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GREENER APPROACH TO LEATHER TECHNIQUES

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ABSTRACT

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The main purpose of this study was to find out greener and more ecological methods of leather tanning. In this thesis, old traditional methods and new developing methods are compared. New alternatives to chrome tanning agent and their benefits are reported. Additionally, efficient way of chrome tanning in presence of masking agents or other catalysts is reported with cleaning techniques using membrane processes such as microfiltration, ultrafiltration (UF), nanofiltration (NF) and reverse osmosis are discussed.

The use of ultrasound in leather production has proved its significance by reducing time and increasing diffusion rate as well as improving leather quality. Eco-friendly approach to tanning process based on amino acids and aldehyde for chrome free tanning are discussed.

Key words
chrome tanning, eco-friendly tanning, leather waste, membrane process, NF, UF, use of ultrasound, vegetable tanning

FOREWORD

I would like to express my humble gratitude to all those who have contributed directly or indirectly to complete this project. Thanks to my supervisor from Centria University of Applied Sciences, Kaj Jansson who gave me useful suggestion and advice during this project.

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The thesis was done in collaboration with KETEK Kokkola. KETEK is an expertise organisation founded in 1987 with primary task to improve the operational preconditions of the companies in the region. I am grateful to KETEK and its staff for supporting me on this project.

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1. INTRODUCTION

Over the past 100 years, leather tanning industry has been into consideration concerning their environmental impact. The low level of cleaning technology standard has given rise to environmental issues awakening the people to think in a new way for the creation of green sustainable process.

Tanning is the most polluting operation during the leather making process. The agents such as chromium can be highly toxic and polluting depending on its existing form. In European countries, EU directives for leather industry have limited the use of chrome tanning which made it important to establish new techniques and strategies to ensure environmental protection.

In leather marketing, the two terms ‘eco-leather’ and ‘bio-leather’ are used to signalize environmental sustainability. The purpose of this study is to investigate how vegetable oils and other re-agents can benefit and provide us better leather without creating any environmental problems. This research aims to find modern alternatives for chrome tanning. Not only this, I will discuss green or ecological methods of tanning leather limiting the cost factors considering the EU directives. The research question is: *How are vegetable oils and other re-agents tanning beneficial to us in-comparison to chrome tanning economically and environmentally?*

The research is carried out with a group of members in Ketek Kokkola with sponsors from all around the world. It is going to be carried out for the next 2 years. Since the research is about the development of new green process, there are many problems concerning the alternatives and process diagram. The readers will get clear-cut idea about chrome tanning and its effect on health and environment. In this research, I will first describe the chemical mechanism of the chrome tanning process and then bring out the solution for its optimum use.

Finally, I will talk about new alternatives and green process and their benefits in leather industry.

2. ENVIRONMENTAL IMPACT

Turning non treated perishable skins and hides into leather of good quality requires the use of chemicals which react with the skins in aqueous phase. Hence it can be assumed that high concentrations of the used chemicals as well as compounds coming from the skin can be found in the wastewater. Organic pollutants from the processed material are of proteic and lipidic nature. It has been reported by Casano et al. that 30 % of organic compounds that are present in waste water originate from the treated raw skin (Cassano, Molinari, Romano & Drioli 2001, 112). Inorganic pollutants are a result of non-reacted chemicals. Conventional treatment methods of wastewater treatment plants fail to recover and reuse the released chemicals. Contaminated water is chemically, physically and biologically treated which results in the formation of sludge. The recycling of this sludge is complex. The sludge will end up in dumps even though it contains resources that could be reused (Molinari 1995, 101).

2.1 FICK'S LAW OF DIFFUSION

In order to react with the fibrous protein collagen which is the main building block of hides and skins, chemicals have to enter the pores. The skin surface is uneven and features several pores of different size. Chemical exposure to the skin involves the diffusion of the chemical substances into the pores which is physically described by the Fick's Law which is depicted in equation 1.0 (Sivakumar, Rao, Swaminathan & Ramasami 2008, 2076-2083.):

$$J = -\frac{\alpha}{\tau} D_i \frac{\partial C_i}{\partial x} \qquad (1.0)$$

with

J = flux which describes the amount of substance crossing unit area of leather in one dimension ‘x’

x = dimension

α = fraction of the volume occupied by the channels or pores

τ = tortuosity which describes the ratio of the length of channel to the direct path

D = diffusion coefficient within the leather matrix

C_i = concentration of the substance in the pores present in the imaginary layer ‘i’.

Diffusion occurs when the chemical concentration of the collagen matrix is different from the concentration inside the tanning medium (Sivakumar and Rao 2001, 29). Fick’s Law describes that the higher is the concentration, the higher is the diffusion rate. Since a high diffusion rate is significant for a good reaction, high concentrations of chemicals are used in leather manufacturing. This excess is accompanied with environmental pollution as the wastewater contains high amounts of chemicals. Especially in the tanning process it is problematic due to use of hazardous tanning agents such as chromium (Sivakumar et al 2001, 29).

2.2 LIMING, UNHAIRING AND DEGREASING AGENTS

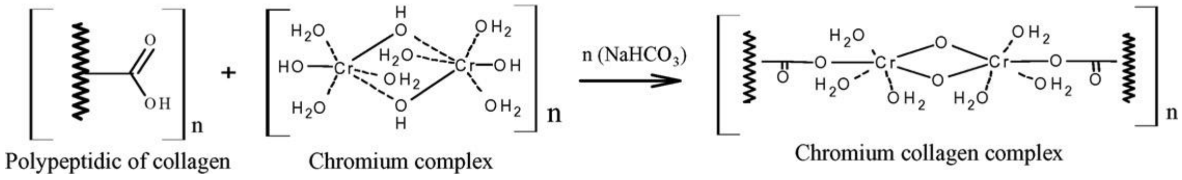
Liming and unhairing agents which are used to pretreat the skin are highly polluting. Sulfides and amins impact the environment and generate by-products when they react with the skin material (Martignone 1997). The chemical oxygen demand (COD) ranges between 20.000 and 40.000 mg/ L of consumed oxygen (Cassano et al. 2001, 113). Organic solvents which are used in the degreasing process affect the environment due to volatile compounds which are released into the air and the water cycle. Additionally, they have a great impact on bacterial life in the wastewater treatment and may inhibit biological degradation of the wastewater (Cassano, Drioli & Molinari. 1997, 251).

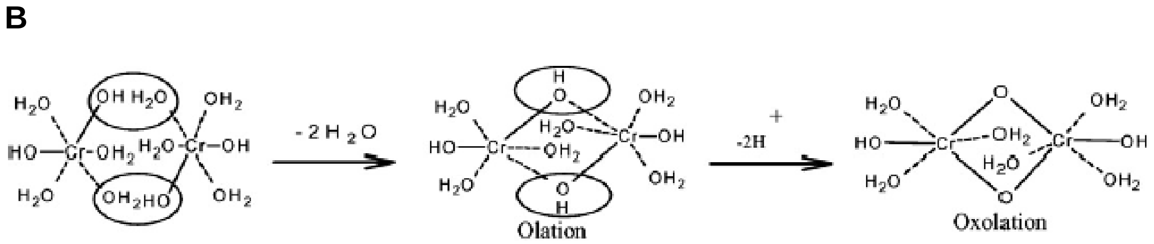
2.3 TANNING AGENT: CHROMIUM

The pickling fluid stream contains high chloride and sulfate amounts up to 9 g/ L which are hard to eliminate by conventional treatment plant. However, the most polluting substance is released after the tanning process. Chrome tanning is one of the most commonly used processes in tannery. Basic salts of chromium are used to guarantee the quality of the produced leather, preventing it from microbial degradation but exhibit/create a significant environmental impact (Cabeza, Mcaloon & Yee 1998, 2990-3135). 25 % of the chromium is present as Cr_2O_3 at 33°S of basicity which causes pollution at a high level (Malek, Hachemia & Didier 2009, 156). About 30 % of the initial salt amount remains in the outcoming fluid stream of the tanning process (Gauglhofer 1986, 11). This chromium leather waste shows high stability and hence causes environmental problems when it is released into the air as gaseous pollutant in the incineration process (Gavend, Bossche & Brun 1997).

