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Recovery of Chromic Oxide from
Leather Chrome Shavings
استرجاع اكسيد الكروم من حلاقة الجلود بالكروم

A thesis
Submitted in fulfillment for the requirements of PhD degree in
leatherengineering

By

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2013

بسم الله الرحمن الرحيم

﴿ وَٱللَّهُ جَعَلَ لَكُم مِّنۢ بُيُوتِكُمْ سَكَنًا وَجَعَلَ لَكُم مِّن جُلُودِ ٱلْأَنْعَٰمِ بُيُوتًا تَسْتَخِفُّونَهَا يَوْمَ ظَعْنِكُمْ وَيَوْمَ إِقَامَتِكُمْ وَمِنْ أَصْوَافِهَا وَأَوْبَارِهَا وَأَشْعَارِهَآ أَثَٰثًا وَمَتَٰعًا إِلَىٰ حِينٍ ۝ ﴾

صدق الله العظيم

سورة النحل : الآية ۝

Dedication

This research is dedicated to the sole of my father

Mother

Brother

Sisters

And

My husband

Acknowledgment

Abstract

A chrome shaving is a process by which the pelt thickness is adjusted according to its utilization purposes.   This chrome shavings which constitute 2.5−5.0 % chromium are mainly disposed at the outside the premises of the tannery and left to dry, posing a hazardous environment. When the chrome shavings are dried, they would be taken by brick - makers and burnt out, a process which will transform chromium III to chromium VI. Chromium VI is 500 times toxic than chromium III and most harmful pollutants in tannery waste. Chromium VI also affects soil quality, more dangerous and carcinogenic. Therefore recovery of chromium VI is very essential. In this study chrome shavings was incinerated at 1000 $^\circ$C to transform chromium III to chromium VI. Leaching of chromium VI in the form of dichromate was carried out in a series of 6 batteries and statistically investigated at different levels of solid/solvent ratios, temperatures, degree of mixing and time. Further evaporation was done in a water bath to raise up the concentration from 40% to 90%. From the statistical analysis it is determined that only the degree of mixing at 200rpm is significant, and other factors are fixed at their low levels, temperature of 37 ºC, time of 1 hour and solid/solvent ratio of 1:10. The leachability was found to be 95%. The hexavalent chromium was reduced to basic chromium sulphate. The basic chromium sulphate obtained was of 33% basicity and 21% chromic oxide with conversion of 96.80%. Experiments on the reaction kinetics were performed to determine the reaction order, the reaction rate and conversion. These were found to be first-order reaction and 100% conversion after ageing the chrome liquor for two weeks. Complete reduction was achieved in three hours with pH of 2.5. A chrome tanning trials were performed using pickled sheep skins. The pelts passed the boiling test indicating that the tannage was completed, and then the pelts

were neutralized, retanned, fat-liquored and left overnight. The dried pelts were conditioned and the crusts produced were subjected to chemical and physical analysis, with chromic oxide 4.4%, moisture content 14%, ash content 4.6%, shrinkage temperature 100 ºC, fat content 3.4% , tensile strength 171kg/cm^2, elongation at break 49% , tear strength 100kg/cm, and load at grain burst 40 kg. The quality of the leather produced using chromium sulphate liquor extracted from chrome shavings was satisfactory with excellent properties.

المستخلص

عملية حلاقة الجلود هي العملية التى يتم بها ضبط سمك الجلد بما يتناسب مع اغراض الاستعمال. هذا الجزء المحلوق يحتوي علي % 2.5-5 من ملح الكروم القاعدي وعادة يتم التخلص منه بوضعه في فناء المدبغة حتي يجف ثم يؤخذ بواسطة اصحاب الكمائن لاستعماله في حرق الطوب , هذه العملية تؤدي الي اكسدة الكروم من الكروم الثلاثي الي الكروم السداسي الذى يتميز بسميته العالية حيث تعادل سميته 500 مرة من سمية الكروم الثلاثي ويتسبب في الاصابة بمرض السرطان بالاضافة لاضراره بالبيئة. في هذه الدراسة تم حرق هذا الجزء المحلوق في درجة حرارة 1000 درجة مئوية لتحويل الكروم من تركيبته الثلاثية الي السداسية ومن ثم استخلاص الكروم السداسي علي شكل صوديوم دايكروميت في سلسلة استخلاص تتكون من ستة وحدات. بعد عملية الاستخلاص تم تركيز المحلول من 40% الي 90% باستعمال حمام مائي . تم تحليل العوامل المؤثرة في عملية الاستخلاص احصائيا وهى درجة الحرارة و الزمن و نسبة المادة الصلبة للسائل و الخلط . ووجد ان عامل الخلط عند 200 دورة في الدقيقة هو العامل الاكثر تاثيرا علي عملية الاستخلاص اما العوامل الاخري فكانت اقل تاثيرا وتم تطبيقها في قيمها الاقل وهي درجة الحرارة 37 درجة مئوية و الزمن ساعة و نسبة المادة الصلبة للسائل 1:10 حيث كانت نسبة الاستخلاص 95%. محلول الكروم السداسى تم اختزاله الي محلول كبريتات الكروم القاعدي. و وجد ان نسبة القاعدية فى كبريتات الكروم القاعدي 33% ونسبة اوكسيد الكروم 21% ونسبة الاختزال 96.8 % تصل الي 100% بعد ترك المحلول لمدة 15 يوما .تكتمل عملية الاختزال خلال 3 ساعات في وسط حمضي عند الاس الهيدروجيني 2.5 . كبريتات الكروم القاعدية المتحصل عليها بو اسطة الاختزال تم استعماله في دباغة جلود محنطة. تم احضاع الجلود المدبوغة الي التحاليل الكيميائية و الفيزيائية حيث كانت النتائج مطابقة للمواصفات وهي محتوي الكروم 4.4%, محتوي الرطوبة 14% , محتوي الرماد 4.6 % ,محتوي الدهون 3.4% و درجة الانكماش 100%. قوة شد الجلد 171 كجم/سم^2 , الاستطالة 49 %, الحمل عند ثقب الجلد 40كجم و قوة التمزق 100كجم/ سم, وقد كانت نوعية الجلود المدبوغة بمادة الكروم القاعدي المتحصل عليه من الحلاقة جيدة وذات خواص ممتازة.

Table of contents

Chapter four

Chapter Five

List of tables

List of figures

Chapter One

Introduction

1.Introduction

1.1 Leather Industry

Leather industry, which is one of the oldest industries in the human history, plays a significant role in today's global economy, leather process transform animal hides/skins into a physically and chemically stable material. By subjecting hides/skins to chemical and mechanical sequential processes, therefore production product to meet various needs of people. The major process of the tanning industry is chrome tanning in which the raw hides and skins are transferred into leather characterized by top handling quality, high hydro-thermal stability and excellent properties[1].

Currently more than 90% of global leather production is produced through chrome tannage, the majority of the shoe uppers are tanned with chromium compound. Leather manufacture is steadily increasing the use of chromium compounds in the manufactures of various types of leathers such as garment, clothing, gloving, bags, textile and furniture [2]

Leather industry has been categorized as one of the high polluting industries and concerns that leather making activity can have adverse impact on the environment [3].

The global production of about 24 million m^2 of leather by 2005 presents a considerable challenge to the industry considering the harmful nature of some of the chemicals used in leather processing. The leather industry is responsible for a large generation of chrome waste during tanning processes. Solid wastes generated from tanning industries contain different chemicals which are used during leather manufacturing process. These tannery solid wastes have different characteristics as different chemicals and mechanical processes are applied to the raw hides/skins. If these solid waste generated during various tanning operations are not properly utilized

or disposed they are likely to cause a number of problems on the environment.

Tanneries produce a great variety of waste, in particular, the solid waste coming from the leather tanning with trivalent chromium salts as trims and shavings. These need special treatment due to environmental regulations and the controlling laws requirements for those wastes. One tone of raw wet hides produces 200 kg of leather but produces over 600 kg of solid waste or by-product. It has been stated that about 600,000 tones of solid waste are generated each year worldwide by the leather industry, this means that approximately 40-50% of hide substance are lost due to shavings and trimmings [4].

The data obtained from FAO reveals that approximately 8.5 million tons of solid waste is generated during the production of 11 million tons of rawhide processed in the world which is in agreement with the fact stated that 60% of solid waste is generated [5].

During chrome tanning process 75-80% of chromium sulphate absorbs into pelts. Up to 33% of chromium is used for tanning by typical tannery is lost in the solid waste in shavings and trimmings [6].

The waste containing chromium are classified as class one hazardous waste , and chromium six is found to be the third most common pollutant hazardous waste [7], therefore they need treatment before disposal. Contamination of soil and groundwater due to chromium six is one of the significant environmental problems to date.

A chrome shaving constitutes 75% of the solid waste containing chromium in the tanning process, beside the 30-35m3 waste water disposed to the environment during the processing of every one ton of raw hides in world leather industry.

Leather production is one of the oldest manufacturing in Sudan, and at its beginning plants and herbs were used in tanning and it evolved over the

centuries with the increasing needs of man and development, and access to modern techniques of leather production. Production of leather is one of the oldest craft in Sudan where processed leather exports from the country, including soft tanned and mummified leather, constitute about 50% of the exports of cattle's rawhide and more than 95% of sheep and goats' rawhide.

Sudan is one of the richest Arab and African countries in animal wealth. Sudan's animal wealth is estimated at 103 million head of livestock, including 30 million head of cattle, 37 million of sheep, 33 million goats and 0.3 million of camels.

The production of rawhide in the country amounts to about 22 million pieces per year of cattle, sheep and goats rawhide. Sudan has exported about 7 million pieces during the current fiscal. The country is characterized by large investments in the areas of tanneries and leather products, where 18 tanneries, large and small, were established in addition to many others under-construction, beside 30 tanneries complex in rural Sudan and 6 large, 6 medium and small factories in addition to 25 large, 250 medium and 350 small workshops for shoe making. Rawhide is assuming economic importance in the sector of exports in Sudan, where it currently brings earnings of $35million annually, as part of the country's plan to generate alternatives to oil exports which, with the separation of the south, are lose some of (36.5%).

Different methods are used for recovery of chromium, including solvent extraction, precipitation, ion exchange and liquid membranes.

The objective of this study is to transform chromium III to chromium VI as a raw material for reduction to basic chromium sulfate, to specify the conditions for optimum leaching of chromium VI and to adjust the basicity of basic chromium sulfate to 33% basicity rendering it suitable for chrome tannage.

Basic chromium sulphate liquor which was reduced from sodium dichromate was used for tanning pickled sheep skin pelts. The chrome tanned pelts were retanned, dried and made into crust. The crust was subjected to chemical and physical analysis.

1.2 Objectives of the study

1- Extraction of chromium VI from chrome shavings.

2- Reduction of hexavalent chromium to basic chromium sulphate from chrome shavings.

3- Application of basic chromium sulphate obtained for tannage of pickled pelts.

4- Protection of the environment from toxic and carcinogenic chromium VI.

Chapter two

Literature review

2. Literature review

2.1 Tanning

Raw hides and skins are transformed into stable finished products by series of chemical and mechanical processes, among these processes tanning is very important. Tanning means the conversion of raw skin into finished leather through technical processes. The collagen proteins will deform when heated, and in water they will turn into gelatin. Thus tanning is an essential process of the conversion of the collagen in a natural skins and hides into stable form, giving the material individual durability by allowing penetration of various tanning agent with different characteristic the structure through mechanical action in floats, and by reaction with reactive groups of collagens. Thus tanning is the main process that protects leather against some environmental effects such as microbial degradation, heat, sweat or moisture [8].

Tanning involves a complex combination of mechanical and chemical processes. The heart of the process is the tanning operation itself in which organic or inorganic materials become chemically bound to the protein structure of the hide and preserve it from deterioration. The substances generally used to accomplish the tanning process are chromium or extracts from bark of trees, such as chestnut. These tanning agents give rise to the two predominant types of tanning operations - chrome and vegetable tanning.

There is a vast array of tanning methods and materials and the choice depends chiefly on the properties required in the finished leather, the cost of alternative materials, the plant available, and the type of raw material [9].

Hides and skins have the ability to absorb tanning acid and other chemical substances that prevent them from decaying, make them resistant to wetting and keep them supple and durable [10].

The conversion from raw hides into leather comprises many steps. The major processes are curing, soaking, fleshing, hair removal, scudding, deliming, tanning, dyeing, and finishing [11].

2.2 Beam-house Operations

2.2.1 Soaking

Tanneries often receive salted rawhides and skins, which must be cleaned and rehydrated through soaking, or by placing the skins or hides in water, usually in paddles or drums. Dirt, blood and dung are also removed in the process. Chemicals used in soaking are 0.2 – 2.0 grams per liter sodium hydroxide, up to 1 gram per liter sodium hypochlorite and/or 0.5 – 2.0 per cent wetting agents, emulsifiers, surfactants etc. The soak bath is often changed every 8 hours to prevent bacterial growth [12].

2.2.2 Liming and unhairing

 The hide is treated with a solution of lime and sodium sulphide or sodium hydrogen sulphide to remove hair and loosen the hide structure. Unhairing is normally carried out by dissolving in a chemical solution. Chemicals generally used are 2-10 per cent calcium hydroxide (lime), 1-4 per cent sodium sulphide or sodium hydrogen sulphide. Some caustic soda may also be used. Enzymatic preparations have been increasingly used in the last years [12].

