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Development of an Eco-friendly and Sustainable Method of Dechroming Leather Wastes

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ABSTRACT

Huge quantities of chromium-containing leather solid wastes are generated during the production of chrome-tanned leather worldwide. Disposal of these huge quantities of leather solid wastes is a major challenge due to the presence of chromium, which is highly toxic (mainly in its hexavalent form) and detrimental to the environment. Sustainable and environmentally friendly methods of their disposal and treatment options for removing chromium are required so that the dechromed waste can be utilized to make useful products, such as fertilizer for soil conditioning, to improve agriculture, or other applications. In this study, therefore, a new method of dechroming leather solid wastes was designed, whose procedure and results were compared with three other commonly used methods. The focus of the various dechroming methods was on the evaluation of the degree of chromium extraction from chrome-tanned leather wastes without destroying the collagen tissues. The average total amount of extractable chromium content (Cr_2O_3) in the dried leather waste samples was found to be 3.67%.

The new method was found to be relatively more efficient, environmentally sound and less cumbersome than all the other methods investigated in this work. At P-Value of < 0.05 , concentrations of chromium extracted and %TKN in residual collagen hydrolysate reached up to 99.89% and 52.89%, respectively. The levels of total ash and total organic carbon were also relatively high in the resultant collagen hydrolysate (i.e. 12.42% and 23.27%, respectively). The t distribution test on the results of the various dechroming methods confirmed that there was a significant difference at 95% confidence interval, since t (calculated) was greater than t (tabulated). It was concluded that nearly all the chromium in chrome-tanned leather wastes can be removed with a simple technology, which is sustainable and environmentally sound.

KEYWORDS

dechroming, hydrolysis, leather waste, sustainable method

INTRODUCTION

Solid waste generation in the leather industry is inevitable. This is due to two major reasons, one of which is the fact that leather processing is primarily associated with the removal of non-collagenous skin components to obtain a single protein, collagen. On the other hand, the intrinsic nature of the leather processing steps coupled with the varied nature of chemicals used is also responsible for the generation of considerable quantities of tannery solid wastes, a majority of which are disposed of through landfill or incineration [1]. However, better options for reutilization of these wastes need to

be explored [2]. Recovery, recycling and reuse of such industrial wastes as raw materials for other applications has posed a great challenge to green chemistry and circular economy for many years [3,4].

According to studies carried out by several researchers [5-7], more than 600 kg of solid waste is generated during the transformation of one ton of raw hide (wet-salted) into leather. A significant proportion of this solid waste is actually tanned waste (200 kg), consisting of shavings, trimmings, splits and buffing dust (with at least 3.5 kg of chromium content for chrome-tanned waste). This situation has been compounded by the fact that more than 90% of the global leather production uses basic chromium (III) sulphate as the tanning agent of choice due to its ability to form stable cross-links with hide collagen carboxyl groups [8,9]. Chrome-tanning is preferred because leather tanned with chromium is versatile (i.e. can be made into a wide variety of finished leathers) and has superior properties as compared to other types of tannages [10]. Besides, the most commonly used chrome tanning salt (basic chromium sulphate) is readily available at a low cost and has been found to be very efficient in leather tanning [3].

It is possible to recycle chrome-tanned solid wastes and even use them as raw materials for different industries, either directly or indirectly [11,12]. Direct recycling means utilizing the chrome-tanned leather waste as a raw material for other industries after only a simple treatment without recovering chromium from the leather waste first. Direct recycling of chromium-containing tanned solid wastes has one serious disadvantage as it poses a very high risk of the chromium being oxidised to Cr (VI), giving rise to secondary pollution [13]. Many scientific groups have oriented their research to find a process to recycle and treat these wastes [14-20]. Chrome-tanned leather scraps and shavings have previously been converted into fertilizers by thermal or enzymatic transformation, but without much success due to the presence of chromium in such waste [1,21-26]. The procedures that have been developed so far, to decontaminate such tannery wastes for re-use as a fertilizer or animal feed additive or for other industrial applications, are complex, time-consuming and expensive. Furthermore, they result in secondary pollution problems [27]. Secondary pollution is a type of pollution that occurs in the atmosphere as a result of reaction of other pollutants emanating from a primary source.

The collagen hydrolysate obtained from the hydrolysis of chromium-containing leather waste has in the past been used in the production of low-cost surfactants, high chrome fixation auxiliaries and fillers for paper [1,26,28-30]. It is against this background, therefore, that an investigation was carried out to develop a sustainable technology of extracting chromium from leather solid wastes and modifying the residual protein fractions for the purpose of enhancing soil fertility.

EXPERIMENTAL

Materials and Methods

Materials

Fresh chrome shavings, trimmings and useless splits were obtained from Alpharama tannery (Athi River, Kenya), spread to dry at room temperature for two days and then conditioned to a moisture content of 50% in preparation for the dechroming process. The reagents required for the dechroming and hydrolysis processes were obtained from OSHO CHEMICALS (K) Ltd. They were all of analytical reagent grade. Commonly available laboratory chemicals were used in the experiments and during all the analyses. The amounts and types of reagents used for dechroming and hydrolysis process in the respective methods that were being compared in this study are summarised in Table 1.