In the following paragraph, the formation of the highly stable chromium leather waste will be explained. GRAPH 1A illustrates the reaction of the used tanning agent chromium with the collagen of the skin resulting in a stabilization of the triple helical structure of collagen matrix. Chromium is cross linked with the carboxylic groups of the polypeptidic chain of the skin collagen resulting in the formation of a chromium collagen complex (Malek et al. 2009, 156-162).

A





GRAPH 1A: Coordinate covalent linkage of chromium complex with the polypeptidic chain of the skin collagen; B: Olation and oxolation process (adapted from Malek et al. 2009, 161)

The following chemical reactions which take place are called “olation and oxolation”. Olation appears as the alkaline milieu of the tanning solution increases resulting in dehydration. This is followed by a dehydrogenation step and the discharge of two hydrogen atoms occur resulting in the covalent linkage of the oxygen-chrome as it is depicted in GRAPH 1B (Martinetti 1995). The obtained oxolation bridges result in high stability of the chromium – collagen complex which causes the adverse environmental impact due to the non degradable toxic material (Robert 1983). The tanning waste contains about 4.3 % of chromium and 14 % of nitrogen (Malek et al. 2009, 156).

Yet, there is no suitable technique that exists which describes an efficient way to recover chromium. The traditional method is alkaline hydrolysis by precipitating the chromium as chromium hydroxide ($Cr(OH)_3$) using sodium hydroxide solution followed by the dissolution in sulfuric acid (Cassano et. al 2001, 118; technical brochure 1992). Another treatment to recover the chromium is acidic hydrolysis (Wojciech, Mieczyslzw & Urszula 1998) and enzymatic hydrolysis (Taylor, Diefendorf, Thompson, Brown, Marmer & Cabeza 1997). However, those treatments generate new waste products of low quality, for example the chrome cake which is a chromium – protein mixture (Malek et al. 2009, 156).

2.4 WASTEWATER TREATMENT PROCESS

Especially tanning agents have a great impact on the environment and hence should be eliminated in the cleaning up process. The common wastewater treatment process consists of three main steps in order to remove tanning substances (Cassano et al. 2001, 121):

1. chemical – physical treatment: coarse screen, equalization and chemical – physical precipitation with sedimentation and sludge separation
2. biological treatment with partial or total recycle of sludge and its separation
3. filtration, stripping, redox processes (Zenon Environmental B.V. 1995).

Wastewater plants which clean the released water from leather industry feature about 10 times higher biomass concentrations compared to conventional wastewater plants (Cassano et al. 2001, 121).

3. APPLIED PROCESSES

The tanning process can be divided into four main steps: pre-tanning to eliminate non-collagenous materials, tanning to stabilize the collagen matrix, post-tanning to impart functional properties and finishing to give aesthetics (Sivakumar, Swaminathan, Rao, Muralidharan, Mandal and Ramasami,. 2010, 1054). Pre-tanning has 5 different steps and post-tanning has 4 different steps. These all processes are discussed below one by one.

3.1 SOAKING

Soaking is the first step in leather processing. In this step the raw skin is exposed to water and chemicals which hydrate the proteins and fibers. Additionally, denatured proteins as well as salts used for preservation are solved in the water phase and removed together with dirt which is attached to the skins. The process duration is about 8 to 20 hours for wet salted skin (Sharphouse 1983, 64) and 24 to 48 hours for dried skin (Sarkar 1991, 99). The wastewater which contains salts, earth, chemical additives and excrements is discharged into a water treatment plant.

3.2 UNHAIRING AND LIMING

The second step in the leather process is the removal of hair and other components from the skin which are not supposed to be transformed into leather.

The treatment affects the structure of the skin which results in a better reactivity of the skin containing collagen when it is exposed to tanning agents. The liming step introduces chemicals such as lime ($Ca(OH)_2$) and sodium sulfide (Na_2S) which open up the fibre structure of the skin (Germann 1997) and hence provides more working surface for treatment with tanning agents (Sivakumar and Rao 2001, 27). Furthermore, natural fats are partially saponified, most of the interfibrillar proteins such as albumins and globulins are eliminated, mucoids are degraded and the derma is swelled (Cassano et al. 2001, 113). Hair loss is introduced by the destruction of the cementing substances, prokeratines and glycoproteins, in the root of the hair. The amino acid cystine is part of the prokeratine structure and features a disulfide bond which is broken by the addition of the liming agent due to SH_2 ion formation. The duration for liming process is about 16 to 20 hours (Sivakumar and Rao 2001, 27).

3.3 DELIMING AND BATING

The deliming step is carried out to reduce the excess of liming agent in the fluid stream. Acids and/ or acidic salts are added to the stream (casano et al. 2001, 116). The bating step involves the addition of proteolitic enzymes. These proteolitic enzymes open the fibrious structure of the derma to make it softer (Casano et al. 2001, 116).

3.4 DEGREASING

A degreasing operation is carried out to eliminate the excess of natural fat substances from the skin. This process step is mainly part of sheepskin processing due to 30 to 40 % of fat substances output in respect to the raw weight

(Cassano et al. 2001, 117). However, it is an essential operation in leather process to avoid quality loss. High amounts of fat cause hardness to touch, loss of physical strength and dyeing imperfections. In some cases, repousse may appear which is demonstrated with the formation of whitish spots on the tanned skin or final product. Organic solvents are employed as degreasing agents in the 2 to 3 hours lasting degreasing process with 1 to 6 hours washing time for removal of the emulsified fat (Sivakumar and Rao 2001, 28).

3.5 PICKLING

The pickling process ensures the removal of the last residual lime in the skin by acidification and dehydration of fibers. Acidification dehydrates the fibers of the skin using sulfuric, hydrochloric, formic and lactic acid in combination with salts such as sodium chloride (NaCl), sodium sulfate (Na_2SO_4) and various salts from the used acids. This may also include chromium basic salts (Casano et al. 2001, 118).

3.6 TANNING

The tanning step guarantees quality, durability, practicability and the stability of the final leather product by treating the skin with inorganic and organic tannins such as chromium, aluminum, titanium, iron and zirconium basic salts as well as high molecular weight vegetable substances, aldehydes, oils and other substances (Krishnamoorthy, G., Sadulla, S., Sehgal, P.K. and Mandal, A.B. 2012, 173; Cassano et al. 2001, 118). This treatment inhibits the biological degradation of the protein containing skin by microorganisms which would result in undesired smell. Furthermore, tanning agents are used in order to prevent the leather from chemical and thermal degradation. The most common tanning agent is chromium sulfate. It enters the pores of the skin by a diffusion process to react with the collagen carboxyl groups and form inter- and intramolecular cross linking which results in physical, chemical and biological stability. This step is followed by a basification step using weak chemical bases which enhances the anionic character of the carboxylic collagen groups and hence increases the attraction towards the chromium cations Cr^{3+} which results in a final covalent bond. The whole tanning process takes about 5 to 6 hours (Sivakumar and Rao 2001, 28).

