CHAPTER1

1. INTRODUCTION

1.1Pollution in water

Natural water pollution is created through the silt that washes down along water beds due to rain carrying dust, dust particles, and other materials into the water. Artificial pollution, until recently, was mostly created by domestic and simple industrial waste. The pollution problems were usually of a local nature. However, as the national growth has increased, the production of goods has increased sharply and with it the production of common industrial waste has increased sharply. Further, new processes in manufacturing have produced new complex wastes that have not been easily handled by the current control technologies.

The increased use of commercial fertilizers and the wide use of a large number of pesticides have contaminated many of our waters. Radioactive materials have entered waters by means of precipitation from the radioactive dust created by nuclear explosions. At present, long stretches of interstate and intrastate streams have become polluted and are continuing to be polluted.[1,Koren,H and Bisesi,M 2003]

1.2Industrial pollution

The use of machinery and factories led to mass production, which in turn led to the development of numerous environmental hazards.The effects on the environment would only be seen clearly years later.While the Industrial Revolution was the cause of positive change for the industrial world, there is no question that it has wreaked havoc on the environment. The depletion of natural resources, the carbon emissions, pollution and human health problems that have resulted directly from the

Industrial Revolution's accomplishments have only been disastrous for the world environment.[2,Ahuti,S.2015]

As the concerns and questions about environmental sustainability grow louder, understanding the determinants of pollution becomes increasingly important, as such detection would make it easier to design and implement appropriate policies against pollution and environmental degradation. Industry, as a highly energy-intensive sector, emerges as a sector that is significantly responsible for carbon emissions, where industry is responsible for more than 30 percent of energy use and 20 percent of total carbon emissions [3,Acar,S and Tekce,M.2014].

The health impact of industrial pollutants is almost equal to or higher than some of the worst global diseases, including malaria and tuberculosis. Industrial pollution depends on several factors, including production technology, quality of inputs, lack of purification equipments, weak environmental regulations and lack of social concern for environmental protection. In this context, determining the responsible factors of carbon emissions in the industrial sector becomes a crucial topic.[3,Acar,S and Tekce,M.2014]

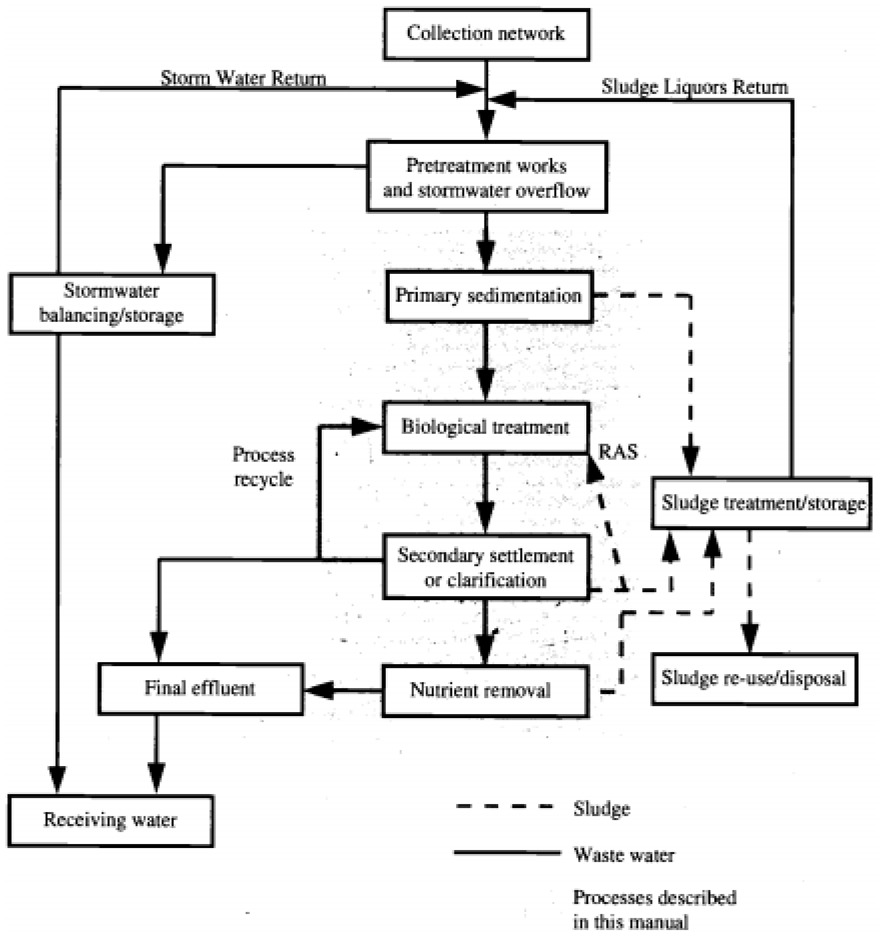
1.3Industrial pollution control

For many years a large part of industrial pollution control has been carried out essentially on an end-of-pipe basis, and a wide range of unit processes (physical, chemical, and biological) have been developed to service the needs of the industry. Such end-of-pipe systems range from low intensity to high intensity arrangements, from low technology to high technology, and from low cost to high cost. Most end-of-pipe systems are destructive processes in that they provide no return to the operating company in terms of increased product yield or lower operating cost, except in those circumstances where reduced charges would then apply for discharge to a municipal sewer. It should be noted that in all cases the size (and hence cost) of end-of-pipe treatment has a direct relationship to both the volume of effluent to be treated and the concentration of pollutants contained in the discharge. For example, the size of most physicochemical reactors (balancing, neutralizing, flocculation, sedimentation, flotation, oxidation, reduction, etc.) is determined by hydraulic factors such as surface loading rate and retention time.

The size of most biological reactors is determined by pollution load, for example, kg BOD (biochemical oxygen demand) or COD (chemical oxygen demand) per kg MLVSS (mixed liquor volatile suspended solids) per day in the case of suspended growth type systems, and kg BOD or COD per m^3 of media or reactor volume in the case of fixed-film type systems. It is evident therefore that the reduction of emissions by action at source can have a significant impact on the size and hence the cost of an end-of-pipe treatment system.On this basis, it should be established practice in industry that no capital expenditure for end-of-pipe treatment should be made until all waste reduction opportunities have been exhausted. This has not often been the case, and many treatment plants have been built that are both larger and more complicated than is necessary.[4,Wang,L, Hung,Y,and Shaammas,N.2010]

1.4Overview of waste water treatment

Waste water treatment can involve physical,chemical or biological processes or combinations of these processes depending on the required outflow standards. A generalised layout of a waste water treatment plant is shown in Figure(1.1).



Fig(1.1) Layout of a waste water treatment plant[Carty,G.,O'Leary,G.and Meaney,B.(1997)]

The first stage of waste water treatment takes place in the preliminary treatment plant where material such as oils, fats, grease, grit, rags and large solids are removed.

Primary settlement is sometimes used prior to biological treatment. Radial or horizontal flow tanks are normally employed to reduce the velocity of flow of the waste water such that a proportion of suspended matter settles out. Biological treatment of waste water takes place in fixed media or suspended growth reactors using activated sludge, biofiltration, rotating biological contactors, constructed wetlands or variants of these processes.

Nitrification/denitrification and biological phosphorus removal can be incorporated at this stage and will reduce nutrient concentrations in the out flow.Chemical treatment is used to improve the settling abilities of suspended solids prior to a solids removal stage or to adjust the properties or components of waste water prior to biological treatment (e.g. pH adjustment, reduction of heavy metals or nutrient adjustment). It may also be used for precipitating phosphorus in conjunction with biological phosphorus treatment.Secondary settlement separates the sludge solids from the outflow of the biological stage.

Tertiary treatment refers to processes which are used to further reduce parameter values below the standards set out in national regulations. The term is often used in reference to nutrient removal. Sludge treatment can be a significant part of a waste water treatment plant and involves the stabilisation and/or thickening and dewatering of sludge prior to reuse or disposal.

1.5 Role of the waste water plant operator

The role of the plant operator in the management, maintenance and operation of each process.The plant operator should manage the plant with the following objectives:

- Meeting the emission limits set in the regulations for secondary treatment systems.
- Meeting the standards for sensitive water where prescribed.
- Minimizing odors.
- Avoiding operating the waste water treatment plant efficiently.

- Minimizing energy consumption.
- Implementing an effective preventative maintenance programme.

1.6 General considerations for the treatment of waste water

1.6.1 Characteristics of waste water

The strength of waste water is normally measured using accurate analytical techniques. The more common analyses used to characterise waste water entering and leaving a plant are:

1.6.2 Parameters by which waste water is measured

Biochemical oxygen demand (BOD): BOD is the amount of oxygen used by organisms while consuming organic matter in a waste water sample. It is possible to assess the performance of a waste water treatment plant by measuring the BOD of the inflow and the outflow. Many factors can influence this test, such as temperature of incubation, dilution rate, nitrification, toxic substances, nature of bacterialseed and presence of anaerobic organisms.

The method of measurement for the BOD test requires:

• The sample is homogenised, unfiltered and undecanted.

• Nitrification inhibitor is added.

The regulations allow for the BOD test to be replaced by another parameter, total organic carbon (TOC) or total oxygen demand (TOD) if a relationship can be established between BOD and the substitute parameter.

Chemical oxygen demand (COD): The COD test uses the oxidising agent potassium dichromate (specified in the UWWT Regulations)

1.7Tanning process:

In the tanning process, the collagen fiber is stabilized by the tanning agents, such that the hide is no longer susceptible to putrefaction or rotting.After tanning, the hides or skins are not subject to putrefaction, their dimensional stability, resistance to mechanical action, and heat resistance increase.

There is a wide variety of tanning methods and materials and the choice depends chiefly on the properties required in the finished leather, the cost of the materials, the plant available, and the type of raw material.The majority of tanning agents fall into one of the following groups:

1. mineral tannages
2. vegetable tannins[6,Rydin,S.2013]

The major public concern over tanneries has traditionally been about odours and water pollution from untreated discharges. Important pollutants associated with the tanning industry include chlorides, tannins, chromium, sulphate and sulphides as addition to trace organic chemicals and increasing use of synthetic chemicals such as pesticides, dyes and finishing agents, as well as from the use of newer processing chemical solvents. These substances are frequently toxic and persistent, and affect both human health and the environment. Tannery effluent is among one of the hazardous pollutants of industry. Major problems are due to wastewater containing heavy metals, toxic chemicals, chloride, lime with high dissolved and suspended salt and other pollutants.[7,Jahan,M et al.2014]

1.8 Chrome tanning:

Chromium salts (particularly chromium sulphate) are the most widely used tanning substances today. Hides tanned with chromium salts have a good mechanical resistance, an extraordinary dyeing suitability and a better hydrothermic resistance in comparison with hides treated with vegetable substances. Unfortunately only a fraction of the chromium salts used in the tanning process react with the skins. The rest of the salts remain in the tanning exhaust bath and are subsequently sent to a depuration plant where the chromium salts end up in the sludge. One of the major emerging environmental problems in the tanning industry is the disposal of chromium contaminated sludge produced. as a by-product of wastewater treatment.At high concentrations chromium is toxic and carcinogenic.Chromium exists in oxidation states of +2, +3 and +6.The trivalent oxidation state is the most stable form of chromium and is essential to mammals in trace concentration and relatively immobile in the aquatic system due to its low water solubility. The hexavalent chromium is much more toxic to many plants, animals and bacteria inhabiting aquatic environments. Most micro-organisms are sensitive to Cr (VI) toxicity but some groups possess resistance mechanisms to tolerate high levels.

A relationship was found between the total chromium content of soil and the presence of metal tolerant/resistant bacteria. In natural waters two stable oxidation states of Cr persist (III and VI), which have contrasting toxicities, motilities, and bioavailability. Cr (VI) is motile and highly toxic and soluble in water and it is a strong oxidizing agent that causes severe damage to cell membranes.Worldwide chromium contamination of soils has arisen predominantly from the common practice of land-based disposal of tannery wastes under the assumption that the dominant species in the tannery waste would be the thermodynamically stable Cr (III) species. However, recent detection of significant levels of toxic Cr (VI) in surface water and groundwater in different part of the world raise critical questions relating to current disposal of Cr-containing wastes. Although Cr III is an essential nutrient for human beings, there is no doubt that Cr (VI) compounds are both acutely and chronically toxic.

The dose threshold effect for this element has not yet been determined accurately enough to allow regulations to be defined. However some risk assessment analysis is currently being undertaken. Cr III is less toxic than some other elements (Hg, Cd, Pb, Ni and Zn) to mammalian and aquatic organism, probably due to the low solubility of this element in its trivalent form. Cr III compounds also have a very low mobility in soils and are thus relatively unavailable to plants.The direct discharge of effluents from tanneries into water bodies has become a growing environmental problem in these days.

Most of these wastewaters are extremely complex mixtures containing inorganic and organic compounds that make the tanning industry potentially a pollution-intensive sector.

Despite the thermodynamic stability of Cr (III), the presence of certain naturally occurring minerals, especially MnO2, can enhance oxidation of Cr (III) to Cr (VI) in the soil environment. This factor is of public concern because at high pH, Cr (VI) is bioavailable and it is this form that is highly mobile and therefore poses the greatest risk of groundwater contamination.

Technologies used to reduce chromium in waste water such as high exhaustion process, direct or indirect chromium recycling cannot eliminate completely from effluent coming from post tanning section. In response to this challenge, replacement of chromium with combinations of metallic cations, for example titanium, magnesium, aluminium and zirconium, was tried but the results obtained at the moment are not completely satisfying for all types of leather. Synthetic organic tanning agents, alone or in combination with a metallic cation can be considered as a substitute for chromium in some types of leather, provided that environmental and workers health regulations are complied with.[8,Ahmed,M and Kashif,M.2014]

1.9Tanning stages

Operation process stages are curing, soaking, liming, deliming, bating, degreasing, picklling, tannage, fat-liqouring, dyeing, drying and finishing.

1.9.1 Curing

This is to shield freshly flayed hides from attacks by microorganisms for them to be stored for long periods through processes such as:air drying, salting, and disinfection. With the exception of air-drying all the cure methods mentioned above employ chemicals.

1.9.2 Soaking

It helps to restore the natural swollen condition of the skin and to remove dirt, blood, dung, soluble proteins and curing agents such as salt. Soaking rehydrates the fibers and tries to bring the skins as close as possible back to the state of green hides.

1.9.3 Liming

The purpose of liming is to loosen hair on the hide, remove the epidermis and separate fibers and fibrils. The hair loosening power of lime is enhanced by adding substances to lime such as sodium sulphide, arsenic disulphide, sodium hydrosulphite, sodium bisulphite.

1.9.4 De-liming

Tends to lower pH to a range between 8.2 - 8.4. Bating – this process makes the grain of the leather clean, smooth and fine resulting in final leather soft pliable and stretchy. Bating is achieved by use of enzymes. The longer the operation the softer and more stretch the final product.

1.9.5 Pickling

Is an acidification process of the delimed and bated pelts and is considered an essential preparatory operation before tanning especial before chrome tanning.

1.9.6 Tannage

It is the means by which hides are preserved into a substance which does not putrefy, dries soft, swell when wetted, which substance is called leather. The object of converting pelt into leather is to enhance its strength properties.

1.9.7 Fat liquoring

The purpose of this process is to surround fiber elements that have been dehydrated by tannage with a fat layer, to render the leather soft again by lubricating and imparting a certain feel and handle to it.The process improves leather properties such as extensibility, tensile strength, wetting properties, water proofness and permeability to air and vapour.[9,Madanhire,I and Mbohwa,CH.2015]

1.10 Post tanning process

To produce finished leather, the finished leather hides must pass through a series of post-tanning processes ,which may include retanning, dyeing and fat-liquoring.Retanning modifies the characteristics leather(such as texture) .The hides also may be immersed in dye to obtain coloured leather. During fat-liquoring, the tanned leather is treated with preparations of natural and synthetic oils to replace the natural oils lost during processing. After post-tanning processing, the hides are dried and pressed; to create the correct shape and surface texture, they may also be trimmed, split, shaved and buffed. A decorative and protective surface coating may also be applied (the finishing process).[10,Balkau,F and Scheijgrond.1991]

1.11Objectives

1. To protect the environment from tannery waste using cheap and effective treatment methods.
2. To reduce cost of chemicals and water through recycling of the effluent.
3. To Provides information on chrome management by recycling and those techniques most frequently used to reduce the amount of chrome in tanneries wastewater.
4. To compare the cost for a new tannery with the conventional treatment method and that use the recycling method.

CHAPTER TOW

2. LITERATURE REVIEW

2.1 Solid waste

Solid waste includes salt from raw skin,hide dusting,hide trimmings,hair, which may contain lime and sulfides; and fleshing from raw skins,hides.Other solid waste from tannery industry includes wet-blue shavings, containing Cr_2O_3, wet-blue trimming, which is generated from finishing processes and contains Chromium oxide (CrO),dye.The reducing characteristics of tannery sludge stabilize Cr(III) with respect to Cr(VI), due to the presence of organic matter and sulfides. Prevention and control measures for solid waste include the following:

- Reduce inputs of process agents (particularly precipitation agents in wastewater treatment) to the extent practically applicable.
- Segregate different waste / residue fractions to facilitate recovery and re-use.
- Recycle sludge in anaerobic digestions for energy generation Process. Sludge may be used for agriculture after appropriate assessment for contaminants and potential impacts to soil and groundwater.
- Fleshing could be degraded through bio-methanation process.[11,Bhat,n.2010]

2.2 Treatment of tannery effluents

The difficulty in treatment of tannery wastewater is due to complex nature of the industry and a large number of chemicals employed in the leather processing. The segregation of each sectional stream and separate treatment therefore requires very high investments in terms of equipment, land etc. hence eliminating or reducing the wastage at the source i.e. at the stage of leather processing, is a promising option for the tanneries.[12,Islam,B et al.2014]

2.2.1Primary treatment

2.2.1.1 Objectives

1. To eliminate the coarse material normally present in the raw wastewater that could clog/block pumps, pipes and possibly sewer lines.
2. To mix and balance well different tannery streams and thus produce homogenized "raw material" that can be treated in a consistent manner.
3. To adjust pH and eliminate toxic substances (sulphides) and avoid shock loads that can negatively affect the rather sensitive biological treatment.
4. To significantly decrease the BOD/COD load and thus simplify the biological treatment phase and reduce its cost.

2.2.1.2 Basic steps

- Screening
- Pumping/lifting
- Fine screening
- Chemical treatment (coagulation, flocculation)
- Settling
- Sludge dewatering[13,Buljan,J and Karl,I.2011]

2.2.1.3 Chemical treatment (coagulation, flocculation)

Chemicals are added in order to improve and accelerate the settling of suspended solids, especially of fine and colloidal matter. In wastewater treatment operations, the processes of coagulation and flocculation are employed to separate suspended solids from water. These terms are often used interchangeably, or the single term “coagulation” or “flocculation” is used to describe both; sometimes “flocculation” is understood as the second stage of “coagulation”. In fact, they are two distinct processes usually carried out in sequence as a combination of physical and chemical procedures. Finely dispersed solids (colloids) suspended in wastewater are stabilized by negative electric charges on their surfaces, causing them to repel each other. Since this prevents these charged particles from colliding to form larger masses, called flocs, they do not settle.

Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative charge of the colloids. As a result, the particles collide to form larger particles (flocs). Rapid mixing is required to disperse the coagulant throughout the liquid.[13,Buljan,J and Karl,I.2011]

Flocculation is the action of polymers to form bridges between flocs and bind particles into large agglomerates or clumps. In this process it is essential that the flocculating agent be added by slow and gentle mixing to allow for contact between the small flocs and to agglomerate them into larger particles. The newly formed agglomerated particles are quite fragile and can be broken apart by shear forces during mixing. Care must also be taken not to overdose the polymer as doing so will cause settling problems.Once suspended particles are flocculated into larger particles, they can usually be removed from the liquid by sedimentation or filtration.The flocculation reaction not only increases the size of floc particles in order to settle them faster, but also affects the physical nature of flocs making them less gelatinous and thereby easier to dewater.

