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The utilization of sodium lignosulphonate extracted from Egyptian rice straw in leather tanning process

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ABSTRACT

Massive quantities of rice straw are burned annually in Egypt and caused environmental hazards. The present study investigated the utilization of rice straw to produce sodium lignosulphonate (SLS) as a water-soluble derivative of lignin in leather tanning and evaluate its usage as a tanning or re-tanning material as well as its effect on leather quality. The results of testing SLS as a leather tanning agent were unsatisfactory due to its slight effect on shrinkage temperature of leathers, unlike its use as a re-tanning material. Four concentrations of SLS (0%, 5%, 10%, and 20%) were used in re-tanning forty of sheep wet-blues. The results showed that using SLS as a re-tanning agent with concentration till 10% from pelts weight enhances some organoleptic properties, such as fullness and general appearance together with slight improvement in physical properties of leathers. Moreover, the addition of SLS with concentration 20% led to an excessive swelling in the collagen fibers as shown from depicted scanning electron micrographs and decreased trends of physical properties.

Keywords: rice straw, lignin, sodium lignosulphonate, tanning leather.

INTRODUCTION

Animal skins or hides considered to be byproduct after slaughtering animals. Leather tanning could be regarded as a process using the produced hides to provide basic raw materials for footwear, apparel or other leather goods (Jayathilakan *et al.*, 2012). Leather producers are interested to improve the quality of leathers and increasing their economic values through different natural sources as a safe and environmental friendly tanning and re-tanning materials (UNIDO, 2010; Deselnicu *et al*., 2012). On the other hand, Egypt produces 5.7 million tons of paddy rice leaving rice straw of about 4 million tons remaining in the fields due to its low nutritional value for livestock feed (FAOSTAT, 2014; Malik *et al*., 2015). In order to get rid of such quantities of rice straw, farmers used to burn them which resulted in environmental destruction, exacerbate pollution, together with negative impacts on ecosystems and the loss of beneficial soil microorganisms (Kanokkanjana & Garivait, 2013). The government had to endorse penalties against those farmers to stop such irresponsible action. Another way to tackle this problem is to convince farmers that rice straw could be taken as an income generating material. Rice straw is the most lignocellulosic materials available contains from 16% to 20% of lignin-based on dry weight. Crude lignin is very much insoluble in water while it is soluble in acid or alkali to some extent according to the type of lignin (Evstigneev, 2011). Lignosulphonate is one of many water-soluble lignin derivatives, have a wide variety of applications and can be used in leather processing (Sjöström, 1993). It has a high molecular size in similarity with vegetable tannins whereas it has a weak tanning reaction and thus it needs to use it in combination with other aromatic products e.g. phenol, naphthol and formaldehyde as synthetic tannins (Gemei *et al*., 1980; Kassa, 2014).

Literature for using lignin in leather tanning indicated that the main problem is the insolubility of lignin in water (Gemei *et al*., 1980). However, some researchers prepared and improved different soluble water derivatives of lignin to be suitable for using in leather tanning (Suparno *et al*., 2005a and 2005b), while few workers applied them in leather tanning as post-tanning material and studied their effects on collagen fiber and leather properties

(Kassa, 2014). On the other hand, previous Egyptian investigators interested to maximize the utilization of cellulosic fibers from rice straws to improve paper industry and neglected the other waste which contains a high amount of lignin (Diab, 2007).

Therefore, the present study has three goals; utilization of rice straw to produce lignosulphonate as a water-soluble derivative of lignin in leather tanning and evaluate the usage of lignosulphonates as a tanning or re-tanning material as well as its effect on leather quality.

MATERIALS AND METHODS

The work plan of this study contained four steps, which were started with extracting lignin from rice straw, preparing sodium lignosulphonate (SLS) from extracted lignin, using SLS in leather tanning and testing leathers as shown in Figure 1. Black liquor was included in this figure since it is available and cheaper as a result of high demand for manufacturers to use crude cellulose in other industries.

Extracting Lignin from Rice Straw

Kraft process was used in this study to extract lignin from rice straw according to Jingjing (2011). Rice straw was dried for five days in an open and shaded place without using any thermal drying treatment. Dried rice straw was cut into small pieces, screened with length of 19-25 mm, kept in paper bags and then extractive-free wood was prepared.

The preparation of extractive-free wood was done by washing it with ethanol, benzene, and boiling distilled water to be freed up from wax according to TAPPI (2011). Washed straw particles were left to dry at room temperature of about 26 ºC. According to Davies (1984), prepared extractive-free wood was used for lignin isolation during Kraft process.

