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Evaluation of chemical compounds in *Plectranthus barbatus* leaves extract for application in reduction of tannery wastewater toxicity

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ABSTRACT

Plectranthus barbatus Andr. grows in Kenya, sub-Saharan Africa, Australia, Brazil and Asia and is one of the most important species of the Lamiaceae family. The plant is widely mentioned in traditional medicine in Africa and Asia. Some of the compounds previously isolated from the plant include diterpenoids, phenolic acids and essential oils. The objective of the study was to evaluate and determine the presence of chemical compounds in *Plectranthus barbatus* Andr. leaves extract of tannin nature that can be beneficial ingredients in processing clean leather and at the same time reduce environmental pollution. The Plant's leaves were collected from Nyamira County then dried and ground to desired mesh before extraction was done with water and 80 % methanol in water. The methanolic solid extract that was recovered after freeze drying was subjected to column chromatography. The pure fractions were analyzed using Nuclear Magnetic Resonance spectroscopy and compared to those previously analyzed using High Pressure Liquid Chromatography. Some of the compounds isolated include phenolics e.g. Para-Hydroxybenzoic acid and Diterpenes. Water solid extract was used in pre-tanning and re-tanning applications followed by analysis of Biological Oxygen Demand, Chemical Oxygen Demand, pH and total chrome content of respective wastewaters. Tannery liquor from re-tanning and pre-tanning combinations with *Plecranthus barbatus* leaves extract showed reduced toxicity to the environment with pH of 7.97 and 2.96 respectively as compared to chrome tannage liquor that recorded a relatively more acidic pH of 2.30. Biological Oxygen Demand, Chemical Oxygen Demand and chrome content levels were 230.00 mg/l, 4520.00 mg/l and 9.69 ppm respectively for effluent from *Plectranthus barbatus* retannage against 320.10 mg/l, 2331.20 and 5.03 ppm respectively from pretannage of the same extract. Permissible limits for pH, Biological Oxygen Demand, Chemical Oxygen Demand and total chrome in discharged tannery wastewater are 5.5 – 10.0, 125 mg/l – 1000 mg/l, 300 mg/l – 3000 mg/l, and 1.0 ppm – 10.0 ppm respectively. Pretanning with *Plectranthus barbatus* leaves extract during leather processing was more effective is reduction of tannery wastewater toxicity although, the use of pretanning and retanning in a single tannage might yield more promising results.

Keywords: Chromatography, NMR spectroscopy, Tanning, Diterpenes, Phenolic acids, Chrome.

INTRODUCTION

Plectranthus barbatus Andr. is one of the most important species of the genus *Plectranthus* in the family Lamiaceae (Labiatae) that grows perennially in the tropics and subtropics of Africa and India. It also grows in parts of Pakistan, Brazil, China and Sri Lanka [1]. The plant which grows as a shrub is also known by various names which include *Omoroka* (Kisii), *Plecranthus forskohlii* Briq, *Coleus forskohlii* Briq, *Mumbu* (Digo) and *malva santa* (Brazil) [2]. The species is also known for a broad range of traditional uses that are not only limited to herbal medicine but also as an insecticide in Kenya and Gabon. Additionally, the shrub is also utilized in conditioning of hides and skins, making manure, animal feed, enhancing ripening of bananas and as vegetable in Yemen [2].

Phytochemistry of *Plectranthus barbatus* together with *Coleus forskohlii* has shown the presence of tannins, terpenoids, flavonoids and alkaloids. Flavonoids are polyphenolic compounds that have been reported by Ganash and Qanash [3] as having antioxidizing properties that have been used medicinally. Furthermore, ongoing studies see the possibility of harnessing the same property in clean manufacturing processes especially leather production. Antioxidizing characteristics of plant extracts have been linked to the activity of phenolics which have been shown to scavenge free radicals and green tea phenolics, ellagic acid together with gallic acid are major compounds in this chemistry. Similarly, p-hydroxybenzoic acid has also been reported as an antioxidant against free radicals [4]. Additionally, other phenolic compounds of interest that have been exclusively mentioned in folk medicine include isoferulic acid, ferulic acid, chlorogenic acid, cinnamic acid and benzoic acid [5].

