RECYCLING OF SPENT SOLUTIONS OF TANNERY LIQUID WASTE

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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 requirements, 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 40% and 75%, chemicals and water, as well as protection of the environment from these polluting chemicals as compared with the standard process without recycling.

The treatment of tannery waste-water is done through addition of the required materials to each process and recycling of the spent solution. After the process is completed the pelts are unloaded, the once-used solution is topped up with the required make-up and reused. The process of recycling is repeated seven times from one batch to another. By this method of recycling there will be saving in water, chemicals and protection of the environment.

The leather processed using recycled solution adjusted with a make-up showed comparatively good physical and chemical properties. The tensile strength obtained is acceptable, and the elongation at grain crack is very good, the load at grain burst is also 200kg/cm2. The elongation at grain crack is equal to the tensile strength.

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: *Tannery Waste, Spent Solution, recycling.*

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 مخلفات مياه المدابغ المستعملة في مراحل البلل والعمليات حتى مراحل إعادة الدباغة كانت موضوع هذا البحث وقد تمت معالجتها بطريقة إضافة المواد المطلوبة في كل عملية وتدويرها بعد إنتهاء عملية الدباغة وتفريغ البراميل من الجلود ويستعمل المزيج المسترجع وتكمل المواد حسب الخلطة اللازمة وتستمر العمليات بنفس الطريقة من دفعة إلي الأخرى سبعة مرات وهكذا حتى مراحل إعادة الدباغة.

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 وقد كان التوفير في الكيماويات والماء 40% و 75% على التوالي بالاضافة الى حماية البنية من هذه المواد الملوثة .

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.

Introduction:

Sudan is one of the Largest Countries in Africa and rich in live stock population. It is estimated to be 142 million heads of Cattle, Sheep, Goats and Camels [(1)]. Due to the races, tropical conditions and grass, the quality of these animals' 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 140,000000 heads of sheep, goats, cattle and camels. in Sudan while the estimated annual production of hides and skins are 20 millions,[(1)].

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 [(2)].

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[(3)].

Over the last decade a lot of work has been undertaken seeking recycling of liming and chromium. Although previous investigations were able to reduce the chromium content below 1 mg/L through precipitation in a conventional tannage, the solid precipitate which contains a considerable amount of chromium remains a problem. A great deal of research data on different precipitation systems and their efficiency exists concerning chromium minimization and COD reduction, but the solid precipitate containing high chromium levels still needs to be treated. An improvement has been achieved through application of high exhaustion tannage followed by precipitation, and although high exhaustion is not economically feasible, the solid precipitate which results still has to be treated to meet the stringent legislations. The application of ion-exchange and membrane-separation have also been investigated, however the separated chromium is still to be removed. Recently research work has been carried out on chromium replacement using combination tannages of vegetable tannins and aluminum salts, but the desired physical. Chemical, properties, handle, strength and chrome leather characteristics are not given by these tannages [(4)].

On the other hand all works on liming recycling, paint unchaining and hair destruction face a problem of filtration and blocking of filter presses.

In this work the recycling starts from the processes of soaking through retannage. The solution was allowed to settle and the sludge was collected and taken to land-fill, keeping the clean solution for recycling. The new contribution of this work is the adoption of sedimentation, filtering for all wet processes in the tannery prior to recycling.

Those tanning materials, and 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 in 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 [(5)].

Objectives are:-

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

Methodology:

In this research all the work was carried out experimentally. The experiments were designed to recycle the spent solution from the process of soaking, liming, deliming, bating, pickling chrome tannage and retannage. The recipes applied were the normal rationalized recipes used in practice. The analysis was carried out by the official method of analysis reproduced by the JSLTC of U.K [5].

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 [6].

Table (1) below show the quantities of Chemicals added.

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 [7].

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

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

Table (1) shows comparison in percentage of chemicals and water added to fresh and used liquors.

The process of deliming and batings:

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 [8].

The process of pickling:

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. In this solution the chrome was added and the pelt, tanned in this pickling [9].

Chrome tannage recycling:

The standard fresh recipe was applied, after basification and after satisfactory boiling test, the pelts were unloaded retannage, as shown in the following figure:

and the spent chromium solution was filtered [10], 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 [11].

