RECYCLING OF CHROME TRIMMINGS & SHAVINGS LEATHER WASTES TO MAKE FERTILIZER

1st Workshop Presentation on Eco-Tanning Processes in Kenya & the East African Region (**17-18th, August 2023**)

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Introduction

- As a matter of necessity, the process of leather making leads to the production of huge quantities of solid wastes.
- A great proportion of these wastes is contaminated with chromium due to the usage of basic chromium (III) sulphate as a major tanning agent in the global leather industry.
- A medium sized tannery operating at full capacity would produce an average of 8.5 tonnes of leather wastes per day; as follows:

Introduction Cont…

- ***Semi-processed leather wastes;***
- ✓ *wet blue first offcuts -----2 tonnes*
- ✓ *wet blue shavings ---------2 tonnes*
- ✓ *wet blue buffing dust------1 tonne*
- ***Finished leather wastes;***
- ✓ *2nd shaving & offcuts-----2 tonnes*
- ✓ *perforation holes----------0.5 tonnes*
- ✓ *lab test samples----------0.25 tonnes*
- ✓ *cutting room offcuts------0.5 tonnes*
- ✓ *mixed product offcuts----0.25 tonnes*

TOTAL----------8.5 tonnes per day.

Introduction Cont…

- Disposal of tannery solid wastes (including chrome-tanned waste) has traditionally been done by landfilling & open dumping. However, in recent years this has become very problematic due to:

i. *acute shortage of landfill sites resulting from rapid increase of human population growth & urbanization;*
ii. *escalating costs of land disposal of hazardous solid wastes, and;*
iii. *increasing risks of environmental pollution & public health issues posed by such wastes.*

Tannery Waste Disposal/Recycling

Tannery	Tannery waste disposal/utilization mode
Nakuru Tanners (Nakuru town)	Landfilling mode of disposal No documented method of recycling or re-using of tannery waste
East Africa Tannery (Nairobi)	Dried fleshings and trimmings are disposed of by: Open dumping, Incineration, Being used as a source of fuel No recycling of tannery waste is done.
Alpharama Ltd. (Athi River)	Landfilling is the only mode of disposal of tannery waste in this tannery. Neither recycling nor re-using of tannery waste is done.
Aziz Tannery Ltd. (Nairobi)	Tannery waste disposal is done by the following methods: Open dumping, Incineration. There is no documented mode of either recycling or re-using of tannery waste in this tannery.
Reddamac Leather Centre (Zingo Investments, Nairobi)	Tannery waste disposal is done by the following two modes:Open dumping, Landfilling. Neither recycling nor re-using of this kind of waste is done.
Bata Shoe Company (Limuru)	Landfilling is the only mode of disposal. Neither recycling nor re-using of leather waste is done. This tannery is currently not doing beamhouse leather processing.

Landfilled chrome-tanned waste

Chrome leather trimmings & shavings dumped in the environment of a tannery

Recycling benefits

There are many benefits of recovering and recycling materials at the end-of-life including;

i. ***the recovery of physical resources that would otherwise be lost to landfill,reducing overall virgin material use as a result;***
ii. ***re-couping of some of the embedded energy and resources within a product;***
iii. ***enhanced economic value of the recycled material and the re-capture of some of this value as the recycled material is sold on the secondary material market;***
iv. ***averting environmental pollution & public health issues.***

Recycling of Chrome Leather Waste

Background Review:

- *Previous studies have shown that for every 1 ton of wet-salted hides processed into finished leather slightly more than 600kg of tannery solid waste is generated.*
- *One-third of this waste is composed of shavings, trimmings, splits and buffing dust with at least 3.5kg of chromium in the waste if the tannage followed was chrome tannage.*
- *Chrome tannage is the most widely practised form of tannage globally due to;*

Recycling of Chrome Leather Waste Cont…

i. The relatively high hydrothermal stability of the resultant leather.
ii. The tanning agent of choice, basic chromium (III) sulphate, has a very high affinity for hide collagen carboxyl groups, and is readily available at a reasonable cost to the tanner.
iii. Versatility (i.e. ability to make a wide variety of finished leathers from this type of tannage).
iv. Superiority of the resultant leather in terms of stretchability, dyeability and resistance to tear and flexural failure.

