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Fatliquor preparation from Karanja seed oil (Pongamia pinnata L.) and its application for leather processing

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Abstract: *Fatliquor affects the physical properties of the leather and makes more flexible and softer. Fatliquor prepared from karanja seed oil by sulphation process followed by addition of sodium hydroxide to maintain pH at 5.0 with conc. sulphuric acid. FT-IR analysis of the sulphated product confirmed the attachment of sulphonic acid group. The physical and chemical properties of the fatliquor were found satisfactory. The prepared fatliquor was applied for the processing of goat skins. The processed goat skins physical and chemical properties compared with the skins processed by fatliquor made from castor oil and all the remaining leather processing chemicals same in both processing. Goat skins processed by these two types of fatliquor found standard leather specification. So fatliqour prepared from karanja seed oil extracted by soxlet extraction method considered as a substitute imported fatliqour.*

Keywords: *Fatliquor, FT-IR, Strength properties, organo leptic properties, sulphation, Karanja seed oil.*

I. Introduction

Karanja (Pongamia pinnata L.) belongs to the family of Leguminaceae. These trees are normally found around coastal areas, river banks, tidal forests and road sides. Karanja is one of the nitrogen fixing tree produces seed kernels containing 27-39 percent of oil. The fresh extracted oil is yellowish orange to brown colour and rapidly darkens on storage. It has a disgusting odour and bitter taste. Karanja oil is mainly used as a raw material for soap manufacturing but the main constrains for its other usage are the color and odor [1]. The oil is used mainly as lubricant, water-paint binder and production of biodiesel by methanolysis [2].

This paper describes the use of Karanja seed oil for the preparation of fatliquor and its uses for leather processing. Most of the fatliquors are imported from other countries and has invested huge foreign currency on imports. In this study we try to prepare substitutes of imported fatliquors by the fatliquors prepared from our local raw materials, Karanja seed oil.

The fatty acid composition of typical Karanja seed oil is shown in the Table-1.

Table-1: The fatty acid composition of a typical karanja seed oil [2]

Fatty acid	**Percentage**
Palmitic acid (C_{16})	11.65
Stearic acid (C_{18})	7.50
Oleic acid ($C_{18:1}$)	51.59
Linoleic acid ($C_{18:2}$)	16.64
Eicosanoic acid (C_{20})	1.35
Dosocasnoic acid (C_{22})	4.45
Tetracosanoic acid (C_{24})	1.09

From the table it is shown that in Karanja seed oil contains higher proportion of oleic acid than other fatty acid. Higher proportion oleic acid content is suitable for fatliquor preparation

II. Material And Methods

2.1 Raw material

Karanja seeds were collected from Rajshahi district, Bangladesh and full grain chrome tanned leathers were collected from commercial hide brokers.

2.2 Reagents

Reagents used for analysis are laboratory or analytical grade and leather processing are commercial grade.

2.3 Oil extraction

Karanja seeds are grained to powder form and shade dried for 10-15 days. The dried powders are subjected to Soxlet extraction using n-hexane as a solvent.

2.4 Sulphation process

A mixture of 40 ml concentrated sulphuric acid and 10 ml of concentrated phosphoric acid are added drop wise in 200 gm of karanja oil with constant stirring at 18-20°C temperature. Reaction was carried out slowly (approximately 3 hours required to complete the reaction). The sulphated products shaken with 400 ml of 10% sodium chloride solution and then keep in a separating funnel overnight and layer was separated. The pH of the separated upper layer sulphated liquor was neutralized at pH 5.0 by adding 30% sodium hydroxide solution and the resulting fatliquor then applied for leather processing.

2.5 Analysis of the fatliquor

Karanja seed oil was analysed and its chemical and physical characteristics are characteristies according to the American Oil Chemists Society Methods [3]. Refractive index, acid value, saponification value and unsaponificable matter were measured.

2.6 FT-IR analysis of Sulphated Product

In order to investigate presence of sulphonic acid group in sulphated fatliquor FT-IR spectra of sulphated fatliquor was taken using a Shimadzu FT-IR [4].