Plectranthus barbatus is one of the most widely studied species and apart from the diterpenoid Forskolin which has numerous biological and pharmacological applications, various compounds have also been isolated [2]. The compounds include abietane diterpenoids for instance plectrinon A, barbatusin, barbitusol, coleon C and 8,13-epoxy-labd-14-en-11-one which is part of the 43 labdane diterpenoids so far studied [7]. In addition, phenolic derivatives such as nepetoidins A and B together with rosmarinic acid have been isolated although nepetoidins are important antioxidants [7] other than the later. Other studies have also documented presence of simple phenolics, phenolic acids, hydrolysable tannins, coumarins, condensed tannins, lignans, stilbenes and lignin [8].

Separately, Nuclear Magnetic Resonance (NMR) studies involving *Plectranthus barbatus* have revealed the presence of Coleon F, Plectrinon B and Plectrinon A in leaves extracts followed by 14-Deoxycoleon U, 9-Deoxyforskolin (7β-acetoxy-1α, 6β-dihydroxy-8, 13-epoxy-labd-14-en-11-one) in root aqueous extracts [1]. Additionally, the following compounds were also isolated from the whole plant in China: 3-Hydroxyforskolin, 3-Hydroxyisoforskolin, Forskoditerpene A (5β,9β,10α,12β-9,12-cyclo-7,13E-labdadien-15-oic acid), 12-Hydroxy-8,13E-labdadien-15-oic acid Coleolic acid (11-ol,13-Me,8(9),13(14)Z-labdadien-15-oic acid), Coleonic acid (11-one,13-Me,8(9),13(14)Z-labdadien-15-oic acid) [9,10,11]. Related research done by Ganash and Qanash [3] used High Performance Liquid Chromatography (HPLC) detection which confirmed the availability of various phenolic acids for instance Gallic acid, Ferulic acid, Coumaric acid, Salicylic acid, Chlorogenic acid and Benzoic acid. This study therefore, was focused on isolating and evaluating compounds that were either derivatives of tannins or those that are of hydrolysable tannin nature and any other compound that may form linkages in situ with collagen to form complex molecules and at the same time minimize residual chrome in effluent and free chrome in leather [12].

Pretanning operation with organic compounds during leather processing has previously posted valuable results in regard to exhaustion of chrome from tanning floats and increase of chrome fixation in collagen [13]. Previous scientific advances focused on controlling of chromium in leather through the use of phenol hydroxyls as pretanning agents showed decreased chromium oxide concentration in tannery wastewater from 1.42 g/l to 0.60g/l [14]. Furthermore, the use of vegetable tannins in preventing formation of Cr (VI) in leather during leather production and eventual release of the mentioned species to the environment found that the hydrolysable type (tara, chestnut, sumac, myrobalans) were more effective compared to condensed tannins (mimosa, quebracho) [15]. Although recycling of chrome floats and chrome recovery through precipitation considerably reduce the threat of chrome pollution, it is evident that much can be done to realize zero or near zero discharge of chrome to the environment. Additionally, pretanning wet leather with organic vegetable tanning compounds has minimized the occurrence of unbound chrome in leather and decreased residual chrome in tanning float due to increased chrome uptake [16]. Elsewhere, such observations have been viewed as better options in realizing a cleaner environment with minimum costs other than treatment of chrome laden effluent.

MATERIALS AND METHODS

Plant material preparation

Plectranthus barbatus leaves were collected by plucking from Gesima ward in Nyamira County in the Nyanza region of Kenya. The leaves were then packed in sisal bags and transported to the Leather testing Laboratory at the Kenya Industrial Research and Development Institute (KIRDI) where they were shredded followed by air drying for two weeks. The dry leaves were then ground in a *wiley mill* to yield fine powder of desired mesh (2 mm) according to SLC 112[17].

Solid extract preparation

Portions of 240 g of the powder were extracted separately with 1,200 ml of water and 80% methanol in water at the Chemistry department in the Faculty of Science and Technology in the University of Nairobi. In addition, the resultant liquid extract originating from 80% methanol in water was concentrated by rotavaping (Buchi Rotavapor R II) to eliminate the organic solvent. The collected reduced liquid extract together with the aqueous extract were further freeze dried using Freeze dryer (MRC instrument) at KIRDI. Subsequently the respective solid extracts were put in zip lock plastic bags and kept frozen awaiting further analysis.

