CLEAN TECHNOLOGY BY RECYCLING OF SPENT SOLUTIONS OF TANNERY LIQUID WASTE

E.Tambal and G.A. Gasmelseed

Email: elsheikhtambal@yahoo.com

Email: gurachigar@hotmail.com

المستخلص

يلاحظ أنه عبر السنين كانت مخلفات مياه المدابغ عبئا كبيراً ومؤثراً في زيادة التكاليف الكلية سواءاً كانت الجلود في مرحلة الحفظ أو مرحلة الدباغة بالكروم أو شبه مصنعة جافة أو مشطبة. بعد الثمانينيات وضعت قوانين صارمة لتحديد نوعية ونقاء مخلفات المياه التي تصرف إلي المجاري. غير أن كمية المبالغ المالية العالية المفروضة لمعالجة هذه المخلفات أجبرت كثيراً من المدابغ أن تغلق. ومع زيادة صرامة القوانين البيئية والمطلوبة، كان علي المدابغ أن تخفض حمل التلوث في مخلفات مياه المدابغ إلي الحد الأدنى. وقد تم ذلك بمعالجة مخلفات مياه المدابغ حيوياً بتكاليف كبيرة حيث لا يوجد دخل في نهاية الأمر من هذه المعالجات. لهذه الأسباب فإن إسترجاع مياه المدابغ المستعملة من عمليات مراحل البلل وحتى مراحل إعادة الدباغة كانت موضع هذا البحث وتطبيق عمليات الإسترجاع. أدت الدراسة إلي توفير ملحوظ يعادل 75% وحوالي40% في الماء والكيماويات علي التوالي مع حماية البيئة من هذه المواد الملوثة. وعليه فإن الإسترجاع يؤدي إلي توفير الكيماويات ويقلل تكاليف الإنتاج وقد كانت الجلود المصنعة بالمياه المسترجعة والمكملة بالمواد اللازمة جيدة الخواص الفيزيائية والكيماوية حيث كانت قوة الشد تعادل 200 كيلو جرام لكل سنتيمتر مربع والإستطالة عند كسر طبقة الحبيبات تعادل نفس قوة الشد للجلود المنتجة بالطريقة العادية وعند تمزق الحبيبات تعادل نفس رقم الجلود المنتجة بالطريقة العادية تقريبا .

وعليه نوصي بتطبيق استرجاع مخلفات مياه المدابغ بعد الإستعمال خلال عمليات البلل وحتى إعادة الدباغة. إن عمليات الإسترجاع تؤدي إلي تخفيض التكاليف الكلية كما يكون هنالك توفير في المواد الكيماوية مع توفير بيئة نظيفة.

Abstract

Over the years, treatment of tannery waste-Water put a considerable burden on the total cost of production, be it pickled, in wet-blue, crust or finished leather. After 1980 a very stringent regulation has been imposed on the quality and purity of the waste waters that go to the drain. The high amount of money charged for effluent tannery waste-water, lead most of the tanneries to close down, With increasingly stringent environmental requipments, it has become necessary to reduce the pollution load in waste-water to a minimum. This has been done by treating tannery waste-water biologically with expensive undertaking as no income or revenue is obtained at the end. For these reasons, recycling of spent solutions from soaking through retannage has been applied in this work with a considerable saving of, chemicals and water, as well as protection of the environment of these polluting chemicals. Hence recycling saves chemicals and reduces the cost of production. The leather that processed using recycled solution that adjusted with a make-up showed a comparatively good physical and chemical properties. The tensile strength obtained is acceptable, the elongation at grain crack is very good, the load at grain burst is also acceptable. In conclusion it is recommended to apply recycling of tannery used solutions from soaking through retanning processes. The total cost will be reduced, then there will be saving in chemicals and clean environment.

Keywords, Recycling clean production, zero liquid waste

Introduction:(8)

The Sudan is a large country in Africa and rich in live stock population. It is estimated to be 142 million heads of Cattle, Sheep, Goats and Camels.

Due to the races, tropical conditions and grass, the qualities of skins are suitable for the production of garment, gloves, shoe and industrial leather goods.

Hides and skins are available as a result of slaughtering animals for meat. hence hides and skins are by-products of meat industry.

Statistics of annual availability and animal population estimated from 1990 to 2010 as total of 140.000 heads of sheep, goats, cattle and camels. While the estimated annual Production of hides and skins are 20 millions.

There are about 20 working tanneries most of them are small tanneries. Most of the tanneries are facing problems such as low capacity utilization, high cost of production, non-availability of liquid money-and low quality of produced leather; they are consuming a big volume of raw hides and skins. The local tanneries are tanning low quality of raw skins and hides.