2.2.3 Fleshing and deliming

Fleshing is the mechanical scraping of adhering connective tissue, fat etc, from the flesh side. On the other hand, deliming solubilizes the absorbed calcium hydroxide and brings the skin to the desired pH, mainly to avoid interference with the subsequent tanning stage. The process is carried out by washing and by using water combined with neutralizing chemicals. Chemicals used are ammonium chloride or sulphate, 0.5– 2.0 per cent acids (lactic, formic, boric and mixtures), acidic salts, sodium bisulphite, hydrogen peroxide. The use of gaseous CO_2 instead of ammonium salts has been increasing [12].

2.2.4 Bating

Bating treats the hides with proteolytic enzymes to purify the material prior to tanning. It loosens the hide structure and removes unwanted proteins, and is often carried out in the deliming liquor. The chemical used is often a 0.5 per cent bating material, which consists of 50 per cent wood flour (or another carrier), 30 per cent deliming agent (ammonium chloride) and 1-5 per cent pancreatic enzyme [12].

2.2.5 Degreasing

Degreasing is the process of removing fats from the skin. This is especially important in sheepskin tanneries as the fat content of their raw material is large.

The process uses solvent degreasing. Solvents, which are increasingly substituted or combined with surfactants and/or enzymes, include perchloroethylene, monochlorobenzene and kerosene [12].

2.2.6 Pickling

Pickling increases the acidity of the hide to a pH value of 3 by addition of acid liquor and salts, enabling chromium tannins to enter the hide. Salts are added to prevent the hide from swelling. For preservation purposes, 0.03-2% by weight of fungicides and bactericides are usually applied [12].

2.2.7 Tanning Processes

The production of leather depends on the generation of complexes between the tanning agent and the skin collagen. The stability of the leather can be ascribed to the strong chemical bonding between the collagen fibers of the skin ridge and the tanning agent. Collagen fibers consist of proteins and have different binding sites available.

The binding sites used differ depending on the respective tanning agent (mineral, vegetable and synthetic tanning agent). The different binding sites are shown in figure (2.1).
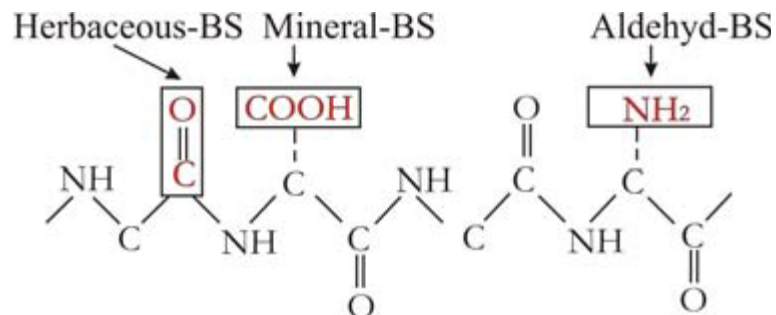
Fig (2.1): Collagen fibers with different binding sites.

The carboxyl groups are the important binding sites for the mineral tanning agents (like chrome) [13]. These binding sites have to be prepared for the tanning step and the collagen has to be activated. This is achieved by a pickle-solution right before the tanning takes place. During the pickle process hair and epidermis are removed from the hide at a pH-value of 2.5.

Proteins are hydrolyzed and washed out. Collagen fibers gain more space and therefore the leather is gaining softness. Due to the low pH-value the collagen starts to swell. The swelling is limited and kind of controlled via buffering salts.

The basis for the tanning solution is the pickle-solution. For a good tanning the pH-value has to be raised to 4. At a pH of 2.5 only some carboxyl groups of the skin collagen are ionized [14]. By raising the pH-value to 4 a maximum binding of chrome and collagen can be reached. Under these conditions 3.8 wt.-% chrome in skin can be reached. Experimentally it was found, that at least 3 wt.-% of chrome have to bind into the skin for producing leather of good quality [15]. The binding of chrome and carboxyl groups generates chrome complexes under formation of water and sulphuric acid. The mechanism is shown in figure (2.2).

$$Cr_2(OH)_2SO_4 + 2R-C\overset{O}{\underset{OH}{\diagup}} \Rightarrow R-C\overset{O}{\underset{Cr_2O_3}{\diagup}}\overset{O}{\diagup}C-R + H_2O + H_2SO_4$$
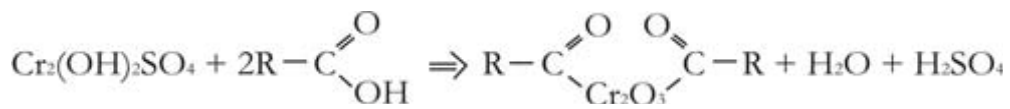
Fig (2.2): The binding of chrome and carboxyl group.

The tanning is carried out in rotating tanning drums. Conventional tanning takes approximately 24 to 35 hours. The products of chrome tanning are called "wet blue" because of their blue color. Tanning is a major step but until finally "leather" is generated, some more finishing and fattening steps are required [16].

2.3 Chrome tanning

Chrome tanning occupies an outstanding position in the tanning industry since its introduction in 1884 by Knapp. 90% of tanning processes use basic chromium sulphate for tanning. Basic chromium sulphate as tanning

material is frequently criticized by the researchers as it causes pollution and suffers with toxicological problems [4].

Chrome-tanned leather tends to be softer and more pliable than vegetable-tanned leather, has higher thermal stability, is very stable in water, and takes less time to produce than vegetable-tanned leather. Almost all leather made from lighter-weight cattle hides and from the skin of sheep, lambs, goats, and pigs is chrome tanned [17].

Chrome is the most used type of tanning materials and widely used over the world. Chrome tanned leathers are characterized by top handling quality, high hydro-thermal stability and excellent properties,   light weight and high tensile strength [18]

Chrome tan cross-links with polypeptide chains by principle valences through coordination bonds with the acidic amino acid side chains of the collagen. The cross-links induce physical and mechanical properties that give the chrome tanned leathers its high quality. Although, there are some disadvantages of chrome tanned leather such as lack of fullness and course nap especially in suede leather. Chrome tannage is still the most widely used method in the tanning industry [19].

Now a day the use of chromium has accelerated in the leather industry as it is enables faster and cheaper production of highly resistance and durable leathers. Today more than 80% of finished goods are tanned using basic chromium sulphate. However high pH value, temperature, UV lights, unsuitable storage conditions and the effect of using lubricants with double bonds in the molecule during production possibly run up the oxidation of the trivalent chromium into the hexavalent form.

After pickling, when the pH value is low, chromium (III) salts are added. To fixate the chromium, the pH is slowly increased through addition of a base. The process of chromium tanning is based on the cross- linkage of

chromium ions with free carboxyl groups in the collagen. It makes the hide resistant to bacteria and high temperature [8].

2.4 Vegetable tanning

Vegetable tanning agent is considered the "green tanning agent" because of its biodegradation, vegetable tanned leather has excellent fullness, moldering properties, wear resistance, air permeability and solidness; hence, it is of great significance to reduce chrome pollution in leather making process. Vegetable tanned leather is used in making heavy leather such as furniture leather, garment leather and shoe upper leather. Worldwide, researchers are paying particular attention to the use of vegetable tanning agents to replace chrome tanning agent and progress has already been achieved. Some plants are preferred for tanning over others due to the level of their tannin content. Tannin is found in various plants' parts such as tree barks, wood, fruits, pods, leaves, roots, tubers and many other plant parts, indicating that different plant parts are used in tanning [20].

2.5 Alternative tanning

Tanning with organic tanning agents, using polymers or condensed plant polyphenols with aldehydic cross- linkers, can produce mineral free leather with high hydrothermal stability similar to chrome- tanned leather. However, organic- tanned leather usually is more full and hydrophilic than chrome- free leather, with equally high hydrothermal stability. This tanning process is carried out with a combination of metal salts, preferable but not exclusively aluminum (III), and a plant polyphenol containing pyrogallol groups, often in the form of hydrolysable tannins [12].

2.6 Shavings

Shaving process is to adjust the thickness to make the wet blue pelts ready for retannage and the following processes. Shaving is carried out by a shaving machine taking off about 20% of the wet- blue pelt weight from the flesh side [21-22].

The quality of finished leather depends to a great extent on the degree of uniformity in shavings. Shaving is undertaken to achieve an even thickness throughout tanned or crusted leather. Shaving is carried out when splitting is not possible or when minor adjustments to the thickness are required. If the thickness of the leather is not uniform throughout the area, the mechanical effects like glazing, staking, ironing, pressing etc., will be un-uniform on the leather surface and the total absorption of season by different portions of the leather surface will be different [23].

2.7 Solid wastes

Tanneries produce a great variety of waste, in particular, the solid waste coming from the leather tanning with trivalent chromium salts as trims and shavings. These need special treatment due to environmental regulations and the controlling laws requirements for those wastes [24] . Large quantities of solid wastes are also generated during leather processing and subsequently during effluent treatment. Although some of the wastes find limited applications, the safe disposal of the bulk of the solid wastes has posed serious problems. Out of which some portion of chromium containing hazardous wastes are also generated. These chrome containing wastes are categorized as hazardous wastes. The main sources of solid wastes are from trimming, fleshing, splitting and shaving processes. The tanned waste contains up to 4.5% of chromium, it can oxidized to

chromium VI which is toxic and carcinogenic. About 3o tons of chromium tannery waste is generated worldwide per year.

The reuse of chromium from tannery waste could help save energy and financial expenditure for chromium ore processing as the energy produced from the combustion may be recovered and used[25] .A further potential source of solid waste is the sludge from the effluent treatment plant. The solid waste generation from tannery process in the world is estimated at 6 million tons per year. At an average 80% of solid waste is generated from tanning industry per ton of raw hide processed. The types of solid wastes generated in a tannery processing one ton of raw skins/hides have been quantified in Table 2.1[22].

Table (2.1): Nature and Quantity of Solid Wastes Produced from Processing

one Ton of Raw Skins/Hides [22] .

S.N	Nature of solid waste	Quantity Kg
1	Salt from handshaking	80
2	2 Salt from solar pans (not realized)	220
3	Hair (pasting ovine)	100
4	Raw trimmings	40
5	Lime sludge (mostly bovine)	60
6	Fleshing	120
7	Wet blue trimmings (grain splits)	30
8	Chrome splitting	65
9	Chrome shaving	95
10	Buffing dust (including shaving bovine after crust)	65
11	Dyed trimmings	35
12	Dry sludge from ETP	125

2.7.1 Suspended Solids

The suspended solids components of an effluent are defined as a quantity of insoluble matter contained in the wastewater. These insoluble material cause a variety of problems when discharge from a site; essentially, they are made up of solids with two different characteristics [12].

2.7.2 Solids with a Rapid Settling Rate (Settleable Solids)

Settle-able solids comprise material that can be seen in suspension when an effluent sample is shaken, but settle when the sample is left to stand. The majority of these solids settle within 5 to 10 minutes, although some fine solids require more than an hour to settle.

These solids originate from all stages of leather making; they comprise fine leather particles, residues from various chemical discharges and reagents from different waste liquors. Large volumes are generated during beam-house processes.

If the waste waters are to be treated in sewage works or undergo traditional effluent treatment, the main problems that arise are due to the large volume of sludge that forms as the solids settle. Sludge often contains up to 97 % water, giving rise to huge quantities of 'light' sludge. Even viscous sludge has a water content of around 93 %, and can easily block sumps, sludge pumps and pipes. All this sludge has to be removed, transported, dewatered, dried and deposited, thus placing an inordinate strain on plant, equipment and resources. If the wastewater is to be discharged into surface water, the rate of flow will determine the distance the material is carried before settling on the stream or river bed. Even thin layer of settled sludge can form a blanket that deprives section of the river or lake bed of oxygen. Plant and aquatic life dies and decomposition set in [12].

2.7.3 Semi- Colloidal Solids

Semi- colloidal solids are very fine solids that, for all practical purposes, will not settle out from an effluent sample, even after being left to stand for a considerable period of time. They can, however, be filtered from solution. Together with the more readily settleable solids, they thus comprise the suspended solids of an effluent that can be measured analytically.

Most of these solids are protein residues from the beam-house operations mainly liming processes; however, large quantities are also produced owing to poor uptake in vegetable tanning processes, another source being poor uptake during retanning.

Semi- colloidal solids will not directly cause a sludge problem. They can be broken down over an extended period by bacterial digestion and they produce solids, which will eventually settle [12].

2.7.4 Settleable Solids

Although suspended solids analysis is the method most commonly used to assess insoluble matter, analysis of the settleable solids content is sometimes required. The settleable solids content is determined by leaving the shaken sample to settle and then filtering a known volume of the semi-colloidal matter remaining in suspension. After drying and weighing, the quantity of semicolloidal matter can be calculated [12].

2.7.5 Gross Solids

Gross solids are large than a sampling machine can handle, hence they are not measured. Their presence, however, is clear to see and the dangers they pose are fully recognized.

The waste components that give rise to this problem are often large pieces of leather cuttings, trimmings and gross shavings, fleshing residues, solid hair debris and remnants of paper bags. They can be easily removed by

means of coarse bar screens set in the wastewater flow. If, however, they emerge from the factory, they settle out very rapidly [12].

2.8 Characteristics of Tannery Solid Wastes

The chemical composition of solid wastes generated from beam-house operations (fleshing, trimmings, and splits) depends mainly on a kind and quality of the raw material, treatment type and process conditions. The main components are proteins and fat, up to 10.5% (w/w) for both groups. Water content is high, moisture amounts up to 60%. These wastes contain small amounts of mineral substances, 2-6% (w/w). Chromium compounds are not present in the material.

The tanned leather wastes are mainly useless splits, shavings and trimmings. These waste groups differ mostly in size and shape, the chemical composition is comparable for each.