About 30 % of the initial salt amount remains in the outcoming stream whereas 70 % reacts within the tanning step (Cassano et al. 2001, 118). The fluid stream is sent to a treatment plant where the chromium basic salt accumulates in the sludge. Further tanning agents which are used in leather manufacturing are vegetable tannins such as chestnut, mimosa and quebracho.

3.7 NEUTRALISING, DYEING AND FAT LIQUORING

The post-tanning process step includes neutralization, dyeing and fat liquoring of the leather product. The commercial value of the leather is increased by dyeing with agents such as acid red, acid black, direct black or metal complex black (Sivakumar and Rao 2001, 30). It has been reported that the dye uptake is about $12x10^{24}$ g per gram of leather when it is exposed to an initial dye concentration of $20x10^{25}$ g/ cm^3.

3.8 DRYING

Drying of leathers is done after all the wet processes. It is done in an isolated condition. Heat can be applied if necessary. But it shouldn’t exceed 30 – 35 ºC for vegetable/synthetical tanned leathers and 55 – 60 ºC for chrome tanned leathers (Pore & Gavend 1978, 145-153).

3.9 FINISHING

Finishing is the final stage of leather production. It makes the leather more suitable, attractive and comfortable for the manufacture of new products. The basic structure of finishing has 3 coats i.e. base coat, pigment coat and top coat (Gerhard 1996, 159).

4. ALTERNATIVE METHODS

With the change in time, we human beings have been more sincere and careful on our environment. We have developed techniques to reduce the use of chrome as well as to replace the use of chrome in the tanning process of leather production. We are now able to determine chromium content with the help of titration which help us to control the excess use of chromium. Some of the alternatives for chrome tanning along with the reduction of the use of chromium are discussed below:

4.1 DETERMINATION OF THE CHROMIUM CONTENT

Quantification of the chromium content is carried out by analyzing chromium leather waste ash. To obtain the ash, the waste is incinerated at 600 ± 25 °C and chemically analyzed according to the American Leather Chemists Association standard ALCA D10 (Malek et al. 2009, 157): Green colored Cr (III) is oxidized to orange colored Cr (VI) using a concentrated mixture of perchloric acid ($HClO_4$) and sulfuric acid (H_2SO_4). The reaction is carried out under boiling conditions to remove the chlorine.

$$Cr^{3+} + 2\,HClO_4 \overset{\Delta}{\rightarrow} Cr_2O_7^{2-} + Cl_2 + H_2O \tag{2.0}$$

The addition of 10 % potassium iodide KI results in the formation of iodine I_2 which is titrated with a 0.1 N sodium thiosulfate solution $Na_2S_2O_3$ using starch solution to detect the endpoint of the reaction (Merrill 1978, 243-251).

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,I^- \rightarrow 2\,Cr^{3+} + 3\,I_2 + 7\,H_2O \tag{3.0}$$

$$2\,Na_2S_2\,O_3 + I_2 \rightarrow Na_2S_4O_6 + 2\,NaI \tag{4.0}$$

The final chromium content is calculated following equation 4.0 (Malek et al. 2009, 157).

$$Cr_2O_3(\%) = \frac{V \times c \times M}{m} \times 100 \qquad (5.0)$$

Chromiumoxide content (%) = (A × N × 0.**02533** × 100)/W
where *A* is the milliliters of titrating reagent used, *N*, the normality of the titrating reagent, *W* is the weight of the specimen in grams and 0.02533 is the standard quantity in grams of Cr2O3 titrated by one milliliter of Na2S2O3 (0.1 N).

As reported in the literature, the chromium content in leather waste exhibits about 4.15 to 4.33 % (Malek et al. 2009, 157).

4.2 ALUMINIUM TANNAGE

This is one of the oldest methods of tanning with simple aluminium chlorides, potassium and aluminium sulphates. This method is not more popular in its application as it doesnot result in real tannage which can be easily washed out by water.(chambard 1978). But nowadays, the chemical industry has been able to make highly basic and partly masked aluminium chloride tanning agents resulting in stable tanning to produce wet white leathers with a very good resistance to light. This tannage improves the density of the fibre texture resulting into its special buffing properties, especially suitable for the production of nubuk and suede leathers. (Gerhard 1996, 68-69.)

4.3 ZIRCONIUM TANNAGE

Zirconium sulphate and/or its basification are the most commonly used tanning agents. The chemical behavior is much more similar to that of aluminium tanning agents. The treatment of leathers with this tanning agent results in leathers with a pure white cross-section and neutral white surface with excellent lightfastness as like aluminium tannage. In this tannage, tanning is more compact and fuller improving the density of fibre texture which points out the special character of this tanning more suitable to treat loose and spongy raw hides. Additionally, it also possess better hydrolysis properties compared to aluminium and chrome tannage (Gerhard 1996, 70.).

4.4 IRON TANNAGE

Iron tannage is the recent discovery in the tanning industry to compensate the economy and fulfill the place/shortage of chromium, due to environmental legislation. Recent findings and trends point out iron tannage to be more suitable in the production of wet brown/wet iron leathers for preliminary tannage (Tonigold, Hein & Heidemann 1990, 8-14). These leathers produced by iron (ıı) tannage show similar handle properties of chrome tanned leathers. But these leathers have low resistance to boiling. Therefore, to fix this defect, they should be retanned using synthetic, vegetable or chrome tanning agents.(Gerhard 1996, 71).

4.5 SULPHUR TANNAGE

Sulphur tannage has no real tanning effect and is not correct term; however, the name is commonly used. This method is used rarely in special cases to make special technical leathers such as belt, picker bands and lace leathers, mostly in combination with other tanning agents like vegetable tanning agents, chrome tanning agents and fat tanning agents. This tannage has the advantage of producing excellent firmness, elasticity and high pliability in the skin (Gerhard 1996, 72).

5. GREEN CHEMISTRY AND NEW INNOVATIVE METHODS

Green Chemistry is an upcoming and emerging field of interest for today’s researcher, tanneries and environmentalist. It represents an environmental friendly procedure applicable in leather manufacturing in order to reduce hazardous chemical material output. Innovative methods promote green chemistry of leather making process. Some of them are discussed below.

5.1 AMINO ACIDS

An alternative process to replace the polluting chrome tanning has been developed by Krishnamoorthy et al. using optically active unnatural d-amino acids (d-AA) with aldehyde. Unnatural d-AA are non-genetically coded. They are naturally occurring but they can also be chemically synthesized. Krishnamoorthy states that unnatural d-AA stabilize protein structures and are less prone to enzymatic reactions than natural peptides (Krishnamoorthy et al. 2012, 174). Hence, they exhibit a suitable feature to stabilize the collagen triple helix of the skins and hides by preventing the skin from proteolytic activity.

Tanning of the skins with glutaraldehyde in the presence of unnatural d-AA such as d-alanine or d-lysine result in high stability of the leather due to the bridging feature of the carboxylic as well as the amine group of the amino acids. Leather collagen molecules are connected to each other and exhibit a reduced reactivity due to the covering of the functional groups by the d-AA reagents. Intra and inter molecular cross linking results in mechanical, thermal and biological stability and exhibits hydrophobicity of the leather due to interfibrillar bonding and isomerisation. The generated d-AA proteins are more stable and resistant towards microorganisms, oxidation, mutation and cancer advancement compared to their l-enantiomeric equivalents due to the essential role of the d-amino acids as bacterial cell wall component (Krishnamoorthy et al. 2012, 181). The wastewater contains no hazardous chemicals as no toxic tanning agents are used during the described process and hence wastewater treatment plants benefit from unproblematic handling and final disposal of the waste.

