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Optimization of Uptake of Tannins Obtained from Piliostigma thonningii by Goat Skin Using Central Composite Design

E. C. Ajah[1], S. O. Idris, I. Akawu[2], I. Y. Magaji[3], J. Abba[4]

[1]Department Chemistry Faculty of Physical Science, Ahmadu Bello University, Zaria, Kaduna State, Nigeria.
[2]Department of Leather Technology, Nigeria Institute of Leather and Science Technology Zaria Kaduna State, Nigeria.
[3]Department of Polymer Technology, Nigeria Institute of Leather and Science Technology Zaria Kaduna State, Nigeria.
[4]Department of Science Technology, Nigeria Institute of Leather and Science Technology Zaria Kaduna State, Nigeria.

Email: kletusemeka3@gmail.com

Abstract:
The study aims at optimizing the uptake of tannins obtained from Piliostigma thonningii by goat skin, using a central composite design. The study was carried out using the central composite design of experiment version 10.0.3.1 which consists of four factors. Bark of Piliostigma thonningii were collected freshly. The barks were dried in an electric oven at a temperature, of 100-105oC and later crushed to powder, to increase the surface area. The samples of goat skin were obtained and were then divided vertically through the backbone into two equal halves, and subjected to the standard procedure of the leather tanning processes. The samples of skin pieces obtained were tanned using the standard procedure of leather tanning. The plant samples were subjected to four experimental conditions, concentration (%), pH, particle size (mm), and time (min). The result indicates that the optimization conditions required for the uptake of tannins by the sample (goat skin) were 20% of plant material, pH of 4.81, 1.988 mm of particle size, and 50 min of time. The optimum responses of the leather produced were 77°C (shrinkage temperature), 27.934 N/mm2 (tensile strength), 13.009 mm (lastomer distention), and 0.293% (water vapor permeability) obtained respectively. Control of these parameters resulted in producing the most stable and flexible leather, which will release fewer contaminants into the environment. Based on the result obtained in the study, Piliostigma thonningii bark can be used as one of the vegetable tanning materials.

Keywords: Collagen, Piliostigma thonningii, Shrinkage temperature, Tensile strength, Vegetable tannins.

I. Introduction

The factors that are mainly responsible for tanning processes are pH, temperature, tannin concentration, salt content, and condition of skins and hides as well as mechanical actions and particle size (Antony et al., 2019). The pH is the most important factor that affects the penetration and fixing of tannins. The reduction of pH in tanning liquor increases the potential of collagen fibers to swell and increases the tendency of tannins to bind with collagen. Temperature is another important parameter that affects vegetable tanning and an increase in temperature results in high diffusion of tannins and gives a high degree of tannage (Colak et al., 2005). The acid and salt content in tannin liquor greatly influences the physical condition of leather. Control of these parameters results in the production of the most stable and flexible leather which results in the release of fewer contaminants and thereby protecting the environment. Hence the current study is an eco-friendly approach that reduces the toxic waste generation compared to the chrome tanning process thereby reducing environmental impacts by contributing to the greener or cleaner development of leather processing (Karanam et al., 2019). Tannins are sufficient enough, for themselves to be used in leather tanning. In that case, the tannin amount of any plant must be large enough for it to be used as a tanning agent. This necessitates the need to study more plants that could be used for tanning operations of skin and hide into leather (Alex, 2015).

PILIOSTIGMA THONNINGII

Piliostigma thonningii grows in open woodland and savannah regions that are moist and wooded grassland in low to medium altitudes. It is widely distributed in Africa and Asia. It is found growing abundantly as a wild uncultivated tree in many parts of Nigeria such as Zaria, Bauchi, Ilorin, Plateau, Lagos, and Abeokuta (Jimoh and Oladeji, 2005). Gimba et al., 2009 report that the bark of Piliostigma thonningii contains about 33.4% tannins. The percentage amount of tannin content in this plant bark shows that it is rich enough to be used as tanning material in leather manufacturing.