Column chromatography separation

The procedure was carried out at the Natural products laboratory at the Chemistry department in the Faculty of Science and Technology in the University of Nairobi. A long cylindrical glass column was set and packed with silica gel (mesh 60-120, Alpha Chemika) using pure hexane for 6 hrs. Methanolic dry solid extract was then adsorbed in silica gel before being ground into fine powder in a mortar. The powder was then loaded slowly into the column and plugged with cotton wool before being countered with 100% hexane. Additionally, the sample was eluted with organic solvents of increasing polarity. This was followed by collecting 500 ml of solvents containing targeted fractions which then were reduced by rotavaping before the fractions were transferred into clean vials and labelled respectively.

Purification of fractions and structure determination

The collected fractions were spotted on Thin Layer Chromatography (TLC) plates to check their profile and those that showed more than one spot were subjected to purification through sephadex. The separate samples were dissolved in 1:1 Dichloromethane: Methanol then introduced keenly on sephadex packed in a column and then eluted slowly using the same solvent system they were dissolved in. Small fractions were then collected and spotted on TLC plates to confirm their purity. Impure fractions were further purified through Preparative Thin Layer Chromatography (PTLC). Later the pure fractions were taken for structure determination using Nuclear Magnetic Resonance (NMR) spectroscopy machine available at the department of Chemistry in the University of Nairobi. Then the resultant NMR spectra were analyzed for structure determination and the names of the compounds were proposed.

Leather processing

Pretanning

Plectranthus barbatus 5% leaves extract and 5% mimosa were separately used in pretanning pickled pelts processed from wet salted goat skins that were later tanned with 8% chrome in 100% float. Triplicate samples measuring 16cm by 16 cm were processed separately and liquors from respective baths collected in clean bottles. Later total chrome residue content, pH, BOD and COD in the resultant effluents were determined and compared with chrome solo tannage.

Retanning

Pickled goat skin pelts were first tanned with 8% chrome until Ø before they were re-tanned with an offer of 5% mimosa and 5% *Plectranthus barbatus* powder separately for a further 120 minutes. Effluent samples were collected respectively from each tannage for analysis of BOD, COD, pH and total chrome concentration. The results were compared among each tannage and also with chrome solo tannage.

Analysis of total chrome in effluent

50 ml of each effluent sample was digested separately after transferring the filtered samples into 250 ml digestion tubes. To each sample 5 ml of Nitric acid (HNO_3) was added together with some pumice boiling chips. After shaking well for two minutes the tubes were then placed in a rack in a block digester and gently heated for 1.5 hours until the mixture had reduced by about 20 ml. Further the mixture was cooled and to it 10 ml of another mixture containing Nitric acid (HNO_3) and Perchloric acid ($HClO_4$) prepared in the ratio of 2:1 respectively was added. Later the tubes were heated in the block digester for 2.0 hours by gently increasing the temperature up to 180℃. Afterwards, the resulting mixture was cooled and to it about 15 ml of deionized water added followed by shaking well before being topped up to 50 ml. Additionally, the mixture was filtered using Whatman filter paper No.1 before the concentration of total chrome in each sample was determined by Atomic Absorption Spectrophotometer (AAS) (Buck Scientific, 210 VGP) [18].

Determination of Biological Oxygen Demand (BOD) in effluent

The quantity of oxygen necessary to biologically stabilize one litre of sampled tannery effluent within five (5) days at 20℃ is considered to be the Biological Oxygen Demand (BOD) of the wastewater. Five litres of distilled water was aerated for 3 hours and 30 minutes. In 300 milliliters (300 ml) BOD bottles, the effluent samples were separately mixed with aerated water and stoppered before being kept in the BOD incubator for 5 days. BOD_5 was then determined according to the method described by Clesceri et al. [19].

Determination of Chemical Oxygen Demand (COD) in effluent

Chemical Oxygen Demand (COD) in effluent analysis is the amount of oxygen (mg) that is needed to completely oxidize chemicals available in one litre of the sample under specified conditions. 2.5 ml of each sample was measured in a tube and to it 1.5 ml of 0.25 N Potassium dichromate solution was added followed by a spatulaful of Mercuric sulphate and a further 3.5 ml of COD acid. The mixtures were then put in the COD incubator at 150℃ for 120 minutes. Later the solutions were cooled and titrated against 0.1 N Ferrous ammonium Sulphate using a ferroin indicator until a reddish brown colour was observed. 25 ml distilled water was used as a blank and then the COD for the 5 samples was determined according to Clesceri et al. [19].

