

SUDAN UNIVERSITY OF SCIENCE & TECHNOLOGY

College of Graduate Studies and Scientific Research

**Application of Novel Method of A Blend of *Acacia nilotica*
Pods Powder and Neem Bark in Full Vegetable and
Semi_chrome Tannage**

تطبيق طريقة جديدة باستخدام بذرة قرن السنط ولحاء النيم في دباغة نباتية كاملة وشبه
الكروم

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DOCTOR OF PHILOSOPHY

By

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الآية

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

أَتَى أَمْرُ اللَّهِ فَلَا تَسْتَعْجِلُوهُ سُبْحَانَهُ وَتَعَالَى عَمَّا يُشْرِكُونَ (1) يُنَزِّلُ الْمَلَائِكَةَ بِالرُّوحِ مِنْ أَمْرِهِ عَلَى مَنْ يَشَاءُ مِنْ عِبَادِهِ أَنْ أَنْذِرُوا أَنَّهُ لَا إِلَهَ إِلَّا أَنَا فَاتَّقُونِ (2) خَلَقَ السَّمَاوَاتِ وَالْأَرْضَ بِالْحَقِّ تَعَالَى عَمَّا يُشْرِكُونَ (3) خَلَقَ الْإِنْسَانَ مِنْ نُطْفَةٍ فَإِذَا هُوَ خَصِيمٌ مُبِينٌ (4) وَالْأَنْعَامَ خَلَقَهَا لَكُمْ فِيهَا دِفْءٌ وَمَنَافِعُ وَمِنْهَا تَأْكُلُونَ (5) وَلَكُمْ فِيهَا جَمَالٌ حِينَ تُرِيحُونَ وَحِينَ تَسْرَحُونَ (6) وَتَحْمِلُ أَثْقَالَكُمْ إِلَىٰ بَلَدٍ لَّمْ تَكُونُوا بِالْغَيْهِ إِلَّا بِشِقِّ الْأَنْفُسِ إِنَّ رَبَّكُمْ لَرءُوفٌ رَحِيمٌ (7) وَالْخَيْلَ وَالْبِغَالَ وَالْحَمِيرَ لِتَرْكَبُوهَا وَزِينَةً وَيَخْلُقُ مَا لَا تَعْلَمُونَ (8) وَعَلَى اللَّهِ قَصْدُ السَّبِيلِ وَمِنْهَا جَائِرٌ وَلَوْ شَاءَ لَهَدَاكُمْ أَجْمَعِينَ (9) هُوَ الَّذِي أَنْزَلَ مِنَ السَّمَاءِ مَاءً لَكُمْ مِنْهُ شَرَابٌ وَمِنْهُ شَجَرٌ فِيهِ تُسِيمُونَ (10) يُنْبِتُ لَكُمْ بِهِ الزَّرْعَ وَالزَّيْتُونَ وَالنَّخِيلَ وَالْأَعْنَابَ وَمِنْ كُلِّ النَّمْرَاتِ إِنَّ فِي ذَلِكَ لَآيَةً لِقَوْمٍ يَتَفَكَّرُونَ (11)

صدق الله العظيم
(سورة النحل)

Declaration

We, the undersigned, hereby declare that the research in this thesis is Mr. Ali's own original work, which has not partly or fully been submitted to any other University in order to obtain a degree.

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Dedication

To my mother Khitma Abd Alsadig and my late father and the smile which is shining my life, Special dedication to my father who has passed away in June 1995. My entire dream was to see your face shining with happiness and satisfaction when I welcome back home as you used to do every time when I visit. This Ph.D. is for you. I love all of you forever. To my wife's and their child Roaa, Braah and Mohammed thank you for your love and support, special dedication for my chemist teacher A. Gurashi.

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Abstract

Vegetable tannage is an eco-friendly method compared with environmental polluting chromium based method of tanning that is commonly used in commercial tanning and which prevents the collagen fibrous protein in animal skins from putrefaction and produces hydrothermal stable product commonly known as leather. Thus study was conducted to improve the tanning efficiency of locally available tanning in the Sudan 'Garad', applying blending method, physico-chemical properties of 'Garad', bark and leaves of 'Neem' and 'Karkady' bark was determined, hide powder method was used in determining the tannins content whereas the analysis t-test and Anova were used to compare the mean values of the physico-chemical properties of vegetable tanning materials, the physico-chemical properties results of 'Neem' bark, crushed 'Garad' and pure powder were found to be acceptable and utilized as raw materials for commercial manufactory purpose, screening results of 'Karkady' calyces and bark show that they contain oxalate organic salts 0.5% which were used to chelate the iron from the tanning liquor the results showed high efficiency, whereas used 5% dry leaves powder of 'Neem' at 60°C eliminated the mould growth for one month and also dropped the viscosity to opposite level and subsequently the liquor of improved indigenous tanning material was produced by blending 80% *Acacia nilotica* pods with 20% *azadirachta indica* barks' and then in spray-drying, various physico-chemical properties were studied and compared with those of conventional indigenous and myrobalan tanning materials. The results showed that the physico-chemical properties of modified indigenous materials are comparable with the myrobalan tanning material and even better than indigenous tanning in total soluble solids (93%), tannin contents (56%), non-tannins contents (36.7%), tannin/nontannins ratio (1.5) and pH (4.6). The results also showed that the material has bright and light brown colour which is consistent with the Indian Standards as

required for industrial usage, yielded powder was used for full vegetable and semi chrome tanning to produce shoe upper leathers. The physico-mechanical properties of improved tanned leather were compared with conventionally tanned leather. Parameters of full vegetable tanned leather were tensile strength (20.0 N/Cm²), tear strength (4.4 N/cm), stitch tear strength (11.8 N/cm), elongation (40.5%), distension and strength of grain (8.9 mm) and shrinkage temperature (>82°C). Whereas factors of semi-chrome tanned leather were tensile strength (21.2-22.0 N/Cm²), tear strength (4.3-5.2 N/cm), stitch tear strength (12.6-11.8 N/cm), elongation (59-57%), distension and strength of grain (9.5-10.6 mm) and shrinkage temperature (98-100°C). The results showed that the 'Garad - Neem' blend significantly enhanced the quality of tanned leather to almost double the level of the leather tanned by conventional pure *Acacia nilotica* pods 'Garad' power. Physico-chemical properties of wastewater of tanning trails showed that the employment of improved powder to produce shoe upper leather is very eco-friendly.

المستخلص

ألدباغة النباتات هي طريقة صديقة للبيئة مقارنة بالعملية التي تستخدم للانتاج التجاري و تبني شيوعا علي الكروم الملوث ألدباغة وهي ألية معألجة ألياف كولاجين بروتين جلود أحيوانات التي تمنع من التعفن وألتي تنتج منتجا مستقرا حراريا يعرف علي الشيوخ بالجلد المدبوغ, لذا أجريت أدراسة لتطوير الفاعلية الدباغية للدابغ المحلي المتوفر في السودان, القرص, بتطبيق نهج المزج, أخواص أفيزيو- كيميائية لقرون أقرص, لحاء و ورق النيم والكركي ولحائه تم تقديرها كما أستخدمت طريقة بدرة أالجلد في تحديد محتوى ألدابغ, في حين أستخدم التحليل الإحصائي لمقارنة قيم متوسطات أخواص أفيزيو- كيميائية للمواد الدباغة النباتية والتي أظهرت أن لحاء النيم ومجروش القرص منزوع البذرة والبذرة الداخلية للقرون لها أخواص تجعلها مقبولة بالقدر الذي يسمح بأستخدامه كخأم لغرض التصنيع التجاري, نتائج تحليل كاسات ولحاء الكركدي أظهر أنهما يحتويان علي 0.5 % من أملاح الأوكسالات أعضوية التي أستخدمت علي أنها كاشف مأسك لأيونات الحديد في مستخلص الدابغ النباتي وألنتائج أظهرت كفاءة عالية في حين 5 % بذرة ورق النيم الجاف مع التسخين إلي 60 م° كبح نموء الفطريات والميكروبات لفترة شهر كما خفض لزوجة المحلول الي مستوءا معاكس كما حفظ المادة الدباغة ضد التكرس. بعد ذلك مستخلص المادة التي تم تطويرها من ال دابغ التقليدي أنتجت بمزج 80% قرص مع 20% لحاء النيم ومن ثم جففت رزازيا, أخواص أفيزيو- كيميائية المختلفة لهذه المادة تمت أدرستها وقورنت بأخواص دابغ القرص التقليدي و دابغ الميروبالان (Myrobalan). ألنتائج أظهرت أن هذه المادة يمكن مقارنتها بأخواص الميروبالان و حتي أفضل من دابغ القرص التقليدي في محتوى المواد الصلبة الذائبة (93%), محتوى الدابغ (56%), محتوى غير دابغ (36.7%), معدل دابغ / غير دابغ (1.5) واس هيدروجيني (4.6) ألنتائج أيضا أظهرت ذلك أن ألامادة لها لون بني فاتح ومشرق متماشيا مع المعيار الهندي ومع إحتياج أأستخدام الصناعي. وقد أستخدمت البذرة المنتجة في نظام دباغة نباتية كاملة اونظام شبه الكروم لإنتاج جلود وجه الحذاء, أخواص أفيزيو- كيميائية للجلود المنتجة تمت مقارنتها بتلك التي تمت دباغتها بالقرص التقليدي والمعلقات للجلود هي قوة الشد (20 نيوتن/ سم²), قوة التمزق (4.4 نيوتن/ سم), قوة التمزق ألتقبيين (11.8 نيوتن/ سم), المرونة (8.9 ملم) ودرجة حرارة الإنكماش أعلي من (82م°). في حين المعلقات لجلود شبه الكروم هي قوة الشد (21.2-22 نيوتن/ سم²), قوة التمزق (4.3-5.2 نيوتن/ سم), قوة التمزق ألتقبيين (11.8-12.6 نيوتن/ سم), المرونة (9.5-10.6 ملم) ودرجة حرارة الإنكماش أعلي من (98-100م°). ألنتائج أظهرت أن خلط القرص- النيم منح جودة بشكل ملحوظ للجلود المدبوعة في الغالب مرتين أعلي من مستوي الجلود المدبوعة ببذرة قرون القرص وأخواص

الفيزيو- كيميائية للمياه العادمة الناتجة عن النشاط الدبغي اظهرت أن خلط القرض- النيم وتوظيفه لإنتاج جلود وجه ألداء هي صديقة للبيئة.

CHAPTER ONE

INTRODUCTION

CHAPTER ONE

INTRODUCTION

Chapter one

Introduction

1.1 Background information

Tanning is one of the major and oldest industries known for the human in the world, where it is carried out from primitive times using vegetable tannin materials to preserve the raw animal hides or skins. Romans tanned their animal's skins with olive oil and alum and occasionally with oak bark. The oak bark was used principally at first and was generally preferred to hemlock. Then tanning remarkably developed through centuries according to human evolution and progress, until the modern tanning is discovered where using machinery and pure chemicals.

The tannery operation consists of converting the raw hide or skin, a highly putrescible material, into leather, a stable material. The whole process involves a sequence of complex chemical reactions and mechanical processes which are described as follows:

Animal's raw hides and skins are treated to remove non-structured proteins and fat using sulphides, NaHS or Na₂S, and lime, then pelts are delimed using ammonium sulphate and then pelts are washed and batted for further purification of hide which leaves an essentially pure collagen matrix which is preserved using tanning in a bath of acid, sulphuric, formic, ...etc, and sodium chloride. This involves the impregnation of the skins with mineral, chromium (III), aluminum, titanium, or vegetable tanning reagents or alternative tanning reagents, which can be subdivided into syntans, aldehydes and oil tanning. After this the wet blue leather is shaved then the fat liquors is added and drying, salting/setting, vacuum drying, stacking/toggling, buffing/shaving, trimming, pressing, and segregation of the leather.

Chromium and vegetable tannins are considered the most common reagents used recently in the world by tanneries. There are more than 85% of the tanneries used chromium (III) salts in their tanning process. So the degree of toxicity of chromium is perhaps one of the most debated issues

between the tanning industry and authorities, therefore the environmental authorities had committed tanneries to use eco-friendly materials which produce high quality leathers and does not harm the environment. However, their mechanical resistance, dyeing suitability and hydrothermal stability were found worth than that for leathers produced by chromium salts tannage.

At the past the vegetable tanned leather are produced by immersing prepared skins in a series pits contained tanning liquors, which are leached from rich vegetable materials, bark, leave, hearts and twigs, in water.

In recent years rapid vegetable tanning usually involve a light pretannage, e.g. syntans, glutaraldehyde, calgon followed by vegetable tannage in more concentrated tannin liquors or extracts in powdered form, spray dried powder, it is carried out at pH ~5 using pits, pits and drums or drums.

The polyphenolic compound which is precipitate the protein from their solution is called tannins and which occur in nearly everly plant from all over the world in all climates and which are divided chemically in the bath into two groups *pyrogallol* and *catechol*.

In the modern classification when discovered the mixed tannins; tannins divided into: firstly hydrolysable tannins, *pyrogallol*, which divided into two groups', *gallo* and *ellago* tannins, according to phenolic acid which was released when it hydrolysis, then secondly condensed tannins, *catechol*, and thirdly mixed types. Manufacture of vegetable tannins materials is essential based on the extraction of tannins using suitable solvent followed by concentration, bleaching and spray draying to get powder

In every country there are large varieties of tannin bearing plants but their practical application for the production of leather, however, is dependent mainly on two important factors: firstly, they must occur in sufficiently amount, and secondly they must contain enough tannin to make its extraction profitable. Wattle; Terminalia, Chebula, Quebracho, Chestnut, Valonea, Tara, Dividivi and Gambiercube...etc is represented as the most important plants that contain a high percentage of tannins which can be commercially used.

Numbers of annual slaughtering animals are 6-7 millions of cattle, 20 millions of sheep and 17 millions of goats, so trading and manufacturing of leathers are very important to national economy. (MAWF, 2014)

In the 1989 approximately 214,800 kg of synthetic tannin material and 169,254 kg of tannin extracted were imported to Sudan, the approximate value of these materials has 1.6 million US\$, and no systematic data has been reported. (MOI, 1996)

Acacia forests abundant in vast area of Sudan is grows along the water source permanent or seasonal; it annually produce large amounts of non-wood product this estimated to be more than thousand tons, these indigenous tanning materials. Some of these, such as pods from *Acacia Nilotica* were used extensively in Sudan by rural tanners. But unfortunately the Sudanese leather industry uses mainly imported tanning materials from *Acacia Mearnsii* or minerals because the *Acacia Nilotica* tanning materials are not available in the high concentration spray dried powder form which is ease of handling and using whereas it do not produce the same quality of leather as 'Wattle' when is used in cruched form.

Many studies have been conducted to characterize tannins of *Acacia nilotica* pods and barks and it using as herbal medicinal or tannins reagents. Researchers studied the influence of subspecies,

soil, climate, cells type, age of the plant and growth stage on the quantity and quality of 'Garad' and barks tannins.

Some studies used pure *Acacia nilotica* pods or mixture of pods and bark to produce high concentrated and 100% soluble tannins as spray dried powder within laboratory use. This tannin was used to produce leathers with distinctive specifications compared to some leather which obtained using international commercial tannins. These studies have not been applied on a commercial scale for a number of reasons, including, high viscosity, nozzles closing on spray drying machine, high sensitivity of tannins materials to oxygen, temperature and iron

Acacia Nilotica pods are contained ~45% of total solids, tanning waste materials, the reminding is insoluble which were consisted of wooden materials it is precipitated and locked the sewage causing an environmental problems within the tanneries when using crushed pods.

Conditions and duration of storage was adversely affected on tannins of *Acacia. nilotica*; it was affected on the production cost, the tannin content was decreased to about half and amount when was stored for long times, whereas it was, consumed more amounts of cruched garad, twice of weight.

Acacia nilotica tannins was classified as a mixture types, it was contain an unspecified percentage of hydrolysable tannins, which was more sensitive to microbial and fungi attack, Fungus was consumed sugar and decomposed tannin molecules. Furthermore *Acacia nilotica* tannin was very sensitive to heat, the temperature should not raise more than 70 °C it was decomposed the tannin molecules and lost astringent powers. Also an iron complex readily with tannins consist highly undesirable blue or blue-green discoloration, which requires mechanical and chemical treatment to minimizing the content and effect of iron contamination in tanning extracts, which was adding extra cost to the production process.

1. 3 Objectives

The aim of this study is:

- * Utilization of local vegetable tanning raw materials such as *Acacia Nilotica* pods 'Garad' and *azadirachta indica* 'neem' barks.
- * Modification of the tanning characteristic of *Acacia Nilotica* pods.
- * Transfer and application of modern technology using local raw materials.
- * Using eco-friendly processes to reduce the pollution load of tannage and produce high quality leather.
- * Improve the physical properties, shrinkage temperature, tensile strength and fullness of the produced leather.
- * Reduction of the cost and replacement of the imported tanning materials

CHAPTER TWO

LITERATURE REVIEW

Chapter two

Literature review

2.1 Botanic description

Acacia is the most significant genus of family *Leguminosae*. It is estimated that there are roughly 1380 species of *Acacia* worldwide, about two- third of them native to Australia and rest of spread around tropical and subtropical regions of the world ((Seigler, 2003).

Acacia nilotica (Sunt) is a member of sub-family *Mimosoideae* of *leguminous* trees. It is of multiple uses in Sudan, Africa and many Arabian countries (Ahmed et al. 2005).

Three subspecies of *Acacia Nilotica* dominated in Sudan. The first one is *Tomentosa* with the pods necklace-like narrowly and regularly constricted between the seeds and grows throughout Sudan. The second subspecies is *Nilotica*, in which glabrous pods are strongly constricted between the seeds and grows along the White Nile. The third subspecies is *Adansonii*, in which the pods are only slightly constricted between the seeds and grows in Western Sudan (Al-Khalifa et al. 2005 and Mahadi et al. 2006).

Acacia Nilotica is one of the major plant species in Sudan there were so far 31 *Acacia Nilotica* in Sudan. Later, two species were added to the previous list, it is an important timber species 40 - 50% sawn timber production (Amos et al. 1999).

Acacia Nilotica wood which is hard and durable is used for many purposes, ranging from railway sleeper, furniture, building construction to boats. *Acacia Nilotica* tree, however, plays an important environmental role in the conservation of water resources along the bank of the river Nile and its tributaries. In addition to that, the tree has also high tannin content (Ibrahim, 2001).

Bargali and Bargali (2009) studied *Acacia Nilotica* as a multipurpose leguminous plant. It was realized to have fast biological nitrogen fixation, ability to establish on nitrogen- deficient and

drought prone soils. In addition, it was found suitable for agro forestry systems and thus can be used in rehabilitation of dry lands.

Acacia Nilotica grows up to 15-18 m in height and 2-3 m in diameter. The bark (appendix.1: Fig.3) is generally slaty green in young trees or nearly black in mature trees with deep longitudinal fissures exposing the inner grey-pinkish slash, exuding a reddish low quality gum (Patrick, 1999).

The leaves as alternate, bipinately compound, 5-15 cm long; axis fairly hairy, with 3-10 pairs of side axes (pinnate) 1.3-3.8 cm long; leaflets 10-20 pairs on each side axis, small, narrowly oblong, 2-5 mm long, blunt at the ends with tiny hairs along edges, grey-green (Raj et al. 2015).

The flowers (appendix.1: Fig.1) in globulous heads, 1.2-1.5 cm in diameter of a bright golden yellow colour, born either axillary or whorly on peduncles 2-3 cm long located at the end of branches (Dorostkar, 2015).

Pods of *Acacia Nilotica* appendix.1: Fig.2, is 7-15 cm long, green and *Tomentose* when immature and greenish black when mature, indehiscent, and deeply constricted between the seed giving a necklace appearance, She reported that the seeds of *Acacia Nilotica* are 8-12 pair pod, compressed, ovoid, and dark brown shining with hard test (Iman et al. 2006).

The yellow sweetly scented flowers are nectar less and found in round heads. Most flowers are functionally male with a few hermaphrodites and are mainly bee-pollinated. Leaf production and fall are affected by rainfall whereas temperature affects flowering and fruiting (Orwa, 2009)

Acacia Nilotica in Sudan flowers irregularly, generally between June and September and seeds fall takes place from March to May. In Australia trees flower from March to June and green pods are produced within four months but ripe pods fall from November to February. Most of the leaf fall occurs during the dry period when the tree bears green pods. (Sayda and Talaat. 1996)

Azadirachta Indica is a fast growing evergreen popular tree found commonly in India, Africa and America. It belongs to the family *Meliaceae* and is related with Chinaberry (*Melia Azedarach*). (Pingale, 2010)

The *Azadirachta Indica* grows in much of Southeast Asia and West Africa; few trees were planted in the Caribbean and several Central American countries. (Musa & Gasm Elseed. 2008)

Azadirachta Indica is a medium sized to large evergreen tree with straight trunk and dark brown to grey bark. It can grow up to 30 m in height and 70 cm in diameter. Its canopy is broad, dense and rounded. Leaves are pinnate with 9 to 15 serrated leaflets each 7 cm long by 2.5 cm wide, shiny dark green. The flowers are small, white, and honey-scented, in terminal clusters that are a good source of nectar for bees. In India the tree flowers profusely between February and May. The fruits are green drupes, smooth, olive-shaped and about 2 cm in length, with a sweet pulp enclosing a seed, which turn golden yellow on ripening in the months of June, July and August. (Mugnai, 2011)

The *Azadirachta Indica* had been used in ayurvedic medicine for more than 4000 years due to its medicinal properties. *Azadirachta Indica* called arista in Sanskrit a word that means perfect, complete and imperishable. Arishtha is the Sanskrit name of the *Azadirachta indica* tree meaning reliever of sickness and hence is considered as sarbarogaribarini. The tree is regarded as village dispensary in India. (Girish and Shankara. 2008)

Azadirachta Indica is the most versatile, multifarious trees of tropics, with immense potential. It possesses maximum useful non-wood products (leaves, bark, flowers, fruits, seed, gum, oil and cake) than any other tree species, known to have antifungal, because of these activities *Azadirachta Indica* has found enormous applications making it a green treasure (Kausik et al. 2002).

Azadirachta Indica became important in the global context because it offered answers to the major concerns facing mankind. It is considered harmless to humans, animals, birds, beneficial insects and earthworms, and had been approved by the United States of Environmental Protection Agency for use on food crops (Debjit et al. 2010).

Hibiscus Sabdariffa (roselle) is a member of the *Malvaceae* family. It has been used in different countries around the world as a culinary and therapeutic resource. It is considered to be one of the most important and popular medicinal plants and it has several properties such as antiseptic, aphrodisiac, cholagogue, digestive and stomachic. (Akindahunsi and Olaleye, 2003)

The *Hibiscus Sabdariffa* (Roselle) also known as 'Guinea sorrel' or 'Indian sorrel' is a medicinal herb cultivated for its seeds, calyx and leaf; and is grown in the tropics, subtropics and other parts of the world (Mounigan and Badrie, 2007).

Hibiscus Sabdariffa is said to have originated in Malaysia but now it is cultivated in many tropical and subtropical regions of the world. It is known by different names in different countries (Mogan and Badrie. 2007).

Hibiscus Sabdariffa plant is about 3.5 m tall and has a deep penetrating taproot, it erects and slightly branched and its stem may be smooth or slightly hispid. The leaves alternate on the stem and have long petioles and palmate divided into 3-7 lobes with serrate margins. (Frimpong, 2008)

Flowers borne singly in the leaf axils are up to 12.5 cm wide, yellow or buff with a rose or maroon eye and turn pink as they wither at the end of the day, 3.2-5.7 cm long and fully enclosed, 1.25-2cm long, which is green when immature, 5-valved, with each valve containing 3-4 seeds. The capsule turns brown and splits open when matured and dry. The seeds are kidney-shaped, light-brown, 3-5mm long and stellate hair. (Mahadevan et al. 2009)

The leaves and the white calyxes are eaten as vegetable after cooking. In Western Indies, the calyxes are freshly used in making jelly, syrup, gelatin, puddings and cakes while the dried calyxes are used in ice cream, butter, pies and sauces. (Bolade et al. 2009)

Hibiscus Sabdariffa L. is an herbaceous plant, cultivated largely in tropical and subtropical areas of both hemispheres. It belongs to the family of *Malvaceae* and is known by different names such as 'Guinea sorrel' or 'bissap' in Senegal, 'karkady' in North Africa, 'roselle' or 'sorrel' in Asia and 'flora' of Jamaica. (Cisse et al. 2010)

The dried calyxes, like any other raw material or food, is susceptible to deterioration by food borne microbes. The deterioration can lead to reduction in quality of the drink in terms of colour, taste and nutrition. Most of the fungal contaminant can cause spoilage and they are known to produce mycotoxins which are detrimental to human health. (Bukaret al. 2009)

The *Hibiscus Sabdariffa* is cultivated mainly for its calyx. The traditional processing activities of the calyx were conducted for the production of jam, concentrated and particularly of drinks/beverages. (Cisse, 2009)

2.2 Vegetable tanning materials

Many researchers have reported the successful usage of tannins materials from plant origins. Different parts of the plants were investigated. Their results have shown that the active materials are the polyphenols (tannins). The efficiency of these tannins materials were found to depend on the kind, structure, pH of tanning liquor, tannin content, nontannin content, and capacity of acid and salt of tannins liquor.

Dutta (2002) mentioned that the astringent organic compounds obtained from plant kingdom and capable to convert raw hides and skins into leather are called tannins. Tannins of different plants are different in composition, structure, and properties and leather obtained from them also possess different properties.

Zivkovic et al. (2009) reported that the plant polyphenols (tannins) constitute a complex group of naturally occurring polymers, and a rigorous chemical definition is difficult. Thus, tannins are considered to be polyphenolic metabolites of plants with a molecular weight larger than 500 and with the ability to precipitate gelatin and other proteins from solution.

Shi & Di (2000) reported that the vegetable tannins constitute one of the most important natural polyphenolic compounds and are widely distributed in root, bark, stalk and fruitage of plant.

Lee (2000) noted that phenolic compounds consist of a wide range of compounds possessing an aromatic ring bearing a hydroxyl (OH) substituent with their functional derivatives inclusive. He reported that food characteristics like taste, palatability, bitterness, astringency, colour, flavor as well as pharmacological and toxic effects are related to phenolic compounds.

Tannins are traditionally used as tanning agent in leather manufacture, according to definition of Bate-Smith (1962) tannin is “water soluble” phenolic compound. In this aspect Anon (2002) mentioned that most tannin is water soluble but very large ones are insoluble.

Yao et al. (2006) reported that the molecular weight of vegetable condensed tannin for leather tanning should be between 500-3000 Daltons: lower molecular weight compounds have weak protein complexation and polymerization abilities, Mavlyanov et al. (2001) noted while higher molecular weight compound poorly penetrate into raw skins, and, consequently, do not bind or bind very weakly to collagen.

Vermerris (2006) substituted the term polyphenols for tannin in attempt to emphasize the multiplicity of phenolic group's characteristic of these compounds. He noted molecular weights as high as 20000 Dalton, and that tannins complex not only with protein and alkaloids but also with certain polysaccharides.

Cornell (2000) reported that the amount and type of tannin synthesized by plants varies considerably depending on plants species cultivars, tissues, stage of development and environmental conditions.

Rao (2001) report that there is no suitable process to isolate tannin in purest form from tannin materials known at present, therefore the properties of a tanning material which are described by chemist and tanners are the overall properties of the mixture of tannins and associated products.

Edwin Haslam (2007) was mentioned that the traditional classification defined by Freudenberg in 1920, has been enlarged to two more classes in the last decades complex tannin and phlorotannins.

There were many attempts were made to classify tannins into different groups according to their different properties but the most important one was classifying them by Griffith (1991) into two groups: pyrogallol type and catechol type.

Edwin Haslam (2001) were reported that modern classification were identified and based on their chemical composition and properties; tannins are divided into two groups: hydrolysable type (pyrogallol) and condensed or poranthocyanidins which belong catechol.

Sarker and Nahar (2007) illustrated that the hydrolysable tannins are non-flavonoids and are split into simple molecules when treated with acids or enzymes while condensed tannins are flavanoids-related and form complex water-insoluble products when treated with acids or enzymes.

Hagerman et al. (2005) mentioned that the tannin was dividing into three main classes. The condensed tannins (proanthocyanidins) are flavan-3-ol base biopolymers that at high temperature in alcohol solutions of strong mineral acid release anthrocyanidins and catechin as end groups. Gallotannin and ellagitannin belong to hydrolysable tannins. Gallotannin is comprised of galloyl

esters of glucose or quinic acid whereas ellagitannin is derivatives of hexahydroxydiphenic acid and complex ones.

Pizzi (2008) reported that the hydrolysable type always undergo hydrolysis in aqueous solutions and are gradually splits up into their different constituents, whereas several molecules of catechol tannin gradually unite together into aqueous solutions and are ultimately separated from the solution as sludge called reds or phlobaphenes. Myrabolan, chestnut galls and valonea are some examples of hydrolysable type of tannins whereas wattle, quebracho, garan, babul (bark) are examples of condensed type.

Lina falcao (2011) reported that hydrolysable tannins consist of a polyolcore, being D-glucose the commonest; multi esterifies with gallic acid (3,4,5-tri hydroxyl benzoic acid) Fig.2.1 or derivative. These tannins undergo hydrolytic cleavage into their components, hence the name. Depending on the phenolic acid formed by hydrolysis they are sub-classified in gallotannin and ellagotannins.

Harzallah et al. (2014) described that Gallotannin, Fig.2.2, to be esters of Gallic acid with carbohydrates D-glucose and quinic acid in chain; in this case one of the hydroxyl groups on the carbohydrate is esterifies by a ploygallic acid, produced by up to four gallic acid, Fig.2.2, residues forming a linear polymer by esterification. While Carbo et al. (2008) reported that the ellagotannins, Fig.2.3, is more complicated chemistry they all tend to precipitate ellagic acid, Fig.2.4. Harzallah et al. (2014) showed that D-glucose core esterified with at least one unit of hexahydroxydiphenic acid. This is formed through oxidative coupling between two gallic acid units. Upon hydrolysis hexahydroxydiphenic acid is released, and spontaneously lactonizes forming ellagic acid.

Muir et al. (2011) noted that the gallic acid units are formed in plants, aromatic amino acids like tyrosine; phenylalanine etc. could be formed in microorganisms through metabolic reaction from 5-dehydroquinic acid.