TYPES OF TANNING MATERIALS

ANIMAL TANNING MATERIALS: Brain-tanned leathers are made by a labor-intensive process that uses emulsified oils, often those of animal brains such as deer, cattle, and buffaloes are used as tanning materials. They are known for their exceptional softness and wash ability (Matthew and

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Darby, 1995). The purpose of brain tanning is to let the hide soak in oils of the brain to lubricate the fibers to make the soft hide, pliable, and elastic and hide is soaked in a brain and water solution for 15 to 20 minutes (at minimum), then squeezed and stretched for approximately 45 minutes to one hour, then the resulting hides are differed greatly from one another in softness and texture (Swarna et al., 2009).

VEGETABLE TANNING MATERIALS: Vegetable tanning, which is also referred to as bark tanning (Selma, 2017) is the time-tested method of using vegetable materials to process animal hides and skins into water-resistant, non-putrefiable, soft, flexible, heat-resistant material. Bark tanning is an ancient method of creating durable, water-repellent leather with a lot of body. It can be done to virtually any skin, but it is generally reserved for tanning grain on leathers from large thick hides such as cattle, horses, buffalo, and pigs. It has been commonly used for saddles, canteens, stiff shoes, belts, wallets, holsters, harnesses, helmets, pouches, trunks, shields, and gun cases. Vegetable tanning involves treating the hides and skins with leaves, roots, and barks containing tannins (Alex et al., 2016) and it is considered a "green tanning agent" because of its biodegradation and environmentally friendly than inorganic tanning.

CHEMICAL TANNING MATERIALS: These are inorganic salt materials that are been used to tan skins/hides to leather. The chemical materials are Chromium i.e. (trivalent chromium), Alum, formaldehyde, glutaraldehyde and etc.

TANNING BY MICROORGANISM (ENZYMES): Enzymes have found uses in various pre-tanning processes of leather manufacture such as soaking, unhairing, bating, dyeing, and degreasing. According to literature reported (Choudhary *et al.*, 2004) an eco-friendly vegetable tanning process combining pickle-free tanning and the application of proteolytic enzymes to improve the exhaustion of vegetable tannins resulted in more than 95% tannin exhaustion in the case of the experimental process, an increase of 10% compared with the conventional vegetable tanning process. Furthermore, the enzymes are successfully employed to make better quality leather production with less pollution impact (Sivakumar *et al.*, 2007).

LEATHER AND ENVIRONMENT: The global environment is continuously deteriorating due to the many socio-economic activities of humans (Thanikaivelan et al., 2005). Processing industries are causing much damage to the environment. Leather processing is one such industry that takes skins from the meat industry and processes them to produce leather through the tanning process. It has a negative impact on society because of its pollution. Leather processing involves various operations which include many chemicals that are expelled in processing. About 40 liters of water is required for processing 1kg of skin which results in the generation of a large amount of effluent leading to an increase in biological oxygen demand, chemical oxygen demand, dissolved oxygen, etc. (Thanikaivelan et al., 2005). It also results in the emission of chromium and sulfate ions.

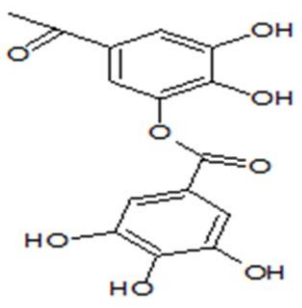
The leather industry also emits an obnoxious smell due to protein degradation of the skin which results in the generation of toxic gases such as ammonia, H2S, etc. (Oruko et al., 2020). Based on this research data, only 20% of the rawhide is used for the production of leather, and the remaining is generated as waste. Hence leather industry is considered one of the major polluting industries that generate huge amounts of solid and liquid wastes. The most important approach to the prevention of environmental pollution is getting idea prevention is better than reuse which is better than the disposal of waste (Şükrü and Mehmet, 2016).