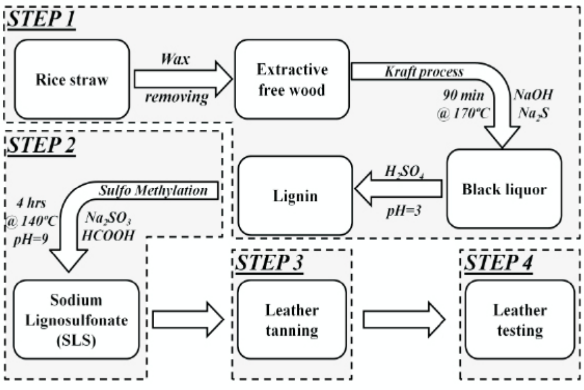

Figure 1. Schematic diagram for the work plan executed in the present study.

In Kraft process, white liquor consisted of 14% NaOH and 35% Na_2S, was used at 170 °C for 90 min to obtain black liquor. The pH of the black liquor was adjusted to pH 3 by adding H_2SO_4 (20%) gradually. The participated lignin was filtered, washed with water for several times, dried at room temperature of about 26 ºC, and then ground mechanically.

Preparing SLS from Extracted Lignin

Lignin is sulfomethylated with a mixture of sodium sulfite and formaldehyde (Kassa, 2014). The addition of formaldehyde and sulfite (molar ratio of 0.6–0.8) to the lignin slurry has increased the pH from about 4 to 9. The contents were heated at 140 °C for about 4 hrs under constant rotation. After cooking, the product was removed, filtered to eliminate insoluble byproducts and then analyzed. The FT-IR spectra of isolated SLS was recorded from 400 to 4000 cm^{-1}, to ensure its chemical structure and fingerprint, using a JASCO 300-E FT-IR spectrometer by scanning 5 times in a resolution of 4 cm^{-1}. The sample was carried out by using the potassium bromide pellet technique (Poletto & Zattera, 2013).

SLS powder was used to determine ash, moisture, yield percentages, pH, SLS solubility in water, and organic solvents. Moreover, to determine shrinkage temperature, five pieces (10 cm x 10 cm) of pickled sheep pelts were tanned with 20% SLS in the laboratory. Pelts were run in a small glass drum with water at pH 4 and Bé 8 for 30 min. The SLS powder was added and drum was run at speed 8 cycles/min for 8 hrs then stopped overnight. Shrinkage temperature was determined next day in tanned samples and compared with un-tanned pickled samples (ASTM D-6076).

Using SLS in Leather Tanning

Forty sheep wet-blues at marketing age were used in this study to evaluate SLS as a re-tanning material. Four concentrations of SLS were used (0%, 5%, 10% or 20%) in re-tanning wet-blues. Thus, wet-blues were divided randomly into four groups, ten pelts in each group. Leather tanning steps were done at El-Shafei's sons tannery, Alexandria, Egypt according to the executed recipe in Table 1.

Table 1. Executed recipe for post-tanning wet-blues.

Step	Description		Time (min.)	Remarks
	%	Added		
Washing	100	Water	10	Drain float
	2	Soap		
Naturalization	100	Water	60	To adjust pH= 6
	2	$NaHCO_3$		
Dyeing & Re-tanning	3	Black dye	90	Adding lignosulphonate with specified percentage.
	X	Lignosulphonate		
Fatliquoring	150	Water	90	
	6	Fatliquor (fish oil)		
Fixation	1	Formic acid	30	
	1	Formic acid	60	
Washing	100	Water	10	Out & overnight as horse up then samming.
Finishing	--	--	--	Drying in shaded place.

Testing Leathers

All finished leathers were assessed for softness, grain smoothness, grain tightness, fullness, and general appearance by standard tangible evaluation technique (Kasmudjiastuti & Murti, 2017). Three experienced tanners rated the leathers on a scale of 1-10 points for each functional property (higher points indicate a superior property). The average of the three tanners was recorded for each sample.

Qualitative and operational properties of the obtained leathers were assessed according to indices of chemical analysis, physicomechanical analysis of the finished leather. Thickness, tensile strength, elongation, split tear strength, pH, ash, and moisture were analyzed (ASTM, 2014). In addition, the morphological characteristics of tanned leathers were analyzed using JEOL JSM-5300LV Scanning Electron Microscopy (SEM). Samples were cut from official sampling position (ASTM- D2813). The specimens were cut with a uniform thickness without any pre-treatment. The micrograph of the cross section was obtained by operating the SEM.

