahl Nitrogen

Coagulation and flocculation are also part of this treatment to remove a substantial percentage of the COD and SS.

Effluent from tanneries after mechanical and physico-chemical treatment is generally easily biodegradable in standard aerobic biological treatment plants. The data in table 3 represent typical values for tannery wastewater treatment efficiency for conventional process liquors for production of finished leather from raw material. [3]

### 3.1.2 Effluent treatment

In order to carry out effluent treatment in the most effective manner, flow segregation<sup>5</sup> is useful to allow preliminary

treatment of concentrated wastewater streams, in particular for sulphid- and chrome-containing liquors. And although a reduction of water consumption does not reduce the load of many pollutants, concentrated effluents are often easier and more efficient to treat. Where segregation of flows is possible, thorough mixing of chrome-bearing effluents and other effluent streams improves the efficiency of the effluent treatment plant because the chromium tends to precipitate out with the protein during pretreatment. The treatment of chrome-containing liquors will be discussed in chapter 4, so only the treatment of sulphide-containing effluent will be described here. It is common practice to keep sulphide-containing effluent from the beamhouse separate and at a high pH until the sulphide is treated, because at a pH lower than 9 the formation of toxic hydrogen sulphide (H<sub>2</sub>S) gas can occur. The sulphides in the delimit-

<sup>5</sup> i.e. keeping wastewater effluents from different process steps separate in order to avoid mixing of different pollutants or dilution of highly polluted streams

ing and pickle liquors can easily be oxidised in the drum by adding hydrogen peroxide, sodium metabisulphite or sodium bisulphite. The associated emission level after treatment of sulphide is 2 mg/l in a random sample in the separate effluent. Where segregation of sulphide-bearing liquors is not possible, the sulphides are generally removed by means of precipitation with iron (II) salts and aeration.

A disadvantage of this precipitation is the generation of high volumes of sludge. The levels that can be achieved in treating the mixed effluent are – depending on the mixing rate – 2 mg S<sup>2-</sup>/l and 1 mg Cr<sub>total</sub>/l. (e.g. if 50% of the mixed effluent consist of the sulphide-bearing effluent, emission levels for the total effluent will be 1 mg S<sup>2-</sup>/l and 0.5 mg Cr<sub>total</sub>/l). [3]

**Table 3: Typical values for tannery wastewater treatment efficiency for conventional process liquors for production of finished leather from raw material [2]**

Parameter % or mg/l	COD		BOD <sub>5</sub>		SS		Chrome	S <sup>2-</sup>	TKN	
	%	mg/l	%	mg/l	%	mg/l	mg/l	mg/l	%	mg/l
<b>Pretreatment</b>										
Grease removal (dissolved air flotation)	20-40									
Sulphide oxidation (liming and rinsing liquors)	10							10		
Chromium precipitation							1-10			
<b>Primary treatment</b>										
Mixing + sedimentation	25-35		25-35		50-70		20-30		25-35	
Mixing + chemical treatment + sedimentation	50-65		50-65		80-90		2-5	2-10	40-50	
Mixing + chemical treatment + flotation	55-75		55-75		80-95		2-5	2-5	40-50	
<b>Biological treatment</b>										
Primary or chemical + extended aeration	85-95	200-400	90-97	20-60	90-98	20-50	<1	<1	50	150
Primary or chemical + extended aeration with nitrification and denitrification	85-95	200-400	90-97	20-60	90-98	20-50	<1	<1	80-90	30-60

COD Chemical Oxygen Demand, BOD<sub>5</sub> Biological Oxygen Demand (in five days), SS Suspended Solids, TKN Total Kjeldahl Nitrogen

### 3.1.3 Post-purification, sedimentation and sludge handling

Post-purification, sedimentation and sludge handling are the last step in wastewater treatment. With sedimentation the sludge in the wastewater treatment plant is separated from the water phase by gravity settlement. After dewatering this sludge by means of filter presses, a sludge cake with up to 40% dry solids can be achieved, whereas belt presses produce a sludge cake with up to 20-25% dry solids.

Centrifuges achieve up to 25-45% dry solids and thermal treatment up to 90% dry solids. Energy is an important factor in these processes.

## 4 Chrome tanning and recovery

### 4.1 Environmental impact of chrome

The environmental impact of chrome (Cr) discharged from tanneries has been a subject of extensive scientific and technical dispute. Cr (VI) compounds are responsible for the majority of the health problems associated with all chromium compounds.

Normally, during the tanning process only Cr (III) salts are used. Nevertheless, under certain conditions the Cr (III) can be transformed into Cr (VI).

However, many studies report that the effluents from tanning industry are often adversely affecting human life, agriculture and livestock. The residents, especially the tannery workers have been the victims of this pollution, which has led to severe ailments such as eye diseases, skin irritations, kidney failure and gastrointestinal problems. For instance, according to an official report of the Environmental Protection Department Punjab (1997), the drinking water supplied by the municipality in Kasur (Pakistan) was found polluted with a high level of chromium. The WHO standard for the acceptable amount of Chromium in drinking water is 0.05 mg/l. The ground water has been stated polluted with chromium up to 5 times of the WHO standard with a varying depth of up to 165 meters. Chromium, extensively used in tanning process, is carcinogenic. Cancer found as cause of death in some cases can be linked to chromium pollution in the groundwater.

