An Eco-Friendly Tanning by Aromatic Sulphonic Acids for Enhancing Chrome Absorption and Reducing the Negative Impact on Environment

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ABSTRACT:

This study was carried out for reducing the environmental effects of chromium and sodium chloride resulting in leather tanning process through salt-free pickling, which is considered as the most important way in reducing pollution of sodium chloride in process of chrome tanning. Two aromatic sulphonic acids (naphthalene sulphonic acid and phenol sulphonic acid) were prepared by sulphonation reaction. Thirty sheep pelts were used in tanning process and divided into ten groups where each group contains three pelts. Group 1 was tanned by traditional method as a control group. While the other groups tanned with prepared aromatic sulphonic acids and sulphonic acid in concentrations (2, 3 and 4%) from bating weight. The results showed that salt free pickling acids have ability to reduce total dissolved solids (TDS), chloride content and chemical oxygen demand (COD) compared to traditional method. Also, results indicated that utilization of sulphonic acid with concentration (4%) enhanced chrome exhaustion from 79.62% to 90.10% and reduced Cr (III) in spent liquor from 6.63% to 2.83%. It had no bad influence on the quality of the finished leather as well and was suitable for using in leather manufacturing.

Keywords: Salt-free pickling; Chrome tanning; Chemical oxygen demand (COD); Naphthalene Sulphonic; sulphonic acid; Total dissolved solids (TDS).

INTRODUCTION

Chrome tanning is one of the most effective and vastly used tanning procedure in manufacture of leather due to the excellent characteristics of their tanned leather such as good physical and mechanical strength, high hydro-thermal stability, nice handing quality and reducing time consuming. These properties cannot be achieved by using other materials of tanning (Zhang *et al.*, 2016), Leathers tanned by chrome were produced for many decades in commercial scale (Sumita *et al.*, 2015). In traditional methods of tanning leather industry, pickling based on the utilization both of sulphuric acid as well as sodium chloride, the spent tanning liquor is loaded with many pollutants such as chlorides, chromium, sulphides and total dissolved solids. These pollutants may lead to environmental pollution (Rao *et al.*, 2004).

Salt, especially sodium chloride with concentration about from 6 to 8% of limed pelt weight can be used before pickling step to prevent skins/hides swelling due to the acid's presence and low pH. Therefore, the spent tanning liquor contained about 20,000 mg/L chloride (Sumita *et al.*, 2015). In fact, according to a recently conducted survey, about 300,000 tons of salt were used in all over the world in leather pickling process to make industry every year (Sundar *et al.*, 2013).

Environmental pollution is a global issue, particularly as a result of industry of leathers that produced large amounts of wastes to land filling. Chromium and chlorides in tannery influents are major environmental issues of leather industry. Treatment systems for removing chlorides from effluents are highly costly and have a significant impact on the tanning industry's viability (Sundar *et al.*, 2013). Long lasting and convincing solution to this problem rests on developing common salt free tanning system with high level of chromium exhaustion. The most common cause of salinity in tannery effluents is sodium chloride (Sundar *et al.*, 2013). Adding large amount of sodium chloride has detrimental impact on mechanical and organoleptic qualities of wet-blue leather. In addition, it causes pickling float to become unmanageable loading with salt effluent in traditional process of pickling. Wastewater discharging with excessive salinization levels would result in a loss in agricultural productivity and a rise in the cost of living in addition to the pollution of drinking water (Bajza and Vrcek, 2001).

Because chrome and chloride tanning agents are used in the process, chromium and chloride are the main contaminants. Salt-free pickling is considered to be an efficient technique for decreasing pollution of sodium chloride in process of chrome tanning and thereby lessen the environmental consequences of chrome tanning and chloride. Instead of formic acid and sulfuric acid, aromatic sulphonic acid products might protect pelts from acidic swelling without the need of NaCl (Bacardit *et al.*, 2008). The avoidance or removal of common salt during tanning has been the subject of extensive investigation. Previously, non-swelling acids such as naphthalene sulphonic acid condensates were used during changes of pH, recycling of pickle liquor and tanning material alteration have all been tried before (Li *et al.*, 2009). To decrease sodium chloride and limit chromium discharge, non-swelling acids are employed. They also guarantee the high quality and characteristics of chrome tanned leather (Zhang *et al.*, 2016).