The leathers produced in the modern and rural tanneries satisfy the local market and they export part of their production as semi processed leather. Those tanneries use tanning materials such as chromium, aluminum salts as well as zirconium, iron salts and vegetable tanning materials, in addition to dyestuffs, oil and fats which are very polluting if drained.

Those tanning materials, chemicals in the effluent if drained without treatment will create health problems to human beings, plant, animals and land. To treat such effluent will cost a lot of money and will increase the cost of production, hence this research work the method of recycling from soaking through retannage will be investigated. This is proposed to save water, chemicals and protect the environment. This procedure will be performed through experimental work on pilot and mass production.

objectives:-

1. To protect the environment from tannery waste.
2. To reduce cost of chemicals and water through recycling of the effluent.
3. To cope with the trend of clean technology in Sudanese tanneries.

Methodology:

Raw Materials(4)

Dry salted raw cattle, sheep and goat skins were used in the following processes, the reagents used for soaking and unhairing are

- Lime (65% ealcium hydroxide).
- Sodium sulphide flakes (62%).
- Soap and preserving agent for soaking process.

UNHAIRING AND LIMMING:(1)

First the skins are soaked properly and then unhairing and limming were carried out.

Deliming and bating:(1)

The PH value of limed pelts is 12.5 to 13.0 by deliming action the PH is lowered to the range of 8.2 – 8.4 to let the skills ready for the bating and pickling process.

Method of sulphide determination (idometric method):(2)

Method of Determination of Calcium (5)

A nalysis of deliming agent(5)

Chemical Analysis of leather:

Sampling location for Skins(5)

Determination Of Moisture(3)

Determination Of Ash Content(5)

Determination of fat content:(5)

Determination of skin substance by total kjeldhal nitrogen analysis(5)

Physical Analysis:-

Preparation of sample (5)

Measurement of Thickness(5)

Measurement of Tensile Strength and Percentage of Elongation:

Tensile Strength(5)

percentage of elongation at break(5)

The recycling Experimental procedure:

chrome tannage recycling:

The standard fresh recipe was applied, after basification and after satisfactory boiling test, the pelts were unloaded and the spent chromium solution was filtered, collected in holding tank and analyzed for cr_2o_3 content. The once – used chrome solution was pumped to the drum already loaded with pickled pelts with addition of fresh make-up chrome. The pelts were tanned, basified and the spent solution is sent to the holding tank. The same was repeated seven times.

The same procedure was applied to all wet processes from soaking through retannage.

Results and Discussions:

Recycling of tannery effluents starting from soaking up to retannage has been carried out in the incubator of Sudan University of Science and Technology.

The incubator consists of a small tannery, chemicals and physical experiment laboratory as well as a workshop for shoe making.

48 sheep,48goat and 24 cattle hides as well as tanning materials.

The skins were soaked and left over night. Next day the skins were drummed for 15 minutes and unloaded.

The process of dehairing and bating:-

In this process of dehairing and liming, 4% of sodium and 4% of lime were used.

The skins were plumped and the hairs removed completely at PH = 12.0,

the spent lime solution was separated and reused.

The average liquor was 2% sodium sulphide and 2% lime make- up to increase the concentration similar to that of the fresh liquor.

The adjustment of used liquors with 25% water based on soaked weight of the raw skins, agrees with the fact that the conventional swelling requires about 20-40% water absorb by skin to open up fiber bundles, It is conclude that the extent of hair removal is 100% for conventional and recycled pelts. There is no significant difference in the swelling between conventional and recycled methods.

Table (4.1) shows comparison in % of chemicals and water added to fresh and used liquors.

The process of deliming and batings:(1)

After the process of unhearing and liming the skins are fleshed by machine to remove the flesh, trimmed and splitted if required.

The PH will be 8 – 8.5 which is favorable for enzyme activity. About 0.6% of bating agent is added and after 45 minutes, the operation is completed. The solution was filtered and recycled 7 Folds.

The process of pickling:(6)

Pickling is the process of treating delimed and bated skins with a mixed solution of acid and salt to bring them into an acid condition.