The diseases found, among the workers of tanning industry and residents of Kasur, were skin irritation, diarrhea, heart burning, respiratory tract infection, sever cough, fever and loss of eyesight. Lung cancer, high blood pressure, and kidney failure were the reported causes of death in many cases.

Allergic contact dermatitis may arise from exposure to either trivalent or hexavalent chromium. Cr (VI) penetrates undamaged skin, and subsequently reduces to Cr (III) which combines with proteins or other skin components to form a whole skin allergen.

Although the legislative limits on the disposal of solid chrome-containing waste have been relaxed in some countries, liquid emissions remain strictly regulated throughout the world. Limits on total chrome discharge in effluent vary widely between 0.05 and 10 mg/l for direct discharges into water bodies and 1-50 mg/l on indirect discharges into sewage systems [5].

The basic scheme of conventional chrome tanning process involves pickling, tanning and basifying. The amount of chrome tanning effluents, including washing waters and sammying water, fluctuates in the range of 3-5 m<sup>3</sup>/t raw hide. Chrome, chlorides and sulphates are the main pollutants. A typical pollution load of these effluents is given in table 2.

### 4.2 High-exhaustion tanning process

Advanced chrome tanning methods primarily aim at reducing the pollution load of chrome. A range of industrially proven methods for reducing the chrome content in effluents discharged are presented below. In this technique the tanning agents used are modified to enhance uptake up to 90%. The method features the following characteristics:

- Use of considerably shorter floats (20-30% related to pelt weight)
- Use of higher temperatures (40-42°C or higher), prolongation of tanning time and higher pH value (4.0-4.7)
- Use of special self-basifying and masked chrome tanning agents.

High-exhaustion and chrome fixing bring about a decrease in chrome discharge and an increase in chrome utilisation. These effects are apparent in table 4.

This example shows that chrome tanning with high-exhaustion and fixing results in:

- a decrease in the chrome offer required from 15 kg/t to 10 kg/t raw hide,
- a decrease in the chrome discharged from spent tanning floats, draining and sammying water from 3.8 kg/t to 0.05-0.1 kg/t raw hide,
- an increase in chrome utilisation in tanning operations from 70% to 98%.

Furthermore, the sulphate load drops from 30-55 kg/t to 17-36 kg/t raw hide, a relevant decrease.

**Table 4: Comparison of chrome discharge and utilisation in conventional and advanced tanning with high-exhaustion and chrome fixing [4]**

Chrome amount (kg/t raw hide)	Technology	
	conventional	high-exhaustion
Offer:	15	10
Spent tanning float	3.2	0.03-0.05
Draining and sammying water	0.6	0.02-0.05
Post-tanning float	0.7	0.1-0.4
Total discharge	4.5	0.15-0.50
Utilisation (%)	70	95-98

The chromium content in the spent float can be reduced to values between 150 mg/L and 600 mg/L of  $\text{Cr}_2\text{O}_3$ , obviously not yielding a concentration low enough to meet the legal standards of most of the countries in the world. Because of the low concentration, the remaining chrome in the effluent is not recovered.

### 4.3 Recycling/reuse techniques

Direct recycling systems can be classified as closed and open. Closed systems are mostly based on reusing only spent tanning floats and sammying water for tanning in successive cycles. They are utilised when working with short floats and powder chrome tanning agents. In open systems, the float volume increases during recycling. The number of cycles is not limited; in practice, however; this depends upon the establishment of an equilibrium in the composition of recycled floats. Several open-system recycling techniques are employed industrially:

- Reuse of separated pickling and tanning floats in successive cycles.
- Reuse of tanning float in the subsequent pickling cycle.
- Reuse of the mixture of tanning float and sammying water partly in pretanning, partly in tanning in the subsequent cycle. The pretanning float is discharged each day.

Float recycling systems require controlling of the relative amount of the float components: acidity (pH) and salt content (density). After about three cycles, the solution normally reaches a certain stability. The eventual enrichment of fat and ferrous ions in the liquor has to be controlled, to avoid stains on the produced leather.

Recycling techniques are mostly used in conventional tanning processes. According to the extent of their use, an increase in chrome utilisation from 70% up to 95% and a decrease in chrome discharge from 2-5 kg/t to 0.1-0.25 kg/t raw hide should be regarded as maxima and minima, respectively.

Recycling systems also decrease the sulphate load in effluents and according to the extent of their use, a decrease from 30-55 kg/t to 10-22 kg/t raw hide can be attained.



