





# STRIDING TOWARDS SELF-SUSTAINABILITY USING ALUMINIUM FROM TANZANIAN KAOLIN FOR COMBINATION TANNING SYSTEM

<sup>a</sup>C. R. China<sup>1, 2</sup>, G. C. Jayakumar<sup>2</sup>, A. Hilonga<sup>1</sup>, S. V. Kanth<sup>2</sup>, K. N. Njau<sup>1</sup>

1 The Nelson Mandela African Institution of Science and Technology, Materials Science and Engineering (MaSE) P. O. Box 447, Arusha, United Republic of Tanzania
2 Tanzania industrial Research and Development Organization, Division of Textile and Leather Technology, P. O. Box 23235, Dar es Salaam, Tanzania.

3 CSIR-Central Leather Research Institute, Centre for Human and Organizational Resources Development (CHORD), chennai, Indi.

a) Corresponding authors:  $\underline{ceciliac@nm-aist.ac.tz} \ and \ \underline{jayakumarclri@gmail.com}$ 

**Abstract.** Sustainability is a key factor which controls future leather manufacture. Developing several new technologies is one of the primary agendas for sustainability. However, developing countries are facing several challenges which not only limited to best practice technologies but also finding self-sustainability in maximizing the available resources. In the present study, an attempt has been made to explore the potential resource of aluminium sulphate from kaolin of Pugu hills, Tanzania for combination tanning. Though, extraction of aluminium sulphate from several resources are available, there is limited literature pertaining to Tanzania resources. Therefore, aluminium sulphate extracted from kaolin was basified and studied for its tanning efficiency. Diffraction and vibrational spectroscopic studies were carried out to assess the confirmation of extracted aluminium. Combination tanning has been carried out with vegetable tannins, which are from natural resources. Leathers tanned with aluminium sulphate and mimosa resulted with a hydrothermal stability temperature beyond 100°C as compared to vegetable tannin alone showed 78°C. Physical strength characteristics met the standard norms. Fiber separation was good, which has been confirmed through microscopic studies. The study provides a new insight on accomplishing self-sustainability through available resources and manufacture eco-friendly system.

Key words: Pugu kaolin, Combination tanning, Aluminium sulphate, mimosa, leather manufacturing

# 1 Introduction

Sustainability is a key factor, which controls future leather manufacture. Today's leather industry is dominated by use of chromium salt as tanning agent. However, Chromium tanning is being debatable owing to reported toxicity of chromium (VI) and associated disposal issues [1]. A new tanning system without using chromium salt is an immediate need for sustainable leather industry. Studies revealed that combination tanning, whereby vegetable tannins are coupled with Aluminium Sulphate [Al2(SO4)3], produce good quality leather mimicking the properties of chrome-tanned leather [1-10]. Al2(SO4)3 currently used in combination tanning is industrially produced by the Bayer and Hall-Herault processes, using bauxitic rocks as raw materials, which contain between 20 and 30% of aluminium [11, 12]. However, bauxite is globally diminishing and also it is often completely absent in known commercial quantity in most developing countries [13]. Kaolin, which is richly available in most developing countries, containing between 10-20% aluminium, can be a reliable source of aluminium for production of Al2(SO4)3 for various applications [12].

Tanzania is endowed the largest kaolin deposit in Africa that entails possible production of Al2(SO4)3 for combination tanning. About 2.3 billion metric tons kaolin deposit of high standard is located in Pugu Hills, 35 km from Dar es Salaam, Tanzania [14-16]. The potentials of Pugu kaolin for industrial use is still untapped [14, 15]. In the present study, an attempt has been made to explore the potential resource of aluminium from kaolin of Pugu hills, Tanzania for combination tanning.

#### 2 Material and Methods

#### 2.1 Materials

Kaolin was collected from Pugu hills, Kisarawe in the coast region of Tanzania, by using quarter sampling technique as described by Sempeho [17]. All chemicals used were of analytical grades purchased from Sigma Aldrich Ltd, India. Industrial chemicals used were of commercial grade, Goatskins pelts were generously donated by CSIR-CLRI pilot tannery, pre-tanning section.