5.2 VEGETABLE / SYNTHETIC TANNAGE

Environmental friendly vegetable tanning includes the use of tannins such as wattle barks, myrobolan nuts, and chestnut. Tannins exhibit highly polymerized and coiled-up structure of plant basis (Sivakumar and Rao 2001, 28-29). The use of natural materials which replace the hazardous chromium illustrates a suitable and eco friendly alternative to chrome tanning in regard to environmental protection.

Since the last century, vegetable tannage has raised to second place in the tanning industry as synthetic tanning agents were invented in 1911 with a number of aromatics. Syntans with very particular properties have also been produced for a few decades. In tanning technique, these syntans improved the vegetable tanning for many cases. This special property of syntan gave rise to the number of combination tannings with vegetable tanning agents resulting in the modification of tanning methods as well as the properties of treated leathers (Gerhard 1996, 73).

5.2.1 VEGETABLE TANNING MATERIALS

Our world is full of vegetable tanning materials like wood, barks, leaves, fruits, roots and growths (gallnuts) containing usable tannin. Plants in the tropical and sub-tropical regions of the world have mostly high content of tannin which is more important in the production of leather. Some of the barks used most commonly worldwide are mangrove, mimosa, eucalyptus, pine and acacia negra where as woods of chestnut, oak and quebracho is also famous for its use. Leaves found in Asian and African countries like sumac and gambir have also good tanning effect. Fruits like valonea and myrobalans also show similar effects like leaves tannin.(Reich 1996, 74-83).

5.2.2 THE MANUFACTURE OF TANNIN EXTRACT

The industrial process of producing tannin extracts is more practical than by leather factories. First the tanning materials are disintegrated by cutting, rasping, crushing and/or coarse grinding. This is followed by the extraction of the disintegrated barks by means of water in accordance with the counter flow principle in extracting boilers usually made of stainless steel. Pump is used to move the weakest liquor towards the fresh new-coming barks in presence of temperature 80 – 130 ºC and suitable pressure (depending on the nature of tanning material). This helps the tannin content in liquor to increase gradually. This liquor is then purified by sedimenting, filtering or centrifugating and then concentrated in vacuum evaporators. These extracts are then turned into powder by spray drying, drum drying or granulate drying and sold with concentrations of about 60-80%. (Gerhard 1996, 74)

5.2.3 TANNING PROPERTIES

Tanning properties of vegetable tanning agents vary from each-other. According to their properties, these agents are classified into two different groups: hydrolysable tanning agents and condensable tanning agents. Hydrolysable tanning agents are also called pyrogallol which means acid former where as condensable tanning agents are called catechol which means phlobaphene former. Oak, chestnut, myrobalan, sumac and valonea are the examples of hydrolysable tanning materials where as pine, mangrove, mimosa and quebracho are the examples of condensable tanning materials (Reich 1996, 74-83).

5.2.4 THE PRODUCTION OF SYNTANS

Syntans are obtained when mononuclear and polynuclear phenols, naphthalene and its derivatives cresols, naphtols, and aromatic ethers are condensed with formaldehyde and then sulphonated. Syntans mainly exist in the form of salts of sodium and/or ammonium and manufactured with particular properties with most of them possessing anionic charge and a few with amphoteric. Syntans have many classification and properties depending upon the products and their procedures of manufacture. Syntans can be used as replacement, shrinking, bleaching, neutralizing as well as filling tanning agents depending on the situations (Suparno, Covington, Philips & Evans 2005, 114-127.).

5.2.5 TANNING METHODS

Vegetable tanning methods are different than chrome tanning methods. Vegetable tanning takes longer time and so, we classify them according to time into four different groups i.e. slow pit tannage, accelerated tannage, quick tanning methods and rapid tanning methods. Slow pit tannage takes 12-18 months and is performed in isolated condition according to the counter-current principle with thin liquor giving good quality of leather. However, this tanning method has an disadvantage of losing high amount of tanning agents due to oxidation and hydrolysis in their prolonged duration where as accelerated tannage takes 2-6 months depending on the process used and is performed by increasing the concentration of tanning agents by using higher percentage tanning agents and tan liquor. But this method has disadvantages of slightly reduced bonding and higher removable of the content of substances by washing in comparison to slow pit tanning method.

Quick tanning methods take 4-20 days depending upon the nature of leather and operational conditions. These conditions are mechanical agitation, concentration, temperature, pressure and pH. Some of the known methods are Italian method, Four step method, Igualada method, Liritan method, West german tanner school method and English hot pit method where as rapid tanning methods take 2-3 days. In this method, powder tanning substances are used. The two known methods are RFP process of BAYER and Rapitan process of BASF. But this method is much more sensitive and should be handle with full attention. The temperature should not rise more than 38ºC, vessels should be well suitable and the hides should be well prepared (Faber, bibliothek des leders, 112-115).

5.2.6 DEFECTS BY VEGETABLE TANNAGE

Vegetable tannins have been reported to accumulate in leather which reduces its applicability in different fields as well as the efficiency of biological degradation which results in high Biochemical oxygen demand (BOD) and Chemical oxygen demand (COD). Furthermore, the limited availability of vegetable tannins and the longer penetration time through the leather matrix illustrate an additional disadvantage for the use of vegetable tannins (Krishnamoorthy et al. 2012, 173-174; Sivakumar and Rao 2001, 28). Different kinds of tanning stains along with case hardening as well as loose cracked and crumbled grain may appear as defects of vegetable tannage but these all defects have causes and most of them can be recovered by following the precautions and knowing the causes.

5.3 ALDEHYDE TANNAGE

Aldehyde tannage is rarely used as tanning methods in its all. But it is used greatly for pretanning and retanning treatments. Aldehydes like glutaraldehyde and some of its modifications have proved to be more competent than others.

5.3.1 FORMALDEHYDE

Formaldehyde is not that popular but it is also used in aldehyde tannage (Wojdasiewicz, Szumowska, Skornicki & Przybylski 1992, 121). When the pH ranges 6.5 to 8.5, formaldehyde gives its best tanning effect. Excessive amount of formaldehyde should not be used to avoid callouses on the grain. Leathers seem to absorb more water in this process giving pure white color of leather with a fine closed appearance of grain (Gerhard 2005, 86).

5.3.2 GLUTARALDEHYDE

Glutaraldehyde and its modifications are more popular in use than formaldehyde as it gives more soft leather with greater fullness and increased fastness to heat, perspiration and washing. The effect of tanning starts at low pH around 2.5 giving the finer appearance of grain. However, this has also some disadvantages like line shrinking effect due to alkaline liquor and bad odours along with slight tinge of yellow which appears occasionally (Gerhard 2005, 86).

5.4 TANNAGE WITH POLYMERS

The use of polymers as a tanning agent has also been more popular for a decade but polymers are not yet recognized as a self tanning agent because they do not have adequate self tanning effect. Polymers are used as pretanning and retanning agents. Some of the examples are polymers of acrylic acid, methacrylic acid, ethyl esters or methyl esters of acrylic or methacrylic acid, copolymers of different monomers, styrene maleic acid and oligomers (Träubel & Slaats 1994, 231-233). All of these polymers have ecological advantages as well as different molecular size with different degree of polymerization (Magerkurth 1987, 183-192). According to their ionic properties, they are classified as anionic products and amphoteric products.