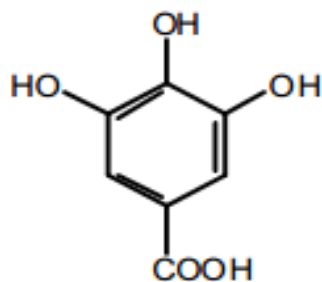


Figure.2. 1: Structure of gallic acid (Majumder and Parihavi, 2013)

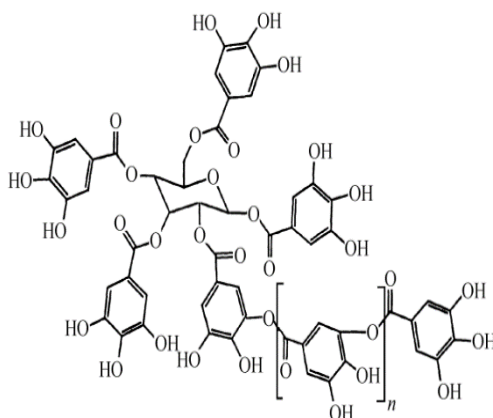


Figure.2. 2: Chain of gallotannin (Xuepin et al. 2003)

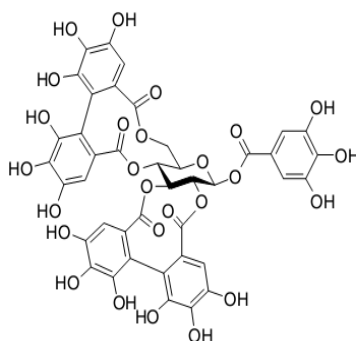


Figure.2. 3: Structure of ellagitannin. (Xuepin et al. 2003)

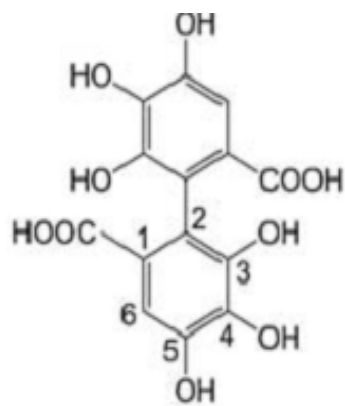


Figure.2. 4: Structure of ellagic acid, (Xuepin et al. 2003)

Flavonoids are the biggest class of polyphenols with more than 4000 different structures identified currently and these have C₆-C₃-C₆ general backbone structure where the two C₆ are phenolic in nature (Tsao, 2010). The different flavonoids come up due to the differences in saturation of the heteroatomic ring C and attachment of the aromatic ring at different positions on the chromane ring in the general structure for flavonoids shown in the following Fig.2.5.

Condensed tannins, also called proanthocyanidins are a result of polymerization of flavan-3-ol units (catechin and epicatechin monomers) joined by carbon-carbon bonds of the monomers (Tsao, 2010) as shown in, Fig.2.5. They are called proanthocyanidins because they produce anthocyanidins when heated under strong acidic conditions in the presence of molecular oxygen, by cleavage of a carbon-carbon bond (Stevanovic et al. 2009).

Shi & Di (2000) noted that the condensed tannins are the polymerized product of flavan-3-ol, and /or flavan-3, 4-diols and mimosa is a representative of it.

Covington (2009) was demonstrated that condensed tannins are oligomeric or polymeric flavanoids consisting of flavan-3-ol (catechin) units, Fig. 2.6, which is commonly linked through C₄, C₅ links, may also occur. Upon treatment with hot alcoholic acid solution this class of tannin

yields red coloured anthocyanidins and insoluble polymeric phlobaphenes example of important condensed tannins for vegetable tanning are extracted from quebracho wood and mimosa bark.

Pizzi (2003) showed that condensed tannin constituting more than 90% of the total world production of commercial tannins (200000 tons per year), are chemically and economically important for the preparation of adhesive and resin.

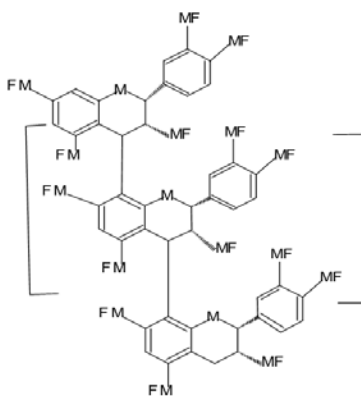


Figure.2. 5 Structure of condensed tannin (Majumder and Paridhavi, 2013)

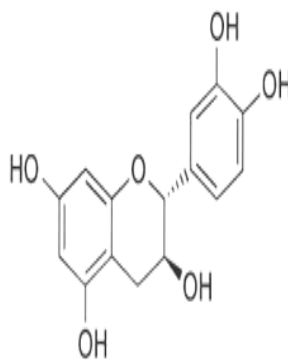


Figure.2. 6 Structure of catechin Shi & Di (2000)

The vegetable tanning liquors not only contain tannins but also many other soluble matters like carbohydrates, acids, salt and phenolic matters, (Bickley, 1999). These soluble matters are called nontannin because they cannot tan but their presence in the tanning liquor is important and essential. (Bajaj, 1998)

Bickley (1991) noted that the nontannin was control the swelling/ plumping of the pelt during tanning and effect significantly on solubility of the higher molecular weight tannins and therefore influence the astringency and rate of the penetration of the tannins into the leather in addition to affecting the viscosity of the tanning solution.

Kuria (2015) demonstrated that if the nontannin content of a tanning material is more than its tannin content the tan stuff is considered unsuitable for tanning, the tan/non-tan ratio of tanning stuff for satisfactory tannage should therefore be always greater than one.

Vegetable tanning liquors contain carbohydrates like glucose, pentose etc, and gums which undergo fermentation, more in the summer season, when kept for some days. The sugary matters are first converted into alcohols by the action of yeast, bacteria, and mould enzymes already present or formed in the tanning liquor. These alcohols are converted into acetic acid. Mould split up hydrolysable tannins into sugar and ellagic acid which is further splitted up into gallic acid.

Gustavson (1990) reported that the pH of tanning liquor is important to control the tanning process for most of the vegetable tanning materials the fixation of tannin by the pelt is minimize within the pH rang 4.0-5.0. He also noted that hydrolysis of hydrolysable tannins and progressive polymerization of condensed tannins are forming sludge/ bloom and Reds/ phlopophane respectively and loss of tannins, also the difficulties due to the formation of gums and mucilages

in the case of *ghatbor* and *garad* are associated with some inherent deviancies which limit the use of these plant materials in the leather industry.

Rao (2001) suggested that for better, fuller, proper and effective utilization, they require modifications by physical and chemical methods, the most effective method is to blend them with other tanning materials for the counteraction of the deficiencies of one material with the advantage of other materials, also treatment/ mixing with syntans and chemical is another effective method of modification.

2.3 Manufacture of vegetable tanning materials

Many researchers have reported the successful extraction of tanning materials from raw plant materials (bark, wood, leaves, fruits, pods...etc); different methods of leaching were investigated using various solvents. Their results have shown that the efficiency of these extraction were found to depend on the kind of solvent, size of raw materials, temperature, solid to solvent ratio, time of leaching and motion through the leaching.

Buelga and Williamson, 2003 reported that some solvents of medium and high polarity, such as ethanol, methanol and water, were found suitable for extraction of tannins.

Sarkar (1991) reported that extraction of tannins from disintegrated plant materials by solid to liquid extraction. Subdivision by grinding or chopping increased the rate of extraction, but if the size of the particles is too small the separation of tanning solution from the solid phase will be made more difficult.

Rao (2001) reported that the removal part of the substrates such as the seeds was found to improve the extraction process, as these substrates may contain substances other than tannin such as starches which interfere with process.

Dutta (1985) reported that the extraction of tannin generally is performed in wooden vats containing tannin-bearing materials connected in series.

Oliveira 2010 described that the selectivity of the extraction process depends on the choice of the appropriate extraction condition, like temperature, solid-to-solvent ratio and type of solvent, among others, the employment of solvent chemical additives, such as sodium hydroxide, tri sodium phosphate, sulfanol, phenol and sulfite salts is recommended in some cases in order to increase tanning extraction yields. In particular, sulfite salts are used with the intention of improving tannin aqueous solubility and of reducing its viscosity, as result of the cleavage of tannin interflavanoid bond with the generation of lower molecular weight procyanidin-4-sulphonated derivative.

In this way, Onifade (2001) studied leaching of tanning materials from the bark using water as solvent, the results showed that the tannin produced varied inversely with the particle size of the bark, better yield were obtained if distilled water, small size and agitation method were used in comparison with tap water and soaking method.

Sundara Rao (2001) noted that generally, extraction is performed in such a way that materials undergo three change of float (water in case) to obtain as high extraction percentage as possible. The temperature of the float has to be maintained at around 70°C. Since tannins in general are sensitive to temperature, the extraction should not be performed at higher temperature and the liquor should not be overexposed to the atmosphere, to avoid possible oxidation. Care should also be taken in the material of construction of process equipment to prevent the contamination of iron with the liquor.

In this aspect, Haj Ali (2007) studied the influence of many parameters (such as, particle size, temperature, duration of process and solid to solvent ratio) on the extraction efficiency using a rotary system to extract tannin from *Acacia Nilotica* pods. The highest efficiency was observed when using 1:3 ratios of crushed materials to soft water at 60°C for 24 hour.

Chew et al. (2011) evaluated the influence of temperature and duration of process on the extraction of tannin from pods using ethanol as a solvent. The temperature was found more effective on extraction than the duration of the process.

Zhekova & Povlov (2012) also studied the Influences of four factors: type of solvent 60% ethanol and 85% glycerin, thyme variety, three subspecies, temperature 20-60 °C and duration of process 1-5 hours. The obtained extracts were determined the content of tannins and flavanoids. The data were presented as four factors analysis the results showed that the thyme variety has the strongest influence on extracted tannins and flavonoids, followed by solvent type, temperature and duration of the process.

Lokeswari and Sujatha (2011) were studied the influence of particle size, temperature, methanol content and time on the extraction of tannins from *Caesalpinia Coriaria* by pressure autoclaving method. The results suggest that a decrease/degradation of these compounds is less noticeable at low temperature 40°C on the other hand the effect of time and substrate concentration on the extraction and evolution of the analyzed compounds that is tannins seemed to be less important than temperature.

Chavan & Amarowicz (2013) in their study, evaluated the extraction capability of methanol-water, ethanol-water and acetone-water for phenolic compounds, condensed tannins and sugar from *Beach pea* seeds using UV spectra, TLC and HPLC analysis. The result showed that acetone-water system was considered far more efficient solvent system to obtain higher amount of phenolic compounds and condensed tannins than the others two systems.

Sivakumar et al. (2007) studied the effect of power ultrasound in the extraction of vegetable tanning material (Myrabolam) at room temperature. The extraction efficiency was found to increase drastically from 77 to 90%.

Gerhard (1996) described the manufacture of tannin extract through a disintegration of tanning materials by cutting, rasping, crushing and/or coarse grinding followed by the extraction of the disintegrated barks by means of water in accordance with the counter flow principle in extracting boilers. Pump was used to move the weakest liquor towards the fresh new-coming barks at temperatures of 80 to 130 °C and suitable pressure (depending on the nature of tanning material). This helps the tannin content in liquor to increase gradually. This liquor was then purified through precipitation, filtration or centrifugation. The liquid extract was then concentrated in vacuum evaporator. This extract was turned into powder by spray drying, drum drying or granulate drying and sold with purity of about 60-80 w/w%.

Rao (2001) reported that the advantages of applying spray dried tannin powder. These include shorter tannage time, ability to fabricate tanning liquor with different concentrations and formations, consistency in quality, availability at off-season periods, and reduction of transportation cost and storage space. He also counted many benefits of spray drying process in the production of tanning materials such as the short drying time (few seconds), materials of quite uniform hollow spheres and bright colour, and the high concentration of tannin in the material powder.

Iron complexes readily with tannin to give highly undesirable blue or blue-green discoloration, the importance of minimizing the content and effect of metallic contamination in tanning extracts has been realized from the earliest days.

Williams & Feist (2004) reported that there are suitable methods are adopted to minimize the collection of soil and other debris with the raw material as this may contain metallic impurities. This applies particularly to tanning materials of fruit origin which may be collected from the ground after falling from tree or shrub. Blue and black spots were formed with hydrolysable

tannins and mimosa tannin in the presence of iron and green or black colour with other condensed tannins.

Gustavson (1990) reported that machinery designed cleaning of tannin containing fruits was useful to keep metallic contamination low. In this process, magnets were employed to extract particular iron from raw material, prior to extraction. Apart from iron, metallic impurities occur naturally in the tannin bearing plant tissue and the water supply should also be removed or minimized to negligible limits.

Dutta (2000) revealed that bleaching and antifungal processing are generally carried out by treating the concentrated liquor with sodium bisulphate or a mixture of sodium sulphate and hydrosulphate for four hours followed by oxalic acid for one hour. The normal bleaching is to treat the tannin liquor (usually contains 45% of tanning material) with about 0.5% sodium metabisulphate and approximately about 0.1% of organic acid such as acetic acid or formic acid.

Haj Ali (2007) applied the previous method of Dutta (2000) on Sudanese indigenous 'Garad' in order to bleach the tanning liquor and to prevent its fermentation. He used either a mixture of 1:1 sodium bisulphate to sodium sulphate or sodium fluoride; this was followed by a treatment with 0.5% oxalic acid for one hour. It was found that addition of 1% bleaching agent was sufficient to prevent fermentation and mould formation as well as the deterioration of the colour.

2.4 Vegetable tanning systems

Many researchers have reported the usefulness of vegetable tannin materials for protein pelts tannage. Many methods of tannage were investigated using kinds of vegetable tanning materials. The results revealed the dependence of tannage quality on the kind of vegetable tanning materials, concentration of tannin, temperature, tannage time, kind of pelts (skins or hides) and motion during the tannage process.

Sivakumar et al. (2010) summarized four tannage steps. These are pre-tanning to eliminate collagenous materials, tanning to stabilize the collagen matrix, post-tanning to impart functional properties and finishing giving aesthetics.

Musa and Gasm elseed (2013_b) reported that the aim of the pretanning is cleaning hides/skins, tanning stabilizes skin/hide matrix permanently, and an esthetic values are added during post tanning and finishing.

Marion and Rey, (2006) reported that the soaking is the first step in leather processing. In this step, the raw skin is exposed to water and chemicals which hydrate the proteins and fibers. Additionally, denatured proteins as well as salts were used for preservation are solved in the water phase and removed together with dirt which is attached to the skins. The process duration of soaking depends on the condition of preserved hides and skins (Yapici *et al.*, 2008).

Sivakumar and Rao (2001) reported that the liming treatment affects the structure of the skin which results in a better reactivity of the skin containing collagen when it is exposed to tanning agents. The liming step introduces chemicals such as lime and sodium sulfide which open up the fibre structure of the skin and hence provides more working surface for treatment with tanning agents. Furthermore, Cassano et al. (2001) noted natural fats are partially saponified, most of the interfibrillary proteins such as albumins and globulins are eliminated, mucoids are degraded and the derma is swelled. The mechanism of unhairing process was described by Sivakumar and Rao (2001) to be through the destruction of cementing substances, such as, prokeratines and glycoprotein, in the root of the hair. The addition of liming agent helps to break the disulfide bond on amino acid cystine, which is part of the prokeratine structure.

Casano et al. (2001) described that the deliming step to reduce the excess of liming agent in the fluid stream. Acids (such as formic acid) and/or acidic salts (e.g. NH_4Cl , NaHCO_3 , etc) are added

to the stream. They also expressed that the bating step involves the addition of proteolytic enzymes. These proteolytic enzymes open the fibrous structure of the derma to make it softer. Furthermore, they detected that the pickling process ensures the removal of the last residual lime in the skin by acidification and dehydration of fibers. Acidification dehydrates the fibers of the skin using sulfuric, hydrochloric, and formic and lactic acid in combination with salts such as sodium chloride, sodium sulfate and various salts from the used acids. This may also include chromium basic salt.

Krishnamurthy et al. 2012 noted that the tanning step guarantees quality, durability, practicability and the stability of the final leather product by treating the skin with inorganic and organic tannins such as chromium, aluminum, titanium, iron and zirconium basic salts as well as high molecular weight vegetable substances, aldehydes, oils and other substances.

Faber, 1990 reported that the vegetable tanning methods are different than chrome tanning methods. Which takes longer time and so they can be classified according to time into four different groups: slow pit tannage, accelerated tannage, quick tanning methods and rapid tanning methods. Slow pit tannage takes 12-18 months and is performed in isolated condition according to the counter-current principle with thin liquor giving good quality of leather. However, this tanning method has a disadvantage of losing high amount of tanning agents due to oxidation and hydrolysis in their prolonged duration, whereas, accelerated vegetable tannage takes 2-6 months depending on the process used and is performed by increasing the concentration of tanning agents by using higher percentage tanning agents and tan liquor. But this method has disadvantages of slightly reduced bonding and higher removing of the content of substances by washing in comparison to slow pit tanning method. Quick tanning methods take 4-20 days depending upon the nature of leather and operational conditions. These conditions are

mechanical agitation, concentration, temperature, pressure and pH. Some of the known methods are Italian method, Four step method, Igualada method, Liritan method, West German tanner school method and English hot pit method. Whereas, rapid tanning methods take 2-3 days, in this method, powder tanning substances are used. The two known methods are RFP process of BAYER and Rapitan process of BASF. But this method is much more sensitive and should be handled with full attention. The temperature should not raise more than 38 °C, vessels should be well suitable and the hides should be well prepared.

Shi and Di (2000) believe the main reaction between vegetable tannins and protein occurs through hydrogen bonds formation between the hydroxyl groups on the polyphenol and oxygen or nitrogen atoms on the protein.

Pankaj et al. (2011) mentioned that the reaction of acid/salt also occur to a lesser extent and more recently it has been suggested that a hydrophobic interaction may also occur whereby the less hydrophilic aromatic parts of both molecules come together with the exclusion of water to form a third type of bond.

SLTC, 1999 suppose that cross-link between collagen and tannin was occurs through hydrogen bonds and the degree of this cross-linkage depends on the polyphenolic molecule size and phenolic group (-OH) number. He also reported that in the pH 5.5-2 ranges there was a marked increase in tannin fixation.

Madhan et al (2001) also in his study presumed that the typical mode of combination is hydrogen bonding between the hydroxyl groups of the tans (phenolic substances) and various reactive groups such as carboxyl, amine and amide groups of collagen.

Rao (2001) reported that the vegetable tanning process through two stages to obtain leather, one of them is penetration and the second is diffusion and fixation, which can be affected with the

size of capillary spaces inside the fiber structure, the size of the tannins particles and the level of affinity between the fiber and the tannin particles.

Gold Farb (1999) did a comparison study between the thermal stability of vegetable tanned leather and chrome tanned leather using types of vegetable tanning materials, mimosa, quebracho and wattle. The results found that the vegetable tanned leathers showed lower thermal stability compared to chrome tanned leather. Luo et al, 2011, but they exhibited lower water swelling and can be colored using direct dyes.

Madhan et al. (2002) had carried out a study to obtain leather of high hydrothermal stability by the treatment with vegetable tannins (*Acacia Mollissima*) in the presence of acrylic polymer the results showed an increase on shrinkage temperature by 25°C when acrylic polymer was applied.

Simon (2003) in their studies suggested that the best alternative to chroming is tanning with synthetic and vegetable tannins because it is so friendly to the environment than chromium tanning although it is cheaper and can easily be applied for various sorts of pelts. On the other hand, chrome method leads to the formation of hazardous waste. Besides, finished products, leather, after exploitation becomes unwelcoming waste by environmental point of view.

Vegetable tannin is often used as a retannage of chromium tanned leathers for the production of shoe uppers. Thus Williams-Wynn (1970) had summarized the type of tanning process. Chromium pretannage increase the reactivity of vegetable tannins, apparently by increasing the availability of amino groups as well as by formation of coordination complexes of both the tannin and non-tans with the chromium. When these leathers are dried and aged, further reaction takes place resulting in an increase in free sulphate and high acidity. The low pH causes hydrolytic degradation of the collagen with loss of strength of the leather. William- Wynn offers suggestion of ways to modify this tanning process to improve the properties of chromium-

vegetable tanned leather. They include reducing the degree of chromium tannage and\ or use of anionic syntans prior to the vegetable retannage. Format masking was very effective in reducing the loss of chromium in the retannage, in reducing the amount of vegetable tannin fixed in the retannage and in reducing the acidity of the resulting leather.

Krause et al. (2005) reported that retannage with condensed tannins was much better than with the hydrolysable tannin while Sarkar (1991) reported that the use of condensed (wattle) with neutralization gave the most stable leather, the wattle tannin were also superior because of the amount of chromium stripped off in the vegetable retannage.

Sah (2013) reported that a rapid tannage combination pit-drum process has also been developed using the same basic process where Athinson (1974) has described other drum processes, which uses wattle tannins in a spray-dried powder form in drum tannage also results in minimal effluent.

Industrial-plant-scale experienced with rapid vegetable tannage processes were reviewed by Exner and Kupka (1982). They demonstrated that a triple glutaraldehyde vegetable–glutaraldehyde tanning process increased the shrinkage temperature a further 5°C and gave leather with very low water- solubility.

Musa and Gasm elseed (2013a) in their study developed an eco-friendly tanning system using a combination of 20% crushed garad and 4% of oxazolidine for the production of upper leathers. It has been observed that above mentioned system provides a shrinkage temperature of 102°C. The characteristics of the leathers indicate that the garad-oxazolidine combination system provides leathers with good organoleptic properties and comparable strength properties. The leathers have been further characterized for chemical analysis such as water soluble matters and degree of tannage.

Aluminum also can complex with carbonyl and amino functions, and hence effective cross linking can be initiated either through the aluminum-collagen or the vegetable tannin- collagen complex. The high degree of thermal stability achieved with vegetable– aluminum tannage is assigned to the complexation between the aluminum and vegetable tannin. This concept was highlighted by Haroun et al., 2009 who showed that many multivalent metals, enhance the shrinkage temperature of vegetable tanned hides.

Toni gold & Heidemann (1982) concluded that the metal retannage involved the formation of extended tannin-metal complexes that effectively crosslink the system rather than the induction of the formation of covalent bonds between the tannin and collagen or within the collagen polymer, as occurs in chromium tannage. Of all processes developed for use of vegetable tanning, the vegetable-aluminum tannage has the most promise of displacing the chromium tannin processes.

2.5 Research updates of *Acacia nilotica*, *Azadirachta Indica* and *Hibiscus Sabdariffa*

Many researchers have reported the successful usage of garad and bark from *Acacia Nilotica* plant origins. Different kinds of garad were investigated. Their results have shown that the active materials of 'Garad' are the mixed tannin types (hydrolysable and condensed). The efficiency of these tanning materials were found to depend on the *Acacia* subspecies, age of the tree, the 'Garad' grown stage, storage of 'Garad', tissues, portion of tissues, kind of leaching system, leaching temperature, time of leaching, solvent, and ratio of materials to solvent.

Ismail et al. (2008) reported that *Acacia Nilotica* pods were applied in Sudan particularly pods of the subspecies *Nilotica* which has been known and used for tannage since long time ago.

Sarkar, 1991 noted that the tannins of *Acacia Nilotica* pods is traditionally used for tanning and retanning in tropical Africa and it is one of the most important tanning materials in Northern India.

Jansen & Cardon. (2005) reported that in India, 10 year old trees yield about 35–40 kg bark, or about 6 t/ha, and plantations of about 600 trees/ha produce 12 ton bark 15 years after planting. Average annual pod yield from the plantations is 8–10 ton/ha. Tinmber lake et al. (1990) reported that in Sudan individual trees yield 18 kg pods per year, where the *Acacia Nilotica* yields about 35 kg of fruit per tree per season in India.

Haj Ali and Ahmed (2007) mentioned that when 'Garad' was used for tanning, a solid deposit known as bloom was found inside the leather and formed insoluble sediment in the tanning liquor. According to tanners conception, this solid deposit was believed to result from long time accumulation of bloom, which produced by hydrolysable tannins.

Musa and Gasm elseed (2013_b) reported that Sudan has various indigenous tanning materials. Some of these, such as 'Garad' pods of *Acacia Nilotica* subsp. *Nilotica* and 'Talh' bark, *Acacia Seyal*, are used extensively in the Sudan by rural tanners. The tannin content of 'Garad' pods is approximately 30 % of the total weight, soluble nontannin are nearly 20 %, while moisture and insoluble make up the remainder.

Ahmed et al. (2005) and Mahadi et al. (2006) in other study evaluated the tannin types and quantity in four indigenous plant *Acacia Nilotica* species *Nilotica*, *Tomentosa*, *Subulatea* and *Adansonii* pods and bark by different methods. The tannins contents of the samples were found more than 10%, which were considered suitable for commercial exploitation. These percentages were found far less than that of standard *Acacia Mearnsii* 'Wattle'. Also the types of tannins

which in the pods of *Acacia Nilotica* subspecies were found hydrolysable-condensed types (mixed).

In contrast to the above findings, Bargali and Bargali (2009), in their evaluation study of tanning materials from leaves and pods including seeds of *Acacia Nilotica* using different methods, reported tannins content of 7.62, 5.45 in leaves and pods, respectively. This purity is considered insufficient for commercial interest. The chemical nature of the *Acacia Nilotica* pods was identified to be mixed type.

Musa and Gasm elseed (2008) reported that the tannin of 'Garad' contains a considerable amount of sugar which causing acid fermentation during long storage. This was assumed to be due to the action of enzyme, which hydrolyzes the ester links releasing sugar and acids such as ellagic and chebulinic acid. For the tannins in such case, 'Garad' tannin behaves like pyrogallol tans. It also gave a red-brown colour, and on a dilution and standing, it deposited a thick reddish-brown sludge similar to reds, phlobaphenes, which is one of the characteristic of catechol tans hence 'Garad' is a mixture of pyrogallol/ catechol.

Bickley (1991) analyzed chromatographically the *Acacia Nilotica* pods tannin. The results showed that the main constituent of tannin is presumably leucocyanidin gallate.

Gaddamwar et al. (2011), in their study, screened the *Acacia Nilotica* pods. They were found to contain high percentages of phenolic constituents consisting of *m*-digallic acid, gallic acid, methyl or ethyl esters of gallic acids, protocatechuic acid, ellagic acid leucocyanidin, dimmers of 3,4,5,7-tetrahydroxyflavan-3-ol, oligomer of 3,4,7-tri hydroxyflavone-3-ol and (-) epicatechol. The results also showed the presence of mucilage and saponin.

Lamb (2007) suggested that the chemical composition of 'Garad' pods tannin to be a mixture of di/tri gallic acid, which consists of five tannins $C_{20} H_{19} O_{10}$, $C_{20} H_{20} O_{10}$, $C_{21} H_{18} O_{10}$, $C_{21} H_{19}$

O₁₀, and C₂₂ H₁₉ O₁₀. These oligo-gallic acids hydrolyze to yield gallic acid, ellagic acid and phlobaphenes C₁₄ H₁₈ O₄.

Nsahlai et al. (2011) noted that *Acacia Nilotica* has been reported to contain condensed tannins in the bark. These condensed tannins were investigated to act as defensive materials in plants against herbivores.

In contrast, Rao (2001) investigated that it is difficult for condensed and hydrolysable tannins to co-exist in one part of the plant. According to his study, he suggested the presence of one type along with low molecular weight compounds of the second type.

Lamb (2007) in his evaluation study on the ground deseeded pods, reported the major constituents to be 34.2% tannins, 18.8% nontannins, 40.7% insoluble materials and 6.3% moisture. The pH of the pods extracts was found to be 4.7.

Ahmed (2005) and Mahadi, et al. (2006) in their studies reported that the mixture of equal proportions of spray-dried extract from *Acacia Nilotica* husk and *Azadirachta Indica* bark was produced and examined; the result showed that the spray dried powder contains ~45% tannins. The produced powder was employed to produce leather which was comparable in the physical and chemical properties to that treated by *Acacia Mearnsii*. But this approach has not yet been adopted commercially.

Ibrahim (2001) in a comparison study examined the tannins content of *Acacia Nilotica* pods and myrabolam, 'dividivi', and 'Wattle' bark. The results identified the tannins content of 'Garad' pods to be fairly high comparable with other natural tannins.

Anon (1992) mentioned that bark of *Acacia Nilotica*, like that of most of the *Acacias*, is a powerful astringent, and it was used, instead of oak bark, for tanning by the European manufactures of leather in Bengal.

Tanner et al. (1990) reported that in India and Pakistan the bark of *Acacia Nilotica* is a by-product of timber plantations, and it is used for tanning and dyeing leather. The tannins from a bark of *Acacia Nilotica* produced heavy leather, which was characterized to be firm, durable and hard. However, when bark tannin was blended with myrobalans from *Terminalia* species produced leather with better quality.

Osman et al. (2014) suggested that the bark of *Acacia Nilotica* in Sudan is discarded as industrial wastes after the manufacturing of railway sleeper, and therefore the extraction of blending of *Acacia Nilotica* pod and bark was found to produce tannin material with a percentage about 29% of the total solid extract.

Osman et al. (2009) in other study, investigated that the spray-dried powder of aqueous extract of *Acacia Nilotica* bark (extracted at 90°C for 24 hours and dried at 175°C) contain 45% tannins.

Sarkar (2005) mentioned that the ratio of tannins to nontannins varies from 1.7-1.9. Whereas. Acid to salt ratio is close to 1. The approximate acid content is 0.9 cc. (N) HCl per gm. of solid extract. Therefore it was cleared that *Acacia nilotica* pods tannin is not highly astringent material and it produced medium firm leather. The pods of the tree called garad contain 20-30 % of tannin when matured and give mellow and plump leather similar to that produced by gambier. (Kuria. 2015)

Haj Ali (2007) studied the effect of pods and bark growth stages on the tannins content. The results showed that the tannins content varies from ~51% of immature pods to ~36% of mature pods, whereas the bark tannins content varies from ~18 % of barks at 6 years to ~15% of barks at 13 years.

Mahadi et al (2006) in a comparison study discussed the influence of the type of *Acacia Nilotica* subspecies on tannin content on pods and barks. The results showed that the tannin contents were

28.8, 26.6, and 39.4% in *Acacia Nilotica* subspecies *Adenosine*, *Nilotica* and *Tomentosa*, respectively. Whereas the tannin content of the barks were 16, 9.5, and 23.6% in *Acacia Nilotica* subspecies *Adenosine*, *Nilotica* and *Tomentosa*, respectively.

Al-khalifa et al. (2005), in comparison study, investigated the effect of many parameters on the tannins content of *Acacia Nilotica*, pods and barks in the Sudan. The studied parameters were subspecies, growth stage, parts of plant (pods or barks), kind of soils, and rainfall ratio. The optimum parameters which produced the highest percentage of tannin (54%) were the subspecies *Nilotica*, immature pods, silty or sandy clay soil type and about 400 mm/year rainfall ratio.

Gaddamwar et al. (2011), in their study, suggested the utilization of *Acacia Nilotica* pods as an eco-friendly bending adhesive in the manufacture of plywood from waste wooden.

Lamb (2008) produced soft plump leather of very light colour when applied 'garad' tannage process. Chemical analysis of produced leather showed that the hide substance, moisture, grease, sulphate ash, tanning matter, water solubility at 25°C, fix tan, degree of tannage, insoluble ash, moisture and sulphated ash of water soluble, were 34.9, 14, 11.4, 4.9, 34.8, 7.0, 28.4, 81.4, 4.3, 7.3 and 0.6%, respectively. Whereas the pH of water soluble components was 3.14 and shrinkage temperature of leather was -75°C.

Haj Ali & Ahmed (2012), in a comparison study of physical and chemical properties of leathers tanned with either spray dried 'garad' or with spray dried mimosa. The results showed that usage of 'garad' powder of 59 % tannins, for tanning goat and cow pelts gave excellent leather and satisfactory results.

Musa and Gasm elseed (2013a) studied the eco-friend combination tanning system using 20% 'garad' and 4% oxazolidine to produce upper shoes leather. The results showed that the eco-

friend tanned provided a shrinkage temperature of 102 °C and the characteristic of the leather indicated that the system provides leather with good organoleptic properties.

The dried mature pods of *Acacia Nilotica* used in local tanneries in Sudan as indigenous materials to produce a pinkish white leather of good quality, thus Musa and Gasm elseed (2013b) were carried out method which improved Sudanese rural 'Garad' tanned crust leathers for the production of semi-chrome shoe upper leathers. The results explained that the leathers produced are full, soft, and flexible with high tensile strength. However, the stripped rural 'garad' tanned leathers retanned with 8% basic chromium sulphate showed high thermal stability (104 °C) and good organoleptic and strength properties.