#### 2.2 Extraction of kaolin

Raw kaolin was grounded to fine particles, activated by heating and dissolved in concentrated sulphuric acid at a definite ratio for 90 minutes. Resultant filtrate was concentrated to obtain white crystals of aluminium sulphate. The latter was analysed by XRD AND FTIR to assess the confirmation of extracted aluminium.

## 2.3 Combination tanning trials

Sample goatskins were treated with mimosa in combination with basified and masked  $Al_2(SO_4)_3$  from kaolin. The recipe for tanning process was adopted from CSIR-CLRI pilot tannery. In summary, 15% of mimosa was used in combination with varying concentrations of  $Al_2(SO_4)_3$  expressed as %  $Al_2O_3$ . Control skin sample treated with mimosa alone.

## 2.4 Determination of shrinkage temperature

The shrinkage temperature test was carried out as per SATRA STD 114 method. A strip of about 2 cm<sup>2</sup> leather were cut from tanned leather sample clamped between jaws of the clamp that in turn was suspended in a solution of water: glycerol mixture (3:1). The mixture was gradually heated and the temperature at which leather sample shrinks to one third of its original length was recorded as a shrinkage temperature. All analyses were done in duplicate.

## 2.5 Post tanning process

After tanning the samples were shaved to uniform thickness of 1.1 mm and conventional post tanning processes where carried out by 13% syntans and 8% fatliquor. Thereafter, leather samples were set, toggled to dry, staked and buffed.

# 2.6 Physical characterization of crust leather

Experiment and control crust leather samples were subjected to physical testing to determine the influence of  $Al_2(SO_4)_3$  from kaolin on physical properties of leather. Tear strength water vapour permeability tests were carried out using SATRA TM 162:1992. All test samples were conditioned at 20°C and 65% relative humidity. Duplicate analyses were performed for each sample.

## 2.7 Scanning Electron Microscopic analysis of Leather Samples

Experiment and control crust leather samples were cut into predefined sampling position and shaped into uniform thickness, coated with gold using Edwards E306 sputter coater followed by scanning process. The micrographs for cross section were obtained by operating the SEM at an accelerating voltage of 5 KV with 150X magnification.

#### 3 Results and discussion

In the present study, Combination tanning using mimosa and  $Al_2(SO_4)_3$  extracted from kaolin was carried out with the main goal of exploring potential utilization of kaolin resource in leather industry (Fig. 1).



**Figure 1.** Step by step preparation of aluminium sulphate from Pugu kaolin (A=Kaolin deposit, B=Preparation and extraction, C=Aluminium sulphate)

# 3.2 Analysis of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> from Pugu kaolin

During extraction process,  $Al_2O_3$  present in kaolin is leached and react with sulphuric acid used for dissolution to form  $Al_2(SO_4)_3$  and water (eq. 1). XRD and FTIR spectra of extract have displayed most characteristic peaks of  $Al_2(SO_4)_3$  signifying that  $Al_2(SO_4)_3$  was formed during extraction process.

Equation 1

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)3 + 3H_2O$$

## 3.3 Determination of shrinkage temperature

The shrinkage temperature of the samples was determined to assess the tanning effect. It was observed that addition of  $Al_2(SO_4)_3$  resulted in significant increase in shrinkage temperature in the order of 78, 115, 118, 114°C for 0, 2, 5 and 10%  $Al_2O_3$ , respectively.

### 3.4 Physical properties of leather samples

It is important to study the influence of the tanning system on the strength properties of leathers. Physical properties analyses carried out are tearing strength and water vapour permeability. Physical characteristic data for leather samples tanned with different concentrations of  $Al_2O_3$  meet standard values recommended by CLRI. Micrographs of leather samples tanned with combination system show better fiber dispersion than those tanned using mimosa alone.

# 4 Conclusion

In the present work, investigation was made to study potential of Pugu kaolin as source of  $Al_2(SO_4)_3$  for combination tanning.  $Al_2(SO_4)_3$  was successful obtained from kaolin using sulphuric acid as dissolution agent. Its application in combination tanning with mimosa gave leathers with shrinkage temperature beyond  $100^{\circ}$ C that can be achieved with as low concentration as 2%  $Al_2O_3$ . Produced leather showed physical properties above recommended values and good fiber structures separation. This study provides useful information on accomplishing self-sustainability through available resources in Tanzania for eco-friendly leather manufacturing.