There are various recycling methods to make generated leather wastes into eco-friendly useful bi-products such as the production of fat liquoring oils and bio-diesel from pre-fleshing wastes, production of activated carbon, gelatin, retaining agents, etc., from shavings and trimmings, the production of grease, methane gas, fertilizers, etc., from fleshing waste (Catalina et al., 2016). Hence cleaner production and recycling are the best options in order to control environmental pollution.

TANNINS

The name ‘tannin’ is derived from the French ‘tannin’ (tanning substance) and is used for a range of natural polyphenols. Since ancient times it has been known that certain organic substances have tanning properties and are able to tan animal skins to form leather (Falcao and Araújo, 2011).

Based on the molecular structures of the currently known tannins, and their origin and role in plant life, the following definition of the tannins may be derived: Tannins are polyphenolic secondary metabolites of higher plants and are either galloyl esters and their derivatives, in which galloyl moieties or their derivatives are attached to a variety of polyol-catechin- and triterpenoid cores (gallo-tannins, ellagitannins and complex tannins), or they are oligomeric and polymeric proanthocyanidins that can possess different interflavanyl coupling and substitution patterns. Since ancient times, it is known that certain organic substances have tanning properties and are able to tan animal skins to form leather or shoe uppers (Pizzi, 2008). Tannins are classified into two (2) basic classifications which are; hydrolysable and condensed tannins (Karamali and Teunis, 2001).



Figures 1: Structure of hydrolysable and catechol moiety of condensed tannins.

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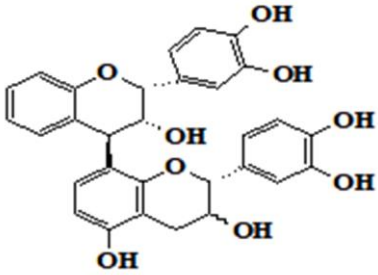

Figures 2: Structure of hydrolysable and catechol moiety of condensed tannins.

TANNING OF LEATHER

Leather is an organic material made of protein fiber, mainly collagen that may break down over time, reducing its durability and proportionally its economic value, affecting directly to leather goods. This problematic property has been resolved with a process called tanning that prevents the decomposition of skin and makes it inalterability and resistance (Marie et al., 2020). Tannins can bind to proteins and stabilize their structure. The main component of skin, collagen, in the presence of about 15% to 40% of tannins is stabilized and provides absorbent and breathable properties to the treated tissues. Tanning is a millenary methodology, considered to be one of the oldest processes used to treat leather; that already existed in northwestern regions of Europe after the Roman conquest.

This technique, known as vegetable tanning, since it uses exclusively tannins throughout the full process, was applied until the end of the 19th century (Falcão and Araújo, 2018). At that moment, a new technique called chrome tanning, based on the combination of mineral salts (chromium (III) salts) and vegetable tannins just applied at some stages of the process commenced being more employed. The historical application of tanning implies many objects over the years thus conservators are very concerned about the use and restoration of tanned leather. Colors obtained with hydrolyzable tannins are lighter than those obtained with condensed tannins.

VEGETABLE TANNING

Vegetable tanning is the use of tannins from plants such as the Piliostigma thonningii (bark) extract and many other higher plants such as chestnut and oak wood, Divi-divi, Sumach, Myrobalaen, Trillo, Valonea or plant galls, depending on their origin and their chemistry varies widely, having a molar mass of up to 20000 Dalton to convert hide or skin into leather. High tannin concentrations are found in nearly every part of the plant, such as in the bark, wood, leaves, fruit, roots, and seed (Musa et al., 2019).

Vegetable tanning is a two-stage tanning that includes penetration and fixing. Penetration involves the diffusion of tannins into the skin whereas fixing makes the penetrated tannins bind with collagen forming stable material. It is mainly affected by several factors such as temperature, pH, mechanical actions particle size, and so on (Appalaraju et al., 2019). Figure 3 shows a structural model of cross-linkage between plants' phenolic and collagen.