Recycling of Chrome Leather Waste Cont…

Recycling of Chrome Leather Waste into Fertilizer:

- *Several attempts have been made at different occasions to formulate organic fertilizers using chromium-containing leather scraps and shavings as the raw material through thermal or enzymatic techniques, but the presence of chromium in such wastes was found to be a limiting factor in the success of those techniques.*
- *The techniques themselves were also found to cause secondary pollution problems in addition to being cumbersome, costly and less efficient to carry out.*
- *Development of a sustainable and environmentally sound technology for dechroming and modifying chrome leather waste to form fertilizer is hereby discussed;*

Recycling of Chrome Leather Waste Cont…

Sample Preparation and Characterization

- *Two (2) categories of leather waste samples, chrome shavings on one hand, and chopped up chrome splits and trimmings on the other, were dried for two (2) days on polythene sheets of paper.*
- *Characteristics of interest(Viz; Cr, moisture, total nitrogen & hide substance, humidity, total lipids, total ash and pH levels) were determined prior to conditioning & wetting back, using appropriate official methods.*
- *The samples were thereafter ground using a laboratory grinding mill (to increase their surface area for enhanced chromium extraction) and then subjected to wetting back to around 50% moisture content.*

Recycling of Chrome Leather Waste Cont…

Detanning of chrome tannery waste samples

- *After wetting back, the ground leather waste samples were then detanned using pure lime (175g for every 5kg of sample mixed with 7.5l of water in a plastic container).*
- *The samples were allowed to mix in the plastic containers for 1 hour after which the pH of the liquor was checked and adjusted to 12.5 with some alkali (lime).*
- *The samples were then put in an experimental tannery drum, allowed to run intermittently 10 minutes every hour for a total period of 12 hours after which they were offloaded & filtered, and thereafter delime-washed with 0.2% ammonium sulphate in 200% fresh float.*

Recycling of Chrome Leather Waste Cont…

New method for extraction of chromium from detanned leather waste samples

- *The new method for dechroming chrome leather waste is a modification of a procedure used previously by Malek et al., (2009), and was very efficient (99.9% Cr extraction in just 24 hours) and environmentally sound.*
- *In this new method, formic acid was used as the major reagent for extracting Cr from such waste as opposed to the use of potassium tartrate in the Malek et al., (2009) method, which achieved only 90% extraction in 36 hrs.*
- *The samples were then dried overnight in the laboratory oven at 40°C in preparation for further Cr extraction & complexation of residual Cr using potassium oxalate.*

Recycling of Chrome Leather Waste Cont…

Hydrolysis and modification of dechromed waste

- *After mechanical dewatering and oven drying of the dechromed leather waste samples, they were given a mild hydrolysis with orthophosphoric acid added at a rate of 100ml perkg of leather waste in 300% float for a period of 1 hour.*
- *The experiment was conducted in a stainless steel tannery experimental drum at a temp. of 50°C as higher temperatures would destroy the collagen fibres making them unusable as a raw material for the intended fertilizer formulation.*
- *The hydrolysed collagenic material was then put in the laboratory oven at 40°C overnight for uniform drying prior to modification with Epichlorohydrin (EPICH).*

Recycling of Chrome Leather Waste Cont...

Hydrolysis and modification of dechromed waste cont...

