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Assessment of Coffee Pulp as a Potential Source of Tannins for Leather Processing

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Article

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ABSTRACT

The leather industry is experiencing environmental challenges due to pollution associated with chromium tanning. Vegetable tanning is considered as an ecofriendly alternative method. Previous research studies have established that coffee contains 1-10% of tannins. In this study coffee arabica pulp was determined for its tannin content and tanning strength for potential use as a source of tanning material. The hide powder method was used and the tannin content of coffee arabica pulp determined as 5.04% with the tanning strength of 2.26 compared to mimosa which had a tannin content of 63.56% with a tanning strength of 2.82. Both coffee arabica pulp and mimosa exceeded the 1.5 tanning strength recommended for tanning agents. It was concluded that coffee arabica pulp sufficient tanning strength to be used as a tanning material.

KEYWORDS

coffee pulp, vegetable tanning, leather

INTRODUCTION

Leather making is an old craft that has been practiced as far back as the Neolithic [1]. Leather processing converts a material susceptible to biodegradation (hides or skins) to one which is resistant to it (leather), has thermal stability and is resistant to abrasion [2]. Leathermaking first utilized vegetable tannins in what was referred to as vegetable tanning before the advent of chromium tanning over 150 years ago [2]. Currently, 90% of all the leathers is produced by using the chrome tanning method and the remaining 10% is mainly produced by using the vegetable tanning method [3]. The use of chromium salts produces leathers with good characteristics but has faced criticism for contributing to environmental pollution. This is because not all the chromium is utilized during the tanning, with 30-40% of it being released into the environment through solids and wastewater. The presence of chromium in the environment negatively affects both plants and animals [4]. Vegetable tanning method is ecofriendly compared to the use of chromium salts, since tannins are biodegradable [5]. The traditional source of vegetable tannins are wattle, mangrove, quebracho and hemlock plants, which are species that contain a higher amount of condensed tannins, with myrobalan and chestnut

plants containing a higher amount of hydrolysable tannins [6]. The current supply of vegetable tannins is, however, not sufficient to sustain the global leather production and, as such, there is need for more sources of tannins to supplement the current production of tannins. Mimosa is the main vegetable tannin used in commercial tanning but has limited supply and is costly. Coffee pulp obtained from coffee cherries from the coffee plant has been suggested as a potential source of these tannins [6].

The coffee plant is a shrub from the rubiciae family which produces coffee berries and was first used in Ethiopia to make the coffee beverage from its beans. There are two species which have been exploited in the production of coffee, coffee arabica and coffee robusta. The two types of coffee undergo different types of processing, with coffee arabica undergoing wet processing, which accounts for more than 70% of the production, and robusta undergoing dry processing [7]. Coffee production begins at the farm where the coffee trees are grown. The production of coffee in sequence includes: planting, harvesting and processing the cherries, drying the beans, milling the beans, exporting the beans, tasting the beans to determine quality, roasting the coffee, grinding the coffee and, lastly, brewing the coffee [8]. Once the coffee berries are mature and ripe, they are harvested and taken to the coffee factory for processing. Coffee processing results in by-products, which include the pulp, the husk and the silverskin. Wet processing produces coffee pulp whereas dry processing produces the husk [9]. In wet processing, the layers of the fruit (cherry) are removed subsequently by several processes, which include pulping, fermentation, washing and drying. The pulping process may be done by using different pulping methods. These include drum pulping, disk pulping and vertical spiral drum pulping which results with the pulp being removed [11]. The coffee pulp produced from this process is the one under study for its potential use in leathermaking.

Coffee pulp contains polyphenolic components, which includes tannins [9]. Tannins are able to bind proteins and as such are used in the leather industry to convert hides and skins to leather [10]. Tannins are polyphenolic compounds that have molecular weights between 500 and 20000 Daltons. They are classified into two categories, namely hydrolysable tannins and condensed tannins [11].

Hydrolysable tannins are grouped into two subgroups, ellagitannins and gallotannins, which are esters of the gallic and ellagic acid, respectively, and glucose. They are referred to as hydrolysable tannins as they undergo hydrolysis to form their individual components when reacting with hot water, acids or bases or tannase enzymes [12]. These tannins are especially found in dicotyledonous angiosperms with some examples being alder leaves, myrobalans, chestnut and tara [13]. They yield leathers that possess light fastness, clarity and of excellent colours.