Determination of pH

The pH of the respective effluent samples was measured using a pH metre (Toledo) by taking three measurements from each category. The pH values were then averaged and recorded in a table for comparison.

RESULTS

Freeze dried *Plecranthus barbatus* solid extract yielded a dark brown powder that was packed in Zip lock bag as shown in the photograph below:

Plate 1: *Plectranthus barbatus* leaves solid extract

Column chromatography indicated that the targeted compounds of tannin nature that comprise phenolic acids were relatively unstable on silica gel, some of the compounds that were detected by the Nuclear Magnetic Resonance (NMR) spectroscopy machine include Diterpenes and 4-hydroxybenzoic acid shown in ^{1}HNMR spectra in fig 1 and 2.

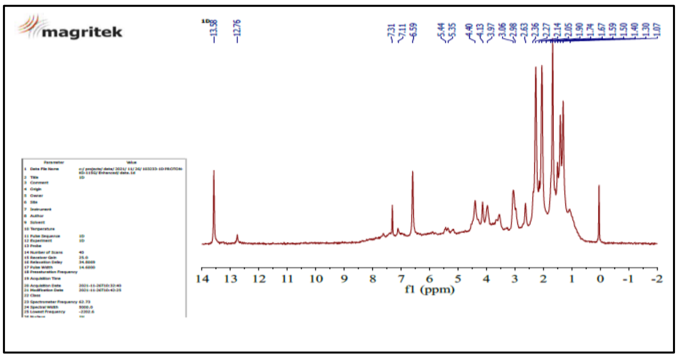

Fig 1: ^{1}HNMR spectrum for diterpene

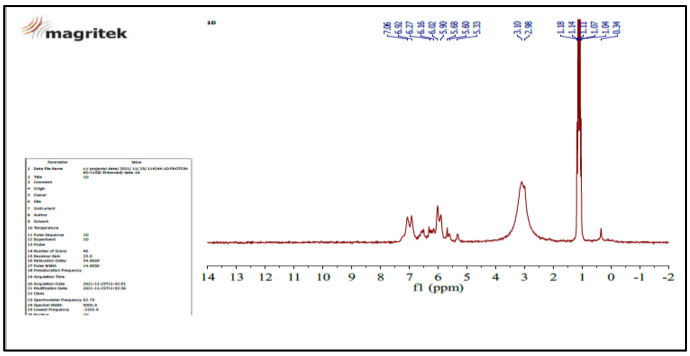

Fig 2: ^{1}HNMR spectrum for 4-hydroxybenzoic acid

The chemical shift shown in the proton Nuclear Magnetic Resonance (^{1}HNMR) spectrum in figure 1 indicated the presence of H-bonding because of the predominant peak arising from a highly deshielded proton with the chemical shift of 13.5. Other peaks signified aromatic protons hence the closest prediction proposed the structure of a diterpene shown in figure 3. Additionally, the analysis of ^{1}HNMR spectrum in figure 2 showed the presence of aromatic protons with chemical shifts between 6.5 to 8.0 with doublet peaks hence the predicted structure is as shown in figure 4.