Green chemicals are used in the tanning process, which can minimize or eliminate hazardous material production while also lowering COD and TDS. Chemical materials and procedures are less harmful to the human body and more ecologically friendly. Green chemicals do not only produce innovative processes that can replace old tanning methods, but they also enhance performance (Zhou *et al.*, 2018 and Gao *et al.*, 2019).

Therefore, the study amims to reduce the negative environmental impacts of sodium chloride and chromium salts resulting from the traditional tanning process by adopting alternative environmentally friendly systems, reduce liquid wastes generated during leather tanning, improve leathers' physical and chemical properties and increase its manufacturing efficiency.

MATERIALS AND METHODS

The experimental study was carried out in Leather Tanning Technology Center in Robbiki Leather City, Cairo, Egypt and Desert Research Center (DRC), Cairo, Egypt.

Materials:-

Thirty sheep pelts were used in this experiment.

Naphthalene, phenol, sulfuric acid, mesitylene, chromium sulphate basicity 33%, sodium chloride, sodium bicarbonate, formic acid and the other tanning chemicals were used in subsequent operations were commercial grade products such as black dye and fish oil.

Methods:-

Preparation of salt free pickling acids (aromatic sulfonic acids) used in the pickling process: -

Naphthalene sulphonic acid preparation:-

Naphthalene sulphonic acid was prepared according to (Zhang *et al.*, 2019). In brief, thirty grams of naphthalene has been added to a three necked flask and also heated at 137 ºC. This mixture has been stirred by using an electric stirrer at the same time. Concentrated sulfuric acid (98%) of 14.5 mL has been added to the flask drop by drop.

Phenol sulphonic acid preparation:-

Phenol sulphonic acid was prepared according to (Ma *et al.*, 2019) as follow:

Phenol sulphonic acid was prepared by phenol dissolving into mesitylene and moved into reactor. After that, concentrated sulfuric acid has been added to solutions drop by drop for keeping concentrated sulfuric acid concentration for being a constant during the reaction course.

Fourier transform infrared spectroscopy (FTIR): -

The structures of naphthalene sulphonic acid and phenol sulphonic acid were characterized by Fourier transform infrared (FTIR-ATR). FTIR-ATR spectra were recorded on KBr pellets using Bruker vertex 80 in the range 400-4000 cm^{-1} with resolution 4 cm^{-1}. KBr pellets were prepared by gently mixing 1 mg sample with 100 mg KBr (1:100).

Pickling and chrome tanning with different salt free pickling acids:-

The aromatic sulphonic acids were used in tanning sheep skins. Thirty sheep pelts were tanned with 100% water and 8% from pelts' weight of chromium sulphate basicity 33%. Pelts were divided into ten groups, 3 pelts in each group.

Bated pelts were pickled using these acids as follows:

G1 (Control): tanned with 1.5% sulfuric acid and 8% sodium chloride.

G2 (NSA 2%): tanned with 2% naphthalene sulphonic acid.

G3 (NSA 3%): tanned with 3% naphthalene sulphonic acid.

G4 (NSA 4%): tanned with 4% naphthalene sulphonic acid.

G5 (PSA 2%): tanned with 2% phenol sulphonic acid.

G6 (PSA 3%): tanned with 3% phenol sulphonic acid.

G7 (PSA 4%): tanned with 4% phenol sulphonic acid.

G8 (SA 2%): tanned with 2% sulphonic acid.

G9 (SA 3%): tanned with 3% sulphonic acid.

G10 (SA 4%): tanned with 4% sulphonic acid.

Wet blue leathers were stored for three weeks and then finishing steps were completed. Post-tanning steps were done at all tanned leathers according to (Kudit *et al.,* 2013) as shown as in table (1).

Determination of composite liquors in spent tanning liquors:-

Composite liquors from experimental leather processing and control have been collected from the chrome tanning. Liquors were analyzed for pickling and basification pH, chemical oxygen demand (COD), total dissolved solids (TDS), chloride content and spent chrome tanning liquors by using the standard procedures for the American wastewater Association method (AWWA, 1998).

Determination of physical and chemical properties for finished leather:-

Operational and qualitative properties of obtained leathers were assessed according to chemical analysis indices and physico-mechanical analysis of finished leather. Tensile strength, elongation, tear strength, thickness, moisture, ash, pH, fat and chromium content were analyzed according to ASTM (2014).

Statistical analysis:-

GLM procedure of SAS (2008) was used to analyze data of physical and chemical properties. This model was used in the analysis as following:-

$Yij = \mu + Ti + eij$

Where Yij is the observation taken on finished leather, μ is overall mean, Ti is a fixed effect of the i^{th} tanning groups and eij is the random error assumed to be normally distributed with mean=0 and variance=σ^2e.