#### 4.4 Recovery/recycling techniques

Since 80 years these techniques are implemented not only for environmental but mainly for economic reasons. In principle, these indirect systems are based on the precipitation of chrome containing effluents with alkalis. Common precipitation agents include  $MgO$ ,  $Ca(OH)_2$ , Soda,  $NaOH$  and others. After settling, thickening and dewatering of the chrome oxide suspension, the filter cake is dissolved in sulphuric acid. After modifying the basicity, the basic chromium sulphate solution can be reused for tanning by recycling into the tanning process and by replacing 20-35% of the "fresh" added chrome tanning salt. It is to be noted that recovery/recycling techniques differ in terms of the precipitating alkalis, flocculation temperatures, settling and dewatering conditions used as well as the manner of handling and reusing the filter cake. With a well-managed effluents collection and processing system, a decrease in the amount of chrome discharged in tanning effluents from 2-5 kg/t to 0.1-0.25 kg/t raw hide can be observed. [3]

From the chemical point of view chrome recovery is a simple process (see figure 3) with excellent environmental results meeting the limits demanded by legislation for discharge of trivalent chromium, but it needs careful analytical control, requires special equipment and chemicals and training of personnel.

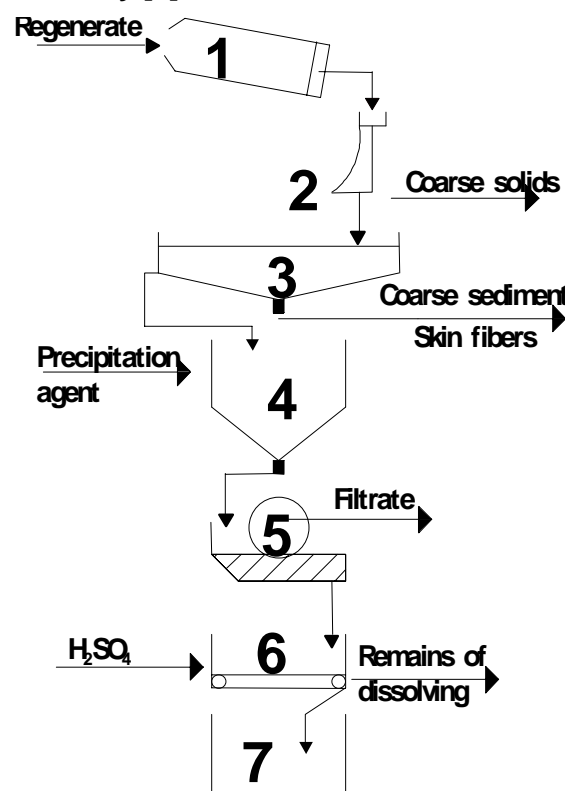
Chromium recycling is not recommended for effluents containing residues of surfactants, fat liquors, dyes and tanning agents other than chromium. Therefore retanning floats cannot be treated in this manner. For these more complex floats, the liquor can be precipitated with calcium hydroxide and flocculates. The separated liquid phase can be discharged into the effluent but remaining chromium sludge has to be disposed safely. Therefore, it is very important to avoid mixing of floats

which can be recycled or combining of a treatment producing sludge which can be disposed of easily with other ones not suitable for recycling. [3]

##### 4.4.1 Costs for chrome recovery

As already mentioned above, chrome recovery is not only an ecologically-friendly process but also an economic one. Based on Greek conditions (year 1990-1991), the maximum payback period for installing a chrome recovery unit was 1.6 years. In India two different examples of running a chrome recovery unit show payback periods of 1 and about 1.6 years (reference years 1994 and 1995). [2]

**Figure 3: Process flow of chrome recovery [8]**



1: Tanning mixer, 2: Bow Sieve, 3: Holding and primary settling tank, 4: Precipitation and settling tank, 5: Filter plant (drum filter), 6: Treatment tank, 7: Storage tank

## 5 References and further information

### 5.1 Literature and useful links

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- <http://www.epa.gov/EPA-WATER/1996/July/Day-08/>  
(Leather Tanning and Finishing Effluent Limitations Guideline)
- <http://www.ifc.org/enviro/FinancialMarkets/FinancialMarkets/Studies/Tannery/tannery.htm>  
(Tannery Case Study)

## 5.2 Organisations

### **Deutsche Gesellschaft für Technische Zusammenarbeit (GTZ) GmbH, German Appropriate Technology Exchange (GATE) - Information Service**

P.O. Box 5180,65726 Eschborn, Germany  
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### **Naturgerechte Technologien, Bau- und Wirtschaftsberatung (TBW) GmbH**

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### **United Nations Industrial Development Organization (UNIDO) Regional Programme for Pollution Control in the Tanning Industry in South-East Asia Leather programme in Eastern and Southern Africa**

UNIDO Vienna International Centre  
P.O. Box 300, A-1400 Vienna, Austria  
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Internet: <http://www.unido.org>

(Access to different interesting documents on tanning and tannery effluents)

- <http://www.unido.org/doc/100453.htmls>  
(India: Treatment of Tannery Effluents in Tamil Nadu State - success story)
- <http://www.unido.org/doc/351434.htmls>  
(Documents on the Industrial Sector with emphasis on Leather Industry)

### **International Union of Leather Technologists and Chemists Societys**

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