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Extraction of Oil from *Aphanamixis polystachya* Seeds for Fat liquor Production

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ABSTRACT

Fat liquor is applied in the wet-finishing stage of leather processing to keep the leather soft and smooth by preventing the adhesion of fibers. This paper represents the prospect of preparation of fat liquor from *Aphanamixis polystachya* seed oil in leather processing. *Aphanamixis polystachya* oil was extracted from the dried seeds of *Aphanamixis polystachya* by the soxhlet extraction method. Fat liquor from *Aphanamixis polystachya* oil was prepared by applying concentrations of sulphuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) to carry out the sulphation process. The sulphation was completed by neutralizing with 30% sodium hydroxide (NaOH) to maintain pH at 5.0. Before and after sulphation, the analysis of the *Aphanamixis polystachya* oil was carried out to confirm the modification of the oil. The physical characterization of the oil and fat liquor was carried out in terms of appearance, odor, and solubility in water. The appearance and odor of the raw and sulphated *Aphanamixis polystachya* oil were completely different from one another. The sulphated *Aphanamixis polystachya* oil also gained the ability to be soluble in water to form an emulsion. The chemical characterization was carried out in terms of acid value, free fatty acid content, saponification value, iodine number, etc. The chemical characteristics showed a marked difference between the raw and sulphated *Aphanamixis polystachya* oil. The acid value, free fatty acid content, saponification value, and iodine number were obtained to be 75.07±2.01 mg KOH/g, 37.76, 229.52±2.72 mg KOH, and 66.54±0.61 g iodine/100 g, respectively in the sulphated *Aphanamixis polystachya* oil. This study could be helpful to utilize sulphated *Aphanamixis polystachya* oil as a fatliquor in leather processing as an appropriate alternative to the patent fat liquor to reduce production costs.

Keywords: *Aphanamixis polystachya* oil, Emulsion, Fat liquor, Soxhlet extraction, Sulphation.

1. Introduction

The leather industry is one of the most prospective industrial domains in Bangladesh due to having available raw materials. It is the second largest export earner after the ready-made garment sector (Rakib et al. 2020). Raw hide/skin is the main raw material of leather that is usually transformed into a non-putrescible and stable material through a series of processing e.g., beamhouse, tanning, and finishing (Maina et al. 2018). Wet processing consists of a series of chemical operations e.g., neutralization, retanning, dyeing, fat liquoring, etc. (Saravanabhavan et al. 2006).

Fat liquoring is a process of oil-coating where the surfaces of leather fibers are lubricated to achieve the ability to slip over one another (Liu et al. 2007). Fat liquor helps to prevent the hardening and breaking of leather on drying and imparts softness, abrasion resistance, and flexibility to the tanned leather fibers (Sivakumar et al. 2012). Applying fat liquor, different strength properties e.g., tensile strength, stitch tear strength, and water-repellant properties are also enhanced in the leather (Kamely et al. 2021). Hence, value-added leather can be manufactured to provide customers with specified aesthetic features by employing fat liquors. Fat liquor is normally comprised of an emulsifier and water-insoluble oil/fatty matter (Kassahun, 2014). Emulsification is usually attained by introducing phosphate, sulfonate, sulfite groups, etc. into the structure of oils/fats (Hassan, 2017; Mekonnen, 2019).

The use of edible oils for the preparation of fat liquor is not feasible in Bangladesh due to the limited source of seeds in terms of annual demand. The sources of common non-edible oils are castor (*Ricinus Communis L.*); Pitraj (*Aphanamixis Polystachya*); Karanja (*Pongamia pinnata*); Neem (*Azadirachta indica*); and Jatropha (*Jatropha curcas*), etc. (Ferdous et al. 2013). Researchers already introduced different oils prepared from different seeds e.g., pumpkin (Ojih et al. 2016); neem (Mekonnen, 2019); castor (Hassan, 2017); Karanja (Quadery et al. 2015); *Citrullus colocynthis* (Sahu et al. 2017), etc. as raw material for manufacturing fat liquor. But all these oils are not cost-effective and available in our country. Utilization of castor oil to prepare fat liquor is also expensive for the unavailability of castor seeds and the higher cost of castor oil (Angeline et al. 2021).

Aphanamixis polystachya (AP) is commonly known as 'Pithraj' in Bangladesh and 'Amoora' in India (Palash et al. 2015). About 40-45% non-edible is yielded from AP seeds. The yield (%) of AP oil is higher compared to other non-edible oil e.g., rubber seed oil (31.8%) (Gui et al. 2008). The AP seed oil does not have any suitable and potential application in our country (Ferdous et al. 2013). Therefore, AP can be applied to prepare fat liquor for leather.