Condensed tannins, which are also referred to as proanthocyanidins are complex polymers of flavan-3-ol units. They are said to be mixtures of oligomers of different degrees of polymerization comprising of catechins (flavan-3-ols) and leucoanthocyanes (flavan-3-4-diols), monomer units and monomeric and polymeric carbohydrates. The proportions of these carbohydrates influence the viscosity and

reactivity of the tanning extract [14,15]. The most commonly commercially used condensed tannin is mimosa.

Coffee is one of the major cash crops in Kenya and constitutes 8% of the agricultural exports [16]. This translated to USD 230 mil. in foreign exchange in 2017 [17]. The coffee processing industry is widespread but mainly located in the central region of Kenya. The processing of a large quantity of coffee produces waste/by-products, a major component of it being coffee pulp, which poses waste disposal challenges.

Studies have indicated that coffee pulp contains tannins and went ahead to propose that they may be used in tanning. However, there hasn't been any study to determine whether these tannins are able to convert collagen to leather [18]. It is for this reason that this study, the aim of which was to analyse the properties of coffee pulp as a tanning material and assess its suitability for leathermaking, was conducted.

EXPERIMENTAL

Materials

The materials used in this study were ferric III chloride (SIGMAALDRICH), potassium hydroxide (Riedel-de Haan), kaolin (LOBACHEMIE), chromium potassium sulphate (LOBACHEMIE), gelatin (THOMAS BAKER), sodium chloride (LOBACHEMIE), acetone (LOBACHEMIE), mimosa powder.

Sample collection

Coffee pulp was collected from Yadini farm, Kiambu county, Kenya. The pulp was from coffee arabica species as it is the species grown commercially in Kenya.

a) b)

Figure 1. a) wet coffee pulp at one of the dumpsites; b) coffee pulp after drying

12 samples were collected across four different days, with the samples collected randomly at three different coffee pulp dumpsites (Figure 1). The collected pulp was in wet condition and was dried under a shade until its weight remained constant, packaged in polythene bags and then transported to the Department of Public Health Pharmacology and Toxicology labs, University of Nairobi for further analysis.

Sample Preparation

The dried pulp was ground with a grinding machine into small particles. The ground pulp was then passed through a 600 micron IS sieve to separate the large particles from the small particles. The small particles were then ready for analysis. Mimosa used for the analysis was already in powder form.

Extraction

Extraction was done by the Procter extraction method. The ground pulp used was sufficient to give 4 g of tanning matter per litre. The ground pulp was first soaked overnight in cold distilled water in the proctor extraction chamber and the extraction commenced the following day. 150 ml was extracted at 40 °C and the temperature was raised to 50 °C. 750 ml was extracted at this temperature and the temperature was further raised to 100 °C. 1100 ml was then extracted at the boiling point to make up two litres of the crude extract. The extract was then cooled in a sink with cold water at 26 °C, with the container being agitated frequently to avoid localized cooling.

Mimosa extract was prepared by measuring the weight of the mimosa powder that was supposed to give the required tanning strength. The powder was then dissolved in 900 ml of hot water to make a liquid extract of mimosa.

Phytochemical screening

Tannin testing

1. Ferric chloride test

One gram of ground coffee arabica pulp was poured into a 100 ml-beaker and 10 ml of distilled water was added, boiled for 5 minutes and then filtered. A few drops of 10%-ferric chloride were then added. Appearance of blue-black or greenish solution indicated the presence of tannins. The test was similarly done to mimosa as a standard.

2. Test for condensed and hydrolysable tannins

A few drops of aqueous potassium hydroxide were added to 2 ml of the extract obtained from the tannin testing. The appearance of the red colour confirmed the presence of condensed tannins. No

observable colour change confirmed the presence of hydrolysable tannins. This was also done for mimosa and used as a standard.