In this way also Mahadi et al. (2009) studied the chrome free tannage methods using indigenous materials (skins, garad powder, and aluminum sulphate). Leathers obtained from this study exhibited high shrinkage temperature (125 °C), elongation at break (65.6 %), tensile strength (38 N/mm²), and tear strength (98 N/mm). The chemical properties of the tanned leathers were found to be quite normal.

Mueller Harvey (2006) screened the *Azadirachta Indica* bark liquors, the results showed the condensed tannins from the bark contained gallic acid, (+) gallo catechin, (-) epicatechin, (+) catechin and epigallocatechin. The study also examined sulphur containing compounds such as cyclic tri-sulphide and tetra-sulphide isolate from the steam distillate of fresh matured *Azadirachta Indica* leaves. The results showed that the extract had antifungal activity against Trichophytin Mentagrophytes.

Obaineh et al. (2013) studied the extracts of leaves and barks of *Azadirachta Indica* which was obtained using 95 % alcohol. The results showed that the highest yield value was recorded in the ethanol leaf extract content ~11 mg/g then ethanol bark extracts content ~6 mg/g.

Debashri and Tamal (2012) examined the *Azadirachta Indica* as a natural, eco-friendly and safe to the non target organism's pesticides used in the agricultural field to control crop pests. The results showed nearly 550 insect pest species were sensitive to *Azadirachtin*, an active compound extracted from the *Azadirachta Indica* tree.

Grover et al. (2011) examined the anti-microbial activity of the leaves of *Azadirachta Indica* extraction using the cup plate agar diffusion method. They were tested against six bacteria and two fungi. The results showed high antimicrobial activities.

Haroun et al. (2013) screened the extract of *Azadirachta Indica* bark. The results showed that the bark contents were 21.1, 24.9, 16.8, 7.6 and 2.2 of total solids, total dissolved solids, tannin, nontannin, catechin number, respectively.

Orwa et al. (2009) reported that the *Azadirachta Indica* bark contains ~12 % condensed tannins and some chemicals which were required by leather industry.

Syed (2000) studied 'Neem' bark tannins for the leather industry the results found that bark was rich in condensed tannin, physical properties of tanned and retanned leathers showed comparability of neem bark tannins with mimosa tannin extract.

Kuriyan et al. (2010) mentioned that the chemical constituents of *Hibiscus Sabdariffa* are citric acid, oxalic acid, tartaric acid, malice acid, hibiscus acid, ascorbic acid.

Obaineh et al. (2013) studied *Hibiscus Sabdariffa* calyx extracts which were obtained using three systems of cold, hot water and 95% of alcohol. The three aqueous were analyzed using standard biochemical procedures. The results showed that the highest yields of all bioactive components were found in the hot water extract especially oxalate yield (8.33 mg/g).

Mahadi et al (2006) reported that the plant contain protein, fats, carbohydrates, flavanoid, acids, minerals and vitamins.

Haroun, et al. (2013) evaluated the bark of *Hibiscus Sabdariffa* using different screening procedures. The results showed that the bark contains 3.5, 3.1, 0.2, 2.9 and 0.7 of total solids, total dissolved solids, tannin, nontannin, catechin number, respectively.

Ijeomah et al. (2012) examined the calyx of *Hibiscus Sabdariffa* which were used as medicinal and food ingredients in many parts of the world. The study showed that calyxes contain 3.11 % alkaloid, 5.54 flavanoid, 16.76 ascorbic acids and 0.45 tannins. On the other hand, it had higher polyphenol (1.10%), anthocyanin (1.15%), oxalate (0.53%) and saponin (1.19%) contents.

Mungole and Chaturvedi (2011) conducted a phytochemical screening of *Hibiscus Sabdariffa* for various medicinally important compounds. They found that phenols, alkaloids, tannins, flavanoids, saponin are present in leaves, stems and roots of the plant. Quantitative analysis of stem leaves and root showed best results in which phenolics have been found to be present more in leaf of the plant.

Haroun et al. (2013) studied the tannins content of 12 indigenous and exotic wood species and two agricultural crops. The extracts of these plants were screened by different methods and the results showed that the tannin of *Hibiscus Sabdariffa* is a condensed type and it contains 0.2% tannins.

CHAPTER TWO
LITERATURE REVIEW

Chapter two

Literature review

3.1 Source of materials

Sinnar city, it lies at the west bank of the Blue Nile north east Singa latitude $13^{\circ} 89\frac{1}{2}''$ N, and longitude $33^{\circ} 57\frac{1}{2}''$ E, approximately 315 Km south of Khartoum, the soil is heavy clay and the rainfall is about 850 mm per year where the *Acacia Nilotica* grows naturally were randomly chosen as the source of the samples, to study.

Khartoum capital of Sudan, latitude, $15^{\circ} 29' 29''$ N, and longitude $32^{\circ} 29' 0''$ E, the rainfall is about 600 mm per year. The soil is generally heavy. Where firstly the *Hibiscus Sabdariffa* cultivable grows was randomly chosen as the source of samples to study and secondly the *Azadirachta Indica* grows naturally was randomly chosen as the source of samples to study.

3.2 The samples collection and preparation

Mature stage of *Acacia Nilotica. Tomentosa* pods were collected in April 2013 from Sinnar state after falling down, 100Kg. The samples collected were dried under shade for three days, then purified and the seeds were discarded from the pods in order to prepare them for grinding, sieving, mesh 10 mm, then dried at 100° C for 2 hours in the oven, then kept in clean labeled samples bottles.

The samples collected of *Hibiscus Sabdariffa*, 10Kg, and *Azadirachta Indica* bark, 30Kg and leaves, 10 Kg, were dried under shade for three days, then purified grinding, sieving, mesh 10 mm, then dried at 100° C for 2 hours in the oven, then kept in clean labeled samples bottles.

The prepared of samples and experimental trails were done in National Leather Technology Center Khartoum, and Industrial Research and Consultancy Center, Khartoum North. Sudan, at April to September 2013.

3.3 Apparatus and chemicals

- **Glass ware**

Barkometer, berkefeled candles, beakers, conical flasks, crucibles, cylinders, and desiccators contain silica gel.

Evaporator's basins 45x105 mm - shallow flat bottomed 7.5 cm diameter; glass and porcelain, funnels, glass rods, mortar, pipettes, Procter extractor, volumetric flasks, washing bottles and incubation bottle 300 ml capacity with ground glass stopper.

- **Instruments**

- Air incubator, thermostatically controlled at $20 \pm 1^\circ\text{C}$ exclude all light to prevent photosynthetic production. Deluxe automatic biological oxygen demand incubator, Sr No 2007, India.
- Coil evaporator, Jain scientific glass wares, 2007, India.
- Chemical oxygen demand digester, Jain scientific glass wares, Sr No 2028, Ca No 1230, India.
- Experimental drum, Ronaldo, Sr No213AS36, 2013, India.
- Grinding Apex construction LTD - Type 116 A. Sr no 15412.
- Hot plate double, Jain scientific glass wares – Sr no 2012- Cat No1197\4, rang 0- 250 °C.
- Heating mantle, Jain scientific glass wares – India- Sr no 2006, Cat No 1196\5, and Rang 0- 100 °C.
- Misuratore di spessori IG\ MS, Torino, Italy – Sr no 13814-prod year 2003.
- Muffle furnace - Gallenkamp registered trade mark – England Amps 8AC \APP Sr No C4192.
- Laboratory Electric Oven – India, 0-500 °C.

- pH 211 Microprocessor pH meter - Hanna Instruments Inc, Sr 08114138 –Romania - Rang 0.00 -14.00.
- Sensitive balance. Ohaus corp ,item No AR3130, max cap 310g, Readability 0.001g China.
- Shaker -V. D. R. L Shaber- Jain Scientific glass wares – India, Sr. No 2010 – Cat No 01229.
- Shrinkage temperature tester, Angelique International limited, India, New Delhi, prod year 2007, Sr. No 1340.1.2.
- Spray Drier machine - Anhydro, Denmark - Qubanhajen; Prod year 1970, Type S LP W-0, 7019.
- Lovibond Tintometer (B.D.H pattern), Tintometer Sali Spuey Limited, England, Rang 0.1-90.
- Thermo Electron, (Karisruhe) GmbH. Type (387.0100). Sr No (387200612206), made in EEC.
- Water bath - Jain scientific glass wars – India – Sr. No 2010 \ Cat
- Chemicals
- Ammonium chloride, 99.5%, AnalaR. BDH Laboratory supplies,
- Calcium chloride, 99.5%. AnalaR. BDH Laboratory supplies,
- Chrome alum, 98%. AnalaR BDH Laboratory supplies,
- Chromium tri-sulphate, commercial. Zschimmer & Schwars .33% basicity,
- Copper acetate, 99.5% AnalaR. BDH Laboratory supplies,
- Dichloromethane, 84.5%, Labchemie. India
- Di-potassium mono hydrate ortho phosphate, 98%, GPR. Hopkin and Williams,
- Disodium mono hydrate ortho phosphate,99.5%, AnalaR BDH laboratory supplies,
- Ferric chloride, 99%. AnalaR BDH Laboratory supplies,

- Ferrous sulphate 99%. AnalaR BDH Laboratory formic acid. 5%, commercial Zschimmer & Schwars,
- Glycerin , 95%, commercial, Sudan,
- Hide powder, AnalaR BDH Laboratory supplies,
- Hydrochloric,36.46%, Blux laboratories,
- Kaolin, commercial, Sudan,
- Magnesium sulfate, 96.0%, Hopkin & William LTD,
- Mercuric sulphate, 99-100%, LOBA chemie,
- Methyl orange, AnalaR BDH Laboratory supplies,
- Nitric acid, 98%. Scharlau chemie SA. Europea. Union/ CElabel,
- Orboron, commercial,
- Silver nitrate, 99%, S.D. Finc. Chem. Limted, India,
- Silver sulphate.99%, Mwt 311.8. AnalaR BDH Laboratory supplies. Pool, England,
- Sodium chloride, 99.9%. Mwt 53.44, AnalaR BDH Laboratory supplies,
- Sodium chloride, commercial, Sudan,
- Sodium di-hydrate ortho phosphate, 99.5%, AnalaR BDH laboratory supplies,
- Sodium formate 99.5%. AnalaR BDH laboratory supplies,
- Sodium sulphate, 99.5%, AnalaR BDH laboratory supplies,
- Sodium sulphate anhydrate 96%, labo chemie, Mumbai,
- Sodium thiosulphate 99.5%, Scharlau chemie SA. Europea union/ CElabel,
- Standard ferrous ammonium sulphate 99.5%,. AnalaR BDH laboratory supplies,
- Standard potassium dichromate, 99.5%, AnalaR BDH laboratory supplies,
- Starch. Scharlau chemie SA. European Union/ CElabel,

- Sulphuric acid, 95-98%, Scharlau chemie SA. European Union/ CElabel,
- Sulphuric acid. 98%, commercial, Zschimmer and Schwars and
- 10-phenanthrol monohydrate 99.5%, S.D. Finc chem. limited.

3.4 Experimental Design

The experimental design was outlined in randomized complete design with two treatments; t_1 indigenous method and t_2 standard treatments replicated three times.

3.5 physico-chemical analysis of raw materials, 'Garad', 'Neem' and 'Karkady' (IS: 5466: 2007 and AOAC: 1996)

3.5.1 Determination of moisture and volatile substance content

The moisture and volatile substance content of samples of 'Garad' were determined by oven-dry method. Two gram of sample weighed in known weight porcelain crucible and then placed in an oven at 100 ± 5 °C for 2 hours, then replaced to the desiccator for 20 minutes to cool and then weighed, the sample and crucible were reweighed continuously until a constant weight obtained, the process was repeated using others samples, the moisture content was determined according to equ (4.1), and the results in tables 4.1 and appendix.2: Table.5.

3.5.2 Determination of ash content

The dried weighed, the sample was reweighed continuously until a constant weight was obtained, and the process was repeated using others samples, the moisture content was determined according to equ (4.1) and the results in tables 4.1 and appendix.2: table.5).

sample above was heated gradually by the flame, then placed in the muffle furnace at a temperature of 450 °C for 2 hours, then cooled in desiccator for 20 minutes and weighed, the ash were reweighed continuously until a constant weight obtained, the process was repeated using others samples, the ash content was determined according to equ (4.2) and the results in tables 4.1 and appendix.2: table.5.

3.5.3 Determination of total solid content

Five gram of 'Garad' powder were dissolved in 1.0 liter distilled water at 70 °C, then stirred and left over night, 50 cm³ of the well-mixed, uniformly turbid tannin was infusion in the weighed evaporating basin to apparent dryness on a water-bath, the residues in the basin were dried in an oven at 100±5 °C for 2 hours, then cooled down in a desiccator for 20 minutes, and weighed rapidly to an accuracy of 0.2 mg, this process was repeated until a constant weight was attained, the process was repeated using others samples, the total solid content was determined according to equ (4.3) and the results in tables 4.1 and appendix.2: table.5 and 10.

3.5.4 Determination of total soluble solid or total dissolved solid

Five hundred cm³ of previous liquor were filtered using Berkefeld candle, then to the filtrate 2.0g of kaolin were added and mixed, and allowed to stand for 5 minutes, then filtered using Whatman filter paper No 41.

Fifty cm³ of filtrate were infused in the weighed evaporating basin to dryness on a water- bath, and then the residue was dried in an oven at 100±5 °C for 2 hours and cooled in a desiccator for 20 minutes and weighed. The process was continued until a constant weight was obtained; the process was repeated using others samples then total soluble solid content was determined according to eques (4.4 and 4.5) and the results in table 4.1 and appendix.2: tables (5, 7 and 9).

3.5.5 Determination of non tannin content

3.5.5.1 Reagents

- Chrome alum solution crystalline and correspond in composition to the formula $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, prepared at lab temperature by dissolved 30g Alum in 1 liter.

3.5.5.2 Procedure

In beaker 7.35 g of hide-powder containing 6.25 g of dry matter were digested with 73.5 cm³ distilled water for 1 hour, then 6.25 cm³ of the stock chrome-alum solution were added and stirred frequently for 2 hours, the mixture was allowed to stand overnight

In the second day the chromed powder was transferred to a clean cotton filter cloth, drained and squeezed, the cloth containing the powder was placed into Tared vessel, then the cloth bag fashion was opened out, 95 cm³ of distilled water were poured on to the powder, the powder and water were mixed thoroughly and digested for 15 minutes, after which the cloth and powder were left out for drainage and squeezed to approximately 75% moisture, the powder was digested three times more in the same manner, using distilled water throughout, at the end of final digestion, the powder was squeezed, then transferred to a third vessel and carefully distilled water was added to give the proper moisture content as determined by weight.

Thoroughly the cake of wet chrome powder was broken up and mixed until became uniform, then transferred to a shaker bottle, 100 cm³ of the sample were added to the cake, and the bottles were tightly locked, the sample was shaken immediately for 10 minutes in a mechanical rotary shaker at 60 rpm. The powder and solution were filtered using a cleaned, dried cotton cloth supported by a funnel, then 1.0 g of kaolin was added to the filtrate and mixed thoroughly, the resulted mixture was poured into a single pleated filter-paper 15 cm, the filtration was repeated until it was cleared, 50 cm³ of the filtrate were added into weighed Tared dish and evaporated to apparent dryness on the water-bath, then dried in an oven at 105 °C for 2 hours, and cooled in desiccator for 20 minutes, the weight was taken to 0.2 mg accurately, the process was repeated using others samples then the nontannin content was determined according to equ (4.6) and the results in table.4.1 and appendix.2: table (4 and 5).

3.5.6 Determination of tannin content

3.5.6.1 Reagent

Copper acetate, prepared at lab temperature by dissolved 50g Alum in 1 liter distilled water.

3.5.6.2 Procedure

Two gram of 'Garad' powder were dissolved in 100 cm³ distilled water at 70 °C, the solution was treated with copper acetate then mixed and left for 10 minutes the solution was filtered, the residues were heated gradually at the flame, then moved to muffle furnace at 450 °C for one hour, then cooled and two drops of concentrated nitric acid were added and removed to the muffle furnace again for one hour, then cooled in a desiccator for 20 minutes and weighed, the process was repeated using others samples then the tannin content was determined according to equ (4.7) and the results in table.4.1 and appendix.2: table (4 and5).

3.5.7 Determination of iron content

One gram of sample 'Garad' was heated gradually on the flame, then ached at 500 °C in muffle furnace, and then cooled, 5.0 cm³ of hydrochloric acid were added and 50 cm³ of distilled water, then the mixture was heated on water-bath for 15 minutes, and filtered, washed and completed to 100 cm³ with water. The Iron was determined using Atomic absorption spectrophotometer, the process was repeated using others samples, and the results in tables (4.1).

3.5.8 Determination the pH of tanning extracts and liquors

Five gram of 'Garad' powder was dissolved with quantity of boiling distilled water; the solution was adjusted to specific gravity of 1.05 at 20 °C with cold water, the pH was determined by the glass electrode using pH meter, the process was repeated using others samples, and the results in table.4.1 and appendix.2: table (4).

3.5.9 Measurement the colour of tanning liquor

Five gram of 'Garad' powders were dissolved in a quantity of boiling distilled water; completed with cold water to 1 liter, and left overnight, the solution was filtrated using Whatman filter paper No 41. The measurement was carried out employed the Lovibond Tintometer (B.D.H

pattern) using a 1 cm. cell, the process was repeated using others samples, and the results in table.4.1 and appendix.2: table (4).

3.5.10 Determination the oxalate content of 'Karkady'

3.5.10.1 Reagents

- Hydrochloric acid
- Ammonium hydroxide
- Methyl orange
- Calcium chloride prepared by dissolved 36.4g of salt in 1 liter of distilled water.

3.5.10.2 Procedure

Oxalate content of samples was determined using the method of Dye (1956) as modified by Oke (1966). A blend of each ground plant sample (1.0 g), 190 ml of distilled water and 10 ml of 6 M hydrochloric acid in 250 ml volumetric flask was digested in a water bath at 90 °C for 4 hours, and then centrifuged at 2000 rpm for 5 min. The supernatant was diluted to 250 ml with distilled water; and then titrated with concentrated ammonium hydroxide solution in drop wise manner, using methyl orange as an indicator which changed from pink coloration to faint yellow at the end point of titration. The resulting solution was heated at 90°C for about 20 minutes on a water bath and 10 ml of calcium chloride solution was added to precipitate oxalate as calcium oxalate. The resulting solution was allowed to stand overnight, centrifuged and the residue dried at 60°C for 48 hours.

The dry precipitate was weighed and triplicate weights expressed as percentage oxalate content. Each determination was done in triplicates and the mean values taken, and then the oxalic content was determined according to equ (4.8) and the results in table (4.1).

3.6 Blending trails of indigenous 'Garad- Neem' tannins

Eleven bottles containing 100, 95, 90, 85 ...and 50g of 'Garad' powder respectively were labeled, then 0, 5, 10....50 g of 'Neem' bark was added to each bottles in the respective order, the bottles content was dissolved in 1000 cm³ distilled water at 60°C. Then stirred gently and left overnight, and then filtered using linen cloths and the tannin content was measured. The process was repeated using others samples, the tannin content was determined according to equ (4.7) and the results are shown in appendix.2: table.2.

3.7 Controlling the viscosity of indigenous 'Garad' liquors and mould growth trails

3.7.1 Controlling the viscosity of indigenous 'Garad' liquors

Eleven bottles containing 100, 99.5, 99, 98.5, 98, 97.5, 97, 96.5, 96, 95.5 and 95 g of blended 'Garad- Neem' powder in the respective order were dissolved in 1 liter distilled water at 60°C were labeled, The one market zero was kept as a control and in the remainder various quantities of dried powder of the 'Neem' leaves 0, 0.5, 1.0, ..., 5 g. was added to each bottles in the respective order. After that 5% of 'Karkady' was added to each bottle and heated to 60°C. The bottles content were stirred gently and left overnight, then filtered using linen cloths and the viscosity was measured using viscometer and the results are shown in appendix.2: table.2.

3.7.2 Controlling growth of mould trails on indigenous 'Garad' tannins

The previous filtered solutions were returned back to his bottles and left one month with daily check up. The liquors were analyzed for mould growth, loss of tannin and nontannin, darkness in colour and pH. The results are in appendix.2: table.3.

3.8 Leaching and powdering of indigenous and blended tanning liquor

A series of five vessels were used for the purpose of leaching. Vessels **1** to **4** contain 500 g of mixture **1** which prepared as the flowing: Firstly 800 g of 'Garad' powder blended with 200 g of 'Neem' bark, secondly 950 g of blending 'Garad-Neem' were mixed with 50 g of 'Neem' leaves

powder, then at last 950 g of previous mixture blended with 50 g of 'Karkady' powders. Vessel **5** was left empty. The whole process is summarized as follows:

- i. The first step of the leaching process was done by adding 1.5 liters of distilled water at 60 °C to vessel **1**, stirred gently for 20 minutes and left for overnight. In the second step, the liquor was decanted into vessel **5**. The first step was repeated for the residue of vessel **1** and the liquor was decanted into vessel **2**. Finally the liquor of vessel **2** was transferred to vessel five. Again the residue of vessel **1** was treated as in the first step and the liquor was transferred to vessel **2** which in turn transferred to vessel **3** and finally to vessel **5**.
- ii. Exactly similar steps were repeated as previously but the liquor from vessel **3** was transferred to vessel **4** and finally to **5**.
- iii. After the end of the whole process in (1) additional vessel which was labeled **6** was introduced. Typical procedure as in (1) was carried out again but this time vessel 1 was excluded and the process starts from vessel **2** to **6**.
- iv. Typical method as in (ii) was followed by introducing vessel **7** and excluding vessel **2**. This process was repeated for the rest of the vessels by introducing a new vessel each time and excluding the first vessel of each step.
- v. The liquor was filtered using cloth filter and their volume, temperature and Barkometer were measured, and the liquors were analyzed for their tannin and non-tannin.
- vi. The liquor obtained previously was mixed, the concentration of liquor was adjusted using distilled water to 25 °Bk, and the solution was filtered for three times until it became clear.
- vii. The liquor was powdered using the spray drier instruments at 170 °C inlet and 100 °C outlet temperatures, at constant pressure of 1.0 Kg/cm³.

viii. The procedure was repeated using the other mixture which prepared as the following: Firstly 800 g of 'Garad' powder blended with 200 g of 'Neem' bark, secondly 950 g of previous blended 'Garad-Neem' were mixed with 50 g of 'Neem' leaves powder, then 950 g of last mixture blended with 50 g of 'Karkady' bark, the powders were collected then analyzed for moisture, ash, total solid, total soluble solid, tannin, and nontannin contains, pH and colour and the results in appendix.2: table.5.

3.9 Tanning trails using indigenous and both improved tannins and semi chrome

3.9.1 Pretannage

Thirty two pieces of wet salted goat pelts were weighed, 32 kg, and soaked in experimental drum for 30 minutes with 32 litres of water. The pelts were re-soaked in a pit using 48 litres of water and then left overnight. In the second day the pelts were placed back into the drum and washed for 10 minutes. The hairs were removed by painting unhearing method using a mixture of 640 g of sodium sulphide and 320 g of lime in paste formed of 12.6 pH and 20 °Be. The pelts were covered with polyethylene and left for 30 hours then scudded manually using scudding knives and washed in drum for 15 minutes. Then transfer to the drum for reliming with 640 g of fresh lime and 32 liters of water and for one hour after that washed. Then pelts were replaced into the drum and washed again followed by delimed with 480 g of sodium formate and 32 liters of water for one hour followed by drain and washed for 10 minutes. The pH of pelts was adjusted to a pH 8.0 followed by bated at 37 °C for 30 minutes in a drum with 160 g of orboron and 32 liters of water then drained and after that washed for 5 minutes. Three thousand and two hundred grams of sodium chloride were dissolved in 32 liter of water and then the pelts were run for 30 minutes followed by addition of 320 g of formic acid diluted (1:10) added to the pelts in the experimental drum and run for 40 minutes. The pH was adjusted to 2.5 using formic acid. The pelts remove

and covered by polyethylene and horsed up. Thickness of the pelts was adjusted using shaving machine to 0.8 mm.

3.9.2 Tannage

3.9.2.1 Full vegetable tannage

Two pieces; weighing 2.0 kg as dry weight; of delimiting pelt were transferred into the experimental drum. Two liters of water and 20g of sodium bicarbonate were added and the pH of pelts adjusted to 5.5. The soaking solution was reduced to 0.8 litres. The pelts were treated with 40 g of sulphonated oil and 125 g of blended; 'garad - neem'; spray- dried powder for 50 minutes. Then the concentration of the bath was raised by adding 125 g of 'garad - neem' spray- dried powder and drumming for 50 minutes. Further 150 g of 'garad - neem' powder were added again into the bath and drummed for 40 minutes. The penetration of the tanning materials into the leather was checked by cross section on the leather. Additional 60 g of oil was added and drummed for 50 minutes. Thirty grams of formic acid were added and drummed for 15 minutes then washed and horsed up and covered with polyethylene left over night and toggled. The method was repeated seven times using two pelts; weigh ~2 kg for one bath and 400 g 240, 260, 280...480 blended; 'garad - neem' respectively and the produced leathers were stored to mechanical and physic-chemical tests.

3.9.2.2 Semi chrome tannage

Two pieces weighing ~2.0 kg as dry weight of delimiting pelt were transferred into the experimental drum. One liters of pickle water and 40 g of basic chrome sulphate were added and drummed for 40 minutes. The content was left to stand for 4 hours during which the content was rotated for 5 minutes each hour. Twenty gram of sodium format was added and drummed further for 10 minutes, drained, and washed. Forty gram of solphonated oil and 70 g of 'garad - neem' spray- dried powder and drumming and drumming for 30 minutes. Then the concentration of the bath was raised by adding 70 g of 'garad - neem' spray- dried powder and drumming for 30

minutes. Further 60 g of 'garad-neem' powder were added and drummed for 30 minutes. The penetration of the tanning materials into the leather was checked by cross section on the leather. Additional 60 g of oil was added and drummed for 50 minutes. Thirty grams of formic acid were added and drummed for 15 minutes then washed and horsed up and covered with polyethylene left over night and toggled. The method was repeated using two pelts; weigh 2 kg and 400 g of crushed 'garad' powder and the produced leathers were stored to mechanical and physic-chemical tests.

3.10 The physical and mechanical analysis of leather (IS: 3376: 2003, 4048: 2008 and 4045: 2008 and ASTM: D. 4705: 2005 and 2261: 2005) and AOAC: 1996)

For all physical tests; half of thimbles were cut along the backbone and the other half along the direction perpendicular to the backbone, all the pieces within the sampling location using sharp knife according to international accepted rule. The test samples were conditioned for 48 hours before tested in an atmosphere of 27°C and 65% humidity in desiccators contained a solution of sulphuric acid, 35.6% by weight, specific gravity 1.270 at 20°C.

3.10.1 Measurement of thickness

The thickness of the specimen form of each tensile, tear, stitch and tongue tears strengths were measured using Misuratore machine and the results in appendix.2: tables (6 and 8).

3.10.2 Measurement of tensile strength and percentage of elongation at break

Sample was attached to two hooks of the Dynamometer and the test was established with turn on the machine then the load at break and length of elongation were reading, the process was repeated using others samples, the tensile strength was determined according to equ (4.9) and the results in appendix.2: tables (6 and 8).

3.10.3 Measurement of stitch tearing strength

Sample was attached to two hooks of the Dynamometer and the test was established with turn on the machine then the load at break was reading, the process was repeated using others samples,

the stitch tearing strength was determined according to equ (4.11) and the results in appendix.2: tables (6 and 8).

3.10.4 Measurement of tearing strength

Sample was attached to two hooks of the Dynamometer and the test was established with turn on the machine then the load at break was reading, the process was repeated using other samples, the tearing strength was determined according to equ (4.10) and the results in appendix.2: tables (6 and 8).

3.10.5 Measurement of tongue tear strength

Sample was attached to two hooks of the Dynamometer and the test was established with turn on the machine then the load at break was reading, the process was repeated using other samples, and the results in appendix.2: tables (6 and 8).

3.10.6 Measurement of distension and strength of grain

Sample was attached to Lastometer and the distention and strength of grain by Ball Burst was measured at crack and at break, the process was repeated using others samples the distention and strength tearing strength was determined according to equ (4.12, 4.13 and 4.14) and the results in appendix.2: tables (6 and 8).

3.10.7 Measurement of shrinkage temperature

3.10.7.1 Reagents

- Glycerin solution prepared at lab temperature by dissolve 50 g of it in 1 liter distilled water.
- Sodium chloride solution prepared at lab temperature by dissolved 50 g salt in 1 liter distilled water.

3.10.7.2 Procedure

Rectangular specimens 50×12 mm were cut and punched a 3 mm hole, 5 mm from each short side on a line parallel to and equidistant from the long sides.

Sample was attached to two hooks, and 350 ± 10 ml of sodium chloride solution was added into the beaker, then heated the solution with stirring at a rate of 2°C/ minute, and then the pointer was observed and the temperature at which the specimen had shrunk to such an extent so to

moved the pointer half a division from the position corresponding to the maximum length of the specimen was taken as the shrinkage temperature.

The procedure was repeated using glycerin solution in place of sodium chloride to determine the shrinkage temperature of semi chroming samples.

The method was repeated for other samples, and then the shrinkage temperature was determined and the results in appendix.2: tables (6 and 8).

3.11 Physico-chemical analysis of indigenous and improved tanned leather

3.11.1 Determination of moisture content of indigenous and improved tanned leather

Ten gram of prepared and grinding skin sample according to SLTC methods was weighed in a previously weighed porcelain crucible and then placed into an oven at $100 \pm 5^\circ\text{C}$ for 2 hours, the hot crucible with the sample was then cooled in the desiccator and weighed, and these steps were repeated twice.

The method was repeated for other samples, and then the moisture content was determined according to equation (4.1) and the results in appendix.2: tables (7 and 9).

3.11.2 Determination of ash content of indigenous and improved tanned leather

The dried samples above were ash similar to method 3.5.4 then the ash content was determined according to equation (4.2) and the results in appendix.2: tables (7 and 9).

3.11.3 Determination of pH of water extract of indigenous and improved tanned leather

3.11.3.1 Reagent

- Buffer solutions 4 and 10.
- Sodium chloride solution prepared at lab temperature by dissolved 0.4 g salt in 1 liter distilled water.

3.11.3.2 Procedure

Ten gram of prepared and grinding skin sample was transferred in a 500 cm³ stopper bottle with 100 cm³. 0.01 M sodium chloride solution and shaken mechanically for 2 hours using mechanical shaker 60 rpm, then diluted with 200 cm³ and allowed to stand in a closed flask for 20 minutes.

The pH of the decanted liquor was determined using the pH meter standardized on buffer solution (4 and 10).

The method was repeated for other samples, and the results are in appendix.2: tables (7 and 9).

3.9.4 Determination of grease and fat content of indigenous and improved tanned leather

Ten gram of prepared and grinding skin sample was transferred to Soxhlet extractor fitted with standard paper thimble, then extracted with dichloromethane for 2 hours at 24°C.

Receiving flask was weighed before extraction after dried in an oven and cooled in a desiccator, and after end of extracted the solvent was removal, the receiving flask was reweighed after drying and cooling in a desiccator.

The method was repeated for other samples, and then the fat content was determined according to equation (4.15) and the results in appendix.2: tables (7 and 9).