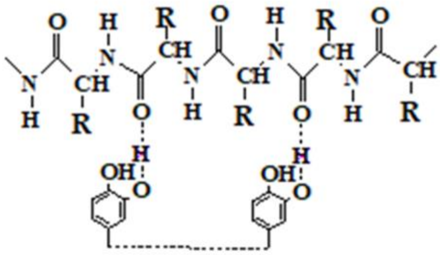

Figure 3: A structural model of cross-linkage between plants' phenolic and collagen.

CENTRAL COMPOSITE DESIGN

The central composite design is the most common fractional factorial design used in the response surface model. In this design, the center points are augmented with a group of axial points called star points. With this design, first-order and second-order terms can be easily estimated. In this design, the center points are eventually augmented with the group of "star points" that allow estimation of curvature. If the distance from the center of the design space to a factorial point is ±1 unit for each factor, the distance from the center of the design space to a star point is ± α with |α| > 1 (Sankha, 2021). The precise value of α depends on certain specific properties required for the design. Since there are many factors available in the CCD model, therefore, the possibility of more than two or many star points within the model is more palpable. The star points represent lower and higher extreme values. The CCD model allows to extension 4 level factors, which have been widely used in optimization. Models of the model used in the optimization process. The first-order model for the optimization can be represented as:

$$Y = \beta o + \beta 1X1 + \beta 2X2 + \epsilon \qquad (1)$$

For quadratic or second order model the optimization can be depicted as:

$$Y = \beta o + \beta 1X1 + \beta 2X2 + \beta 12X1X2 + \beta 11X12 + \beta 22X22 + \epsilon \qquad (2)$$

where βo, β1X1, and β2X2 represents factors responses such as pH, concentration, particle size and time, also tensile strength, shrinkage temperature, distension and water vapor absorptivity, while ϵ represent down to infinity.

STATISTICAL ANALYSIS

A medium randomized design (factorial arrangement 2 × 2 × 2 × 2) was used in the experiments. The data were subjected to statistical analysis by Gomez and Gomez, (1983) using the statistical package for experiment design version 10.0.3.1 program.

II. Methods

SAMPLE COLLECTION AND PREPARATION

Bark of Piliostigma thonningii were collected freshly from farmland at Basawa, Sabon Gari Local Government Area of

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Kaduna state. The bark was dried in an electric oven at a temperature of 100oC after which it was then crushed to 2mm powder particle size, to increase the surface area. Eleven fresh goat skin samples were obtained from an abattoir at Samaru, Zaria, Kaduna state, Nigeria. The eleven fresh goat skin were divided into two equal halves through the vertebral column to get a total of twenty-two goat skin samples which were then subjected to the standard procedure of the leather tanning processes (Karanam et al., 2019).

DESIGN OF EXPERIMENT

Table1 independent variables which are, time (X1: 50, 0, and 90 min), particle size (X2: 1, 0, and 2 mm), plant sample concentration (X3:20, 0, and 40%), and pH (X4: 4.5, 0 and, 5.5). The design of experiment version 10.0.3.1 software aided the experimental. Design, modeling, and optimization. It was also used to perform the statistical analysis of variance (ANOVA).

The required minimum, center, and maximum points are -1, 0, and +1, respectively. Each independent variable was incorporated into the central composite design, which allows for the design of the experiment and the concentration of a second-order quadratic model equation (a) for the dependent response variable, Yn. Yn = bo+b1X1+b2X2+b3X3+b11X12 +b20X20 +b21X21 +b12X2+b13 X1X3 + b20X2X3 (b) where Yn represents the response variables for each factor response, bo is the error, b1, b1, and b3 are the co-efficient for the linear effects and b11, b12 and b22 are the quadratic coefficients, while b12, b13 and b23 are the coefficients for interaction effects [7]. Hence, the total number of experiments was 21, and four center points

$$\propto = [2^K]^{1/4} \quad (3)$$

Where K = 2, α = 1.4142. Total number of runs:

$$R = 2^K + 2K + n \quad (4)$$

where K is the number of factors, and n is the number of center points, (2^4) + 2*4+ 1 = 25). The values in the bracket represent the coded values and predicted values in Table 1.