5.5 TANNING WITH FATTY SUBSTANCES

One of the oldest methods of tanning is tanning with fatty substances. The oil of different marine fish and animals has reactive double bonds which makes the real tanning possible with fatty substances. This tanning is further divided into three groups which are:

5.5.1 CHAMOIS TANNAGE

This tannage process treats the skin of lamb, sheep, red deer, chamois, reindeer and elks to make garment leathers, mostly leather for Tyrol trousers. Fish oil is used under controlled temperature not exceeding 45 ºC in a hot air drum. Formaldehyde and/or glutaraldehyde can be used as a pretanning agent to get more softness in the leather (Gerhard 1996, 89)

5.5.2 TANNAGE WITH FATTY ALCOHOL SULPHATES

This tannage has pretanning and retanning effect. It does not have self tanning effect. This method is still in use because it gives very soft and elastic leathers in conjunction with mineral tanning agents. But this process has disadvantage of increasing wettability (Gerhard 1996, 89).

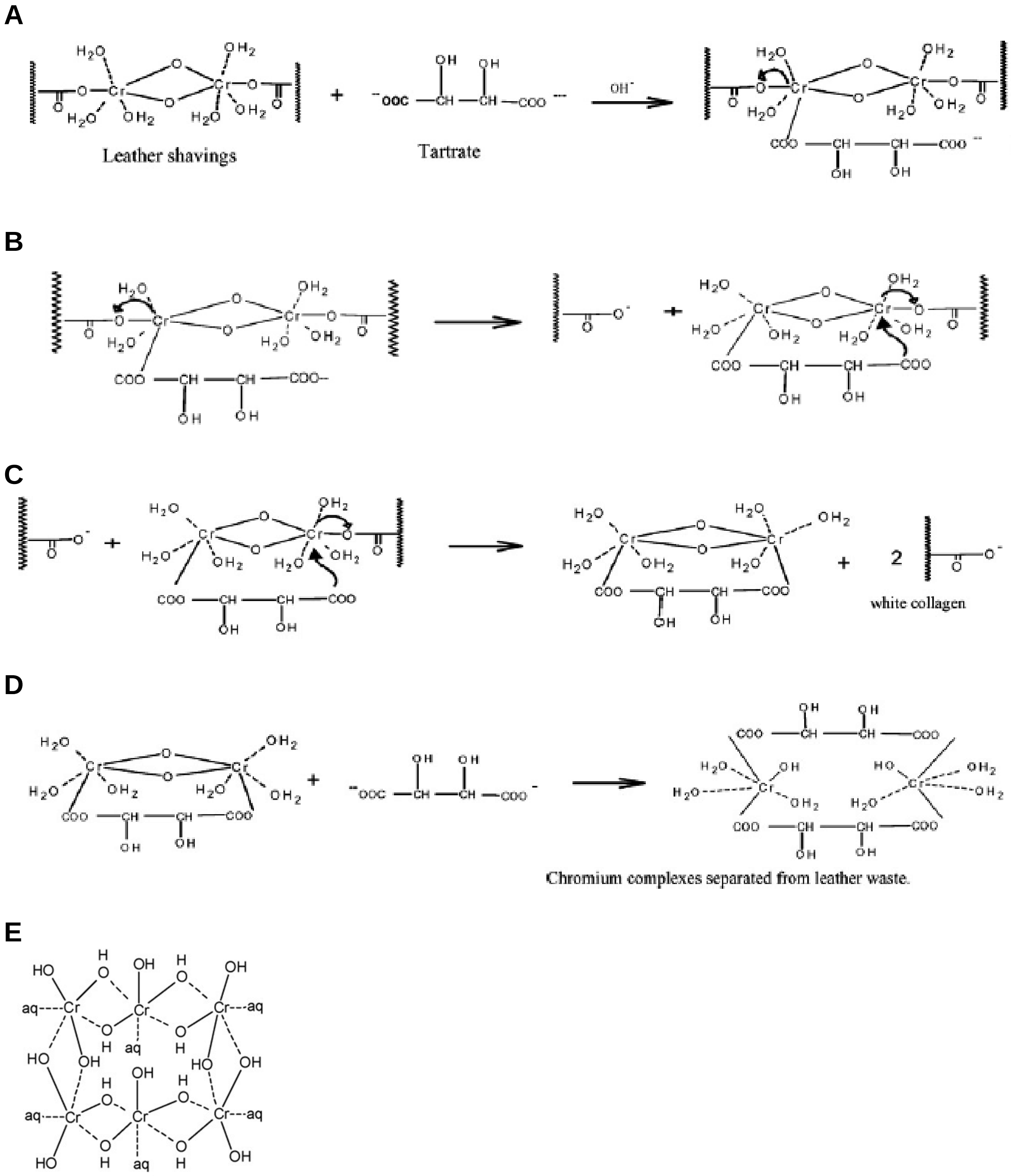
5.5.3 TANNAGE WITH SULPHOCHLORIDES

In this tannage, paraffin sulphochlorides are used. The tanning effect is gained by attachment to the amino group of the collagen. This tannage gives pure white leathers, properties similar to the chamois leather as this tannage is mainly combined with aluminium tanning agents (Gerhard 1996, 89).

5.6 MASKING AGENTS

An approach to lower the chromium output is to increase the efficiency of the tanning process. Optimal reaction of chromium with the treated skin can be achieved by the addition of masking agents. Organic chelates like mono – or polycarboxylic organic salts and acids exhibit high reactivity due to their carboxylic groups. The initial chromium content of about 4.30 % is reduced to 0.24 to 1.1 % using potassium oxalate, potassium tartrate, acetic or citric acid in alkaline milieu. However, organic salts feature higher efficiency compared to the organic acids. Potassium tartrate is the most effective extracting agent removing about 94.3 % chromium from the leather waste (Malek et al. 2009, 158). Extensive research about the influence of pH, organic chelate concentration, reaction temperature and reaction time has been carried out by Malek et al. and can be found in the literature (Malek et al. 2009).

As reported in section 2.3 above, the leather shavings show high stability due to the strong binding between the chromium and the collagen on the one hand, and the formation of strong oxygen bridges which are formed by olation and oxolation on the other hand. The extraction of the toxic chromium requires the destruction of these stable chemical bonds which may be theoretically obtained by the following chemical reactions depicted in GRAPH 2 below. An aqua group from the chromium collagen complex is replaced by one ionized carboxylic group of the tartrate salt (GRAPH 2A) resulting in the elimination of the bond polypeptidic chain of the skin collagen (GRAPH 2B). The other ionized carboxylic group of the tartrate salt interacts with the second chromium atom of the complex and effects the elimination of the second polypeptidic chain of collagen as it is illustrated in GRAPH 2B and C. The generated chromium structure still consists of the strong oxygen bridges which cause high stability of the leather shavings. Protonation of the oxygen atoms using the aqua groups of the chelate complex results in the disruption of the chemical bonds. The exposed oxygen atoms can further react with additional tartrate or interconnect with other chromium tartrate chelate. The final chromium complex which is separated from the leather shavings can be seen in GRAPH 2D, respectively. A second chromium complex 6 $Cr(OH)_3(H_2O)$ which is assumed to be formed is depicted in GRAPH 2E. However, it is less stable due to the high amount of bond hydroxyl groups which make the complex more vulnerable to condensation processes resulting in aggregation and precipitation. The chromium complex which is demonstrated in GRAPH 2D is protected by the tartrate chelate formation and hence, it will not precipitate but it will be extracted in the leather waste treatment.