2.7 Fatliquoring process

After shaving the leather at 0.9 mm, it was wet back by adding water and wetting agent in the drum. After 30 minutes run the water was drained off. Then by adding 2% neutralizing syntan in the drum it was run for another 15 minutes at approximately 10 rpm in the ambient temperature. There after 0.5% sodium bicarbonate was added and the drum was run for an additional 15 minutes at the same speeds maintaining the pH at 5.0-5.5. The neutralized leather was washed with water and dyed with 1% acid dye for 30 minutes [5], [6].

Then 6% fatliquor was added to the dye bath at room temperature and was run at 10 rpm for 40 minutes. The dyed leather was then washed with water and removed from the drum. After samming and settling out it was air dried at room temperature and was used for various physical properties investigation. The fat liquoring process of skin is illustrated by the Table-2.

Table-2: Practical recipe for fat liquoring of skin

Process	%	Product	Duration (min)	Remarks
Wet back	200	Water at 35°C		
	0.2	Ethoxylated Fatty Alcohol		
	0.2	Oxalic Acid	Drum 30 min	pH 3.8
Neutralization	100	Water at 35°C		
	0.5	Sodium bicarbonate		
	2	Neutralizing Agent	Drum 30 min	pH 4.6
Dyeing-Fatliquoring	60	Water at 30°C		
	1	Dye (Beige)	Drum 30 min	
	100	Water at 60°C		
	6	Sulphated Vegetable Oil (Karanja oil)	Drum 60 min	
	1.0	Formic Acid	Drum 10 min	
	1.0	Formic Acid	Drum 10 min Run-off and Wash 10 min	pH 3.9

III. Result and Discussion

3.1 Analysis of Karanja seed oil

3.1.1 Physical properties

The physical properties of Karanja seed oil, sulphated Karanja seed oil and sulphated Castor oil (which is conventionally used as fatliquor in leather processing) are shown in Table-3.

Table-3: Physical properties of Karanja seed oil, sulphated Karanja seed oil and sulphatedn Castor oil

Parameter	**Karanja oil**	**Sulphated Karanja oil**	**Sulphated castor oil**
Appearance	Dark brown liquid	Brown liquid	Pale amber liquid
Solubility in water	Insoluble	Soluble	Soluble
Refractive Index (20.5^0 C)	1.4686	1.467	1.479
Specific Gravity at (20.5^0C)	0.880	0.861	1.029

Mean ± SD triplicate analysis

From the table it can be shown that the appearance of sulphated Karanja seed oil and sulphated Castor oil are distinct. Both the sulphated oil is soluble in warm water. The refractive index value, specific gravity values are higher in case of sulphated castor oil. Thus the physical properties of Karanja seed oil are in agreement with the reported values [3], [7].

3.1.2 Chemical properties

The chemical properties of Karanja seed oil and sulphated Karanja seed oil compared with sulphated Castor oil are shown in the Table-4.

Table-4: Chemical properties of Karanja seed oil, sulphated Karanja seed oil and sulphated Castor oil

Parameter	Karanja oil	Sulphated Koranja oil	Sulphated castor oil
pH of 10% solution	8.1	6.2	7.0
% Fatty matter	91.04	60.9	70.1
Saponification value	185	187	176
Iodine Value	86.5	81.5	81
Acid Value	7.1	5.06	8.0
SO_3 content	--	4.1%	5.1%
Ash content	--	6.2%	2.8%

Mean ± SD triplicate analysis

From the table-4 it is shown that Karanja seed oil contains high percentage of fatty matter, which indicates the use of this oil for preparation of fatliquor.

Iodine value shows that the oil has high quantity of unsaturated fatty acid. The iodine value is used to determine the degree of unsaturation of fatty acids. It is also reported that the oleic acid is the main fatty acids of this oil.

Karanja seed oil has been found to have the higher saponification value (Table-4). Since saponification value is inversely proportional to the molecular weight of the fatty acid present in oil. So it is found in liquid form at room temperature. Karanja seed oil also represents the higher acid value which makes this oil suitable ingredient for fatliquor.

Colloidal emulsion is indicative of low to medium degree of sulphation. This physical observation confirms that there is percentage of SO_3 incorporated in the sulphated compound. The combined SO_3 or emulsifier is the fuel which drives the oil droplets into the leather. Anionic emulsifier ensures a great degree of fixation [8], [9] since they will be attracted to the positively charged leather.