TANNING PROCESS

In this study, eleven fresh skins from mature goats were used. The eleven fresh skins were divided into two equal halves through the vertebral column to get a total of twenty-two goat skins. All the pre-tanning, tanning, and post-tanning processes were the same and included: Dirt soak with 200% water at 20oC for 20 minutes and main soak with 200% water for four hours. Unhairing and liming were done with 150% water at 20°C, 1.5% Sodium sulfide, and 1% lime, and the drum ran for one hour. After one hour, 50% water at 20°C, 1% sodium sulfide, and 2% lime were added and the drums ran for eight hours. The tanning drum was drained and limed pelts were washed with clean water. The pelts were then fleshed before deliming. During the deliming process, 150% water at 20oC, 2% ammonium sulphate and 1% sodium metabisulphite were used and the drum run for one hour. The delimed pelts were then bated with 1% bate powder in a 100% water at 35oC for one hour. Tanning was done with 150% water and vegetable (Piliostigma thonningii bark powder) added in two steps based on the percentage concentrations, particle sizes and pH design by CCD. The drum was run based on the timing design by CCD. Then penetration was checked through a cut on the cross-section of the skins. Formic acid (1%) was then added and the drum runs for one hour. The tanned skins were washed and left overnight for ageing. The next morning fat liquoring was done with 100% warm distilled water, 4% oil and the drum run for two hours. It was then fixed with 1% formic acid for one hour, then drained, washed and horsed up overnight. They were then dried using toggle drying method (Alex et al., 2016).

PHYSICAL TESTING ON LEATHER PROPERTIES

MEASUREMENT OF WATER VAPOR PERMEABILITY: The measuring principle was based on the fact that distilled water, approximately 5g was introduced to a special measuring vessel. After that, a sample of leather (the disc with an appropriate diameter) was introduced to the vessel. The vessel was moved to the analyzer. Required temperature of moisture analyzer and duration of stay of leather sample was set at 40°C and 2hrs respectively. Water vapour permeability was calculated as:

$$P = M1\text{-}M2 \div M01\text{-}M02 \times 100\% \quad (5)$$

Where: P = water vapour permeability, M1 = initial mass of distilled water used for the leather sample test, M2 = final mass of distilled water used for the leather sample test, M01 = initial mass of distilled water for the blank and M02 = final mass of distilled water for the blank test (Krzysztof et al., 2014).

MEASUREMENT OF TENSILE STRENGTH: The specimen was cut due to the required shape and size from both at parallel and perpendicular directions to the backbone of leather. Measurement of width was taken for the test piece to the nearest 1.0 mm at three places on the grain side (i.e. on the surface where hair was removed). And also thickness was measured in three points on the surface. The specimen was placed in the electronic universal tensile machine of model WDW-100 KN, the machine was run until the specimen broken. Then readouts were taken by equation 3.5.

Tensile strength = breaking load ÷ cross-sectional area

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TABLE 1: DESIGNED EXPERIMENTAL CONDITIONS OF FACTORS

S/No	Factor 1	Factor 2	Factor 3	Factor 4
Runs	A: Concentration (%)	B: pH	C: Time (min)	D: Particle size (mm)
1	20	5.5	50	1.7
2	30	5.8	70	1.4
3	30	5.0	70	0.5
4	30	5.0	70	1.4
5	30	5.0	104	1.4
6	30	5.0	70	1.4
7	30	5.0	70	1.4
8	40	5.5	90	1.0
9	40	5.5	50	1.0
10	47	5.0	70	1.4
11	30	5.0	70	1.4
12	30	5.0	70	2.0
13	30	5.0	36	1.4
14	20	4.5	90	1.0
15	40	4.5	50	1.7
16	20	5.5	90	1.7
17	13	5.0	70	1.4
18	30	4.2	70	1.4
19	40	4.5	90	1.7
20	20	4.5	50	1.0
21	30	5.0	70	1.4

DISTENTION (LASTOMETER TEST): The specimen was cut of 44.5 mm diameter from the sampling location of shoe upper leather. The specimen was clamped tightly in the electronic lastometer of model 5077-ET (MUVER) and forced the plunger at a rate of 20 ± 0.05 mm per sec. This was done by turning the hand wheel clockwise at one revolution per second. When the spear cracked the sample, the force and detention were recorded.