The inorganic coagulants are compounds that break colloidal suspensions and help floc forming. The most frequently used coagulants in tannery effluent treatment are:

- Industrial aluminium sulphate $Al_2 (SO4)_3 \cdot 18H_2O$
- Industrial iron sulphate: $Fe(SO)_4 \cdot 7H_2O$
- Industrial iron chloride: $FeCl_3 \cdot 6H_2O$
- Lime: industrial calcium chloride $Ca(OH)_2$.

Coagulant aid flocculants are water-soluble organic (anionic) polyelectrolyte that support agglomeration of colloidal and very fine suspended matter thus enhancing the impact of coagulation.

2.2.1.4 Settling – primary sedimentation

The main objective at this stage is the removal of suspended solids; however, various constituents such as fats, waxes, mineral oils, floating non-fatty materials, etc, not already removed are also separated here. Primary settling tanks (clarifiers) are either circular (more commonly used) or rectangular with continuous grease (scum) removal at the top and sludge removal at the bottom.[13,Buljan,J and Karl,I.2011]

2.2.2 Biological (secondary) treatment:

2.2.2.1 Objectives and basic principles:

The main objective at this stage is to further reduce the amount of organic (expressed as BOD and COD).and other substances still present in the effluent after the primary treatment and thereby satisfy the standards/limits for discharge into surface waters (rivers, lakes).

The biological treatment duplicates processes that take place in nature, but under controlled conditions and, especially, at a highly accelerated pace,however, the efficiency of this treatment largely depends on the biodegradability of the polluting substrate, i.e.,its inherent capacity to decompose by biological processes.The remaining suspended and colloidal solids are removed by flocculation and adsorption.

While biological treatment may be aerobic, facultative or anaerobic (or some combination),in practice, almost only aerobic systems are used; exceptionally, in countries with a hot climate and where a lot of land is available, facultative (preferably aerated/facultative) lagoons are also used.

Due to the inherent characteristics of tannery effluents, primarily their sulphide/sulphate content, in practice, anaerobic treatment is used only in sludge digestion. Among many variations of the aerobic process, the most widely used method is (complete-mix) activated sludge treatment with extended aeration; despite some very interesting features, membrane bioreactors (MBRs) have not made significant inroads in the tanning sector.The activated sludge process is an aerobic, biological process, which uses the metabolism of microorganisms to remove substances causing oxygen demand. The qualitative biochemical reaction taking place in the organic matter stabilization process can be summarized in the following manner:

Inert matter + organic matter + oxygen + nutrients + micro-organisms give a new micro-organisms + CO_2 + H_2O + additional inert matter Simply said, we stimulate micro-organisms to convert (eat and digest) harmful, oxygen-demanding organic compounds into an environmentally more acceptable form (micro-organisms) and low-energy, stable compounds like water and carbon dioxide.[13,Buljan,J and Karl,I.2011]

The microbial community that does that job comprises various species of bacteria, fungi, protozoa, sometimes rotifers (multicellular animals only found in very stable activated sludge with long retention times), even nematodes, the composition of the population depending on a plethora of factors.Let us recall that BOD is defined as the quantity of oxygen required during the stabilization of decomposable organic and oxidizable inorganic matter by aerobic biological action under standard conditions, usually over only five days instead of 20.[13, Buljan,J and Karl,I.2011].

COD is the quantity of oxygen consumed for the total oxidation of the oxidizable matter (organic and inorganic) with dichromate as the oxidizing agent. The COD is always greater than its BOD. Generally, the biological stage is the most complex part of the overall effluent treatment process, with highest investment and operational costs, its day-to-day running requiring considerable skills and experience.[13,Buljan,J and Karl,I.2011]

2.2.3 Advanced (tertiary) treatment

In certain cases, despite extensive physical-chemical and biological treatment, the quality of the final effluent does not meet the promulgated discharge limits. The usual culprit is the recalcitrant COD, i.e., compounds that the micro-organisms present in the flow are unable to decompose.In such cases, it is necessary to resort to additional, usually more sophisticated and rather expensive treatments such as mineralization of organic compounds by oxidation with H_2O_2 in the presence of ferrous sulphate.Ozonation is sometimes included not so much to kill potentially harmful micro-organisms but to destroy part of the residual COD. [13, Buljan,J and Karl,I.2011]

2.3Mechanical sludge dewatering

The main purpose of sludge dewatering is not only to reduce the volume and weight of material to be transported but also to attain the dry matter content required for disposal at landfills. The equipment used for this purpose recessed-plate filters, belt presses and decanter centrifuges. Here is a short comparative overview of the main characteristics and efficiencies of the various systems throughout the treatment process.

- Polyelectrolyte (usually cationic)
- (Sludge conditioning with inorganic chemicals (iron salts and lime) is not strictly necessary,but recommendable for enhancing filtration rate and general performance.

2.4Utilization and disposal

In comparison with sanitary sludges, tannery sludge has greater inorganic matter content, greater heavy metal content, especially chromium and greater sulfur compound content. However, the main stumbling block is the chromium content, with legislation and practice varying a lot from country to country.

A number of solutions for utilization and/or safe disposal of tannery sludge have been proposed, practiced, tested, and applied at pilot and industrial scale include the landfill, land application, composting, anaerobic digestion, thermal treatment, pyrolisys, etc., none of them proving satisfactory enough.There is certainly no universal solution for sludge utilization application.

The sludge of specific characteristics and different regions and countries has quite different regulations regarding sludge utilization. In any case, handling, storage and transport of sludge and solid wastes should also be safe and not contaminate the surroundings; thus, for example, the collection points should be protected against bad weather (rain, for example).[13,Buljan,J and Karl,I.2011]

2.5Air emissions from tanneries

Air emissions from tanning facilities include the following:

Table (2.1) Sources of air emissions and preventive methods[11, Bhat,N et al.2010]

Emission to Air	Source Operations in Tannery	Suggestive Methods of Prevention
Organic Solvents	-Degreasing -Finishing	-Usage of water-based formulations for spray dyeing. -Usage of roller coating techniques or curtain coating machineswherever applicable. -Usage of spraying units with economizers and high volume / low pressure spray guns.
VOCs	-Spray finish -Machines Dryers	-Avoid Usage of internationally banned solvents. -Usage of wet scrubbers, activated carbon adsorption, bio-filters (to remove odors), cryogenic treatment, and catalytic or thermal oxidation materials. -Add manganeese sulphate to treated effluent. -Use adequate ventilation

Table(2.1)continued

Ammonia	-Beamhouse -Deliming -Dehairing,Drying after dye penetration	-Adequate ventilation followed by wet scrubbing.
Dust	-Storage handling of powdery chemicals. -Dry shaving -Machines Milling drums,Stalking	-Centralized system -Employing cyclones -Usage of scrubbers/bag filters, as needed.

Emissions of sulfur dioxide may occur during bleaching, post-tanning operations, or carbon dioxide (CO2) deliming, but they are not typically a significant source of emissions.

Table (2.2)Odor Emissions to Air[11, Bhat,N et al.2010]

Odorous Emissions to Air	Source Operations in Tannery	Suggestive method of prevention
NH_3	Beam house operations	-Quick the curing of raw hides - Reduce the time that sludge remains in the thickener, dewater thickened sludge by centrifugation or filter press, and dry the resulting filter cake. Sludge containing less than30%solids may generate especially strong odors. -Ventilate tannery areas and control exhaust from odorous areas (e.g.,
H_2S	Beam house operations ETP collection tank. ETP primary treatment units. ETP sludge dewatering system. ETP anaerobic lagoons	
VOC_S	Finishing operations	

Table(2.2) continued

CH_4	ETP anaerobic lagoons	where wastewater sludge is thickened and dewatered), through use of a biofilter and / or a wet scrubber with acid, alkali, or oxidant

ETP=effluent treatment process

2.6Waste water production and treatment

Table (2.3) 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.[15,Naturgerechte Technologyien.2002]

Table (2.3) Water consumption in individual processing operations[15, Naturgerechte Technologien, Bau- und Wirtschaftsberatung (TBW) GmbH. 2002]

Operation	Discharge (m^3/t raw hide)	
	Conventional	Advanced
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

Table (2.3)continued

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 m3/t of raw hide under conditions of very good housekeeping.[15,NaturgerechteTechnologien,BauundWirtschaftsberatung (TBW) GmbH.2002]

2.7 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 0.05mg/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[15, Naturgerechte Technologien,Bau undWirtschaft sberatung(TBW) GmbH. 2002].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[15, Naturgerechte Technologien, Bau- und Wirtschaftsberatung (TBW) GmbH. 2002].

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 3-5m^3/t raw hide[15,Naturgerechte Technologien,Bau-undWirtschaftsbe ratung(TBW)GmbH. 2002].Chrome, chlorides and sulphates are the main pollutants.

2.8 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)[15, Naturgerechte Technologien, Bau-undWirtschaftsberatung(TBW) GmbH. 2002].

• 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.[15]

High-exhaustion and chrome fixing bring about a decrease in chrome discharge and an increase in chrome utilization. These effects are apparent in table (2.4).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[15,Naturgerechte Technologien,Bau-undWirtschaftsberatung (TBW) GmbH. 2002].

• 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[15, Naturgerechte Technologien,Bau-undWirtschaftsberatung (TBW) GmbH. 2002].

• An increase in chrome utilization 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 [15, Naturgerechte Technologien, Bau- und Wirtschaftsberatung (TBW) GmbH. 2002].

Table(2.4)Comparison of chrome discharge and utilisation in conventional and advanced tanning with high-exhaustion and chrome fixing[15, Naturgerechte Technologien, Bau- und Wirtschaftsberatung (TBW) GmbH. 2002].

Chrome amount in the	Technology	
	Conventional(kg/t raw hide)	High exhaustion(kg / t raw hide)
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	0.15.50
Utilization	70	95-98

The chromium content in the spent float can be reduced to values between150mg/Land600mg/L of Cr_2O_3[15,NaturgerechteTechnologien, Ba u-undWirtschaftsberatung(TBW)GmbH.2002].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.

2.9 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 utilized 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 of raw hide ,should be regarded as maxima and minima, respectively. [15, Naturgerechte Technologien, Bau- und Wirtschaftsberatung (TBW) GmbH. 2002]. 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- 22kg/t of raw hide can be attained.

2.10Recovery/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 25 kg/t to 0.1-0.25 kg/t raw hide can be observed.[15,Naturgerechte Technologien,Bau-undWirtschaftsberatung(TBW)GmbH. 2002].From the chemical point of view chrome recovery is a simple process 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.

For these more complex floats,the liquor can be precipitated with calcium chloride 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.

2.11 Chrome recovery

Chrome management in a tannery may comprise any of the following methods and sometimes a combination of these:

2.11.1 Direct recycling of spent chrome

The direct reuse method envisages reuse of exhaust chrome liquor directly after simple screening as tanning Liquor for the next batch. Additional chromium is supplied to compensate the deficiency.the main constraint in adopting this method is that the salts and other impurities are accumulated due to repeated reuse and will have negative effect on the leather quality. After afew reccles the exhaust chrome liquor has to be discharged as waste.[16,Rajamani,S]

2.11.2 Recovery of chromium and its reuse indirect reuse method

Under the indirect reuse method, chromium is recovered by precipitation as chloride using an alkali and the precipitated chrome slurry is dissolved subsequently in sulphuric acid. The solution can be used as tanning liquor. The advantage of this method is a more efficient use of chromium and a cleaner reusable solution which normally does not affect the leather quality.

2.11.3 Separation of chromium compounds

In principle, by this method, recovery of chromium can be achieved by separating the chromium compounds from other salts in the waste liquor.The chrome liquor may be cleaner than by the direct reuse method, but this system requires rather sophisticated techniques such as electrodialysls, membrane separation, ion-exchange etc.and has limited scope for implementation in tanneries.

2 .12Use of alternative chemical(s) for tanning

Various alternative chemicals like aluminum and zirconium based salts have been tried in the tanning industry, but these have certain limitations on the quality of finished leather required. Accordingly these are applied on a limited scale only.

Of all the options described above, the chrome recovery and reuse system using MgO as alkali has found much favor in India, particularly among the small tanners, as it can be used either for an individual tannery (if the quantum of spent chrome liquor discharged justifies it) or for a group of small tanneries (each bringing its spent chrome liquor once in 2 or 3 days to the recovery unit and taking back the recovered chromium for reuse). This technology package dwells on recovery of chrome and its reuse by indirect reuse method only.[16,Rajamani,S]

In the following figure, the process flow chart of recovery of chrome and regeneration for reuse may be seen, The spent chronic liquor from the tanning drum is discharged through a special door fixed with flexible hose pipe to the collection trap. The flexible hose pipe will be as long as required depending on the location of the collection trap.

A screen chamber is provided at the end of collection drain before discharge into the collection tank. From the collection tank, the spent liquor is pumped into the main reactor. Before entering the main reactor, it is screened again In the main reactor the alkali, magnesium oxide (in solution form) is added slowly, when the stirrer is operational.

This process takes one hour. The stirrer is thereafter stopped and the precipitated chromium settles in the form of a compact slurry in the bottom in about 4hours. Supernatant is discharged through side valves at different levels in the main reactor and the chrome slurry is discharged from the bottom by opening the bottom valve.The chrome slurry is redissolved and acidified in the chrome regeneration tank by adding sulphuric acid keeping the stirrer on. The recovered chrome after natural cooling for 3-4 hours is pumped from here to the recovered chrome storage tank. The recovered chromium in the form of solution is collected in buckets and used in normal chrome tanning operation, generally in the ratio70 % market BCS to 30 % recovered chromium. The whole process can start afresh from here. .[16,Rajamani,S]

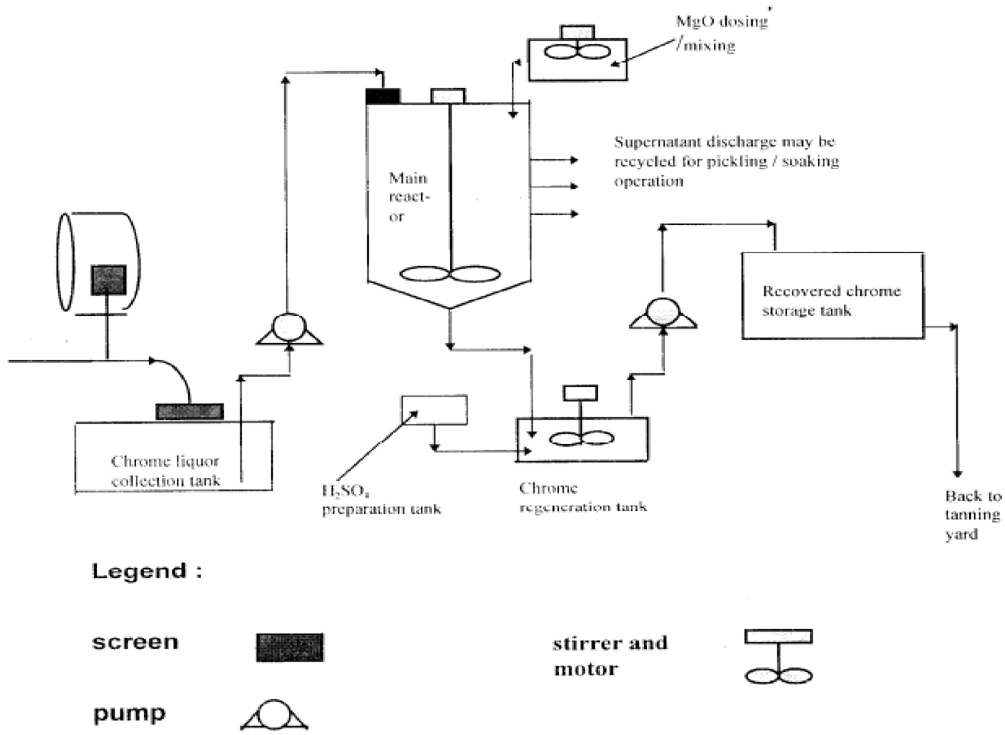


Fig (2.1) Chrome recovery[16, Rajamani,S]

2.13Costs 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).[15,Naturgerechte Technologien ,Bau-undWirtschaftsberatung(TBW)GmbH. 2002]

2.14 Source of waste

Leather tanning is a production process in which animal hides are transformed by using of water, chemicals and mechanical process. Therefore, waste water from the process will contain a high concentration of pollutants. Moreover, this process also generates solid waste. In this respect, the character of wastewater, the pollution load as well as the amount of solid waste depends on the type of production process including the source of the tanning. The main steps which produce waste are concluded as follows [17,Leather tanning group,1997]

2.14.1 Raw hide preservation

Preservation of raw hides is not part of the actual tanning process, but is necessary to preserve raw hides from decomposition. Salt, about 20% of the weight of raw hides, is normally used for pickling of raw hides. In the preservation step, the hides will lose moisture, about equal to the amount of salt added. In addition, bactericides and insecticides are also used for preservation of hides. Therefore, prior to the actual tanning process, the salt must be removed which is normally carried out by shaking of the raw hides. This salt is the first type of solid waste generated by the leather tanning process. If the removed salt is disposed off in an environmentally unsound way it will negatively affect plant growth, aquatic life, and will increase salinity in the water bodies including ground water which may become unfit for drinking purpose or steaming tanks.

2.14.2 Hide washing and soaking

During this step hides are rehydrated. Surfactants and alkaline are added for the removal of dirt. The effluent from this process contains

BOD, COD, salt, insecticides and bactericides, flesh scraps, hair, skin and dirt .High values of BOD and COD indicate high water pollution.

2.14.3 Unhairing and liming

Liming and unhairing is one of the steps which produce effluent with very high pollution load. Wastewater discharged from this step contains residues of hair, epidermis as well as other dirt accumulated in the hides. The combination of lime (to swell the hides), salt and sodium sulfide (for unhairing) together with bactericides and insecticides accumulated in the hides will be also discharged along with the effluent. The effluent will have high pH, high concentration of BOD, COD, salt, sulfide, insecticides and bactericides, ammonia, alkaline and suspended solids. Solid waste generated is hair-sludge, lime and sludge. Hydrogen sulfide gas (rotten egg gas) is emitted in case insufficient alkaline is added resulting in a pH lower than 9.5[17, Leather tannery working group. 1997].

Ammonia gas causes irritation of the respiratory system and results in breathing problems. Hydrogen sulfide gas has very strong smell and is highly toxic. Discharge of suspended solids will reduce the depth of water ways and in addition will create anaerobic conditions due to the decomposition of organic material in the sediment. Hair, lime and sludge will contribute to the clogging of water way.

2.14.4 Fleshing and spliting

Hide which has been limed/unhaired will be fleshed by a scraping machine.Subsequently the defleshed hide will be split by “splitting machine”. Main waste generated from this step is fleshings and scraps from the lower part of hides. These hide scraps have dark green color due to the chemical reaction during the step of unhairing and liming. The liquid effluent from this step is small in volume, and has similar composition as the waste water generated from the liming step but with lower concentration.

2.14.5Deliming of splittings

For deliming of splittings, ammonium chloride is added to reduce leather swelling.Acid is introduced for neutralising purposes, reducing the pH to 7-8.At the same time the splitting is decoloured by using hydrogen peroxide as oxidizing agent. The waste water generated has muddy white color containing BOD, COD, salt, sulfate, ammonium,alkaline,suspended solid and chloride.This production step may be omitted in some tanneries. Chloride is compound of salt. If discharged into the water, the water will be brackish and has only limited usage.

2.14.6 Pelt Deliming and Bating

Pelt deliming and bating is used to reduce pH level of the pelt with the addition of ammonium chloride and/or ammonium sulfate. Addition of these chemicals must be sufficient to eliminate the action of lime completely.Enzyme or bate is added to smooth and soften hide tissues. Therefore, wastewater generated from this step will contain BOD, COD, salt,sulfate, ammonium, alkaline, suspended solid, and chloride.Ammonia gas is also emitted at this step.[17, Leather tannery working group. 1997].

