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Possible Application of Using Modified Black Liquor from Rice Straw in Leather Tanning

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ABSTRACT

Ensuring environmental and human safety is a crucial requirement in modern industrial practices. Consequently, the utilization of natural substances in the tanning industry could serve as a reliable approach to prevent chemical contamination associated with the use of traditional chromium salts during the tanning process. This study aimed to assess the potential application of black liquor derived from rice straw as a tanning agent for leather. The black liquor was prepared using the Kraft method, and a modified version called modified black liquor (MBL) was created by gradually reducing the pH from 13 to 7. Subsequently, MBL was employed in the tanning of pickled sheep pelts using four different concentrations: 10%, 20%, 30%, and 40% of the pelts' weight. The physical, chemical, and organoleptic properties of the resulting MBL-tanned leathers were compared with those of leathers tanned with quebracho extracts to evaluate the suitability of MBL as a tanning agent. The findings demonstrated that MBL leathers exhibited slightly lower physical and organoleptic properties when compared to the quebracho-tanned leathers. Increasing the concentration of MBL up to 30% was sufficient to enhance the properties of the tanned leathers, while concentrations exceeding this threshold did not yield any significant improvements in the leather's properties. Consequently, the study recommends the use of MBL in leather tanning either in combination with other tanning agents or as a re-tanning agent to enhance the fullness, smoothness, and overall physical quality of the leather, thereby elevating its overall quality.

Keywords: Kraft, Leather quality, Leather properties, Lignin, Vegetable tanning.

INTRODUCTION

The history of leather tanning dates back thousands of years, with evidence of tanning practices found in ancient civilizations such as Egypt. The development of modern tanning techniques in the 19th and 20th centuries, such as chrome tanning and synthetic tanning agents, revolutionized the leather industry and made it possible to produce large quantities of leather more quickly and at a lower cost (Abbas, 2017; Haddad et al., 2018). Therefore, the quality of leather can be influenced by various factors such as the type of animal hide used, the tanning process, the skill of the tanners, and the type of material used in the tanning process (Valeika et al., 2010). Different methods of tanning involve the use of different materials, such as chromium salts for mineral tanning and oils for oil tanning (Haroun et al., 2012; Sai Bhavya et al., 2019). Vegetable tanning, also known as plant extract tanning, requires tannin-rich barks, roots, leaves, and other plant materials (Koloka and Moreki, 2011; Ahmed et al., 2021). This traditional method involves treating raw hides with natural tannins and chemicals with large molecular weights, such as lignin and its derivatives from plants (Falcão and Araújo, 2018; Abid et al., 2020). Leather that has been vegetable-tanned is known for its strength, resilience, and ability to age gracefully. It is also considered a more environmentally friendly alternative to chrome-tanned leather, which requires chemicals and is faster but less beneficial to the environment (Haroun et al., 2009).

Lignin, a complex organic polymer and a vital component of cell walls, is present in many plants, including agricultural waste materials like cotton lugs, maize husks, and rice straw (Gopalakrishnan et al., 2010; Taha et al., 2016; Klett, 2017). Lignin can be removed from these waste products and utilized for various industrial processes, such as the creation of biofuels and other chemicals (Di Francesco et al., 2021). Furthermore, lignin can potentially be used as a tanning agent in the leather industry due to its phenolic structure (Mastrolitti et al., 2021). By utilizing lignin from black liquor in the leather tanning process, it may be possible to reduce the reliance on imported raw materials and promote a more sustainable and environmentally friendly leather industry (Balasubramanian et al., 2018; Mili et al., 2022).

The Kraft process, which utilizes alkaline solutions to dissolve the cellulose and hemicellulose components of biomass and leave behind lignin (Gopalakrishnan et al., 2010; Olgun and Ateş, 2023), is the most widely used technique for extracting lignin (Hamaguchi et al., 2012). Depending on the optimization of process parameters, the finished product may contain lignin that is dissolved in water, particularly at or near neutral pH. In the tanning of leather, lignin is a promising substance (Kihlman, 2021). In addition to fragmented lignin, the black liquor produced by the Kraft process also contains phenolic compounds, Na_2SO_4, and other chemicals that, when burned, produce Na_2S and CO_2 (Merlea et al., 2019; Mastrolitti et al., 2021; Sharma et al., 2023; Jardim et al., 2022).

