

APPLICATION OF INFUSION FROM LEAF OF *HIBISCUS SABDARIFFA* IN DELIMING

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ABSTRACT

For efficient control, and to produce a particularly fine grain in the leather, ammonium sulfate (or boric acid) is conventionally used as a delimiting agent. It is used in the amounts necessary to neutralize the alkali in pelts after the liming and unhairing processes in leather manufacture. A 5% infusion from leaf of *Hibiscus Sabdariffa* was evaluated as an alternative delimiting agent in leather processing. After extraction, the pH of the infusion was found to be 3.18. The delimiting value of the infusion was determined by titrating the infusion against 20ml solution of 3% Calcium hydroxide. The volume of the infusion required and optimum time taken to delimit 50g of limed pelt was also determined. Several delimiting trials were also undertaken; complete delimiting of limed pelt was achieved with 50ml of the infusion within a period of 40 minutes as against the delimiting period of 1 hour recorded for solution of ammonium sulfate. From results obtained after delimiting trials and from physical observations made on the pelts, the infusion was discovered to effectively delimit pelts almost competing and compared favorably to the conventional delimiting agents such as ammonium sulfate. The infusion of *Hibiscus Sabdariffa* can thus be introduced, after further investigation, for use as a delimiting agent in the leather industry.

RESUMEN

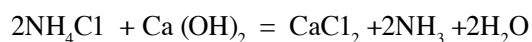
Para un control eficiente, y para producir una flor particularmente fina en el cuero, sulfato de amonio (o ácido bórico) es utilizado convencionalmente como un agente de desencalado. Se emplean en las cantidades necesarias para neutralizar el álcali en las pieles después de los procesos de encalado y pelambre en la fabricación del cuero. Una infusión de 5% a partir de la hoja de *Hibiscus Sabdariffa* fue evaluado como un agente desencalante alternativo en el tratamiento del cuero. Luego de la extracción, el pH de la infusión era 3,18. El valor de desencalado de la infusión se determinó mediante titulación de la infusión con una solución de 20 ml de 3% de hidróxido de calcio. El volumen de infusión requerido y el tiempo óptimo para desencalar 50g de piel encalada también fue determinado. Varios ensayos de desencalado se llevaron a cabo también con desencalado completo de pieles encaladas obtenidos con 50 ml de la infusión en un período de 40 minutos frente a un período de desencalado de 1 hora tomado para la solución de sulfato de amonio. De los resultados obtenidos tras el desencalado de los ensayos y observaciones físicas realizadas en las pieles, la infusión se descubre como un desencalante eficaz que compite y se compara favorablemente con el agente desencante convencional, sulfato de amonio. La infusión de *Hibiscus Sabdariffa* puede entonces ser introducida, luego de investigaciones adicionales, para su uso como un agente desencalante en la industria del cuero.

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INTRODUCTION

Deliming is the process of neutralizing alkali, used during liming and unhairing of hides and skins in leather manufacture. It is accomplished by running the hides or skins in a drum or paddle to which has been added water and a proprietary compound consisting of a mixture of an ammonium salt (preferably ammonium sulfate).^{1-3, 6, 23} For effective processing of leather, the swollen limed pelt is reversed by washing and chemical deliming. Whereas washing only removes the free lime, the chemically bonded lime is often removed by chemical reaction using conventional delimiting agents such as ammonium sulfate or chloride by conversion into readily soluble salt⁴⁻⁶ as shown in the equation below:



The ammonium salt neutralizes the bonded lime in the pelt, thus the delimiting process is said to be achieved by reduction in alkalinity and pH of the pelt to 8-8.5.^{7,21,22} The progress of delimiting is monitored by checking of pH values of process liquors and in the cutting of a pelt cross-section. This is often confirmed using phenolphthalein indicator showing colorless at a cut cross-section of the neck region of the pelt. In the leather industry, 1.5 – 2% delimiting agent is used on the basis of the weight of the limed pelt and the process is usually completed within 45-60 minutes.⁸⁻¹⁰ The amount of delimiting agent in g necessary for neutralizing 1 g calcium hydroxide is referred to as the delimiting value.¹⁹

Weak organic acids and their salts are also used to neutralize limed pelts during delimiting.²⁰ It is practical to choose a weak acid with pK value near to the required pH. For example formic, acetic and boric acid with pH of 3.7, 4.7 and 9.2 respectively.¹¹ The delimiting process can be done with these acid can be rapid and may require pH adjustment.