3. Quantitative analysis of tannins

The analysis of tannins was conducted using the hide powder method as described in the IS 5466: 2013 standard, Vegetable tanning materials - Methods of test. The moisture content, total solids, total soluble solids, non-tans, tans and pH were analysed. The tanning strength, which is the ratio of tans to non-tans, was also determined.

Hide powder preparation

A bovine hide was collected from Dagoretti slaughter house and processed to make hide powder. The bovine hide was soaked, limed, fleshed, delimed, bated and pickled before being neutralized with acetone to bring the pelt to pH 5.5. The pelt was then airdried under a shade until it was dry and then one kilogram of it was shredded into powder with a star mill.

Chromed hide powder preparation

Approximately 6.25 g of hide powder were mixed with an amount of distilled water 10 times the weight of the powder in order to create a reaction. 1 g of chrome alum per gram of dry hide powder was added and the mixture was stirred for several hours and then left to stand overnight. The following morning the chromed hide powder was transferred to a clean linen and then washed and drained. The linen containing the chrome hide powder was then placed in a suitable beaker and opened. An amount of distilled water equal to 15 times the weight of the powder was added and mixed with the powder. The mixture was then left to react for 15 minutes after which the linen with the powder was lifted up, the beaker drained and the linen squeezed until the powder remained with approximately 75% of moisture. This process of creating a reaction between distilled water and the powder was repeated three times and then the cake powder was mixed until there were no more lumps visible. The powder was then weighed.

Determination of moisture (IS 5466)

Five grams of finely ground coffee arabica or mimosa was placed in a tared-mouth weighing bottle and weighed on an analytical balance accurately. The bottle containing the sample was transferred to an oven and the sample dried at 100 ± 2 °C for 3 to 4 hours and then cooled in a desiccator for 20 minutes. The process was repeated until the difference in weight of the first weight and the subsequent weight after one hour was not more than 2 mg.

$$the\ moisture\ content\ percentage\ by\ weight = \frac{(w1-w2)\times 100}{w2} \quad (1)$$

$$total\ solids\ percentage\ by\ weight = \frac{w2}{w1} \times 100 \quad (2)$$

Where: w1 is the weight in g of the material taken for the test; w2 is the weight in g of the residue left after drying.

Determination of total solubles

One gram of kaolin was added to the bottom of a fluted filter paper with the aid of 50 ml of extract. After the addition was complete, 500 ml of fresh extract was filtered with the filtrate collected as soon as it was optically clear. 50 ml of the filtrate was pipetted into a tared porcelain basin and was evaporated in a water bath to dryness. The porcelain basin was then placed in an oven and dried at 100 ± 2 °C for 3 to 4 hours and then cooled in a desiccator for 20 minutes. The drying and cooling was repeated until two subsequent weights differed only by 2mg.

$$Total\ solubles\ percentage\ by\ weight = \frac{w2}{w1} \times \frac{v1}{v2} \times 100 \quad (3)$$

Where: w2 is the weight in g of the residue left after drying, v1 is the volume in ml made up originally, w1 is the weight in grams of the tanning material taken and v2 is the volume in ml of the test solution pipetted out.

Determination of non-tannins

Wet chrome hide powder containing 6.25 g of dry hide powder was weighed accurately and transferred to a round bottomed flask containing 100 ml of unfiltered coffee pulp extract. 20 ml of distilled water was then added into the flask. The flask was then vigorously shaken by hand for 15 seconds and was then taken to a mechanical rotary shaker and shaken for 10 minutes at 50-65 revolutions per minute. The powder and the solution were poured onto a clean linen covering a funnel. Once the filtrate was collected, the powder was squeezed to remove the remaining filtrate. 1 g of kaolin was then added to the filtrate and transferred to a fluted filter paper. Once the transfer was completed, the filtrate was collected as soon as the filtrate was optically clear. 50 ml of the filtrate was then transferred to a porcelain basin and left to evaporate in a water bath. Once the evaporation was complete, the porcelain basin was transferred to an oven and dried at 100± 2 °C for 3 to 4 hours and then cooled in a desiccator for 20 minutes. The process was repeated until two consecutive weights after an hour had the same weight, or the difference in weight was not more than 2 mg.

$$Non - tannins\ percentage\ by\ weight = \frac{w2 \times v1}{w1 \times v2} \times 100 \quad (4)$$

Where: w2 is the weight in g of the residue left after drying, v1 is the volume in ml made up originally and w1 is the weight in g of the taken material.