- *The oven dried collagen hydrolysate (10kg) was put back into the stainless steel tannery experimental drum containing 50% float, and the pH of the float adjusted to 11.0 with 0.01M sodium hydroxide.*
- *Appr. 10ml of EPICH (99%) was then added, drum temp. set at 60°C, allowed to run for I hr and then stopped. After resting for I hr and checking pH (the pH was maintained at 11.0), an extra 10ml of EPICH) (99%) was added and the temp. increased to 120°C (to trigger the reaction of the EPICH oxirane ring); the drum was then allowed to run for I hour, contents offloaded and spread on polythene papers to cool down (overnight).*

Recycling of Chrome Leather Waste Cont…

Modification of dechromed waste with EPICH

- *After cooling, the EPICH modified collagenic material was vacuum dried at 80°C for 2minutes using a tannery vacuum drier to mechanically squeeze out excess water present.*
- *This mechanical removal of excess water was meant to allow for concentration of the protein fractions and further modification of the relevant amino acids.*
- *The modified collagenic material was thereafter dried at 40°C for 3 days using the laboratory oven to ensure complete drying.*
- *The dried samples were analysed to identify different functional groups of interest using Infrared (IR) spectroscopy (both before and after EPICH modification.*

Recycling of Chrome Leather Waste Cont…

Formulation of the new organic fertilizer

- *Maize cobs powder was used as filler material in the formulation of this new organic fertilizer.*
- *The milled maize cobs powder was selected as filler material after conducting some preliminary laboratory tests and relevant literature review.*
- *Dry maize cobs were shredded and milled to make powder and samples of the EPICH modified collagenic material were blended at different rates of this filler material.*
- *The use of maize cobs powder keep the resultant slow-release fertilizer from drying out, hardening and clumping during storage. The filler was also intended to contribute to the nutrient value of this new fertilizer.*

Results & Discussion

Nutrient content of the new organic fertilizer

(unmodified and EPICH modified as well as the filler)

Type of nutrient	unmodified collagen hydrolysate	Modified collagen hydrolysate	Filler
Total N (%)	35	44	2.8
Available P (% P_2O_5)	8.27	21.02	14.04
Exchangeable K (% K_2O)	0.25	0.1	0.3
Mg	0.002	0.2	7.5
Ca	0.03	1.8	1.6
TOC (%)	22.15	27.0	38.12
C:N ratio	0.47	0.61	13.61
pH	6.79	6.79	6.76

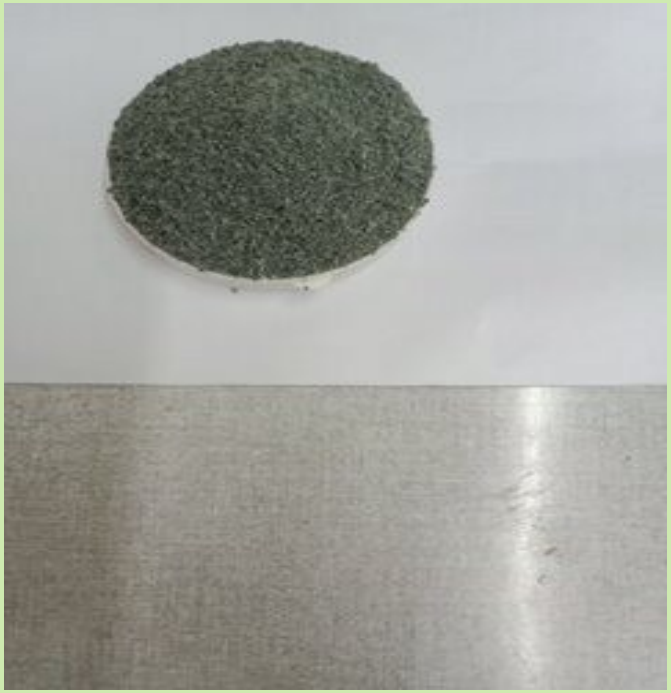
Results & Discussion Cont...

- *It can be seen from the table that EPICH modification improved the nitrogen, phosphorus, magnesium and calcium content of the collagenic fertilizer.*
- *Total N in modified collagen hydrolysate increased to a mean value of 44% from 35% in the unmodified form after modification with EPICH.*
- *The two-stage process of EPICH modification of collagen hydrolysate favoured the development process for a slow-release nitrogen fertilizer that was being investigated in this study.*
- *Available phosphorous (% P_2O_5) in the developed slow-release fertilizer increased from 8.27% (in the unmodified collagen hydrolysate) to 21.02% after modification with EPICH*