RESULTS AND DISCUSSION

Characterization of naphthalene sulphonic acid and phenol sulphonic acid:-

An unknown molecule's chemical structure and/or bonding can be determined using FTIR-ATR. Figure (1) is the FTIR-ATR spectrum of naphthalene sulphonic acid:-

The peaks at 3449 cm^{-1}, 3358 cm^{-1}, 3311 cm^{-1} and 3153 cm^{-1} are assigned to -OH stretching vibrations. At 2861 cm^{-1} and 2586 cm^{-1} the peaks are assigned to C-H and C-H_2 vibrations. At 1695 cm^{-1}, 1658 cm^{-1} and 1557 cm^{-1} the peaks are assigned to aromatic ring characteristic absorption band. The bands at 1340 cm^{-1}, 1292 cm^{-1} and 1127 cm^{-1} are attributed to the stretching vibrations of the SO3 moiety. The peaks at 1042 cm^{-1} and 1015 cm^{-1} should be the C-H absorption. The peaks at 860 cm^{-1}, 822 cm^{-1} and 744 cm^{-1} are assigned to the isolated hydrogen from benzene ring. It can be illustrated that the typical absorption peaks of sulphonic acid group are shown at 593 cm^{-1}, 530 cm^{-1}, 498 cm^{-1}.and 437 cm^{-1}.

On the other hand, Figure (2) is the FTIR-ATR spectrum of phenol sulphonic acid. It can be illustrated that the typical absorption peaks of sulphonic acid group are shown at from 415 cm^{-1} to 545 cm^{-1}. The intense band at 609 cm^{-1} and 683 cm^{-1} are attributed to the C–S aromatic stretching vibrations. The peaks at 756 cm^{-1} and 831 cm^{-1} are assigned to the isolated hydrogen from benzene ring. The peaks from at 974 cm^{-1} to 1088 cm^{-1} should be the C-H absorption. The bands from at 1117 cm^{-1} to 1321 cm^{-1} are attributed to the stretching vibrations of the SO3 moiety. At from 1435 cm^{-1} to 1679 cm^{-1} the peaks are assigned to aromatic ring characteristic absorption band. The peak at 2831 cm^{-1} is assigned to C-H and C-H_2 vibrations. The peaks at 3094 cm^{-1} and 3300 cm^{-1} are assigned to –OH stretching vibrations of phenol.

These results indicate the successful preparation of naphthalene sulphonic acid and phenol sulphonic acid. This is in agreement with (Nasr, 2011; Zhang *et al.,* 2017; Zhou *et al.,* 2018; Huang *et al*., 2019 and Wu *et al.,* 2020).

Impact of salt free pickling acids on chrome tanning:-

Naphthalene sulphonic acid, phenol sulphonic acid and sulphonic acid compared to the traditional method were used in the pickling process without adding any salts. This can be shown as follows:-

Effect of salt free pickling acids on chrome exhaustion:-

The chromium content was estimated quantitatively in exhaust liquor and tanned leathers in each group. Data in figure (3) showed that all treatments caused the reduction of Cr (III) in the spent liquor compared to control, but phenol sulphonic acid 4% and sulphonic acid 4% recorded the highest rate of the reduction in Cr (III) in the spent liquor, where the proportion of the reduction in Cr (III) were 52.45 % and 51.42 % for phenol sulphonic acid 4% and sulphonic acid 4%, respectively. This is in agreement with Zhang *et al.,* (2017) who explained that treatment with aromatic sulphonic acid decreased Cr (III) in spent liquor. Also, these results are near to results obtained by Zhang *et al.,* (2016) who reported that the concentration of residual Cr (III) in spent tanning liquor after pickling with phenol sulfone sulphonic acid (PSSA), naphthalene sulphonic acid (NSA), or naphthol sulphonic acid (NOSA) reduces Cr (III) in spent tanning liquor at least 60% compared to process of conventional pickling, temperature of shrinkage of tanned leather with corresponding chrome has also a little increase. The carboxyl and hydroxyl on benzene ring of sulfo salicylic acid molecular can coordinate with ion of Cr^{3+} according to (Song *et al.,* 2007) and also can form a hexatomic ring chelate. For this, the impact of stronger masking on ions of Cr^{3+} is achieved, that is not conductive to of Cr^{3+} ions combination with collagen.