Determination of tannins

Tannins were determined by calculating the difference between total solubles and non-tans.

$$tannins\ percentage\ by\ weight = x - y \quad (4)$$

Where: x is the total soluble percentage by weight (Equation 3) and y is the non-tannins percentage by weight (Equation 4).

Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR) analysis

Vibrational infrared spectroscopy was conducted for both the coffee pulp extract and mimosa by an ATR-FTIR spectrometer (IRAffinity 1-S). The powders were put in direct contact with the diamond. The spectra were recorded in 4000-600 cm^{-1} spectra with a resolution of 0.5 cm^{-1}, using 32 scans. Labsolutions IR software was used for processing and evaluating the spectra.

Determination of pH

The relative density of the extract was adjusted with cold water to 1.05 g cm^3 at 27 °C. The pH was then measured with a pH meter.

Statistical analysis

The experiments were performed in duplicates, the data was entered in EXCEL and the means were presented in tables. The data was then exported to General statistics (GENSTAT) 14th Edition for analysis. A statistical t-test was used for the comparison of means between mimosa and coffee pulp. Differences between the two means were considered to be significant at $p<0.05$.

RESULTS AND DISCUSSION

The amount of tannins yielded at different temperatures was recorded as follows:
The yield of tannins at 50 °C, as can be observed from Figure 2, was the highest, when compared to the yield at 40 °C and 80 °C.

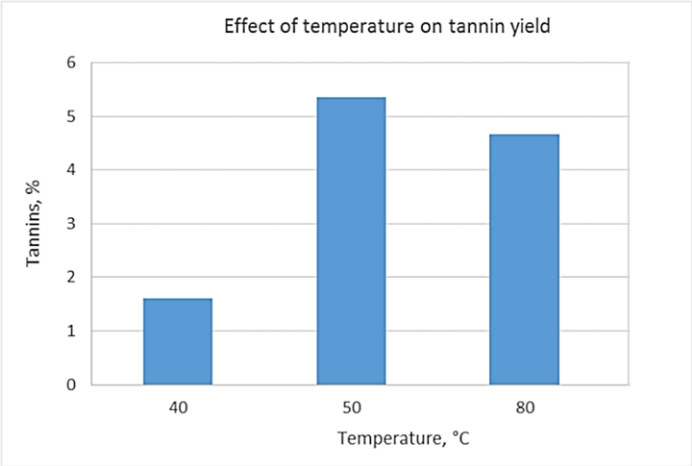

Figure 2. The effect of temperature on the yield of tannins in the coffee pulp extract

Naima et al. observed in their study of moroccan Acacia mollissima barks that, at 60 °C, the tannin yield by water extraction was at its peak compared to 40 °C and 80 °C [20]. Arina and Harisun, in their study of Quercus infectoria, observed that the tannin yield peak was at 75 °C [21]. These observations agree with other studies which show that the tannin yields from most plant sources begin to decline after the temperatures reach 80 °C. This is because prolonged exposure of tannins (phenolic compounds) to temperatures above 80 °C could lead to degradation.

Table 1. Phytochemical results for the tannin test and test for condensed or hydrolysable tannins

Phytochemical	Test	Coffee Pulp	Mimosa
Tannins	Ferric III Chloride test	+	+
Hydrolysable tannins	Potassium Hydroxide test	-	-
Condensed tannins	Potassium Hydroxide test	+	+

(+) - the presence of the phytochemical; (-) - the absence of the phytochemical

Table 2. Results for moisture content, total solids, soluble solids, non-tans, tannins, tanning strength and pH for coffee arabica pulp