3.11.5 Determination of total soluble matter of indigenous and improved tanned leather

Thirty gram of prepared and grinding skin sample was transferred into stopper bottle with large neck and 2.0 liters of distilled water were added, and shacked mechanically using shaker machine at 55 rpm for two hours, the solution and sample was poured into glass cylinder, the Berkefeled candles 130 mm long and 28 mm diameter was used, filtration was continued until 250 cm³ was collected in the filter flask; this quantity was rejected, then filtration was continued until a filtrate perfectly cleared and collected 1750 cm³ of liquor, then 250 cm³ was treated with 1.0 g of kaolin, stirred 5 minutes then allowed for 10 minutes and filtered, 50 cm³ of filtrate was placed in weighed Tared basin for evaporation to apparent dryness on a water-bath, the residues were dried in an oven at 105°C for 2 hours, and cooled in a desiccator for 20 minutes and weighed, the process was continued until a constant weight obtained.

The method was repeated for other samples and then the total soluble content was determined according to equation (4.4) and the results in appendix.2: tables (7 and 9).

3.11.6 Determination of hide substances of indigenous and improved tanned leather

3.11.6.1 Reagent

- Standard sodium hydroxide solution 0.05 M was prepared at lab temperature by diluted the ampoule content in 500 Cm³ of distilled water.
- Standard sulphuric acid 0.05 M was prepared at lab temperature by diluted the ampoule content in 500 Cm³ of distilled water.
- Mixture of 1:1 potassium sulphate to copper sulphate

3.11.6.2 Procedure

After determination of total matter soluble in water, the leather sample was completely dried, and 0.6 g were taken and placed into a dry 250 ml Kjeldahl flask with 15 to 20 ml of concentrated sulphuric acid, as well as some glass beads. The flask was heated gently in the inclined position. The flask was equipped with a small funnel to prevent loss of acid during hide destruction. 10 g of the mixture was added to the flask, and heated up to boiling until the solution became clear and the colour stopped changing. This procedure took about 30 minutes. After cooling, the solution was quantitatively transferred into ammonia distillatory. Through a dropping funnel, sodium hydroxide solution (0.05 M) was added until the solution colour became black. During the distillation, the quantity of ammonia was reduced to one third. The ammonia was distilled into 100 ml of Boric acid (0.05 M) in the presence of methyl orange as indicator. Usually, after obtaining about 150 ml distillate it can be considered that all ammonia has been distilled and this procedure takes about 40 minutes. The excess acid was back titrated with 0.05 M sodium hydroxide.

The method was repeated for other samples and then the degree of tannage was determined according to equation (4.16) and the results in appendix.2: tables (7 and 9).

3.11.7 Determination of degree of tannage of indigenous and improved tanned leather

Degree of tannage was calculated as difference between 100% and summation of moisture, ash and total soluble percentage.

The calculation was repeated for other samples and then the degree of tannage was determined according to equation (4.17) and the results in appendix.2: tables (7 and 9).

3.11.8 Determination of chrome content of indigenous and improved tanned leather

3.11.8.1 Reagents

- Standard sodium thiosulphate solution (0.1N) prepared at lab temperature by diluted ampoule content in 500 cm³ distilled water.
- Potassium iodide solution prepared at lab temperature by dissolved 100 g of salt in 1 litre distilled water.

3.11.8.2 Procedure

Two gram of prepared and grinding skin sample was transferred in to 250 ml conical flask then 10 ml of concentration nitric acid were added and take it for 10 minutes.

A mixture of 5 ml of sulphuric acid and 10 ml of peroxychloric acid was added to the flask, placed a small funnel in the neck of the flask heated to boiling on a flame until the colour was changed to orange, cooled for a short time in the air and then rapidly in the cool water, dilute the contents to approximately 200 ml. then boiled for 10 minutes.

Fifteen ml of orthophosphoric acid and 20 ml of potassium iodide solution were added and the flask was stoppered, and leaved to stand for 10 minutes in the dark. Then titrated with 0.1 N sodium thiosulphate solution until the solution in the flask is light green, 5 ml of starch was added as indicator and the end point is the blue. The results were determined according to equation (4.18) and the results are in appendix.2: table.8.

3.12 Physico-chemical analysis of indigenous and improved tannage wastewater

3.12.1 Determination of biological oxygen demand

3.12.1.1 Reagents

The reagents necessary for this test are:

- Phosphate buffer solution: was prepared by dissolving 8.59 g of KH_2PO_4 , 21.75 g of K_2HPO_4 , 33.4 g of $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ and 1.7 g NH_4Cl in distilled water and made up to 1 litre.
- Magnesium sulphate solution: was prepared by dissolving 22.5 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water and made up to 1 litre.
- Calcium chloride solution: was prepared by dissolving 27.5 g CaCl_2 in distilled water and made up to 1 litre.
- Ferric chloride solution: was prepared by dissolving 0.25 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in distilled water and made up to 1 litre.
- Sodium hydroxide 1 N.
- Sulphuric acid 1 N.
- Manganese sulphate solution: was prepared by dissolving 48g MnSO_4 , in distilled water filtered and made up to 1 liter.
- Iodide – azide reagent: was prepared by dissolving 500 g of NaOH and 135 g NaI in distilled water and made up to 1 liter and 10 g sodium azide NaN_3 in 40 ml distilled water were added.
- Sulphuric Acid, Conc. 36%
- Starch indicator solution: was prepared by dissolving 5 g of starch and 0.01 g of mercuric iodide in 30 ml of cold distilled water, the solution was then made up to 1 liter using boiling distilled water.
- Standard sodium thiosulphate solution: was prepared by dissolving 6.205 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in distilled water and made up to 1 liter, then it was standardized against potassium dichromate.

3.12.1.1 Test procedure

In one litre volumetric flask 2ml of each of the following solutions phosphate buffer, magnesium sulphate, calcium chloride, ferric chloride were poured and then 5ml of the sample was added and made up the mixture to 1 liter with oxygenated water. Then the pH of the mixture was adjusted to 7.0 using 1N either sodium hydroxide or sulphuric acid, and then two samples from the mixture above were taken in biological oxygen demand bottles, one of them was tested immediately to determine the dissolved oxygen and the other sample was kept in incubator for 5 days at $20 \pm 1^\circ\text{C}$.

The dissolved oxygen was determined by adding 2 ml of manganese sulphate and 2 ml of iodide-azide reagent into first sample, then the bottle was stopper and shaken tightly to ensure proper mixing, then the mixture was allowed to settle and 2 ml of sulphuric acid was added and then the shaking was continued gently until solution was homogenous. And then 200 ml of sample was titrated with standard sodium thiosulphate solution until pale yellow colour was seen, then 1-2ml of starch solution was added (which turned the mixture colour to blue) and the titration was continued until the first disappearance of the blue colour, which was end point (DO1).

After 5 days the dissolved oxygen steps were repeated and the (DO2) were determined. The biological oxygen demand was determined according equation (4.19) and the results are in appendix.2: table (10).

3.12.2 Determination of chemical oxygen demand

3.12.2.1 Reagents

- Standard potassium dichromate 0.25N ($\text{K}_2\text{Cr}_2\text{O}_7$) solution: was prepared by dissolving 12.259g in distilled water and made up to 1 litre.
- Sulphuric Acid, H_2SO_4 , reagent: 1 Kg of Sulphuric acid 36% containing 22 g Silver sulphate.

- Standard ferrous ammonium sulphate (FAS) $\text{Fe}(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ solution: was prepared by dissolving 39 g in distilled water before adding 20 ml of concentrated Sulphuric acid then cooled and made up to 1 litre.
- Ferron indicator solution: was prepared by dissolving 1.485 g of 10-phenanthroline monohydrate together with 0.695 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water and made up to 100 ml.
- Mercuric sulphate (Annular) HgSO_4 powder.

3.12.2.2 Procedure

In an air refluxing tube contained pumice stone 48 ml of distilled water was added to 2 ml of sample and then was shaken well. 1g of mercuric sulphate and carefully 5 ml of sulphuric acid reagent were added and then was stirred to ensure homogeneity, then 25 ml of potassium dichromate was added and stirring was continued then the refluxing tube was attached to the condenser and 70 ml of sulphuric acid was added to the mixture and stirring was continued to avoid explosion.

Gradually heated the refluxing tube on chemical oxygen demand digester till the mixture was brought to the boiling point, and then closed the condenser and reflux for 2 hours at the boil. The tube was removed from the digester and was lifted to cool down, then the mixture was transferred into the 500 ml of volumetric flask and completed to the mark using distilled water. The excess of dichromate was determined using back titration with volume B ml of standard FAS, using 2-3 drops ferroin indicator bluish green to reddish brown.

A blank, 50 ml of distilled water, was treated in the same manner as in the above step, and the volume A ml of FAS was determined.

The chemical oxygen demand was determined according to equation (4.16) and the results are in appendix.2: table (10).

3.13 Statistical data analysis (Gomez and Gomez, (1984)).

The data collected from experimental observation and results was analyzed using descriptive statistics such as percentages and mean. The data was subjected to analysis using the statistical package for social science (SPSS). A student t-test was used to test the level of significant for the means tannins levels and the resultant physical properties of the vegetable tanned leathers. The $p < 0.05$ value indicated a significant difference between the means. And the results are in tables (4.2, 4.3, 4.4, 4.5, 4.6, 4.7 and 4.8).

CHAPTER FOUR

RESULTS AND DISCUSSIONS

Chapter four

Results and discussions

4.1 Evaluation of physico-chemical properties of tannins raw materials

Many parameters have been considered before selecting any plant material for tanning or re-tanning purposes. These parameters include: sustained availability, nature of tannins and their molecular weight, colour, yield of leather, tannin to nontannin ratio, astringency (which control tanning power), rate of penetration and buffering capacity of the salts present, proneness to oxidation and acid/salt content. The as-mentioned parameters were studied using *Acacia nilotica*, *Azadirachta indica* and *Hibiscus sabdariffa* and the results are calculated using the flowing equations and which demonstrated in Table (4.1).

4.1.1 Calculations of physico-chemical properties

4.1.1.1 Moisture content

The percentages of moisture and volatile substances were determined by adapting methods (3.5.1 and 3.11.1) and were calculated by equation (4.1). The results are listed in Tables (4.1 and appendix.2: 5, 7 and 9) for the two portions of pods, barks, 'Garad-Neem' spray powder and leather.

$$\text{Moisture \%} = \frac{\text{Weight of sample} - \text{Weight of dried sample}}{\text{Weight of sample}} \times 100\% \quad \text{equ.4.1}$$

4.1.1.2 Ash content

The percentages of ash content were determined using method (3.5.2 and 3.11.2) and were calculated by equation (4.2). The results are listed in Tables (4.1 and appendix.2: 7 and 9) for the two portions of pods, barks, 'Garad-Neem' spray powder and vegetable and semi chrome tanned leather.

$$\text{Ash \%} = \frac{\text{Weight of ash} \times 100 \%}{\text{Weight of dried sample}} \quad \text{equ.4.2}$$

4.1.1.3 Total solids, TS, content

The percentages of total solids content (TSC) were determined according to method (3.5.3) and were calculated by equation (4.3). The results are listed in Tables (4.1) for the two portions of pods, and barks.

$$\text{TSC \%} = \frac{\text{Weight of residue} \times \text{diluted volume} \times 100\%}{\text{Weight taken} \times \text{volume taken}} \quad \text{equ.4.3}$$

4.1.1.4 Total soluble solid, TSS or Total dissolved solid, TDS content

The percentages of total soluble solid (TSS) were determined conducting to the methods (3.5.4 and 3.11.5) and were calculated by equations (4.4 and 4.5). The results are listed in Tables (4.1 and appendix.2: 5, 7 and 9) for the two portions of pods, barks and 'Garad' leaching, spray powder and leather.

$$\text{TSS\%} = \frac{\text{Weight of residue} \times \text{diluted volume} \times 100\%}{\text{Weight taken} \times \text{volume taken}} \quad \text{equ.4.4}$$

$$\text{Or TDS} = \text{Weight of residue mg} \times 1000 / \text{volume taken} \quad \text{equ.4.5}$$

4.1.1.5 Nontannin content

Nontannin percentages determine conducting the method (3.5.5) and were calculated by equation (4.6). The results are listed in Tables (4.1 and appendix.2: 2 and 7) for the raw tannins materials and spray dried powder.

$$\text{NTC \%} = \frac{\text{Weight of residue} \times \text{diluted volume} \times 100\%}{\text{Weight taken} \times \text{Volume take}} \quad \text{equ.4.6}$$

4.1.1.6 Tannin content

Tannin percentages were determined conducting the method (3.5.6) and were calculated by equation (4.7). The results are listed in Tables (4.1 and appendix.2: 2, 4 and 7) for the raw tannins materials and spray dried powder.

$$\text{TC \%} = \frac{\text{Weight of residue} \times \text{diluted volume} \times 1.35 \times 100\%}{\text{Weight taken} \times \text{volume taken}} \quad \text{equ.4.7}$$

4.1.1.7 Oxalate content

The percentages of oxalate were determined conducting the method (3.5.10) and were calculated by equation (4.8). The results are listed in Table (4.1), for the *Hibiscus sabdariffa*.

$$O C \% = \frac{\text{Weight of Precipitate} \times 100\%}{\text{Weight of sample}} \quad \text{equ.4.8}$$

4.2 Physico-chemical properties of raw materials, 'Garad', 'Neem' and 'Karkady'

Table.4. 1: Physico-chemical properties of *Acacia nilotica*, *Azadirachta indica* and *Hibiscus sabdariffa*

No	Description	<i>Acacia nilotica</i>			<i>Azadirachta indica</i>		<i>Hibiscus sabdariffa</i>	
		Husk	Powder	De-seed pods	Bark	Leaf	calyx	Bark
1	Moisture content%	3.5	5.2	7.5	6.8	7	6	5.7
2	Ash content%	1.6	1.2	1.1	2	0.9	1.1	2.3
3	Total solid content%	94.8	96.40	96.9	93.2	93	94	94.3
4	Total soluble solid content%	30.75	68.78	64.4	25.0	-	-	3.1
5	Non tannin content%	19.5	25.6	28.8	7.8	-	-	2.9
6	Tannin content%	11.7	43.58	35.6	17.0	-	0.45	0.2
7	Tannin/Nontannin ratio	0.6	1.7	1.2	2.2	-	-	0.07
8	Oxalate content %	-	-	-	-	-	0.45	0.52
9	Colour	Yellow	6.2	6.5	6.2	3.8	6 ^{ab}	8.4
		Red	2.1	2.8	2.1	2.1		0.6
		Blue	1.2	1.8	1.2	1.5		-
10	pH	4.2	4.3	4.2	6	6	2.5	6
11	Iron content ppm	0.65	0.711	0.467	0.32	-	-	0.35

Tannins liquor of *acacia nilotica* pods 'Garad' contains carbohydrates, glucose, pentose and gum.

It is more sensitive to mould and microbial enzyme action. It can undergo fermentation more in the moderated temperature and at high moisture content, more than 10%, during long storage at the summer season. The mould and microbial enzyme split up hydrolysable tannins into sugar and ellagic acid which is further split up into gallic acid and causing high tannin lose. Therefore, the moisture should be adopted through the storage and should not be raised more than the range.

Important particulars of *acacia Nilotica* pods, *azadirachta indica* 'Neem' bark, leaves and *hibiscus sabdariffa* calyx, bark were carried out and given in Table (4.1) The results showed that the values of moisture and ash contents are more acceptable and are considered within the required range of Indian standards of tannin materials, IS. No: 5127 (1969). However, increasing of the value of ash content beyond the standard requirement could indicate the co-existence of some inorganic ions such as copper and iron with vegetable tannins materials which are expected to form green-blue or blue complexes.

The tannins contents are listed on Table (4.1) which show that the inner powder of *Acacia nilotica* contain higher amount of tannins content compared to the de-seeded pods and husk. However, all materials contain more than 10% tannins and thus according to Seigler et al (1986) conception they can be used for manufacturing purposes.

The purity of tannins is usually calculated as ratio of tannin to total soluble solids or. The results show that all samples, except husk of *acacia nilotica*, were within the Seigler et al (1986) conception. The materials are considered good tannin materials if their tannins purity is greater than 0.6.

Non-tannins act as an important component in tannins liquor, they presence as large amount of small molecular weight tannins and semi-tannins. These materials impact on the fullness, flexibility and grain crack index of the leather. The non-tannin contents of raw tannins materials samples have been included in Table (4.1) These results show that the deseeds and inner powder of *Acacia nilotica* pods and *Azadirachta indica* bark contain less amount of non-tannin based on Indian standards requirements so that the materials are suitable for tanning purpose. According to Sarkar and Sorcar (2005) investigation, if the tannin/non-tannin ratio is less than one, the

material is desirable for retannage whereas if it is greater than one the material is suitable for tannage purpose.

In generally the colours of *Acacia nilotica* tannin liquors are pleasant light biscuits colours and consist of mixtures of red and yellow colours. These colours were measured and the values which indicate the colours are illustrated in Table (4.1). The registered values for de-seeded pods, husk, and *acacia nilotica* and *Azadirachta indica* were 5.3/1.5/1.4, 5.0/0.9/1.2, 4.7/1.0/1.8 and 2.3/0.6/1.5, respectively. These values were found corresponding to red, yellow and black colours. It is important to note that although the red and yellow colours are within the range of the Indian standards requirements, IS. 5127-1969, however, the presence of iron or copper could be the reason for changing these colours to darker ones. In order to avoid the irons contamination, oxalic acid or its salts can be used as masking reagent to chelate the irons from tannin liquor. Analysis showed that boss calyces and bark of the *Hibiscus sabdariffa* 'karkady' contain oxalic salts which were found sufficient to chelate the iron species from tannins liquor.

The pH values of tan liquors are listed in Table (4.1). It is very obvious that *Acacia nilotica*, de-seeds, inner powder and husk extracts showed slightly lower pH values. Whereas, bark and leaves of *Azadirachta indica* and *Hibiscus Sabdariffa* bark extracts exhibited relatively high pH values. The leather which was tanned in liquor of low pH was generally hard and firms. Whereas softer leather should be produced by sweet tan liquor which was prepared by blending of vegetable tannin materials together at pH values of 4.5-5.5.

4.3 Controlling of mould growth trail and physico-chemical properties of controlled and uncontrolled indigenous tannins liquors

4.3.1 Controlling mould fermentation trail on indigenous tannins liquor

Control mould growth trail on indigenous tannins liquor using 'Neem' leaves are shown in fig (4.1). The result showed that 5% of dried Neem leaf powder eliminates the mould grows for 30 days.

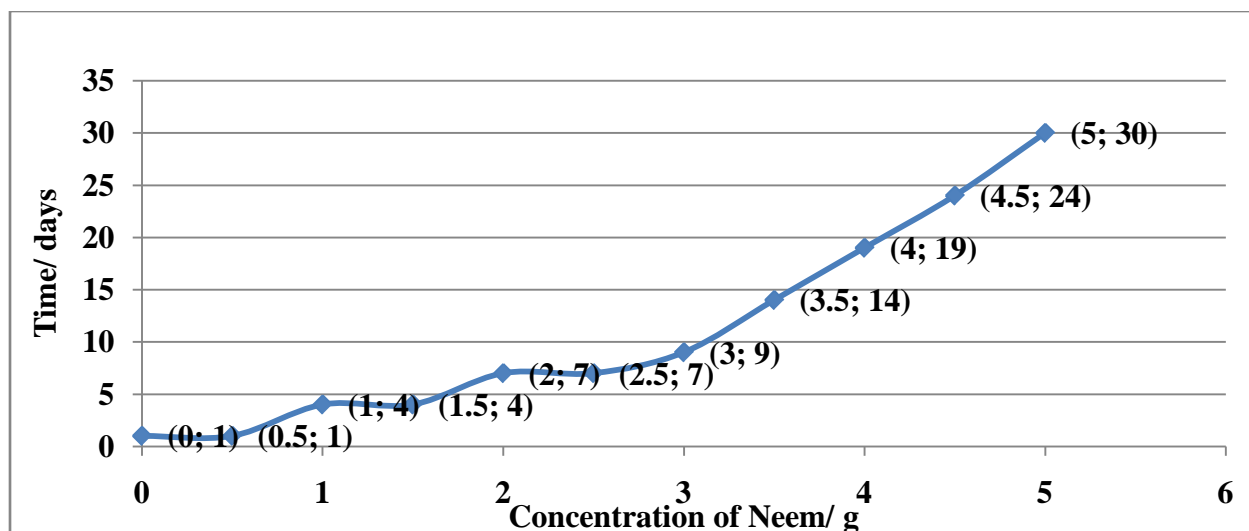


Figure.4. 1 Controlling mould growth on *Acacia nilotica* tannins liquor using Neem leaves

These results showed that fermentation of tannin liquors started on the second day in the beakers contained 0 and 0.5 g of *Azadirachta indica* leaves, whereas in the cases of others beakers no mould formation was observed up to the third day. For beakers of 1 g and 1.5 g materials, the mould commenced on the fourth day whereas for beakers of 2 and 2.5, materials, the mould formation is started on the 7th day. For beakers of 3 g, mould formation was observed on the 9th day whereas for beakers of 3.5-4 g, mould formation was observed on the 12th-19th day, whereas for the beaker of 4.5-5.0 g, there was no mould formation on the liquor even after 24th days. Therefore, addition of 5.0% of *Azadirachta indica* leaf eliminates fermentation and mould formation completely for more than 30 days. The result agreed with Debashri and Tamal (2012) conception that used dried *Azadirachta indica* leaves to control the mould growth. Their experiments, illustrated that the *Azadirachta indica* leaves contain sulphur organic compounds, which control and eliminate the fungi and moulds growth. Also *Azadirachta Indica* barks contain condensed tannins type in high sufficient amount, which has high stability to hydrolysis and micro-organism thus blended *Acacia nilotica* pods with 20% of *Azadirachta Indica* barks produce acceptable stability tannins materials, this agree with Dai and Mumper, (2010)

conception who suggested that the stability of condensed tannins due to strong covalent bonding between individual carbon atoms and absence of ester links and biological degradable material, glucose, in the tannin molecule.

4.3.2 physico-chemical properties of controlled and uncontrolled tanning liquors

4.3.2.1 Tannin content of controlled and uncontrolled indigenous tanning liquor

Tannin contents of controlled and uncontrolled indigenous tanning liquor are shown in fig (4.2).

The results showed that tannin content of controlled indigenous is highest compared to uncontrolled one.

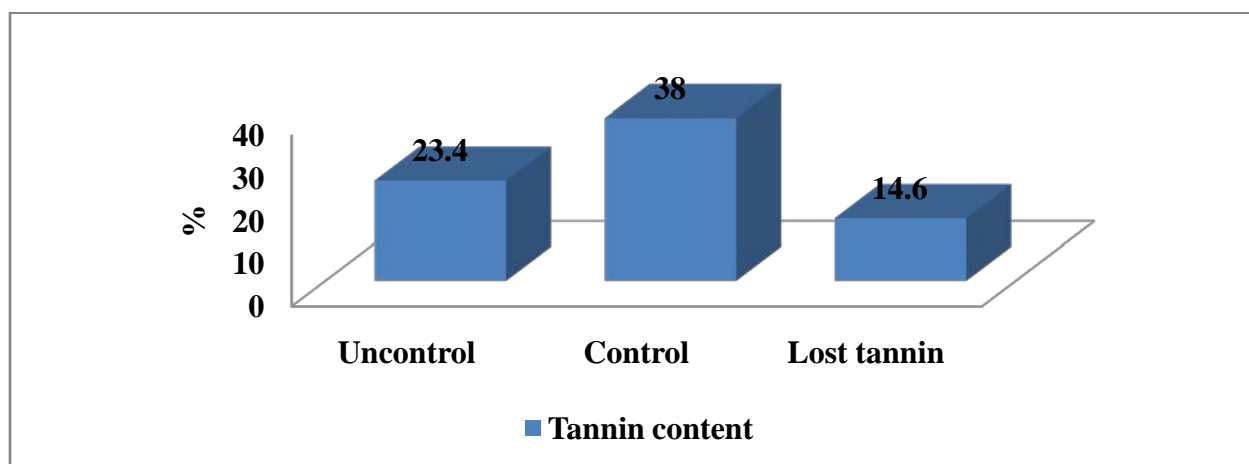


Figure.4. 2 : Tannin content of controlled and uncontrolled mould fermentation of *Acacia nilotica* tanning

These results showed that using the 5% of 'Neem' leaf powder to prevent tannin liquors decomposition through standing and leaching prevented ~15% tannin content which is equivalent to 38% of the total tannins; This finding is quite consistent with the investigation of Grover et al (2011) for dried powder of 'Neem' leaves which were found exhibit a good efficiency to control the mould growth. This fermentation is assumed to be due to the action of enzyme, which hydrolyzes the ester links of tannins releasing sugar and acids such as ellagic and chebulinic acid. Dutta revealed that antifungal processing are generally carried out by treating the concentrated liquor with sulphate, bisulphate and hydrosulphate salts followed by organic acid for specific time.

4.3.2.2 Nontannin content of controlled and uncontrolled mould fermentation on indigenous tanning materials

Nontannin content and the pH of controlled and uncontrolled indigenous tanning liquor are shown in figs (4.3 and 4.4). The results showed that nontannin content of controlled indigenous tanning liquor is lowest than of uncontrolled one whereas the pH of controlled liquor is highest compared to uncontrolled.

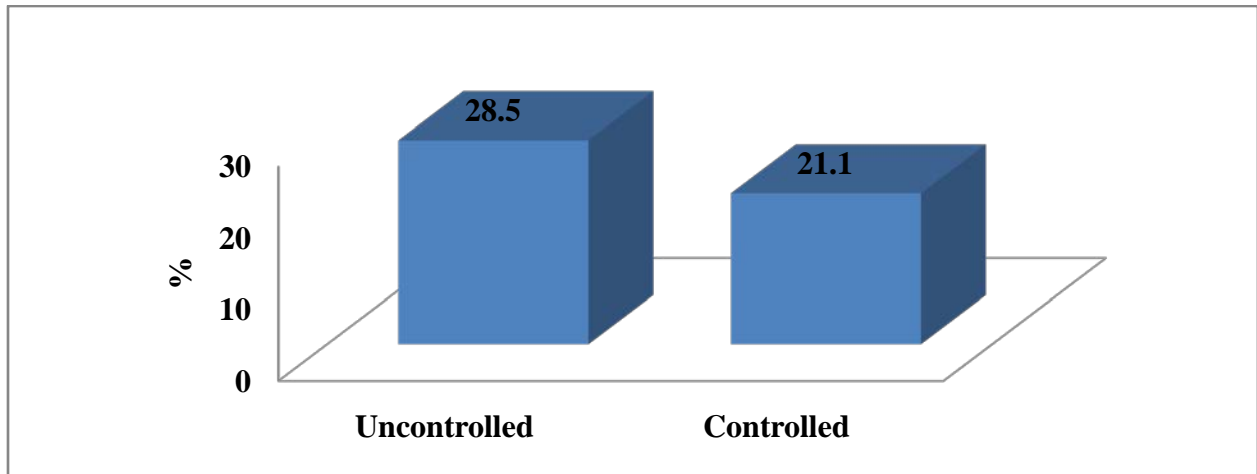


Figure.4. 3 Nontannin content of controlled and uncontrolled tanning solution

These results suggested that the fermentation is assumed to be due to the action of enzyme, which hydrolyzes the ester links of tannins releasing sugar and acids such as ellagic and chebulinic acid which raised the nontannin content and dropped the pH value.

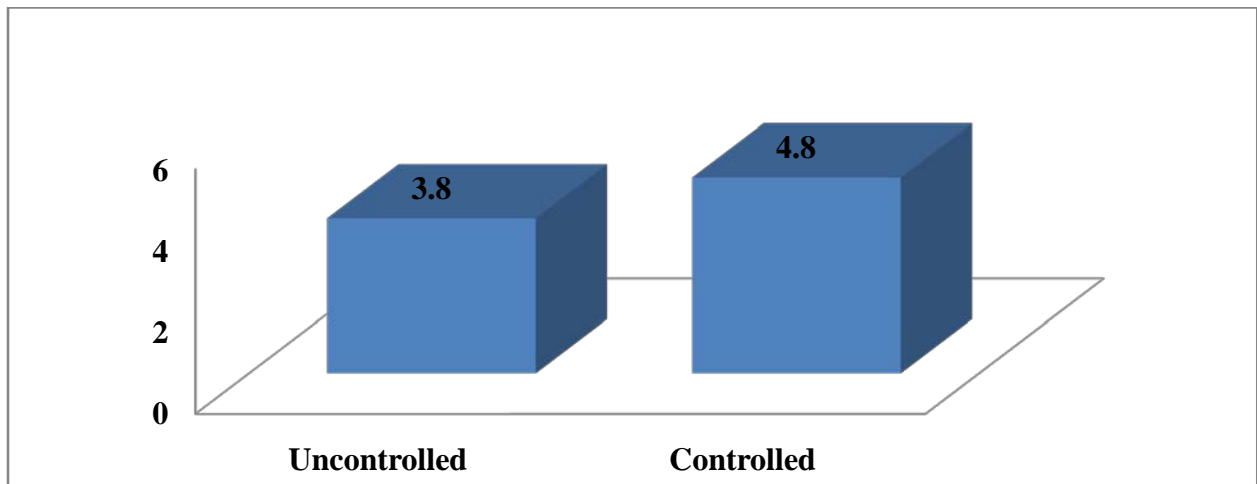


Figure.4. 4 the pH of the controlled and uncontrolled indigenous tanning liquor

Thus it is essentially prevent the indigenous tanning liquor during standing and leaching, thus blended 20% of 'Neem' condensed tannin changed indigenous 'Garad' tannins nature and increase the tanning stability to microbial attacked contributed to adding 5% of dried 'Neem' leaves powder which eliminate mould fermentation this agree to Mueller Harvey (2006) investigation who proved that *Azadirachta indica* leaves contain sulphur organic compounds and had antifungal activity.

4.3.2.3 Colour content of controlled and uncontrolled mould fermentation of indigenous tanning materials

The colour of controlled and uncontrolled indigenous tanning liquor was shown in fig (4.5). The results showed that controlled tanning liquor reflected light colour compared to uncontrolled one which reflected brown colour due to present of 0.6 blue colour.