They contain 3-6% (w/w) of fat and about 15% (w/w) of mineral components, including 3.5- 4.5% (w/w) of chromium as Cr_2O_3. Sludge from wastewater treatment plants contains mostly water (up to 65% (w/w)), organic substances (30% (w/w)) and chromium (III) compounds (about 2.5% (w/w) [26].

2.9 Environmental Impacts of Tannery Solid Wastes

Solid wastes generated from tanning industries contain different chemicals which are used during leather manufacturing process. These tannery solid wastes have different characteristics as different chemical and mechanical processes are applied to the raw hides/skins. If these solid waste generated during various tanning operations are not properly utilized or disposed they are likely to cause a number of problems on the environment. Salt dust or de-dusted salt if stored in heaps outside the tanneries or dumped in open dumping area is likely to be washed away during rains and cause

groundwater pollution. Hair waste and lime sludge if discharged along with the effluents are likely to choke the drains. Raw and green fleshing, limed fleshing, splits (splitting waste) and trimmings putrefy easily and give rise to noxious smells. In many tanneries, it is the foul odour which emanate from some of these putrescible solid wastes which accounts for much of the smell traditionally associated with tannery wastes. Some of the bio-degradable tannery solid wastes are sources of pathogenic bacteria and volatile organic compounds emission. Vegetable and chrome tanned shavings and splits do not easily decompose. If they are not utilized, problems of disposal are encountered. Primary and secondary sludge obtained during the treatment of tannery wastes are also putrescible

Excess heavy metal accumulation in soil is toxic to humans and other animals. Exposure to heavy metals is normally chronic (exposure over a longer period of time), due to food chain transfer. Acute (immediate) poisoning from heavy metals is rare through ingestion or dermal contact, but is possible. Some of tannery solid waste contains chromium metal which is the most widely used in tanning industries as chromium salt and it causes carcinogenic effect when it enters human body through food chain. The standard safe limit for chromium metal in the soil is 150ppm.

In general where tanning industries have long been established there has been usually a simultaneous growth in industries which can use tannery solid wastes to produce some valuable products. This pattern is especially helpful to the tanning industry in the case of obnoxious rag and limed fleshings, trimmings and splits which are lifted by glue and gelatin units.

When solid waste is disposed off on land in open dumps or in improperly designed landfills (e.g. in low lying areas), it causes the following impact on the environment [26].

1. Ground Water Contamination by the Leachate Generated by the Waste Dump

2. Surface Water Contamination by the Run-off from the Waste Dump

3. Bad odour, Pests, Rodents and Wind-Blown Litter in and Around the Waste Dump

4. Generation of Inflammable Gas (e.g. Methane) Within the Waste Dump

5. Bird Menace above the Waste Dump Which Affects Flight of Aircraft

6. Fires within the Waste Dump

7. Erosion and Stability Problems Relating to Slopes of the Waste Dump

8. Epidemics through Stray Animals

9. Acidity to Surrounding Soil And

10. Release of Green House Gas

2.10 Solid Waste Management

Solid waste management is the collection, transportation, storage, recycling or disposal of solid waste, or the subsequent use of a disposal site that is no longer operational. It is a complex process because it involves many technologies and disciplines. These include technologies associated with the generation (including source reduction), on-site handling and storage, collection, transfer and transportation, processing, and disposal of solid wastes.

All of these processes have to be carried out within existing legal, social, and environmental guidelines that protect the public health and the environment and are aesthetically and economically acceptable. The objective of solid waste management is to reduce the quantity of solid waste disposed off on land by recovery of materials and energy from solid waste [26].

2.11 Chrome recovery

The environmental impact produced by the chromium discharge from tanneries has been subject of extensive scientific and technical dispute, without the existence of a unique criterion at the present time for fixing regulatory limits. Thus, different countries of the world have established total chromium maximum values that vary between 0.05-10 mg /L for discharges into water (direct discharge) and 1-50 mg/ L for discharge into sewage systems (indirect discharge). Besides the place in which the discharge of liquid effluents containing chromium is made, that is considering of the metal oxidation state. Although chromium III oxidation to chromium VI occurs under environmental specific conditions special attention is devoted to this transformation because chromium VI causes adverse effects for the human health. Even when the tanning wastewater has chromium only in trivalent form since the tannage process does not generate chromium VI, some countries fixed regulatory limits for the two species.

This criterion appears from the assumption that the oxidation would be produced during storage and subsequent treatment of the liquid effluent to reduce its total chromium content [27].

In recent years, there have been reports that hexavalent chromium can be detected in leathers. While tanning process uses only chromium III, the presence of chromium VI is due to utilizing processing conditions which oxidize chromium III to chromium VI [28].

The chrome tanning is done by adding Basic Chromium Sulphate in pickle bath. In the chrome tanning, about 100% water on the basis of pelt weight, 6% to 8% BCS and 2% Sulphuric acid are added. After chrome tanning, exhaust liquor is discharged as waste. This liquor contains about 30-40% of the chrome.

The chromium in the effluent may be reduced in several ways:

(1) improved chromium uptake/exhaustion.

(2) Chromium reuse.

(3) Wet white pretanning.

(4) Chromium substitution .

(a) High chrome exhaustion techniques

Several commercial systems for high-exhaustion tanning exist. Chrome fixation during tannage is favoured by the following: (1) short float;

(2) increased temperature;

(3) Increased time of tanning; (4) increased basification; and (5) decrease in neutral salts.

The chromium fixation level may be raised using a combination of these techniques and with self-basifying chrome compounds.

High-exhaustion tanning enables the exhaustion of 80-98 per cent of chromium from the liquor. The concentration of chromium in the total effluent is reduced to 4-25 mg per liter. In terms of weight of raw material, this means a reduction of chromium discharge in effluent from 5-6 kg chrome per ton hide (using conventional tanning) to 0.2-0.5 kg per ton (using high-exhaustion tanning).

(b) Chromium re-uses

As an alternative, recovery and re-use of chromium is possible. This is done by the precipitation of chromium with alkali, and adjusting the temperature to accelerate settling. After filtration the supernatant liquor can be discharged, while the precipitate is redissolved in sulphuric acid, adjusted to the required basicity and re-used in the tannery. Magnesium oxide and sodium carbonates are the most commonly used precipitating chemicals and considered the most efficient. The amount of chromium in the effluent could be reduced from 5-6 kg per ton hide (conventional tanning) to less than one kg per ton.

The investment costs for chromium precipitation and re-dissolving plant depend on the size of the tanning operations. Experience in developing countries has shown that direct and indirect savings in terms of chemical costs, treatment costs and product quality justify the payback period of chrome recovery investment. In addition, it is environmentally friendly.

The chemical reactions of a typical chrome recovery process are:

$$Cr_2(SO_4)_3 + 3\,MgO + 3H_2O \rightarrow 2Cr(OH)_3 + 3\,MgSO_4 \quad \ldots\ldots\ldots\ldots(2.1)$$

$$2\,Cr(OH)_3 + 3\,H_2SO_4 \rightarrow Cr_2(SO_4)3 + 6\,H_2O\ldots\ldots\ldots\ldots\ldots\ldots..(2.2)$$
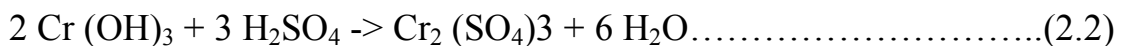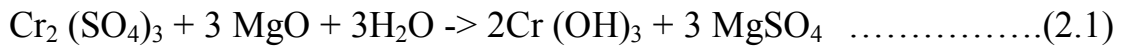
(c) Chromium substitutes

A fourth possibility is to use an alternative to chrome, such as aluminum, titanium and iron. These materials have so far mainly complemented chrome tanning and are used either as pre-tanning or as re-tanning agents. Vegetable tanning is normally applied to heavy hides for the production of sole or industrial leather.

In summary it can be concluded that the most realistic and economic ways to reduce chromium is to apply a high-chrome exhaustion tanning or use precipitation of chrome [29].

2.12 Incineration

Incineration is the process of direct burning of wastes in the presence of excess air (oxygen) at temperatures of about 800ºC and above, liberating heat energy, inert gases and ash. It is a waste treatment process that involves the combustion of organic substances contained in waste materials. The ash is mostly formed by the inorganic constituents of the waste, and may take the form of solid lumps or particulates carried by the flue gas. The flue gases must be cleaned of gaseous and particulate pollutants before they are dispersed into the atmosphere. Net energy yield depends upon the density and composition of the waste; relative percentage

of moisture and inert materials, which add to the heat loss, ignition temperature, size and shape of the constituents, design of the combustion system. In practice, about 65 to 80 % of the energy content of the organic matter can be recovered as heat energy, which can be utilized either for direct thermal applications or for producing power via steam turbine generators [26].

The combustion temperatures of conventional incinerators fuelled only by wastes are about 760ºC in the furnace and in excess of 870ºC in the secondary combustion chamber. These temperatures are needed to avoid odour from incomplete combustion but are insufficient to burn or even melt glass. To avoid the deficiencies of conventional incinerators, some modern incinerators utilize higher temperatures of up to 1650ºC using supplementary fuel. These reduce waste volume by 97% and convert metal and glass to ash. Ash is the weight of residue after combustion in an open crucible. By resource recovery facilities, several solid residuals are produced including bottom ash and fly ash. Bottom ash is the unburned and non burnable portion. It can contain considerable amounts of metals and glass as well as unburned organics. Fly ash is composed of the micron and submicron particulates that have been collected by the air pollution control system, it must be handled very carefully to avoid fugitive dust emissions, which may be harmful to workers and the surrounding environment.

Wastes burned solely for volume reduction may not need any auxiliary fuel except for startup. When the objective is steam production, supplementary fuel may have to be used with the pulverized refuse, because of the variable energy content of the waste or in the event that the quantity of waste available is insufficient. While incineration is extensively used as an important method of waste disposal, it is associated with some polluting discharges which are of environmental concern, although in varying degrees of severity. These can fortunately be effectively controlled by

installing suitable pollution control devices and by suitable furnace construction and control of the combustion process [27].

One of the most attractive features of the incineration process is that it can be used to reduce the original volume of combustibles by 80 to 95 %. Air pollution control remains a major problem in the implementation of incineration of solid waste disposal. In the United States, the cost of best available technology for the incineration facility may be as high as 35 % of the project cost. The cost of control equipment will, however, depend upon the air pollution regulations existing in a given lesser developing country. Waste incineration may be advantageous when a landfill cannot be sited because of a lack of suitable sites or long haulage distances, which result in high costs.

Incineration plants can be located close to the centre of gravity of waste generation, thus reducing the cost of waste transportation.

Incineration provides the best way to eliminate methane gas emissions from waste management processes. Furthermore, energy from waste projects provides a substitute for fossil fuel combustion [27].

2.13 Chemical controls in chrome tanning:

2.13.1 Basicity

All types of chrome compounds cannot tan protein it must have hydroxyl group in the complex directly attached to the chromium atom, such compound are called basic compound.

The basicity of chrome can define as" the percentage valence of chromium attached to hydroxyl group [9].

$Cr_2(SO_4)_3$	non tanning	1%
$Cr_2(OH)_2 SO_4$	tanning	33%
$Cr_2(OH)_4 SO_4$	too astringent	66%
$Cr_2(OH)_6$	insoluble and nontanning	100%

Tanning takes place with basicities between 33% and 55%. Above 55% basicity there is a danger of chrome precipitation and subsequent staining of the hides.

Chromium sulphate in solution has a strong attraction for hydroxyl ions OH which associate with molecule by replacing one or more of the sulphate ions SO_4. As more OH is made available (i.e., as the pH rises), it enters the chromium sulphate molecule and the molecules reactivity towards collagen increases. However when the pH rises beyond about pH 4.3 all the sulphates radicals are removed and chromium hydroxide is formed. Chromium hydroxide is insoluble and has no tanning power at all.

It's useful to note that below pH 4 the amount of acid used in pickling will need an equivalent amount of alkali to add for basification.

Low basicity chrome liquor has good penetration properties, but poor fixation, high basicity liquors have high fixation and consequently poor penetrating power. To achieve both penetration and high fixation the basicity is raising during the tannage in a process called basification, it involves the addition of alkali, sometimes combined with increasing the temperature. The amount of alkali to be added depends to considerable extent on the state of the pelt at the start of the tanning stage. This is controlled by the preceding deliming , bating and pickling [30].

2.13.2 Effect of pH value

The tanning behaviour of chrome is related directly to its pH value, salt content and acidity. Basic chromium salts, as used for chrome tanning, when dissolved in water, result in pH of solution of about 2.5-3.5 depending on the basicity, concentration and nature of the salt used .the basic chromium sulphate complexes in the solution combine with hide protein to greater or lesser extent, depending on the pH of the solution within the practical chrome tannage pH range. The higher the pH, the

greater is the tendency for chrome tanning to take place. When pickled pelt enter the chrome tanning bath at pH value of about 2.0, they don't have a strong attraction for chromium salt in the solution [31].

2.13.3 Masking agents

Masking agents are any materials which, when added to the chrome liquor, will raise the precipitation, buffer the solution and reduce the tanning affinity of the chrome. The organic anions of the masking salt form complexes with the basic chromium ions the solution and thus reduce their tanning power. The effect of these complexes to allow more uniform penetration of the chromium tanning agent. Using a mild – masking agent such sodium formate, the penetration of the chromium can be accelerated, and then, upon raising the pH, fixation, smooth, full leather can be obtained.

The forming of tanning complexes by the reaction of basic chromium salt with the masking agent is a fast reaction, for these reasons many tanners prefer to added masking salt to stock chrome liquor and allow it to age for a time before use. Others add the masking agent to the chrome liquor and heat before adding the chrome liquor to the tannage. Some tanneries prefer to add the masking agent to drum with the chrome liquor [31].