Statistical Analysis

Data were analyzed using GLM procedure of SAS (2008) to evaluate the differences among produced leathers. The following model was used in the analysis:

$$Y_{ij} = \mu + T_i + e_{ij}$$

Where Y_{ij} is the observation taken on finished leather, μ is overall mean, T_i is a fixed effect of the i^{th} SLS concentration treatment (1 = 0%, 2 = 5%, 3 = 10% and 4 = 20%) and e_{ij} is the random error assumed to be normally distributed with mean = 0 and variance = $\sigma^2 e$.

RESULTS AND DISCUSSION

FT-IR Analysis of Sodium Lignosulphonate (SLS)

The FT-IR spectrum of prepared SLS was given in Figure 2. The fingerprint region lied between wave numbers ranging from 600 cm^{-1} to 1700 cm^{-1} and typical stretching of chemical groups was observed at 2800 cm^{-1} to 3500 cm^{-1}. As presented in Table 2, the broad band at 3398 cm^{-1} was due to the presence of hydroxyls. The band at 2960 cm^{-1} was contributed to methylene and methyl groups. The adsorption of aromatic methoxy group was located at 2854 cm^{-1}. At fingerprint region, the ad-

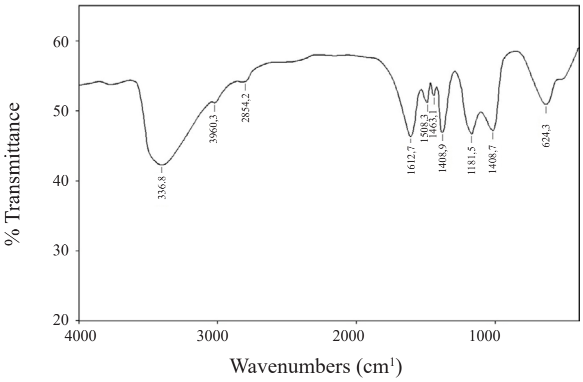

Figure 2. The FT-IR spectrum of prepared sodium lignosulphonate (SLS).

Table 2. The assignment list of infrared bands of sodium lignosulphonate.

Absorption peak (cm^{-1})	Band
3398	O-H stretching vibration
2960	C-H stretching
2854	C-H vibration of methyl group
1612	C=C ring skeletal vibration
1508	C–C ring skeletal vibration
1463	C-H vibration
1408	C–H ring skeletal deformation
1181	C–O stretching
1048	$-SO_3$ adsorption
624	$-SO_3$ deformation

sorption bands at 1612 cm^{-1} and 1508 cm^{-1} were characteristic of phenyl ring skeletal vibrations of lignin macromolecules. The vibrations of methylene and methyl groups were bands at 1463 cm^{-1} and 1408 cm^{-1}. The bands at 1048 and 624 cm^{-1} were assigned to the adsorption and deformation of sulfonated group, respectively. These bands were in agreement with corresponding bands obtained for lignin and lignosulphonate by other researchers (Kamoun *et al*., 2003; Diab, 2007; Shen *et al*., 2008; Zhili & Yuanyuan, 2011; Poletto & Zattera, 2013 and Darweesh, 2014). These results might suggest that the obtained extract of this study is for lignosulphonate.

SLS Properties

The properties of SLS powder were determined and presented in Table 3. Ash, moisture percentages and pH values were 9.8%, 3.9% and 9% respectively, which appeared to be close to the corresponding values obtained by other investigators (Diab, 2007; Jingjing, 2011). Obviously, the obtained SLS was soluble in water and characterized by high yield (68.88%). Due to chemical structure of lignosulphonate, it is an organic material with a high molecular weight such as in vegetable tanning materials (Covington, 2009). Usually, shrinkage temperature of vegetable tanning materials ranges from 70°C to 85°C and considered to be the weakest tanning materials (BASF, 2007). Therefore, SLS was lower than vegetable tanning material in shrinkage temperature (63°C), thus, the present results excluded the possibility of using it as a main tanning material in leather tanning. On the other hand, the colors of SLS powder and pickled pelt treated with 20% SLS were dark and light brown respectively, which considered to be acceptable color in leather tanning such as vegetable tanning materials (BASF, 2007).

Organoleptic Properties

Table 4 presents organoleptic properties for the control (SLS 0%) and treated leathers (SLS 5%, 10% and 20%). Leathers treated with 10% SLS showed the highest general appearance, where other leathers were similar in this property. With

Table 3. Properties of sodium lignosulphonate (SLS) powder.