Experimental leathers have a higher percentage of exhaustion of chromium compared to control leathers. Saravanabhavan *et al.,* (2003) demonstrated that the increased exhaustion of chromium may be because of carboxyl groups of collagen presence in a form of ions at a higher pH during the pickle entire course and basification free chrome tanning.

Effect of salt free pickling acids on composite liquor analysis:-

Pickling and basification pH were measured in all experimental groups. In general basification pH values were higher than pickling pH values as shown in figure (4). Values of pickling pH ranged from (2.30 to 4.10). The highest value was recorded by Sulphonic acid 2%, while control group recorded the lowest value of pH. On the other hand, values of basification pH ranged from (3.80 to 4.70). The highest value was recorded by Sulphonic 2% treatment, while control group recorded the lowest value of pH.

Also, figures (5, 6 and 7) illustrated that PSA 4% group showed the highest chemical oxygen demand (COD) values (2687.00 ppm). While, control group showed the highest values of total dissolved solids (TDS) and chloride content (45968.30 mg/L and 520.00 ppm) respectively. Chloride content, chemical oxygen demand (COD) and total dissolved solids (TDS) reduced by (96.0 %, 23.39 % and 72.42 % respectively) after being treated with salt free pickling. Thus, salt free pickling were more effective to reduce the negative effects of COD, TDS and chloride content on environment. Moreover, chlorides and total dissolved solids (TDS) reduction was because of eliminating of conventional pickling operation. But, chloride was eliminated completely from the waste streams. The decreasing of total dissolved solids (TDS) is about more than 70%. This was because of common salt elimination and also eliminating of pH steep differences (Sundar *et al.,* 2013).

This was in the same trend with Thanikaivelan *et al.,* (2003) who reported that the discharged large amounts from total dissolved solids (TDS) and chemical oxygen demand (COD) produced by pollution control boards in many countries were 2100 and 250 ppm respectively. It can be illustrated that to produce one ton of raw hides in processing of conventional leather, the allowed emission leads for total solids and chemical oxygen demand range from 52.5 to 105 and from a 6.25 to 12.5 kilograms respectively. Demand values of TS and COD for the control leather processing are higher than these of the experimental leather processing, despite of using low water in experimental leather processing. Reducing of total dissolved solids and chemical oxygen demand emission loads by the adopting experimental tanning process including soaking are 74 and 52%, respectively compared with control leather processing (Saravanabhavan *et al.*, 2003).

Our values are in the same trend with Rao *et al.,* (2004) who found that chemical oxygen demand (COD) of various leathers which were tanned by using naphthalene sulphonic acid and prepared by naphthalene sulfonation about from 2090 to 2640 ppm. But chloride values for the conventional treatment were 25000 and 24250 ppm, after that they reduced to 750 and 780 ppm. In addition, TDS reduced from 64550 to 21540.

Properties of chrome tanned leathers:-

Physical and chemical properties of tanned leathers by using various salt free pickling acids were presented in table (2 and 3).

Leather thickness did not differ significantly among all experimental tanned leathers. It was in a narrow range between 0.92 and 0.94 mm. That gave an indication to the similarity among traditional pickle chrome tanning method and salt-free pickling in the fullness effect with collagen. Table (2) shows that the differences among tensile strength valueswere highly significant. The minimum values were recorded with various concentrations of naphthalin sulphonic acid (119.00, 106.50 and 100.82 Kg/cm^2 for 2, 3, 4%, respectively). While, the maximum values (227.20 and 223.19 Kg/cm^2, respectively) were found in control and sulphonic acid 4 % group. These differences gave an indication to difference of salt free pickling acids in attracting collagen fibers.

Tear strength values of all tanned leathers were highly significant differed, which ranged between 11.91 and 24.15 Kg/cm. This indicates the different effect between traditional pickle chrome tanning method and salt free pickling acids on attracting collagen fiber bundles.

Elongation values differed significantly among of all tanned leathers in this study, which ranged between 39.97 and 71.90 %. Sulphonic acid 3% recorded the highest value of elongation (71.90 %) followed by sulphonic acid 4% which recorded (70.40 %). This referes to the different effect of salt free pickling acids and traditional pickle chrome tanning method on collagen fiber elasticity when using it in tanning leathers.