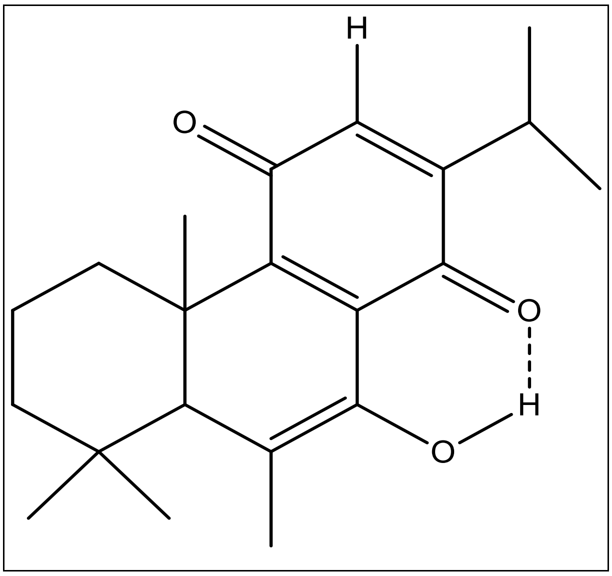

Figure 3: Diterpene

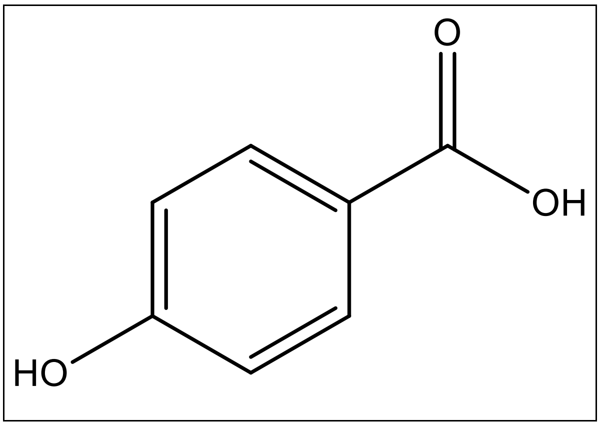

Figure 4: 4-hydroxybenzoic acid

Table 1: Results for total chrome content of respective effluent from pretanning, retanning formulations and chrome solo tannage

Parameter	T-R$^{p.b}$	T-R^{m}	PRE$^{p.b}$-T	PRE^{m}-T	CT	DSL
Total chrome (ppm)	9.69	29.43	5.03	16.83	27.80	1.0-10.0

Key: T-R$^{p.b}$ – Tanning (chrome) – Re-tanning (*P. barbatus*); T-R^{m} - Tanning (chrome) – Re-tanning (*mimosa*)

PRE$^{p.b}$-T – Pre-tanning (*P. barbatus*) - Tanning (chrome); PRE^{m}-T - Pre-tanning (*mimosa*) - Tanning (chrome)

CT – Chrome Tannage; DSL – Discharge to Sewer Limit

Average total chrome concentration was highest in effluent samples from the tanning formulation where mimosa was used in retanning and this observation was unexpected as compared the reading recorded from chrome solo tannage wastewater that was expected to have the highest load of chrome. Pretanning formulation using the two plant organic extracts separately posted lower concentrations of total chrome of 5.03 ppm and 16.83 ppm for *Plectranthus barbatus* and *mimosa* respectively

Table 2: Results for pH of respective effluent from pretanning, retanning formulations and chrome solo tannage

Parameter	T-R$^{p.b}$	T-R^{m}	PRE$^{p.b}$-T	PRE^{m}-T	CT	DSL
pH	7.97	4.25	2.92	2.85	2.30	5.0-10.0

The average pH values recorded from various tannages did not conform to the Discharge to Sewer Limit (DSL) except for the sample collected from effluent where *Plectranthus barbatus* powder was used in retanning that recorded a slightly alkaline pH of 7.97. The most acidic effluent was measured in effluent sample taken from the chrome solo tannage. Wastewater sampled from the tanning formulation that used mimosa as a retanning agent posted the second best result that missed the lowest limit of DSL by 0.75. Pretanning leather with either mimosa or *Plectranthus barbatus* organic extracts showed poor quality wastewater in terms of pH which yielded acidic effluent with pH values of 2.85 and 2.92 respectively.

Table 3: Results for BOD_5 of respective effluent from pretanning, retanning formulations and chrome solo tannage

Parameter	T-R$^{p.b}$	T-R^{m}	PRE$^{p.b}$-T	PRE^{m}-T	CT	DSL
BOD_5 (mg/l)	230.00	350.00	320.10	294.00	198.20	125-1000

Biological Oxygen Demand (BOD) average values of all effluent sampled from the five tannages complied to the DSL (125- 1000 mg/l) although, the most impressive result of BOD_5 was 198.20 mg/l posted by chrome solo tannage. This showed that besides the toxic nature of chrome in wastewater, it does not encourage microbial proliferation that deplete oxygen dissolved in water. The least recommendable tannage in respect to BOD_5 of tannery wastewater was that using mimosa as a retanning agent.