Properties	S1o	S2f	S3f	S4f	S5o	S6f	S7f	S8f	S9f	S10f	S11o	S12f
Moisture content, %	10.81	10.53	10.32	9.64	11.21	10.12	11.14	10.92	8.51	9.81	10.01	10.74
Total solids, %	89.19	89.47	89.68	90.36	88.79	89.88	88.86	89.08	91.49	90.19	89.99	89.26
Soluble solids, %	6.84	7.69	7.45	7.13	6.53	7.39	7.01	7.41	7.85	6.97	7.73	7.30
Non-tans, %	2.06	2.58	2.29	2.12	1.88	2.35	1.94	2.28	2.67	2.04	2.50	2.21
Tannins, %	4.77	5.11	5.16	5.01	4.65	5.04	5.07	5.13	5.18	4.93	5.23	5.09
Tanning strength	2.31	1.98	2.25	2.36	2.47	1.94	2.59	2.25	1.94	2.41	2.09	2.30
pH	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7

s - sample; o - pulp that had remained on the dumpsite for a prolonged period of time; f - fresh pulp from processing

The coffee pulp samples at the point of sample collection were a mixture of red and yellow in colour when fresh but upon being dried their colour changed to dark brown. This was attributed to the oxidation of the phytochemicals present in them, affecting their structural composition, which was observed by the change in colour [21].

The extraction process was conducted at the temperature ranging from 40 °C to 100 °C with water being used as the solvent. The high temperatures were used to enhance the tannin yield from the extraction.

Table 3. Summary of tanning strength, tannins and non-tans of coffee arabica and mimosa

Properties	Coffee pulp	Mimosa
Moisture content, %	10.31 ± 0.76	8.05 ± 0.19
Total solids, %	89.69 ± 0.76	91.95 ± 0.19
Total soluble solids, %	7.28 ± 0.39	86.04 ±0 .17
Soluble non-tans (NT), %	2.24 ± 0.25	22.54 ± 0.49
Tannins (T), %	5.04 ± 0.17	63.56 ± 0.58
Tanning strength (T/NT)	2.26	2.82
pH	4.7 ± 0.00	4.6 ± 0.00

The tannin analysis was conducted in two stages with the first being the detection by metal salts and the second being the quantification by the gravimetric hide powder method [22,23]. The detection stage showed that both the coffee arabica pulp from Yadini farm and the commercial mimosa contained tannins of the condensed type as shown in Table 1. These findings were in agreement with what was found in literature, the observation of the coffee pulp containing condensed tannins but no hydrolysable tannins [24]. Condensed tannins are more suitable for the tanning process as they are more reactive than hydrolysable tannins because of their high molecular sizes and them providing more phenolics groups for bonding.

ATR-FTIR results

The spectra in Figure 3 showed several functional groups for coffee pulp tannins. These were an O-H stretching at 3259.70 cm^{-1} due to intermolecular bonds, C-H stretching at 2918.30 cm^{-1} attributed to an alkane, C-H group at 2848.86 cm^{-1} attributed to an alkane. There was a C=C group at 1548.84 cm^{-1} attributed to a cyclic alkene and C-H bending on an alkane due to a methyl group.