2.13.4 Temperature

The control of the temperature in chrome tanning process is important. With increased temperature (up to 40 $^\circ$C), there is an increase in the fixation of chrome. Temperature of tanning tanning bath in a drum tannage may be adjusted by heating the solution with steam during the tannage. The temperature control in drum tannage can be best accomplished by control of the temperature of the solution entering the drum and careful attention to

the liquor ratios. The mechanical heat developed by the action of the mill usually causes the tannage to seek its own temperature level [31].

2.14 Basification

In order to get good exhaustion of chrome the chrome must be basified by some means or other. As more chrome is fixed the shrinkage temperature increases. This is usual way to ascertaining the degree of tannage. The simple way to do this is applying the boiling test. If an actual shrinkage temperature is required a glycerine solution or liquid paraffin is used. Temperature in excess of $120^{o}C$ can thus be obtained.

There is a range of options available with which to bring about basification.

1- To have sufficient alkali remaining in the pelt by using a low acid pickle.

2- To add simple alkali such as sodium bicarbonate or sodium carbonate solution (10 % solution). Sodium carbonate is cheap source of alkali. This has to be added as a series of small additions to prevent the pH rising to a point at which precipitation takes place (pH greater than 4.3). A continuous slow feed is preferred and can be achieved with modern systems. Slow feed is ensures that the pH remains at a safe level and chromium is gradually and uniformly taken up.

3 - To use a low solubility alkali such as magnesium oxide. The acid in the system reacts with the alkali and is slowly consumed, thus the pH rises gradually and safely increases the stringency and fixing the chrome. In this way, any sudden increase in pH above a safe level is avoided. However, if all the magnesium oxide (or similar material) is not completely consumed before drumming is stopped there will be localized spots of alkali which will continue to raise the pH and create spots of dark coloured chromium hydroxide on the surface. They may appear as stains but when examined under a lens will be seen to be discrete spots. The stains are impossible to

completely remove and will be highlighting if the leather is dyed (other than black) [32].

To avoid this:

a) Don't use too much basifying alkali. Commercial products may claim that it is impossible for the product to cause stains. This should be viewed with caution.

b) Give mechanical action for sufficient time.

c) Utilize an increase in temperature to accelerate the decomposition of the alkali.

d) Using a built-in basification by using self-basifying chrome powder [3].

2.15 Self Basified chrome liquor/ powder

Chrome liquor is called a self basified when the basicity in the tanning drum automatically increases gradually with time without addition of any basifying agent.

Self basified chrome powder is actually an ordinary basic chrome sulphate powder then gradually reacts with those ores and thus basicity of liquor slowly but uniformly increases.

At the initial stage of dry chrome tanning the concentration of the small quantity of liquor produce by the surface water of the pickled pelts is so high that the hydrolysis is practically nil. This high concentrated liquor of low basicity develops an osmotic pressure by which water from the pelts gradually comes out diluting the external liquor and at the same time, chromium penetrates the pelt due to osmotic diffusion and gets uniformly distributed throughout the cross-section of the pickled pelt. Chrome liquor thus penetrates and chromium gets uniformly distributed in the pelt far before appreciable degree of hydrolysis start.

Once hydrolysis starts, its rate gradually increases due to removal of acid by the ores from the sphere of reaction and thus chromium gets fixed to protein in all layers of the pelts and the bonds strength between protein and chromium continuously increases till the leather stands the boil test [32].

2.16 The effect of thickness of the pelt

Tanning recipes frequently fail to mention the effect of the pelt thickness on the process details. It's fairly obvious that a process suitable for 1mm sheep skin is not going to be the same as one coping with 8mm cattle hide. The rate of diffusion of the float and chemicals determines the rate of tanning.

Formic acid is useful where chrome penetration is proving difficult, added to the chrome bath it assist penetration more effectively than will sulphuric acid and without lowering the pH as much.

When dealing with a thicker hide the weight is high in relation to surface area.

Thus in basifying, for instance, it may require a substantial quantity of basifying agent to adequately raise the pH. If this is added in one shot, or too fast, the pH in the bath and surface layers could reach precipitation point even though the inner layers still contain acid. Even when using a safe slow release type of basifying agent there may be a problem if insufficient running time is given for equilibrium to be reached and for all the basifying material to be consumed [32].

2.17 Forms Chromium

Chromium salts are considered to be the most heinous element which is used in chrome tanning stage as basic chromium sulphate. So polluting

nature of chromium salts has placed chrome tanning under severe criticism owing to ecotoxicological objections [33].

Chromium (Cr) is a transition metal present in group VI-B of the periodic table. Although it can exists in nine valence states, from −2 to +6 only trivalent chromium Chromium III and hexavalent chromium Chromium VI are ecologically important because these are the most stable oxidation states in the natural environment. Hexavalent chromium polluted anthropogenic effluents are principally answerable for environmental contamination by toxicity and carcinogenicity [34].

Chromium polluted soils and sediments are usually the result of sewage sludge disposal or dumping of chromate wastes from industrial and manufacturing activities. Chromium contamination of the environment is of concern because of the mobility and toxicity of Chromium VI [35].

Trivalent and hexavalent chromium differ widely in physicochemical properties and biological reactivity. While Cr VI species and dichromate's are extremely water-soluble and mobile in the environment, Cr III species are much less soluble and comparatively immobile [30]. Moreover, Cr VI is recognized to be highly toxic, carcinogenic, mutagenic and teratogenic for mammals including humans [36], whereas Cr III is an essential trace element necessary for glucose, lipid and amino-acid metabolism as well as a popular dietary supplement. Studies have revealed that Cr VI is approximately 100 times more toxic and 1000 times more mutagenic than Cr III [37].

Among the different oxidation states of chromium, Cr VI is acutely toxic and carcinogenic [38]. The Cr III ion on the other hand has a high tendency to form strong complexes with soil minerals. Incineration of chromium III to chromium VI and its reduction back to basic chromium sulphate is considered to be an important step towards overcoming chromium pollution [39].

2.18 Toxicity of chromium

Due to its wide industrial use, chromium is considered a serious environmental pollutant. Contamination of soil and water by chromium (Cr) is of recent concern. Toxicity of Chromium depends on its valence state: Cr VI is highly toxic and mobile whereas Cr III is less toxic.

Chromium and its compounds have multifarious industrial uses. They are extensively employed in leather processing and finishing, in the production of refractory steel, drilling muds, electroplating cleaning agents, catalytic manufacture and in the production of chromic acid and specialty chemicals. Hexavalent chromium compounds are used in industry for metal plating, cooling tower water treatment, hide tanning and, until recently, wood preservation. These anthropogenic activities have led to the widespread contamination that chromium shows in the environment and have increased its bioavailability and bio mobility.

The leather industry is the major cause for the high influx of Cr to the biosphere, accounting for 40% of the total industrial use.

Basic chromium sulfate containing trivalent chromium has been recognized as a less toxic compared with the hexavalent form which is more toxic and carcinogenic. Many noxious residues are routinely treated for recovery of heavy metals, with techniques that include conventional neutralization, precipitation, reduction, separation and solvent extraction [40].

Several studies have shown that chromium VI compounds can increase the risk of lung cancer. Animal studies have also shown an increased risk of cancer. The World Health Organization (WHO) has determined that chromium VI is a human carcinogen. The Department of Health and Human Services (DHHS) has determined that certain chromium VI compounds are known to cause cancer in humans [41].

2.19 Leaching

The extraction of a soluble constituent from a solid by means of a solvent is generally referred to as leaching. The process may be employed either the production of a concentrated solution of a valuable solid material, or in order to free an insoluble solid from a soluble material with which it is contaminated. The method used for the extraction will be determined by the proportion of soluble constituent present, its distribution throughout the solid, the nature of the solid.

Generally the processes which is responsible for limiting the extraction rate can be considered one of three parts, first the change of phase of the solute as it dissolves in the solvent, secondly its diffusion through the solvent in the pores of the solid to the outside of the particle, and thirdly the transfer of the solute from the solution in contact with the particles to the main bulk of the solution.

The selection of the equipment for an extraction process will be influenced by the factors which are responsible for limiting the extraction rate [42].

2.19.1 Factors influencing the rate of extraction:

1- **The particle size:**

 The smaller size of particle has a greater interfacial area between the solid and liquid and therefore the rate of transfer of material is high. Further the smaller is the distance the solute must diffuse within the solid as already indicated. It is generally desirable that the range of particle size should be small so that each particle requires approximately the same time for extraction, and in particular the production of a large amount of fine material should be avoided as it may wedge in the interstices of the larger particles and impede the flow of the solvent [42].

2- **The Solvent**:

The liquid chosen should be good selective solvent and its viscosity should be sufficiently low to circulate freely.

3- **The temperature**:

In most cases, the solubility of the material which is being extracted will increase with temperature to give a higher rate of extraction. Further the diffusion coefficient will be expected to increase with raise in temperature and this will also improve the rate.

4- **The agitation of the fluid**:

Agitation of the solvent is important, it increase the eddy diffusion and therefore increases the transfer of material from the surface of the particles to the bulk of the solution.

2.19.2 Types of equipment

Three distinct processes are involved in the normal leaching operation. They are:

a) Dissolving the soluble constituent.

b) Separating the solution, so formed, from the insoluble solid residue.

c) Washing the solid residue in order to free it of unwanted soluble matter or to obtain, as product, as much of the soluble materials as possible.

The type of equipment employed will depend on the nature of the solid, whether it granular or cellular and whether it is coarse or fine. The normal distinction between coarse and fine solids is that the former have sufficiently large settling velocities for them to be readily separable from the liquid whereas the latter can be maintained I suspension with the aid of only a small amount of agitation. Generally the solvent can be allowed to percolate through beds of the coarse materials whereas the fine solids offer too high a resistance.

The rate of extraction will in general be a function of the relative velocity between the liquid and the solid. In some plants the solid is stationary and the liquid flows through the bed of particles, in some continuous plants the solid and liquid move counter-currently [42].

2.19.3 Extraction from cellular materials

With seeds such as soya beans, containing only about 15% of oil, solvent extraction is often used because mechanical methods are then not very efficient. Light petroleum fractions are generally used as solvent. A plant for the extraction of oil from seeds is illustrated in fig (2.3) and consists of vertical cylindrical vessel divided in to two sections by a slanting partition. The upper section is filled with the charge of seeds which is sprayed with fresh solvent from a distributor. The solvent percolates through the bed of solids and drains into the lower compartment where together with any water extracted from the seeds, it's continuously boiled off by means of a steam coil. The vapours are taken to an external condenser and the mixed liquid is pass to a separating box from which the solvent is continuously fed back to the plant and the water is run to waste. By this means a concentrated solutions of the oil is produced by the continued application of pure solvent to the seeds [42].
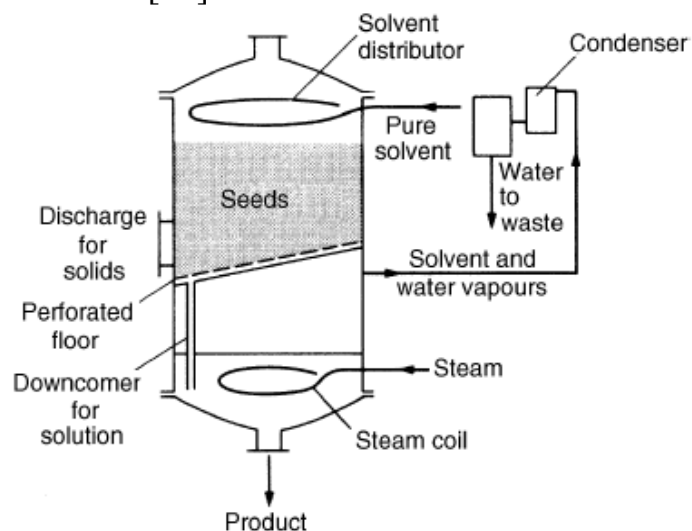
Fig 2.3: plant for extraction of oil from seeds

2.19.4 Leaching of coarse solids

 The simple batch plant is used for coarse solids consists of a cylindrical vessel in which the solids rest on a perforated support. The solvent is sprayed over the solids and, after extraction is complete the residue is allowed to drain. If the solids contains such a high proportion of solute that is disintegrate, it's treated with solvent in tank and the solution is decanted.

In the simple counter-current system, the solid is contained in a number of tanks and the solvent flows through each in turn. The first vessel contains solid which is almost extracted and the last contains fresh solid. After a time, the first tank is disconnected and a fresh charge is introduced at the far end of the battery. The solvent may flow by gravity or be fed by positive pressure, and is generally heated before it enters each tank.

A continuous unit in which counter-current flow is obtained is the tray classifier (fig 2.4). Solid is introduced near the bottom of a sloping tank and is gradually moved up by means of a rake. The solvent enters at the top and flows in the opposite direction to the solid and passes under a baffle before finally being discharged over a weir , the classifier operates satisfactorily provided the solid does not disintegrated , and it can be arranged so that the solids are given simple time to drain before they are discharged . a number of these units can be connected in series to give counter-current flow.

The leaching plant consists of an open tank 10 ft in diameter, into the outer portion of which the solid is continuously introduced from an annular hopper. Inside the tank a 6 ft diameter vertical pipe rotates very slowly at the rate of about one revolution every 40 min. it carries three ploughs stretching to the circumference of the tank, and these gradually the solid through holes into the inside of the pipe. A hollow shaft, about 3 ft in diameter, rotates in the centre of the tank at about one revolution in 3 min and carries a screw   conveyor which lifts the solid and finally discharges it through an opening. So that it falls down shaft and is deflected into a waste

pipe passing through the bottom of the tank. Leaching takes place in the outer proportion of the tank where the reheated mother liquor rises through the descending solid. The make-up water is introduced under the flouts of the screw elevator, flows down over the solid and then joins the reheated mother liquor. The counter-current extraction takes place in the outer part of the tank and counter-current washing in the central portion. The plant described operates efficiently and gives between 85 and 90% extraction, as compared with only 50% in the batch plant [42].