Table 4: Results for COD of respective effluent from pretanning, retanning formulations and chrome solo tannage

Parameter	T-R$^{p.b}$	T-R^{m}	PRE$^{p.b}$-T	PRE^{m}-T	CT	DSL
COD (mg/l)	4520.00	8850.00	2331.20	7792.20	5357.10	300-3000

The tanning experiments did not show whether the proposed approaches were likely to reduce the Chemical Oxygen Demand of the receiving waters. Although, the tanning procedure that used *Plectranthus barbatus* as a pretanning agent seemed promising with a COD value of 2331.20 mg/l that appeared closer to the upper limit of DSL and further from the lower limit of DSL (300 mg/l). The highest figure of COD (8850.00 mg/l) was recorded from effluent where goat skin pelts were first tanned with basic chrome followed by retanning with mimosa. Pretanning operation with mimosa recorded a higher COD value of 7792.20 mg/l as compared to 4520.00 mg/l from the same operation that used *Plectranthus barbatus* powder.

DISCUSSION

Plant tannins have been applied in the leather processing from ancient times firstly because the polyphenols are able to stabilize collagen and improve its versatility for various uses. Although the use of vegetable tannins was overtaken by mineral tanning especially the use of chrome solo tannage about a century ago, the backlash of environmental contamination and increased quest for adoption of green chemistry proposes the revival of organic tanning materials [20]. The evaluation of organic compounds in *Plectranthus barbatus* leaves extract identified important compounds that previously were applied in ethno medicine [21] but the findings of this study have proposed their application in reduction of leather toxicity together with minimizing of tannery wastewater contamination.

Phenolics isolated in this study include 4-hydroxybenzoic acid (Fig 4) although such compounds are relatively unstable on silica gel and heat of above 60℃ [22], it is possible to isolate similar compounds if the period of isolating them through silica gel packed column is greatly reduced. Related studies targeting phenolic acids conducted by Ganash and Qanash [3] using High Pressure Column Chromatography (HPLC) isolated Caffeic acid, Benzoic acid, Ferulic acid, Gallic acid and Chlorogenic acid among others. Additionally, one of the diterpenes isolated in the study is shown in fig 3 and previous review conducted by Alasbahi and Melzig [1] documents similar compounds not limited to abietane diterpenoids and 8,13- epoxy-labd-14-en-11-one diterpenoids. With the evidence of the presence of phenolic acids and other organic compounds in *Plectranthus barbatus* crude leaves extract, it is possible to suggest the possibility of the role of such compounds in increasing the stability of leather through increasing the density of bonds surrounding collagen and even improved fixation of chrome when applied in combination tanning.

Leather processing through various formulations of combination tanning involving *Plectrathus barbatus* crude powder yielded results showing possible increased uptake and fixation of chrome. The formulation starting with pretanning of pelts with the leaves extract favoured chrome tanning at the pH values between 5.5 to 7 where collagen's reactivity is elevated. This observation agrees with research done by Jian et al. [23] that suggested the substitution of rechroming by pretanning that considerably reduced the amount of chrome released by leather into effluent during post tanning operations. The same study supported such observations due to possible improved collagen-chrome interaction. This study further suggests the likelihood of similar stabilization through Colagen-chrome-phenolic interaction although the order and the pattern of the proposed bonding is not clear at least at the moment.

The quality of tannery wastewaters benefits from reduced influx of residual chrome from spent liquors. Results from this study recorded average chrome concentration of 9.69 ppm posted by samples retanned by *Plectranthus barbatus* powder as compared to 29.43 ppm measured in effluent collected from a similar formulation that used mimosa. The effluent from formulations where *Plectranthus barbatus* and mimosa were used in pretanning posted mean chrome concentrations of 5.03 ppm and 16.83 ppm respectively as compared to chrome solo tannage with a mean value of 27.80 ppm. Chrome in tannery wastewaters is one of the most toxic heavy metals that results into serious environmental pollution if left unregulated. Effective chrome exhaustion from tanning liquor is one of the most effective approaches in minimizing its discharge [24].

Pretanning pelts with *Plectrathus barbatus* powder which contains phenolic acids and diterpenes evidently improved chrome uptake by remarkably reducing the concentration of chrome (5.03 ppm) in the collected effluent as compared to other experimented tannages including chrome solo tannage. Furthermore, retanning leather with either *Plectrathus barbatus* powder or mimosa did not post better results as compared to pretanning formulations in terms of reducing chrome in effluent. Although, wastewater originating from the formulation where *Plectranthus barbatus* was used in retanning recorded a lower value of 9.69 ppm as compared to 29.43 and 27.80 from mimosa pretannage formulation and chrome solo tannage respectively. Notably, chrome concentration in effluent from mimosa retannage surpassed that measured from chrome solo tannage because of possible de-tanning caused by the presence of phenolic hydroxyls that have a higher affinity to collagen carboxyl groups than chrome [25]. Generally, leather processed from formulations using *Plecranthus barbatus* yielded less toxic wastewaters in terms of the level of chrome concentration against the set discharge to sewer limit of 1.0 ppm to 10.0 ppm.