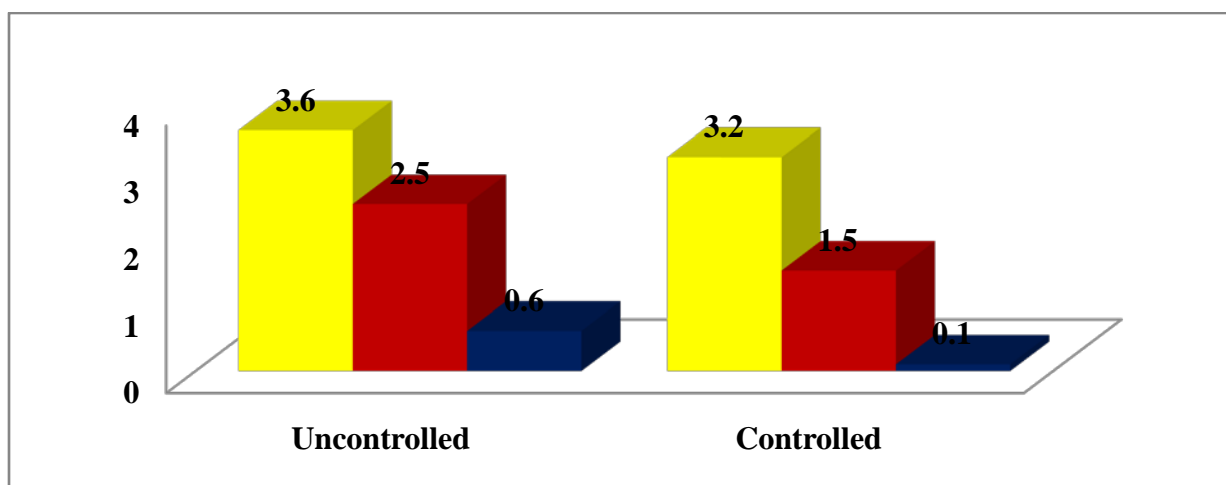


Figure.4. 5 Colour content of controlled and uncontrolled mould fermentation of indigenous tanning materials

These results suggested that blended indigenous tannins using control mixtures, bark and leaf of 'Neem', cycles or bark of *hibiscus sabdariffa* controlled the colour deterioration of tanning liquor, and enhanced the original biscuit colour, *hibiscus sabdariffa* cycles or bark contain sufficient amount of organic oxalate salt which eliminate undesirable blue or blue-green discoloration, iron-tannins complexes, this agree with Williams, (2004) who suggested that oxalic acid will

remove the blue–black discoloration. Apply a saturated solution (0.5 kg of oxalic acid per 4 L of hot water) to the stained surface

4.3.5 Statistical assessment of controlled and uncontrolled of indigenous tanning materials

Table 4.2 Paired samples of T test for mechanical and physico-chemical properties of controlled and uncontrolled tanning liquor. Statistical data of SPSS analysis shows that there are significant differences of physico-chemical properties of controlled indigenous tanning liquor comparing uncontrolled indigenous tanning liquor. Table (4.2) showed statistical analysis at $P < 0.05$ level as described by Gomez and Gomez, (1984) to evaluate the significant differences between the treatments.

Table.4. 2 Statistical assessment of indigenous, modified and myrobalan tannins analysis

No	Description	Mean	Std	Sig. 0.05
1	Tannin	29.7	7.8	0.03
2	Non tannin	17.1	4.3	0.00
3	Colour	Red	2.0	0.58
		Yellow	3.4	0.72
		Blue	0.35	0.28
4	pH at 25°C	4.5	-	0.03

4.4 Modification of indigenous 'Garad' tannins, *Acacia nilotica* pods

4.4.1 The controlling system to modify tannin nature of indigenous tanning materials

The tannins content of blended 'Garad-Neem' tanning liquors was shown in fig (4.6). The results showed that tannin content of blended tanning liquors were decreased gradually according to increase of 'Neem' bark amount which was added thus blended '80% Garad- 20% Neem' recorded acceptable tannin content which agree with the standard of myrobalan tanning material and sufficient amount of condensed tannins components.

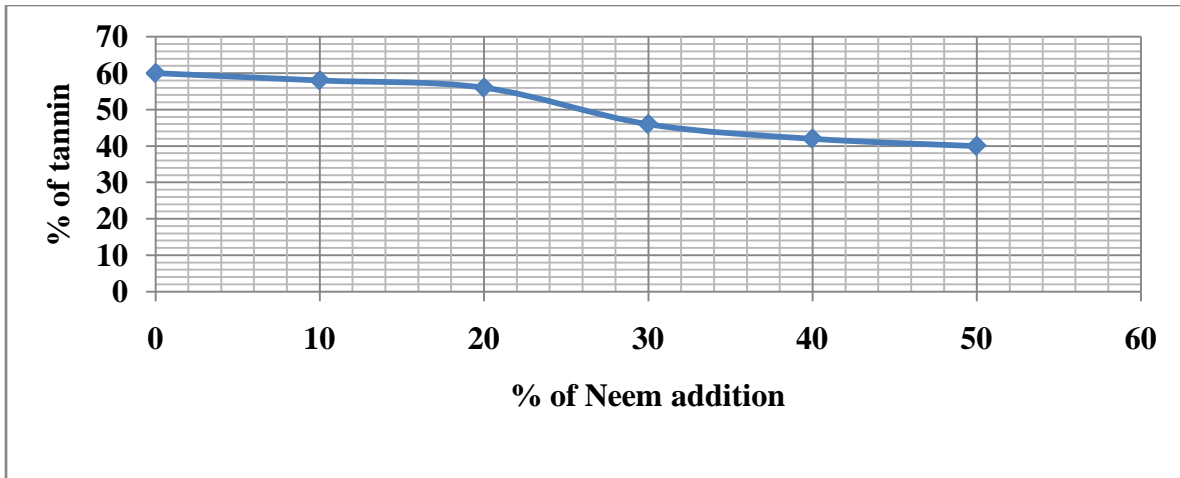


Figure.4. 6 The effectiveness of 'Neem' bark additions on the modified 'Garad-Neem' tannin content

These results assumed that blended 'Garad-Neem' although it was decreased the indigenous tannin content but also it increased the tanning potential of indigenous Garad' where the 'Neem' bark is rich in condensed tannin while 'Garad' is highly content hydrolysable tannin this agree with Schmutterer, (2005) found that condensed tannins bind and complex strongly with carbohydrates and proteins such binding is quite powerful and difficult to reverse, ended with astringency of leather and high power of tannage. Covington. (2006) investigated that condensed tannins create leather with high thermal stability and ideal shrinkage temperature (80-85°C) than hydrolysable tannins (75-80 °C) Larsen *et al*, (2009).

4.4.2 The controlling system to reduce the viscosity of indigenous tanning liquor

4.4.2.1 Viscosity controlling system

The viscosity of modified blending 'Garad-Neem' tanning liquors was shown in fig (4.7). The results showed that viscosity of indigenous tanning liquor was decreased gradually according to change of 'Neem' leaves amounts which was added, thus adding 5% of *Azadirachta indica* leaves and heating to 60°C were dropped the viscosity to minimum range.

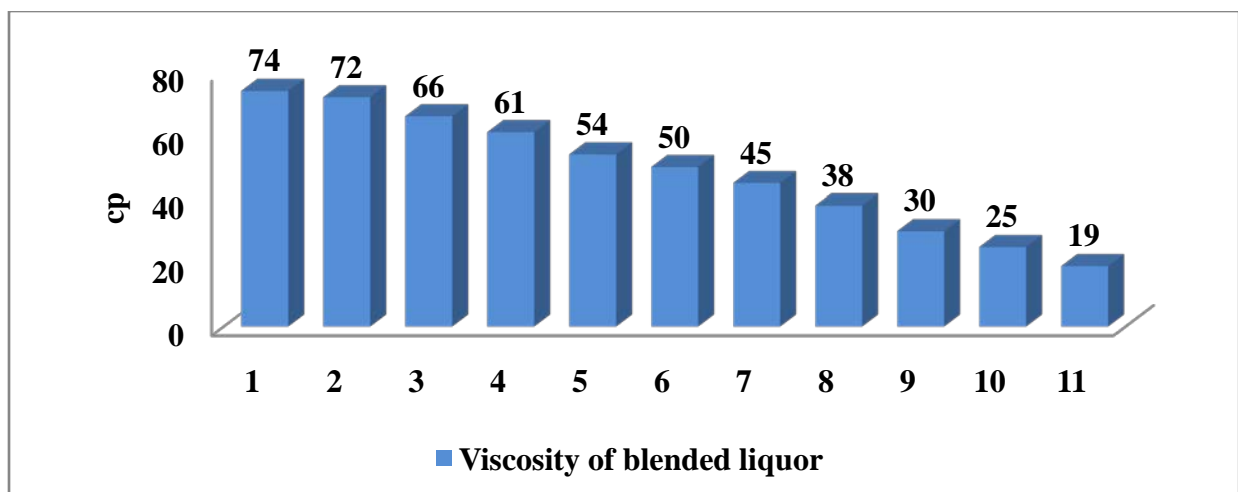


Figure.4. 7 Viscosity of modified 'Garad-Neem' tanning liquors

These results assumed that heated and sulphur organic compounds on 'Neem' leaves are used to introduce sulphonic acid groups into the tannin molecules which are expected to reduce the level of polymerization and aggregation. High molecular weights particles are converted into low molecular weight particles containing soluble sulphonic acid groups, this agree with Dutta, (2002) who revealed that bleaching and antifungal processing are generally carried out by treating the concentrated tanning liquor with sulphur compounds, bisulphate sulphate and hydrosulphate, followed by oxalic acid. Thus applied experimental of Dutta to reduce the indigenous 'Garad' viscosity using two mixtures of either 1:1 dried powder of 'Neem' leaves and *hibiscus sabdariffa* cycles or 1:1 bark at 60°C showed reduced of the tendency of tannin particles to form hydrogen bonds within each other forming aggregates at high tannin concentration and low pH.

4.4.2.2 Statistical assessment of modified tanning viscosity

Table 4.3: Paired samples of T test for viscosity of indigenous tanning liquor. Statistical data of SPSS analysis shows that there are significant differences of viscosity of indigenous tannins according to addition amount of control blended. Table (4.3) showed statistical analysis at $P <$

0.05 level as described by Gomez and Gomez (1984) to evaluate the significant differences between the treatments.

Table 4. 3: Statistical assessment of modified tannins viscosity

No	Description	In group		
		Mean	Std	Sig. 0.05
1	Blended 1	49.2	19.63	0.00
2	Blended 2	44.7	19.79	0.00
-	within groups	45.1	20.54	0.60

4.5 Physio-chemical properties of indigenous and modified tanning materials

The tanning materials were extracted and powdered using the method in section 3.7. The spray dried powders were analyzed according to American Society Official Methods and the results are illustrated in appendix.2: Table (5).

4.5.1 Moisture and total solid content of indigenous, both modified and myrobalan tanning materials

Moisture and total solid contents which represented as the summation of tanning waste materials and total soluble solid of indigenous and both modified tanning materials are shown in fig (4.8). The results showed that moisture content and total solid of indigenous and both modified types agree with the standard of myrobalan tanning materials and fell in the recommended range (6%, 94%) respectively. Thus results suggest that moisture and total solid contents seemed to be less important than other physio-chemical properties.

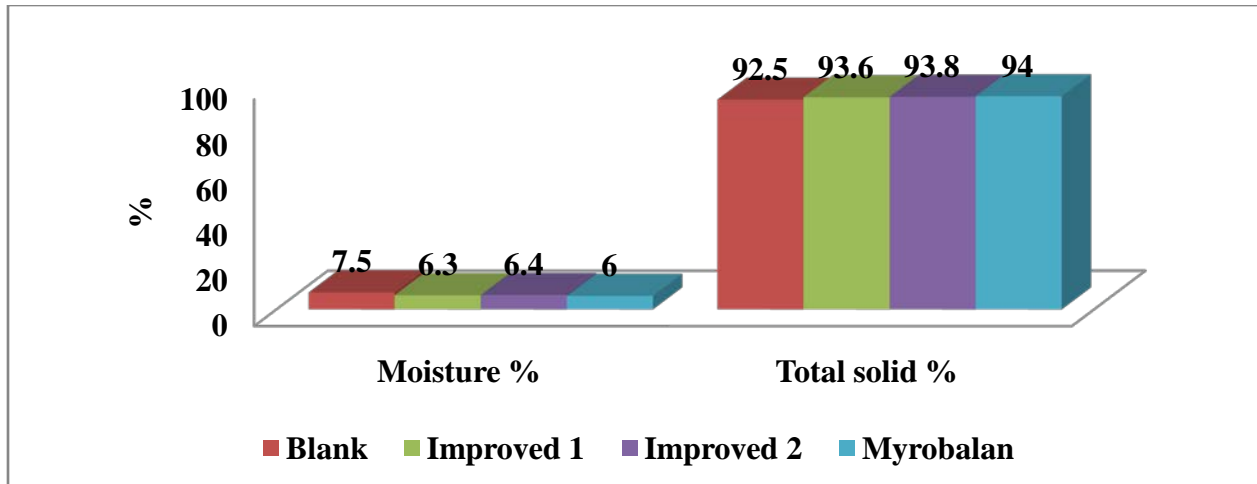


Figure.4. 8 Moisture and total solid contents of indigenous, both modified and myrobalan tanning materials

4.5.2 Total soluble solid content of indigenous, modified and myrobalan tanning materials

Total soluble solid, TSS, of the indigenous, both modified and myrobalan tanning materials are shown in fig (4.9). The results showed that both modified tanning materials is highest in TSS compare to indigenous tannins and excellent compare with the standard of myrobalan tannins and felt in the recommended range (96).

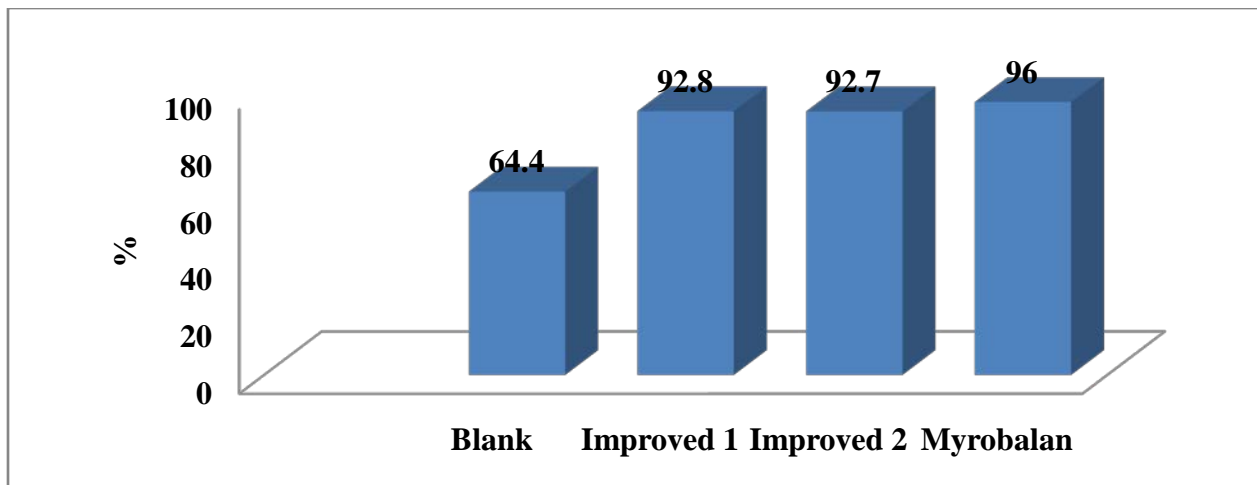


Figure.4. 9 Total soluble solid of indigenous, improved and myrobalan tanning materials

These results suggested that application of rotary system as leaching method and spray dried blended leaching raised the TSS of the both modified tannins compared to indigenous tanning

material. This because insoluble wooden materials in indigenous tanning precipitate and block the sewerage system; this result agreed with Lamb, (2008) evaluation in his study on the ground deseeded 'Garad', and he reported that the insoluble materials of 'Garad' found to be high as 40.7%, where modified tannins produced 0 % percentage of insoluble materials. And spray dried powder is extremely soluble 100% and has no any effect on blocking of sewerage system.

4.5.3 Tannin content of indigenous, both modified and myrobalan tanning materials

Tannin content of indigenous, both modified and myrobalan tanning materials are shown in fig (4.10). The results showed that modified tanning materials contains high tannin content in comparison with the indigenous and standard of myrobalan tanning material and felt in the recommended range.

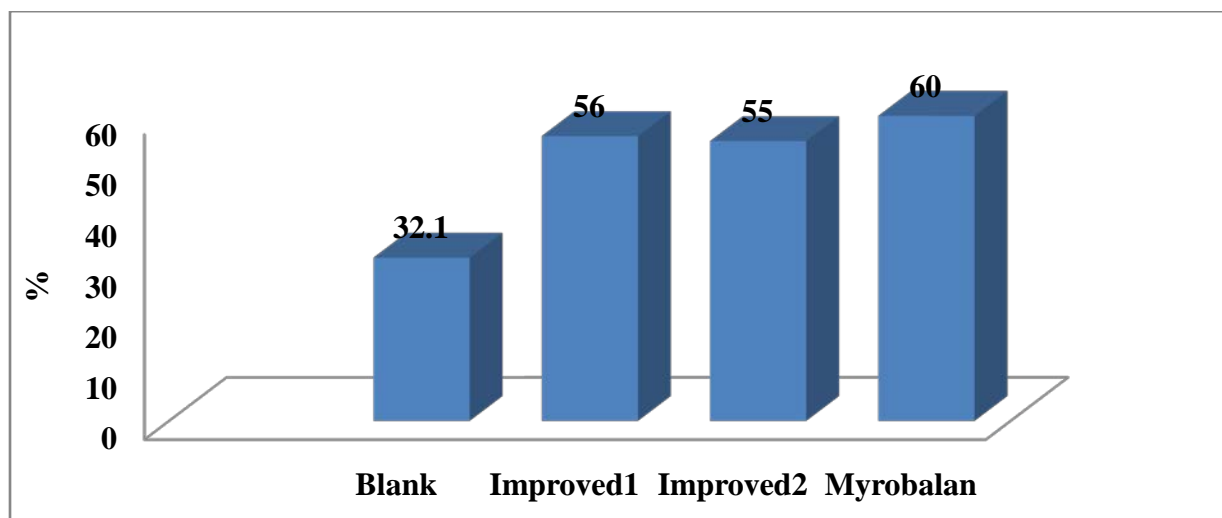


Figure.4. 10 Tannin of indigenous, modified and myrobalan tanning materials

As depicted in Fig. (12), applied rotary system as leaching method and using spray drying machine improve chemical properties of tannin in both modified tannins compare to indigenous tanning. Moreover addition of 20% *Azadirachta indica* bark to 80 % *Acacia nilotica* raised the level of tannin content significantly this could be due to the change occurred in the nature of tannin. *Azadirachta indica* bark contains considerable amount of condensed tannins, these

species believed to add more varieties of tannin species and hence increase the percentages of condensed tannins in the mixture. The presence of high level of is expected to improve the tannage power of *Acacia nilotica*. It was reported by Syed, (2000) that *Azadirachta indica* bark is rich with condensed tannins. Schmutterer, (2005) found that condensed tannins bind and complex strongly with carbohydrates and proteins such binding is quite powerful and difficult to reverse, ended with astringency of leather and high power of tannage. Covington, (2006) investigated that condensed tannins create leather with high thermal stability and ideal shrinkage temperature (80-85°C) than hydrolysable tannins. Larsen *et al*, (2009) also found that leather tanned with condensed tannins characterized with ideal shrinkage temperature (75-80 °C).

4.5.4 Nontannin content of indigenous, both modified and myrobalan tanning materials

Nontannin content of indigenous, both modified and myrobalan tannins materials are shown in fig (4.11). The results showed that both modified tannins materials contain high nontannin content compared with indigenous and the standard of myrobalan tannins and felt in the recommended range (36%).

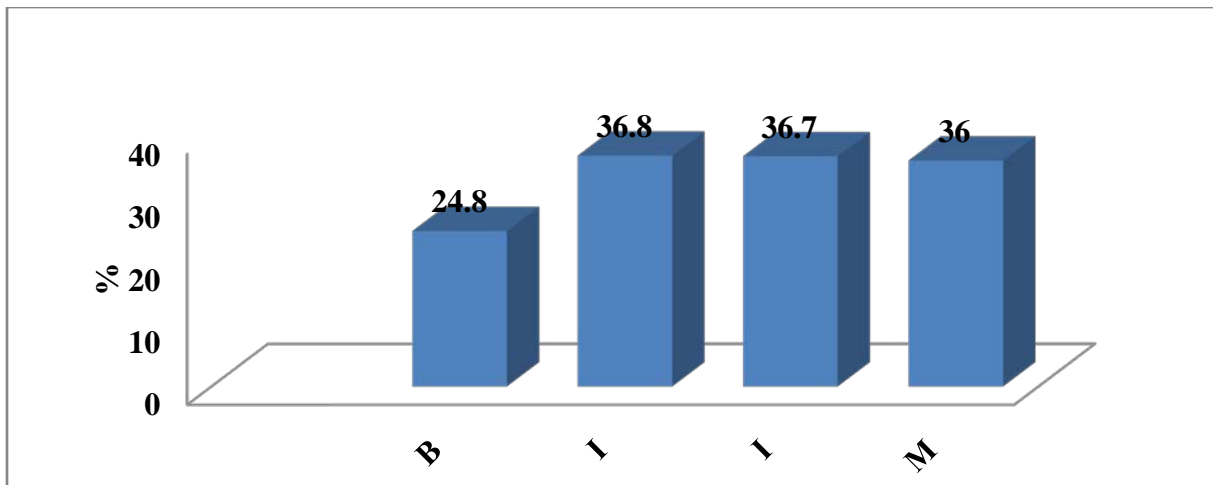


Figure.4. 11 Non tannin content of indigenous, both improved and myrobalan tanning materials

These results suggested that application of rotary system as leaching method and using spray drying machine improve chemical properties of tannin in both modified tannins compare to indigenous tanning. Moreover addition of 20% of *Azadirachta indica* bark changed the nature of *Acacia nilotica* hydrolysable tannin due to *Azadirachta indica* condensed tannin that increased tannage power. These agree with Rao, (2001) who suggested that most effective method is to blend vegetable tannins materials with other for the counteraction of the deficiencies of one material with the advantage of other materials. That agreed with Orwa *et al.* (2009) who mentioned that 'Neem' bark rich with condenses tannins whereas *Acacia nilotica* contain sufficient amount of hydrolysable tannin which hydrolysis releasing carbohydrates, acids, salts, and phenolic compounds. Carbohydrates, acids salts, and phenolic compounds are called non-tannin materials and had no tanning power but their presence in tannin liquors is very important and essential to control the tanning process.

4.5.5 Tannin to nontannin ratio of indigenous, both modified and myrobalan tanning materials

Tannin to nontannin ratio of indigenous, both modified and myrobalan tanning materials are shown in fig (4.12). The results showed that modified tanning materials contain high tannin/nontannin ratio in comparison with the standard of myrobalan tanning materials (1.7).

These results indicates that spray dried powder of modified tannins compare with indigenous addition of 20% of *Azadirachta indica* bark changed the nature of tannin and increase tannage power of *Acacia nilotica*. Results agree with Haroun *et al.* (2013) who reported that bark of *Azadirachta indica* is rich with catechin (condense tannin). And Sarkar and Sorcar, (2005) postulation that explains a tannage with condensed tannins was much better than with the hydrolysable tannin and gave the most stable leather.

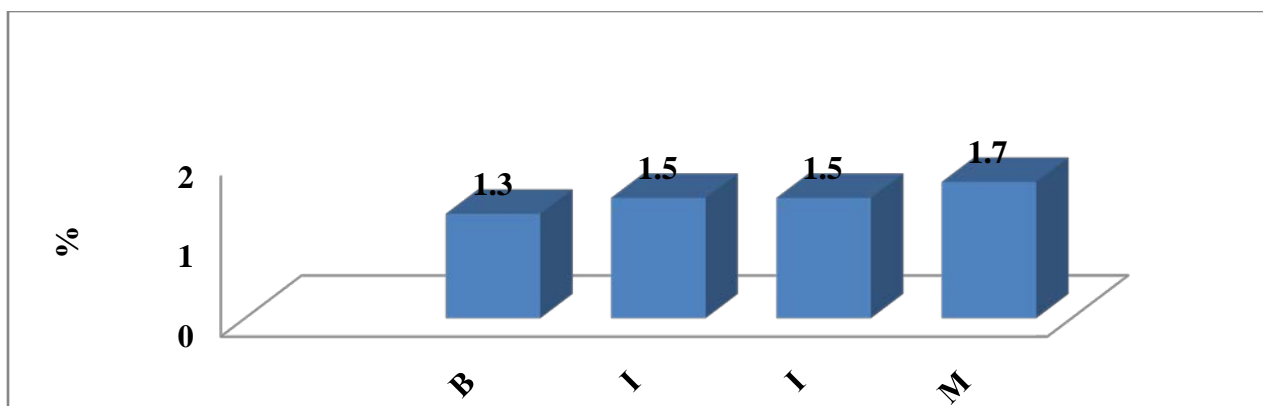


Figure.4. 12 Tannin/Nontannin ratio of indigenous, both modified and myrobalan tanning materials

The high stability of tannins molecules is believed to be due to the strong covalent bonding and to the absence of ester links which are degradable materials. Hydrolysis of ester links cause loss of tannin molecules and increases the percentage of non-tannins, and consequently decreases the ratio of tannin/nontannin which in turn results in a decrease of tanning quality. Simon and Pizzi, (2003) investigated that tannin/non-tannin ratio of the tan stuff should always be increased beyond one in order to get excellent and satisfactory tannage power.

4.5.6 The pH at 25°C of indigenous, both modified and myrobalan tanning materials

The pH of indigenous, both modified and myrobalan tanning materials are shown in Fig. (4.15). The results showed that the modified tanning material exhibits higher pH than the standard of myrobalan tanning material. (3.5 to). These results suggested that addition of 20% of *Azadirachta indica* bark changed the tanning nature as indicated by the increment in pH of both modified tanning material (pH 4.1- 4.6) compared to indigenous *Acacia nilotica* tannins (pH 3.8). The elevation of pH is attributed to the presence of *Azadirachta indica* which contains high percentages of non-hydrolysable condensed tannins. The pure *Acacia nilotica*, however, rich with hydrolysable tannins which undergo hydrolysis during tannage realizing sugar and organic acids that lead to drop the pH to a minimum value.

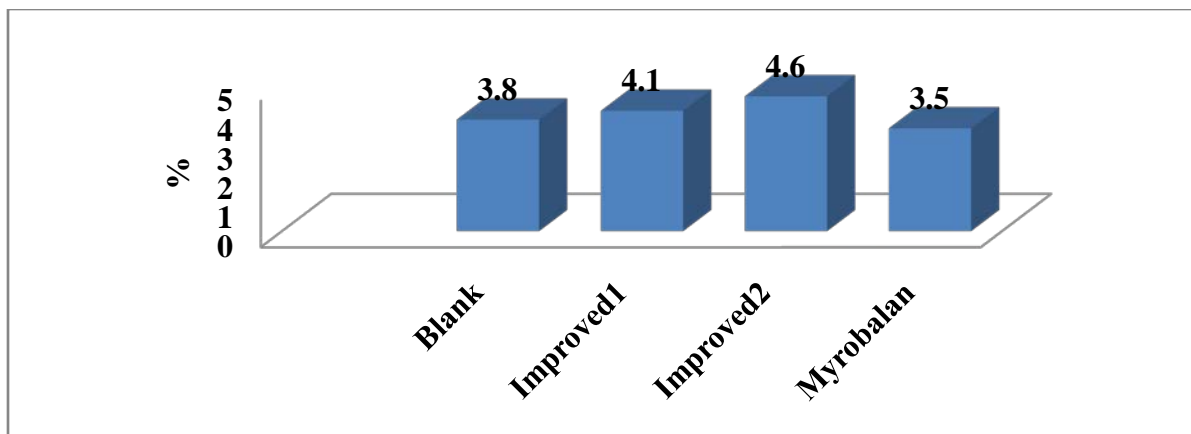


Figure.4. 13 pH of indigenous, both modified and myrobalan tanning materials

This result is coinciding with Dutta, (2002) who found that solutions of hydrolysable tannin have pH range of 2.8 - 3.6 whereas solutions of condensed tannins shows pH range of 4.1 - 5.2.

4.5.7 Colour of indigenous, both modified and myrobalan tanning materials

The colour of indigenous, both modified and myrobalan tannins materials were shown in fig (4.14). The results showed that modified tannins materials reflected light colour felt within the standard myrobalan tannins colour, while indigenous one reflected brown colour due to present of 0.6 blue colours.

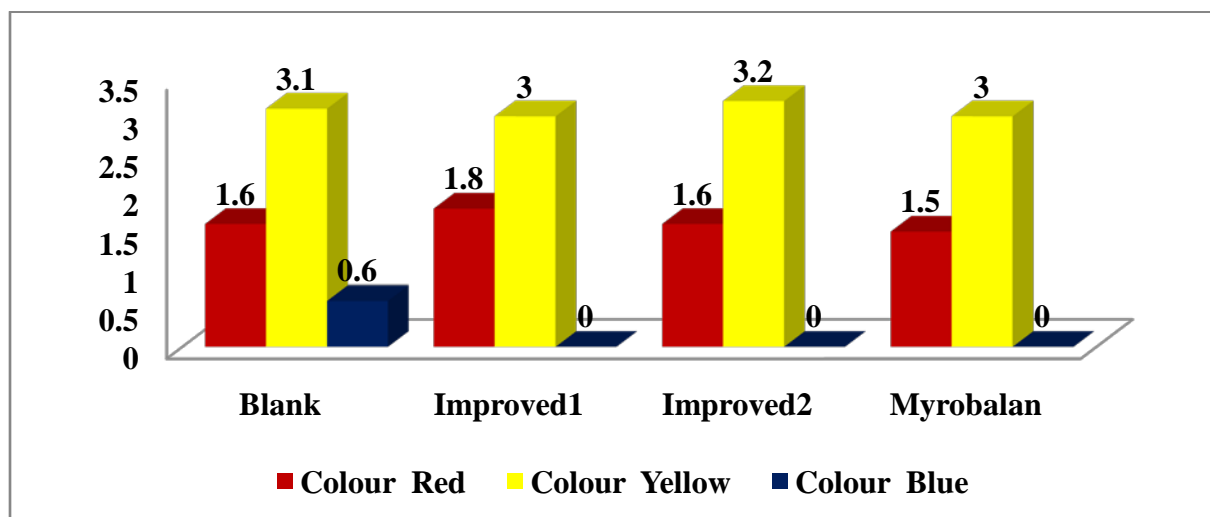


Figure.4. 14 Colour of indigenous, both improved and myrobalan tanning materials

Generally, the colour of hydrolysable and condensed tannins varies from yellow to yellow-brown biscuit colour, which is mixture of red and yellow colours only. The presence of any other

colours, such as blue or blue-green is undesirable in the tanning liquors. The observance of other colour, such as blue, indicates the presence of iron ions in tanning liquors. These iron species are undesirable and expected to react with tannin to produce undesirable complexes. The modified method bleached out all impurities and hence avoided contamination of liquors with iron and therefore save the bright colour of leather which is desirable for tannage power, good shiny leather and ease of painting by bright colours.

4.5.8 Statistical assessment of indigenous, both modified and myrobalan tanning materials analysis:

Table 4.4 Anova test for mechanical and physicochemical properties of tanned leathers using either improved or indigenous tannins. Statistical data of SPSS analysis shows that there are significant differences of physicochemical properties of improved indigenous tannins comparing indigenous tannin. Table (4.4) showed statistical analysis at $P < 0.05$ level as described by Gomez and Gomez, (1984) to evaluate the significant differences between the treatments.