2.14.7 Pickling and Chrome Tanning

Pickling is done to adjust pH level of the pelt to the range of 1.4 - 3.0 which is suitable for subsequent chrome tanning. Sodium chloride or sodium sulfate and sulfuric acid are added for the pH adjustment. The pickling takes 1-2 hours[17, Leather tannery working group. 1997]. Subsequently, basic chromium sulfate is added as tanning agent, reacting with protein in the hide.Normally 70% of chromium added will remain in the chrome tanned hide [17, Leather tannery working group. 1997]. Some tanneries add “tanning aid”during pickling (for high chromium up-take and reduction of chromium concentration in the wastewater).Chromium chemical fixation will be more effective if the pH and temperature levels are increased. The wastewater from this step will contain acid, salt, suspended solid,BOD, COD, and chromium. Float residues will contain chromium, and will be discharged along with the effluent.(The concentration of chromium in the effluent is about 2,0004,000mg /l) [17, Leather tannery working group.1997].Chromium is a heavy metal hazardous to living creatures and dangerous to the nervous system.[17]

2.14.8 Sammying and Shaving

Sammying generates a certain amount of effluent which the composition is similar to the effluent from chrome tanning. Shaving generates ‘chrome shavings’ which is solid waste containing chromium. These shavings create a big problem to the environment and have to be disposed off at a secured landfill site. Disposal at domestic garbage landfills or by incineration is not recommended.

2.14.9 Neutralization, Re-tanning, Dyeing and Fat Liquoring

For chrome tanned “wetblue” Neutralization is to increase the pH level to between 5and 6 by adding sodium carbonate for the removal of residue chromium and to prepare wet-blue for subsequent retanning and dyeing processes. Therefore, chromium is present in the effluent from this step along with suspended solids.Re-tanning is performed simultaneously with fat liquoring.

Formic acid, syntans(synthetic tanning agent) and fat liquor are added. The chemicals which are not absorbed by the hides will be discharged along with the effluent in which chromium is also found.Wet dyeing is usually applied to chrome tanned hides. It is to dye the entire hide. It is not similar to colour spraying or painting which are usually applied to vegetable tanned hides.Chemicals, dyes, organic acid and hot water is applied for the completion of dyeing. All these substances are to be found in the effluent. Even though this step generates a very small effluent volume, it must be segregated and pre-treated in a sedimentation tank for removal of suspended pigment.[17, Leather tannery working group.1997].

2.15Vegetable Tanning Process

Vegetable tanning is carried out in rotating wooden tanks, or in a series of concrete tanks, by adding tanning agent extract from eucalyptus bark,quebraco tree, etc. Owing to the high prices of chemicals, vegetable tanning liquid is usually not discharged but re-used.Only vegetable tanning agent is added to the tanning pit. Therefore, there is no negative effect to the environment, since there is no effluent emission.

The effluent from the subsequent two-stage washing step creates more problem. Washing of vegetable tanned hides is carried out with the addition of oxalic acid which will be discharged with the effluent along with the surplus vegetable tanning agent.Shavings from vegetable tanning contain no chromium, and can be disposed off as normal garbage. Hence, they do not create any problems to the environment.

Coloring of vegetable tanned leather is carried out by painting /spraying color on the leather surface. It creates only a small effluent volume.This wastewater may be treated with plain sedimentation method for removal of suspended solids. Then the supernatant will be discharged to the combined wastewater treatment system of the tannery.

Table(2.5)Summary – Average characteristics of combined wastewater generated from tanneries(unit is in mg/l except for pH value) [17, Leather tannery working group. 1997].

average		minimum-maximum
pH	8.15	6.67-8.64
BOD	1,535	958-4,200
COD	4,150	2,433-8,100
SS	2,097	1,027-4361
TS	13,857	9,118-21,881
Cr	77.68	18-204.4

2.17Methods for minimization of solid waste and water pollution from production process

Minimization of solid/liquid waste from the production process is to reduce the amount of waste to be taken for disposal or treatment. Accordingly, pollution load and disposal costs are reduced. Minimization applies to all media i.e. liquid waste (wastewater), solid waste and gaseous emissions.

There are 4 main methods of waste minimization called 4R as follows:

1. Replace. If it is known which chemical or raw material will create a lot of problems, others should be used instead, for instance, aluminum may be used instead of chromium for tanning.

2. Reduce. If it is still needed, its use should be reduced, for instance, using less water to wash the tank. Or it could mean to reduce the waste, for instance, recycling of water or chemicals repeatedly without discharging as waste water, etc.

3. Reuse. Means, i.e. collecting spent chemicals or any material already used, in a tank and use it again.

4. Recycle. Various processes can be used to extract some substances from the waste then use them in the production process again. For instance, chromium extracted from spent liquor from the chrome tanning process can be recycled to the tanning drum.[17, Leather tannery working group. 1997].

This 4R method can be used in every step of a tannery's production process and is described in detail below:

2.18Minimisation of Wastewater Volume and Pollution Load

Wastewater volume and pollution load can be reduced by:

- minimizing water consumption (which will also reduce the volume of wastewater).

- using chemicals effectively, and

- reuse/recycle chemicals.

2.18.1Techniques for reducing water consumption

The techniques which can be easily applied are:

-Use a suitable size of container to reduce the problem of water overflow.

- Install flow meters to measure the use of water in every step, and record the daily use of water. This will help monitor whether there is over-use of water.

- Use mechanized system for chemical dosage and water filling.

- Use the counter-current system of washing, i.e., use clean water to wash rather clean leather or piece of work (already washed briefly), then use more dirty water (already used for leather washing) to wash very dirty leather or piece of work. This will save a lot of water.

- Avoid excessive water consumption for washing purposes.

- Do not use the system of soaking hides in a tank and allow continuous water overflow. It should be improved by soaking hide firstly in water for a long time, and using the wash water in that tank repeatedly until it becomes too contaminated and has to be discharged.

- Reuse water (after pre-treatment) in operations which do not require high water quality,for instance, hide soaking, lime mixing, floor cleaning, tank cleaning, etc.

2.18.2 Reduction of sulfide in liming and unhairing

Sulfides can generate the emission of “rotten egg” gas which has not only a very bad smell but is dangerous to the respiratory system. It is highly toxic and poses a severe health risk at relatively low concentrations. Therefore, minimization of sulfide application should be considered.

One possibility for the reduction of sulfide application is the use of “enzymes” in the unhairing process. This method will reduce the amount of sulfide required for unhairing and subsequently leads to lower concentration of sulfide in the wastewater as well as a reduced risk of high H_2S emissions However, this enzyme unhairing process is slightly costlier than the conventional sulfide unhairing process.[17, Leather tannery working group. 1997].

2.18.3 Recycling/reuse of lime solution

In the unhairing step hides are soaked in a lime solution, containing sodium sulfide. Hairs will be gradually decomposed in this chemical solution and will form a hair sludge, which also contains non decomposed hair and hide parts. In normal practice, the spent unhairing solution will be discharged after use. Reuse of the unhairing solution is possible if the hair sludge is removed by fine screening and adding fresh lime and sodium-sulfide to ensure sufficient chemical concentration. This reuse method will reduce sulfide load in the waste water but requires that the hides are thoroughly cleaned in the washing step, thus needing more water in the washing process.

The unhairing solution can be reused about 10 times and requires, besides the screening equipment, sufficient storage capacity as well as equipment for the analysis of lime and sulfide in the spent solution.

The disadvantage of this method is that the wastewater from this unhairing procedure will contain a higher concentrations of organic substances (indicated by an increased COD value) and in addition has a strong smell.

The advantages of this reuse method are:

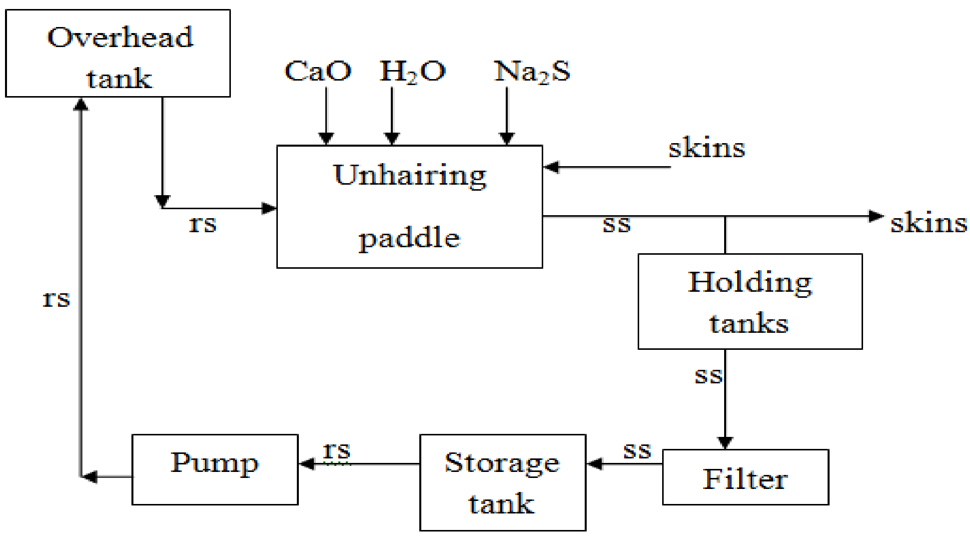
- Does not require changes in the production process

- Easy operation

- Has no negative effect on the quality of leather[17, Leather tannery working group. 1997].

2.18.3Reuse-method

The spent unhairing solution will be pumped from the rotating tank to a fine screen (filter) for separation of the hair sludge. Then, this "filtered" lime solution will be pumped back to the rotating tank (See Fig.2.2), where lime and sodium sulfide is added to the required concentration. This method can be also applied with the paddle tank. This screen (filter) used can be of rotating type made of stainless steel or plastic. [17, Leather tannery working group. 1997].



Fig(2.2):Lime solution recycle

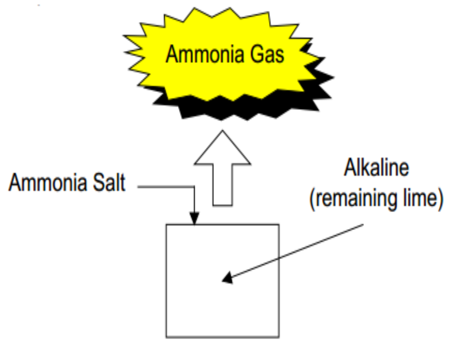
2.18.3.1Cost of recycling of spent unhairing solution

Unhairing time requirements are usually one day for cow hides and two days for buffalo hides. Water consumption is about 3 cubic meters per ton of raw hide[17,Leather tannery working group.1997]. Usually, the quantity of hide unhaired each time is 6 tons, therefore, the wastewater generated by each unhairing batch is about 18 cubic meters[17,Leather tannery working group.1997].The construction costs for a spent solution storage tank including the screens is about30,000-40,000Baht.[17,Leather tannery working group.1997].Cost recovery is normally within two years.

2.18.4 Deliming with carbon dioxide (instead of using ammonium salt)

After unhairing it is necessary to adjust the hide condition (pH) to make it suitable for the subsequent tanning process. This is achieved by deliming using ammonium salt and diluted sulfuric acid. Therefore, the deliming process generates high ammonia gas emissions, which irritate eyes, nose and lungs, etc.

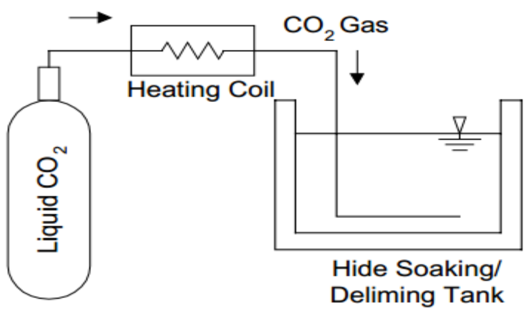
Ammonia compounds in the wastewater are toxic to fish and have to be treated properly prior to final discharge. Therefore, the amount of ammonium salt used for deliming should be controlled carefully to avoid negative health and environmental impacts.



Fig(2.3): Emission of ammonium gas in the conventional process of deliming[17,Leather tannery working group.1997].

In order to eliminate both, the discharge of ammonium salt in the effluent as well as ammonia gas emissions in the tannery, the method of carbon dioxide (CO2) deliming can be applied. . The carbon dioxide gas will chemically react with lime and will form “lime stone” (SeeFig(2.4).

This method is suitable for split hides with a thickness not exceeding 3 mm. Investment costs for this deliming method is high. Limitations are the longer deliming time requirements and the risk of H2S gas emissions because of lowering of the pH value.Therefore, hydrogen peroxide has to be added to the deliming process to ensure the oxidation of sulfide, avoiding rotten-egg gas odour problems.



Fig(2.4): Carbon dioxide gas deliming system. [17,Leather tannery working group.1997].

2.18.5 Reduction of chromium in effluent

Prior to the chrome tanning process, the delimed hides are pickled with sulfuric acid for pH adjustment. Subsequently the tanning agent, basic chromium (III) sulfate with a chromium content of 26 % (as Cr2O3) is added[17,Leather tannery working group.1997].The amount of chromium required for tanning is in the range of 8-10 % of hide weight. Time required for chrome tanning carried out in wooden drums,is about 8-10 hours. [17,Leather tannery working group.1997].

Chromium will chemically react with the carboxyl group of the protein in the hides. The fixed chromium makes the hides stable and gives the necessary strength. However, the hides will absorb only 65-70% of the chromium added. Therefore, chromium will remain in the spent chrome tanning liquid, which is normally discharged as waste water. The overall discharge of chromium from a typical tannery is shown below: [17, Leather tannery working group.1997].

- 20% remaining in the effluent from chrome tanning, can be reused/recycled.

- 2% in the liquid remaining in the tanned hide layer.

- 8% in the effluent from sammying (sammying float).

- 3-5% in the shavings, hide tissues and scraps.

- 2-7% in the re-tanning liquid.

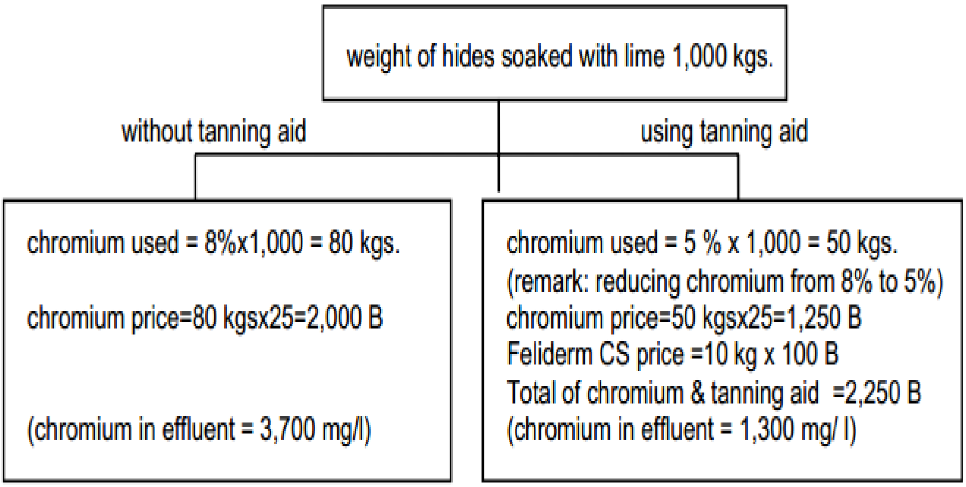
The volume of waste water generated by the chrome tanning process (residue float) is about one cubic meter per ton of raw hide. The residue float has an average chromium content of about 3 g/ l (or 3,000 mg/l) [17, Leather tannery working group.1997].If the conventional (standard) chrome tanning process is applied.

The concentration of organic substances and suspended solids in this wastewater is relatively low. Therefore, methods for residue float utilization and/or chrome discharge minimization should be introduced and applied .The following three methods for chromium discharge minimisation have been proven and are applied successfully:

2.18.5.1 High-exhaustion chrome tanning process

At present so-called “tanning aids” or “chromium absorption aids” are used in the high exhaustion chrome tanning process. By using these agents, which improve the chromium uptake, the total amount of chromium required for tanning can be reduced. This subsequently results in reduced chromium content in the residue float (wastewater).

One brand name of these tanning aids is Feliderm CS. A comparison of tanning chemicals required in the standard tanning process and the high exhaustion process is shown below:



Fig(2.5):Comparison between standard and high-exhaustion chrome tanning process(using Feliderm-CS)[17,Leather tannery working group .1997].

The above diagram indicates that the chromium content in the effluent from the high exhaustion chrome tanning process is only 1,300 mg Cr/l) as compared to 3,700 mg/l from the standard chrome tanning process[17,Leather tannery working group.1997]. However, the reduced chromium concentration is still by far too high for direct discharge and has to be further reduced by proper treatment, by chemical precipitation and sedimentation.

Moreover, the application of a complex organic compound like the tanning aids has shown to make chromium precipitation and sedimentation more difficult. In addition, the application of tanning aids requires good process control to achieve satisfactory leather quality.

2.18.5.2Tanning solution reuse

After tanning a high concentration of chromium still remains in the "residue float" If this liquid is collected and refurbished with fresh tanning agent (basic chromium sulfate) the residue float can be reused for tanning purposes. This will lead to reduced chromium load discharged from the tannery.

However, the residue float must be correctly analyzed for its remaining chromium content as well as salt content and concentration of organic substances. The residue float has to be discharged whenever the content of salt and organic substances reaches a pre-determined maximum concentration.Usually, the residue float can be reused for a period of up to 3-4 months [17,Leather tannery working group.1997].

2.18.5.3 Recycling of chromium

Chromium recycling is carried out by separating chromium from the residue float by means of chemical precipitation using Magnesium oxide (MgO).The chromium chloride sludge is separated from the solution by sedimentation and dissolved in sulfuric acid for subsequent use as tanning agent.[17, Leather tannery working group. 1997].

Using “quick methods” for the analysis of chromium in the “residue float”the required amount of MgO-solution/suspension can be determined by using the following table:

Table (2.7)Analysis of chromium in residue float[17,Leather tannery working group.1997].

the value of chromium readable (g / l)	1	1.5	2	2.5	3
the volume of MgO to be added (l)	100	150	190	240	290

-Residue float volume = three cubic meters

-10% MgO solution, prepared by using MgO 30kg and 300 liters of water the solution must be prepared 1day before and must be stirred all the time during working period. [17, Leather tannery working group.1997].

It can be concluded that at an investment cost in the range of 300,000-500,000 Baht (depending on the size of tannery) and if the high-exhaustion tanning process (tanning aid Feliderm-CS) is not used, the payback period of the chrome recycling system is around 2-3 years.

However, if the high exhaustion chrome tanning process is used, the chrome recycling system will not cover costs, which is mainly resulting from the comparatively low chromium concentration in the high-exhaustion “residue float”.Table(2.8)indicates the amount of chromium which can be recycled (indicated as chrome tanning agent) at different volumes and concentrations of the recycled chrome solution.

Table(2.8):Volume of chromium recycle in the form of tanning agent in kilograms[17,Leather tannery working group.1997].

Chrome solution (liter) / Chrome conc. (gram / liter)	300	350	400	450	500	550	600	650	700	750	800
15.0	18	21	24	27	30	33	36	39	42	45	48
20.0	24	28	32	36	40	44	48	52	56	60	64
25.0	30	35	40	45	50	55	60	65	70	75	80
30.0	36	42	48	54	60	66	72	78	84	90	96
35.0	42	49	56	63	70	77	84	91	98	105	112
40.0	48	56	64	72	80	88	96	104	112	120	128
45.0	54	63	72	81	90	99	108	117	126	135	144
50.0	60	70	80	90	100	110	120	130	140	150	160
55.0	66	77	88	99	110	121	132	143	154	165	176
60.0	72	84	96	108	120	132	144	156	168	180	192

2.18.5.4Replacing chromium with other chemical tanning agents

Aluminum, zirconium, titanium and ferrous salts (II) can be used as replacement for chromium as leather tanning chemical. But the leather which is tanned using these chemicals has a lower quality than chrome-tanned leather both in terms of softness and thickness.In addition, chrome tanned leather has higher resistance to heat, indicating that leather tanned with other chemicals (replacing chromium) may not be suitable for the shoe industry.