Obtaining raw materials from imports can be challenging due to various reasons, such as economic conditions, trade agreements, supply chain disruptions, and competition for resources (Vakkilainen and Välimäki, 2009; Tsega et al., 2023). For this reason, the current study aims to analyze the black liquor generated from the Kraft process in the leather tanning process.

MATERIALS AND METHODS

Collecting rice straw

Rice straw was obtained from Abu Homs city, Buhaira governorate, Egypt and thoroughly washed with running water to remove any dust or suspended particles. It was then air-dried for a week at room temperature and cut into small pieces of less than 1mm. The samples were stored in a dry and isolated environment to protect them from moisture and other contaminants until the extraction process could be carried out.

Preparation of modified black liquor

The Kraft method, as described by Rodríguez et al. (2008), involves treating rice straw with a white liquid solution consisting of a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) to extract black liquor. The mixture is then heated to a temperature of 150°C to 170°C and a pH of 9 to 13, gradually increasing the temperature until the lignin is fully broken down. The soluble lignin is separated from the mixture according to Balasubramanian et al. (2018), with the initial pH of the black liquor being 13.0 and the pH gradually reduced to 7.0 by slow addition of 1N sulfuric acid. The mixture was then filtered to remove any insoluble materials, and the resulting modified black liquor (MBL) was ready to be used in the tanning process.

FT-IR analysis

Brucker alpha FT-IR spectrometer (Thermo FTIR 200) was used to analyze chemical structure and fingerprint of both black liquor and MBL. A small quantity of the samples in liquid phase was scanned directly on the instrument stage.

Tanning pickled sheep pelts

The tanning experiments were conducted at El-Shafei Sons' Tannery in Alexandria, Egypt. Four increasing concentrations of tanning materials (10, 20, 30 and 40% from pelts weight) were used for tanning pickled sheep pelts. Therefore, a total of 12 pickled sheep pelts were used, with each pelt divided into two halves along the backbone. The right half of the pelt was tanned with quebracho extract as a control groups, while the left half was tanned with the prepared black liquor.

Thus, the number of repetitions for each used concentration was three repetitions. Table 1 shows the experimental groups and concentrations used for tanning with either quebracho extract or the MBL. The pickled pelts of each group were tanning separately in a small drum according to the recipe outlined in Table 2.

Tanned leather properties

Various tanned leathers were subjected to physical and chemical testing in accordance with ASTM methods (ASTM, 2014). The specimens were conditioned for 48 hours at a temperature of 20°C ± 2°C and a relative humidity of 65% ± 4%. Physical properties such as thickness, tensile strength, elongation percentage at break, and split tearing strength were measured, with reported values being the average of three specimens. Chemical properties such as pH, moisture content, and ash content were also analyzed. The organoleptic properties of the tanned leathers were assessed by five experienced tanners using the standard tactile evaluation technique (Kasmudjiastuti and Murti, 2017). These properties included softness, grain smoothness, grain tightness, fullness, and general appearance, each rated on a scale of 1 to 10 points, with higher scores indicating better quality.

Statistical analysis

To evaluate the differences among the various tanned leather properties, the data was analyzed using the statistical package for social science (SPSS) version 25 (IBM, 2017). The fixed model employed in the analysis of the effect of tanning material type, tanning material concentration and interaction effect is described by the following equation:

$$Y_{ijk} = \mu + T_i + C_j + TC_{ij} + e_{ijk} \quad (1)$$

where: Y_{ijk} represents the observation taken (k),
μ is the overall mean,
T_i represents the fixed effect of the tanning material (either quebracho or MBL),

Table 1. The experimental groups and concentrations used for tanning with either quebracho extract (QE) or the modified black liquor (MBL)

Experimental group	Tanning material	Tanning material concentration (%)*
QE-10	Quebracho (control)	10
MBL-10	Modified black liquor	10
QE-20	Quebracho (control)	20
MBL-20	Modified black liquor	20
QE-30	Quebracho (control)	30
MBL-30	Modified black liquor	30
QE-40	Quebracho (control)	40
MBL-40	Modified black liquor	40

Note: * Tanning material concentration calculated based on pelt's weight.

Table 2. Executed recipe for tanning pickled pelts

Step	Description		Time (min)	Remarks
	%*	Added		
Tanning	100	Water	120	- Tanning material is quebracho extract or modified black liquor, which added in two batches. - After rotating for two hours, drum is left for 24 hours with 5 minutes of rotation per hour.
	X	Tanning material		
Washing	200	Water	10	
Fatliquoring	150	Water	90	
	6	Fatliquor (fish oil)		
Fixation	1	Formic acid	30	Check fatliquor in float.
	1	Formic acid	60	
Washing	100	Water	10	Out & overnight as horse up then samming.
Finishing	--	--	--	Drying in shaded place.