It is found that the iodine value of the raw Karanja seed oil decreases after sulphation, while the acid value increases showing the hydrolysis of fatty molecule.

The pH value of sulphated Karanja seed oil and sulphated Castor oil was found to be 6.2 and 7.0 respectively. This may result of neutralization carried out during the sulfating process.

The result showed that in sulphated Karanja seed oil the percentage of organically combined SO_3 [6] is relatively lower than the sulphated castor oil.

The sulphated Karanja seed oil showed higher ash content than sulphated Castor oil. This value referred to the sodium salt produced by neutralization of acid during sulphation.

3.2 FT-IR Analysis [4]

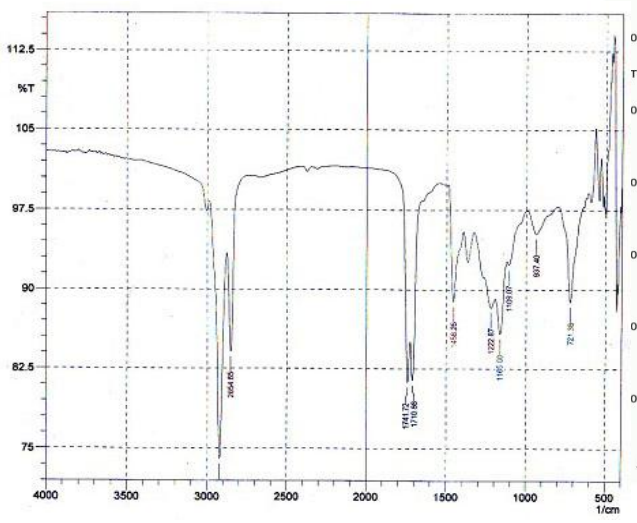

Fig. 1(a) The FT-IR spectra of sulphonated oil

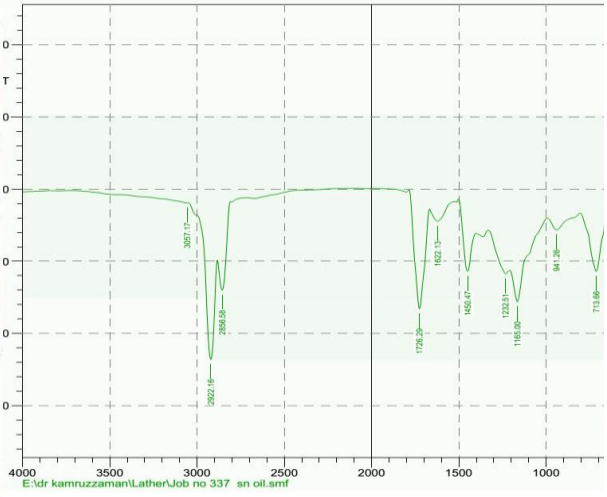

Fig. 1(b). FT-IR spectra of unsulphonated oil

Fig. 1(a) & 1(b) illustrates the IR spectrum of sulphated and unsulphated Karanja seed oil (Pongamia pinnata L.). The peaks at Fig.1(a)2854.65cm^{-1}, 1165.00cm^{-1} & 1222.87cm^{-1} represent the presence of C-H, C-O & -SO_3 groups respectively.

The peaks at Fig.1(b). 2922.16cm^{-1}, 1726.29cm^{-1} & 1165.00cm^{-1} are due to the presence of =C-H, C=O & C-O respectively.

3.3 Stability of Karanja seed oil

The stability of the prepared fatliquor in different solution is shown in Table-5.

Table-5: Stability of 10% solution

Solution	**Sulphated Karanja seed oil**
5% NaCl	Stable
5% Na_2SO_4	Stable
5% Basic Chromium Sulphate	Stable 1-2 hours
5% MgO	Stable
5% Formic Acid	Not stable

From the Table it can be shown that the prepared fatliquor is stable in salts, tanning and basification agent. This makes it possible using in re-tanning and fatliquoring steps. The stability of the emulsion of the experimental fatliquor is due to the poly hydroxyl sulphate group which is resistance to hydrolysis.