Table.4. 4 Statistical assessment of indigenous, modified and myrobalan tannins analysis:

No	Description	Mean	Std	Sig. 0.05
1	Moisture	7.9	0.5	0.00
4	Total soluble solid	74.5	1.56	0.00
5	Non tannin	33.15	4.77	0.00
6	Tannin	43.36	1.06	0.00
7	Tannin/Nontannin Ratio	1.5	0.16	0.03
8	Colour			
	Red	1.98	0.71	0.53
	Yellow	3.04	0.22	0.01
	Blue	0.36	0.33	0.02
9	pH at 25°C	4.9	0.44	0.00

4.6 Mechanical and physico-chemical properties of indigenous, improved and myrobalan tanned leathers

To evaluate the modification processes which are applied to improve the tannin power of the *Acacia nilotica* pods thus the quality of leathers which are produced using these modified tannins

materials applying the methods in section (3.10), mechanical and chemical parameters, are measured using the methods in section (3.11) and the results have been listing on appendix.2:

Table.6. Each factor of them is discussed individually and the discussions are showed as flowing:

4.6.1 Calculations of mechanical and physico-chemical properties of leather

4.6.1.1 Tensile strength

The tensile strengths were determined conducting the method (3.10.2) and were calculated by equation (4.9). The results are listed in appendix.2: Tables (6 and 8) for the leather samples:

$$\text{Tensile strength N/ cm}^2 = \frac{\text{Breaking load (N)}}{\text{Cross section (sq. cm)}} \quad \text{equ.4.9}$$

4.6.1.2 Tear strength

The tear strengths were determined conducting the method (3.10.4) and were calculated by equation (4.10). The results are listed in appendix.2: Tables (6 and 8) for the leather samples:

$$\text{Tear strength N/ cm} = \frac{\text{Tearing load (N)}}{\text{Leather thickness (cm)}} \quad \text{equ.4.10}$$

4.6.1.3 Stitch tear strength

The stitch tear strengths were determined conducting the method (3.10.3) and were calculated by equation (4.11). The results are listed in appendix.2: Tables (6 and 8) for the leather samples.

$$\text{Stitch tear strength N/ cm} = \frac{\text{Tearing load (N)}}{\text{Leather thickness (cm)}} \quad \text{equ.4.11}$$

4.6.1.4 Distention and strength of grain

The distention and strength of grain were determined conducting the method (3.10.6) and were calculated by equation (4.12, 4.13 and 4.14). The results are listed in appendix.2: Tables (6 and 8) for the leather samples:

$$\text{Grain crack strength N/ cm} = \frac{\text{load at crack in N}}{\text{Leather thickness in cm}} \quad \text{equ.4.12}$$

$$\text{Grain bursting strength N/ cm} = \frac{\text{Load at bursting in N}}{\text{Leather thickness in cm}} \quad \text{equ.4.13}$$

$$\text{Distention and strength of grin} = \frac{\text{Grain crack strength} + \text{Grain bursting strength}}{2} \quad \text{equ.4.14}$$

2

4.6.1.5 Grease and fat content

The fat percentages were determined conducting the method (3.9.4) and were calculated by equation (4.15). The results are listed in appendix.2: Tables (7 and 9) for the leather samples.

$$\text{Fat content \%} = \frac{\text{Weight of extracted fat} \times 100}{\text{Weight of sample}} \quad \text{equ.4.15}$$

4.6.1.6 Skin substances content

The skin substances content percentages were determined conducting the method (3.11.6) were calculated by equation (4.16).

$$\text{Skin substances content\%} = \frac{\text{Volume of 0.05 M sodium hydroxide} \times 6 \times 10}{\text{Weight of sample}} \quad \text{equ.4.16}$$

The results were determined in appendix.2: Tables (8, 10 and 12) for the leather samples.

4.6.1.7 Degree of tannage

The degree of tannage percentages were determined conducting the method (3.11.7) and were calculated by equation (4.17). The results are listed in appendix.2: Tables (7 and 9) for the leather samples:

$$\frac{100 - \sum (\text{Moisture} + \text{Ash} + \text{Fat} + \text{Organic lost by washing} + \text{Skin substance}) \times 100}{\text{Skin substance}} \% \quad \text{equ.4.17}$$

4.6.2 Mechanical properties of indigenous, both improved and myrobalan tanned leathers

To evaluate the two kinds of modified tannins materials and discuss their penetration and fixation power, time, their capability and efficiency on tanning trials thus the vegetable tanned leathers were producing using the methods in section (3.9), the leather samples are assessed using mechanical analysis as following:

4.6.2.1 Thickness of indigenous, both improved and myrobalan tanned leathers

The thickness of the goat leather treated with either indigenous *Acacia nilotica* pods as the control or both spray dried of blending of 20% *Azadirachta indica* and 80% *Acacia nilotica* were shown in Fig (4.15). The results showed that thickness of leather treated with the both modified spray- dried characterized with an excellent cross and fullness compared to the standard of shoe upper leather and it felt in recommended range IS, (2003) and SS, (2003).

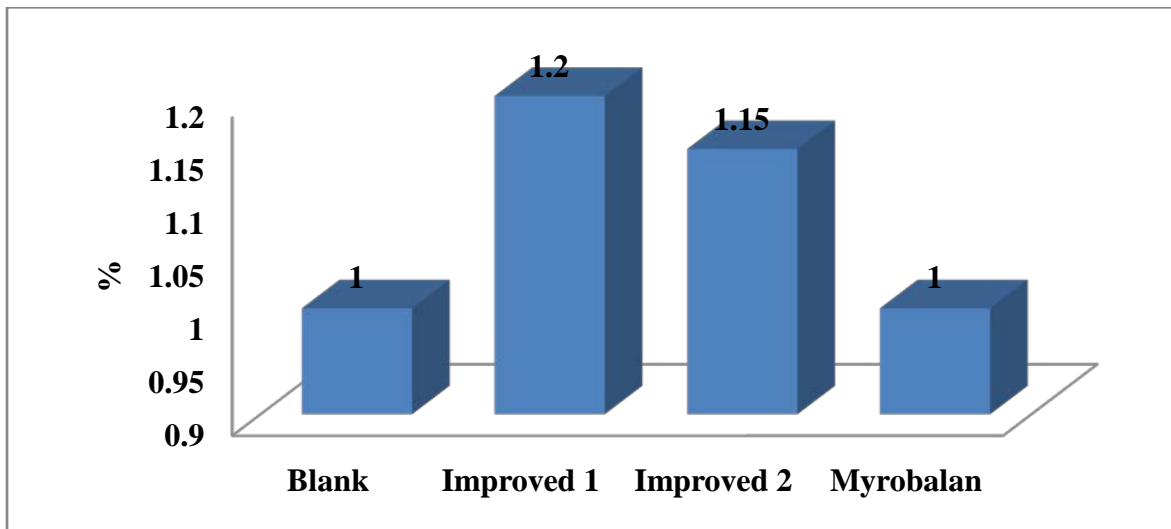


Figure.4. 15 Thickness of indigenous, both improved and myrobalan tanned leathers an

These results suggested that 20% of *Azadirachta indica* change the behavior of tannin and raised tannage power of *Acacia nilotica* by reducing the amount of consumed tannin to half with an increment of leather strength than addition of *Acacia nilotica* alone. Because *Acacia nilotica* contains hydrolysable tannin which is better for thickness while *Azadirachta indica* bark contains condensed tannin which impact the strength properties of the tanned leather. Overall collective actions of the power quality of the leather by using 'Garad – Neem' tannage materials increased the homogenous interaction of strength, fullness and fellness that recommended for good leather. These results were agreed with Musa and Gasm elseed, (2008) whom mentioned that pods of *Acacia nilotica* contain a considerable amount of hydrolysable tannins which undergo hydrolysis

in the acid solution. Therefore leathers which were tanned with only conventional 'Garad' are characterized with drawn grain decrease in strength and low shrinkage temperature. Therefore blended *Azadirachta indica* bark rich with condenses tannins Haroun et al, (2013) controlled the swelling/plumping of yielding leather with thickness closed to standard

4.6.2.2 The strengths of (Tensile, Tear, and Stitch Tear) of indigenous, both improved and myrobalan tanned leathers

The results of tensile, tear and stitch tear strengths values of the goat leather treated by either *Acacia nilotica* pods or both blending; 20% *Azadirachta indica* and 80% *Acacia nilotica*; were shown in Figures (4.16-4.18).

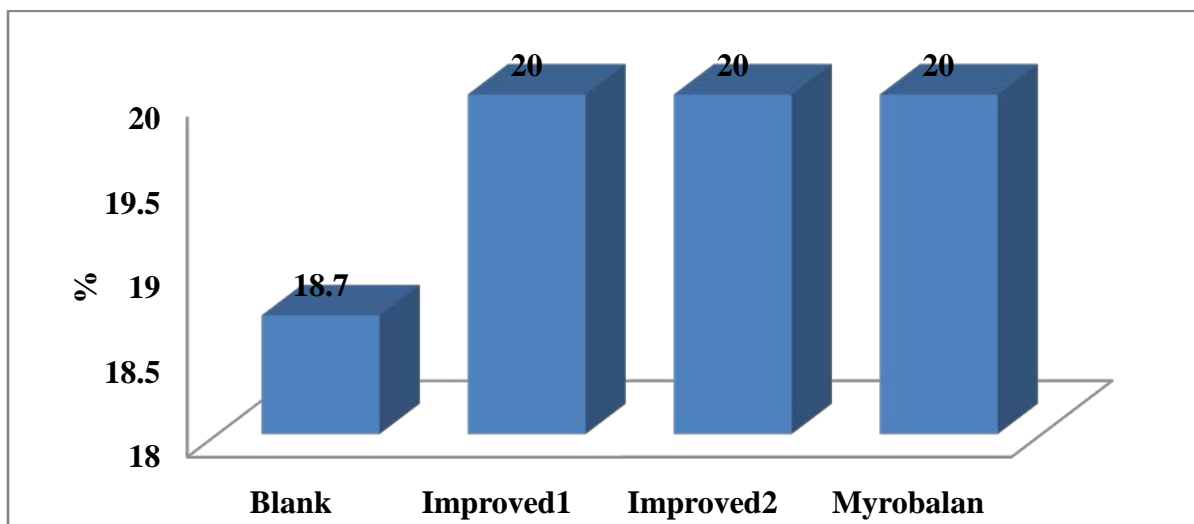


Figure.4. 16 Tensile strength of indigenous, improved and myrobalan tanned leathers

The leathers treated with the blended powder showed better strength in compared with the standard of shoe upper leather which closed in agreement with standard BIS, (2003) and SS, (2003). The strengths values of goat tanned leathers increase by applying a blend of 20% *Azadirachta indica* and 80% *Acacia nilotica*. These results suggested that the presence of 20% of *Azadirachta indica* modifies the tannin conduct and raised the tannage power of *Acacia nilotica* to almost double its normal power.

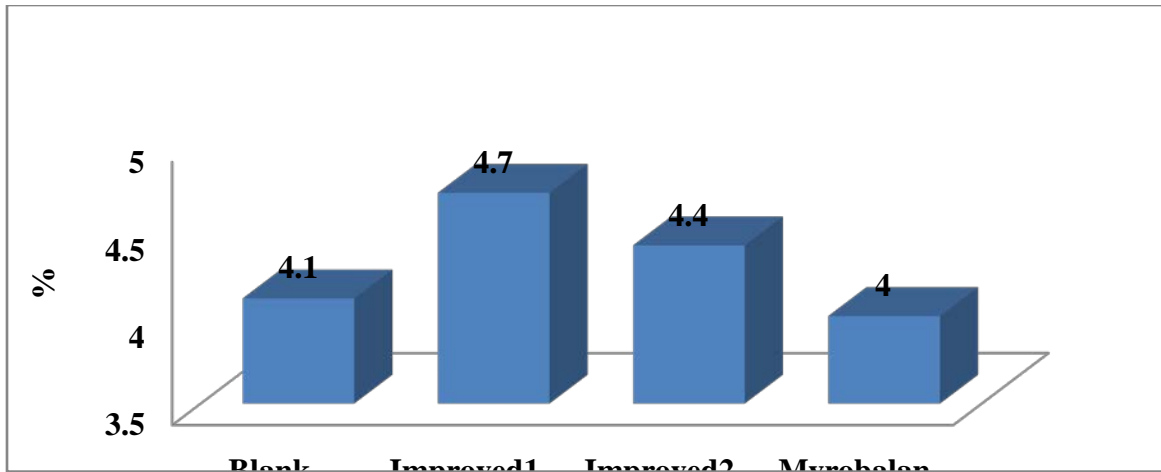


Figure.4. 17 Tear strength of indigenous, improved and myrobalan tanned leathers

This could be attributed to the existence of considerable amounts of condensed tannins in *Azadirachta indica* bark which seem to be very important to strengthen the leather beside the customary benefits of hydrolysable tannin in *acacia nilotica* required for fullness and color. Orwa *et al.* (2009) reported that *Azadirachta indica* bark contains considerable amounts of condensed tannins, whereas Lamb, (2008) found that pods of *Acacia nilotica* contain hydrolysable types. Therefore, it is quite obvious that the types and contents of tannins together are quite crucial to strengthen the fibres of the leather. Generally collective actions of the power quality of the leather increase with homogenous interaction of strength, fullness and fellness that recommended for good leather. Hence good leather strengths due to the behavior of condensed tannins. Condensed tannins penetrate rapidly and aggregate more readily in the pelt fibres deposited a very large molecules that cross-linking through hydrogen bond to the peptide groups of the collagen.

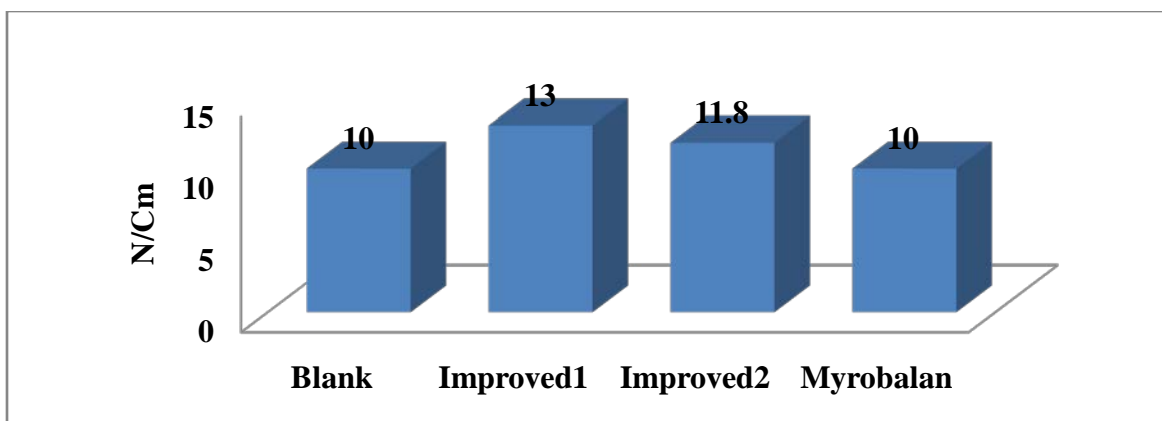


Figure.4. 18 Stitch tear strength of indigenous, improved and myrobalan tanned leathers

The degree of cross-linkage depends on the size of the polyphenol molecules and number of –OH groups where hydrolysable type not condensate but hydrolysis deposited sludge with low molecules. Sarkar and Socar, (2003) conception that tannage with condensed tannins was much better than with the hydrolysable tannin and gave the most stable leather. However, extensive and deep studies are needed to investigate the actual role played by each type of tannin species, and the mechanism of the overall tannage process.

4.6.2.3 Elongation and distension and strength of grain of indigenous, both improved and myrobalan tanned leathers

The elongation and distension and strength of grain of the goat leather tanned using either 100% of *Acacia nilotica* pods as the control or both spray dried of blending; 20% *Azadirachta indica* and 80% *Acacia nilotica*; were shown in Figs (4.19 and 4.220). The result showed better elasticity, softness and flexibility of blended tanned leather agree with the standard of shoe upper leather and felt in recommended range, BIS, (2003) and SS, (2003).

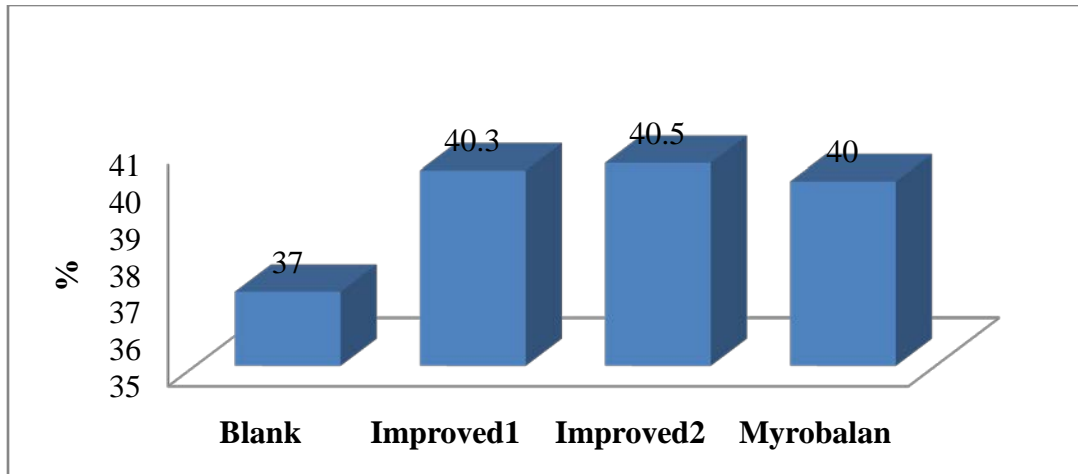


Figure.4. 19 Elongation of indigenous, improved and myrobalan tanned leathers
 These results postulate that addition of 20% *Azadirachta indica* vary the nature of tannin and raised tannage power of *Acacia nilotica* and reduced consumption of tannin to the half than using *Acacia nilotica* alone. *Acacia nilotica* contain consider amount of hydrolysable tannin which

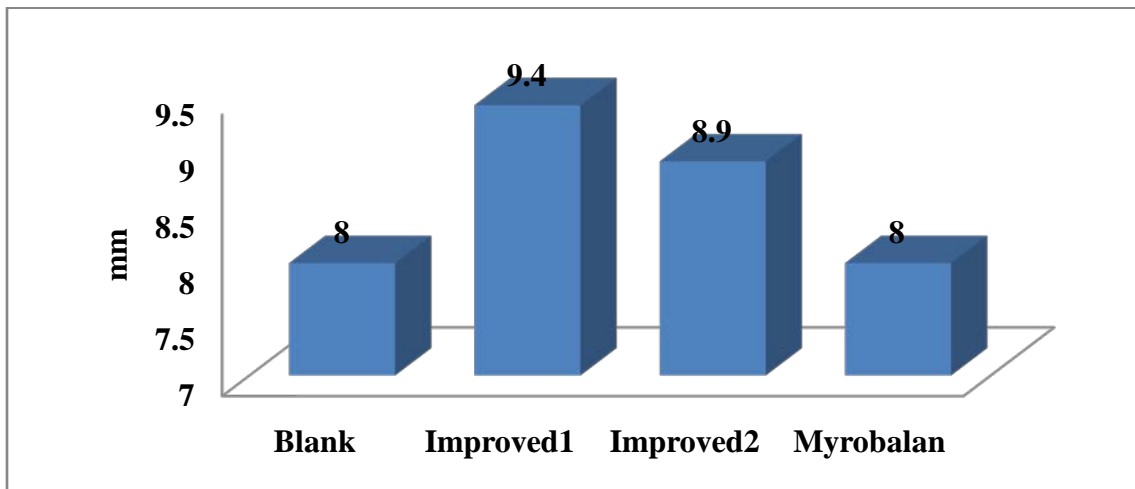


Figure.4. 20 Distension and strength of grain of indigenous, improved and myrobalan tanned leathers

undergo hydrolysis releasing nontannins molecules which reduced the tannin liquor acidity causes an osmotic effect, protein swell and plumps, that accelerates the penetration whereas drop the fixation of the tannin producing very firm leather. Thus it is essential to control the pH of the tanning liquor using blending method, 'Garad – Neem' and natural salt, which organized the

protein swelling/ plumping and developed physical properties such as softness, flexibility, strength and thermal stability of yielded leather. This result is coincided with Dutta, (2002) who mentioned that increase in acid swelling/ plumping ruptures stabilizing cross-links in the fibre structure, short links, and releases additional hydrogen bond sites, peptides groups, for tannin fixation. Whereas final pH values of 3.6-3.6 produce flexible leather, pH of 3.2 produce very firm leather (Orwa et al, (2009).

4.6.2.4 The shrinkage temperature of indigenous, both improved and myrobalan tanned leathers

The hydrothermal stability of the goat leathers tanned using either 100% of *Acacia nilotica* pods control or both spray dried of blending of 20% *Azadirachta indica* and 80% *Acacia nilotica* were shown in Fig (4.21).

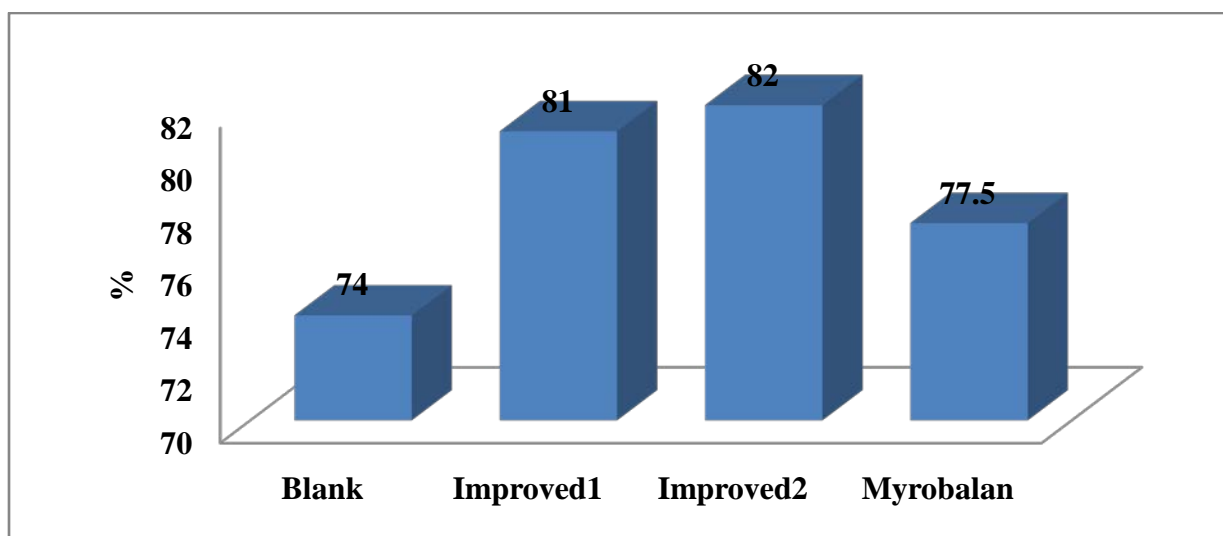


Figure 4. 21 Shrinkage temperature of indigenous, improved and myrobalan tanned leathers

These results proposed that 20% of *Azadirachta indica* modify the tannin nature and increased tannage power of *Acacia nilotica* and reduced amount of consumption tannin to half. *Azadirachta indica* bark wealthy in condensed tannin which acts as strength agent of the tanned leather while *Acacia nilotica* contain high hydrolysable tannin which is reduced thermal stability.

Shrinkage temperature assesses the amount of tannin and can enhance the deposition through the cross-section of tanned leather, ended with better elasticity, softness and flexibility of leather.

The increment of temperature depends on the size of the polyphenol molecules and the numbers of –OH groups which is consistent with Covington *et al*, (2006) postulation who concluded that shrinkage temperature is determined by the effectiveness of tanning molecules to produce high molecular weight cross-linked moieties. Also they reported that thermal stability of leather depends on the kinetic stability of the interaction between the tanning molecules and the protein side chains. Larsen *et al*, (2009) reported that typical shrinkage temperature for new leather tanned with condensed tannins is 80-85°C while hydrolysable shrinkage temperature is 75-80 °C.

4.6.3 Physico-chemical properties of indigenous and both improved or myrobalan tanned leathers

To evaluate the two kinds of modified tannins materials and discuss their penetration and fixation power, time, their capability and efficiency on tanning trials thus the vegetable tanned leathers were producing using the methods in section (3.7) and the leather samples are assessed using physico-chemical analysis as following:

4.6.3.1 Moisture and Fat Contents of indigenous, improved and myrobalan tanned leathers

The moisture and free fat content of the goat leather tanned using either 100% of *Acacia nilotica* pods or both spray dried blended 20% *Azadirachta indica* and 80% *Acacia nilotica* were shown in Fig (4.22 and 4.23). The results showed that elasticity and flexibility of leather agree with the standard of shoe upper leather, IS (2003) and SS, (2003). Above mentioned results suggested that both moisture and fat increase the tensile strength and flexibility of leather for a certain limit, firstly, tensile strength is depend on angle of the fibre and their splitting value so low angle and high splitting value yielding high tensile strength.

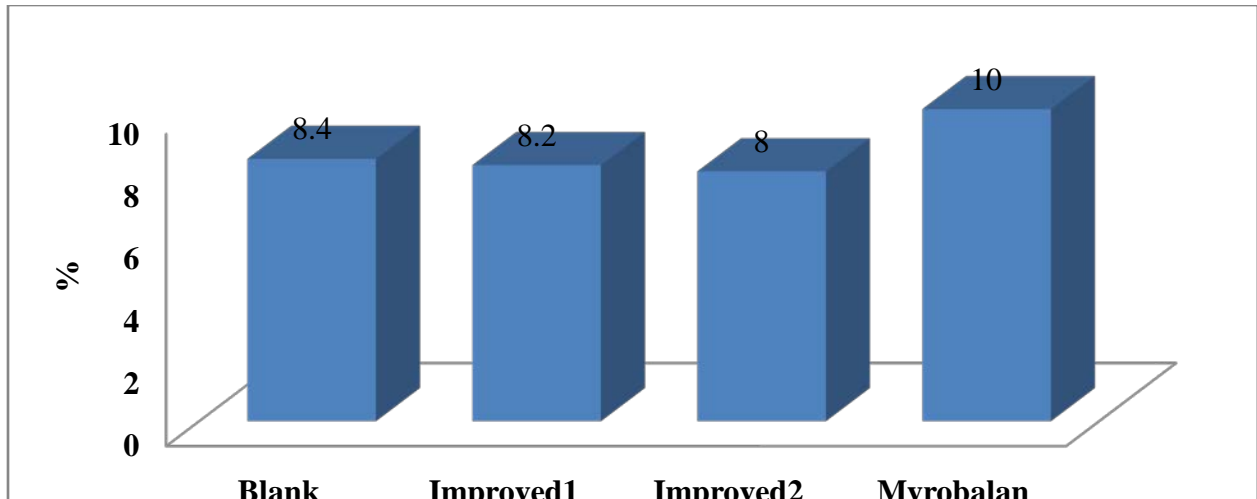


Figure 4. 22 Moisture of indigenous, improved and myrobalan tanned leathers

In contrast of that when fibre has lower tensile strength the addition of fat liquor does not lower the fibre bundles angle of weave; but it improve the splitting value of the fiber and its strength. Secondly the leather is flexible when its fibre slid one above the other.

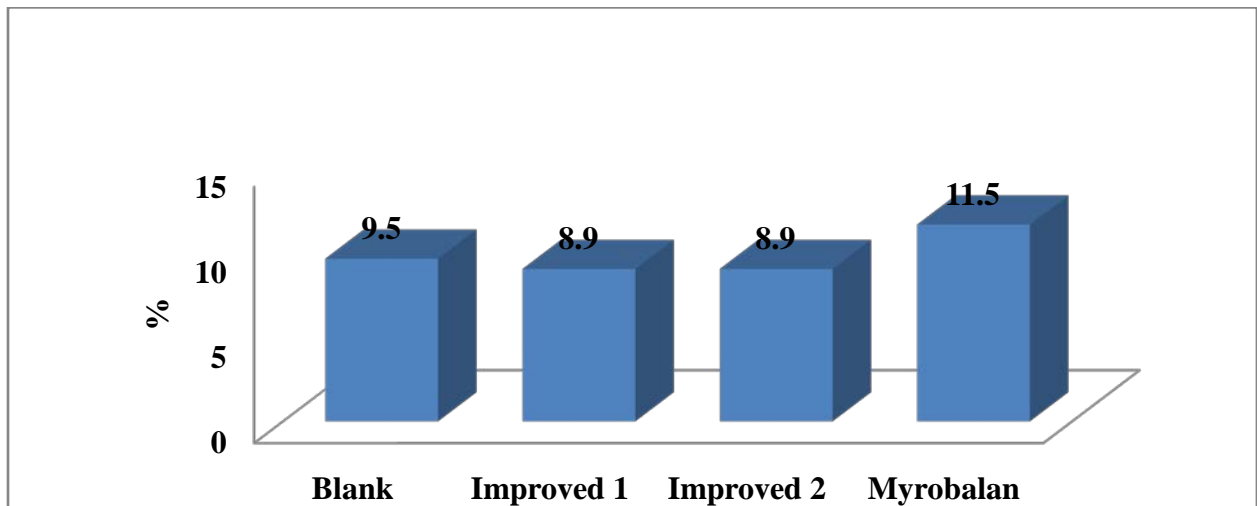


Figure 4. 23 Fat content of indigenous, improved and myrobalan tanned leathers

The amount of flexibility is estimated using elongation, distension and strength of grain values which indicate if the amounts of moisture and fat content were reasonable in the fibers or not. This coincided with Hai Quadery et al, (2015) who reported that both tensile strength and flexibility changed with the oil content of the leather increased with the increase of its oil content

and then decreased after a certain limit. In generally the moisture and fats values present in improved tanned leather are comparable to those of normal standard values.

4.6.3.2 Total Soluble and Degree of Tannage of indigenous, improved and myrobalan tanned leathers

Total soluble matter and degree of tannage of the goat leather treated using either 100% of *Acacia nilotica* pods or blended 20% *Azadirachta indica* and 80% *Acacia nilotica* were shown in Figs (4.24 and 4.25). The results showed that both total soluble and degree of tannage represented the fixation of tannins on the collagen fibers and the stability of leather.

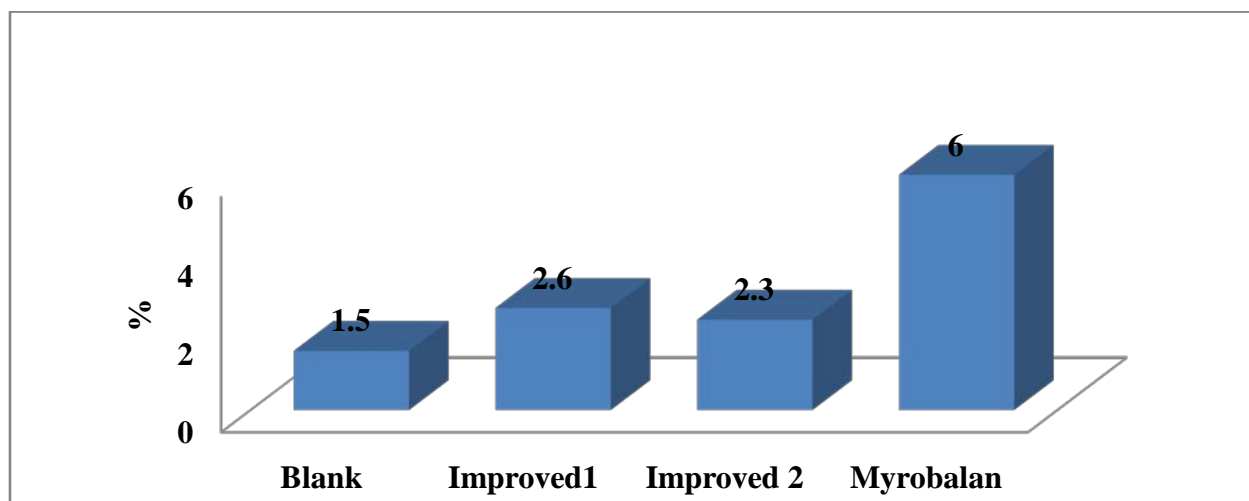


Figure 4. 24 : Total soluble solid of indigenous, improved and myrobalan tanned leathers
Leather treated with the both blended powder showed high stability due to fixation and low soluble matter of condense tannin which agrees with the recommended standard of shoe upper leather IS, (2003) and SS, (2003). These results suggested that blended 'Garad – Neem' improved the tanning power of indigenous tannin of *Acacia nilotica* and decreased amount of spending tannin to half. Condensed tannins, 'Neem' is more stable to hydrolysis and microbial attack than indigenous 'Garad' tannins, contain consider amount of hydrolysable tannins, this due to strong co-valent bonding between individual carbon atoms and the absence of ester links.