The moisture percentage, pH value and fat content did not differ significantly among all experimental tanned leathers. That might be due to the similarity in tanning steps for all groups.Table (3) shows that the differences among total ash values were highly significant. The trend of these changes was similar to that found with the changes of chromium content. The minimum value of total ash was noticed with naphthalin sulphonic acid 3% where it recorded (9.86%), while the maximum value was noticed with sulphonic acid 4 % where it recorded (12.13%). That might be due to the change of chromium content in different experimental tanned leather. Also, chromium contents differed significantly among all experimental tanned leathers. The minimum value was recorded with Phenol sulphonic acid 2%. While the maximum value was found with tanned leathers by sulphonic acid 4 %. These differences gave an indication to difference of salt free pickling acids in attracting collagen fibers and improving chromium absorption.

CONCLUSION

The results of the current study illustrated that the eco-friendly tanning process decreases pollution because of the impact of chromium and chloride salts by using salt free pickling process and therefor, participates in developing the clear tanning process. Sulphonic acid (4%) enhanced chrome exhaustion from 79.62% to 90.10% and reduced Cr (III) in spent liquor from 6.63% to 2.83%. Also, it is suggested that it had no negative influence on the quality of the finished leather and was suitable for using in leather manufacturing.

Generally, sulphonic acid with concentration 4% was more effective than NSA and PSA in reduction of the environmental impacts of Cr (III) in spent liquor, COD, TDS and chloride.

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Table 1: Tanning and post tanning steps recipe.

Step	Description		Time (min)	Notes
	%*	Added		
Pickling	150 8 1.5	Water Salt Sulphuric acid or untraditional methods	90	• Skins were drummed with water and salt for about 15 min then acids added gradually. • pH = 3.5 – 4 • Bé = 7 – 8
Tanning	8	Chrome sulphate	90	Chrome 33% basicity
Fixation	1	$NaHCO_3$	60	Overnight, pH = 3.8- 4.2
Washing	100 2	Water Soap	60	Drain float
Naturalization	100 2	Water $NaHCO_3$	60	pH= 5.5 Drain float
Dyeing & Fat liquoring	150 3 6	Water Black dye Fish oil	90	Bath temperature 40°C
Fixation	0.5 0.5	HCOOH HCOOH	30 30	Overnight
Washing	100	Water	10	Horse up - samming - dry hanging

* Percentages were calculated based on the pelt weight of the previous step.

Table 2: Physical properties of tanned leathers with different addition of salt free pickling acids.

Group	Physical properties			
	Thickness (mm)	Tensile Strength (Kg/cm2)	Tear Strength (Kg/cm)	Elongation (%)
Control	0.92	227.20[a]	24.15[a]	69.49[a]
NSA 2%	0.93	119.00[d]	12.73[d]	39.97[d]
NSA 3%	0.94	106.50[d]	14.85[Cd]	51.52[bcd]
NSA 4 %	0.92	100.82[d]	11.91[d]	46.16[cd]
PSA 2%	0.94	169.02[bc]	13.55[d]	67.06[a]
PSA 3%	0.94	134.49[cd]	14.89[cd]	57.47[abc]
PSA 4%	0.93	176.91[abc]	17.96[bc]	49.27[bcd]
SA 2%	0.94	188.22[ab]	19.98[ab]	62.59[ab]
SA 3%	0.93	177.80[abc]	21.76[ab]	71.90[a]
SA 4%	0.93	223.19[a]	22.34[a]	70.40[a]
SEM	0.015	23.478	1.951	7.037
Sig	NS	**	**	**

Means in the same row having different superscripts are significantly different (P<0.05).
*SEM: standard error of the mean, Significance: NS Not significant, * P<0.05, ** P<0.01*

Table 3: Chemical properties of tanned leathers with different addition of salt free pickling acids.

Group	Chemical properties				
	Moisture (%)	Ash (%)	pH (ml mol/L)	Fat (%)	Cr (%)
Control	17.26	10.09[c]	3.86	7.21	2.99[bcd]
NSA 2%	17.33	10.26[c]	3.92	7.52	3.09[bcd]
NSA 3%	17.20	9.86[c]	3.85	7.37	2.83[d]
NSA 4 %	17.35	10.38[bc]	3.89	7.41	2.93[cd]
PSA 2%	17.20	10.35[bc]	3.88	7.49	2.78[d]
PSA 3%	17.10	10.50[bc]	3.85	7.36	2.89[cd]
PSA 4%	17.14	10.35[bc]	3.88	7.41	3.18[bc]
SA 2%	17.00	10.20[c]	3.89	7.19	2.95[cd]
SA 3%	17.23	11.25[b]	3.90	7.23	3.32[ab]
SA 4%	17.02	12.13[a]	3.86	7.25	3.57[a]
SEM	0.771	0.411	0.049	0.372	0.144
Sig	NS	**	NS	NS	**