5 Acknowledgements

This work was financed by the Centre for Science and Technology of the Non-Aligned and Other Developing Countries (NAM S&T Centre) under Research Training Fellowship for Developing Countries Scientists (RTF-DCS) 2016-2017 Scheme [Grant number NAM – 05/74/2015] and Africa Development Bank through The Nelson Mandela African Institution of Science and Technology [Grant number 2100155032816]

#### Reference

- 1. Madhan, B., et al., Interaction of aluminum and hydrolysable tannin polyphenols: An approach to understand the mechanism of aluminum vegetable combination tannage. Vol. 101. 2006. 317-323.
- 2. Musa, A. and G. Gasmelseed, Combination tanning system for manufacture of shoe upper leathers: cleaner tanning process. Journal of the Society of Leather Technologists and Chemists, 2012. **96**(6): p. 239-245.
- 3. Musa, A. and G. Gasmelseed, Development of eco-friendly combination tanning system for the manufacture of upper leathers. International Journal of Advance Industrial Engineering, 2013. 1(1): p. 9-15.
- 4. Musa, A. and G. Gasmelseed, Eco-friendly vegetable combination tanning system for production of hair-on shoe upper leather. Journal of Forest Products & Industries, 2013. **2**(1): p. 5-12.
- 5. Musa, A., et al., Studies on combination tanning based on henna and oxazolidine. Journal of the American Leather Chemists Association, 2009.
- 6. Choudhury, S.D., S. DasGupta, and G.E. Norris, Unravelling the mechanism of the interactions of oxazolidine A and E with collagens in ovine skin. International journal of biological macromolecules, 2007. **40**(4): p. 351-361.
- 7. Hassan, E.A. and M.T. Ibrahim, Innovation of New Cleaner Technology: Tannage by Local Tanning Agent Acacia Nilotica (Garad) and Aluminum Retannage. 2014.
- 8. Mahdi, H., et al., Vegetable and aluminium combination tannage: aboon alternative to chromium in the leather industry. 2008.
- 9. Covington, A.D., Modern tanning chemistry. Chemical Society Reviews, 1997. 26(2): p. 111-126.
- 10. E Musa, A. and G. A Gasmelseed, Combination Tanning System for Manufacture of Shoe Upper Leathers: Cleaner Tanning Process. Vol. 96. 2013. 239-245.
- 11. Pinna, E.G., et al., Hydrometallurgical extraction of Al and Si from kaolinitic clays. REM-International Engineering Journal, 2017. **70**(4): p. 451-457.
- 12. Chigondo, F., B.C. Nyamunda, and V. Bhebhe, Extraction of water treatment coagulant from locally abundant kaolin clays. Journal of Chemistry, 2015. **2015**.
- 13. Aderemi, B.O., L. Edomwonyi-Otu, and S.S. Adefila, A new approach to metakaolin dealumination. Australian Journal of Basic and Applied Sciences, 2009. **3**(3): p. 2243-2248.
- 14. Akwilapo, L.D. and K. Wiik, Ceramic properties of Pugu kaolin clays. Part I: Porosity and modulus of rupture. Bulletin of the Chemical Society of Ethiopia, 2003. 17(2).
- 15. Kimati, B., Massive kaolin deposits untapped at Pugu hills, in Daily News. 2012, Tanzania Standard Newspapers Ltd:
  Dar es Salaam.
- 16. Schwaighofer, B. and H. Muller, Mineralogy and genesis of the pugu hill kaolin deposit, Tanzania. Clay Minerals, 1987. **22**(4): p. 401-9.
- 17. Sempeho, S., E. Lugwisha, and L. Akwilapo, Suitability of kaolin and quartz from Pugu and feldspar from Morogoro as raw materials for the production of dental porcelain [MS thesis]. University of Dar es Salaam, Dar es Salaam, Tanzania, 2012.