Results & Discussion Cont…

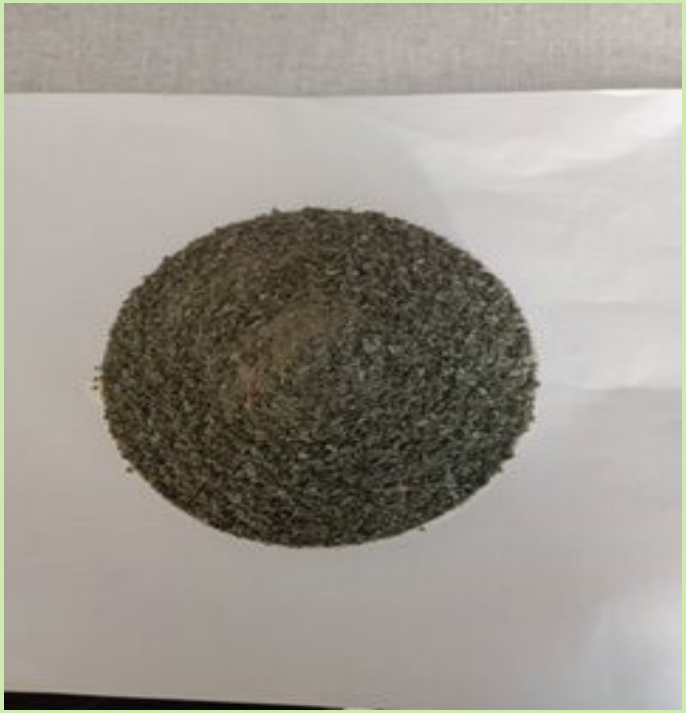
- *EPICH modified collagen hydrolysate was slightly lighter in appearance as compared to the unmodified form due to the presence of relatively more available phosphorus after this modification process.*

(Collagen hydrolysate fertilizer (unmodified)



Results & Discussion Cont…

Collagen hydrolysate fertilizer (EPICH modified)



- *EPICH modification improved the nitrogen, phosphorus, magnesium and calcium content of the collagenic fertilizer.*
- *The amount of carbon content in the EPICH modified collagen hydrolysate increased significantly from 22.15 to 27%. However, C:N ratio & potassium remained low.*

Results & Discussion Cont...

Collagen hydrolysate fertilizer (EPICH modified and blended with filler)

- *Fertilizer filler derived from ground maize cobs is cost effective, ecofriendly & 100% biodegradable.*
- *High C:N ratio (13.6) of the filler makes the slow-release fertilizer more effective.*
- *Improves uniformity in particle size of the fertilizer.*
- *adds more plant nutrients.*
- *enhances ease of application.*

Kale crop under different treatments of greenhouse fertilizer trials (8 weeks old)

- *Treatment 1 (second row to the left)*
- *Treatment 2 (Foreground row)*
- *Treatment 4 (Extreme row to the left)*
- *Treatment 6 (Extreme row to the right)*

Treatment 4 (1769.28kg/ha Fertilizer + 0.00kg/ha Filler) gave the highest kale vegetative growth.

Capsicum crop under optimal fertilizer application rates (8 weeks old)

- *Treatment 5 (the first 3 pots in the middle row)*
- *Treatment 6 (the first 3 pots in the left row)*

The new fertilizer formulation (if applied at optimal rates as seen in Treatment 5) was significantly better than DAP and CAN conventional fertilizers

5 = 1238.50kg/ha Fertilizer + 530.79kg/ha Filler

Conclusions

- *Large quantities of tannery solid wastes are generated by tanneries during leather production.*
- *Significant proportion of this waste is tanned & contaminated with chromium (about 8.5 tonnes per tannery are produced daily) due to the use of chrome as the tanning agent of choice.*
- *Disposal; landfilling.*
- *An efficient, cost effective & environmetally sound method of exracting Cr from chrome leather waste was developed.*
- *Phosphoric acid hydrolysis &EPICH modification of such waste gave rise to an effective slow-release fertilizer.*
- *It was blended with maize cobs powder as the filler.*

THANK YOU
BE BLESSED