Means in the same row having different superscripts are significantly different (P<0.05).
*SEM: standard error of the mean, Significance: NS Not significant, * P<0.05, ** P<0.01*

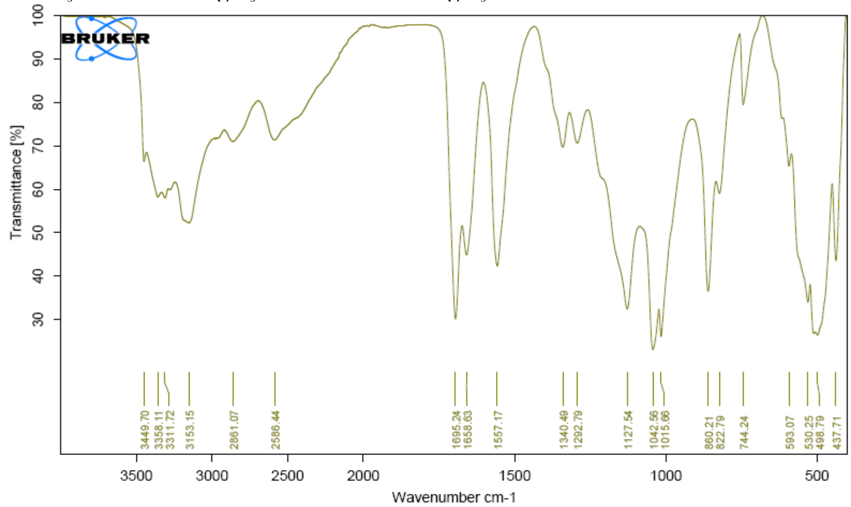

Figure 1: FTIR-ATR spectrum of naphthalene sulphonic acid.

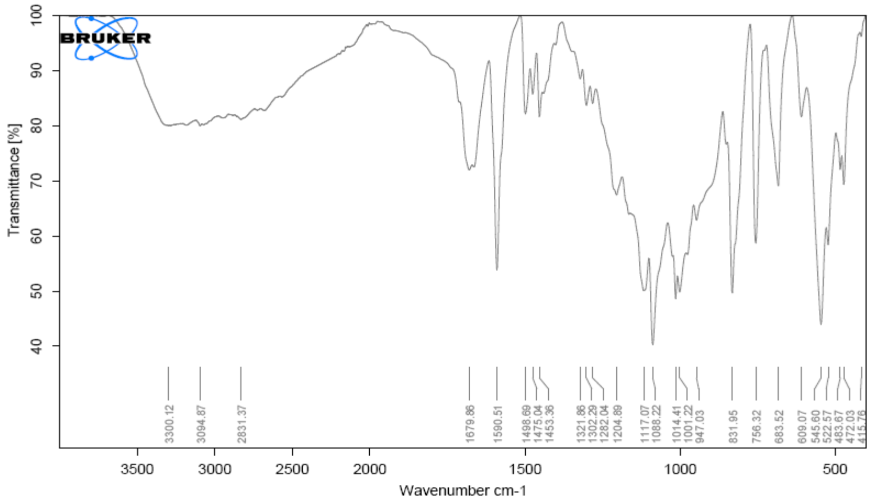

Figure 2: FTIR-ATR spectrum of phenol sulphonic acid.