CHEMICAL ENGINEERING
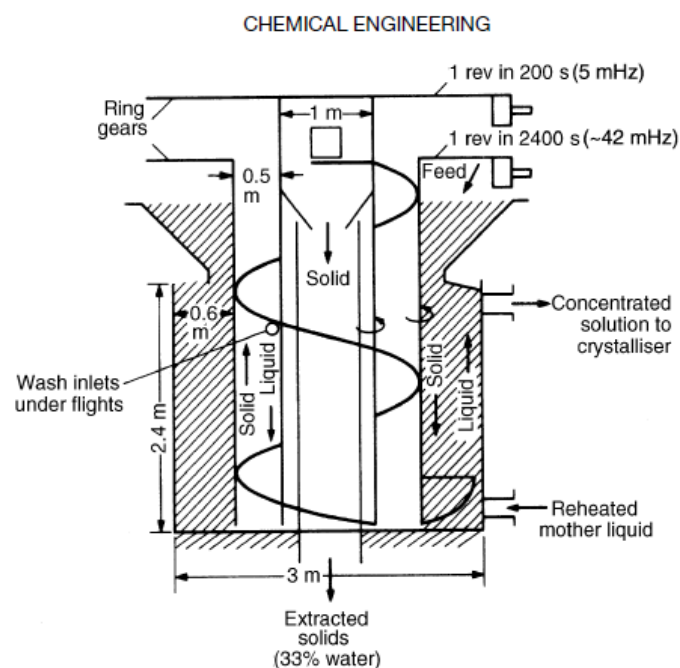
Fig 2.4: continuous leaching tank

2.19.5 Leaching of fine solids:

Whereas coarse solids can be leached by causing the solvent to pass through a bed of the material, fine solids offer too high a resistance to flow. Particles less than 200 meshes may be maintained in suspension with only a small amount of agitation, and as the total surface area is large an adequate extraction can be effected in a reasonable time. Because of the low settling velocity of the particles and their large surface, the subsequent separation and washing operations are more difficult for fine materials than for coarse solids.

Agitation can be achieved either by the use of a mechanical stirrer or by means of compressed air. If a paddle stirrer is used, precautions must be taken to prevent the whole of the liquid being swirled, with very little relative motion occurring between solids and liquid. The stirrer is often placed inside a central tube (fig2.5) and the shape of the blades so arranged that the liquid is lifted upwards through the tube, the liquid then discharges at the top and flows downwards outside the tube, thus giving contiguous circulations.

The Dorr agitator uses a compressed air for stirring; consist of a cylindrical flat-bottomed tank fitted with a central air lift inside a hollow shaft which slowly rotates. To the bottom of the shaft are fitted rakes which drag the solid material to the centre as it settles, so that it is picked up by the air lift. At the upper end of the shaft the air lift discharges into a perforated launder which distributes the suspension evenly over the surface of the liquid in the vessel. When the shaft is not rotating the rakes automatically fold up so as to prevent the plant from seizing up if it is shut down full of slurry. This type of agitator can be used for batch or contiguous operation. In the latter case the entry and delivery points are situated at opposite side of the tank. The discharge pipe is often in the form of a flexible connection which can

arranged to take off the product from any desired depth. Many of these agitators are heated by steam coils [42].
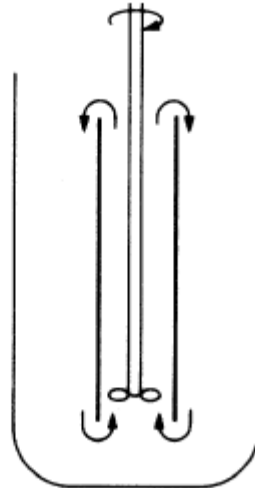
Fig 2.5: simple stirred tank

2.20 Counter-current washing

Where the residual solid after separation is still mixed with an appreciable amount of solution, it's generally desirable to pass it through a battery of washers, arranged to give counter-current flow of the solids and the solvent (fig 2.6). if the solids are relatively coarse a number of classifiers may be used, and with the more usual case of fine solids thickeners are generally employed. In each unit a liquid, referred to as underflow, and a mixture of insoluble residue and solutions, referred to as underflow, are brought into contact so that intimate mixing is achieved and the solution leaving in the under flow has the same composition as that associated with the solids in the underflow. Each unit then represents an ideal stage.

By means o a series of material balances, the composition of all the streams in the system can be calculated on the assumption that the whole of the solute has been dissolved and that equilibrium is reached in each of the thickeners.

In order to define such a system completely six quantities must be specified:

1- The composition of the solvent fed to the system, in particular the concentration of soluble material already present.

2- The quantity of solvent used, alternatively the concentration of the solution to be produced may be specified, and the corresponding amount of solvent calculated from a material balance.

3- The composition of the solid to be leached.

4- The amount of sold fed to the system alternatively, the amount of soluble or insoluble material requires as product may be specified, and the necessary amount of solid feed then calculated from a material balance.

5- The amount of liquid discharged with the solid in the underflow from each of the thickeners.

6- The number and arrangement of the units, the purity of the product from the plant can then be calculated, alternatively the required purity of the washed solid may be stated, and the number of units can then be calculated [39].
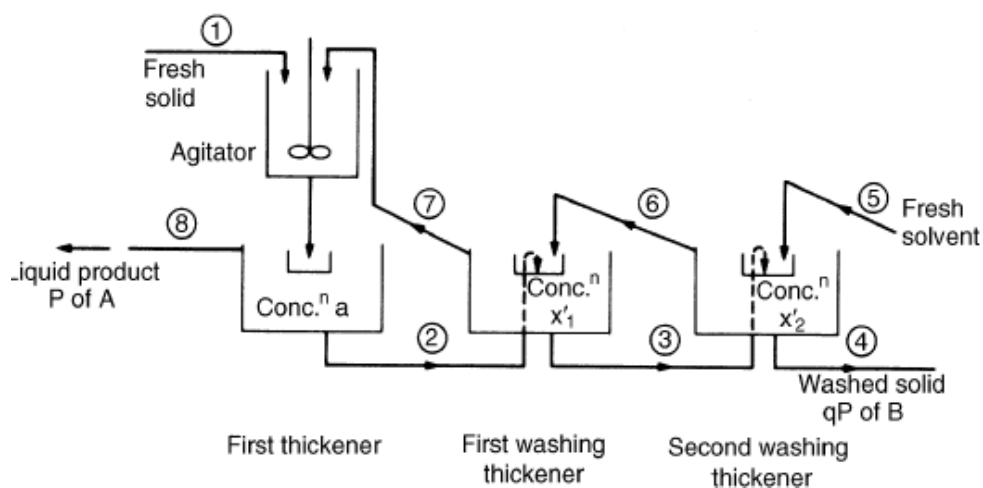
Fig 2.6: agitator and washing system

2.21 Evaporation

Evaporation means vaporization of a liquid or that of solvent from a solution.

Principals of evaporation and evaporator are that a solution boils in an evaporator to give off the vapour and thereby becomes concentrated.

2.21.1 Single and multiple- effect evaporators:

1-single- effect evaporator:

The simplest method of evaporation is to feed the solution to the evaporator which is provided with sufficient heat transfer area. The vapour generated is condensed using a surface condenser or a direct contact condenser. The concentrated product is drawn from the bottom; this is called a single-effect evaporator.

A single-effect evaporator is simple in operation and doesn't utilize steam efficiently. More than a kilogram of steam is needed in order to vaporize 1kg of water from the solution. The reasons are:

a- The feed temperature remains below its boiling point. Apart of steam is utilized to raise the feed to its boiling point.

b- Steam condensing in the steam chest is at higher temperature than that of the solution. So the latent heat released by condensation of 1 kg steam is less than that required for vaporization of 1 kg of water from the boiling solution.

c- Some amount of heat loss from the evaporator to the ambient always occurs.
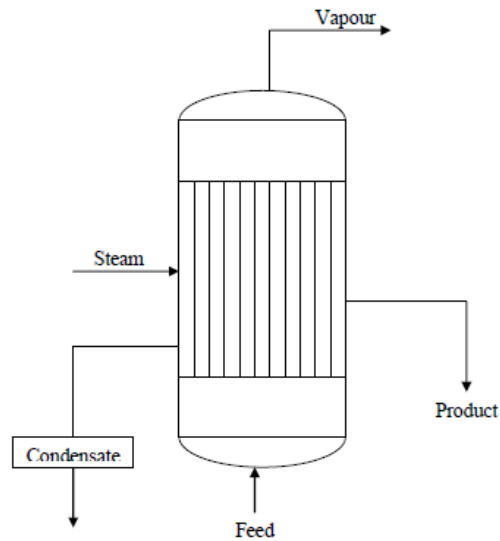
Fig 2.7: single-effect evaporator

2.21.2 Double –effect evaporator

These are two evaporators that arranged in series such that the vapour generated in one is fed to the steam chest of the second for heating. Partly concentrated solution flows from the first to the second where it attains the desired final concentration. The vapour generated in the second evaporator is sent to a condenser.

It must be noted that the vapour leaving evaporator 1 is at the boiling temperature of the liquid leaving the first effect, hence heat transfer occurs from the condensing vapour (evaporator 1) to the boiling liquid in evaporator2, the liquid in evaporator 2 must boil at a temperature less than the condensation temperature of the vapour in order to ensure driving force for the transfer of heat. A method of achieving this is to maintain a suitable lower pressure to evaporator 2 so that the liquid boils at a lower temperature [42].
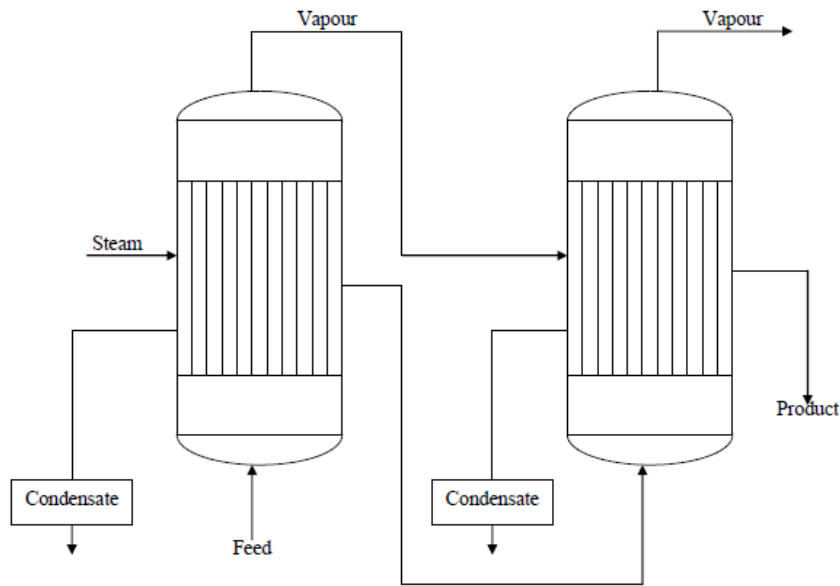
Fig 2.8: Double-effect evaporator

3- Multiple -effect evaporator:

The arrangement can be extended by arranging more evaporators in series to have a triple-effect or quadruple-effect evaporator in the multiple –effect operation. Several operators are connected by suitable piping in order that the vapour from one effect passes to the next in series. The vapour produced in the first effect is used to vaporize water from the solution in the second effect. This goes sequentially until the vapour from the last effect is discarded in the condenser. In most situations the solution also flows from one effect to the next and gets partially concentrated in each effect. The net result of this arrangement is multiple reuse of heat supplied to the first effect, thereby improving the steam economy [42].
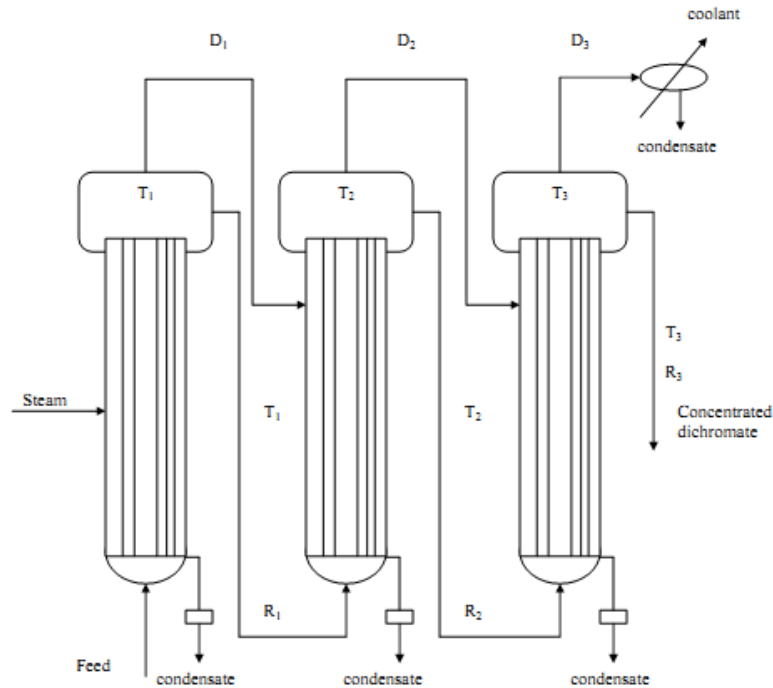
Fig 2.9.: triple-effect evaporator

2.22 Capacity and economy:

Capacity of an evaporator means the number of kilograms of water it can vaporize per hour. The steam economy is the number of kilograms of water vaporized from all the effects taken together for each kilograms of steam fed to the first effect. The ratio of capacity to economy gives the steam consumption of the evaporator per hour [42].