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

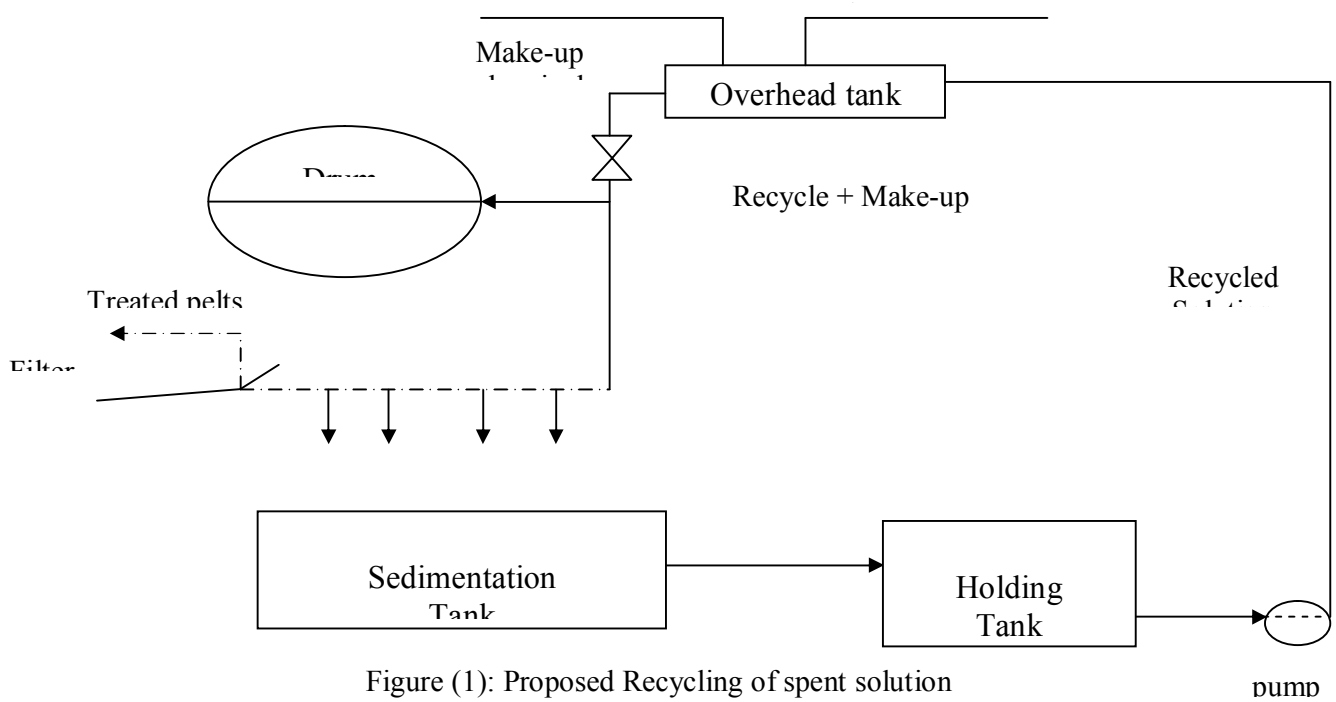

Figure (1): Proposed Recycling of spent solution

cheaper compared to conventional method [12].

This means the selling prices of finished leather will be, competitive a fact which will promote the marketing From the results obtained, (Table 2 through 6) the tanneries can operate the recycling system adopted in this research. Using such technique will minimize the load to the effluent treatment plant which is expected to work at a low capacity. Maintenance time and operation will be at a minimum level and waste-water from rinsing and washing will be much cleaner and can be used for irrigation of a green belt [13].

Experimental work

Discussion of the results:

Results obtained from chemical and physical analysis of crust and finished leather processed by recycling method are comparatively similar to the leather processed by conventional methods. The tensile strength and percentage of the elongation results are satisfactory. The flexibility of leather as well as the feel and the break are acceptable. The quality of the leather is acceptable and almost identical to leather produced by conventional methods. In addition to this advantage of good quality there is save in tanning materials and chemicals used in the processing of leather, almost by 50% this means the cost of production is

Table (2): 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 (3):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 (4): 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 (5):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 (6): 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/mm	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

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 [14]. 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 [15]. 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 [16]. 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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