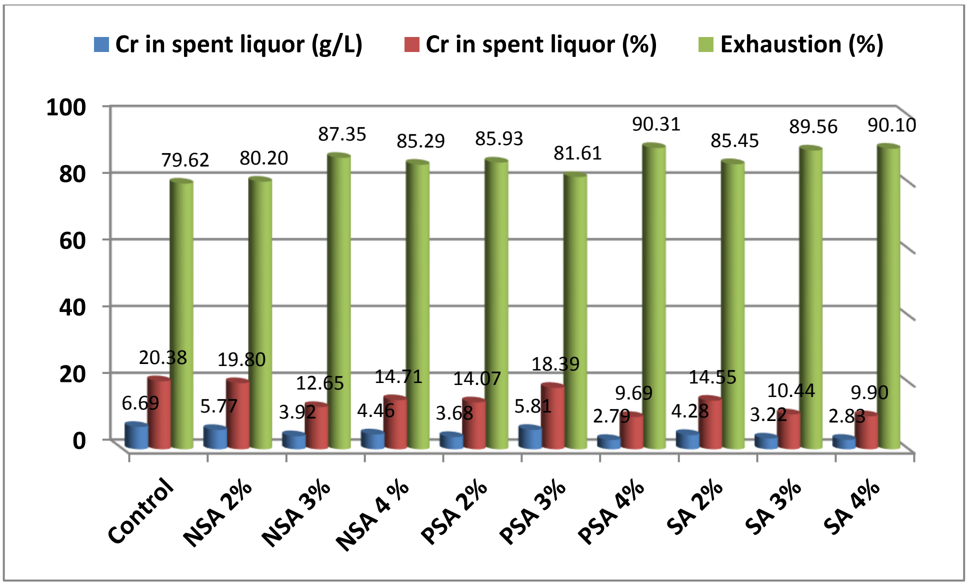

Figure 3: Effect of salt free pickling acids on chrome in spent liquor (g/L), chrome in spent liquor (%) and Exhaustion (%)

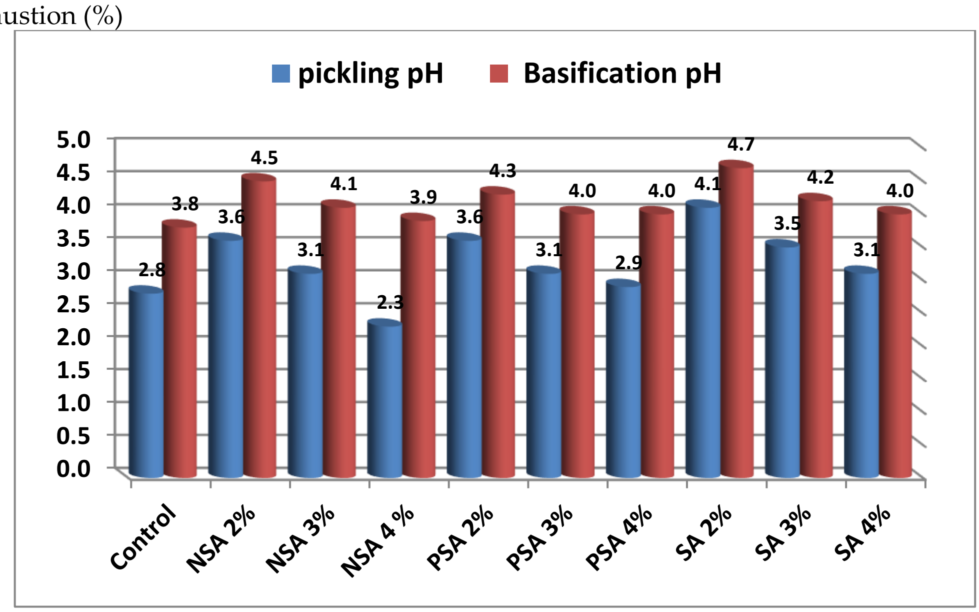

Figure 4: Effect of salt free pickling acids on pickling pH and basification pH.

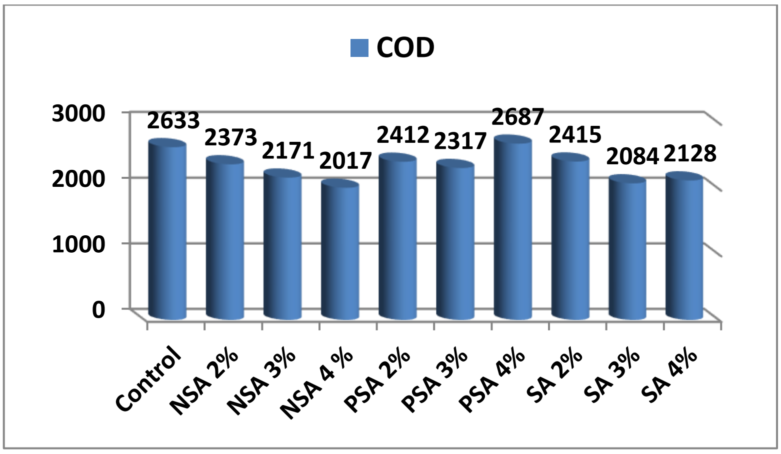

Figure 5: Effect of salt free pickling acids on chemical oxygen demand (COD).