2.23 Boiling point elevation (BPE):

It is the difference of boiling point of concentrated solutions produced by evaporators and boiling point of pure water at the pressure prevailing in the vapour space.

2.24 Enthalpy of solutions:

Enthalpy concentration data of solution are required for making the energy balance calculations of an evaporator. The integral heat of solutions is defined as the change in enthalpy of solution when one mole of solute is dissolved in n_1 moles of solvent at 25 C^o and atmospheric pressure. The enthalpy of a solution at temperature T relative to the pure solvent and solute at temperature T_0 is expressed as :

$$H_s = n_1 H_1 + n_2 H_2 + n_2 \Delta H_{s2} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2.3)$$

That is

$$H_s = n_2 \Delta H^0_{s2} + (n_1+n_2)(S)(T - T_0) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2.4)$$

2.25 Classification of multiple-effect evaporators:

Depending upon the directions of flow of the heating medium and of the feed or the liquor multiple-effect evaporators can be classified into four categories: forward feed, backward feed, mixed feed and parallel feed [42].

2.25.1 Forward feed:

The feed is induced to the first effect. Partly concentrated liquor flows to the second effect and then from the second to the third effect. Thick liquor is withdrawn from the last effect. Steam is fed to the shell of the first effect and the vapour generated therein flows to the shell of the second effect and acts as the heating medium there. Vapour generated in the second effect supplies heat for boiling the liquor in the third effect. The vapour from the third effect is condensed in a barometric condenser connected to a steam-jet ejector. The final condensate is discarded with the water supplied to the barometric condenser.

2.25.2 Backward feed:

The feed is introduced to the last effect. Partly concentrated liquor flows to the second and then to the first effect from which the thick liquor is withdrawn. Pumps are used to maintain the flow of liquor against a positive pressure.

2.25.3 Mixed feed

In the mixed feed arrangement, the dilute feed enters an intermediate effect and flows to the next higher effect till it reaches the last effect. On this section, the liquid flow occurs in the forward feed mode. Partly concentrated liquor is then pumped to the effect before the one to which the feed is introduced. It then flows towards the first effect in the backward feed mode. Thick liquor is withdrawn from the first effect [42].

2.26 Evaporator Selection:

The more important factors for selection of an evaporator for a particular service are:

1. Solution viscosity.
2. Heat sensitivity of the solution.
3. Scaling or fouling characteristics of the solutions
4. Corrosiveness.
5. Presence of suspended solids.
6. Foaming characteristics.

The choice of evaporation temperature, vacuum and residence time or contact time is of great importance as these parameters influence the product quality and economy.

2.27 Vapour Recompression:

The basic objective of the multiple effect evaporator configurations is to achieve a high steam economy by multiple reuse of the heat supplied to the first effect in the form of steam. Similar results can be obtained in a single-effect evaporator if the steam generated by evaporation of the solution is compressed to a higher pressure (simultaneously raisin its temperature) using a suitable device, so that the compressed steam can be re-circulated to the steam chest. This is the idea behind vapour recompression that essentially pumps heat from a lower level to a higher level. In fact, there are certain applications where the evaporation of solutions has to be done only at a moderate temperature. The vapour recompression system is a practical alternative for an achieving good steam economy in such a case [42].

Chapter three

Materials and Methods

3.Materials and Methods

3.1: Materials

1. Concentrated H_2SO_4 (98% , Sp.gr. 1.84).
2. Concentrated $HClO_4$ (70% , Sp.gr. 1.41).
3. Concentrated HNO_3 (60% , So.gr. 1.54).
4. KI (10%)
5. $Na_2S_2O_3$ (o.1 N)
6. $K_2Cr_2O_7$
7. NaOH (0.1N)
8.

3.2: Equipment and Insroments

1. Thermolyne Benchtop Muffle Furnace.
2. Soxhlet Unit
3. Digital Spectrophotometer (Cary 100 Perkin-Elmer UV-visible spectrophotometer).
4. Water bath unit
5. Digital pH meter

3.3: Methods

3.3.1 Percentage of chrome shavings waste

To determine the percentage of wet chrome shaving waste generated per kilogram of raw wet salted hide processed, a sample of ten pieces of wet blue hides were randomly taken from ten different batches and shaved to a thickness of 1.70mm which is the average thickness of finished leather for shoe upper made from cattle hide. The samples were weighed before and after shaving.

3.3.2 Analysis of chrome shavings

Chrome shavings was collected from the incubator of the faculty of engineering of Sudan University for Science and Technology fig (3.1), dried at room temperature for seven days and analyzed using official methods of analysis [43] for chromic oxide, pH, moisture and ash content.

Fig (3.1): chrome shavings waste

3.3.3 Determination of pH

The pH of the sample of chrome shavings wastes were determined by shaking five gram of sample of chrome shavings in 100ml of distilled water for 16 – 24 hours followed by direct measurement of the pH according to the standard method of official methods of analysis.

3.3.4 Determination of Moisture Content

Moisture content of solid waste is usually expressed as the mass of moisture per unit mass of wet or dry materials. In order to determine the moisture content of the solid wastes, samples of the solid waste was first weighed and put in an oven at 105 ^{o}C for 24 hours. It was kept in desiccators for about 30 minutes and then weighed and recorded. The wet-mass moisture content is expressed as follows:

Moisture content (%) = ((w-d) /w) x 100……………………………….…..3.1

Where

 w = initial mass of sample as delivered

d = mass of sample after drying.

3.3.5 Determination of Volatile Organic Compound and Ash Content

The volatile organic compound and ash content were determined after burning the dry chrome shaving in a furnace at 850 to 1000 ºC for 2 hours. The samples were again sent to desiccators for about 30 minutes and weighed.

Ash Content (%) = (W1 / W2) × 100……………………………….........3.2

Volatile organic compound (%) = (W2 – W1/W2) × 100 ……………....3.3

Where: W1 is the weight of the chrome shavings left after burning.

W2 is the weight of the chrome shavings before burning.

3.3.6 Transformation of chromium III to chromium VI

The chrome shavings was burnt in a furnace (Thermolyne Benchtop Muffle furnace) for two hours at 1000 ºC to transform chromium III to chromium VI.

3.3.7 Analysis of chrome shaving ash, Chromium content and Total soluble

 10 gram of chrome shavings ash was weighed accurately and then put in an extraction unit (soxhlet) using 250 ml distilled water until the recycled solution becomes clear .The residue was taken and weighed , and the solution is analyzed using spectrophotometer (Cary 100 Perkin-Elmer UV-visible spectrometer). The analysis is shown in table (4.1).

3.3.8 Preparation of standard solutions for Spectrometry

Standard solution that contains 1000 ppm of chromium was prepared; 10 ppm was taken and diluted to 100 ml. Five working standard solutions of 5, 10, 15, 20, 25 ppm are prepared in 50 ml volumetric flask.

3.3.9 Factorial experiments of leaching

Leaching of dichromate is carried out using distilled water in a series of single contact batch experiments to determine the effect of the various factors on leachability of dichromate from shavings ash. Factors which normally influence the rate of extraction of a solute from a solid are:

A. Time of leaching

B. Leaching temperature

C. Solvent-solid ratio

D. Degree of mixing

Two level factorial experiments are carried out to investigate the effects of the above factors and their significance as shown in table (4.3).

The actual levels are:

a (1, a) time, 1 hour and 3 hours.

b (1, b) temp 38^0C and 70^oC.

c (I , c) solid/solvent ratio, 1:10, 1:30

d (1, d) without mixing, with mixing at 200 rpm

The number 1 indicates that the chosen factor is at its low value, and a,b,c,d indicate that the factors are at their high values. Each experiment is replicated.

3.3.10 Leaching method

The chrome shavings ash was fed into a wooden vat $(0.25 \times 0.25 \times 0.5)$ m^3, the vat was then filled with normal water at $37\,^0$C with solid to liquid ratio of 1: 10 and left for one hour with a mixer rotating at 200 rpm to insure that the equilibrium was realized . To produce stronger concentrated liquor, a battery of several leaching vats was used as shown in fig (3.1). The liquors were run on a counter-current basis to increase the efficiency of leaching. A battery of six vats were used, all interconnected. When the chromium VI was fully extracted as in C the vat was emptied and recharged again and then became the front leach, with B the bottom leach and the next to be discharged.

A	B	C
Fresh ash strong liquor from B	Once used ash & liquor from C	Twice extracted ash & fresh water
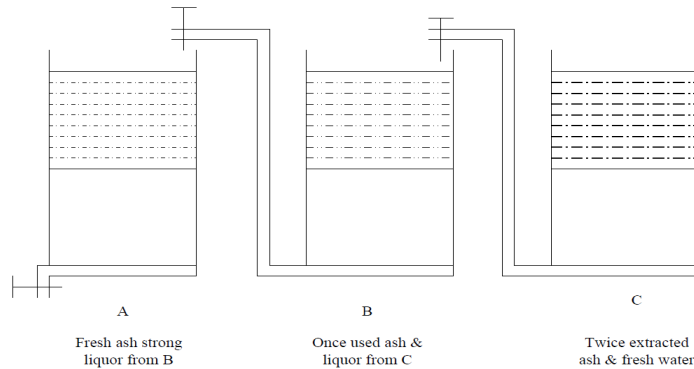
Fig (3.2): press leach for chrome shavings ash

Figure (3.2) shows the leaching pattern for a six stage system. Each of the circles stands for leaching followed by phase separation. **W** for leaching solvent (water), **C** for solids being leach (chrome shavings ash), **E** for extract solution and **R** for the raffinate. Subscripts refer to stage numbers.

Starting with at stage 1 a weight **C** of chrome shavings was leached for 1 hour with an amount **W** of water, the extract E_1 was withdrawn while the raffinate R_1 was extracted with a fresh amount of water **W** in contact number 2. From stage 2, the extract E_2 was used for leaching a fresh amount **C** of chrome shavings ash in leaching 3, the raffinate R_2 was leached with fresh water in stage 4and so on. It is essential to allow enough

time for drainage of all extract in order to effect a substantially complete phase separation.

The first complete cycle of the operation was represented by leaching 16-20. The cycles were continued until 5 consecutive extract analyses were constant within experimental errors.
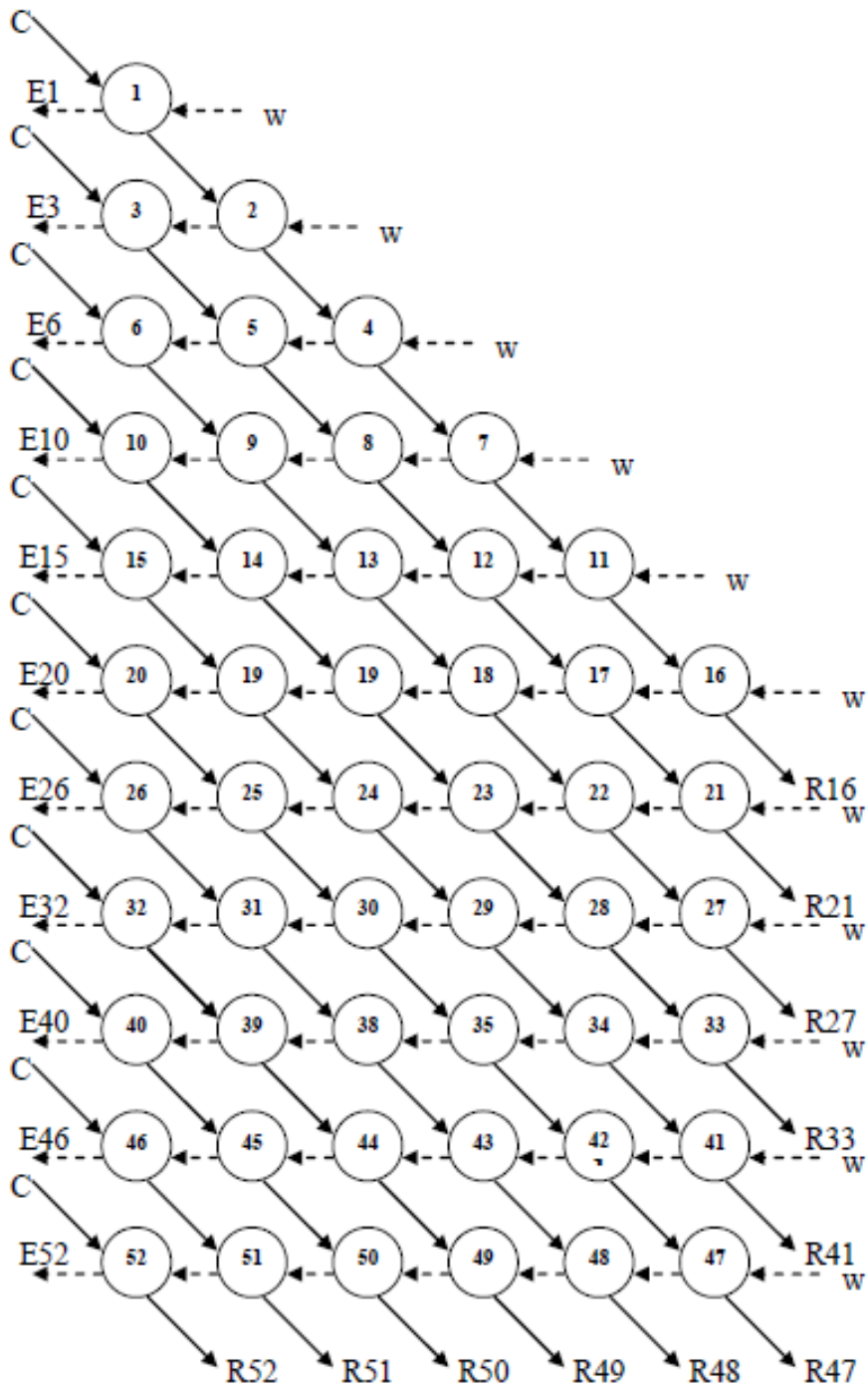
Fig (3.3): Leaching pattern for a six stage system

C: fresh chrome shavings ash

E: Extract

R: Raffinate

W: Solvent (Water)

3.3.11 Time of leaching

10 g of chrome shavings ash is taken in a beaker, 100 ml of distilled water is added at 37 ºC and left for 1 hour with mixing, the beaker contents is filtered, the extract is analyzed for concentration of dichromate and then subjected to more leaching using the same conditions described above, this process is repeated 10 times until the recycled solution is clear.