SHRINKAGE TEMPERATURE: The shrinkage temperature of the experimented leathers was determined using the shrinkage tester of model STD-114 SATRA (Musa et al., 2019). About 2 cm sample that was cut out from the leather was clamped between the jaws of the clamp, which in turn was immersed in a solution of water. The temperature of the solution was gradually increased and the temperature at which the sample shrunk was noted. Triplicate test was carried out for each sample and the average values were recorded.

III. Results and Discussion

Tanning is a chemical process by which additional crosslinks are introduced into collagen, binding active groups of tanning agents to functional groups of protein (Haroun *et al.*, 2009). Hence, the tanning effect mainly depends on the extent of cross-linking between collagen molecules and the thermodynamic stability of the cross-linking bonds. Animal skins or hides generally have a substantial thickness; thus, penetration of tanning agents is also very important for characterizing the tanning process. Only complete penetration and uniform distribution of tanning materials along the skin cross-section can lead to a satisfactory tanning effect as seen in Table 2.

Table 2 below describes the four responses in each run of the experiment. It suggests the best shrinkage temperature obtained in all the twenty-one (21) runs to be 80^{o}C which is in run eight (8th), with a plant material concentration of 40% and time, 90 min. It also inferred that the best tensile strength of 38.30 was found in run seventeenth (17th) with plant material concentration of 13%, although the shrinkage temperature value is at the minimum acceptable value of 60oC as compared with the international standard (Dennis et al., 2020).

It divulged that the best distention was 14.37 mm as seen in run Nineteenth (19th) with plant material concentration of 40%, which is within the recommended standard value, and above the minimum value of 7.0 mm. The (8th) run has the best shrinkage temperature of 800C, water vapor permeability value of 4.12%, tensile strength of 19.39 N/mm2, and time of 90 minutes when compared with the values obtained in the remaining twenty (20) runs. Observing table 2, with respect to plant material concentration, run 1, 14, 16, and 20 have the minimum amount of plant material of 20% shrinkage temperature of 66, 77, 66, and 71 (OC), pH of 5.5,4.5, 5.5, and 4.5, the particle size of 1.0, 1.7, 1.7 and 1.0, when compared with the remaining seventeen runs in the experiment. The best among the four runs is the 20th run with pH value of 4.5, time of 50-minutes, particle size of

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1.0 mm and water vapor permeability of 4.92% with respect to time (Dennis et al., 2020).

TABLE 2: PHYSICAL TESTING RESULTS OF THE LEATHER

No. of Runs	Response 1 Shrinkage temperature (^{0}C)	Response 2 Tensile strength (N/mm^2)	Response 3 Distention (mm)	Response 4 Water vapor permeability (%)
1	66	3.14	11.24	7.22
2	69	15.25	10.36	3.66
3	61	14.29	13.31	12.92
4	68	14.46	11.06	6.84
5	62	7.93	11.11	6.63
6	79	15.97	11.21	4.18
7	70	17.88	13.97	0.29
8	80	19.39	10.15	4.12
9	68	10.15	9.91	0.96
10	64	5.54	12.49	6.27
11	76	4.31	12.45	2.08
12	74	6.09	10.21	1.80
13	60	13.06	13.99	12.75
14	78	8.93	8.92	3.21
15	64	9.68	16.39	8.58
16	66	13.83	10.42	3.57
17	60	38.30	13.93	2.19
18	68	6.28	9.58	4.73
19	65	5.48	14.37	3.35
20	71	5.50	11.24	4.92
21	72	12.91	9.50	2.48

RESULTS OF STATISTICAL ANALYSIS OF VARIANCE (ANOVA)

The central composite design for ANOVA results is presented in TABLE 3. The results of the regression model inferred that the model was significant at P< 0.0301 and the lack of fit was not significant at P>0.3670 due to a large p-value.