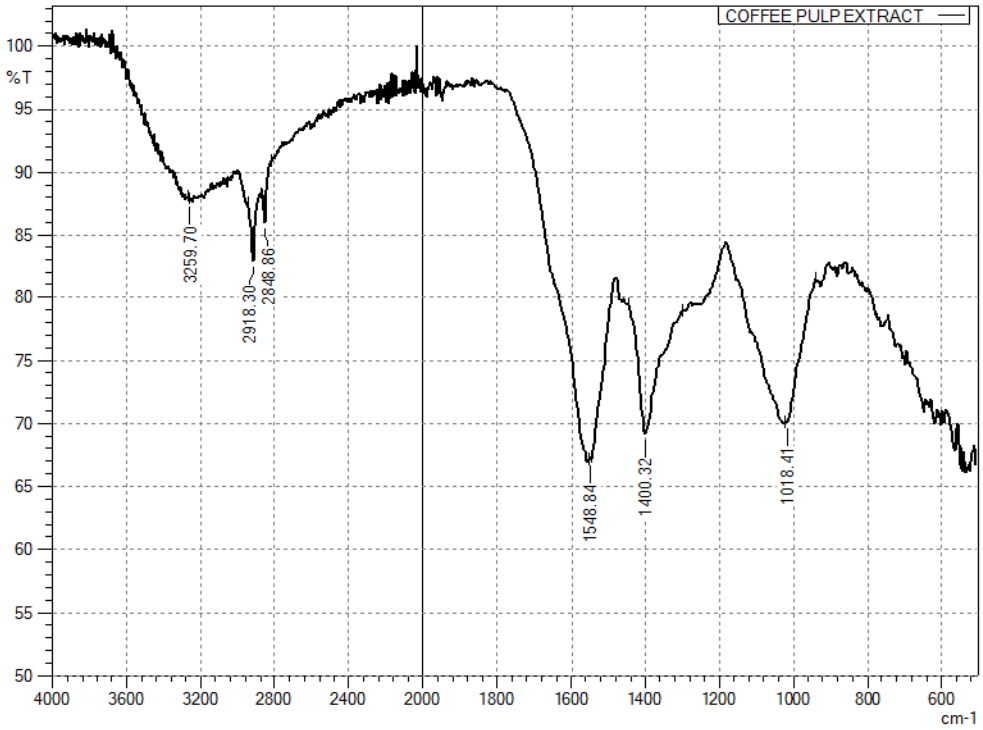

Figure 3. ATR-FTIR spectrum of the coffee pulp extract

The spectra in Figure 4 showed several functional groups for mimosa tannins. These were O-H stretching at 3236.55 cm^{-1}, C=C stretching of aromatic rings at 1606.70 cm^{-1}, C=C stretching at 1506.41 cm^{-1} attributed to a cyclic alkene, C-H bending at 1448.54 cm^{-1}, C-O stretching of aromatic ester at 1309.67 cm^{-1}, C-O stretching of ester at 1197.79 cm^{-1} and 1157.29 cm^{-1} and C=C bending of an alkene at 837.11 cm^{-1}.

The ATR-FTIR spectra in Figure 3 and Figure 4 showed similarities between coffee pulp tannins and mimosa tannins. There were three peaks which were at the same spectra ranges. These spectra ranges were 3550-3200 cm^{-1}, 1650-1500 cm^{-1} and 1450-1375 cm^{-1} attributed to an O-H stretching, C=C stretching and C-H bending. The spectra for mimosa tannins, however, recorded more functional groups compared to the spectra of coffee pulp tannins, with mimosa having eight functional groups compared to the three of coffee pulp in the fingerprint region.