Commercial sulphated oil may give either a solution or emulsion with water. Such an emulsion may be either transparent or opaque. This variation in types of emulsion is dependent on the degree of sulphation and to a subsequent treatment and the neutralization. In general the more opaque types of conclusion are considered to due taken up better in fat-liquoring. The prepared fat-liquor gives colloidal emulsion with warm water.

3.4 Strength properties

The strength properties [10] like tensile strength tongue tear strength were tested using an instron tensile tester and grain crack & grain brust using lastometer of two matched side leather those were fat liquored by using sulphated Karanja seed oil and imported sulphated castor oil have been compared which is shown in the

Table-6: Strength Properties

Properties		Prepared fat-liquor	Imported fat-liquor
Tensile strength (N/mm^2)	Parallel	15.05	19.03
	Perpendicular	17.93	21.40
Elongation at break (%)	Parallel	53.0	49.0
	Perpendicular	28	24
Tear resistance (nm)	Parallel	4.9	5.01
	Perpendicular	7.2	7.11

From the strength properties analysis conducted, it is evident that the leather fatliquored using sulphated Karanja seed oil comparable to sulphated castor oil.

Some difference was observed in the physical test of leather however, results were found under the limit of standard specification which confirmed [6], [8] the suitability of prepared fatliquor. As the strength properties of the leather are also decided by the Cr_2O_3 and fat content, the leather have been physically tested for tensile strength, elongation at break, stitch tear strength and the results are reported in table-6.

The chromic oxide content and fat content in leather seems to have acceptable value for both the sulphated Karanja seed oil and Castrol oil. The enhancement in mechanical properties of treated leather using sulphated Karanja seed oil is due to good lubrication of [6], [11] fibers. The prepared fat-liquor possesses good penetration power and emulsion stability.

Tensile strength is the value of load the sample cross section can bear when load by the axial load and it is related with the leather sample state of collagen fibers. Therefore, the tensile strength can characterize the flexibility of fibers beside for the strength of collagen fibers.

Flexibility is one of the most important properties of leather achieved from fat-liquor. Fat-liquor reduce the friction between fiber is mainly related to the nature of sulfated oil and the quality of introduced oil. The elongation at break can characterize the softness, flexibility [5], [6], strength and toughness of leather matrix.

3.5 Physical testing and Hand Evaluation of leather

Experimental and control crust leather were assed for fullness, softness, grain tightness (break) by hand and visual examination. The leathers were rated on a scale of 0-10 points for each functional property by experienced leather technologist, where higher points indicate leather property.

3.6 Organo leptic properties

Leather made with sulphated Karanja seed oil and imported fatliquor based on castor oil were analysed for their organo lepltic properties which are shown in the Table-7.

Table-7: Organo leptic properties

Properties	Trial with prepared fatliquor	Trial with imported fatliquor
Softness	3.5	4.5
Fullness	4.0	4.5
Surface touch	4.5	4.5
Grain tightness	4.5	4.5
Odor	Odorless	Distinct

From the Table it can be shown that the leather made with the sulphated Karanja seed oil has the similar softness, fullness with the fatliquor based on Castor oil. Leather will be full if fiber sickening of the tanned fiber structure is well avoided.

Firmness or looseness of the grain seems also be coupled with the amount of fat [12], [13] in the grain. If the papillary layer is externally softened the grain may become loose and poor break occurs. For fullness, firmness is more critical issue; it requires proper adjustment of combination of fatliquor, dyeing and subsequent mechanical operation.

IV. Conclusion

The leather processed by the prepared fatliquor and conventional fatliquor are very closer in respect of physical, chemical, strength and organo leptic properties. Firmness or looseness of the grain coupled with the amount of fat in the grain. If the papillary layer is externally softened the grain may become loose and poor break occurs. For fullness, firmness is more critical issue; it requires proper adjustment of combination of fatliquor, dyeing and subsequent mechanical operation. Firmness value of prepared fatliquor less than convention liquor firmness value but higher percentage of fatty matter content ensures its suitability for preparing fatliquor. On the other hand prepared fatliquor is stable in salt, tanning and basification agent. Moreover the physical and chemical properties of the prepared fatliquor are very much closer to those of conventional fatliquor. Thus Karanja seed oil may be considered as an important source of fatliquor material.

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