The aim of this study is the extraction of oil from AP seeds to prepare noble fat liquor for leather. The extracted oil and fat liquor were physically characterized in terms of appearance, odor, and solubility in water and chemically characterized in terms of acid value, free fatty acid content, saponification value, and iodine number.

2. Materials and methods

2.1 Raw material

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The AP seeds were collected from the local market, in Khulna, Bangladesh. The seeds were washed with distilled water. Fig. 1 represents the AP tree, fruits, and seeds.

Fig. 1 AP tree (a), fruits (b), and seeds (c)

2.2 Reagents

The reagents that were used in this experiment were ethanol (C_2H_5OH, Merck Specialties Private Limited, Worli, Mumbai), phosphoric acid (H_3PO_4, Merck Specialties Private Limited, Worli, Mumbai), sulfuric acid (H_2SO_4, Merck Specialties Private Limited, Worli, Mumbai), sodium chloride (NaCl, Merck, India), sodium hydroxide (NaOH, Loba, India), sodium sulphate (Na_2SO_4, Loba, India), magnesium oxide (MgO, Loba, India), formic acid (HCOOH, Merck Specialties Private Limited, Worli, Mumbai), basic chromium sulphate (Merck, India), phenolphthalein (Loba Chemie, India), potassium hydroxide (KOH, Merck, India), hydrochloric acid (HCl, Merck Specialties Private Limited, Worli, Mumbai), sodium thiosulphate ($Na_2S_2O_3$, Merck, India), starch solution (Loba, India), potassium iodide (KI, Merck, India) and chloroform ($CHCl_3$, Merck Specialties Private Limited, Worli, Mumbai). All of the reagents were collected from a local scientific store, in Khulna, Bangladesh.

2.3 Oil extraction

The collected seeds were sun-dried in the open air for five days and then the kernels were ground with mortar properly. Then ground AP seeds were screened to separate the coarse ones from the finer ones. The coarse ones were again ground to obtain a finer powder. The oil was extracted from the powders using ethanol as solvent employing the Soxhlet apparatus. About 50 g of AP seeds powder was mixed with 300 mL C_2H_5OH in the soxhlet extraction kit and heated at 60ºC for about 5 h.

Table 1 Properties of AP oil (Banik et al. 2015).

Parameters	Unit	Value
Color Index		0.5
Density @ 15°C	g/cc	0.8473
Kinematic Viscosity @ 40°C	cSt	2.0304
Sulfur Content	% (w/w)	8.091
Water Content	% (v/v)	Nill
Carbon Residue	% (w/w)	0.0593
Ash Content	% (w/w)	0.00255

The process of extraction in the soxhlet extractor was repeated until a sufficient quantity of AP oil was obtained. After extraction, the AP oil was kept in an oven at 60ºC for about 5 h to obtain solvent-free oil. After oil extraction, it was filtered. The viscous AP oil was found to be dark brown in color. It was then stored at room temperature. This extracted AP oil was employed as raw material for fatliquoring production. The properties of the AP oil are shown in Table 1.

2.4 Sulphation process

At first, a mixture of 20 mL of concentrated H_2SO_4 and 5 mL of concentrated H_3PO_4 was prepared to carry out the sulphation. Then, the mixture of acids was added to 100 g of AP oil with constant stirring at 18±2°C temperature to carry out the reaction slowly (Quadery et al. 2015). The time was approximately 2.5 h requiring to complete the reaction of sulphation. After that, the sulphated products were shaken with 200 mL of 10% NaCl solution (Quadery et al. 2015). Finally, the solution was kept in a separating funnel overnight and the layer was separated. The pH of the separated upper layer sulphated liquor was carefully neutralized at pH 5.0 by adding 30% NaOH solution (Quadery et al. 2015). Then the resulting fat liquor was bottled and stored at room temperature. The stability of the fat liquor was analyzed against 5% NaCl, 5% Na_2SO_4, 5% basic chromium sulphate, 5% MgO, and 5% HCOOH.

2.5 Physical characterization of oil and fat liquor

AP oil and prepared fat liquor were physically characterized in terms of different organoleptic properties e.g., physical state at room temperature, appearance, odor, and solubility in water. At first, the appearance and odor of the oil and fat liquor were observed. The solubility of the AP oil and prepared fat liquor was checked in warm water.