Note: * Chemical addition percentage calculated based on pelt's weight.

C_j the fixed effect of the tanning material concentration (10, 20, 30 or 40%), and
TC_{ij} the interaction effect between tanning material and the concentration and
e_{ijk} represents a random error that is assumed to be normally distributed with a mean of 0 and a variance of σ^2e.

RESULT AND DISCUSSION

Characteristics of modified black liquor

Table 3 shows the properties of the rice straw black liquor extract (MBL), which has a high ash content (14.4%) and moisture content (48.4%). These values are comparable to those found in previous studies (Diab, 2007; Jingjing, 2011), which is expected due to the use of chemical alkaline and acid in preparation.

The MBL is also soluble in water and other solvents. This is because the main component of the MBL is lignin, which is soluble in water down to a pH value of 5.5 (Savy et al., 2015; Matiz et al., 2020). The solubility of the MBL in water is important for its use in tanning, as the tanning process is carried out in water (BASF, 2007; Covington, 2009). The color of the MBL is dark brown, and the color of the tanned leather sample is light brown. Both colors are acceptable in leather tanning, as they are similar to the colors produced by traditional vegetable tanning materials (Dutta, 2008).

FTIR of MBL

Fourier transform infrared (FT-IR) spectroscopy was used to investigate the structural changes that occurred in black liquor when the pH was changed. The FT-IR spectra of black liquor at pH 13 and MBL at pH = 7 are shown in Figure 1, and the corresponding assignments and bands are presented in Table 4. The two spectra have the same basic functional groups. The spectrum shows the characteristic bands of natural fibers, including strong broad hydroxyl (OH) stretching from 3400–3450 cm^{-1}, C=O stretching at 1634 cm^{-1}, and OH bending at 1412, 1413, and 1361 cm^{-1}. The regions between 1800 and 1100 cm^{-1} are typically assigned to the main components of wood and natural fibers; cellulose, hemicelluloses, and lignin. The results showed that the main component of MBL is lignin, which is consistent with previous studies of black liquor from different sources (Risanto et al., 2014, Ramalingam et al., 2015, Maisarah et al., 2015, Vedhanayagam et al., 2015; Taha et al., 2016).

Table 3. Modified black liquor properties

Parameter	Value
Ash	14.4%
Moisture	48.4%
pH	7.2
Solubility in water:	
• in water	soluble
• in organic solvents*	soluble
Color:	
• solution color	dark brown
• Pelts treated with 20% MBL	light brown

Note: *Organic solvents were acetone, alcohols, chloroform, hexane and ethyl acetate.

Evaluation of shrinkage temperature

The statistical analysis of the data from the shrinkage temperature test showed significant differences ($P < 0.01$) among the studied tanned leathers, which attributed to the effect of the tanning agent ($P < 0.01$), while the concentration of the tanning agent had no significant effect. The leathers tanned with commercial quebracho extract outperformed their counterparts tanned with MBL in terms of shrinkage temperature, with an average shrinkage temperature of 85.4 °C and 69 °C, respectively (Figure 2). These findings suggest that quebracho extract is a more effective tanning agent than MBL for enhancing the shrinkage temperature performance of leather. On the other hand, the mean values of the different concentrations, 10%, 20%, 30%, and 40%, were 71.3, 74.7, 80.7, and 82.2 °C, respectively (Figure 2). These results indicate that increasing the concentration of the tanning agent improved the shrinkage temperature, although the differences between the concentrations were insignificant.

Figure 3 shows the shrinkage temperatures of different studied tanned leathers vs. untanned pelt. The shrinkage temperature values for all the leathers tanned with either quebracho or MBL were higher than the corresponding value for the untanned pelt, indicating that the tanning agents had effectively bound to the collagen fibers in the leather. This finding is consistent with previous studies of Covington, (2009), Ibrahim et al. (2013) and Unango et al. (2021), which have