The data obtained for shrinkage temperature in all the experimental runs were analyzed with respect to particle size (D), concentration, and pH (AB) by the The F value of 4.28 depicts that the model was significant and there was a 3.01% probability that an F-value that large could occur due to noise. The values of "probability > F" less than 0.0500 indicate model terms were significant.

The analysis of variance test was carried out on the data obtained for tensile strength was done to test the significance of the four factors such as concentrations, pH, particle sizes, and time, on the quality of leathers produced as presented in

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TABLE 4 below. The result hints that the tensile strength was significant (P<0.0089), but the Model F-value is 4.92. The values of "probability > F" less than 0.0500 suggest that the model terms were also significant, A, B, and BD were significant model terms. Lack of fit was not significant (P>0.4412).

TABLE 3: SHRINKAGE TEMPERATURE

Source	Some of Squares	Df	Mean Square	F Value	p-value Prob> F	
Model	46.49	4	11.62	5.95	0.0039	Significant
C-Time	6.99	1	6.99	3.58	0.0767	
AB	18.56	1	18.56	9.51	0.0071	
BD	13.13	1	13.13	6.73	0.0196	
B^2	7.81	1	7.81	4.00	0.0628	
Residual	31.23	16	1.95			
Lack of fit	20.07	12	1.67	0.60	0.7784	not significant
Pure terror	11.16	4	2.79			
Correlation total	77.72	20				

Df = degree of freedom

TABLE 4: ANALYSIS OF VARIANCE FOR TENSILE STRENGTH

Source	Some of Squares	Df	Mean Square	F Value	p-value Prob> F	
Model	656.00	4	164.00	4.92	0.0089	Significant
A- Concentration	523.21	1	523.21	15.68	0.0011	
B- pH	418.97	1	418.97	12.56	0.0027	
D- Particle size	36.71	1	36.71	1.10	0.3098	
BD	416.38	1	416.38	12.48	0.0028	
Residual	533.74	16	33.36			
Lack of fit	423.50	12	35.29	1.28	0.4412	not significant
Pure terror	110.23	4	27.56			
Correlation total	1189.74	20				

Df = degree of freedom

Analysis of variance response of the data obtained for the distention experiment was carried out by the central composite design to determine the significance of the factors (C (time), AB (concentration and pH), BD (pH and particle size), and B-squared) on the tanning of the leather as narrated in TABLE 5 above. The results suggest that (P<0.0039) is a significant model and the lack of fit was not significant (P>0.7784). The results show that the model F-value of 5.95 infers that the model was significant. The values of "probability > F" less than 0.0500 indicate model terms were also significant. In that case, AB, and BD are significant model terms. Water vapor permeability is one of the most important physical properties of leather, which impacts the essential functional properties such as the breathing ability and comfortability of leather products (Giorgio, 2015). This test was analyzed by the central composite design of the experiment. It was carried out with respect to factors (A (concentration), B (pH), C (time), D (particle size), AB (concentration and pH), and C-squared. The narration of the result obtained in the test is described in Table 6.

TABLE 5: ANALYSIS OF VARIANCE FOR LASTOMETER

Source	Some of Squares	Df	Mean Square	F Value	p-value Prob> F	
Model	241.54	2	120.77	4.28	0.0301	Significant
D- Particle size	79.54	1	79.54	2.82	0.1103	
AB	237.44	1	237.44	8.42	0.0095	
Residual	507.41	18	28.19			
Lack of fit	427.41	14	30.53	1.53	0.3670	not significant
Pure error	80.00	4	20.00			
Correlation	748.95	20				

Df = degree of freedom

The Analysis of variance of the water vapour permeability results, shows that the model was significant (P<0.0150) and lack of fit was not significant (P>0.5542). The values of "probability > F" less than 0.0500 indicated that the model terms were significant. In that case, D, AB and C^2 were significant model terms because values greater than 0.1000 infers that the model terms are not significant.