2.6 Chemical characterization of oil and fat liquor

AP oil and prepared fat liquor were chemically characterized in terms of different chemical properties e.g., acid value, free fatty acid (%), saponification value, and iodine number.

2.6.1 Acid value

At first, absolute ethanol alcohol was prepared. To determine the acid value, 1 g of oil/fat liquor was mixed with 5 mL of absolute ethanol alcohol. About 1-2 drops of phenolphthalein were added to it. Then heated with shaking in a water bath for 10 min and cooled. Finally, titration was performed using 0.1 N KOH until a pink color appeared. The volume of KOH used was noted. Calculation of acid value is usually performed from milliliters of KOH required, normality of KOH, and weight of the sample which is shown in Eq. 1. The value of % of free fatty acid is calculated from the acid value which is represented in Eq. 2.

Where V is the volume of KOH (mL), N is the normality of KOH and w is the weight of the oil/fat liquor.

$$\text{Acid value} = \frac{V \times N \times 56}{w} = \text{mg of KOH} \qquad (1)$$

$$\%\text{ of free fatty acid} = \text{acid value} \times 0.053 \qquad (2)$$

2.6.2 Saponification value

To determine the saponification value, 25 mL of alcoholic KOH was added with 1 g of oil/fat liquor. Then heating was performed for 1 h with occasional shaking. Finally, titration was performed using 0.5 N HCl with a phenolphthalein indicator. The volume of HCl used was noted. Similarly, under the same condition, a blank determination was set up and the volume of HCl used was noted. The calculation was performed from the value of milliliters of HCl required by blank, milliliters of HCl required by sample, normality of HCl, and weight of the sample which is shown in Eq. 3.

$$\text{Saponification value} = \frac{56.1 \times (B - S) \times N}{w} \qquad (3)$$

Where N is the normality of HCl, B is the amount of HCl required for blank (mL), S is the amount of HCl required for sample (mL), and w is the weight of the oil/fat liquor.

2.6.3 Iodine number

At first hanus solution was prepared from iodine, glacial acetic acid, and bromine water. To determine the iodine value, 10 mL chloroform was added with 0.25 g oil/fat liquor. Then, 30 mL hanus solution was added to it and left for 30 min with shaking continuously. After that, 10 mL of 15% KI and 100 mL of distilled water were added. Finally, titration was performed using 0.1 N $Na_2S_2O_3$ solution till the yellow color formed, then 2/3 drops of the starch solution were added where the blue color formed and continued with titration till the blue color disappeared. The volume of $Na_2S_2O_3$ used was noted. Similarly, under the same condition, a blank determination was set up and the volume of $Na_2S_2O_3$ used was noted. At last, the iodine number was calculated from Eq. 4.

$$\text{Iodine value} = \frac{(B - S) \times N \times 0.127 \times 100}{W} \qquad (4)$$

Where N is the normality of $Na_2S_2O_3$, B is the amount of $Na_2S_2O_3$ required for blank (mL), S is the amount of $Na_2S_2O_3$ required for sample (mL), and w is the weight of the oil/fat liquor.

2.7 Economic Viability Analysis

The advantages of AP oil fat liquor in terms of cost in the market were evaluated. The price was calculated from the unit prices of all the reagents employed in the preparation of fat liquor. Finally, the total cost for the preparation of fat liquor was compared with the commercial fat liquors used in the leather industry.

3. Results and discussion

3.1 Physical characteristics of oil/fat liquor

AP oil and prepared fat liquor were physically characterized in terms of physical state at room temperature, appearance, odor, and solubility in water. The physical properties of AP oil and prepared fat liquor are shown in Table 2.

Table 2 Physical properties of AP oil and prepared fat liquor

Parameter	AP oil	Prepared fat liquor
Physical state at room temperature	Liquid	Semi-liquid
Appearance	Dark brown	Brown
Odor	Pungent	Light
Solubility in water	Insoluble	Soluble

From Table 2, it can be found that the appearance, odor, and solubility of AP oil and prepared fat liquor were different. The AP oil was found to be dark brown in color however the fat liquor was brown colored. After sulphation, the AP oil gained the ability to be soluble in warm water.

3.2 Chemical characteristics of AP oil/fat liquor

The extracted AP oil and prepared AP oil fat liquor were chemically characterized by acid value, free fatty acid (%), saponification value, and iodine number. The chemical properties of AP oil and prepared fat liquor are represented in Table 3.