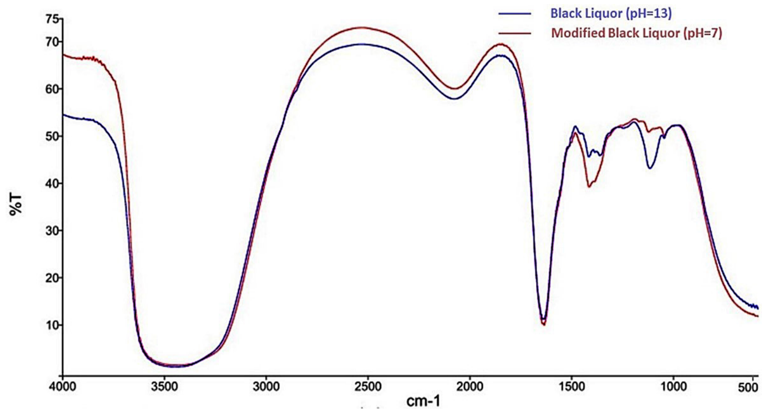

Figure 1. FTIR spectra of black liquor (pH = 13) and modified black liquor (pH = 7)

Table 4. FT-IR Absorption bands and assignments for black liquor and modified black liquor from rice straw

Assignments	Absorption peak (cm^{-1})		
	Band range (cm^{-1})	Black liquor (pH = 13)	Modified black liquor (pH = 7)
O-H stretching (phenolic OH and aliphatic OH)	3400–3450	3436	3436
C=O bond stretching	1600–1650	1634	1634
O-H bending	1410–1330	1412	1413
O-H bending (phenol)	1310–1390	–	1361
Ar-CH in-plane deformation (syringil)	1115	–	1115
C-O(H) and C-O(C)	1030–1085	1043	–

shown that one of the important properties of tanning agents is to form bonds between collagen fibers in leather, thereby improving its shrinkage temperature, strength and occupying the active sites, which prevents water absorption and ensures that the leather does not decompose later on. However, the results suggest that MBL has a weaker affinity for collagen fibers compared to quebracho extract, which is reasonable given the differences in their chemical composition, with quebracho extract consisting primarily of tannins. As for the difference between the leathers tanned with quebracho extract and those tanned with MBL, it can be observed that the highest shrinkage temperature value for the leather tanned with 40% prepared black liquor (77°C) was lower than the lowest value for the leather tanned with quebracho extract at 10% concentration (83.3°C). Nevertheless, the use of 30% and 40% concentrations is considered appropriate for tanning, as they exceed the minimum threshold required for materials suitable for tanning according to the Indonesian National Standard (SNI) (Nurichsanto et al., 2023). However, the shrinkage temperature of

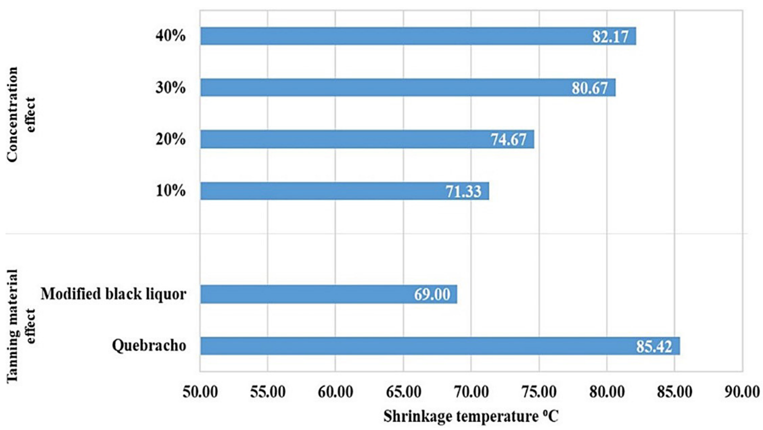

Figure 2. Effect of tanning material and concentration on the shrinkage temperature

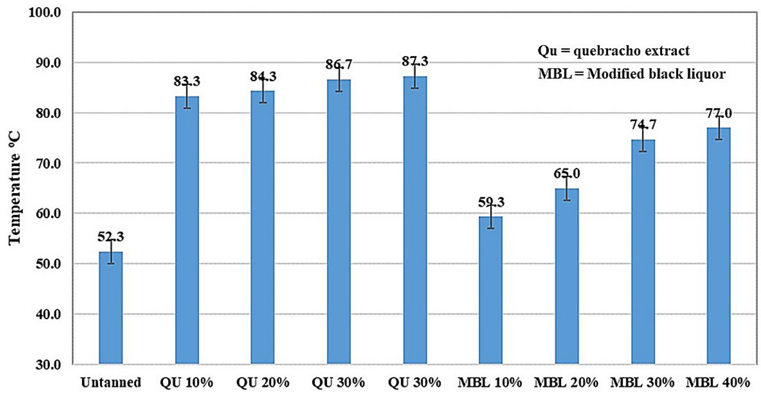

Figure 3. Interaction effect between tanning material and the tanning material concentration on shrinkage temperature of tanned leathers

vegetable tanning materials usually ranges from 70°C to 85°C (BASF, 2007), which considered to be from the weakest tanning materials. Therefore, MBL has a lower shrinkage temperature, ranging from 59.3 and 77°C, makes it a good agent for use in re-tanning.