The rate of transfer from the particles to the bulk of the liquid is correlated and found to be:

$$C = C_s (1 - e^{-t}) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 3.4$$

where :

C: concentration of the solute at any time t.

C_s: chromium VI content in chrome shavings ash.

t: time

3.3.12 Evaporation

200 gram of 40% sodium dichromate solution was introduced into a crucible to raise the concentration of the dichromate to 90%. The solution obtained was 88.9 gram and the water evaporated is 111.1 gram, saturated steam from the water bath at atmospheric pressure and 100 ºC was recorded and used for heating in macro-scale this is usually carried out in a triple-effect evaporator as shown in fig 3.3.
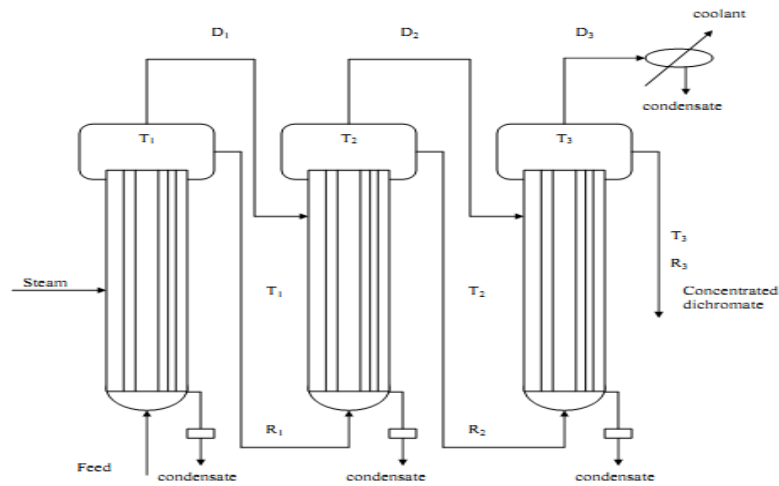
Figure (3.4): Flow sheet of triple- effect evaporator

3.3.13 Triple-effect evaporator calculations

This is usually carried out as follows:

Saturated steam (Flow rate = M_s, temperature = T_s, pressure = P_s) enters the steam chest of the first effect, the liquid in the first-effect boils at temperature Tb_1. This is also the temperature of vapour generated in this effect. The pressure in the vapour space was maintained at P_1 the boiling point of pure solvent at this pressure is Tw_1, so the boiling point elevation in the first-effect is ($Tb_1 - Tw_1$), and the vapour generated is a superheated vapour. The saturation temperature is Tw_1 which is the boiling point of pure water at pressure P_1 prevailing in the vapour space.

Solution from first-effect flows to second-effect where the liquor boils at temperature Tb_2 and the pressure in the vapour space is maintained at P_2. The boiling point of water at a pressure of P_2 is Tw_2 and the boiling point elevation is ($Tb_2 - Tw_2$), the vapor from first –effect enters the steam chest of the second-effect with a degree of superheat. But lost it is superheat quickly by transfer of sensible heat and attains its saturation temperature of Tw_1. The amount of sensible heat transferred is negligible

because of practical purpose, so the temperature driving force for heat transfer to the boiling liquor in the second effect is ($Tw_1 - Tb_2$). The vapor from second effect enters the steam chest of third-effect at temperature Tb_2. This vapor has superheat of temperature ($Tb_2 - Tw_2$, and lost the superheat quickly and attained the saturation temperature of Tw_2 the temperature driving force in this effect was consider to be ($Tw_2 - Tb_3$) where Tb_3 was the boiling point of the liquor in the third-effect operating at pressure P_3. The boiling temperature of water at pressure P_3 was Tw_3 , and the boiling point elevation in the third effect was ($Tb_3 - Tw_3$)

3.3.14 Reduction of Sodium Dichromate to Basic Chromium Sulphate

250 gram of sodium dichromate was taken from leached chromium VI in a beaker; 230 g of concentrated sulphuric acid (Sp. Gr. 1.84) were added carefully and stirred well. The beaker was placed in a reactor under cooling with continuous stirring while 62.5 g of sugar were added slowly in 10 lots over three hours. During the reaction the colour of the liquor changed gradually from orange to green and finally to bluish green indicating the completion of the reduction [11]. The reaction proceeded as follows:

$4Na_2Cr_2O_7 + 12H_2SO_4 + C_6H_{12}O_6 + 26H_2O = 8Cr\ (OH)\ SO_4 + 4Na_2SO_4 + 40H_2O + 6CO_2$...3.5
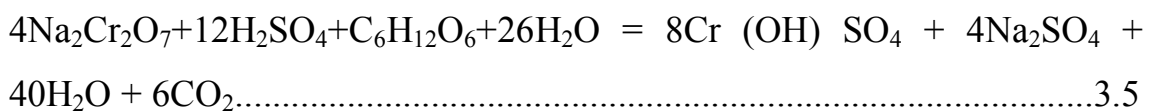
The following figure show the schematic diagram of the process
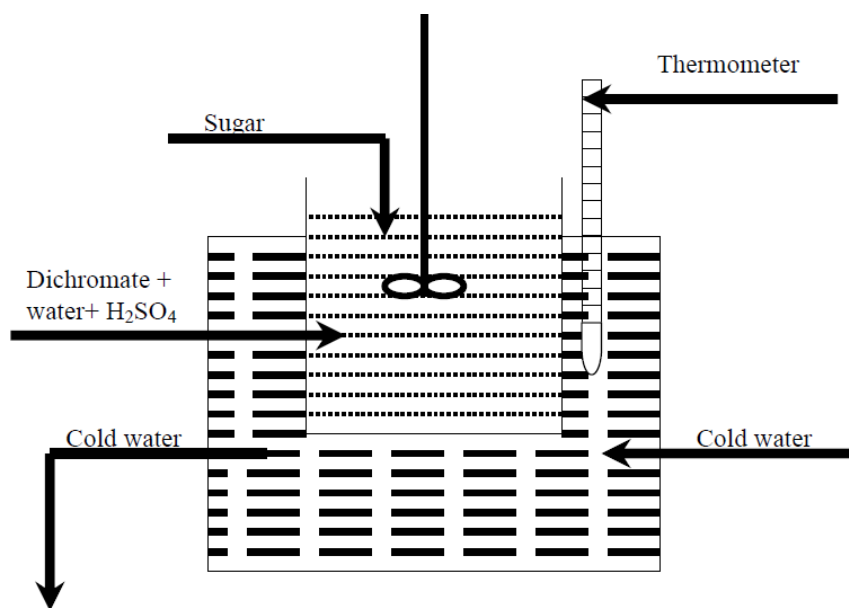
Fig (3.5): schematic diagram of the reduction process

3.3.15 Tests for Complete Reduction

Three drops of reduced chrome liquor were taken in a beaker, diluted with distilled water, ammonia was then added and the mixture was boiled and filtered. No yellow colour was observed in the filtrate indicating complete reduction.

3.3.16 Determination of Chromic Oxide

25 ml of the chrome liquor was transferred into a conical flask and diluted with 100 ml distilled water. 2N caustic soda solution was added drop by drop until the precipitated chromium hydroxide formed was just dissolved. 25 ml of hydrogen peroxide solution (3%) was added. Some boiling stones were then introduced into the vessel and the contents were allowed to boil. A small funnel was suspended in the neck of the conical flask to avoid any loss due to bubbling. The boiled solution (yellow chromate) was cooled and made up to the mark.

50 ml of the yellow chromate solution was pipetted into an iodine flask to which concentrated hydrochloric acid was added in excess (5 ml excess) , followed immediately by 10 ml of 10% potassium iodide, the closed flask was left in a dark for 10 minutes. The liberated iodine was titrated with 0.1 N sodium thiosulphate using freshly prepared starch as indicator; the disappearance of the blue colour indicated the end point.

1 ml of 0.1 N sodiumthiosulphate = 2.533 mg chromic oxide 3.6

3.3.17 Determination of Bacisity

 3 ml of 1% phenonaphthalein solution was added to 300 ml distilled water in a large porcelain bowel and adjusted to pink colour with three drops of 0.1 N sodium hydroxide solution. 25 ml of solution was prepared as described above and titrated with continuous stirring at the boil to effect further hydrolysis of the chromium salt, with 0.1 N sodium hydroxide until the distinct pink colouration was obtained.

Bacisity = (A-B) / A× 100 ....3.7

A = ml of 0.1 sodium thiosulphate.

B = ml of 0.1 sodium hydroxide.

3.3.18 Tanning process

 Pickled sheep skins were tanned using the reduced basic chromium sulphate, obtained by the above process.

Table (3.1): Recipe for chrome tannage,

Percentage was based on pickled pelt weight. Cr_2O_3: 21%, Basicty: 33%

Material	Percentage %
Float	100
Reduced chrome liquor	10
Sodium bicarbonate	1
Mimosa	10
Syntan	10
fatliquor	5

Chapter four

Results and Discussion

4.Results and Discussion

4.1 Sample Collection

Chrome shavings were collected from the Incubator of the faculty of engineering of Sudan University of Science and Technology.

The percentage of shavings material was determined as shown in table 4.1:

Table (4.1) Shavings produced per kilogram from wet blue hides processed

Batch No	Weight of a single piece of wet blue hide before shaving (kg)	Weight of a single piece of wet blue hide after shaving (kg)	Weight of Shavings (kg)	Percentage
1	10.80	5.8	5.00	46
2	6.00	4.20	1.80	30
3	8.20	5.60	2.60	32
4	8.60	5.4	2.70	32
5	10.00	5.80	4.50	45
6	8.60	5.00	3.30	38
7	8.60	6.20	2.10	28
8	7.60	4.60	2.70	36
9	8.60	6.20	2.70	31
10	7.60	4.60	2.60	34
Average Weight (kg)	85.5	59.8	30.00	36

Determination of percentage of chrome shavings showed that 36% on average of pelt weight was taken off in the process of shavings; this means that 0.36 kg of shaving is produced per kilogram of wet blue hides processed to produce wet blue pelts.

4.2 Analysis of Chrome shavings

The chemical analysis of chrome shavings shows that chromic oxide content in chrome shavings is 2.75% which is quite significant as shown in table (4.2).

Table (4.2): Analysis of Chrome shavings
Percentages are on dry weight

Characteristic	values
Average moisture (%)	13.90
Ash content (%)	6.50
Chromic oxide (%)	2.75
pH	4.2

4.3 Transformation of chromium III to chromium VI

The incineration of chrome shavings at 1000 $^{\circ}$C oxidized all chromium III to chromium VI.

The analysis of chrome shavings ash for dichromate and total soluble are shown in table (4.3).

Table (4.3): Analysis of chrome shavings ash on dry basis

Item	Content
Dichromate (g/g)	0.4
Total soluble (%)	50.85
Chromium recovery as Cr VI (%)	95

4.4 Development of Calibration Line

Standards solutions of potassium dichromate of different concentration were prepared and analyzed with atomic absorption spectrophotometer as shown in fig (4.1) with a correlation of :

$$y = 0.005\ X - 0.012 ....4.1$$
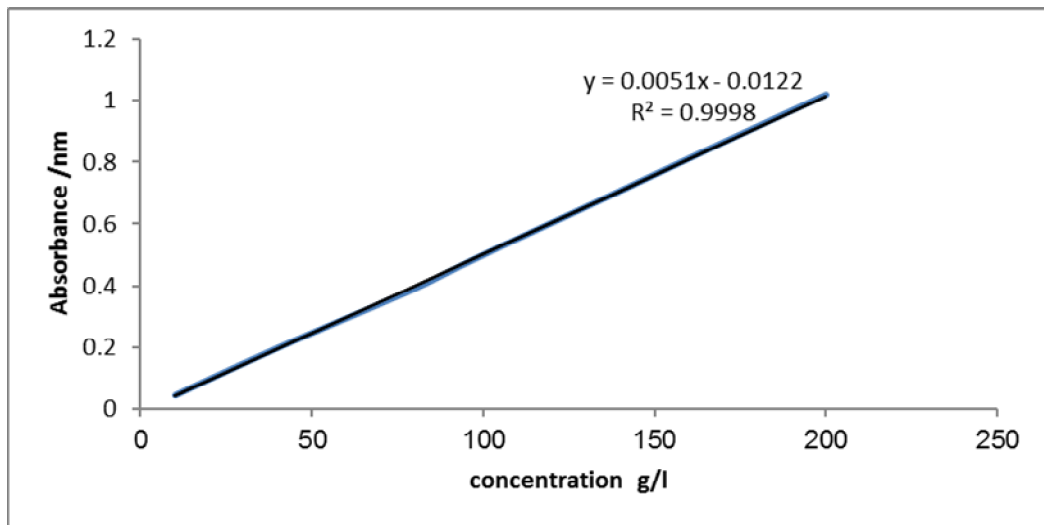
Fig (4.1): calibration and correlation of chromium VI

4.5 Factorial experiments and statistical analysis

Two level factorial experiments were carried out to investigate the effects of the factors which normally influence the rate of extraction of a solute from a solid   these are shown in table (4.3).