The advantage of this chrome-free tanning process is the absence of chrome shavings. Shavings from this process, therefore, can be either taken to a domestic landfill site for disposal, or can be reused for the production of leather board or fertilizer or roof tiles.

2.19Wastewater and solid waste treatment

Tanneries in general will discharge wastewater from the various production areas into a single collection drain, leading to the wastewater treatment system. However, because of the type and amount of chemicals applied in the different production steps, as well as because of the different reactions taking place in the various productions steps, the composition/characteristics of wastewater generated in each production step, shows big variances.

Therefore, separate treatment (or pretreatment)of waste water generated at the different production steps should be considered, which could reduce overall wastewater treatment costs for a tannery. The main process steps at which wastewater should be pre-treated prior to mixing with other wastewater streams are the unhairing process in the beamhouse and the chrome tanning process in the tanyard.

2.19.1Sulfide wastewater pre-treatment from the unhairing step

Unhairing is a production step in which a very high pollution load is generated. About nine cubic meters of wastewater per ton of raw hides (9 m3/ton) [17,Leather tannery working group.1997]are generated, having the following characteristics:

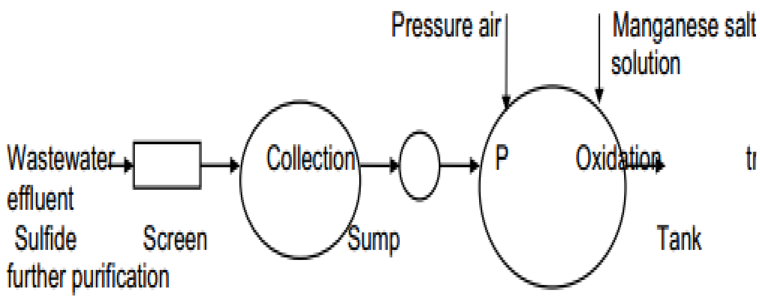
Table(2.9)Waste water characteristics[17,Leather tannery working group .1997]

Pollutants	Concentration
BOD	13,000 - 50,000
pH	12 - 13
sulfide	500 - 1,400

The high content of sulfide in this waste water is of particular concern. Sulfide treatment systems applied both in Europe and USA are oxidization and chemical precipitation/sedimentation.These treatment methods are described as follows:

2.19.1.1Sulfide Oxidation with Manganese Salt as Catalyst (Air Oxidation)

Sulfide containing waste water (spent unhairing liquor) is collected in a suitable tank. A predetermined amount of Manganese (Mn2+) salt is added and the tank content is aerated by introducing air by means of a blower-diffuser system. Sulfide will be oxidized and transformed into thiosulfate, sulfite and sulfate which are more inert than sulfide.Details of system design and operation are shown in Fig(2.6) and Table(2.10)respectively



Fig(2.6)Sulfide Oxidation Treatment Process[17,Leather tannery working group.1997]

Table(2.10)Design and Operation of Sulfide Oxidation.

% of Plant Flow Treated	Catalyst Mn^{++} Type mg/l	Batch Oxidation Time (hour)	Aeration Equipment HP/1000ft^3	KW/1000m^3
100	$MnSO_4$ 31	3-10	1.5	(40)
40	$MnSO_4$ 9.1	4	-	(-)
40	$MnSO_4$ 55	7	4.2	(110)
15	$MnSO_4$ 91	8	1.8	(47)
25	$MnSO_4$ 302	8	1.3	(34)
40	$MnSO_4$ 51	8	3.8, 5.2	(100, 137)
100	$MnCl_2$ 0.3	24	1.5	(40)
100	$MnSO_4$ 79	960	0.14	(4)
40	$MnSO_4$ -	2-3	1.5	(40)

* batch means the total period of time required for complete chemical reaction - tank emptying - tank filling and chemical addition etc.. Indicating that this is not a continuous process.

In general, this waste water contains sulfide with a concentration in the range of 1,200-1,400 mg/l which can be treated by the introduction of air at the ratio of 1 m^3 air/minute/m^3 of waste water or 20 m^3/hour/m^2 (m^2 of water surface area)at a tank depth of not less than 4-6 meters [17,Leather tannery working group.1997].Pressurized air is supplied for a period of 6-12 hours and Manganese sulfate is added in the range of 50 and 100 g per m^3 of waste water - both, mechanical surface aerators as well as submersible aerators can be used for the supply of air[17,Leather tannery working group.1997].

The collection tank must be equipped with a bottom scraper for the collection and removal of sediments. During the introduction of air, hydrogen sulfide gas (rotten egg gas) and ammonia gas will escape from the tank causing odor problems. The correct method is to cover the tank and withdraw the contaminated air,by means of an exhaust fan, to a biofilter purification system – the air disposal rate should be 1.5 m^3/hour per m^2 of water surface area.

If pH is lower than 8, there will be the problem of hydrogen sulfide gas (badsmell, can lead to death at a concentration of 2,000 ppm) If pH is higher than 10, there will be the problem of generation of ammonia gas ,pH should be managed in the range 9-10

Sulfide concentration in the treated effluent can be lower than two (2) mg/l. [17,Leather tannery working group.1997]

1.19.1.2Oxidation of Sulfide with Hydrogen Peroxide (H_2O_2)

This method is used successfully to oxidize sulfide in tannery wastewater. Investment costs for construction of the chemical reaction tank and purchase of chemical dosing equipment are low, however the cost of Hydrogen peroxide is rather high. Therefore, this method is suitable for small tanneries with little effluent from Unhairing activities (for instance discharging Unhairing liquor 1-2 times a week) [17,Leather tannery working group.1997].

In this oxidation method, the effluent is collected in the chemical reaction tank,pH of the liquid is adjusted to below 8, followed by the addition of Hydrogen peroxide. At a pH value below 8.0, sulfide will be oxidized to sulfur.If the pH is higher than 8, sulfide will be oxidized into sulfate. However, oxidation to sulfate requires 3 times more Hydrogen peroxide than oxidation to sulfur. Therefore, it is important for economic reasons to adjust the pH of the waste water below 8 before adding the peroxide solution. [17,Leather tannery working group.1997]

About 200mg/l of Hydrogen peroxide is required to reduce sulfides from an initial concentration in the range of 100-300 mg/l to less than one (1) mg/l in the treated effluent.

2.19.3Chemical Precipitation with Iron Salt

Precipitation of sulfide with iron salts is another effective method of reducing sulfide concentration.There might be incidental removal of other pollutants in this process too, i.e. suspended solids and BOD. The iron salts may be available at a low price from the steel industry - using their spent pickling liquor (acid). However, this method has disadvantages, i.e. bad smell, effluents with very black color, high chemical requirements, and a rather high cost for Ferrous-sulfate (in case spent acid from the steel industry is not available and the chemical has to be purchased).

In addition, this process generates a voluminous sludge which has to be taken for further treatment. Since this sludge is not suitable for agricultural purposes the treatment and disposal costs are quite high.

2.19.3Chromium Wastewater Treatment

The treatment method used for the purification of wastewater from chrome tanning,sammying of wet-blue, re-tanning and dyeing is chemical precipitation of chromium with alkaline solution(such as lime) and discharge of the supernatant for further biological treatment.Atank similar to the one which has been designed for recycling of chromium can be used.

The alkaline used for chromium treatment does not have to be MgO (which is much more expensive than other alkaline chemicals – in particular CaO) since the created chromium chloride sludge is not taken for reuse in the tanning process.[17,Leather tannery working group. 1997]

The most suitable chemicals for chromium treatment are lime (CaO), Sodium Carbonate ($Na_2(CO)_3$) and caustic soda (NaOH).To achieve rapid sedimentation of the precipitated chromium-chloride sludge (adding lime solution until a pH of about 8.5 is achieved) either Anionic Polyelectrolytes or Ferric chloride can be added[17,Leather tannery working group.1997].

The chromium removal efficiency by this physico-chemical treatment system is more than 98%.

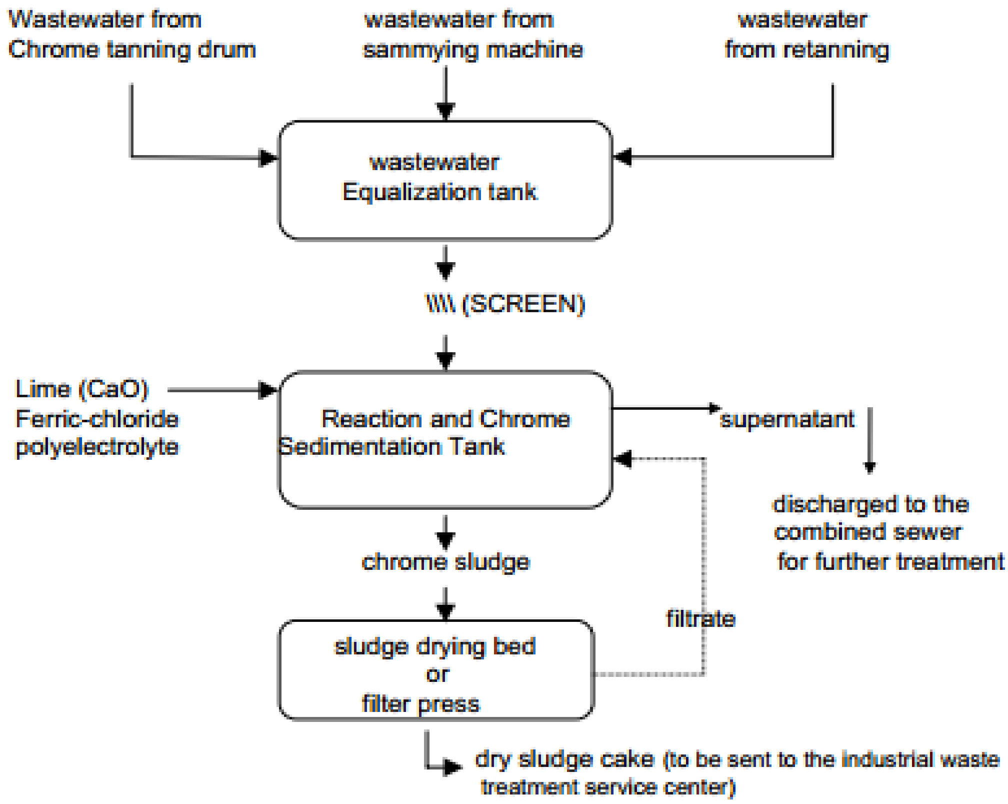
The settled chromium-chloride sludge should be dewatered either by means of a filer press or at a drying bed. The dried sludge cake should be properly packed, signed and sent to the Industrial Waste Treatment Service Center for further treatment and final disposal.

The supernatant from either the chromium treatment system or the chromium recycling system still has a high concentration of organic substances and has to be sent to the biological wastewater treatment system for further purification.

However, it has to be emphasized that the volume of hazardous sludge (chrome containing) produced from this chrome treatment step is much less compared with the volume of sludge generated by a combined wastewater treatment system without a pre-treatment system for chrome containing waste streams.

In addition, if chrome pre-treatment systems are installed, the excess sludge generated from the joint wastewater treatment system will contain very low chromium concentrations and, hence, can be used as fertilizer or disposed off at a domestic landfill site. This excess sludge then is not classified as hazardous waste anymore. Therefore,the costs which have to be paid to the Industrial Waste Treatment Service Center for special treatment of sludge with excessive chromium concentrations can be reduced substantially. [17, Leather tannery working group.1997].

The hazardous waste related costs are then only for transportation and treatment of sludge produced by the chrome tanning wastewater pre-treatment system to the Industrial Waste Treatment Service Center. It is estimated that about 0.12-0.25 ton of sludge/ton of raw hides are generated by the chrome treatment system[17,Leather tannery working group.1997].The total chrome-sludge disposal cost thereby depend on the distance the sludge has to be transported i.e. from the tannery to the Service Center.



Fig(2.7)Chromium Wastewater Treatment System Chemical Precipitation[17,Leather tannery working group.1997]

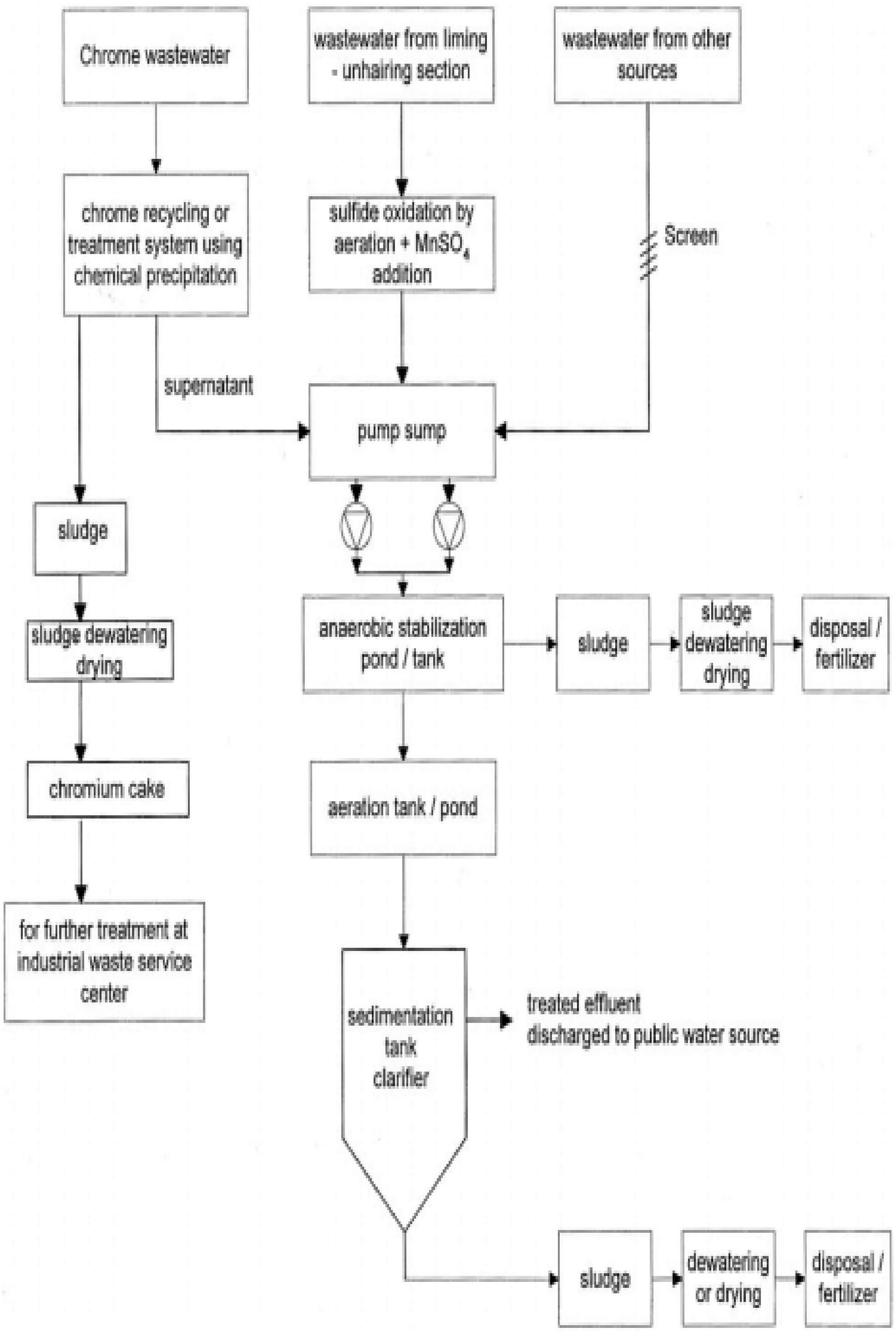
Volume of chrome effluent is about 0.5-0.75 m3/ton of raw hides.Volume of chromium sludge is about 0.2-0.3 m3/m3 effluent or about 0.1-0.2 m3/ton of raw hides,or about 0.12-0.24 ton/ton of raw hides [17,Leather tannery working group.1997].

2.19.3 Combined Wastewater Treatment

The treatment system applied in the leather tanning industry normally emphasizes on the removal of organic substances (BOD), sulfide and chromium.A schematic diagram of the treatment process is shown in the following figure indicating chromium wastewater segregation and separate chromium treatment. Subsequently, the pre-treated effluent from this precipitation/sedimentation process will be combined with the wastewater from unhairing step and with overall tannery wastewater to be discharged into the pump sump from where it will be transferred for further biological treatment.

The first step of the biological treatment is an anaerobic system (no mechanical aeration equipment and hence no electricity consumption at this step). In this process bacteria which do not require oxygen will digest organic compounds in the wastewater and purifying the same. However, treatment efficiency of the anaerobic system is not sufficient to allow discharge of the effluent to a water body. Therefore, the pre-treated effluent from the anaerobic treatment is further purified in an aerobic system. This method is characterized by the requirement of oxygen for biological oxidation. Oxygen is supplied by mechanical aeration systems resulting in high electricity cost. At this treatment step, another kind of bacteria (aerobic) will further digest organic compounds of the wastewater until it is clean enough for discharge into a public water source.

Operational data obtained from the combined wastewater treatment system of the tannery cluster indicate average electricity costs of about 420,000 Baht/month - total operating cost i.e. including personnel cost, chemical cost, etc. are reported as 900,000 Baht/month equal to a total wastewater treatment cost of about 3 Baht/cubic meter(excluding costs for chemicals, personnel, water analysis,equipment maintenance,etc.) [17,Leather tannery working group .1997].



Fig(2.8)Combined Wastewater Treatment System of Tannery Industry[17,Leather tannery working group.1997].

2.19.4 Disposal of Chromium Containing Solid Waste

2.19.4.1 Sludge from Chromium Treatment System

Dewatered sludge from the chrome treatment (precipitation) system contains high concentrations of chromium exceeding the standard prescribed for landfill or agricultural use. Therefore, this sludge is considered as hazardous waste and must be treated at the Industrial Waste Treatment Center.

Table (2.11) Recommended standards for Chromium (III) concentration in soil and sludge for agricultural use(by UNIDO/UNEP)[17,Leather tannery working group.1997]

concentration in soil, mg/kg dry soil	150-200
concentration in sludge, mg/kg dry sludge	1000-1500
total metal added in agricultural area	300-600 (a), (c)
amount added in agricultural area per year (kg/hector/year)	45 (b), (c)

For the soil with background concentration of 50 mg/kg, the increase of concentration is allowed to be 100-200 mg/kg, at 25 cm depth and soil density of 1.20. The total metal accumulation in a period of 100 years must not exceed 450 kg/hectare. The total increased value must not exceed the concentration standard in the soil.[17,Leather tannery working group.1997]

2.19.4.2Excess sludge from combined biological wastewater treatment system

After segregation and separate treatment of chromium wastewater, the combined wastewater will contain only minimal chromium concentrations. Therefore, the excess sludge produced in the combined / joint biological treatment system will contain a chromium content not exceeding 800 mg/kg dry solids (experience from Germany).This sludge can be either disposed off at a domestic landfill site, or used for agricultural purposes.[17,Leather tannery working group.1997]

The disposal costs for this type of solid waste consist mainly of the transportation cost to the landfill site (or to the agricultural area) and landfill costs which are much lower than treatment cost for hazardous waste landfills.

2.19.4.3Solid waste containing chromium

Chromium containing solid waste, such as chrome shavings, (if these chrome shavings are reused) has to be sent for treatment and landfill at the Industrial Waste Treatment Center. Incineration is prohibited because it will result in the creation of highly toxic and carcinogenic Cr(+6) compounds. Hence, transferring solid waste pollution problems into air pollution problems.[17, Leather tannery working group. 1997]

2.20Monitoring and control

In order to minimize the environmental impact from tanneries it is necessary to introduce suitable measures for pollution related to both the production process and the wastewater treatment system, including proper operation and supervision. To achieve this in both, individual tanneries and tannery the environmental management guidelines for the leather tanning and finishing industry must be applied.