Table 3 Chemical properties of AP oil and prepared fat liquor

Parameter	Unit	AP oil	Prepared fat liquor
Acid value	mg KOH/g	70.99±1.63	75.07±2.01
Free fatty acids	-	35.71	37.76
Saponification value	mg KOH g	231.12±2.51	229.52±2.72
Iodine value	iodine/ 100 g	68.70±0.41	64.54±0.61

From Table 3, it is found that the acid value of AP oil fat liquor was higher than the AP oil. The higher acid value of sulphated AP oil indicates that sulphated AP oil is suitable for fat liquoring (Quadery et al. 2015). The value of free fatty acids (%) is also higher in the case of sulphated AP oil compared to AP oil which may be a positive sign of sulphated AP oil to be used as fat liquor.

Sulphated AP oil has been found to have a higher saponification value than AP oil (Table 3). The smaller the saponification number the larger the average molecular weight of the triacylglycerol present, which meant the saponification value is inversely proportional to the molecular weight of the fatty acid present in oil/fat liquor (Quadery et al. 2015). The AP oil was found to be in liquid form at room temperature but the sulphated AP oil was not found to be in liquid form. Though the sulphated AP oil was in a semi-liquid form, it was possible to make an emulsion using hot water easily.

The iodine value is usually used to determine the degree of unsaturation of fatty acids. AP oil contains both saturated and unsaturated fatty acids. From Table 3, it can be found that the iodine value was greater in sulphated AP oil. It is known that an increase in iodine value indicates high susceptibility of lipids to oxidative rancidity due to a high degree of unsaturation. The iodine value of raw AP oil decreases after sulphation, while the acid value increases showing the hydrolysis of the fatty molecule. The value of pH in AP oil was found to be near 6.0. This may be due to the neutralization carried out as a part of the sulfating process using NaOH. Usually, the patented fat liquors give an emulsion with water. The type of emulsion may be either transparent or opaque. The variation in the type of an emulsion depends on the degree of sulphation and subsequent treatment and neutralization (Quadery et al. 2015). Sulphated AP oil produced an opaque emulsion in hot water which was brownish in color. There was no change in the emulsion of sulphated AP oil with patent fat liquor excepting color.

3.3 Stability of fat liquor

The stability of the 10% solution of AP oil fat liquor was analyzed employing NaCl, Na_2SO_4, basic chromium sulphate, MgO, and HCOOH solutions which are represented in Table 4.

Table 4 Stability of AP oil fat liquor.

Solutions	Stability
5% NaCl	Stable
5% Na_2SO_4	Stable
5% Basic Chromium Sulphate	Stable for 1h
5% MgO	Stable
5% HCOOH	Not stable

From Table 4, it can be found that the AP oil fat liquor was stable in NaCl and Na_2SO_4 salts, basic chromium sulphate tanning salt, and MgO basifying agent. So, AP oil fat liquor can be used in re-tanning and fat liquoring steps.

3.4 Cost Analysis

The production cost of fat liquor from AP oil was calculated which is shown in Table 5. Considering the cost of the reagents employed in the preparation of AP oil fat liquor, the total cost of the fat liquor is about 1.74 USD/L. However, the total cost required for the preparation of commercial fat liquors is required about 2.05-2.33 USD/L (Saranya et al. 2020). So, the AP oil fat liquor can save 0.31-0.59 USD/L compared to the commercial fat liquors.

Table 4 Economic cost of AP oil fat liquor

Reagents	Price (USD/L of fat liquor)
H_2SO_4	1.32
H_3PO_4	0.41
NaOH	0.0027
NaCl	0.011
Total cost of fat liquor	1.74 (USD/L)

Therefore, tanneries would be gone down to employ AP oil fat liquor for the advantages in terms of cost competitiveness.

4. Conclusion

This investigation provided a viable option to use sulphated *Aphanamixis polystachya* oil as fat liquor in the leather industry. *Aphanamixis polystachya* seeds are available material for the extraction of oil to prepare fat liquor. The economical assessment of the *Aphanamixis polystachya* oil in the fatliquoring process for tanneries was investigated. The investigation on the chemical properties of this fat liquor has cleared that sulphated *Aphanamixis polystachya* had better chemical properties. After the extraction of valuable oil, the seed-cake can be used for composting and adsorbent preparation. *Aphanamixis polystachya* oil can be converted into a value-added product of the leather industry from the easy extraction and sulphation process of oil. The prepared *Aphanamixis polystachya* oil fat liquor would provide a reduction in the cost of procurement of fat liquor and also on over-dependence on patented fat liquor for leather processing.

5. References

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