Parameter	Value
Ash	9.8%
Moisture	3.9%
pH	9
Yield*	68.88%
Solubility in water	Soluble
Solubility in organic solvents**	Soluble
Color of SLS powder	Dark brown
Color of pelts treated with 20% SLS	Light brown
Shrinkage temperature of pickled pelt (T_{S1})	48 °C
Shrinkage temperature of tanned pelt with 20% SLS (T_{S2})	63 °C
$\Delta T_S = (T_{S2} - T_{S1})$	15 °C

* Yield calculated as percentage from lignin in black liquor.
** Organic solvents were acetone, alcohols, chloroform, hexane and ethyl acetate.

Table 4. Organoleptic properties of control and treated tanned leathers with different concentrations of sodium lignosulphonate (SLS).

Property	Control	Treated		
	SLS 0%	SLS 5%	SLS 10%	SLS 20%
Fullness	7	8	9	10
Grain tightness	7	7	8	9
Grain smoothness	8	8	7	6
Softness	9	9	7	6
General appearance	8	8	9	8

respect to other organoleptic properties, fullness and grain tightness properties tend to increase by increasing SLS concentration, while the opposite trend was observed with grain smoothness and softness properties. That might be due to similar effect of SLS with vegetable tanning material as an organic tanning material as a result of swelling in collagen fibers, increase their hardness and also increase roughness in surface layer of finished leathers (Heidemann, 1993; Covington, 2009). As far as organoleptic properties, it is obvious that the treated leathers with SLS 5% and 10% were close in most organoleptic properties. The superiority of SLS 10% leathers might due to its high general appearance property, while SLS 20% leathers had the lowest values among treated leathers.

Physical and Chemical Properties

Physical and chemical properties of control and treated tanned leathers were presented in Table 5. All properties differed significantly as a result of addition of SLS as a re-tanning material. The treated leathers (SLS 5%, 10%, and 20%) had higher thickness values ($P<0.05$) than control leathers (SLS 0%), where the differences among treated leathers were not significant. Regarding physical properties, tensile and tearing strength values tend to significantly decrease ($P<0.01$) in 20% SLS leathers, whereas leathers treated with 0%, 5% and 10% SLS showed no significant differences. This trend was expected due to swelling and fullness effects of SLS in addition to the negative relation between thickness and strength (Kotb, 1987; Abdelsalam *et al*., 1998). The percentages of elongation tend to decrease by increasing SLS concentration, which might be due to increase collagen fiber hardness (Heidemann, 1993; Covington, 2009).

Chemical properties showed that pH and ash percentage values increased significantly ($P<0.01$) between the control and treated leathers because of the effect of alkalinity and the content of ash in SLS powder (Table 3). For this reason, pH and ash values tended to increase by increasing SLS concentration.

As far as physical properties of tanned leather,

Table 5. Physical and chemical properties of control and treated tanned leathers with different concentrations of sodium lignosulphonate (SLS).

Property	ASTM	Control	Treated			SEM	Significance
		SLS 0%	SLS 5%	SLS 10%	SLS 20%		
Physical properties							
Thickness (mm)	D1813	1.17^{b}	1.35^{a}	1.41^{a}	1.43^{a}	0.31	*
Tensile (kg/cm^2)	D2209	283.60^{a}	284.02^{a}	291.96^{a}	222.06^{b}	6.72	**
Tearing (kg/cm)	D4704	40.28^{a}	42.42^{a}	35.88^{a}	26.20^{b}	0.98	**
Elongation (%)	D2211	65.25^{bc}	84.89^{a}	76.73^{ab}	55.93^{c}	2.52	**
Chemical Properties							
pH	D2810	3.63^{c}	4.34^{b}	4.59^{ab}	4.81^{a}	0.11	**
Moisture (%)	D6403	17.26^{a}	15.78^{a}	16.40^{a}	14.01^{b}	0.35	*
Ash (%)	D2617	5.44^{a}	6.61^{b}	7.51^{c}	8.26^{d}	0.26	**

^{a,b,c,d} Means in the same row having different superscripts are significantly different ($P<0.05$)