The optimum responses in table 6 are the predicted or optimized optimum results of the data obtained from all the results of the analysis carried out. This analysis was carried out to ascertain the best conditions for the vegetable leather processing technique that should produce leather of international standard based on standard physical properties of veg-tanned leather such as shrinkage temperature, tensile strength, lactometer distention, and water vapor permeability.

Desirability function (DF) is a generic term for a variety of different methods that transform response variables to a scale-free value, dir, usually between 0 and 1 where i = 1, . . .,N and r = 1, . . . ,m. Data collected with designed experiments allow interpolated solutions to be used as well. In the trivial case with one objective, the response with the largest desirability is then selected (Calhoun, 2022). The desirability results describe the ten best leather and their properties among hundred results of optimum analysis carried out. The results also infer the best factor conditions if employ, would produce leathers of this qualities using vegetable tannins of this plant.

The optimum responses of the leather produced predicted were 77°C (shrinkage temperature), 27.934 N/mm2 (tensile strength), 13.009 mm (elastomer distention), and 0.3 % approximation of water vapor permeability, obtained respectively. Therefore, based on the result obtained in this study, the plant Piliostigma thonningii bark could be used as one of the vegetable tanning materials in Nigerian leather tanneries for vegetable leather production. Vegetable-tanned leather has excellent fullness, moldering properties, wear resistance, air permeability, and solidness; hence, it is of greater significance to reduce chrome pollution in the leather-making process. Vegetable-tanned leather is used in making heavy leather such as furniture leather, garment leather, and shoe upper leather (Selma, 2017). The vegetable tanning method does not require the prior preparation of pickling and therefore the contributions to pollution load from sulfate salts are lower. In addition, vegetable tannins have several advantages such as its make leather hard to biodegrade, and hence wastes bearing vegetable tannins degrade slowly (Musa and Gasmeleed, 2013), ingredients (no harmful chemicals) are used when dying the hides are lighter in color and can be converted into pastel shade leathers, high softness, good lightness, natural sensation, pleasant touch, beauty over the time environmentally friendly and can be recycled, each leather product that is dyed using vegetable tanning is completely unique, rich, warm-tone colors which look completely natural and high-performance leather can be obtained, often better than chrome tanning. Therefore, based on the result obtained in this study, the plant Piliostigma thonningii bark could be used as one of the vegetable tanning materials in Nigerian leather tanneries for vegetable leather production.

TABLE 6: ANALYSIS OF VARIANCE FOR WATER VAPOUR PERMEABILITY

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Model	145.73	6	24.29	4.02	0.0150	Significant
A- Concentration	1.74	1	1.74	0.29	0.5997	
B- Ph	2.71	1	2.71	0.45	0.5138	
C-Time	22.74	1	22.74	3.76	0.0728	
D-Particle size	69.49	1	69.49	11.50	0.0044	
AB	65.40	1	65.40	10.82	0.0054	
C^2	39.31	1	39.31	6.51	0.0231	
Residual	84.58	14	6.04			
Lack of fit	60.20	10	6.02	0.99	0.5542	not significant
Pure error	24.39	4	6.10			
Correlation total	230.31	20				

Df = degree of freedom

IV. Conclusion

Central composite design version 10.0.3.1 factorial is an appropriate and effective method for optimizing the uptake of tannins obtained from the plant, Piliostigma thonningii (bark). It could be concluded here that the best leathers produced in this study are the leathers found at run 6th, 8th, 11th, 12th, 14th, and 21st, of the twenty-one pieces of leathers produced. The results of regression models of Shrinkage temperature were significant at $P<0.0301$, tensile strength was significant at ($P<0.0089$), lactometer which suggests that ($P<0.0039$) is a significant model, and water vapor permeability was significant at $P<0.0150$. Each experimental run consumes a minimum of 20% to 40% maximum of plant material at a pH range of 4.5 to 5.5 as described in Table 2 respectively and particle size ranging from 1.0 to 2.0 at a time range of 70 to 90 minutes' maximum to produce leathers with such physical properties as presented in Table 2.

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