GRAPH 2. A: Attack of Tartrate on leather sheavings, B: elimination of one polypeptidic chain of the skin collagen, C: elimination of the second polypeptidic chain of the collagen, D: protonation of the oxygen bridges and binding of additional tartrate resulting in a chromium complex separated for the leather shavings, E: second structure of chromium complex which is produced during the leather waste treatment (adapted from Malek et al. 2009, 160-161)

5.7 ULTRASOUND (US) AIDED LEATHER PROCESSING

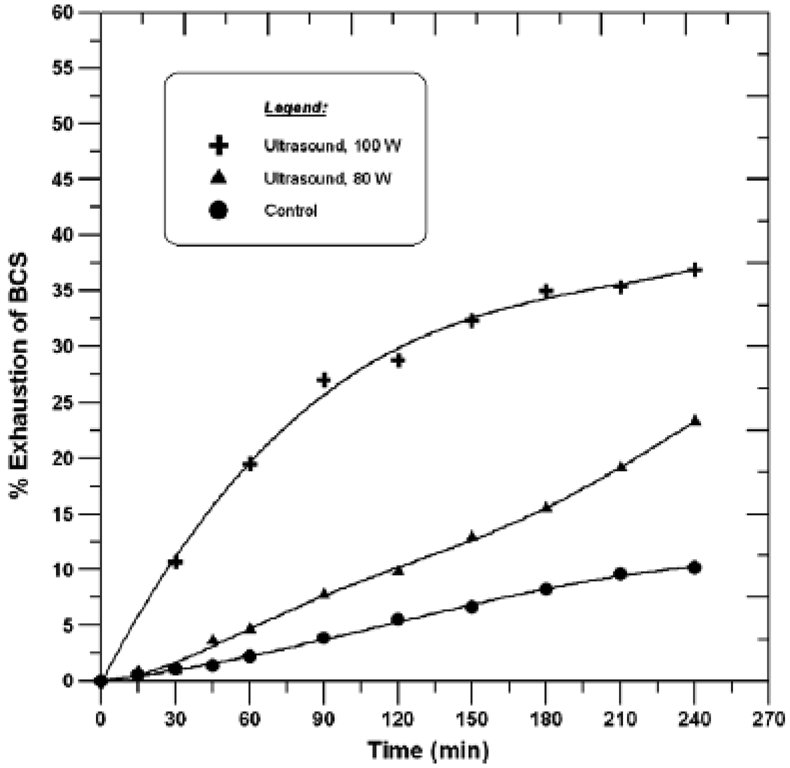
Ultrasound describes an effective tool to improve the efficiency of the conventional process by using sound waves in a frequency higher than16 kHz which affect the chemical substances as well as the treated skin. In addition, the processing time is reduced and leather quality is improved. These properties are further enhanced using power ultrasound with frequencies in a range of 20 kHz to 100kHz (Sivakumar and Rao 2001, 25). US support the conventional leather manufacturing process in order to reduce the environmental impact. It has been reported that the ultrasonic field affects the particle size and particle distribution of the used chemicals. Enhanced penetration through the pores of the leather matrix which range in size from 3 Å to 150 µm (Sivakumar and Rao 2001, 26) is achieved by a decrease in particle size and a uniform distribution of the particles. Furthermore, this results in higher tanning agent uptake which is accompanied by less chemical load in the output waste stream preventing environmental pollution. US also impart better dispersion of the chemicals (Sivakumar et al. 2010, 1055 and 1058).

In chrome tanning process, chrome tanning agent diffuses through the leather pores in order to crosslink with the carboxylic groups of the collagen and stabilize the final leather product physically, chemically and biologically. Applying US improves the diffusion rate of the tanning agent which results in a reduction of the process time and enables the adjustment of chromium sulfate in order to employ just the needed amount for tanning and to avoid the release of excessive tanning agent (Sivakumar and Rao 2001, 28).

US in a frequency range of 80 to 100 W deploys a two to three fold increase in chromium uptake compared to control experiments which can be seen in GRAPH 3 below. The exhaustion of basic chromium sulphate $CrOHSO_4$ (BCS) in percentages is plotted against time in minutes. The chromium amount has been determined experimentally with the spectrophotometry (Sivakumar et al. 2010, 1058). The exhaustion of BCS in respect to time has been calculated using the depicted formula 6.0.

$$Exhaustion\ of\ BCS\ (\%) = \frac{Initial\ BCS\ offered - BCS\ in\ spent\ liquor\ at\ time\ t}{Initial\ BCS\ offered} \times 100 \qquad (6.0)$$

The increase in chromium uptake is referred to be a result of a good dispersed medium and improved diffusion through the leather matrix.



GRAPH 3. Plot of the exhaustion of BCS in % in respect to time t in minutes describing the effect of US on chrome tanning agent (adapted from Sivakumar et al. 2010, 1059).

Previous studies also revealed the beneficial properties of US in the chrome tanning process which resulted in faster operations of olation and oxolation which have been described in section 5.6 (Sivakumar and Rao 2001, 28). Also other leather manufacturing process steps benefit from the deployment of US as it is excessively discussed in the literature (Sivakumar and Rao 2001; Sivakumar et al. 2010). For example, US influences enzymatic aided unhairing processes of the skin in tannery by decreasing the size of the enzyme (Sivakumar et al. 2010, 1058) and supports hair loss at the same time (Sivakumar and Rao 2001, 27). It has a positive effect on the diffusion coefficient of dye diffusion through the collagen matrix of the skin due to stable cavitation as well as on pre-tanning processes which show higher efficiency in terms of cleaning and the creation of fat-in–oil emulsions (Sivakumar et al. 2010, 1055).

5.8 MEMBRANE PROCESSING

Raw or wet-blue skins are transformed into clothes, shoes and other leather goods using diverse chemicals such as acids, alkalis, chromium, salts, tannins and sulfides. Membrane processes offer a possibility to remove the salts as well as organic material using a chemical-physical process. The previous separation of reusable and non-reusable substances facilitates the recycling process and enables a more efficient treatment of the produced sludge which can be used as fertilizer in agriculture (Molinari 1995, 101).

5.8.1 ULTRAFILTRATION (UF)

Ultrafiltration (UF) represents a good preliminary treatment method to remove particles which are larger than 200 to 300 nm in size. 90 % of the solids will be retained while the suspension passes a filter membrane (Cassano et al. 2001, 113). Using UF systems, fluid streams can be released from suspended particles. The produced filter cake further supports the removal of organic material as it accumulates in the sludge. The salt containing permeate could be reused in the pickling and liming step. This method results in lower costs and a reduction of the environmental impact in regard to the ability of recycling the wastewater and avoiding a step in wastewater treatment.

Each kilogram of treated leather requires an input of 0.012 kg of sulfides. 20 % of sulfide is used for the unhairing process and attached to the leather. Hence, the outcoming fluid stream contains about 60 % of sulfides (Cassano et al. 2001, 123). The efficiency of the UF membrane to recover the sulfides is 55 to 60 % whereas 70 % of water can be recycled. Hence, the environmental impact is reduced as the excess liming agent which is retained by the UF membrane can be returned into the process cycle after adjusting the salt concentration. In addition, the raw material input is reduced and the waste-water plants benefit from less contaminated wastewater.