Moreover, the tanners should cooperate closely with government officers, responsible for supervision, follow up and control of pollution control measures at the production process and the wastewater treatment system. This regular co-operation will result in continuous improvement of the environmental management system at the tanneries and will correct any operational problems and deficiencies.

2.20.1 Process Control

Tanners should pay special attention to the Good housekeeping, Development of production process, applying clean technology or less polluting technology, Improvement of control and supervision of the different production steps in order to ensure proper operation of the different equipment and avoid the discharge of pollutants to the environment. Introduce wastewater segregation, especially separating the wastewater stream from the chrome tanning section from other wastewater, Chromium recycle system should be installed in case of the tannery without application of chromium absorption agent.

However, when Chromium absorption agent is applied, it is necessary to install and operate a chromium pre-treatment system to remove chromium to the prescribed level of 30 mg/l[17,Leather tannery working group.1997],Measure and control the volume of water and chemicals applied in each production step, keep records of consumption ratios in relation to the amount of hides processed, train operators and workers in the safe handling of chemicals and cleanliness of the tannery and install signboard to show the name of chemicals used in the production process and their potential danger. Introduce proper storage of chemicals. [17, Leather tannery working group. 1997]

2.20.2End of Pipe Treatment Control

Correct collection of samples from end-of-pipe wastewater treatment systems is required to avoid the generation of wrong information concerning operation, efficiency and compliance of the final effluent quality with the prescribe standards.

2.21Waste minimization and management

Process-integrated techniques to reduce waste production inside installations are essential for an optimized waste treatment system. Waste treatment is still necessary for materials which cannot be reused.Various solid or liquid waste fractions have to be considered. A large amount of waste consists of organic materials such as hair or wool, trimmings, fleshing, splits, shavings, fats and grease. As long as these fractions are not contaminated or hardly contaminated with chemicals, recovery options can be considered that offer economic as well as environmental advantages.[18,Rydin,S et al.2013]

Recovery of proteins and fat or the production of other raw materials is feasible. The further processing can be done off site by other industries. Sometimes plants can be used by a number of tanners or on site on a small scale.The optimum arrangement has to be found depending on the local environment and the local options available.

Since the implementation of the EU Directive on the landfill of waste(1999 /31/ EC)[18,Rydin.S,Black.M,Scalet.BandCanova.M.(2013)] ,the landfill of untreated organic waste has become more difficult and in some Member States, effectively banned. One of the treatment methods for organic wastes which have become popular as a result is composting. Some tannery wastes are unsuitable for composting or require specific pretreatment.

2.21.1 Organic waste fractions and by-products

Organic materials are separated from the main product stream at various process stages. Some of these materials are by-products for which there are established uses, while others are wastes for which a disposal route must be found. This distinction is not a simple matter because users of particular by-products may not be available within an economic transport distance of a given tannery. Furthermore, the closure of secondary leather producers may preclude the processing of some by-products.

Some tannery by-products can be processed for human consumption in which case, food hygiene rules apply to their handling and storage (EU Regulation853/2004).Collagen can be obtained from,e.g. limed trimmings and splits. Collagen has various uses as meat and bakery product additives, in the manufacture of pharmaceuticals,cosmetics and as additives to rubber products. Food grade gelatin can also be produced.

Materials or wastes separated before liming must be handled so as not to endanger animal health (EU Regulation 1069/2009). Rendering (in a plant licensed under those regulations) is often the only disposal route for such materials, but approval/licensing for the generation of biogas from raw fleshing may be available where suitable precautions are taken.Waste and by-product streams not intended for food use and not needing treatment in a licensed plant may be subjected to rendering or other treatment:

- Technical gelatin and glue can be produced from untanned materials.
- Tallow recovery from limed trimmings, fleshing, and splits can be performed in rendering plants or on site. Limed trimmings, fleshing and splits may need pretreatment with acids before conversion. In some cases, tallow can be separated and recovered after a thermal pretreatment. Tallow may be used as a substitute fuel.
- Recovery of protein (protein hydrolysate), e.g. from splits, for conversion into fertilizer.
- Tanned wastes can be used in leather fiberboard production.

Further treatment options for organic waste and sludges from waste water treatment dependent on the composition are composting, recycling in agriculture, anaerobic digestion, and thermal treatment.Treatment to reduce the water content may be applied. Landfilling of tannery wastes is prohibited or severely restricted in some Member States.

2.21.2Hair and wool use/disposal

If there are no options for reuse, the hair has to be disposed of. In some cases, the hair is not separated and is sent for disposal together with the waste water treatment sludges.The hair residues from the unhairing step using hair-saving techniques are partially destroyed. Depending on rinsing and cleaning procedures, the chemicals from the unhairing step are attached to the hair. After washing, therefore, sulphides sometimes have to be removed by oxidation. Hair residues can be compacted to reduce volume before further treatment or disposal. The options for recycling and reuse of hair are summarized in Table (2.12)Hair can be used as a fertiliser because of the nitrogen content. Hair may also be landfilled after composting.

Table(2.12)Options for dealing with hair[18,Rydin.S,Black.M,Scalet.B and Canova.M.(2013)]

	Hair options
Uses as a by-product	Filling material
Reuse after preparation	Protein hydrolysate
Recycling as	Fertilizer
Other recovery	Generation of biogas by anaerobic digestion

Sheep wool can be used by the textile industry, e.g. in carpet manufacture.Wool can also be composted together with other wastes (although the temperature of spontaneous ignition has to be taken into account).

Achieved environmental benefits are some reductions of the environmental impact of disposal when hair or wool is used.The cross-media effects are sulphide odour production may cause problems at composting sites.[18,Rydin.S,Black.M,Scalet.BandCanova.M.(2013)]

2.21.2.1Technical considerations relevant to applicability

Utilization of wool in the textile industry is only practical where the tannery is located near textile manufacturers.External anaerobic digestion facilities may be reluctant to accept any wastes from a tannery.

2.21.3Options for the reuse, recycling and disposal of trimmings

An overview of options dealing with raw limed and tanned trimmings are given in Table (2.13)

Table(2.13)Options for dealing with raw, limed, and tanned trimmings [18,Rydin.S,Black.M,Scalet.B and Canova.M.(2013)]

	Raw trimmings	Limed trimmings	Tanned trimmings
Uses as a by-product		Collagen production	Patchwork, small leather goods,etc.
Reuse after preparation		Production of technical gelatine, or tallow, or protein hydrolysate	Leather fibreboard production for non-finished trimmings.

Table(2.14)continued

Recycling as	Hide glue	Hide glue	
Other recovery	Generation of biogas by anaerobic digestion	Generation of biogas by anaerobic digestion	Generation of biogas by anaerobic digestion

2.21.4 Options for the reuse, recycling, and disposal of fleshing.

Fleshing are produced either before (green fleshing) or after liming. The sulphide and lime content and the high pH from limed fleshing may reduce the acceptability of the residues in recycling facilities and make the technical processing more difficult.

Options for dealing with fleshing are listed in Table(2.14)

Table(2.14)Options for dealing with fleshing[18,Rydin.S,Black.M,Scalet .B and Canova.M.(2013)]

Uses as a by-product	Type of by-product
Reuse after preparation	Protein hydrolysate, tallow
Recycling as	Hide glue
Other recovery	Generation of substitute fuel Generation of biogas by anaerobic digestion

Limed fleshing should not be subjected to anaerobic digestion without pretreatment to remove sulphides, unless the digestion plant is designed to cope with hydrogen sulphide production. Animal health controls restrict the disposal routes for green fleshing. Energy can be recovered from fleshing (in a mixture with some other wastes) by the generation of biogas as a fuel and the production of tallow as a fuel .Achieved environmental benefits are the reduction of wastes sent for disposal and the production of energy or useful by-products. Cross-media effects is that anaerobic digestion of limed fleshing has a potential to produce foul odours.

2.21.4.1Technical considerations relevant to applicability

Availability of facilities or buyers in the vicinity of the tannery may affect availability. Animal health controls restrict the disposal routes for green fleshing.[18,Rydin.S,Black.M,Scalet.BandCanova.M.(2013)]

2.21.4.2Economics

There may be a savings on disposal costs. There may be some return from the sale of by-products. Energy recovery may be economically beneficial. Fees are charged for composting and rendering.

2.21.5 Options for the reuse, recycling and disposal of splits.

The splitting process can be performed in either the limed or the tanned condition. Depending on where the splitting takes place within the process line, further processing in different ways is feasible. Table (2.15) summarizes the waste treatment options for untanned splits and for tanned splits together with shavings: composting and anaerobic treatment together with other waste fractions. Depending on the quality, untanned splits can be used to produce hide glue, gelatine and sausage casings.

Table (2.16) Options for dealing with untanned and tanned splits and trimmings[18,Rydin.S,Black.M,Scalet .B and Canova.M.(2013)]

Uses as a by-product	Untanned splits	Tanned splits and trimmings
	-Processed further to leather. -production of sausage casings. -Collagen production -Dog chews	Finished for use in patchwork small leather goods Collagen production
Reuse after-preparation	-Production of technical gelatin -Protein hydrolysate	Leather fibreboard production (from non-finished materials); Protein hydrolysate
Recycling as	Hide glue	
Other recovery	Generation of biogas by anaerobic digestion	

The achieved environmental benefit is the reduction of wastes sent for disposal.

2.21.5.1Technical considerations relevant to applicability

Leather production is carried out at only a few locations in Europe. Parts of the tannery must comply with food safety legislation if limed materials are processed for edible collagen production. Rendering plants and hide glue manufacturers may not be available in all cases. Fees are charged for composting and rendering. The reduction of wastes sent for disposal is the principal reason for using the technique.

2.21.6 Options for the reuse, recycling and disposal of shavings.

Shavings are produced in different sizes. Many of the recycling routes available for shavings are the same as for tanned splits. Chrome-tanned splits and shavings can be hydrolysed to produce chromium-containing sludge, fat and protein hydrolysate. Outlets have been found for the hydrolysate in various chemical and technical products. Certain tanned leather wastes are biodegradable,such as wet white shavings and vegetable-tanned shavings.This allows for a recycling route to produce soil improvers and fertilisers.Energy is recovered from shavings in several Scandinavian tanneries.

2.21.6.1Achieved environmental benefits

Reduction of wastes sent for disposal.

2.21.6.2Technical considerations relevant to applicability

Leather fibreboard production is carried out at only a few locations in Europe. Rendering plants and hide glue manufacturers may not be available in all cases. The economics of the process is that the fees are charged for composting and rendering.

2.21.7 Options for the disposal of fats, greases and oils

Fats, grease and oil are by-products from hides or residual process chemicals from the process steps of degreasing and post-tanning operations, particularly from fatliquoring,as that is where they are separated from waste water effluents.Grease from sheepskin dry degreasing can be recovered from the organic solvents and sold on the commodity market. The grease emulsions may be cracked if aqueous degreasing has been applied, either in solvent emulsion or in solvent-free emulsion using surfactants. However, no market has been identified for the recovered grease, from the aqueous degreasing process with the use of surfactants.[18,Rydin.S,Black.M,Scalet.BandCanova.M.(2013)]

Grease from hides is generally separated in grease traps.This grease has no commercial value.Fats and greases can be treated by anaerobic digestion. If these residues are not recycled or reused, they give a good energy yield in a thermal treatment and anaerobic digestion. Options for dealing with fats, grease and oil are shown in Table(2.17).

Table (2.16) Options for dealing with fats,grease and oil[18,Rydin .S, Black M,Scalet .B and Canova.M.(2013)]

Uses as a by-product	Type of by-product
Reuse after preparation	Commodity market(grease from solvent degreasing)
Recycling as	
Other recovery	Thermal treatment Generation of biogas by anaerobic digestion

The achieved environmental benefits for this process are some reduction of wastes sent for disposal is possible.

2.22 Disposal of other residues

Other residues require further (off-site) treatment, apart from the options discussed above for recycling and reuse in the process units themselves. This includes the following wastes: salt, organic solvents, and chemicals used as process chemicals, auxiliaries, or cleansers, sludge from finishing and packaging material.

The achieved environmental benefits are the appropriate disposal of non-reusable wastes is environmentally beneficial. The cross-media effects of this process are disposal is still required.

Table (2.18)Waste treatment and disposal for other waste fractions[18, Rydin.S,Black.M,Scalet .B and Canova.M.(2013)]

Waste Material	Treatment and disposal options
Chemicals	Obsolete chemicals require specific treatment, according to their content.
Finishing sludge	The sludge generated in finishing requires specific treatment, according to the content.
Sludge from wet-scrubbers	The content of the sludge from wet scrubbers depends on the off-gas streams collected for abatement.The sludge requires specific treatment, according to their content.
Other residues from air abatement	Activated carbon filters are mainly used for the abatement of organic solvents (in water and air). The filter can be regenerated by desorption several times. After exhausting the regeneration capacity, they have to be disposed of in an incineration plant.

2.23 Energy

The efficient generation distribution and use of energy is beneficial in environmental and economic terms. Some energy efficiency measures have applications in many industry sectors.

- In German tanneries,the energy consumption for processing bovine hides from raw to finished leather is up to 12 GJ/t of raw material. About 37 % of the total energy (i.e. ~ 4.5GJ) is used in the process steps from raw to wet blue or wet white[18,Rydin.S,Black.M, Scalet.B and Canova.M.(20 13)]

- In Austrian tanneries, the energy consumption for coated vegetable leather from raw hides in the automotive industry varies in the range5.4 –7.2GJ/t,covering all the processes, including waste water treatment. [18,Rydin.S,Black.M,Scalet .B and Canova.M.(2013)]

2.24 Use of short floats

The use of short floats to reduce energy use.The use of short floats entails the starting and rotation of less balanced process vessels. There is an increase in the rate of use of electrical energy, but this is balanced by the shorter process times involved.

2.24.1 Achieved environmental benefits

Because it reduces process water heating the use of short floats can make an obvious difference to the energy use in a tannery.The driving force for implementation is this technique is used to achieve a reduction in the use of water and process chemicals, as well as energy.

2.25 Energy recovery from process fluids

Energy savings can be achieved by heat pumps incorporating recovery systems. Waste heat can be used from and for other processes. By means of heat exchangers, energy can be recovered from the waste process water, from condensate from vacuum dryers, from evaporated water from high frequency drying, or from exhaust air from drying. The cooling water from the vacuum dryer, which is not polluted, can be used in the hot water supply.

2.25.1 Achieved environmental benefits

Reduced energy use may be achieved.The environmental performance and operational data is Up to 75 % of waste heat from drying may be recovered.About 10 – 20 % of the energy consumption of vacuum drying may be recovered for hot water supply needs.[18,Rydin.S,Black.M,Scalet .B and Canova.M.(2013)].

2.26Improved drying techniques

The improvement of drying techniques to reduce energy use. Low temperature drying (LTD) machines are available with reduced energy consumption, although in some cases they can lengthen the drying process (e.g. LTD drying tunnels may require all night to dry leathers, compared with 4 hours in conventional hang drying tunnels, but may have three times the capacity).

Considerable reductions in energy consumption can be achieved by optimizing the mechanical dewatering processes prior to drying. Temperature and humidity during the drying need to be carefully controlled. Elimination of the greatest possible amount of water in samming may mean energy savings of 0.5 – 1 GJ/t raw hide in drying. Keeping drying temperature low and drying time and amount of exhaust air at the necessary minimum will keep heat losses to a minimum (although, consideration of leather properties will have priority).

In order to avoid energy losses for reheating, drying installations should be run as continuously as possible. The heat capacity and heat transmission of new installations are as low as possible. Without the use of a heat pump, the energy consumed is mainly thermal energy. The only exception is high frequency drying, which uses electrical energy exclusively. Due to the high costs of electrical energy and to the high investment cost, this method has only gained a limited acceptance. It is obvious the natural drying of the leather is the method with the lowest energy consumption but it is impractical for much of the year in many parts of Europe due to climatic conditions. These include low temperatures, high rainfall and the associated humidity, combined with unpredictable variations in all these factors.For finish drying, infrared heating is an energy-saving method.The achieved environmental benefits are reduced energy use may be achieved.

2.26.1 Environmental performance and operational data

For example, a study carried out on a paste drying unit and on a hang drying unit showed that the overall thermal efficiency of the first machine was approximately 2.9 kg of steam per unit of water evaporated, whereas the second machine required approximately 2.5 kg of steam per unit of water evaporated. The poorer performance of the paste drying unit was found to be related to 30 % heat losses due to leaks, and insufficient insulation of the unit. In this case, energy savings were achieved by improving the insulation of the unit, reducing heat losses and optimising the operating procedures.The figures given in Table (2.18) are for the energy consumption of various drying methods, without and with the use of heat pumps.

Table(2.18)Energy consumption of various drying methods[18,Rydin.S, Black.M,Scalet .B and Canova.M.(2013)]

Drying methods	`MJ/kg water evaporated	
	Without heat pump	With heat pump
Theoretical minimum	2.48	
Toggling	8.17	
Pasting	6.37	

Table(2.18)continued

Chamber drying	5.83	1.62
Vacuum drying	7.20	1.37
Through-feed drying	5.22	1.12
High-frequency drying	6.84	

2.27Energy recovery from waste by digestion

Anaerobic digestion of organic waste fractions to produce a fuel gas.Anaerobic treatment of wastes is a well known technique which can be used to produce energy from waste and by-products from the leather industry.Green fleshing are suitable for biogas production. The achieved environmental benefits are the reduction of fossil fuel use, a reduction of CO2 emissions and a reduction of the volumes of waste for disposal.

2.26.2 Environmental performance and operational data

It is possible to recover around 3 GJ per ton of raw hide through digesting limed fleshing and waste water sludge.The cross-media effects is the formation of hydrogen sulphide can occur during the process.The final disposal routes for digestates from tannery wastes may be more restricted than those from anaerobic digestion of other wastes.

2.26.3 Technical considerations relevant to applicability

The technique is applicable to both new and existing installations. In practice, the technique will normally use waste material from several different sources.

2.26.4 Economics

The cost-benefit calculation depends on many parameters such as the amount of waste, cost of disposing of fleshing, gas or electricity price.

2.26.5 Driving force for implementation

Increasing energy prices and possible CO_2 emissions trading contribute to the case for energy recovery by biogas. Another driving force for the installation of a biogas plant is the increasing costs for the disposal of waste.

2.27 Energy recovery from waste by combustion

Fat recovered from wastes is burnt as a fuel. Fleshing (and other fatty wastes) are minced to approximately 5 – 10 mm, heated to 75 – 85 ºC and separated e.g. using tricanters into tallow (10 – 20 %), solids 'greaves' (35 – 55 %), and a water fraction (35 – 55 %). The tallow contains up to 99 % fat and can be used in an appropriate burner as a direct substitute for oil fuel; the calorific value is about 85 – 90 %.[18,Rydin.S, Black.M,Scalet .B and Canova.M.(2013)]

2.27.1 Achieved environmental benefits

A reduction of fossil fuel use and a reduction of the volumes of waste for disposal can be achieved. The environmental performance and operational data is the emissions from burning the substitute fuel generated from fleshing do not show significant differences regarding CO_2,or CO compared to gas oil.

Combustion of fat from the fleshing can cover 50 – 70 % of the total demand for thermal energy. The cross-media effects is the technique also generates two different waste fractions which have to be disposed of. The water fraction represents an additional load on effluent treatment facilities, while the greaves have to be disposed of as waste.

2.27.2 Technical considerations relevant to applicability

The method can be used on or off site. For on-site operation, the heat generated can be used in the tannery. Depending on the status of the material being burnt, compliance with waste incineration legislation will require a more complex plant.[18,Rydin.S, Black.M,Scalet .B and Canova.M.(2013)]

2.27.3 Economics

The cost-benefit analyses depend on local conditions. Important factors are the amount and the composition of the fleshing, the cost for disposal of the fleshing, the cost saved on the fuel which is replaced and the possibilities and costs for the disposal of the residue. The capital cost of the plant can be high, especially if compliance with waste incineration legislation is required. The driving force for implementation is the drivers are increasing energy prices and costs of disposal.