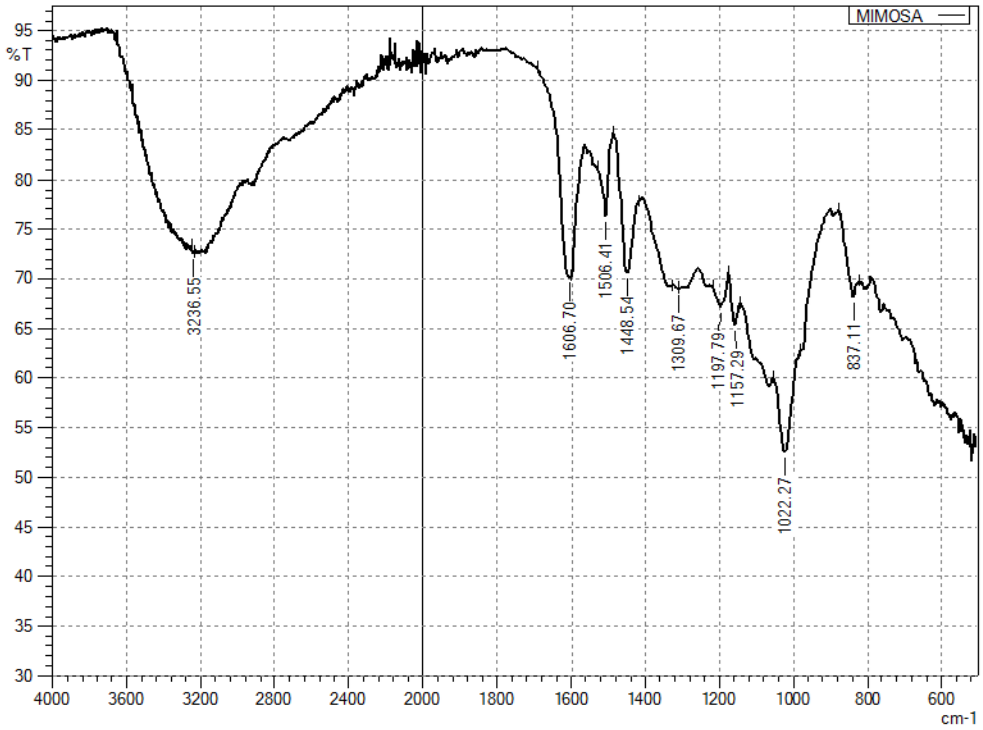

Figure 4. ATR-FTIR spectrum of MIMOSA

The moisture content was obtained as 10.31%, which slightly differed with a study by Peña-Lucio et al., which showed the moisture content of coffee pulp to be 11.6 ± 1.8% [25]. The dry matter at 89.69% was slightly different from that obtained by Pleissner et al., which was 86.8±6.3%, and differed with Moreira et al. who found it to be 81.64% [26,27].

The tannin content of coffee arabica pulp was found to be 5.04%. Kieu Tran et al. recorded the tannin content of the coffee pulp between 1.8 to 8.56%, whereas a study in india by Bhoite and Murthy reported a tannin content of 8-10% [21,28]. The differences can be attributed to differences in environmental factors, such as the type of soil and differing climatic conditions. The tannin content of coffee pulp at 5.04 was found to be lower when compared to commercial mimosa, for 63.56%. The tanning strength (a ratio of tans to non-tans) of the coffee pulp exceeded the minimum tanning strength of 1.5 recommended for vegetable tanning materials. This ratio means that the amount of tannins is higher compared to the non-tans. There was a significant difference, $p<0.05$, between the tanning content and tanning strength of mimosa and the coffee pulp.

It is worth noting that the tannin content of the coffee pulp of samples 1, 5 and 11 (pulp that had stayed at the dumpsite for a longer period) was lower compared to the fresh coffee pulp from the factory. This can be attributed to the leaching action of water as it sips down to the ground. This is because water, being a polar solvent, has the ability to extract phytochemicals, including tannins, from the pulp and, because these samples had remained in contact for a prolonged period of time, the

phytochemicals were degraded by being reduced in quantity. The samples that had not remained at the dumpsite for a longer period of time had a higher tannin content as the phytochemicals were not extracted by water. It is, however, important to note that the coffee production involves the use of water and as such some of the phytochemicals might also have been degraded during processing.

The pH of the coffee pulp extract was observed to be 4.7. The pH for vegetable tanning is recommended to be in the range from 2 to 8 [5]. Vegetable tanning occurs by either covalent or hydrogen bonding between the tannins and the functional groups of collagen. The reactivity of these functional groups is affected by the pH and, as such, the pH of the extract directly contributes to the pH of the tanning liquor [30]. A pH lower than 4, in regards to condensed tannins, results in their coalescing and formation of large molecules known as phlobaphenes [31]. This is because the extracts contain tannins with various molecular sizes and as the pH is lowered towards 2, the tannins begin to combine, thus forming these large molecules. Phlobaphenes are astringent and react quickly with the collagen functional groups on the surface leading to surface tanning.

CONCLUSION

The coffee pulp was found to contain 5.04% tannins of the condensed type. The tanning strength of coffee pulp at 2.26 was comparable to mimosa with a tanning strength of 2.82. Both of them were above the minimum tanning strength of 1.5 for tanning materials. Coffee pulp was found to have a tanning strength that is capable of being used in the tanning process. The tannin content was, however, lower than the 10% required for commercialization. The use of coffee pulp tannins from arabica coffee would not only encourage eco-friendly tanning practices but would also solve the problems associated with disposing of coffee pulp as waste.

Author Contributions

Conceptualization-Mutuku M, Ombui JN and Onyunka A, Methodology- Mutuku M and Ombui JN, Investigation and Resources- Mutuku M, Writing original draft presentation- Mutuku M, Ombui JN and Onyunka A. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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