The filter material is of great importance as it influences the substances in the fluid stream. Tubular membranes that are made of carbon fibers retain up to 60 to 85 % of proteic substances whereas non-cellulosic membranes and flat sheet membranes eliminate sulfides by 2% and more than 85% of proteic and colloidal substances is obtained (Cassano et al. 2001, 116).

Regarding the elimination of sulfides, 5 to 10 % of the initial sulfide amount is retained by the filter cake whereas 60 to 65 % is still present in the permeate after passing the membrane filter. As a result, 55 to 60 % of sulfide can be recycled using the UF method. In the degreasing step, Casano demonstrated that the initial fat content in pickled skin could be reduced by 55 %. A traditional dry-degreasing process with tetrachloroethylene shows similar elimination rate. Hence, UF systems are comparable in efficiency to commonly used processes (Cassano et al. 2001, 117). In addition, the loss of water supply is minimized in repeated washing steps to remove the fat from the degreasing fluid stream.

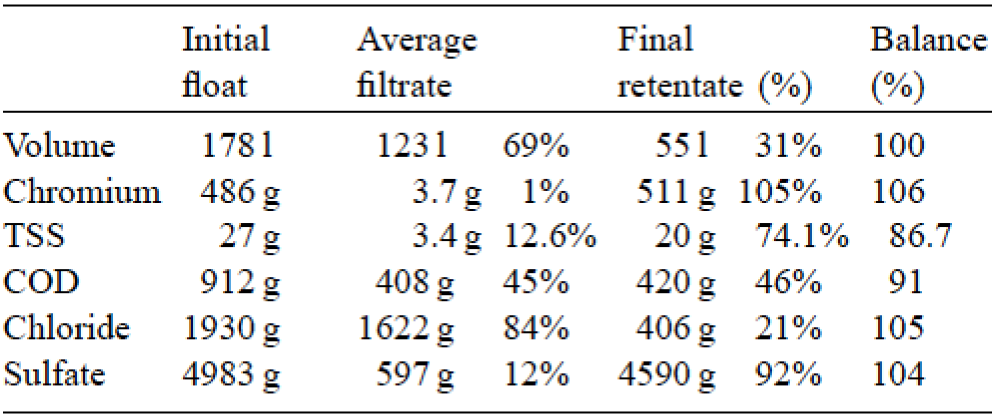
5.8.2 MICROFILTRATION AND CENTRIFUGATION

Microfiltration and centrifugation exhibit other preliminary process techniques to eliminate larger particles from the wastewater. In a recent study by Casano, an effective way of unhairing using an enzyme resulted in a sulfide reduction from 10 % to 1.5 % in terms of dry skin compared to the traditional process. In comparison to the former process, the hair remains in its initial state preventing the formation of hazardous by-products. Using these new innovation techniques, pollution which is caused by sulfide containing wastewater is reduced and hence, it results in environmental protection as well as in safer work conditions for employees. However, as this result is based on a pilot industrial scale, tanners have to adjust their own procedure by testing and evaluating (Casano et al. 2001, 116-123).

5.8.3 NANOFILTRATION (NF)

The recovery of the chromium amount in the outlet stream after the tanning process step requires an efficient process. Experimental tests by Casano et al. illustrated that nanofiltration (NF) is an effective method (99.9 %) in regard to the removal of chromium (Cassano et al. 2001, 118). TABLE 1 shows a material balance of the NF process for some substances.

TABLE 1. Material balance of the NF process (adapted from Cassano et al 2001, 120)

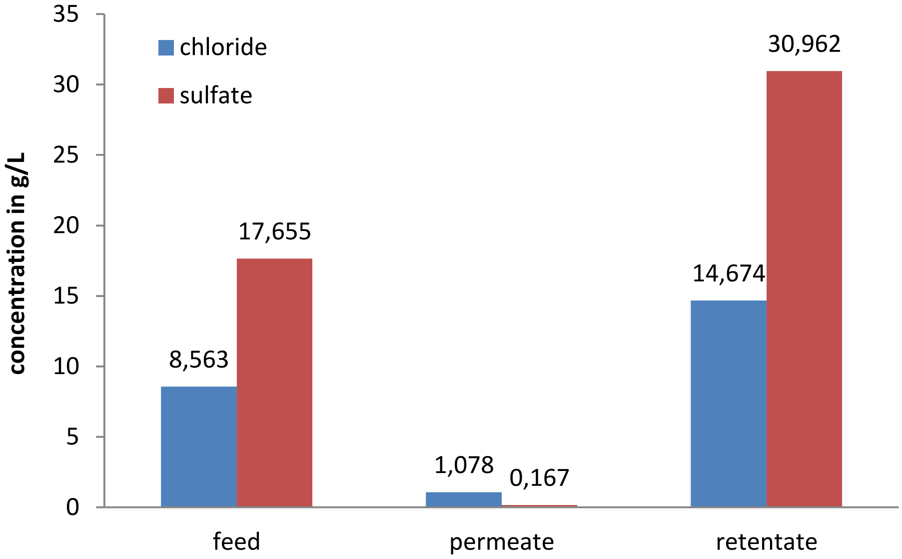


	Initial float	Average filtrate		Final retentate	(%)	Balance (%)
Volume	178 l	123 l	69%	55 l	31%	100
Chromium	486 g	3.7 g	1%	511 g	105%	106
TSS	27 g	3.4 g	12.6%	20 g	74.1%	86.7
COD	912 g	408 g	45%	420 g	46%	91
Chloride	1930 g	1622 g	84%	406 g	21%	105
Sulfate	4983 g	597 g	12%	4590 g	92%	104

In addition, the retained chromium can be returned into the process after additional concentration. The recovered chromium has been observed to be of similar effectiveness in the process than using a fresh chromium solution (Cassano et al. 2001, 120). Furthermore, NF membranes can be applied in vegetable tanning to recycle the used tannins after adjusting the concentration. Tannins which are 300 to 800 Da in molecular weight aggregate and hence, they can be separated from salts (Cassano et al. 2001, 121). The permeate will be sent to a wastewater cleaning plant.

5.9 REVERSE OSMOSIS

The pickling fluid stream features an osmotic pressure of 12 to 15 bar and hence enables the application of reverse osmosis. The salt is concentrated in the retentate and reused in the pickling process after adjusting the salt level. The permeate can be used as washing water or returned into the soaking step. As the recovery of dyeing substances is well established in the textile industry (Cassano et al. 2001, 121) and as the chemical parameters are comparable to the dyeing step in leather manufacturing, reverse osmosis represents an efficient method to separate dyeing agents from the fluid stream.