2.28Noise and vibration control

Techniques to control the emission of noise and vibration. Good practice to control the emission of noise and vibration may use one or more of the techniques listed below.

- The prevention of noise generation at source. Preventative maintenance and replacement of old equipment can considerably reduce the noise levels generated.
- Change of operating speeds so as to avoid creating resonances. Avoiding operation of several machines of the same type at the same speed.
- Placing as much distance as possible between the noise source and those likely to be affected by it.

- Use of resilient machine mountings and drives to prevent the transmission of vibration.
- Using a building designed to contain the noise or a noise barrier.
- Silencing of exhaust outlets.

2.28.1Technical considerations relevant to applicability

In determining the degree of control required, it is usual to calculate or measure the sound pressure level close to the source and, knowing the desired end-point, calculate:

- The attenuation at the sensitive location.
- The additional attenuation required.

The desired end-point must be calculated taking into account the existing noise emissions from external sources. Noise which is particularly annoying because of its tonal character will need greater attenuation. Economics is the noise and vibration control measures can be costly to implement, especially in existing plants.

2.29Monitoring

Monitoring techniques are appropriate for the operation of a tannery. Monitoring of the environmental outputs and emissions from an industrial activity is essential to their effective control.

This monitoring deals with techniques specific to the leather making industry. Water–Standardized analysis and measurement methods exist for waste water effluent parameters such as COD , BOD ,SS , ammonia, total chromium, sulphides, chloride, conductivity, pH and temperature that are set in the permit for tanneries or determined by the requirements of the waste water treatment plant they discharge to.

Particulate matter emissions do not require frequent precise monitoring once the efficacy of the equipment has been proved. Indicative or secondary monitoring can be used to check for correct operation. For example, the functioning of filtration equipment can be monitored by measuring the pressure drop across the filter.

Where emissions of hydrogen sulphide, ammonia or volatile organic compounds are sufficient to need abatement equipment, correct operation of that equipment must be checked by indicative monitoring. Alternatively secondary indicators such as the pH or redox potential of the liquid at the outlet from a wet scrubber can be used for day to day monitoring.The keeping of an organic solvent inventory is necessary to establish the total solvent emissions per m^2 of leather produced.At sites where annoyance is likely to be caused, monitoring of hydrogen sulphide, ammonia and other odorous substances at the downwind boundary of the site may be required.

Since H_2S and NH_3 are detectable by humans in concentrations below the operational limits of portable measuring equipment, olfactory monitoring may be the only technique available. It is usual to deploy staff who do not work in the production areas for olfactory monitoring. For other gaseous emissions, specific monitoring might be required, for example if energy is generated on site by combustion plants, or waste treatment plants are installed.[18,Rydin.S, Black.M,Scalet .B and Canova.M.2013]

Waste fractions arising from the processes in the tannery need to be recorded according to type, amount, hazard and recycling or disposal route.A chemical inventory is essential as part of good housekeeping techniques, and is essential in good environmental management of emissions and in accident preparedness programmes.

The consumption of water, electricity, heat (steam and heating), and compressed air,should be recorded, as part of a program to manage these resources. A total of all energy use at the installation should be calculated .Where there are residences or other noise-sensitive locations near to the tannery, sound levels should be measured outside the tannery buildings on appropriate parts of the site. The measurement should include narrow band frequency analysis.

When new equipment is installed, new measurements should be taken to detect any increase in the sound emissions or a change in their character. Monitoring is expensive and adds to process costs.

2.30 Decommissioning

Techniques for the decommissioning of a tannery. When decommissioning a plant in general, all provisions and measures have to be taken into account to prevent environmental impact during and after the shutdown process. The aim is to prevent impact on the environment in general and in particular on the immediate surroundings, by remediation techniques, to leave the area in such a way that it can be reused.

This includes activities from the shutdown of a plant itself, the removal of buildings, equipment, residues, etc. from the site, and contamination of surface waters, groundwater, air or soil. Records must be kept during the operation of the tannery of the location on the site at which each process step is undertaken.

Drainage routes and waste storage locations must be included. These records should be preserved systematically to allow the efficient planning of decommissioning. Additional records should be made each time activities or equipment are relocated, or when changes are made to process chemistry.[18,Rydin.S, Black.M,Scalet .B and Canova.M.(2013)]

The legal framework for the decommissioning of installations varies greatly and any provisions and duties laid down in a permit will depend strongly on the local environment and on the legislation to be applied, in particular with respect to liability. Thus, general guidelines can be given on the possible impacts and the provisions to prevent impacts at three stages:

- The conditions in the permit for processing at a site can be set to prevent negative long-term effects on the environment during operation and after decommissioning
- What has to be taken into account consequently during operation.
- The prerequisites to be considered for the final shutdown
- The contamination might be caused.

The large quantities of raw materials and wastes handled by tanneries mean that the prevention of soil and groundwater contamination is a high priority with regards to spillage, storage, processing, and final decommissioning. Furthermore, for floors in general, not only in storage rooms, it is common practice that surfaces are used that facilitate cleaning and removal of spillage and have limited permeability. Retention tanks for process liquors, chemicals, and waste water effluents, basins and drainage systems for the collection of effluents, and storage containers for waste are mostly impermeable to prevent leakage to the soil and surface water.

2.30.1End of operation

The decommissioning operations may include:

- Clean-up , dismantling of installations, clean-up and demolition of buildings.

- Recovery, treatment and disposal of material derived from general clean-up,plant demolitions,demolition of buildings,and dismantling of environmental units,
- Survey of possible contamination,
- Traffic due to transport and demolition activities.

The first step upon closing a production facility is a general clean-up involving the emptying of containers and process units of liquors, chemicals and residues, draining liquors from piping and retention units, and emptying storage and cleaning the equipment, storage, and buildings. The components of a plant are dismantled and sorted according to the material generated[18,Rydin.S, Black.M,Scalet .B and Canova.M.(2013)]

Separating the specific waste generated in the clean-up and demolition of buildings allows for optimized recycling and disposal. The amounts of waste generated in these operations are generally large. Residues from the general clean-up have to be sorted for further reuse, recycling, treatment or disposal similar to the residues generated during processing. Similarly, material from the dismantling or demolition of the equipment and buildings can be separated into reusable and recyclable material and material that has to be disposed of.

Good organizational management will avoid storage of material for long periods .It is not possible to identify contamination from the clean-up and demolition that would be exclusive to tanneries. There might be amounts of hazardous waste from residues of chemicals, wastes, equipment contaminated with the chemicals and from the demolition of buildings. Chemicals and equipment, in particular, may be sold to third parties. Any material which cannot be recycled has to be classified. It is disposed of via authorized dealers or treatment or disposal facilities.

All environmental abatement installations which might still have been needed during the dismantling of the plant must be dismantled and disposed of. Contamination of air may arise from inappropriate waste disposal due to spreading of dusty materials or toxic substances, odours or releases of, e.g. hydrogen sulphides. Such impact can,however, be readily prevented and is unlikely to have a long-term effect. Site-specific long term contamination in tanneries, in particular to soil (and groundwater), and surface water can arise from:

- Organic solvents
- Oil
- Chromium
- Substances contained in waste.

Contamination from these sources might have been caused much earlier when the possible environmental impact was not yet understood. Halogenated hydrocarbons in degreasing and other (non-halogenated) organic solvents can cause severe soil and groundwater impacts. Specifically, halogenated hydrocarbons were often handled carelessly because they do not have high acute toxicity for humans. Waste which was inappropriately disposed of onsite might have caused contamination from infectious material or process chemicals. A survey of this possible contamination is mandatory to prevent long-term adverse effects on the environment.Restoration of the site following the cessation of operations. A robust and properly documented decommissioning program enhances the value of the land[18,Rydin.S, Black.M,Scalet .B and Canova .M .2013].

2.31 Recycling of unhairing liming solutions

2.31.1 Raw materials:

Wet salted Sheepskins of average weight 2 kg were used in all trials. The reagents, added to unhairing lime liquors are the following:

Lime (65% calcium chloride).

Sodium sulphide (60% flake). [19, Mohamed,K.2003]

Forty-eight wet salted sheepskins were used in eight trials, six skins in each; they were treated in 1.5 m diameter wooden drum operating at 8 revolutions per minute.

All processes were carried out as in micro scale trial except cycle 7, which was treated with 0.75% caustic soda.Degree of unhairing and swelling were assessed and after completion of tanning operations, the produced leathers were subjected to physical tests.[19,Mohamed,K.2003]

As lime has a limited solubility of 0.125 %, undissolved lime remains in solution, the amount of lime chemically fixed to the skin is 2%of soaked weight (Sorkar, 1981). However, it is customary to use aquantity of lime in excess of that suspended in liquor to maintain the strength of the liquor regardless of the soluble lime absorbed by the skin,the quantity in excess of that chemically fixed to the skin remains in used liquor.

A 300% float was used in all trials because similar floats are used in most tanneries, but Simncini et al; (1972) used 400% water and higher percentages of lime and sodium sulphide based on skins weight while Money and Adiminis (1973) used 200% float based on hide weight. However, the float must be enough to enhance the mechanical action of the drum and should not be too high to affect the diffusion rate.

The adjustment of used liquors with 30% water based on soaked weight, agrees with the fact that the conventional swelling requires 20-

40% water absorbed by skin to open up fibre bundles (Thanikaivelan etal., 2001). These amounts to only one tenth of the amount of water employed during the conventional unhairing method.The average replenishment with 1.4% sodium sulphide and 2%lime based on the soaked weight is applied to increase the concentration similar to those in fresh liquors.[19, Mohamed,K.2003]

They attributed that to the increasing concentration of sodium chloride in the used liquor during recycling.

The addition of caustic soda in cycle 7 had improved the swelling to a degree similar to that obtained in conventional method and this was due to the strong alkali action of caustic soda.

Table (2.19) Chemical Analysis of fresh and used lime-sulphide liquors . [19, Mohamed,K.2003]

	Sulphide (S- -) mg/L	Ca(OH)2 mg/L	pH
Fresh	3200	6500	13
Used	2100	2500	12.4

Chemical analysis of both fresh and used liquors are given in table(2.19).The analysis showed that about 65% and 33% from the total amount of sulphide and lime respectively remained in the used liquor.The amount of sodium sulphide found in the used liquor is due to the amount in excess, in addition to the fact that pulping reaction induced by sodium sulphide had produced sludge containing keratin sulphide reaction products.

Table (2.20):Total amount of the sulphide,lime and pH of recycled Liquors.[19, Mohamed,K.2003]

	Sulphide (S- -) mg/L	Ca(OH)2 mg/L	pH
Cycle 1	2100	2500	12.4
Cycle 2	2100	2350	12.3
Cycle 3	2000	2400	12.3
Cycle 4	1900	2500	12.3
Cycle 5	2000	2400	12.3
Cycle 6	2000	2450	12.3
Cycle 7	2000	2400	12.3

Table(2.20) shows that the amount of sulphide and lime in recycled liquors remains approximately constant from one cycle to another, due to the addition of make-up of each compound. The consistency of the amounts of chemicals after each cycle indicates that the liquor may be recycled indefinitely.The amount of water, sodium sulphide and lime added to the conventional and recycled liquors are given as a percentage based on soaked skins in table (2.21).

Table(2.21):Comparison of recycling and conventional methods [19 , Mohamed,K.2003]

	Water %	Sulphide %	Lime %
Conventional (control)	300	4.0	3
Cycle 1	30	1.5	2
Cycle 2	32	1.5	2
Cycle 3	30	1.3	2
Cycle 4	29	1.4	2
Cycle 5	29	1.3	2
Cycle 6	30	1.4	2
Cycle 7	30	1.4	2

Table(2.22):Conventional unhairing method versus recycling method[19, Mohamed,K.2003]

	Consumption without recycling %	Net consumption with recycling %	Saving %
Water	300	30	90
Sodium sulphide	4	1.4	65
Lime	3	2	33

The consumption of the chemicals and water for both conventional and recycling unhairing methods are shown in table (2.23).The average consumption of recycling unhairing liquors based on soaked weight was 30% water, 1.4% sodium sulphide and 2% lime. That saving was about 90% water, 65% sulphide and 33% lime compared with conventional method. This will make a reduction in the total cost of unhairing and liming process.Even if the unhairing liquors were discharged after eight cycles there could an overall a 7-fold reduction in unhairing effluent pollution.However, the recycling process could be applied indefinitely with some tight control of filtration and make-up addition.

2.32Chrome tannage recycling

The standard fresh recipe was applied,after basification and after satisfactory boiling test, the pelts were unloaded and the spent chromium solution was filtered (10), collected in holding tank and analyzed for Cr2O3 content. [20,Tambal,E and Gasmelseed,G.2013].

The once – used chrome solution was pumped to the drum already loaded with pickled pelts with addition of fresh make-up chrome. The pelts were tanned, basified and the spent solution is sent to the holding tank. The same was repeated seven times.

Table(2.24):The chrome tannage process result[20,Tambal,E and Gasmelseed,G.2013]

Cycle No	PH	Penetration	Relaxation	Completeness
1	3.8	Full	100c°	v. good
2	4.0	Full	100c°	v. good
3	4.2	Full	100c°	v. good
4	3.9	Full	100c°	v. good
5	3.9	Full	100c°	v. good
6	4.4	Full	100c°	v. good
7	4.3	Full	100c°	v. good

CHAPTER THREE

3. MATERIALS AND METHODS

Experiments had been carried out in Amatong tannery in Khartoum South, to recycle the spent solutions form soaking through retannage.

3.1The soaking process

Three wet salted goat skins with approximately equal size and grade were weighted and washed with two hundred percent of water based on skins weight to remove dirt, salt, dung and blood.

The weight of the water used for the first rinsing was two hundred percent by the weight of wet salted skins

The weight of skins=5kg.

The volume of water used for the first rinsing=2*5=10L.

The skins had been washed again with another ten liters of water (V_{w2}) to remove any remaining salt.The first and second rinsing solutions had been collected together.The concentrations of NaCl,total suspended solids (TSS)and pH of the washing solutions and final solutions had been measured.

The washed skins were soaked in two hundred fifty percent of water,0.5% of soda ash, 0.5% of soap and 0.2% of bactericide (based on weight of skins).

V_s=2.5*5=12.5L.

V_s is the volume of water used for soaking.

W_{sa}=5*0.005=0.025kg.

W_{sa} is the weight of soda ash used for soaking.

V_{soap}=5*0.005=25ml.

V_{soap} is the volume of soap used for soaking.

V_b=5*0.002=0.01kg

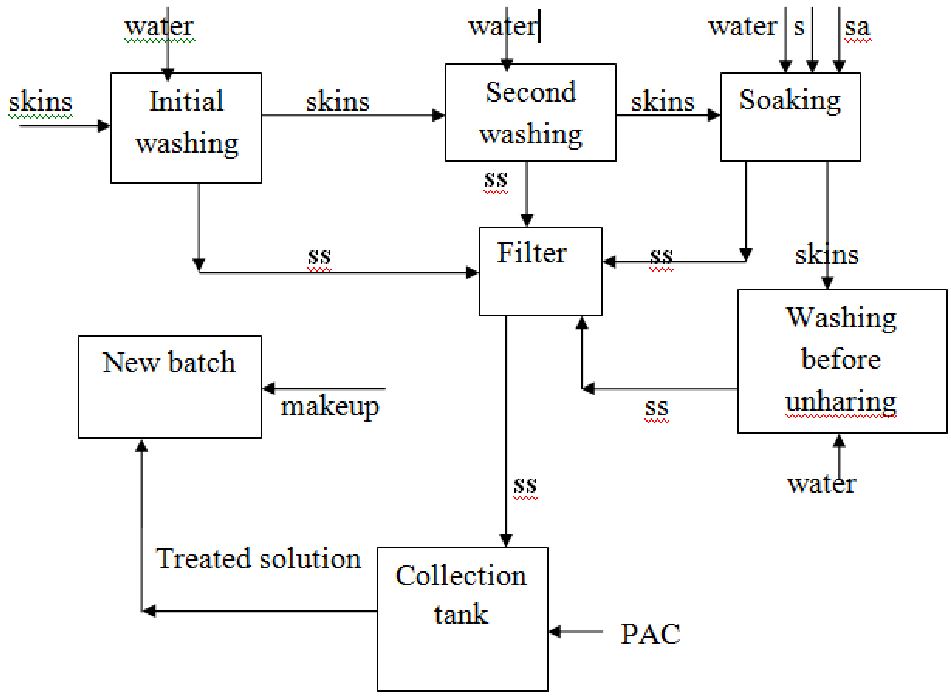
V_b is the volume of bactericide had been used for soaking.

The soaking process was continued to the next morning (twenty four hours).The skins from soaking solution was transferred further to the unhairing process after rinsing with ten liters water (W_f), these ten liters together with rinsing and soaking spent solutions were collected ,filtered and treated with PAC(poly aluminum chloride) and was saved to the next runs.

The pH and TSS of the soaking and treated solutions were measured.The amount of the PAC used is one percent of the amount of the spent solution

The weight of PAC that was used for treatment=0.001*42=0.0042kg.

In the next runs the required amount of treated solution was used together with seventy percent of the original quantity of the soda ash, soap and the same amount of bactericide had been used with extra 2ml (because of bad smell of treated solution).



Fig(3.1)Flow sheet of the recycling process of soaking using spent solutions

ss=spent solution, s=soap, sa= soda ash

3.2The deliming process

The three skins were fleshed in the fleshing machine and were weighted,The weight was found to be about four kilograms.Then1.5 percent of ammonium chloride (NH_4Cl) based on weight of the fleshed skins was added to the skin with continuous stirring for ninety minutes.

The weight of ammonium chloride that had been used=0.015*4= 0.06kg.

The bating agent was added after ninety minutes(0.8 percent) based on the weight of the fleshed skin with continuous stirring for forty minutes.

The weight of the bating agent that had been used=0.008*4=0.32kg

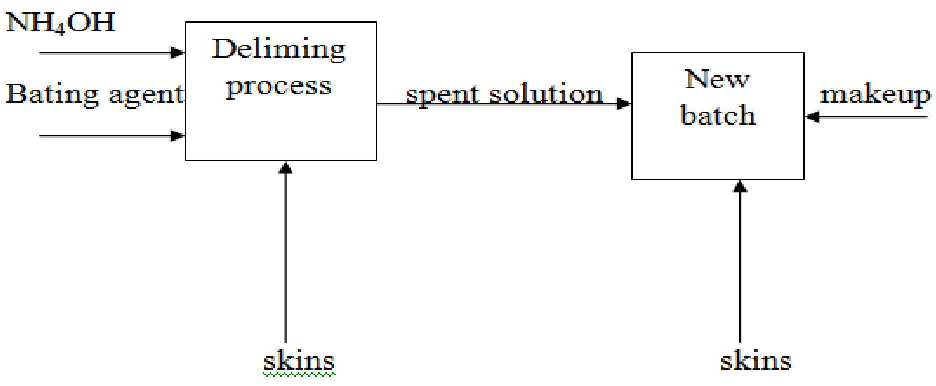
Two hundred percent of water based on the fleshed skins weight had been added in the first run.

The volume of the water that had been used=2*4=8L.

The deliming process was continued in the same solution of ammonium chloride and bating agent,with another three skins four kilograms weight.In the next runs seventy percent of the original weight of the ammonium chloride and the same amount of bating agent were used.The volume of water that was saved from the first run was found to be about six liters, two liters of the water was added to the second run.The volume of water that had been saved from the second run was found to be about seven and half liters,only two and half liters of the water had been added to the third run.

- Extent of deliming had been estimated by making a clean cut in the skin and the pH had been checked by dripping phenolphthalein in the cross section of the pelt, and it had been turned into completely colorless.
- Thumb test: the bated pelt had been pressed with thumb and it left a print.
- Bubble test: the bated skin had been wrapped and bubble was come out.