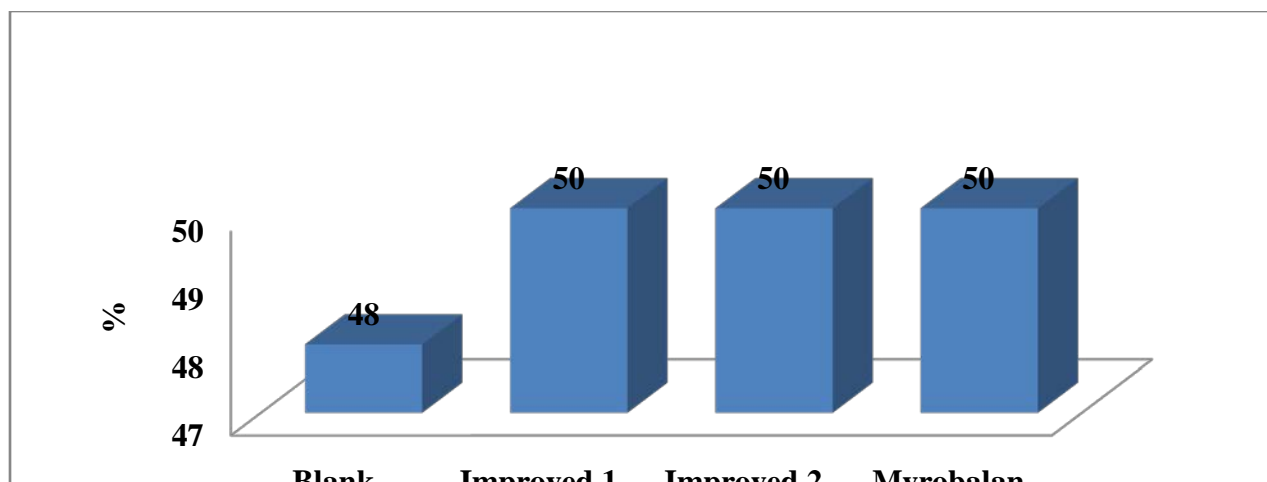


Figure 4. 25 Degree of tannage of indigenous, improved and myrobalan tanned leathers
indigenous 'Garad' tannins hydrolysis decomposed the tannin and released sugar and organic acid that increased the soluble matter and decreased the degree of tannage, where condensed tannins are deposit large molecules size of the polyphenol, Reds, contained high numbers of –OH groups which deposit into the pelts fibre and cross-link through large amount of hydrogen bonds to peptide groups in collagen. As reported by Rao, (2001) these phenol-peptide strong interactions improve the leather stability.

4.6.4 Statistical assessment of indigenous, both improved and myrobalan tanned leathers

Table.4.5 Anova test for mechanical and physicochemical properties of tanned leathers using either improved or indigenous tannins.

Statistical data of SPSS analysis shows that there are significant differences of mechanical and physico-chemical properties of produced leathers using both improved tanning materials comparing to indigenous tanned leathers. Table (4.5) showed statistical analysis at $P < 0.05$ level as described by Gomez and Gomez, (1984) to evaluate the significant differences between the treatments.

Table 4. 5 Statistical assessment of indigenous, improved and myrobalan tanned leathers

No	Description	Mean	Std	Sig. 0.05
1	Thickness mm	1.18	0.197	0.000
2	Tensile strength	19.34	1.390	0.000
3	Elongation	43	8.276	0.000
4	Tear strength	3.9	0.413	0.000
5	Stitch tear strength	11.6	1.230	0.000
6	Distension and strength of grain /mm	8.4	1.340	0.000
7	Shrinkage temperature	83	9.155	0.000
8	Moisture	8.35	1.14	0.00
9	Fat	8.72	1.37	0.00
10	Total soluble matter	1.88	1.03	0.00
11	Degree of tannage	49.5	2.17	0.00

4.7 Mechanical and physico-chemical properties of leathers which produced using semi chrome and either indigenous or modified tannins

4.7.1 Calculation physico-chemical properties of leathers

4.7.1.1 Chrome content

The chrome content percentages were determined conducting the method (3.11.8) and were calculated by equation (4.18). The results are listed in appendix.2: Tables (9) for the leather samples and waste water:

$$\text{Chrome Content\%} = \frac{\text{Volume of 0.1 N sodium thiosulphate} \times F \times 100\%}{\text{Weight of dried sample}} \quad \text{equ.4.18}$$

Where F is factor = 0.00253

4.7.2 Mechanical properties of leathers which produced using semi chrome and either indigenous or both modified tannins

To evaluate the modification processes which are applied to improve the tannin power of the indigenous tannins thus the quality of leathers which are produced using the methods in section (3.9) is examined, mechanical parameters, using the methods in section (3.10 and 3.11), the results have been listing on the appendix.2: Table (8). Each factor of them is discussed individually and the discussions are showed as flowing.

4.7.2.1 Thickness of semi chrome and either indigenous or both improved tanned leathers

The thickness of the goat leather treated with semi chrome and either indigenous *Acacia nilotica* pods as the control or spray dried of blending of 20% *Azadirachta indica* and 80% *Acacia nilotica* was shown in Fig (4.26). The results showed that thickness of semi chromed leather treated with either unmodified and modified spray-dried materials characterized with an excellent cross-section and fullness compared to the standard of shoe upper leather and it felt in recommended range, IS, (2003) and SS, (2003).

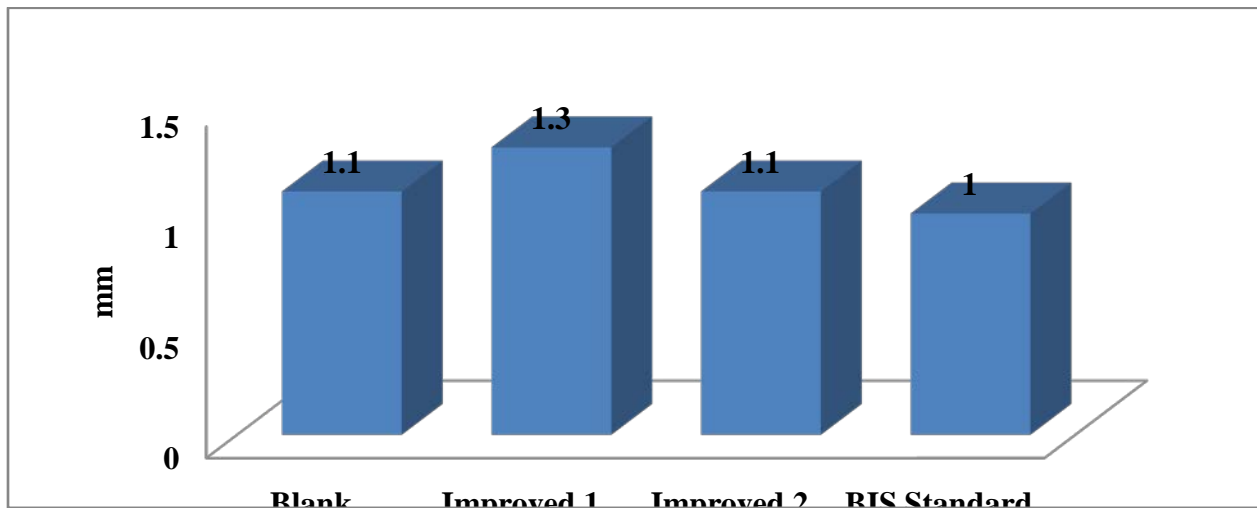


Figure 4. 26 Thickness of semi chrome and either indigenous or improved tanned leathers and BIS standards

Although of high strength of semi chrome tanned leather but there are some disadvantages of such as lack of fullness, filling and softening; therefore, indigenous tanning materials as

retanning agents were developed to improve the chrome tanned leather properties and the results suggested that modified 'Garad – Neem' materials increased the homogenous interaction of strength, fullness and fellness that recommended for good leather. These agreed with Nilay et al 2014 vegetable tannins are opted in leather industry for their mechanical properties they gain to the leathers such as fullness, filling and softening.

4.7.2.2 The strengths of (tensile, tear, and stitch tear) of semi chrome and either indigenous or both improved tanned leathers

The results of tensile, tear and stitch tear strengths values of the goat leather treated by either *Acacia nilotica* pods or both blending; 20% *Azadirachta indica* and 80% *Acacia nilotica*; were shown in Figures (4.27-4.29).

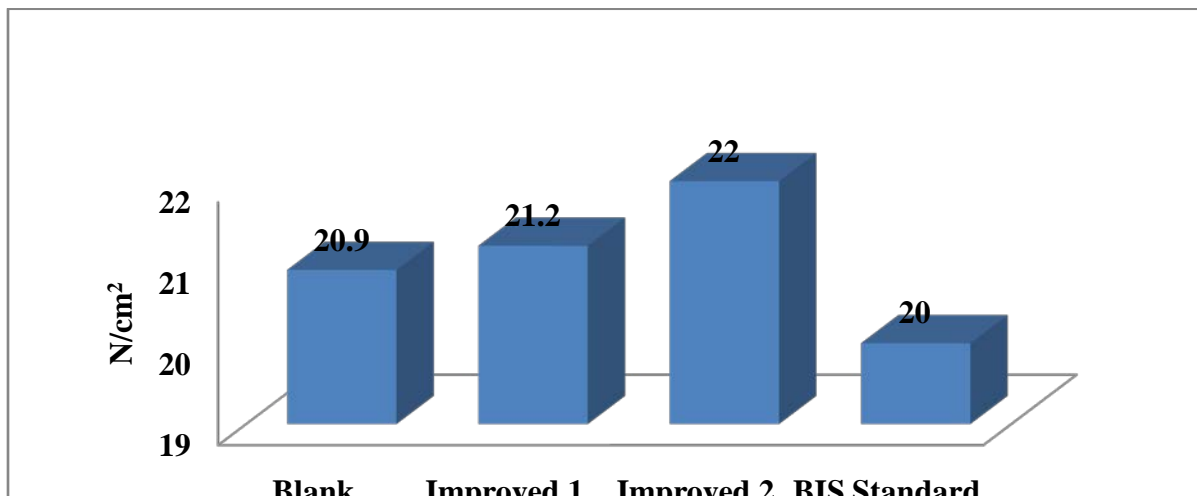


Figure 4. 27Tensile strength of semi chrome and either indigenous or both improved tanned leathers and BIS standard

The leathers treated with the semi chrome and both improved tanning materials showed highest strength than those treated with indigenous 'Garad' and better in compared with the standard of shoe upper leather which closed in agreement with standard, IS, (2003) and SS, (2003). The strengths values of goat tanned leathers increase by applying a blend of 20% *Azadirachta indica* and 80% *Acacia nilotica*.

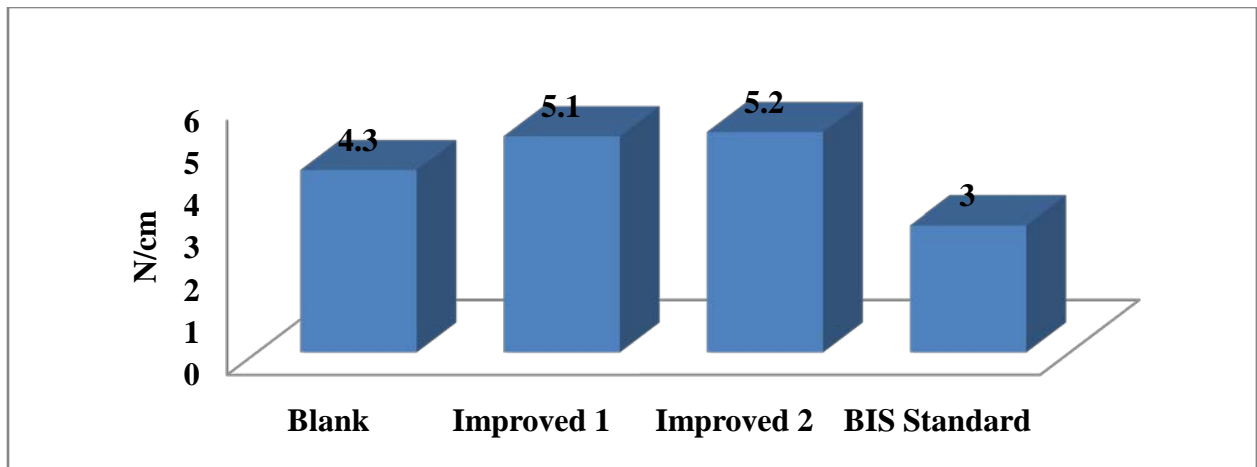


Figure 4. 28Tear strength of semi chrome and either indigenous or both improved tanned leathers and BIS standard

These results suggested that the presence of 20% of *Azadirachta indica* modified the tannin conduct and raised the tannage power of *Acacia nilotica* to almost double its normal power.

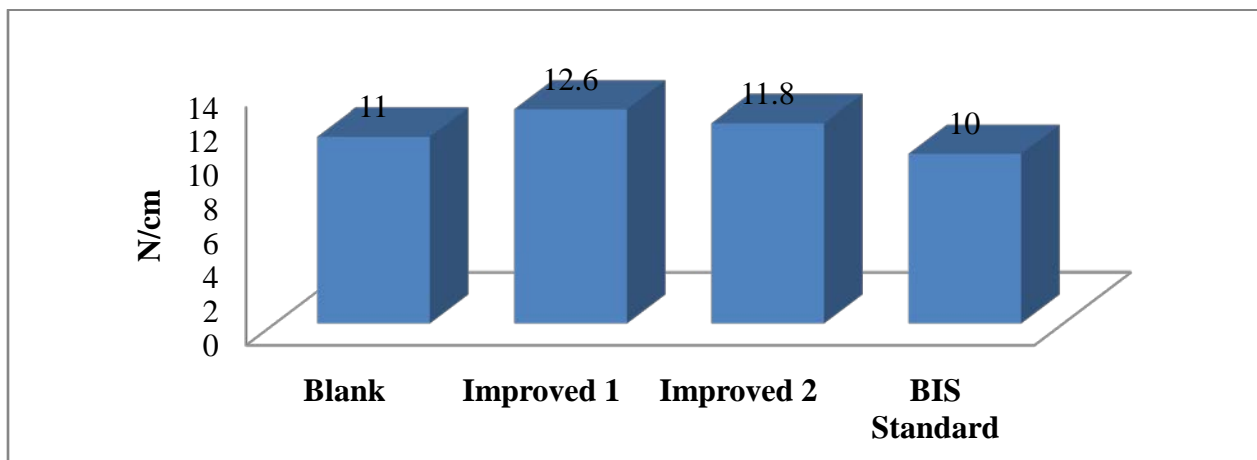


Figure 4. 29Stitch tear strength of semi chrome and either indigenous or both improved tanned leather and BIS standard

This could be attributed to the existence of considerable amounts of condensed tannins in *Azadirachta indica* bark which seem to be very important to strengthen the leather beside the customary benefits of hydrolysable tannin in *acacia nilotica* required for fullness and color. These agree with Nand *et al*, (2013) who reported that *Azadirachta indica* bark contains considerable amounts of condensed tannins. Therefore, it is quite understandable that the types and contents of tannins together are quite essential to strengthen the fibres of the leather. Generally collective actions of the power quality of the leather increase with homogenous

interaction of tensile; tear and stitch tear strengths that recommended for good leather. Hence good strengths leather due to the behavior of chrome and condensed tannins. Condensed tannins penetrate rapidly and aggregate more readily in the pelt fibres deposited a very large molecules that cross-linking through hydrogen bond to the peptide groups of the collagen. While chrome tan cross-links with polypeptide chains by principle valences through coordination bonds with the acidic amino acid side chains of the collagen cross-links induce strengthens properties that give the chrome tanned leathers its high quality. This agree with Srearam and Ramasami, (2004) which reported that the cross-links induce physical and mechanical properties that give the chrome tanned leathers its high quality chrome tanned leathers which are characterized by their light weight and high strength and disapproves to Roig et al 2012 conception that the trivalent chromium salts interact by chemical bonding with the carboxylic groups of collagen in the skin, giving to the leather its strength and stability properties. This process gives the leathers with excellent physical properties and high stability for the footwear manufacturing processes this agree to Sykes et al. (1982) who report that the metal retannage involved the formation of extended tannin-metal complexes that effectively crosslink the system rather than the induction of the formation of covalent bonds between the tannin and collagen or within the collagen polymer.

4.7.2.3 Elongation and distension and strength of grain of semi chrome and either indigenous or both improved tanned leathers and BIS standard

The elongation and distension and strength of grain of the goat leather tanned using semi chrome and either 100% of *Acacia nilotica* pods as the control or spray dried of blending; 20% *Azadirachta indica* and 80% *Acacia nilotica*; were shown in Figs (4.30 and 4.31). The result showed better elasticity, softness and flexibility of indigenous and blended tanned leather is fairly similar, it is agree with the standard of shoe upper leather and felt in recommended range,

IS, (2003) and SS, (2003). These results assume that the nature of indigenous tannin was changed since addition 20% 'Neem' it raised tannage power of 'Garad' and reduced consumption of tannin to the half than using 'Garad' alone. *Acacia nilotica* contain consider amount of hydrolysable tannin which undergo hydrolysis releasing nontannins molecules which reduced the tannin liquor acidity causes an osmotic effect collagen swell, likely plumps, that accelerates the penetration and fixation of the tannin producing very firm leather

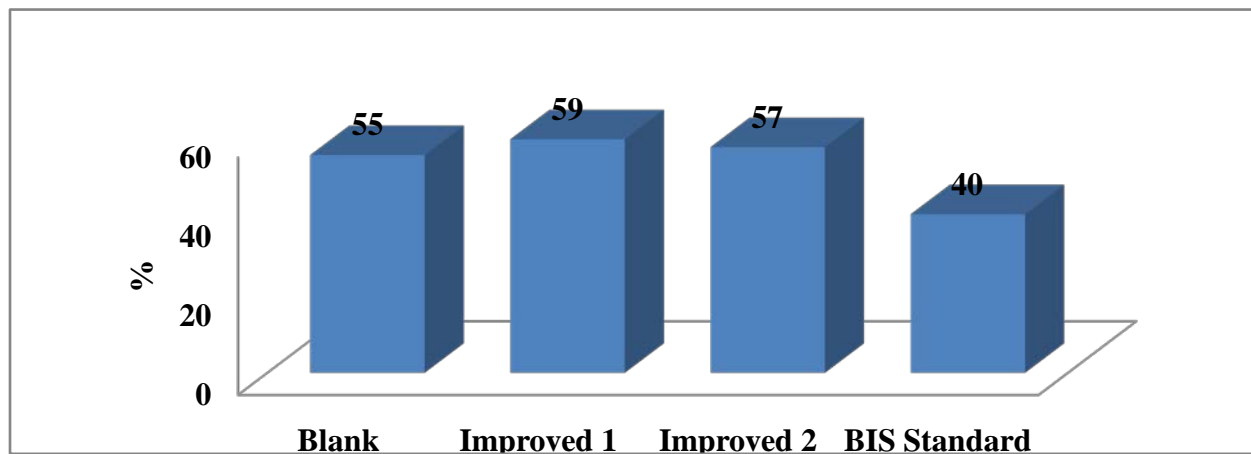


Figure 4. 30Elongation of semi chrome and either indigenous or both improved tanned leathers and BIS standard

Thus it is essential to control the pH of the tanning liquor using blending method, 'Garad – Neem' and natural salt, which organized the pelts swelling/ plumping and developed physical properties such as softness, flexibility, strength and thermal stability of yielded leather. This result confirm that increase in acid swelling/ plumping ruptures stabilizing cross-links in the fibre structure, short links, and releases additional hydrogen bond sites, peptides groups, for tannin fixation.

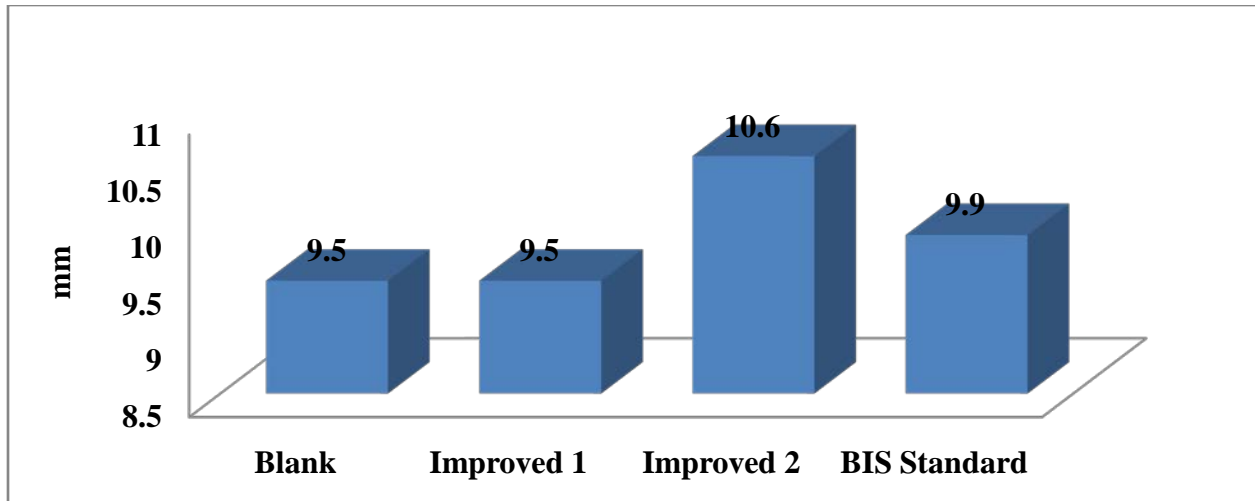


Figure 4. 31 Distension and strength of grain of semi chrome and either indigenous or improved tanned leathers and BIS standard

This is coincided with Looney, (2002) who mentioned that final pH values of 3.5-4.0 produce flexible leather where decreasing of the pH below than 3.0 produce very firm leather. Also the results assume that there are another reason to discuss achieved percentage of elongation, at break, values it is increase as a function of the amount of chromium present in the leather matrix this agree to Ravichanadran and Natchimuthu, (2005) conception.

4.7.2.4 The shrinkage temperature of semi chrome and either indigenous or improved tanned leathers

The hydrothermal stability of the goat leathers tanned using semi chrome and either 100% of *Acacia nilotica* pods control or spray dried of blending of 20% *Azadirachta indica* and 80% *Acacia nilotica* were shown in Fig (4.32). These results proposed that 20% of *Azadirachta indica* modify the tannin nature and modified 'Garad' tannage power and reduced amount of consumption tannin to half. *Azadirachta indica* bark wealthy in condensed tannin which acts as strength agent of the tanned leather while *Acacia nilotica* contain high hydrolysable tannin which is reduced thermal stability. Shrinkage temperature assesses the amount of tannin and can enhance the deposition through the cross-section of tanned leather, ended with better elasticity, softness and flexibility of leather.

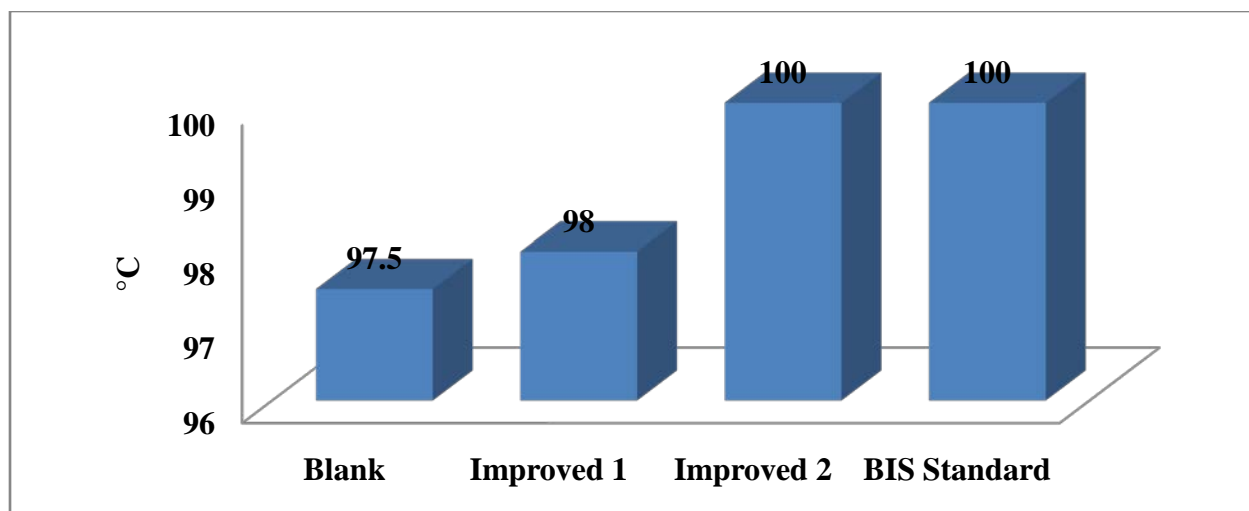


Figure 4. 32Shrinkage temperature of semi chrome and either indigenous or improved tanned leather and BIS standard

The results show that, the shrinkage temperature of the semi chrome/ modified tanned leather is higher degrees than that of semi chrome/ indigenous tanned leather one. Thus, the incorporation of the condensed into leather increases the thermal stability of the chrome/improved leather over that of the semi chrome/ indigenous tanned leather. This improvement in thermal stability can be attributed to the formation of condensed–collagen composite. Which can be explained by brought about multiple weak hydrogen bonding between the numerous hydroxyl groups (-OH) of the polyphenols and the countless hydrogen atoms of (NH) peptide groups, which support of the junction between the grain and corium. These results indicate that condensed filling up the empty parts of leather and tightness the leather fibers. This is consistent with Covington *et al*, postulation who concluded thermal stability of leather depends on the kinetic stability of the interaction between the tanning molecules and the protein side chains. Musa *et al* (2013) reported that typical shrinkage temperature for new leather tanned with vegetable tannins/ semi chrome is 104 °C.

4.7.3 Physico-chemical properties of leathers which produced using semi chrome and either indigenous or both modified tannins

To evaluate the modification processes which are applied to improve the tannin power of the indigenous tannins thus the quality of leathers which are produced using the methods in section (3.10) is examined, physico-chemical parameters, using the methods in section (3.11) and the results have been listing on the appendix.2: Table (8). Each factor of them is discussed individually and the discussions are showed as flowing

4.7.3.1 Moisture and fat contents of semi chrome and either indigenous or both improved tanned leathers

The moisture and free fat content of the goat leather tanned using semi chrome and either 100% of *Acacia nilotica* pods or spray dried blended 20% *Azadirachta indica* and 80% *Acacia nilotica* were shown in Fig (4.33 and 4.34). The results showed that elasticity and flexibility of leather agree with the standard of shoe upper leather, IS, (2003) and SS, (2003).

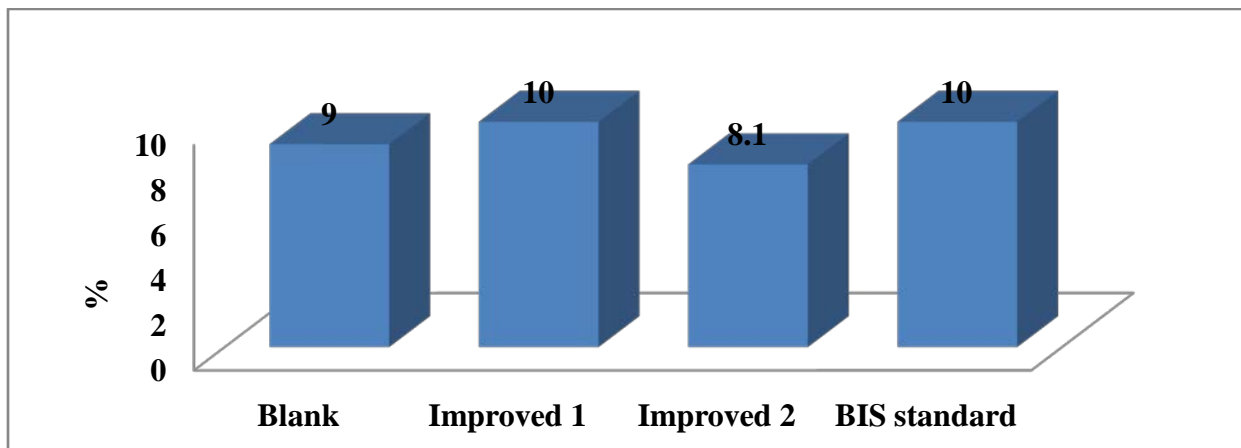


Figure 4. 33 Moisture content of semi chrome and either indigenous or both improved tanned leathers

Mentioned results suggested that both moisture and fat increase the fibre strengthens and flexibility of leather for a certain limit, firstly, strength is depend on angle of the fibre and their splitting value so low angle and high splitting value yielding high tensile strength. The amount of

flexibility is estimated using elongation, distension and strength of grain values which indicate if the amounts of moisture and fat content were reasonable in the fibers or not.

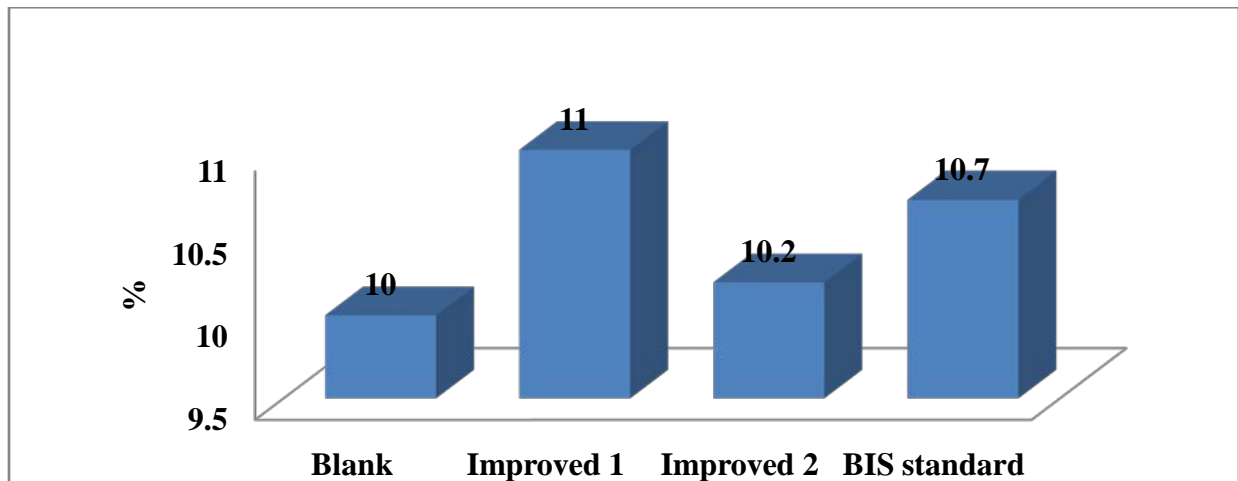


Figure 4. 34 Fat content of semi chrome and either indigenous or improved tanned leather
This coincided with Bitlisli et al. (2004) who reported that both physico-chemical properties changed according to amount of the fat content of the leather which increased with the increase of its fat content and then decreased after a certain limit. In generally the moisture and fats values present in both indigenous and both improved tanned leather are comparable to those of normal standard values.