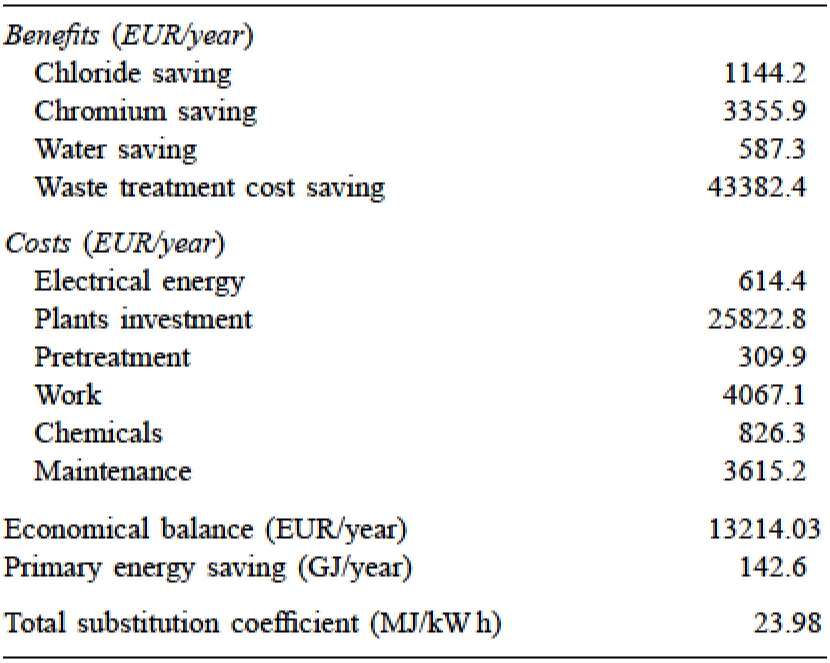


GRAPH 4 Chloride and sulfate concentrations using reverse osmosis (Modified from Cassano et al. 2001, 122)

6. ECONOMIC AND ENERGY ANALYSIS OF THE TANNING PROCESS

Innovative techniques for the chromium tanning process are of economical and energical benefit compared to the commercial process. Analysis carried out by Cassano et al. reported that the energy consumption is reduced by the integration of membrane systems into the tanning process. Cost for energy and investment are lowered. In TABLE 2 the energetic analysis concerning the tanning process is illustrated. It is considered that 1 kWh of electrical energy requires 10.5 MJ of primary energy from combustion. Cassano et al. pointed out that the innovative process with included membrane operations is energetically convenient when the substitution coefficient is greater than 10.5 MJ/ kWh. The calculated factor for the tanning process is 23.98 MJ/ kWh representing an energetically convenient process.

TABLE 2. Energetic analysis for the chromium recovery by integrated membrane operations (adapted from Cassano et al. 2001, 124)



Benefits (EUR/year)	
Chloride saving	1144.2
Chromium saving	3355.9
Water saving	587.3
Waste treatment cost saving	43382.4
Costs (EUR/year)	
Electrical energy	614.4
Plants investment	25822.8
Pretreatment	309.9
Work	4067.1
Chemicals	826.3
Maintenance	3615.2
Economical balance (EUR/year)	13214.03
Primary energy saving (GJ/year)	142.6
Total substitution coefficient (MJ/kW h)	23.98

7. DISCUSSION AND CONCLUSION

Considering the high amount of produced leather waste which contains toxic and polluting chemicals such as chromium, it is of great interest to develop and investigate new methods and alternatives for the commercial tannery to realize environmental protection and sustainable development. In this thesis, the commercial leather manufacturing process as well as new innovations and implements have been discussed which could replace the traditional processing.

Malek et al. developed an innovative tannery solid leather waste process which includes the disruption of the stable chromium collagen bonds using masking agents such as organic salts and acids (Malek et al. 2009). It has been pointed out that potassium tartrate is the most efficient decontamination agent to destroy the chemical bonds and to separate chromium from the leather shavings resulting in an chromium extraction yield of about 95 %. The integration of tartrate treatment inside the commercial treatment process illustrates an efficient way for chromium removal. Since the leather waste is not incinerated, the process is more eco-friendly, more effective in chromium recovery and less power consuming. It is of economic, ecological and energetic benefit and supports the long-term goal of sustainable development.

Reduction of tanning operations should be carried out using new technology and strategies such as membrane processes. Those applications offer new and interesting perspectives for the leather industry to protect the environment and reduce pollution. The integration of UF systems into the leather manufacturing process is of economical, ecological as well as of energetic benefit for the leather industry, the environment and the wastewater treatment plants. The recovery of the used polluting agents and the water in leather processing reduces the raw material input. Hence process input materials are saved leading to raw material cost reduction. Recycling and reuse of the chemicals decreases the output of contaminated wastewater into the environment, protects the eco system and reduces the need of primary resources. In addition, wastewater treatment plants are disencumbered and do not have to cope with environmental problems coming from sludge with high chemical concentration. The resulting simplification of the wastewater treatment process leads to a reduction of the wastewater treatment costs.

Another beneficial option features enzymatic treatment in the unhairing process. The combination with UF systems reduces the chemical concentration in the permeate stream (55 to 60 %) including a partial substitution of the agents (1 % in respect to dry leather weight) by the enzyme (Cassano et al. 2001, 123).

The most significant problem that leather industry has to cope with is the output of hazardous chromium. Since chromium is the most common agent used in the tanning process, the chemical output is high. The released chromium will end up in the sludge of the wastewater treatment process. Hence, it is of importance to establish chromium recovering and recycling systems to gain an economic and ecological benefit. Applications using membrane systems have been described in section 5.8 above and exhibit a possibility of clean chemical operations. Energetic analysis of the chromium tanning process show that innovative processes are convenient as it has been shown in section 6. Their employment would be of benefit for the leather industry as well as for the wastewater treatment plants.

These new techniques exhibit also good applications for the wastewater treatment plants. The integration of these methods into the treatment process of the wastewater would result in the elimination of harmful substances. Cassano et al. reported the set up of a membrane bioreactor which consists of a biological treatment process as well as of an integrated UF system (Cassano et al. 2001, 121). This application enables a refinement, clarification and disinfection step. Dissolved organic material is biologically degraded by microorganisms resulting in the formation of nitrogen, water and carbon dioxide. Suspended substances which are high in molecular weight can be separated from the fluid by UF membrane. Furthermore, reverse osmosis illustrates an efficient possibility for the reduction of salts in the wastewater treatment process as described in section 4 above.

The aim of reducing the chemical output of hazardous polluting chromium has been of great concern for environmental activists and the tanning industry. Tanners try to minimize their chromium output and not to exceed the required maximum values in the output stream taking considerable expenses into account (Krishnamoorthy et al. 2012, 173). However, further research and optimization has to be carried out to ensure proper working systems.

Implementation of ultrasound technologies contributes to environmental protection by making the conventional tanning process more efficient and cleaner. This is attributed to better diffusion rate, dispersion and conversion of the chemical substances obtained by the decrease of the particle size and the generation of a uniform particle distribution. Since the optimal amount of tanning agent is employed in the tanning process, an excess of hazardous chemicals in the effluent is avoided; processing time is shortened due to increased diffusion rate through the skin pores and easier quality control management can be applied in regard to the manufacturing of high quality leather (Sivakumar and Rao 2001, 25-26). Additionally, performance of the US tool is effective in numerous steps of the leather manufacturing process e.g. dirt removal from the untreated skin and hair loss of the hides during the soaking step as well as emulsification of the fats which are naturally present in the skin during the degreasing process (Sivakumar and Rao 2001). As US technology is already successfully applied in textile, chemical and polymers, it may become an effective, beneficial tool in leather tannery (Sivakumar and Rao 2001, 30-31). It is of economic and environmental benefit as it contributes to the development of a cleaner process by reducing the pollution load in the output stream and the chemical material input for processing.

Another discussion that has arisen within the last years exhibits the complete replacement of hazardous chemicals by nontoxic substances. Green chemistry describes an approach to clean and environmental friendly leather manufacturing and it benefits the environment as well as the tanning industry. Conventional tanning processes which release toxic and polluting substances into the environment are replaced by cleaner production. It includes a chrome free, non toxic tanning process which generates nontoxic and simple disposable effluents and feature more efficient reaction processes to gain higher tanning agent conversion and physical, chemical and biological stability. The realization of a toxic, hazardous and polluting free tanning process by using and establishing technical environmental friendly innovations is setting the fundaments for a sustainable growth.

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