Table (4.4): factorial experiments for the factors influencing leaching

These are:

A = time of leaching in hours

B = temperature in degree centigrade

C = solid/solvent ratio

D = degree of mixing (with, without)

Treatment combination	Time Hour	Temp °C	Solid/solvent Ratio w/w	Mixing rpm	Concentration Mg/l
1	1	37	1:10	Without	37.2
a	3	37	1:10	Without	38.2
b	1	70	1:10	Without	37
c	1	37	1:30	Without	45.6
d	1	37	1:10	With mixing*	36.2
ab	3	70	1:10	Without	37.4
ac	3	37	1:30	Without	49.8
ad	3	37	1:10	With mixing	39.8
bc	1	70	1:30	Without	52.8
bd	1	70	1:10	With mixing	35.4
cd	1	37	1:30	With mixing	55.2
abc	3	70	1:30	Without	55.2
abd	3	70	1:10	With mixing	45.4
bcd	1	70	1:30	With mixing	56
acd	3	37	1:30	With mixing	47.4
abcd	3	70	1:30	With mixing	55.6

1: all factors were in their high value.

a : time in the high value and the rest of factors in their low value.

b: temperature in the high value and the rest of factors in their low values.

c: solid/solvent ratio in the high value and the rest of factors in their low value. d: mixing in the high value and the rest of factors in their low value

ab: time and temperature in their high value and the rest of factors in their low value

ac: time and solid/solvent ratio in their high value and the rest of factors in their low value

ad: time and degree of mixing in their high value and the rest of factors in their low value

bc: temperature and solid/solvent ratio and the rest of factors in their low value

bd: temperature and degree of mixing and the rest of factors in their low value

cd: solid/solvent ratio and degree of mixing and the rest of factors in their low value

abc: time and temperature and solid/solvent ratio and the rest of factors in their low value

abd: time and temperature and degree of mixing and the rest of factors in their low value

bcd: temperature and solid/solvent ratio and the rest of factors in their low value

acd: time and solid/solvent ratio and the rest of factors in their low value

abcd: all factors were in their high value.

* With mixing means that rpm = 200

From the statistical investigation it's found that only the degree of mixing of 200 rpm was significant, this is due to rapid contact of the solvent with the solute inside the batteries. Other factors of time, temperature and solid/solvent ratio were non-significant and they were used at their low level as shown in table (4.4).

Table (4.5): Concentrations of chromium six at different factors and their significance.

The factor	N	mmean	Std.devition	Std.error mean	Gnificant
Solvent/liquid ratio **Concentration:** **Low** **High**	 8 8	 42.56 44.25	 8.44 9.23	 2.98 3.26	 **NS***
Temperature **Concentration:** **Low** **High**	 8 8	 42.88 43.94	 8.40 9.32	 2.97 3.29	 **NS***
Time **Concentration:** **Low** **High**	 8 8	 41.69 45.12	 8.48 8.91	 2.99 3.15	 **NS***
Degree of mixing **Concentration** **Low** **High**	 8 8	 35.62 51.19	 1.97 3.98	 0.699 1.40	 **Sig**

*: Not significant

4.6 Concentration of the dichromate

Having statistically determined the factors that affect the process of leaching, leaching was carried out according to the statistical analysis shown in table 4.4 . The solution of dichromate was concentrated in a crucible.

4.7 Reduction of Sodium Dichromate to Basic Chromium Sulphate

Sulphuric acid was used in the reaction of sodium dichromate with sugar to produce basic chromium sulphate. Sugar was used as a reducing agent; the reaction was as shown in equation (3.4).

Basic chromium sulphate was produced gradually over three hours. To measure the reaction rate, a sample of the chrome liquor was taken every 10 minutes until complete reduction. The concentration of the chrome liquor as chromic oxide was determined using the hydrometer (Baume). The composition was obtained using a calibration chart as shown in fig (4.2). This calibration chart was determined using chromsal B as standard sample.

The correlation model is: $y = 0.705 \, x - 0.185$.................................4.2

The conversion was = 250 – 8 / 250 × 100 = 96.8%

Where:

250 gm of dichromate was used.

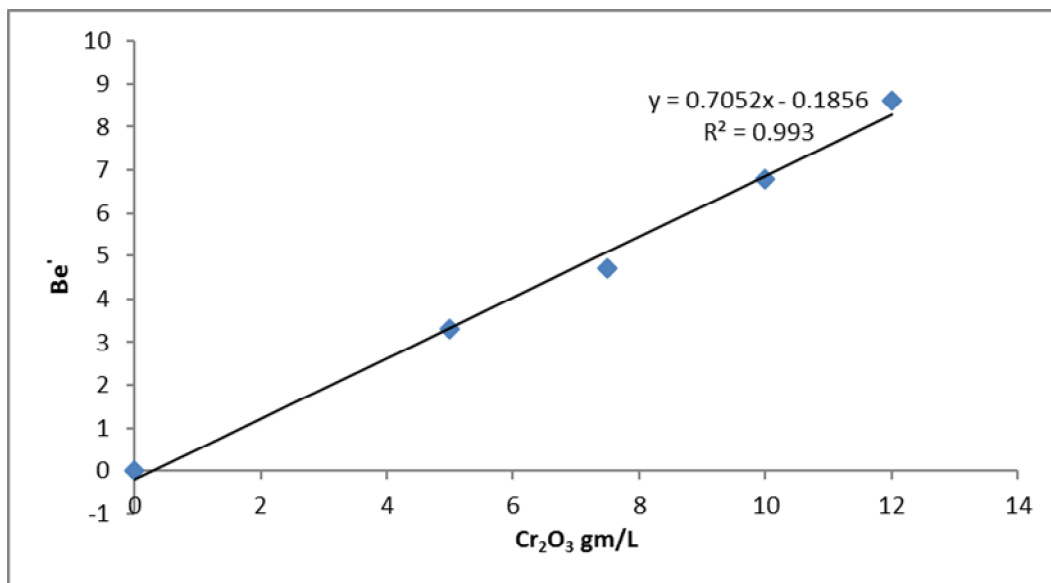8   gm of dichromate was left unreacted.

Fig (4.2):calibration and correlation of chromic oxide Vs degree Boume

In the process of reduction the chromic acid mixture yielded oxygen that oxidized the reducing agent ($C_6H_{12}O_6$) producing unstable (CO_3) and the hexavalent chrome in the form of CrO_3 in the dichromate was reduced to trivalent form as follows

$12CrO_3 + C_6H_{12}O_6 \rightarrow 6Cr_2O_3 + 6\ CO_3 + 6H_2O$ 4.1
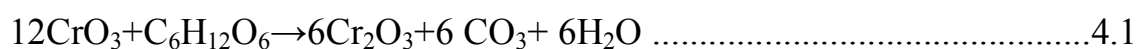
The chromic oxide thus formed combined with concentrated H_2SO_4 to produce basic chromium sulphate (Cr2 (OH)$_2$ SO$_4$) of 33% basicity.

$Cr_2O_3 + 2H_2SO_4 \rightarrow 2Cr\ (OH)\ SO_4 + H_2O$ 4.2
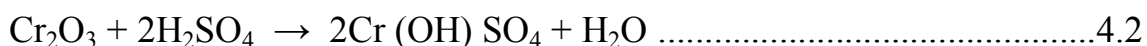
The conversion was found to be 96.8% indicating that 3.2% of chromium six was left in the liquor of basic chromium sulphate, to raise the conversion from 96.8% to 100% the chrome liquor was aged for two weeks and the chromic oxide was measured every week. The result was that 100% conversion was obtained, and hence no chromium VI was found in the produced basic chromium sulphate.

Hence ageing is very important due to the environmental effect of chromium VI produced in the process of reduction. Therefore the

reduction- oxidation reaction should be carefully observed to be free from chromium VI as chromium six is toxic and carcinogenic. It is found that ageing of the basic chromium sulphate liquor completed the conversion to 100 % therefore eliminating the presence of chromium six.

The result from the process of reduction gave the best percentage basicity (33%) and chromic oxide of 21% which are acceptable compared with the usual concentration.

4.8 Tanning processes

The chrome liquor produced was used in tanning trails in wet-blue, retannage and drying to crust. The pelts and crust were subjected to chemical and physical analysis.

Table (4.6) Applied Process Recipe of Tanning Processes

Material	%	Quantity Kg	Duration Min	Remarks
Float	100	15	30	
Reduced chrome liquor	10	1.5	240 left overnight	pH 2.8
Sodium bicarbonate	1	0.15	120	pH 5.5 piled 24 hours
Mimosa	10	1.5	240	
syntan	10	1.5	240 left overnight	
fatliquor	5	0.75	240	Paste-dried

4.9 Chemical analysis of the leather produced

Shrinkage temperature, chromic oxide, total ash, moisture and fat content were measured using standard method [40], and the results showed acceptable properties compared with standard results as shown in table (4.5).

Table (4.7): chemical analysis of the leather produced

Item	Values
Shrinkage temperature ^{o}C	100
Chromic oxide%	4.4
Total Ash %	4.6
Moisture %	14
Fat and oils%	3.4

4.10 Physical analysis

Samples for physical testing were cut and conditioned as per the official methods of analysis (Official methods, 1996), temperature of 20 ± 2 ºC and the percent relative humidity of 65 ± 2 for 48 hours. The physical properties of the crust leathers were measured as shown in Table (4.6). The physical testing results showed that the method of reduction was 100% conversion. The tensile strength, elongation at break, tear strength and load at grain burst are very good and were within the standards.

Table (4.8) Physical analysis of the crust leathers

Item	Values	Standards
Tensile strength(kg/cm2)	171	150
Elongation (%)	49	20-50
Tear strength (kg/cm)	100	80
Load at grain burst (kg)	40	20

The analysis of chrome shavings showed that 36 % of the chrome tanned pelt was removed in the shavings process. Thus a tannery producing 10 tons of wet blue per day would get chrome shavings of 3.6 tons of shavings per day. The analysis also showed that 2.75% chromic oxide content accompanied the chrome shavings, which is equivalent to 99.0 kg per day. This is a considerable amount of chromium III that is wasted to the environment and may be transformed to chrome VI which affects people, animals and the environment.

The leachability of chromium III was 95 % thus 95.5kgs of chromic oxide was recovered. This amount is equivalent to 250 kg of chrome powder of 26% chromic oxide. This amount justified the leaching and processing of chrome shavings and recycling it for chrome tannage.

It is concluded that chrome shavings instead of being taken by brick makers and producing chromium VI, it must be incinerated and reduced to basic chromium sulfate which can be recycled for chrome tannage. The heat liberated in the incinerator can be used to make hot water for fatliquoring and drying processes. The environment is thus protected from any possibility of disposing chromium VI which is toxic and carcinogenic.

Chromium is normally nontoxic in the trivalent state, but the research studies indicate the oxidation of the trivalent chromium to the hexavalent state, that is recognized to be highly toxic, carcinogenic, mutagenic and teratogenic for mammals including humans. Chromium is a valuable resource and its extraction and reuse is environmentally friendly. In the present study, it is seen that the reduction of chromium VI to chromium III is the better way for protecting the environment from the contamination with hexavalent chromium. The completion of reducing dichromate through ageing showed no appearance of chromium VI in the basic chromium sulphate produced. The reducing agent i.e., sugar, can be

replaced with molasses from sugar cane industry, which is cheaper and available.

Also in the present study, an attempt has been made to produce upper leather using tanning process based on reduced chrome liquor. It is seen that tanning system with reduced chrome liquor resulted in leathers with shrinkage temperature of $100^{o}C$ giving a complete tannage.

Chapter five

Conclusions and Recommendations

5.Conclusions and Recommendations

5.1 Conclusions

It is observed that the chrome shavings of wet blue leathers constitute 36% of the shaved pelt, it's also known that the chromic oxide content in wet blue is about 2.5% based on the wet blue pelt weight. From these fact the chrome shavings which is thrown out to the tannery premises with considerable amount of chromium III, these chrome shavings were taken by brick-makers and incinerated producing chromium VI which is toxic and carcinogenic.

The aim of this research is to collect the chrome shavings and transform chromium III to chromium VI. The produced chromium VI is reducing by molasses to basic chromium sulphate which is recycled for chrome tannage.

The heat generated during incineration it can be use to make hot water for retannage and dying. These methods save some of the chrome and protect the environment and if the chrome shavings in all tanneries in Khartoum was collected, incinerated and reduced to basic chromium sulphate, there will be saving in chemicals and there will be protection of the environment.

5.2 Recommendation

1- It is recommended that chrome shavings at any tannery in Sudan should not be allowed to be taken for incineration for whatever reasons.

2- To raise the quantity of basic chromium sulphate produced from chrome shavings, chrome shavings should be blended with an

appropriate amount of chromite's to be obtained from the area where the chrome ore is available (Angassana) .

3- A feasibility study has to be carried out to see the economic visibility of the production of basic chromium sulphate, from a xblended shavings and chrome ore, barring in mind that the heat produced by chrome shavings will be enough for heat required for the roasting process, which is necessary to convert chrome ore to sodium chromate.

4- The kinetics reaction rate and design of the reactor for chrome roasting and reduction should be studied and designed.

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