4.7.3.2 Total Soluble of semi chrome and either indigenous or improved tanned leathers
Total soluble matter of the goat leather treated using semi chrome and either 100% of *Acacia nilotica* pods or blended 20% *Azadirachta indica* and 80% *Acacia nilotica* were shown in Fig (4.35). The results showed that both total soluble and degree of tannage exposed the fixation of tannin particles on the collagen fibers and the stability of leather.

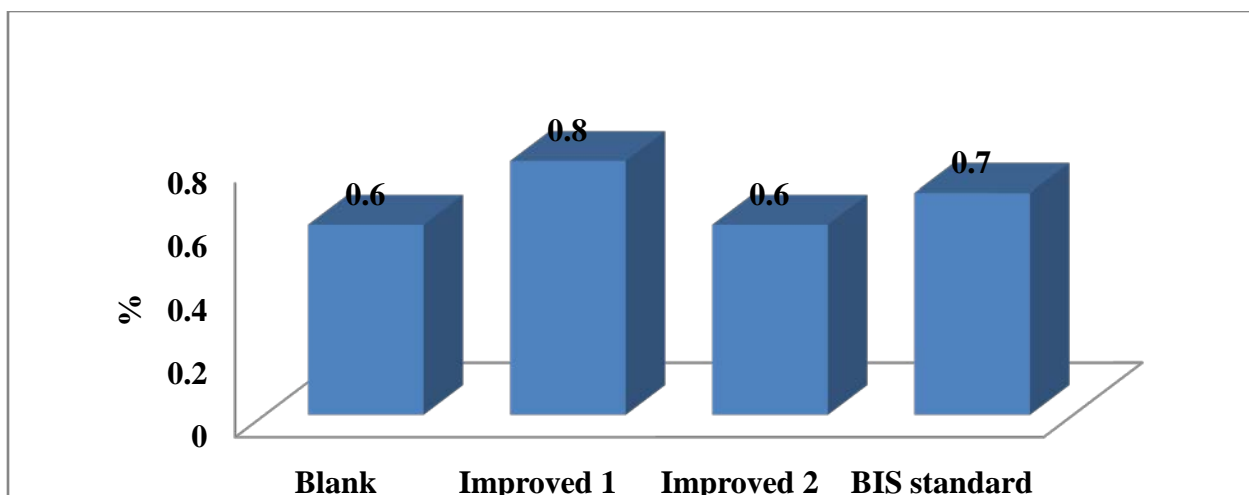


Figure 4. 35 Total soluble content of semi chrome and either indigenous or both improved tanned leathers and BIS standard

Semi chrome leather treated with the blended 'Garad-Neem' powder showed high stability due to fixation and low soluble matter of leather which agrees with the recommended standard of shoe upper leather, IS, (2003) and SS, (2003). These results suggested that semi chrome tanning developed the optimal condition of the formation of tanning matrix including the amount of tanning agents, outside and inside conditions of collagen and the reaction order with collagen. Where blended 'Garad-Neem' improved the tanning power of indigenous 'Garad' tannin and decreased amount of spending tannin to half. Condensed tannins, 'Neem' is more stable to hydrolysis and microbial attack than indigenous 'Garad' tannins, contain consider amount of hydrolysable tannins, this due to strong co-valent bonding between individual carbon atoms and the absence of ester links. Indigenous 'Garad' tannins hydrolysis decomposed the tannin and released sugar and organic acid that increased the soluble matter and decreased the degree of tannage, where condensed tannins are deposit large molecules size of the polyphenol, Reds, contained high numbers of -OH groups which deposit into the pelts fibre and cross-link through large amount of hydrogen bonds to peptide groups in collagen. As reported by Rao, (2001) these phenol-peptide strong interactions improve the leather stability.

4.7.3.3 Ash content of semi chrome and either indigenous or both improved tanned leather

Ash of the goat leather treated using semi chrome and either 100% of *Acacia nilotica* pods or blended 20% *Azadirachta indica* and 80% *Acacia nilotica* were shown in Fig (4.36). The results showed that ash content represented the inorganic content on the collagen fibers which is agree with the standard of shoe upper leather, IS, (2003) and SS, (2003).

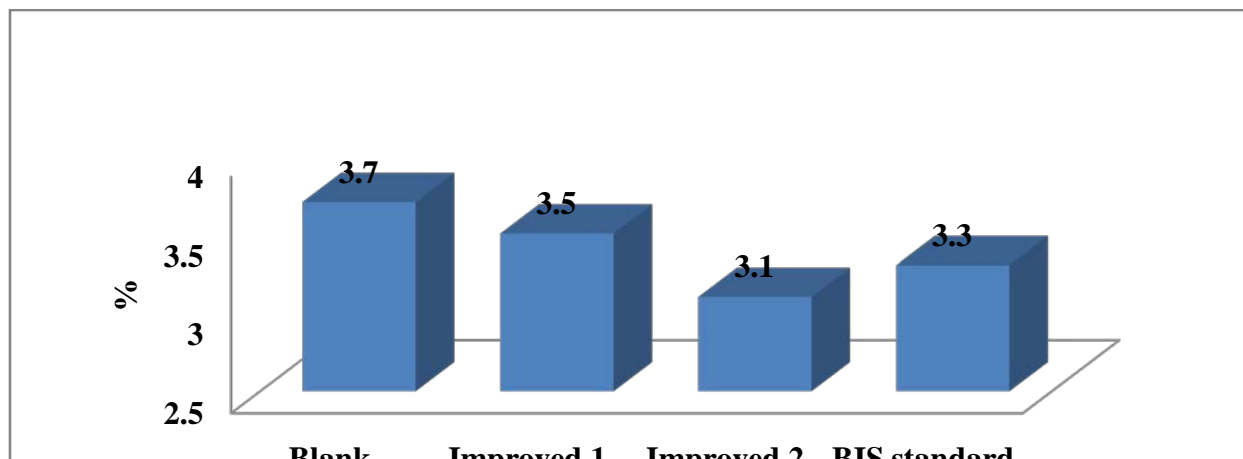


Figure 4. 36Ash content of semi chrome and either indigenous or both improved tanned leathers and BIS standard

4.7.3.4 Chrome content of semi chrome and either indigenous or improved tanned leathers

Chrome content of the goat leather treated using semi chrome and either 100% of *Acacia nilotica* pods or blended 20% *Azadirachta indica* and 80% *Acacia nilotica* were shown in Fig (4.37). The results showed that there were insignificant differences in chrome content represented between the semi chrome and either indigenous or improved tanned leathers and it is lower than standard

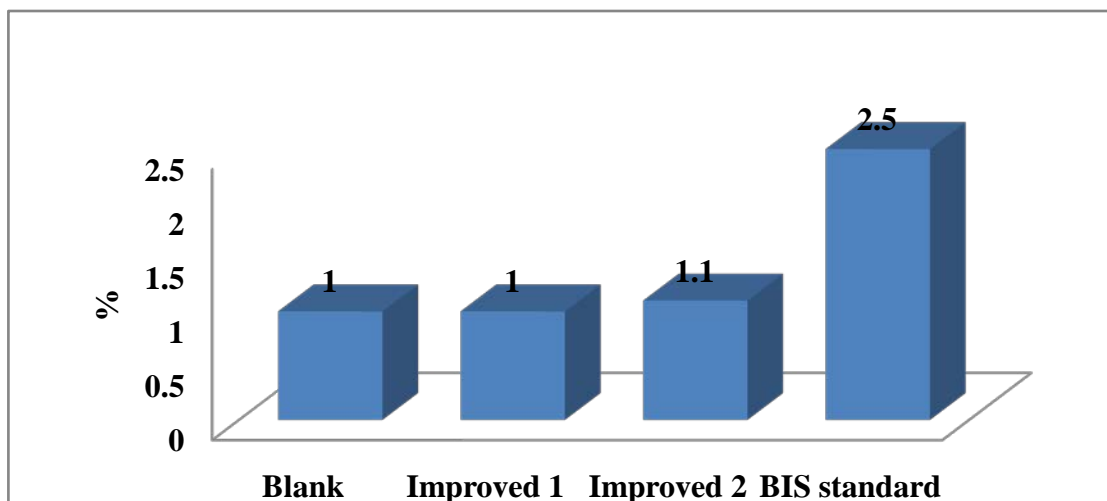


Figure 4. 37 Chrome content of semi chrome and either indigenous or both improved tanned leather

4.7.4 Statistical assessment of semi chrome and either indigenous or both improved tanned leathers

Table 4. 6 Anova test for mechanical and physicochemical properties of tanned leathers using either both improved or indigenous tannins

No	Description	Mean	Std	Sig. 0.05
1	Thickness	1.30	1.1	0.00
2	Tensile strength	21.2	22.0	0.00
3	Elongation	59	50	0.00
4	Tear strength	4.3	5.2	0.00
5	Stitch tear strength	12.6	11.8	0.00
6	Distension and strength of grain	9.5	10.6	0.00
7	Shrinkage temperature	98	100	0.00
8	Moisture	9.2	1.04	0.00
9	Fat	10.7	0.44	0.00
10	Total soluble matter	0.7	0.11	0.08
11	Chrome content	1.1	0.07	0.08

Statistical data of SPSS analysis shows that there are significant differences of mechanical and physico-chemical properties of produced leathers using both improved tannins comparing indigenous tanned leathers. Table (4.6) showed statistical analysis at $P < 0.05$ level as described by Gomez and Gomez, (1984) to evaluate the significant differences between the treatments.

4.8 Physico-chemical properties of indigenous and both improved tanning wastewater

4.8.1 Calculation of physic-chemical properties of indigenous and both improved tanning wastewater

4.8.1.1 Biological oxygen demand

The BOD were determined conducting the method (3.10.1) and were calculated by equation (4.19). The results are listed in appendix.2: Table (10) for the waste water:

$$\text{BOD} = \frac{(\text{DO1} - \text{DO2}) \times 1000}{\text{Volume of sample taken}} \text{ mg/liter} \quad \text{equ.4.19}$$

Where;

DO1 is initial dissolve oxygen in the sample.

DO2 is dissolve oxygen in the sample after 5 days.

4.8.1.2 Chemical oxygen demand

The COD were determined conducting the method (3.10.2) and were calculated by equation (4.20). The results are listed in appendix.2: Table (10) for the waste water:

$$\text{Chemical oxygen demand} = \frac{(\text{A} - \text{B}) \text{M} \times 8000}{\text{Volume taken}} \text{ mg/liter} \quad \text{equ.4.20}$$

Where;

A is the volume of FAS used in blank.

B is the volume of FAS used in sample.

M is the molarities of FAS.

4.8.2 Total solid of indigenous and both improved tanning waste water

Total solid, TS or tanning waste materials of the yielded waste water of goat leather treated using either 100% of *Acacia nilotica* pods or blended 20% *Azadirachta indica* and 80% *Acacia nilotica* were shown in Fig (4.40). The results showed that total solid of indigenous tanned waste water is greater high compare to total solid of both improved tanned leather waste water.

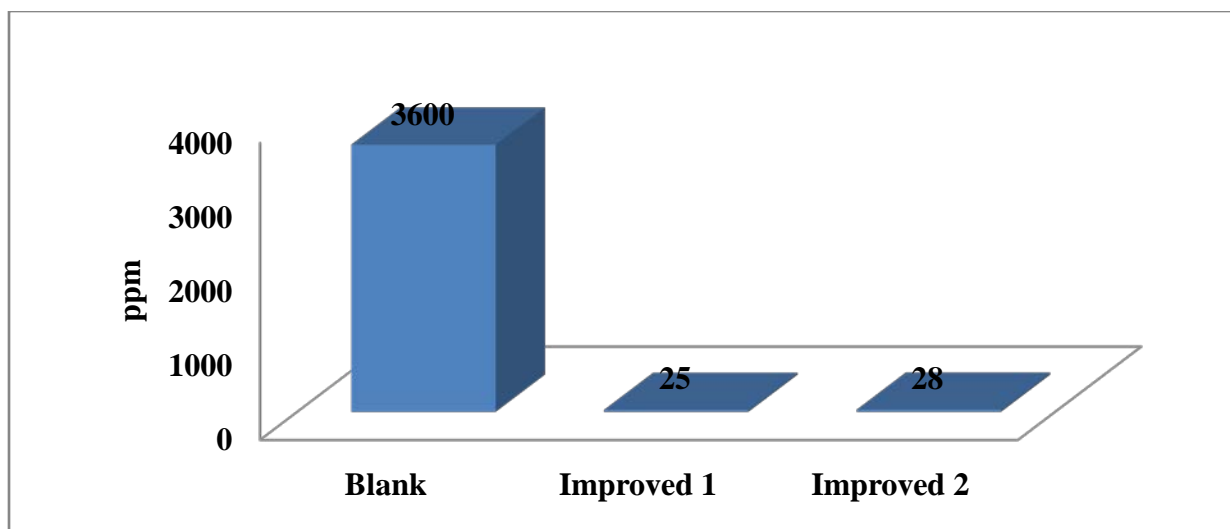


Figure 4. 38 Total solid of indigenous and both improved tanning wastewater

The result suggested that devolvement of indigenous tanning and diverts to spray drier form widely decrease tanning waste materials of the both modified tannins compared to indigenous tanning material. The insoluble wooden materials in indigenous tanning are responsible about highest values of decrease tanning waste materials on drain wastewater which undergo precipitate as sludge and block the sewerage system; this result agreed with Barman, (2008) estimated in his study on the deseeded 'Garad', and he reported that the insoluble matters of 'Garad' found to be more than 40%, where modified tannins produced 0 % percentage of insoluble matters. And spray dried powder is extremely soluble 100% and has no any effect on blocking of sewerage system.

4.8.3 Total dissolve solid of indigenous and both improved tanning waste water

Total dissolve solid, TDS, or residual tannin levels of the yielded waste water of goat leather tanned using either 100% of *Acacia nilotica* pods or blended 20% *Azadirachta indica* and 80% *Acacia nilotica* were shown in Fig (4.41). The results showed that there are insignificant differences in residual tannin levels between both improved tanned leather wastewater in compare to indigenous tanned wastewater.

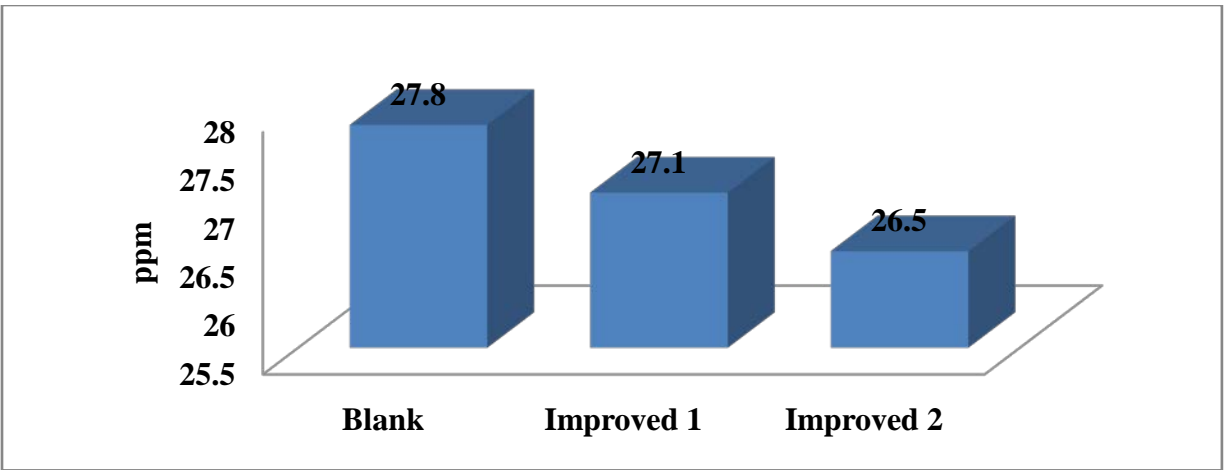


Figure 4. 39Total dissolve solid of indigenous and both improved tanning wastewater

4.8.4 Biological oxygen demand of indigenous and both improved tanning waste water

Biological oxygen demand, BOD, of the yielded waste water of goat leather tanned using either 100% of *Acacia nilotica* pods or blended 20% *Azadirachta indica* and 80% *Acacia nilotica* were shown in Fig (4.42). The results showed that there are significant differences in BOD. The biological oxygen demand of both improved tanned waste water were lower in compare to indigenous waste water.

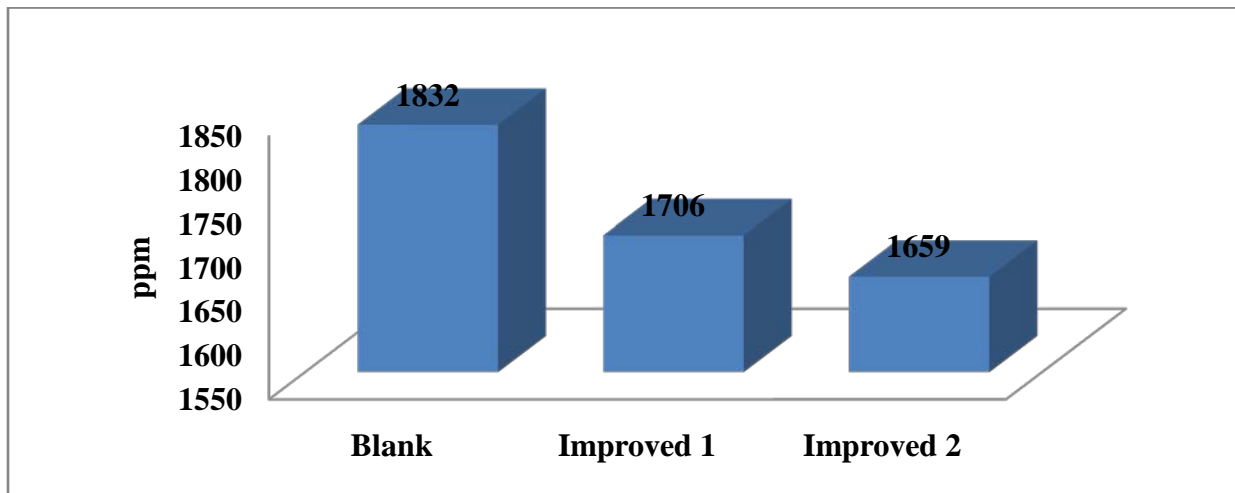


Figure 4. 40 Biological oxygen demand of indigenous and both improved tanning waste water

The results suggested that the addition of 20% *Azadirachta indica* changed the tannin behavior and elevated tanning power of *Acacia nilotica* which increased the affinity of tannins to collagen fibre where the pelts absorbed high amount of tannins and as a result of that the wastewater

carried appositely BOD level, Generally BOD is a measure of the oxygen consuming capacity of water containing organic matter. Organic matter by itself does not cause direct harm to aquatic environment, but it exerts an indirect effect there by depressing the dissolved oxygen content of the water. The oxygen content is an essential water quality parameter and its reduction causes stress on the ecosystem. As an indigenous tanned wastewater, a total lack of dissolved oxygen as a result of high BOD which can kill all natural life in an effected area. This agree with Svoboova et al. 1993 who reported that

4.8.5 Chemical oxygen demand of indigenous and both improved tanning waste water

Chemical oxygen demand, COD, of the yielded waste water of goat leather tanned using either 100% of *Acacia nilotica* pods or blended 20% *Azadirachta indica* and 80% *Acacia nilotica* were shown in Fig (4.43). The results showed that there are significant differences in both improved tanned wastewater COD in compare to indigenous tanned wastewater.

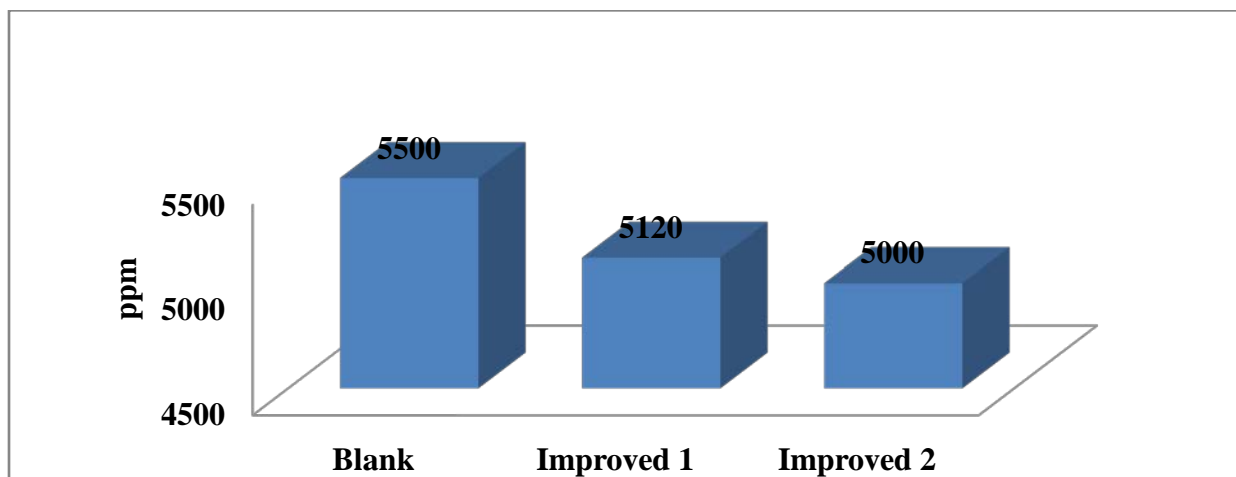


Figure 4. 41Chemical oxygen demand of indigenous and both improved tanning wastewater

The results postulate that addition of 20% *Azadirachta indica* vary the nature of tannin and either tanning reactivity of *Acacia nilotica* which accelerate the fixation of tannins on collagen fibre whereas lower of improved tanned wastewater COD are indicates that the amount of organic wastes and the other chemicals are lower compare to indigenous tanned wastewater. If effluent

with the high demand oxygen the sensitive balance maintained in the water becomes overloaded. Oxygen is stripped from the water causing oxygen lack so dependent plants, bacteria, and fish impel to die. The outcome is an environment populated by non-oxygen dependent (anaerobic) bacteria leading to toxic water conditions. These agree with Soha Nassar, (1999) she reported that the healthy wastewater can tolerate substances with low levels of oxygen demand.

4.8.6 Statistical assessment of either indigenous or both modified tanning materials analysis

Table 4.7 Anova test for physico-chemical properties of tanned wastewater using either both improved or indigenous tannins. Statistical data of SPSS analysis shows that there are significant differences of physicochemical properties of improved indigenous tannins comparing indigenous tannin. Table (4.7) showed statistical analysis at $P < 0.05$ level as described by Gomez and Gomez, (1984) to evaluate the significant differences between the treatments.

Table 4. 7 Statistical assessment of wastewater of indigenous and modified tanning analysis:

No	Description	Mean	Std	Sig. 0.05
1	Chemical oxygen demand	520	226	0.00
2	Biological oxygen demand	1170	16	0.00
3	Total dissolve solid	24.3	2.63	0.36
4	Total solid	1217	1726	0.00

CHAPTER FIVE
CONCLUSION AND RECOMMENDATION

Chapter five

Conclusion and recommendation

5.1 Conclusion

Physico- chemical properties of 'Garad', leaves and bark of 'Neem' and calyxes and bark of 'Karkady' were determined. The results showed that deseeds and powder of 'Garad' and bark of 'Neem' had a high tanning power whilst leaves of 'Neem' does not contain tannins but it rich in organic sulpher compounds and nontannins materials, whereas screening of calyxes and bark of 'Karkady' showed that both of them contained traces amount of tannins and plenty amount of oxalate salts, which showed high efficiency to chalet the iron.

Controlling system using dried leaves of 'Neem' powder and heating to 60°C were designed and the results showed that the system was very effectiveness to control mould growth and dropped the viscosity of '80% Garad – 20% Neem' tanning liquor to apposite level and then the produced liquor of rotary system was subsequently spray-drying and the physico-chemical properties of the spray-dried powder showed that the modified tanning material is completely water soluble material and yields liquor with pleaser brown colour, high tannin content as well as acceptable tannin/non-tannin ratio.

The spray-dried powder of 80% 'Garad' and 20% 'Neem' was applied for full vegetable and semi chrome tanning to produce shoe upper leathers so the mechanical and physio-chemical properties of tanned leathers were determined and compared to those of control leather the results explained that the leather had good thermal stability and organoleptic properties that is important for commercial viability of the tanning system. Large collective actions of the power quality of the leather increase with homogenous interaction on hydrothermal stability are recommended for good leather. The physical properties of the leathers prepared compiled quite well with the standard requirements. As far as the physical and technical properties of the crust leather

concerned; the experimental trial revealed the best performance in terms of softness, fullness, grain stability and general appearance. This sequence, besides the good properties of the final leather is also easily applicable from an industrial point of view. Whereas physico-chemical properties of wastewater revealed tanning using improved powder is very eco-friendly tannage. Involve leaves and bark of 'Neem' which available as the timber waste and bark of 'Karkady' harvesting waste to improve the indigenous 'Garad' tannins are very feasible and adding economical value to utilization this raw material

5.2 Recommendations

The research recommends that:

- It is highly recommended that scientific methods must be adopted in harvesting and storage of *Acacia nilotica* pods; because it is seasonal crop contains high tannin concentration that susceptible to microbial damage when harvested and stored in wet climate conditions
- It is highly recommended that scientific leaching methods must be studied and adopted on other Sudanese natural tannins containing plants with economical invitation.
- Researches must be conducted to utilize the blended national tanning materials for eco-friendly tannage with better properties.
- Research's to be conducted to utilize the blended national tanning materials in recommended having eco friendly tannage with better properties with different plants and concentrations. Phyto-chemical investigation of tannins in Sudanese plants is recommended.
- Research's to be conducted to evaluate the economical feasible of utilization of leaves and bark of 'Neem' and bark of 'Karkady' in indigenous 'Garad' tannins manufacture.
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APPENDIXES

Appendixes

1. Appendix 1



Appendix 1 Photo.1 Twigs and flowering of *acacia nilotica*



Appendix 2 photo .2 Pods of *acacia nilotica*



Appendix 3 Photo.3 Bark of *acacia nilotica*

2. Appendix 2

Appendix.2: Table 1 Tannin content of blended 'Garad-Neem' according to 'Neem' addition

Description	1	2	3	4	5	6	7	8	9	10	11
Addition of Neem %	0	5	10	15	20	25	30	35	40	45	50
Tannin content %	60	59	58	57	56	51	46	43	42	41	40

Appendix.2: Table 2 The effectiveness of 'Neem' leaves on the viscosity of indigenous 'Garad' tanning materials

Description	1	2	3	4	5	6	7	8	9	10	11
Addition of Neem leaves %	0.0	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5
Viscosity of blended liquor	74	72	66	61	54	50	45	38	30	25	19

Appendix.2: Table 3 The effectiveness of controlling mould growth on 'Garad' tanning liquor staying

Description	1	2	3	4	5	6	7	8	9	10	11
<i>Acacia Nilotica</i> pods/ g	100	99.5	99	98.5	98	97.5	97	96.5	96	95.5	95
<i>Azadirachta Indica</i> leaves/ g	0	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5
Times/ days	1	1	4	4	7	7	7	7	12	12	>30

Appendix.2: Table 4: Physio-chemical properties of controlled and uncontrolled tanning liquors

No	Description	Untreated	Treated	Lost tannin	
1	Tannin %	23.4	38.0	14.6	
2	Nontannin %	28.5	21.1		
3	Colour	Yellow	3.6		3.2
		Red	2.5		1.5
		Blue	0.6		0.1
4	pH at 25°C	3.8	4.8		
5	preventing tannins%	38.4			

Appendix.2: Table 5 Physio-chemical properties of indigenous 'Garad' and both improved tanned leathers and myrobalan standard

No	Description	Blank	Improved 1 [*]	Improved 2 ^{**}	Myrobalan	
1	Moisture %	7.5	6.3	6.4	6	
2	Total solid %	92.5	93.6	93.8	94	
3	Total soluble solid %	64.4	92.8	92.7	96	
4	Non tannin %	24.8	36.8	36.7	36	
5	Tannin %	32.1	56.0	55.0	60	
6	Tannin/Nontannin Ratio	1.3	1.5	1.5	1.7	
7	Colour	Red	1.6	1.8	1.6	1.5
		Yellow	3.1	3.0	3.2	3
		Blue	0.6	0	0	0
8	pH at 25°C	3.8	4.1	4.6	3.5	

*Improved₁ = bleached with 5% *Hibiscus sabdariffa* cycles.

**Improved₂ = bleached with 5% *Hibiscus sabdariffa* bark

Appendix.2: Table 6 physical properties of leathers of indigenous 'Garad' and both improved tanned leathers and myrobalan standard

No	Description	Blank	Improved 1*	Improved 2**	Myrobalan
1	Thickness mm	1.00	1.20	1.15	1.0
2	Tensile strength N/cm ²	18.7	20.0	20.0	20.0
3	Elongation %	37	40.3	40.5	70
4	Tear strength N/cm	4.1	4.7	4.4	4.0
5	Stitch tear strength N/cm	10.0	13.0	11.8	10
6	Distension and strength of grain /mm	8.0	9.4	8.9	8
7	Shrinkage temperature °C	74	81	82	77.5

Appendix.2: Table 7 Physio-chemical properties of indigenous 'Garad' and both improved tanned leathers and myrobalan standard

No	Description	Blank	Improved 1	Improved 2	Myrobalan
1	Moisture%	10.4	10.2	10.0	<10*
2	Ash%	1.7	1.9	1.5	2
3	Fat%	9.5	8.9	8.9	8-15
4	Total soluble%	1.5	2.6	2.3	≤ 6
5	Hide substance%	46.2	51	49.3	-
6	Degree of tannage%	48	50	50	≥ 50

Appendix.2: Table 8 Mechanical properties of semi chrome /indigenous 'Garad' and both improved tanned leathers and myrobalan standard

No	Description	Blank*	Improved 1 **	Improved 2 **	BIS Standards ***
1	Thickness mm	1.1	1.3	1.1	1.0±0.1
2	Tensile strength N/cm ²	20.9	21.2	22.0	20.0
3	Elongation %	5.5	59	50	40-65
4	Tear strength N/cm	4.3	4.3	5.2	30
5	Stitch tear strength N/cm	11.0	12.6	11.8	100
6	Distension and strength of grain /mm	9.5	9.5	10.6	7
7	Shrinkage temperature °C	97.5	98	100	102±2

* = Leather samples which tanned using 2% chrome and 24% of 'Garad'.

**= Leather samples which tanned using 2% chrome and 12% of modified tannin of 'Garad'.

***= Indian Standard

Appendix.2: Table 9 physico-chemical properties of semi chrome/indigenous 'Garad' and both improved tanned leathers and myrobalan standard

No	Description	Blank*	Improved 1 **	Improved 2 **	Previous studies
1	Moisture%	9.0	10	8.1	9.2
2	Ash%	3.7	3.5	3.1	3.3
3	Fat%	10	11	10.2	10.7
4	Total soluble%	0.6	0.8	0.6	0.7
5	Chrome content%	1.0	1.0	1.12	1.1

Appendix.2: Table 10 Physico-chemical properties of wastewater of indigenous and both improved tanned methods

No	Pollutant	Blank	Improved 1	Improved 2
1	Chemical oxygen demand /ppm	5500	5120	5000
2	Biological oxygen demand /ppm	1832	1706	1659
3	Total dissolve solid mg/l	27.8	22.6	22.5
4	Total solid mg/l	3600	25	28