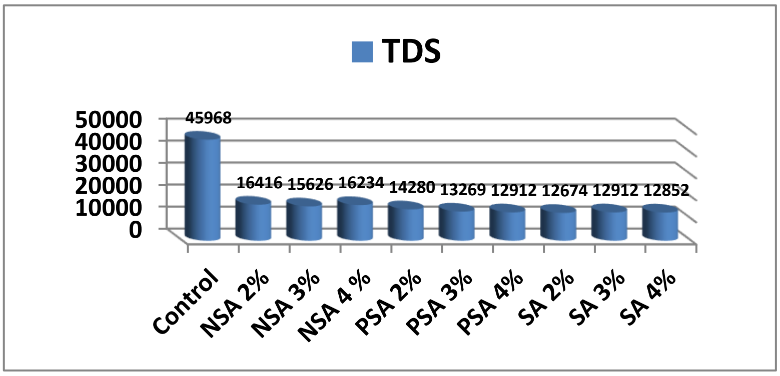

Figure 6: Effect of salt free pickling acids on total dissolved solids (TDS).

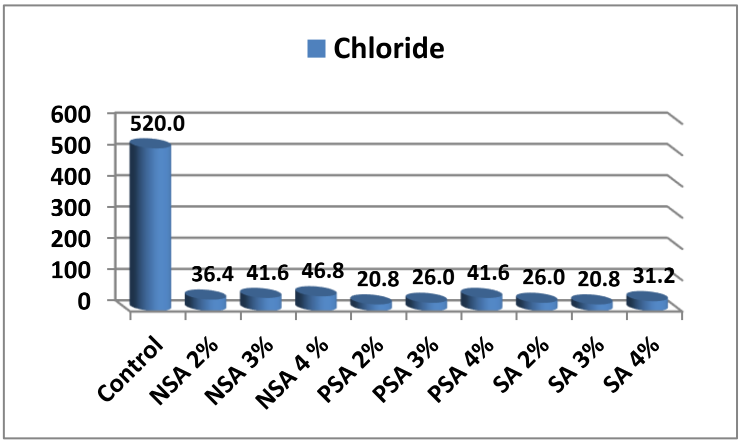

Figure 7: Effect of salt free pickling acids on chloride content.

دباغة صديقة للبيئة باستخدام أحماض السلفونك الأروماتية لتحسين امتصاص الكروم وتقليل التأثير السلبي على البيئة

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الملخص العربي:

أجريت هذه الدراسة لتقليل التأثيرات البيئية للكروم وكلوريد الصوديوم الناتجة عن عملية دباغة الجلود وذلك من خلال عملية الدباغة الخالية من الأملاح والتي تعد واحدة من أكثر الطرق فاعلية في خفض التلوث بكلوريد الصوديوم في عملية الدباغة بالكروم. وقد تم تحضير كل من حمض النفثالين سلفونك وحمض الفينول سلفونك باستخدام تفاعل السلفنة. وقد استخدمت أحماض السلفونك الأروماتية المحضرة وكذلك حمض السلفونك في عملية التأسيس بدون إضافة أي أملاح لمقارنتها بالطريقة التقليدية بتركيزات مختلفة وهي 2 و3 و4٪ من وزن الجلود. وقد تم دباغة ثلاثين قطعة من جلود الأغنام تم تقسيمها لعشر مجموعات كل مجموعة تحتوي على ثلاثة جلود. وقد تم دباغة المجموعة الأولي بالطريقة التلقيدية كمجموعة كنترول بينما تم دباغة باقي المجموعات بحمض النفثالين سلفونك وحمض الفينول سلفونك وحمض السلفونك بتركيزات (2% ، 3% ، 4%) من وزن الجلد وقد أظهرت النتائج أن الأحماض المستخدمة في عملية الدباغة الخالية من الأملاح لها القدرة علي خفض قيم كل من الطلب علي الأكسجين الكيميائي (COD)، إجمالي المواد الصلبة الذائبة (TDS) ومحتوى الكلوريد مقارنة بالطريقة التقليدية، كما أظهرت النتائج أن استخدام حمض السلفونك (4٪) قد حسن امتصاص الكروم من 79.62% إلى 90.10% وتقليل الكروم (III) في السائل المتبقي من 6.63% إلى 2.83%، بالإضافة الي أنه لم يكن له أي تأثير سئ على جودة الجلود المشطبة وكان مناسبًا للاستخدام في صناعة الجلود.

الكلمات الاسترشادية: تأسيس خالٍ من الأملاح، الدباغة بالكروم، الطلب على الأكسجين الكيميائي، النفثالين سلفونيك، حمض السلفونيك، إجمالي المواد الصلبة الذائبة.