Despite the advantages associated with the use of ammonium salts during delimiting, its use is often accompanied by the emission of the obnoxious ammonia gas, thus the need to seek for alternative delimiting agents which would emit no such gas while achieving the desired delimiting process.

Hibiscus Sabdariffa is a wood based perennial subshrub used for the production of basic fiber¹⁰ and the calyces used commonly as beverage. The plant is commonly cultivated in the Northern part of Nigeria. The leaf material is also available worldwide with China and Thailand being the highest producers of the plant but the world best variety comes from Sudan. Other countries where *Hibiscus Sabdariffa* leaf material is grown and used include Malaysia, India, Jamaica, Guyana, Grenada, Trinidad and Tobago, Mali, Benin, Egypt, and Tanzania.^{10, 12} The leaves are long and grow alternately

along the stem of the plant and are used in the preparation of soups, salad and local diet commonly called “gwote” in parts of Nigeria. Several studies have indicated that extract of *Hibiscus Sabdariffa* have medicinal applications; Two diuretic ingredients ascorbic and glycolic acid. Because it contains citric acid, it is used as a cooling herb, providing relief during hot weather by increasing the flow of blood to the skin’s surface and dilating the pores to cool the skin.¹⁵ the leaves and flowers are used as a tonic tea for digestive and kidney functions. The heated leaves are applied to cracks in the feet and on boils and ulcers to speed maturation. The calyces and seeds are diuretic, laxative and tonic.¹⁶⁻¹⁸

This study is aimed at determining the suitability of infusion of *Hibiscus Sabdariffa* as an alternative for the above mentioned conventional delimiting chemicals especially in the face of scarcity or escalating price of these chemicals due to import restrictions. Moreover the proposed alternative delimiting agent contains weak organic acids, is bio-degradable, and a naturally cultivable renewable resource which can be more environmentally friendlier than the conventional delimiting agents.

METHODOLOGY

Sample Collection and Preparation

Leaves of *Hibiscus sabdariffa* was harvested from a farm in Basawa-Zaria, Kaduna State and identified at the Department of Biological Sciences, Ahmadu Bello University, Zaria-Nigeria. The sample was washed thoroughly with water, sundried for eight hours and further dried in an oven at 80°C for a period of 6h after which it was pulverized and sieved through a mesh with aperture of 0.75mm.

Preparation of Infusion

Infusion of the leaves of the plant was prepared in accordance with the official method prescribed by the Society of Leather Trade and Chemists (SLTC 2/2)⁶. 50 grams of the sample was soaked in 100ml of distilled water in a 2500ml beaker and the extraction process was carried out using the Procter extraction apparatus. The process of extraction was continued until 1000ml representing. 5% solution of *H. Sabdariffa* of the infusion was obtained. The extract was kept in a refrigerator until needed.

Determination of pH of Infusion and of Conventional Delimiting Agent

The pH of the 100cm³ infusion of *Hibiscus sabdariffa* and 100ml of 0.2% solution of the conventional delimiting agent (ammonium sulfate) was determined with a pH meter (Henna Model H18734). pH values of 3.18 and 6.68 was obtained and recorded for the infusion and the control delimiting agent respectively.

Determination of Deliming Value

The delimiting value of the infusion was determined by titrating the infusion against 20cm³ solution of 2% and 3%Ca(OH)₂ using phenolphthalein as indicator until the disappearance of the pink color. The pH of the mixture was determined and recorded intermittently after addition of 1ml of the infusion. The volume of the infusion required to neutralize solution of calcium hydroxide at pH 8 – 9 upon the disappearance of the pink color of phenolphthalein indicator was calculated from plotted graphs and recorded as the delimiting value. Similar experiment was set up as control using 2% solution of ammonium sulfate.