The following figure shows the recycling process of deliming spent solution.



Fig(3.2) Flow sheet of the recycling process of deliming process using spent solutions

3.3The retannage process

3.3.1The wetting back process

The skins had been weighted, their weight was found to be four kilograms and wetted back with hundred percent of the water,0.5 percent of soap and 0.5 percent of formic acid, based on the weight of the wet blue skin.

The volume of the water that was added=4*1=4L.

The volume of the soap that was used for the wetting back=4*0.005 =20ml.

The volume of the formic acid that was used for the wetting back=4* 0.005=20ml.

The wetting back was continued for fifteen minutes with stirring,Then the skins were rinsed with two hundred percent of water based on the weight of the wet blue skin.

The volume of the water that had been used for the washing after wetting back=4*2=8L.

The spent solution from wetting back process WAS saved as make up for the new wetting back,the volume of the saved solution was found to be seven and half liters.The skins then had been transferred to the rechroming and neutralization process.

3.3.2The rechroming process

The rechroming process had been done with the addition of eighty percent of the water, two percent of chrome and tow percent of chrome syntan,based on the weight of the wet blue skin.

The volume of the water that was added for the washing process after wetting back=4*0.8=3.2L.

The weight of the chrome that was added for the rechroming process=4*0.2=0.8kg

The weight of the chrome syntan that had been added for the rechroming process=4*0.2=0.8kg

The process of rechroming was continued for an hour. The skins then had been transferred to the neutralization process.

3.3.3Neutralization:

The neutralization process was done with addition of one percent soduim formate, and 0.25 percent sodium bicarbonate,based on the weight of the wet blue skin.

The weight of the sodium formate that had been added for the neutralization process=4*0.01=0.04kg.

The weight of the sodium bicarbonate that had been added for the neutralization process=4*0.0025=0.01kg.

The process of the neutralization was continued for thirteen minutes with continuous stirring.At the end of the netralization process the pH of the solution was measured,The pH the of the solution was found to be five (pH=5).After the neutralization process ten percent of garad and hundred percent of water were added based on the weight of wet blue skins.

The weight of the garad that had been added for the retannage process=4*0.1=0.4kg

The volume of the water that had been added for the retannage process=4!=4L.

The process of the retannage was continued to the next day(twenty four hours) ,then the liquid and powder syntans and dye were added in the same garad solution.

Two percent of the liquid syntan was added and stirred for half an hour,then two percent of the powder syntan was added and stirred for half hour,and one percent of the dye was added.all percentage were based on the weight of the wet blue skin.

The volume of the liquid syntan that was added for the retannage process =4*0.02=80ml.

The weight of the powder syntan that was added for the retannage process =4*0.02=0.08kg.

The weight of the dye that was added for the retannage process=4*0.01 =0.04kg.

The retannage process was continued for ninety minutes with continuous stirring,then six percent of the fatliquir was added based on the weight of the wet blue skin.

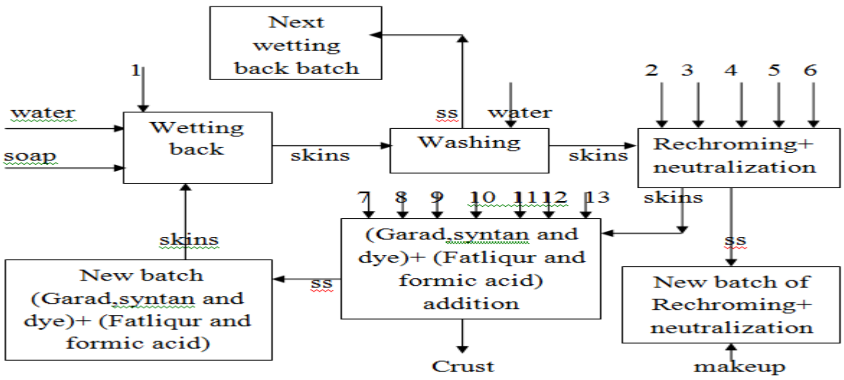
The weight of the fatliquor that was added for the retannage process=4*0.06=240ml.

The process was continued for two hours then one and half percent of the formic acid was added based on the weight of the wet blue skin. The process of the retannage was continued for forty five minutes.

The volume of the formic acid that had been added for the retannage process=4*0.015=60ml.

The retanage process for the next runs was done with the addition of required quantity of the water from the saved water from the previous run and , and seventy percent of the original volume of the other chemicals.

The recycling process of the retannage process had been shown in the figure below.



Fig(3.3)Flow sheet of the retannage recycling process

ss=spent solution

1,2,3,4,5,6,7,8,9,10,11,12 are formic acid ,basic chromium sulphate , syntan,sodium formate, sodium bicarbonate ,water ,garad ,water, liquid and powder, syntan,dye,fat liquor,formic acid

The skins had been then dried and tested for the thickness,tensile strength,elongation at break,tear strength,load at grain crack,destination at grain crack.

4.4 The development of a new tannery that used the recycling of spent float

3.4.1Introduction

The pressure to adopt cleaner technologies normally emanates from environmental imperatives such as the need to meet specific discharge norms, reduce treatment costs or comply with occupational safety and health standards.The typical primary targets are:

Lower water consumption, improved uptake of chemicals,better quality/re-usability of solid waste, and reduced content of specific pollutants such as heavy metals and electrolytes.

The spread of cleaner technologies and processes has been neither spontaneous nor extensive. For all the claims about favorable cost-benefit ratios and/or environmental benefits to be derived from many of these technologies, tanners are not quick in adopting them, be it due to inertia, higher costs or the limitations mentioned earlier.

Due to variations in raw material, process, chemicals, water consumption, etc., it is small wonder that figures about pollution load in the literature vary a lot and should be interpreted very cautiously.[24,Wikipedia.2019]

3.4.2The recycling process development

The tanning process was designed to recycle the spent solution from the soaking to the retannage processes with the addition of a makeup of water and chemicals.The quantities of the water and the chemical that had been required for the recycling process was calculated for each process.The additional equipment required for the recycling process also was included.

The quantities of water and chemical for tanning process were calculated based on a thousand kilograms of the raw skins or hides.

3.4.2.1 The soaking recycling process

Two hundred percent of the water based on the weight of wet salted skins or hide had been required for the first rinsing process.

The volume of the water that had been required for the first rinsing process=2*1000=2m^3.

Two hundred percent of the water based on the weight of the wet salted skins had been required for the second washing process.

The volume of the water that had been required for the second washing process=2m^3.

Two hundred and fifty percent of the water based on the weight of the wet salted skins had been required for the soaking process.

The volume of the water that had been required for the soaking process=2.5*1000=2.5m^3.

Total amount of water that had been required for the soaking and washing processes=6.5m^3.

0.5 percent of the soda ash and soap based on the weight of the wet salted skins had been required for the soaking process.

The weight of the soda ash that had been required for the soaking process=0.005*1000=5kg.

The volume of the soap that had been required for the soaking process=5L.

The volume of the bactericide that had been required for the soaking process=0.002*1000=2L.

The skins after the soaking process had been transferred to the unhairing process.The spent solution of the soaking process had been used in the next runs with the addition of a makeup of water, soda ash ,soap and bactericide.

Ninety percent of the water had been saved.The saved solution had been collected in a storage tank and treated with 0.01 percent of the (PAC).the treated solution had been used in the next runs with the addition of a makeup of ten percent of water and seventy percent of the other chemicals.

The volume of the water that had been saved in each run=6.5*0.9=5.85m^3

The weight of the PAC that had been added=0.001*5.85=0.0585kg.

3.4.2 The unhairing and liming recycling process

The weight of the skins after the soaking process=1100kg.

One hundred and fifty percent of water had been required for the unhairing process.

The volume of water that required for the unhairing process=1.5*1100= 1.65m^3.

2.5 percent of the sodium sulphide had been required for the unhairing process.

The weight of the sodium sulphate=0.025*1100=27.5kg.

5 percent of calcium hydroxide had been required

The weight of the calcium hydroxide=0.05*1100=55kg.

The spent solution of unhairing and lime had been used in the next runs with the addition of a makeup of ten percent of water and seventy percent of sodium sulphide and calcium hydroxide.

3.4.3 The deliming and bating recycling process

The skins after unhairing had been fleshed and weighted.

The weight of the fleshed skin=800kg.

1.5 percent of the ammonium chloride had been added.

The weight of the ammonium chloride=800*0.015=12kg.

The skins had been stirred for one hour then 0.8 percent of the bating agent(oropon) had been added.

The weight of the bating agent=800*0.008=6.4kg.

In the next runs seventy percent of ammonium chloride had been added as make up, and the same amount of the bating agent had been used.

3.4.4 The tannage recycling process

3.4.4.1The pickling recycling process

The skins had been washed after bating,then pickled with hundred percent of water.

$$VH2Op = 8 * 100 = 800L = 0.8m3$$

The volume of the water that used for pickling=8*100=0.8m^3.

Ten percent of the sodium chloride had been added.

The weight of sodium chloride=800*0.1=80kg.

0.4 percent of the formic acid had been added.

The volume of the formic acid=800*0.04=3.2L.

0.8 percent of the sulphuric acid had been added.

The volume of the sulphuric acid=800*0.08=8L.

The next runs had been done with the addition of a makeup of water about ten percent,and seventy percent of the sodium chloride,formic and sulphuric acid.

3.4.4.2The chroming recycling process

The same solution of pickling had been used for the chroming process.With 0.15percent of the fungicide,0.4 percent of the sodium formate,and six percent of the chrome for six hours, 0.8 percent of the Sod bicarbonate.

The weight of fungicide had been added=800*0.0015=1.2kg.

The weight of sodium formate=800*0.004=3.2kg.

The weight of basic chromium sulphate=800*0.06=48kg.

The weight of sodium bicarbonate=800*0.008=6.4kg.

The next runs had been done with addition of makeup of a ninety percent of the water and seventy percent of other chemicals.

3.4.5 The retannage recycling process

The skins then had been billed for one day after boiling test have been done,then the following process had been done.

3.4.5.1The wetting back process

The wetting back process had been done with the addition of a hundred percent of the water and 0.5 percent of the soap.

The volume of the water used for the wetting back=800*1=0.8L.

The volume of the soap used for the wetting back=800*0.005=4L.

The next runs had been done with addition of a makeup of ninety percent of water,and seventy percent of soap.

3.4.5.2 The rechroming recycling process

The rechroming process had been done with the addition of an eighty percent of the water and two percent of the chrome and the chrome syntan.

The volume of water had been required for the rechroming process= 800*0.8=0.64m^3.

The weight of chrome had been required for the rechroming process = 800*0.02=16kg.

The weight of chrome syntan had been required for the retannage process =16kg.

The next runs had been done with addition of a makeup of ninety percent of the water, and seventy percent of the other rechroming chemicals.

3.4.5.3 The neutralization recycling process

The neutralization process had been done with the addition of one percent of the sodium formate and 0.25 of the sodium bicarbonate.

The weight of sodium formate=800*0.01=8kg.

The weight of sodium bicarbonate=800*0.0025=2kg.

The pH had been measured and found to be (4.5-5).The next runs had been done with addition of a makeup of ninety percent of the water, and seventy percent of the other neutralization chemicals.

3.4.5.4 The retannage process of syntan addition

The process had been done with the addition of two percent of the liquid syntan and four percent of the powder syntan.

The volume of liquid syntan=8008*0.02=16L.

The weight of powder syntan=800*0.04=32kg.

The next runs had been done with the addition of a makeup of seventy percent of chemicals.

3.4.5.5 The retannage recycling process the garad and dye addition

The process of the garad and dye addition had been done with fifty percent of the garad,one hundred and fifty percent of the water and two percent of the dye.

The weight of garad=800*0.15=120kg.

The volume of the water that had been used for the neutralization process=800*1.5=1.2m^3.

The weight f the dye=800*0.02=16kg.

The next runs had been done with the addition of a makeup of ninety percent of the water,and seventy percent of the other chemicals.

3.4.5.6 The retannage process fatliquor and formic acid addition

The process had been done with the addition of a six percent of the fatliquor and 1.5 percent of the formic acid.

The volume of fatliquor=800*0.06=48L.

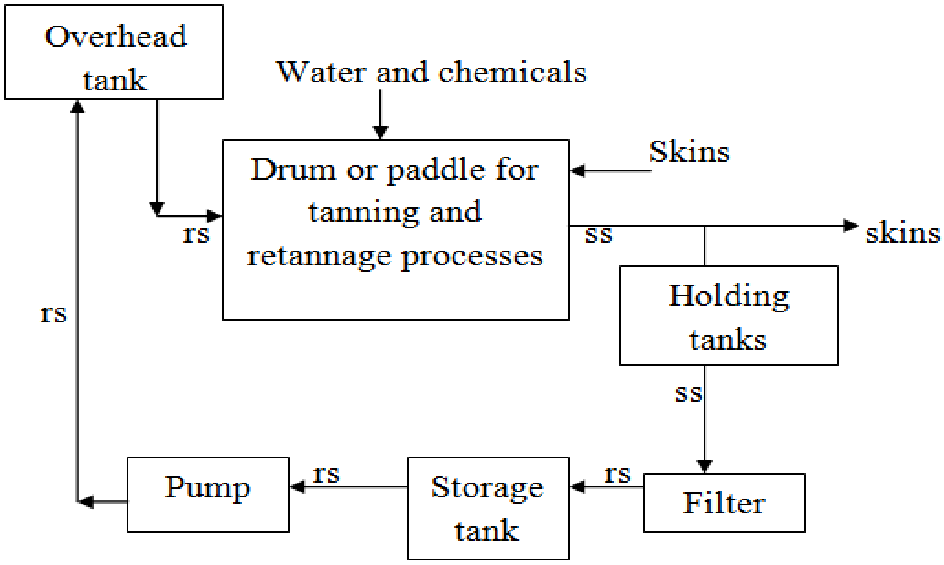
The volume of formic acid=800*0.015=12L.

The next runs had been done with the addition of a makeup of seventy percent of the chemicals.

The following additional equipment are require for the recycling of the spent solutions of the wet processes.

1. Storage tank to save the collected solution.
2. Filter to filter the spent solution.
3. Holding tank.
4. Pumps to pump the solution.
5. Overhead tank.

The following figure shows the recycling for the spent solution of the wet processes.



Fig(3.4) The recycling process of the spent solutions

ss=spent solution, rs=recycled solution.

3.5 The cost estimation for the conventional treatment and recycling of the spent float methods

3.5.1Introduction

Cost benefit analysis is a systematic approach for estimating the strengths and weaknesses of alternatives used to determine options which provide the best approach to achieving benefits while preserving savings.

The cost benefit analysis may be used to compare completed or potential courses of actions, or to estimate the value against the cost of a project.It is commonly used in commercial transactions,business or policy decisions and project investments.

Cost analysis has two main applications:

1. To determine if an investment and by how much its benefits outweigh its cost.

2. To provide a basis for comparing investments, comparing the total expected cost of each option with its total expected benefits.

The cost benefit analysis is related to cost-effectiveness analysis. Benefits and costs are expressed in monetary terms and are adjusted for the time value of money.all flows of benefits and costs over time are expressed on a common basis in terms of their net present value, regardless of whether they are incurred at different times.

Cost benefit analysis is often used by organizations to appraise the desirability of a given policy. It is an analysis of the expected balance of benefits and costs.also helps predict whether the benefits of a policy outweigh its costs, relative to other alternatives. This allows the ranking of alternative policies in terms of a cost benefit ratio.

Generally, accurate cost benefit analysis identifies choices which increase welfare from a utilitarian perspective.Although cost benefit analysis can offer an informed estimate of the best alternative, a perfect appraisal of all present and future costs and benefits is difficult, perfection in economic efficiency and social welfare, is not guaranteed.

Cost benefit analysis attempts to measure the positive or negative consequences of a project.

A similar approach is used in the environmental analysis of total economic value. Both costs and benefits can be diverse. Costs tend to be most thoroughly represented in cost–benefit analyses due to relatively-abundant market data.

The net benefits of a project may incorporate cost savings, public willingness to pay, or willingness to accept compensation for the policy's welfare change. The guiding principle of evaluating benefits is to list all parties affected by an intervention and add the positive or negative value that they ascribe to its effect on their welfare.

Revealed preference is an indirect approach to individual willingness to pay. People make market choices of items with different environmental characteristics, for example, revealing the value placed on environmental factors.

The value of human life is controversial when assessing road-safety measures or life-saving medicines.Controversy can sometimes be avoided by using the related technique of cost-utility analysis, in which benefits are expressed in non-monetary units such as quality-adjusted life years. Road safety can be measured in cost per life saved, without assigning a financial value to the life. However, non-monetary metrics have limited usefulness for evaluating policies with substantially different outcomes. Other benefits may also accrue from a policy, and metrics such as cost per life saved may lead to a substantially-different ranking of alternatives than cost benefit analysis.

Another metric is valuing the environment, which in is typically assessed by valuing ecosystem services to humans such as air and water quality and pollution.Monetary values may also be assigned to other intangible effects such as business reputation, market penetration, or long-term enterprise strategy alignment.[24,wikibedia,cost-benefit analysis,2019]

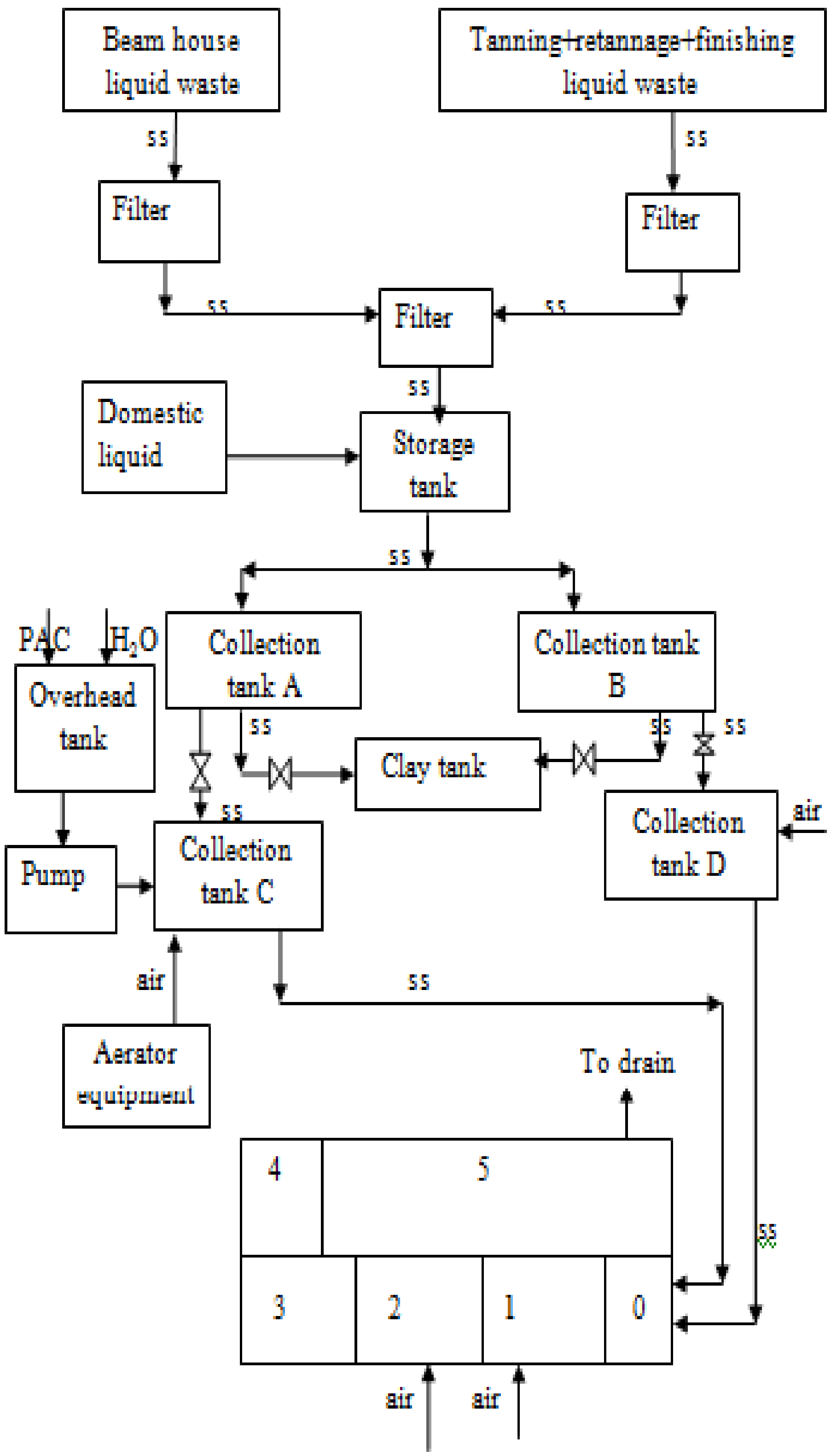
The capital cost estimation is an essential part of investment assessment. Many types of capital cost estimates are made, from initial estimates to detailed estimates which require the collection of accurate technical data.[26,KayodeCoker,A.2007]

The total capital investment for any process consists of fixed-capital investment for equipment and facilities in the plant plus working capital which must be available to pay for salaries, raw materials and products on hand, and other special items requiring a direct cash expense.Thus in the cost analysis of industrial processes,capital-investment costs, manufacturing costs, and general expenses including income taxes must be taken into consideration. [27,Peter,M and Timmerhaus,K,1991]

3.6The chemicals cost for the recycling and conventional method

The cost of the water and the chemicals required for the tanning processes is calculated per thousand kilograms of raw skins or hides. The costs for the chemicals used in the tanning process are obtained from the Alibaba.com website. [27,Peter,M and Timmerhaus,K,1991]

The following figure shows the treatment unit that had been established in the Amatong tannery.