Evaluation of physical and chemical properties of tanned leathers

Table 5 presents the physical and chemical properties of tanned leathers produced using quebracho or MBL extracts at different concentrations. The interaction effect of the tanning agent and concentration was found to have a significant impact ($P < 0.01$) on all physical and chemical properties of the tanned leather, except for moisture content. The differences observed between the tanned leather groups can be attributed to the interaction between the independent effects of the tanning agent and concentration.

The interaction effect on the physical properties of the tanned leather was primarily influenced by the concentration, while the chemical properties were mainly affected by the tanning agent. Regardless of the tanning agent used, all physical properties of the tanned leather, except for tearing strength, significantly increased ($P < 0.01$) by increasing concentrations of the tanning agent. However, the type of tanning agent had a significant impact ($P < 0.01$) on the pH and ash content of the tanned leather.

In terms of the tanning agent effect, the results showed that quebracho leathers exhibited significantly higher tear strength ($P < 0.01$) compared to MBL leathers, with values of 57.80 kg/cm and 48.99 kg/cm, respectively. Although the physical properties of quebracho leathers surpassed those of MBL leathers, there were no significant differences in thickness, tensile strength, and elongation. This suggests that quebracho extract may have a more favorable effect as a tanning agent than MBL extract since the improvement in the physical properties of quebracho leathers aligns with the increase in shrinkage temperature, as previously explained. This indicates that the active tannin compounds in quebracho extract form stronger bonds with collagen fibers compared to the active lignin compounds in MBL extract, resulting in more durable collagen fibers in quebracho leathers. Additionally, MBL leathers had higher ash and pH values compared to quebracho leathers, with values of 7.09% vs. 2.03% and 4.68 mmol/L vs. 2.76 mmol/L, respectively. This was expected due to the higher ash content and pH in MBL agent.

Regarding the effect of tanning agent concentration, the properties of thickness, tensile strength, and elongation were influenced by increasing tanning agent concentration ($P < 0.01$), but there were no significant differences between the concentrations of 30% and 40%. On the other hand, tearing strength and chemical properties showed no significant differences based on tanning agent concentrations.

In summary, the results indicate that MBL leathers are not as durable or strong as quebracho leathers, and increasing the concentration of the tanning agent can enhance the leather quality, but only up to a certain point. Once the tanning agent concentration reaches 30%, there is no significant further improvement in leather quality.

From a technical perspective, the physical property values obtained in this study were comparable to those estimated in previous studies that utilized tanning agents prepared differently from black liquor. The tensile strength and tear strength

Table 5. Least square means ± standard error of the mean of physical and chemical properties of tanned leathers affected by tanning material, concentration and their interaction