4.6 The process of chrome tanning:

As residual chrome from tanning operation acts as a considerable pollutant in waste waters, it is necessary to remove it prior to drainage. For reasons of economy and saving chrome can easily be used and recycled to reduce the cost of production of leather :

This can be achieved in two ways:

1. Chrome precipitation
2. Recycling of chrome

4.6 .1 Chrome precipitation (7)

Chrome can be separated from spent floats by precipitation in the form of chromium hydroxide by the addition of an alkali such as sodium hydroxide or $Na_2 Co_3$ The sludge is filtered and the cake obtained is redisolved using H_2So_4 The liquid can be stored in a reservoir from which it can be used the next day. The H_2So_4 added should be calculated to obtain a liquid of determined basicity.

Recycling of chrome (10)

The collected filtered used tanning chrome liquor may be utilized in different ways.

1. As a float in pickling bated pelts:

The spent chrome solution was acidified to lower the PH to 1.5. Then spent chrome used as a float for pickling. Salt was adjusted to avoid swelling. The spent float of chrome was mixed with sulphuric acid, formic acid and sodium chloride in a mixeding tank and pumped into the drum containing the bated skins and drum for 90 minutes, 6% of charmosal powder 33% basicity 26% chromic oxide is added and the process was then proceeded as normal.

2. As a source of high bascity chrome salt (for normal picked pelts)

Table (1): Chemical analysis of fresh and used lime- sulphide liquors.

PH	Calcium Hydroxide (mg/l)	Sodium sulphide (mg/l)	Item
13.2	520	520	Fresh Lime
12.0	260	260	Used Liquor

Discussion of the results

Results obtained from chemical and physical analysis of crust and finished leather processed by recycling method are similar to leather processed by conventional methods.

The tensile strength and percentage of elongation results are satisfactory. The flexibility of leather as well as the feel and the break acceptable. The quality of leather is acceptable and almost identical to leather produced by conventional methods.

In addition to this advantage of good quality there is a save in tanning materials and chemicals used in the processing of leather, almost by 50% this means the cost of production is cheaper compare to conventional method.

This means the selling prices of finished leather will be cheaper. This will promote the marketing. .

Conclusion and Recommendation

Conclusion:

The process of recycling tannery effluent is carried out to process hides and skins to finished leather proved to be possible. The leather produced by this method of recycling is of good quality and very similar to the leather produced by conventional methods.

This conclusion is based on physical and chemical analyses of the leather and on visual assessment. The feel of the leather is soft, of good quality and can be used as shoe upper, garment, gloves, industrial leather and other types of leathers.

There is saving in tanning materials, chemicals used in the processing of leather as well as saving in the water used in tanning processes. The environment is also protected from these harmful chemicals.

5.2 Recommendation:

It is recommended to introduce the recycling process of the tannery effluents in sudanese tanneries for the following advantages over the conventional methods:

1. The quality of leather produced by this method of recycling is almost similar to the one produced by conventional method and the quality is good and acceptable.

2. The cost of production is less than the cost of the conventional method due to saving in tanning materials and chemicals used.

3. Less water is used in the processing of leather which means less waste effluent.

4. No additional machines and equipment are required to introduce the recycling in the tanneries except filters, pumps and pipes.

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Table (1): Recycling of lime solution

Cycle No	PH	Hair removal	Degree of Swelling	
1	12.7	Complete	40	
2	12.5	Complete	38	
3	13.0	Complete	38	
4	12.9	Complete	35	
5	12.6	Complete	33	
6	12.5	Complete	37	
7	12.7	Complete	40	

Table (2):Deliming

Cycle No	PH	Finger print	Relaxation	6Completeness
1	8.0	permanent	flat grain	Colourless to phenolphthalein
2	8.2	permanent	flat grain	Colourless to phenolphthalein
3	8.0	permanent	flat grain	Colourless to phenolphthalein
4	8.5	permanent	flat grain	Colourless to phenolphthalein
5	8.3	permanent	flat grain	Colourless to phenolphthalein
6	80	permanent	flat grain	Colourless to phenolphthalein
7	8.4	permanent	flat grain	Colourless to phenolphthalein

Table (3):Chrome tannage :-

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

Table (4):Retannage :-

Cycle No	PH	Exhaustion		
1	4.8	clean solution		
2	5.0	clean solution		
3	5.2	clean solution		
4	5.5	clean solution		
5	5.0	clean solution		
6	4.9	clean solution		
7	5.0	clean solution		

Table (5):Physical Testing Of The Leather After The 7th Cycle: Sheep Skin :-

Batch No	Thickness, mm	Tensile strength Kg/cm2	Load at grain crack / Kg	Elongation at grain break	Load at burst /Kg
1	1.2	180	35	40	38
2	1.1	200	34	42	40
3	1.2	190	33	45	39
4	1.0	200	40	39	41
5	1.1	190	32	44	37