Delimiting Trails

Six pieces of limed pelt each weighing about 50 grams were placed in six separate conical flasks containing 10, 20, 30, 40 and 50ml infusion of the leaf. Flasks were agitated with a mechanical shaker for a period of 45 minutes after which the progress of delimiting was tested by observing a cut cross-section to the pelt with phenolphthalein indicator. The appearance of pink color in the cut cross-section indicates incomplete delimiting while the appearance of no color to the cut cross section of the pelt on the addition of phenolphthalein indicator is an indication of complete delimiting.

Determination of Volume of Infusion to Effectively Delime Pelt

The maximum volume of the infusion of *Hibiscus Sabdariffa* and that of the ammonium salt (NH₄)₂SO₄ required to delime the six limed pelt used during the delimiting trial was also determined after the period (1hr) stated in the experiment.

Optimum Time for Delimiting by Infusion

The Optimum time taken for the infusion to delime completely a pelt was determined by treating the pelt with 6ml infusion of the leaf which was recorded as the delimiting value. A cut cross-section of the pelt was observed periodically after 10 minutes with phenolphthalein. Indicator for color change after a period of 1hr; a limed pelt was similarly treated with 2% solution of ammonium sulfate and the color change on cut cross section observed after 1hr.

RESULTS AND DISCUSSION

The pH values of 3.18 and 6.68 obtained for the infusion and 0.2% solution of ammonium sulfate respectively indicate that solution of the former is more acidic than later. This can be attributed to the fact that the infusion may contain weak organic acids particularly dihydroxybenzoic acid, a type of phenolic acid¹⁴. The delimiting value of infusion of *Hibiscus Sabdariffa* after titration against 2% and 3% Ca(OH)₂ is presented in figures I. From the plotted graphs it can be observed that the delimiting value in terms of volume of the infusion used was found to be 3.60 and 4.50ml respectively. This gives an average figure of about 4.10ml and at this value,

the infusion can neutralize or delime pelt with pH 12.10 to pH8-9. The sudden drop in pH in the two graphs from 10.2 to 7.3 for 2% and 11.3 to 7.0 on addition of 3 and 4ml of the infusion respectively simply explains the behavior of equivalent point in a typical acid and base titration. Moreover the infusion having low pH value of 3.18 may be responsible for such result. The volume of delimiting agent (ammonium sulfate) used in the control experiment was 6.8ml. This figure is significantly higher than the volume of the infusion of *Hibiscus Sabdariffa* (3.60ml) that neutralized 3% lime solution. This means that lower concentrations of the infusion could be used in effectively delime pelts probably due to the presence of organic acids in it. The gradual drop in pH of the experiment carried out with the conventional delimiting agent can be as a result of the slow dissociation of the ammonium salt and its buffering effect¹⁰ during the process as shown in figure 1.

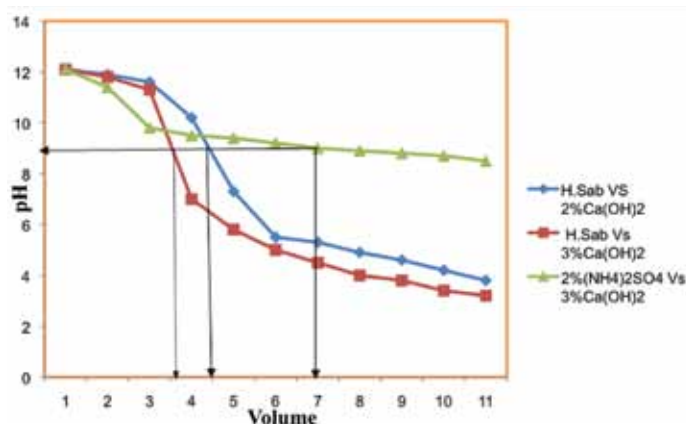


Figure 1. Delimiting Values of Infusion of H.Sabdariffa and Ammonium Sulphate.