Item		Physical properties				Chemical properties		
		Thickness	Tensile strength	Elongation	Tear strength	Moisture	Ash	pH
Unit		mm	kg/cm^{2}	%	kg/cm	%	%	mmol/L
ASTM		D1813	D2209	D2211	D4707	D6403	D2617	D2810
Material effect (T)								
Quebracho		1.65	255.64	69.89	57.80^{a}	15.07	2.03^{b}	2.76^{b}
MBL		1.48	248.43	66.32	43.99^{b}	15.50	7.09^{a}	4.68^{a}
Significance		ns	ns	ns	**	ns	**	**
Concentration effect (C)								
10%		1.45^{b}	210.13^{b}	58.09^{b}	43.80	15.10	3.16	3.49
20%		1.59^{a}	221.43^{b}	69.47^{a}	52.10	14.21	5.05	3.26
30%		1.52^{a}	287.49^{a}	70.90^{a}	52.56	15.83	4.70	3.85
40%		1.71^{a}	289.07^{a}	73.95^{a}	55.13	15.99	5.33	4.26
Significance		**	**	**	ns	ns	ns	ns
Interaction effect (T×C)								
10%	Quebracho	1.68^{ab}	213.86^{c}	58.33^{c}	53.24^{abc}	15.88	1.83^{c}	2.41^{e}
	MBL	1.21^{e}	206.40^{c}	57.85^{c}	34.37^{e}	14.33	4.49^{b}	4.57^{b}
20%	Quebracho	1.82^{a}	234.40^{b}	74.87^{a}	60.22^{a}	14.13	2.02^{c}	2.64^{de}
	MBL	1.35^{de}	208.47^{c}	64.08^{bc}	43.97^{d}	14.29	8.09^{a}	3.88^{c}
30%	Quebracho	1.44^{cd}	283.88^{a}	70.88^{ab}	58.74^{ab}	15.56	2.08^{c}	2.92^{de}
	MBL	1.60^{bc}	291.10^{a}	70.92^{ab}	46.38^{cd}	16.10	7.33^{a}	4.79^{b}
40%	Quebracho	1.65^{ab}	290.40^{a}	75.46^{a}	59.03^{ab}	14.70	2.21^{c}	3.05^{d}
	MBL	1.76^{ab}	287.74^{a}	72.44^{ab}	51.24^{bcd}	17.28	8.44^{a}	5.47^{a}
Significance		**	**	**	**	ns	**	**
Over all means		1.56	252.03	68.10	50.90	15.28	4.56	3.72
SEM		0.05	7.93	1.60	1.89	0.24	0.59	0.23

Note: MBL – modified black liquor, SEM – standard error of means, ns –not significant, * – significant at $P < 0.05$, ** – significant at $P < 0.01$. Means in the same column having different superscripts are significantly different ($P < 0.05$).

values of this study were similar to those reported by Ramalingam et al. (2015), who used black liquor in re-tanning goat wet-blues, and Taha et al. (2016), who used ligosulphonates prepared from rice straw black liquor in re-tanning sheep wet-blues. However, they were slightly lower than the values obtained in the study by Vedhanayagam et al. (2015), who used syntan prepared from black liquor in the re-tanning of goat chrome wet-blues.

Generally, the physical properties of the MLB leathers obtained in this study were in an acceptable range for vegetable-tanned leather used for shoe uppers and upholstery (UNIDO, 1994; BASF, 2007). This is because the leather had good values of strength and elongation.

Evaluation of organoleptic properties of tanned leathers

The organoleptic properties of the tanned leathers were examined and presented in Table 6. The results indicated that quebracho tanned leathers exhibited superior characteristics compared to MBL tanned leathers. Specifically, the quebracho tanned leathers were found to be more plump, with a tighter grain, softer texture, and a better overall appearance. However, MBL tanned leathers showcased a smoother grain when compared to quebracho tanned leathers. Furthermore, it was observed that increasing the concentration of the tanning agent led to an enhancement in the organoleptic properties. Notably, the differences between the leathers tanned at 30% and 40% concentrations were minimal, as the organoleptic values were similar for both concentrations.

From previous investigations on the re-tanning agents prepared from black liquor, the obtained organoleptic properties were in coincided with Vedhanayagam et al. (2015), whereas they tended to be slightly lower than those obtained values by Taha et al. (2016).

Table 6. Organoleptic properties of studied tanned leathers

Group	Fullness	Grain tightness	Grain smoothness	Softness	General appearance
Quebracho 10%	4.6	5.6	7.4	5.6	6.0
MBL 10%	4.0	4.8	7.6	4.6	3.6
Quebracho 20%	5.6	6.8	8.2	6.6	6.4
MBL 20%	4.8	5.4	7.8	5.6	4.4
Quebracho 30%	8.0	7.2	8.6	7.4	7.4
MBL 30%	5.8	5.4	8.8	6.8	7.0
Quebracho 40%	8.4	8.4	9.0	8.4	8.4
MBL 40%	7.6	7.2	9.0	7.6	8.0

Note: MBL – modified black liquor.

CONCLUSION

This study investigated the potential of using black liquor from rice straw as a tanning agent. The results showed that black liquor from rice straw can be used for leather tanning after it is chemically modified to a pH of 7. The study found that modified black liquor is suitable for use as a sole tanning agent at a concentration of at least 30%. However, it is preferable to use it in combination with other tanning agents or as a re-tanning agent at unspecified concentrations. Using modified black liquor improves the fullness and smoothness of the leather surface, as well as the physical properties of the leather, making it of higher quality.

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