Fig(3.5)the treatment unit of the Amatong tannery

3.7 The comparison a new tannery using the conventional treatment of waste water and the same using recycling of the spent float

3.7.1The cost for new tannery with conventional treatment method

The capacity of the tannery and the equipment were specified.Then the free on board cost (f.o.b) cost of the major equipment were obtained from the design data. The total major equipment was estimated as a base of 22.9 percent of the total fixed cost. Once the fixed cost is calculated the working capital investment is estimated as well as the total capital investment. For the recycling method there are no running cost, labor and maintenance cost. Therefore the working capital investment is estimated to be fifteen percent of the total capital investment and that for the recycling method is 12.5 percent.[26,KayodeCoker,A.2007]

The capacity of the tannery has been assumed to be thousand wet blue pelts. The f.o.b cost had been estimated using the capacity and design data from vendors. The soaking, liming unhairing processes has been carried out on paddles, three paddles were needed with a capacity of two thousands skins, also three drums are required for the deliming, tanning and retannage processes with the same capacity, as well as two fleshing and unhairing /scudding machines.

Table(3.1) The major equipment f.o.b cost [prices from vendors]

Equipment	Cost ($)
The paddles	25,000
The drums	75,000
The fleshing machine	25,000
Unharing machine	25,000

Table(3.1)continued

The cost of the treatment plant	100,000
The total cost of the major equipment	250,000

The total cost of the major equipment=$250,000

Table(3.2)Determination of the fixed capital investment[27,Peter,M and Timmerhaus,K,1991]

The items	Percentage on fixed capital investment (FCI)	The cost($)
Purchased equipment	22.9	250,000
Equipment installation	8.3	90,611
Instrumentation	9.2	100,436
Piping	7.3	79,694
Electrical	4.6	50,218
Engineering and supervision	7.3	79,694
Construction expense	9.2	100,436
Legal expense	1.8	19,650
Contractors fee	1.8	19,650
Contingency	7.3	79,694
The total fixed cost	99.9	1,090,606

Total capital investment=fixed cost+working capital

TCI=1,090,606+WC……….(1)

W.C=15%TCI……………....(2) [27,Peter,M and Timmerhaus,K,1991]

0.85TCI=1,090,606

TCI=$1,283,065

3.7.1.1The total production cost

1. The direct manufacturing cost

Table(3.3)The direct manufacturing cost[27,Peter,M and Timmerhaus, K,1991]

The items	The cost
The raw material	0.50TPC
Operating labor	0.15TPC
Direct supervision	0.0275TPC
Maintenance and repairs	0.06FCI
Operating supplies	0.009FCI
Laboratory charges	0.015TPC
Utilities	0.045TPC
Total	0.7375TPC+0.069FCI

2. The fixed charges

The total fixed capital charges=d.p+2%FCI.(d.p is deprecation)

d.p=(internal cost-s.v)/service life(service life of tannery=25years

s.v is the salvage value=zero.

3. The plant overhead:

Plant over head=0.075TPC

4. The general expenses

a. Administrative cost=0.0375TPC

b. Distribution and marketing=0.0095TPC

c. Research and development=0.003TPC

The total general expenses= 0.0375TPC+0.0095TPC+ 0.003TPC= 0.0473 TPC.

The total production cost(TPC)=0.7375TPC+0.069FCI+d.p+2%FCI+ 0.075 TPC+0.0473TPC= 0.8598TPC+0.089FCI+d.p

0.1402TPC=0.087FCI+d.p

TPC=(0.089 FCI+d.p)/0.1402 [27,Peter,M and Timmerhaus,K,1991], [28,Sinnott,r.2005]

d.p=(250,000-0.00)/25=10,000$

TPC=(0.089 FCI+d.p)/0.1402=((0.089*1,090,606)+10,000)/0.1402 =$763,651.

The rate of production=5000W/B Pelts/day

With 5% losses the rate of production= 4,750W/B pelts/day=4,750 * 300 =1,425,000W/B pelts/year.

The rate of production=1.425,000*4=5,700,000 ft^2/year.

The selling price=$0.6/$ft^2$.

The sale=0.6*5,700,000=$3,420,000.

3.7.1.2The gross profit

Gross profit=revenues-total cost and expenses[28,Sinnott,r.2005]

Gross profit=3,420,000-763,651=$2,656,349.

3.7.1.3The net profit

Net profit= gross profit – tax.[29,Hays,A.2020]

The tax=17%.

The net profit=2,656,349(1-0.17)=$2,204,769.67.

3.7.1.4The rate of return(IRR)

IRR=((Cumulative net cash flow at end of project)/(TCI))*100 percent IRR=2,204,769/1,283,065=171.8%.

3.7.1.5the pay-back period estimation

Pay-back time (as the annual savings are constant, the pay-back time will be the reciprocal of the IRR).

The payback period= 1/IRR[30,wikibedia.netincome2020]

Payback period =1/171.8%=0.58years

3.7.1.6The break-even point

The breakeven point=FCI/(unit sale price -cost per unit)[31, wikibedia.break-even point(economics).2020]

Cost per unit for conventional method=TPC/rate of production=763,651 /5,700,000=$0.133/unit.

The break-even point=1,090,606/(0.6-0.133)=2,320,438units/year

3.7.2The cost for new tannery with the recycling of the spent float method

The fixed cost of the new tannery with the recycling will be the same as that of the conventional treatment with the addition of filters, storage tanks ,overhead tanks and pumps.

Estimated equipment cost for the recycling=$40,000[vendors].

3.7.2.1The fixed capital investment and the total production cost

The total equipment cost=150,000+40,000=$190,000

Referring to table (2) the fixed cost is calculated as follows:

The total fixed investment=(100/22.9)*190,000=$829,694

TCI=FCI+WC

W.C=12.5% TCI

0.875TCI=$829,694

TCI=$948,221

d.p=(190,000-0.00)/25=$7,600

TPC=(0.089*948,221+7,600)/0.1402=$656,145

3.7.2.2The gross profit

Gross profit=3,420,000-656,145=$2,763,855.

3.7.2.3The net profit

Net profit=1,243,854*(1-0.17)=$2,293,999.

3.7.2.4The rate of return

IRR=1,032,339/948,221=241.9%.

3.7.2.5The payback period

Payback period=1/1.08= 0.41years.

3.7.2.6The break-even point

Breakeven point=FC/(unit sale price -cost per unit),Cost per unit =TPC/rate of production=656,145/5,700,000=0.12$

Break-even point=829,694/(0.6-0.12)=1,728,529 unit/year.

CHAPTER FOUR

4. RESULTS AND DISCUSION

4.1Introduction

The crust that was tanned by the recycling process of the spent float was dried and tested and the result was found to be satisfactory.the development of a new tannery with the recycling of the spent float method,show the advantages of using this method.

4.2 The experimental work

Table(4.1)The rinsing solutions analysis

Run 1		pH	NaCl concentration (%)	TSS(ppm)
	Initial washing	8.00	5.0	7000
	Second washing	8.00	1.5	6660
	Final solution	7.95	2.0	6800
Run2		pH	NaCl concentration (%)	TSS(ppm)
	Initial washing	8.10	6.1	7500
	Second washing	7.90	2.0	7000
	Final solution	7.95	2.5	6500
Run3		pH	NaCl concentration (%)	TSS(ppm)
	Initial washing	7.50	6.9	7850
	Second washing	7.95	2.0	7320
	Final solution	7.90	3.0	6940

The initial rinsing solution had a high sodium chloride concentration as shown in the tables (4.1),(4.2),(4.3),due to the fact that the skins were wet salted.

Table(4.2)The soaking and the treated solution analysis

Run		pH	TSS (ppm)
1	Soaking solution	9.55	3360
	Washing+soaking solution	8.78	4643.3
	Treated solution	8.97	756
2			
	Soaking solution	9.50	3900
	Washing+soaking solution	8.00	4955
	Treated solution	8.76	781
3			
	Soaking solution	9.55	3997
	Washing+soaking solution	8.36	5026
	Treated solution	8.35	799.5

Table (4.3) The tanning and retannage processes water and chemicals quantities

Soaking process								
Run	Water(L)		bactericide		Soda ash(g)		Soap(ml)	
	Treated	saved	required	added	Required	Added	Required	Added
1	-	-	10	10	25	25	10	10
2	41.5	9	10	12	25	17.5	10	12
3	41.6	18.1	10	12	25	17.5	10	12
Deliming process								
	Ammonium chloride(g)			Bating agent(g)			Water(L)	

Table(4.3)continued

1	Added	Saved	Added	Saved	added	Saved
2	60	18	32	-	10	6
3	42	18	32	-	4	7
	42	18	32	-	3	7
	pH test		Thumb test		Bubble test	
1	colorless		pass		pass	
2	colorless		pass		pass	
3	colorless		pass		pass	
Retannage wetting back process						
	Water (L)		Formic acid(ml)		Soap(ml)	
	Added	Saved	Added	Saved	Added	saved
1	4	3.6	20	6	40	10
2	0.4	3.5	14	6	20	10
3	0.5	3.5	14	6	20	10
Retannage rechroming process						
	Water (L)		Chrome		Chrome syntan	
	added	Saved	Added	saved	Added	saved
1	3.2	2.3	80	32	80	32
2	0.9	2.6	48	32	48	32
3	0.6	2.5	48	32	48	32

Retannge neutralization process								
	sod formate		Sod bicarbonate		Garad		Water	
	Added	Saved	Added	Saved	added	saved	added	saved
1	40	-	10	-	400	80	4	3.8
2	40	-	10	-	320	80	0.2	3.7
3	40	-	10	-	320	80	0.3	3.8

Table(4.3)continued

Retannnage syntan and dye addition process						
	Liquid syntan		Powder syntan		Dye	
	Added	Saved	Added	Saved	Added	saved
1	80	24	160	48	40	12
2	56	24	112	48	28	12
3	56	24	112	48	28	12

Retannage fatliquor and formic acid addition process				
	Fat liquor		Formic acid	
	added	Saved	Added	Saved
1	240	72	60	18
2	168	72	42	18
3	168	72	42	18

Table(4.4)The crust physical test[22, Sudanese Standards and Metrology Organization,garment leathers,SDS 579:2016,23, Musa, A and Gasmelseed, G.2013]

Test name	**Run 1**	**Run 2**	**Run 3**	**SSMO Standards**	**BIS standards**
Thickness(mm)	1.2	1.0	0.8	1	-
Tensile strength(kg/cm^2).	200	243	149	100	200
Elongation at break%.	34	51	34	60	40-65
Tear strength (kg/cm).	73	70	43	-	30
Load at grain crack (Kg).	20	22	20	-	20
Destination at grain crack (mm).	10	6	6	-	7

All the tanning and retannage processes was carried out at room temperature (about 35c°).According to the previous results from the following table more than ninety percent of the water was saved in each run.The skins that had been used are wet, so no significant loss in water occurs for the soaking process.The treated solutions had a bad smell, so additional amount of the bactericide was added to the second and third run(two ml had been added).

The neutralization processes was started with seventy percent of the sodium carbonate and sodium formate, for the second run, but the solution pH was four, so the total amount of them had been added. As shown in table below about eighty nine percent of the water has been saved in each run.

The wetting back process had been continued for a short time and need less amount of the water because the skins were wet. A small part of the quantity of water that had been saved from the washing process had been used as make up for wetting back process.

4.3the recycling process development

Table(4.5) The water and chemicals quantities for the soaking process

Soaking process					
Run	**Water (m^3)**	**Sodaash(kg)**	**Soap (L)**	**Bactericide (L)**	**PAC(kg)**
1	6.5	5	5	2	
2-10	0.65	3.5	3.5	2	0.00585
Unhairing process					
	Water (m^3)	**Sodium sulphide(kg)**		**Calcium oxide(kg)**	
1	1.65	27.5		55	

Table(4.5)continued

2-10	0.165	19.25	38.5		
Deliming process					
	Ammonium sulphate(kg)	Bating agent(kg)			
1	12	3.2			
2-10	8.4	3.2			
Tanning process(pickling)					
	Water (m^3)	Sodium chloride(kg)	Formic acid(L)	Sulphuric acid (L)	
1	0.8	80	3.2	8	
2-10	0.08	64	2.24	5.6	
Tanning process(rechroming)					
	Fungicide(L)	Sodium formate(kg)	BCS(kg)	Sodium bicarbonate(kg)	
1	1.2	3.2	48	6.4	
2-10	0.84	2.24	33.6	4.48	
Retannage process(wetting back and rechroming)					
	Water (m^3)	Soap (L)	Water(m^3)	Chrome(kg)	Chrome syntan(kg)
1	0.8	4	0.64	16	16
2-10	0.08	2.8	0.64	16	16
Retannage process(neutralization,syntan garadand dye addition)					
	Sodium formate(kg)	Sodium bicarbonate(kg)	Water (m^3)	Garad(kg)	Dye (kg)
1	5.6	1.4	1.2	120	16
2-10	5.6	1.4	0.12	84	11.2
Retange process(syntan,fatliquor and formic acid addition)					
	Liquid syntan(L)	Powder syntan(kg)	Fatliquor(L)	Formic acid(L)	
1	16	32	48	12	
2-10	11.2	22.4	33.6	8.4	

4.6The chemical cost for the conventional treatment method

Table(4.6)the soaking,unhairing,deliming and tanning chemicals cost

Soaking chemicals cost

Water (m^3)	Cost ($)	Soda ash(kg)	Cost ($)	Soap (L)	Cost ($)	Bactericide (L)	Cost ($)	Total cost for ten runs ($)
6.5	0.2054	5	1.4	5	1.7	2	10	133.054

Unharing chemicals cost

Water(m^3)	Cost ($)	Sodium sulphide(kg)	Cost ($)	Calcium oxide(kg)	Cost ($)	Total cost ($)
1.65	0.05214	27.5	13.75	55	5.5	193.0214

Deliming chemicals cost

Ammonium sulphate(kg)	Cost ($)	Bating agent(kg)	Cost ($)	Total Cost ($)
12	4.2	3.2	1.536	57.36

Pickling chemicals cost

Water (m^3)	Cost ($)	Sodium chloride kg)	Cost ($)	Formic acid(L)	Cost ($)	Sulphuric acid(L)	Cost ($)	Total cost ($)
0.8	0.02528	80	6.8	3.2	1.088	8	3.84	117.5328

Chroming chemicals cost

Fungicide (L)	Cost ($)	Sodium formate kg)	Cost ($)	BCS(kg)	Cost ($)	Sodium bicarbonate(kg)	Cost ($)	Total cost ($)
1.2	6	3.2	2.56	48	18.24	6.4	0.832	276.32

8	6.4	2	0.26	1.2	0.03792	120	48	16	240	3013.579

Table(4.6)continued

Retanage wetting back and rechroming chemicals cost								
Water (m^3)	Cost ($)	Soap (L)	Cost ($)	Chrome(kg)	Cost ($)	Chrome syntan (kg)	Cost ($)	Total cost ($)
1.6	0.05056	4	1.36	20	7.6	20	40	486.2288

Retanage wetting back and rechroming chemicals cost

Neutralization garad and dye addition chemicals cost										
Sodium formate((kg)	Cost($)	Sodium bicarbonate(kg)	Cost($)	Water ((m^3)	Cost($)	Garad(kg)	Cost($)	Dye(kg)	Cost($)	Total cost($)
8	6.4	2	0.26	1.2	0.03792	120	48	16	240	3013.579

Syntan ,fat liquor and formic acid addition process								
Liquid syntan(L)	Cost($)	Powder syntan (Kg)	Cost($)	Fatliquor(L)	Cost ($)	Formic acid(L)	Cost ($)	Total cost ($)
16	38.4	32	576	60	6	15	5.1	6255

The total chemical costs for the conventional method= 10435.62$

The total chemical costs for the recycling method= 7637.889$

4.7The cost estimation of a new tannery using the conventional and recycling method

The following table shows the advantages of using the recycling method

Table(4.7)The recycling method versus the conventional treatment method

Items	The conventional method	The recycling method
TCI	$1,283,065	$948,221
TPC	$763,651	$656,145
Gross profit	$2,656,349	$2,763,855
Net profit	$2,204,769	$2,293,999
IRR	171.8%	241.9%
Payback period	0.58 year	0.41 year
Breakeven point	2,230,438 unit/year	1,728,529 unit/year

The difference of the total capital investment and the total production cost of the conventional and the recycling method show the advantage of using the recycling over the conventional treatment.

The saving in the TCI=1,283,065-948,221=$334,844

The saving in the total production cost=763,651-656,145=$107,506

4.8Discussion of the results

Ninety percent of water and thirty percent of chemicals is saved by using the recycling of the spent float method.

The working capital investment for the conventional treatment plant and that for the recycling method are different due to the fact that there are saving in chemicals and water upon using the recycling method. It must be observed that the conventional treatment method needs treatment plant to construct with operating cost without any returns.

The recycling of the spent float ensures the decreasing of the levels of the liquid discharges that cause the environment pollution to the acceptable international standards.

By using the recycling method there will be a decrease in the total capital investment and the total production cost, also there will be an increase in the net and gross profit as shown in table (4.7).

CHAPTER FIVE

5. Conclusion and Recommendations

5.1 Conclusion

1. The recycling of the spent solution is done for the wet processes from soaking through the retannage ,the physical tests had been done for the resulted crust and the result was found to be satisfactory.
2. The cost analysis of two tanneries with conventional and recycling method show the advantages of using the recycling method , because the use of the recycling process decrease the total capital investment and the total production cost as there will be no need for establishing treatment unit with its running cost.

5.2 Recommendations

1. It is recommended that the initial washing water should be treated separately as it contains a lot of dirt, blood and dung,salts.
2. The first rinsing water contains high concentration of sodium chloride (due to the fact that the skins were wet salted),so it can be used in the pickling process after treatment.
3. Using the water shower will decrease the amount of the H_2S and ammonia gas that evolved during the deliming process.
4. The recycling of the spent float should be used to minimize the hazardous chemicals exist in the spent floats and hence protect the environment.
5. The process of recycling has to be generalized to all tanneries in the Sudan for protection of the environment.
6. The solid waste obtained from sludge has to be treated and used as fertilizer.

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