The main significance of measuring BOD values of the effluent samples is to determine the likelihood of such wastewater in polluting receiving waters due to the amount of biodegradable organic materials therein. The higher the BOD value of tannery discharge the more polluting it will be if released without treatment [26]. BOD values for the effluent sample collected from the *Plectranthus barbatus* pretanned formulation was 320 mg/l and slightly higher that the tannage that used mimosa in pretanning that recorded a value of 294.00 mg/l. Waste water from the *Plectranthus barbatus* retannage posted the lowest value of 230. 00 mg/l compared to 350 mg/l recorded from the effluent emanating from mimosa retannage. The BOD values do not clearly show whether retanning leather with either of the two organic materials was superior over pretanning formulations but generally without looking at the four formulations separately then the lowest BOD_5 value of 230 mg/l posted by *Plectranthus barbatus* retannage was recommendable. However, notably all the BOD_5 values from all the tanning formulations were within the limit of discharge to sewer (125- 1000 mg/l) although, none was within the limit for direct discharge to inland waters set at 5-200 mg/l [27].

Reduction of oxygen dissolved in water is an important parameter used in determining the suitability of surface waters in sustaining healthy aquatic organisms. Chemical Oxygen Demand (COD) in mg/l is the amount of oxygen utilized by reducing matter present in one litre of effluent sample. The COD levels recorded were 4520.00 mg/l, 2331.20 mg/l, 8850.00 mg/l and 7792.20 mg/l respectively for effluent samples collected from *Plectranthus barbatus* retannage, pretannage, mimosa retannage and pretannage formulations as compared to 5357.10 mg/l that was characteristic of the chrome solo tannage. All the observed values except that measured in wastewater from *Plectranthus barbatus* pretannage (2331.20 mg/l) were above the permissible limits of 300-3000 mg/l and 50-450 mg/l for discharge to sewer and direct discharge to inland waters respectively [27]. Elsewhere, the World Health Organization (WHO) has set the COD limit at 250 mg/l [28]. Chrome solo tannage recorded a COD value of 5357.10 mg/l against higher levels recorded from effluent originating from mimosa treated tannages. Therefore, tanning formulations treated with *Plectranthus barbatus* comparatively decreased the toxicity posed by this parameter albeit not to limits stipulated by WHO but will also still reduce the cost of wastewater treatment.

The pH tested for wastewater from different tanning formulations as shown in table 1 partly complied to the set limits (5.0-10) [26] for direct discharge to the sewer or inland water in absence of dilution, mixing and assumed reaction in the tannery wastewater stream. Neat effluent collected from the tanning drum in which tanning was first done with chrome followed by retanning with *Plectranthus barbatus* powder registered a slightly neutral pH of 7.97 against the formulation that used *Plectranthus barbatus* in pretanning that recorded an acidic mean pH value of 2.92. Effluent from tannages that utilized mimosa in pretanning and retanning recorded pH values of 2.85 and 4.25 respectively as compared to the value of 2.30 from chrome solo tannage. On the basis of WHO permissible limit range of between 5.5 to 9.0 [28] then the only recommendable tanning formulation would be the use of *Plectranthus barbatus* leaves extract in retanning. However, analyzing other effluent parameters that affect the quality of tannery wastewater then it seems that further balancing of the proposed formulations will have to be tested in order to arrive at a formula that will yield the least toxic tannery effluent.

CONCLUSION

Pretanning goat skin pelts with *Plectranthus barbatus* leaves extract powder during leather processing considerably reduced total chrome content in tannery wastewater but did not keep the effluent pH within the discharge limits. However, experimenting use of this extract in pretanning and retanning in the same tannage might yield promising results of the two mentioned parameters. Both retanning and pretanning kept BOD of tannery effluent at desired discharge limits although only the later reduced the COD of the wastewater. Therefore, the use of *Plectranthus barbatus* leaves extract in various combinations with chrome will remarkably improve the quality of tannery effluent.

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Conflict of Interest

There is no conflict of interest.

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