The result obtained also indicate that 5% of the crude *Hibiscus Sabdariffa* can be extracted to be used in the neutralization of 3% Ca(OH)₂ and about 3.60cm³ would be adequate to neutralize 25ml of 3%Ca(OH)₂ or delime pelts to pH 8- 9. However it would be expected that increasing the amount of the infusion would further lower the delimiting period but the pH of the pelt after the process would go beyond that which is required prior to bating process. This would adversely affect the efficacy of bating enzymes. The optimum volume of the infusion required to completely delime pelt and that of the conventional delimiting agent used is presented in table I and II respectively. From the results obtained it can be deduced that the amount of the infusion to delime completely 50g of the pelt was found to be in the range of 40-50ml while the control delimiting agent could not delime completely the pelt on addition of 60ml. This can be understood from the fact that the infusion being more acidic (pH3.18) would naturally require smaller volume to delime the pelt than the solution of ammonium sulfate (pH6.68). This simply implies that more of the ammonium sulfate solution would be required to achieve complete delimiting of the pelt than the infusion. This result correlates with the behavior of both solutions as depicted in figure 1.

Table III and IV represent optimum time taken to delime 50g of limed pelts with the infusion of *Hibiscus sabdariffa* and the conventional deliming agent (ammonium sulfate). Shorter time (40minutes) was observed to be taken to completely delime the pelt with the infusion than with the ammonium salt

used. This is against time (1hr) recorded for the same process using ammonium sulfate. This can be also be attributed to the presence of organic acids which could be responsible for it faster penetration through cross section of the pelt. Moreover, the infusion was observed to penetrate through the cross-section of the pelt faster than the solution of the ammonium salt.

TABLE I

Influence of Volume of *H. Sabdariffa* on Physical Appearance of and color change in Cross section of Pelt during Deliming.

Volume of Infusion (ml)	Observation (Extend of de-swelling Pelt)	Color Change at cut cross-section with Phenolphthalein
10	No effect	No change in color (pink)
20	No effect	No change in color (Pink)
30	Slight reduction in swelling	Slight color change
40	Slight reduction in swelling	60% colorless
50	Complete de-swelling	Completely colorless
60	Complete de-swelling	Completely colorless

TABLE II

Influence of Volume of Ammonium Sulphate on Physical Appearance and color change in Cross section of Pelt during Deliming.

Volume of Infusion (ml)	Observation (Extend of deswelling Pelt)	Color Change at cut cross-section with Phenolphthalein
10	No effect	No change in color (pink)
20	No effect	No change in color (Pink)
30	Slight reduction in swelling	Slight color change
40	Slight reduction in swelling	30% colorless
50	Slight de-swelling	50% colorless
60	Slight de-swelling	80% colorless

TABLE III

Effect of Time taken by Infusion on Physical Appearance and color change in Cross section of Pelt during Deliming.

Time (Minutes)	Observation (Extend of deswelling)	Color Change at cut cross-section with Phenolphthalein
10	No effect	No change in color (pink)
20	No effect	No change in color (Pink)
30	Slight reduction in swelling	Slight color change
40	Significant swelling reduction	Completely colorless
50	Complete de-swelling	Completely colorless
60	Complete de-swelling	Completely colorless

TABLE IV

Effect of Time taken by Ammonium Sulphate on Physical Appearance and color change in Cross section of Pelt during Deliming.

Time (Minutes)	Observation (Extend of deswelling)	Color Change at cut cross-section with Phenolphthalein
10	No effect	No change in color (pink)
20	No effect	No change in color (Pink)
30	Slight reduction in swelling	Slight color change
40	Slight reduction in swelling	50% colorless
50	Significant reduction de-swelling	75% colorless
60	Complete de-swelling	Completely colorless

CONCLUSION

Based on these results, the infusion of *Hibiscus Sabdariffa* can be said to have a great potential to serve as an alternative delimiting agent for the leather industry. Apart from being a renewable and bio-degradable resource, it would also prevent the emission of gaseous product such as ammonia, which is attributed to the use of ammonium salts as delimiting agents. Further work on this research is thus recommended.

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