Significance: *$P<0.05$, ** $P<0.01$

SEM: standard error of the mean

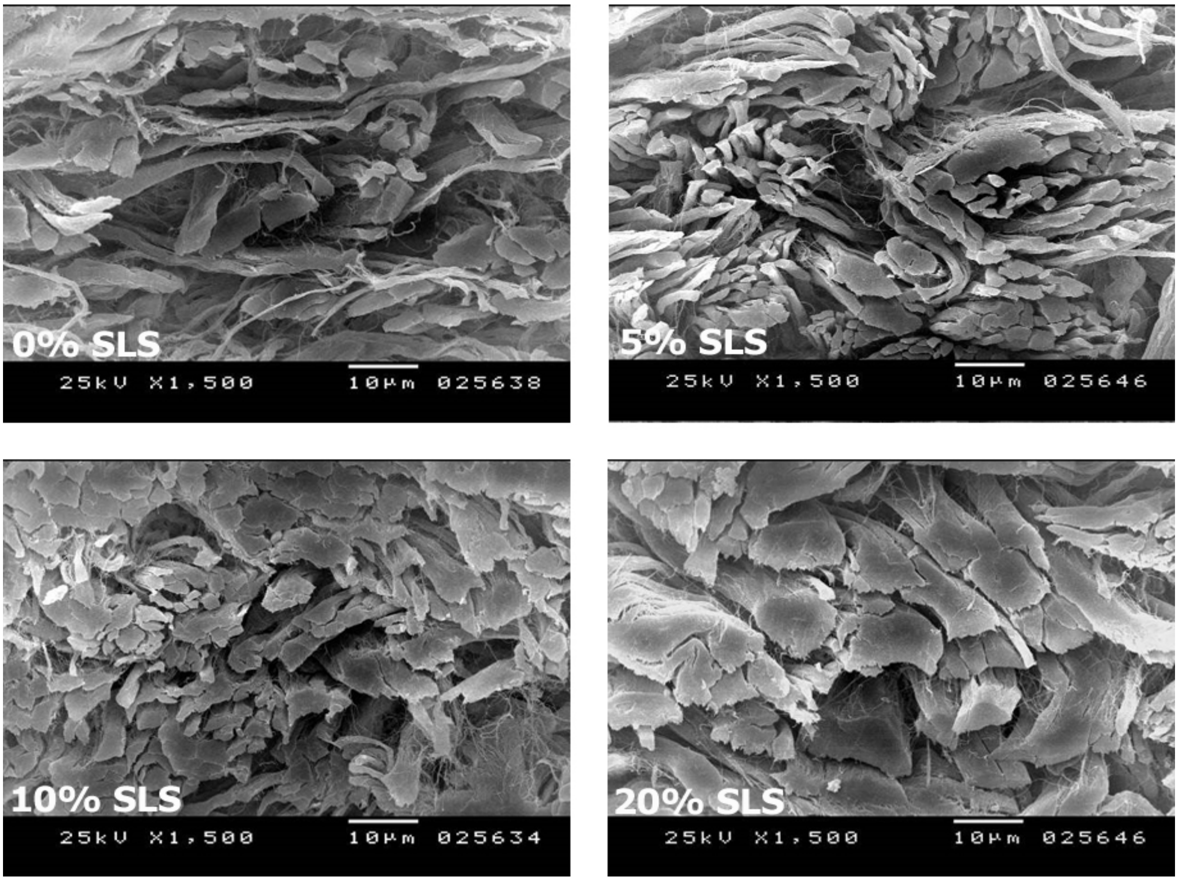

Figure 3. Scanning electron micrographs (magnification of 1500X) for treated tanned leathers with different concentrations of sodium lignosulphonate (SLS).

it is observed that addition of SLS with concentrations of 5% and 10% would improve physical properties, while the concentration of 20% would deteriorate such properties (Table 5). The high concentration of SLS (20%) might lead to weaken leathers as a negative effect of excess swelling on collagen fiber.

Scanning Electron Microscopy

Figure 3 shows the depicted micrographs from the cross-section of tanned leathers treated with different concentrations of SLS. The control leathers (0% SLS) showed the highest separation of fibers, while increasing the concentration of SLS led to decrease the spaces among fiber bundles due to fiber swelling, which increased the fibers diameters to about the double in 20% SLS leathers. This extra increase in fiber swelling and compactness in 20% SLS leathers resulted in increasing in some other properties such as thickness, fullness and grain tightness and decreasing tensile strength, tearing strength and softness. On the other hand, 5% and 10% SLS leathers showed moderate changes in fiber swelling and compactness, which explained the improvement occurred on their organoleptic and physical properties, especially concentration 10% of SLS as described previously.

CONCLUSIONS

Using sodium lignosulphonate (SLS) extracted from Egyptian rice straw in leather tanning was investigated. The solubility of SLS in water allows its utility in leather tanning. The addition of SLS with concentration 20% from pelts weight led to an excessive swelling in the collagen fibers and thus caused a decrease in physical properties of leathers, but SLS can be used as a re-tanning agent with concentration till 10% to improve leather quality. SLS enhances some organoleptic properties, such as fullness and general appearance together with slight improvement in physical properties of leathers. Therefore, producing SLS considered to be an important complementary step for Kraft process in other industries which might be suitable in Egypt in order to reduce some environmental hazards and on other hand enhance the profitability of leather industry.

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