Table 1. Amounts and types of reagents used for leather waste dechroming and hydrolysis process in the respective methods

Method & Amount of sample	Amount & Type of reagent	Amount & Type of reagent	Amount & Type of reagent	Amount & Type of reagent	Amount & Type of reagent
1 100g/l sample (aq)	10% w/v Sodium sulphate (x2)	10% w/v Sodium carbonate	8% v/v Hydrogen peroxide 0.2% v/v Hydrogen peroxide	6% w/v Sodium chloride (x3)	1% v/v Sulphuric acid
2 20g/100ml sample (aq)	5% w/v Sodium sulphate 10% w/v Sodium sulphate (x5)	4% w/v Sodium carbonate	3% w/v Calcium hydroxide	6% w/v Sodium chloride (x3)	1% v/v Sulphuric acid
3 20g/100ml sample (aq)	5% w/v Sodium carbonate	2% w/v Sodium hydroxide	15% v/v Hydrogen peroxide	10% w/v Sodium sulphate (x5)	6% w/v Sodium chloride (x3) 1% v/v Sulphuric acid
4 10kg/15l sample (aq)	350g Calcium hydroxide + 15l Water (initial float)	0.2% w/v Ammonium sulphate + 200% Water (fresh float)	200ml Formic acid + 100% Water (fresh float)	250g Potassium oxalate + 100% Water (fresh float)	1000ml Phosphoric acid + 100% Water (fresh float) x2

Key

Method 1 – Dechroming method according to Sun *et al.*, 82.9% Cr extracted in 16 hours [31].

Method 2 – Dechroming method according to Paul *et al.*, 71.5% Cr extracted in 36 hours [32].

Method 3 – Dechroming method according to Adeoye *et al.*, 90.0% Cr extracted in 36 hours [33].

Method 4 – New method of dechroming developed in this study; 99.9% Cr extracted in 24 hours.

Methods

A new method of detanning chrome leather waste was designed, the procedure and results of which were compared with three other commonly used methods, namely the standard method of dechroming leather waste as described by Sun *et al.*, the alkaline hydrolysis method by Paul *et al.* and the dechroming method according to Adeoye *et al.* usually known as modified alkaline hydrolysis [31-33].

Sample collection and preparation

Collection of leather waste samples consisting of fresh chrome leather shavings (10 kg), trimmings and useless splits (10 kg) was carried out at Alpharama tannery (Athi River, Kenya) and then the samples were thoroughly mixed together following the procedure described by Ozgunay *et al.* [34]. The trimmings and splits were first chopped into tiny pieces so as to increase their surface area. The respective samples were then spread on polythene sheets of paper for two (2) days to dry. The moisture content for the dried samples was determined using the International Union of Leather Technologists and Chemists Society (IULTCS) official methods of analysis as well as according to Aneja [35,36]. The estimation of chromic oxide concentration in the dried leather waste samples was determined by the wet oxidation method as described in the International Union of Leather Technologists and Chemists Society (IULTCS) official methods of analysis [37]. The details of the wet oxidation method are summarised as follows:

Step 1 – Some of the prepared chrome leather waste samples were weighed accurately (2.5 g) in a conical flask, after which 15 ml of a mix of sulphuric and perchloric acid and a few anti-bumping granules were added.

Step 2 – A funnel was then placed in the neck of the conical flask and the contents were heated to a boiling point on a wire gauze over a moderate flame. As soon as the reaction mixture started to turn orange, the flame was lowered.

Step 3 - After a complete change of colour, the contents of the flask were heated gently for two minutes, allowed to cool in air for five minutes and then diluted to approximately 200 ml.

Step 4 – Boiling was then done for ten minutes to eliminate any chlorine and the flask was then allowed to cool, after which 15 ml of orthophosphoric acid was added to mask any iron. Potassium iodide solution (20 ml) was also added at the same time, and the flask was then stoppered and left to stand in the dark for ten minutes.

Step 5 – Titration with 0.1 M sodium thiosulphate solution was then carried out until the solution in the flask turned light green after using 5 ml of starch indicator solution (added toward the end of the titration).

The results for this determination are indicated in Table 2 (Results and Discussion section).

The levels of Total Kjeldahl Nitrogen (TKN) and hide substance, total lipid - fat content, humidity, total ash and pH were also determined [38-41].

Thereafter, the samples were conditioned to a uniform moisture content of 50%. 10 kg of dried and conditioned samples in each category were further divided into two (2) similar samples of 5 kg each for the purpose of getting representative data for statistical analysis. The duplicated samples were then milled using the laboratory grinding mill (before wetting them back) for further increase of surface area. The purpose of wetting back of the samples before detanning was to speed up the detanning process so as to trigger an increased rate of chromium extraction in the ensuing process step that was to follow after detanning.

Dechroming method according to Sun *et al.* (usually known as normal alkaline hydrolysis or standard dechroming method [31])

The aim of this dechroming method was to remove the chromium without affecting the properties of the original fibres [31,42]. Prepared chrome leather waste sample (100 g/l) was stirred in a mixed solution of sodium sulphate (10%) and sodium carbonate (also 10% used as opposed to the conventional 8% of Na₂CO₃). After 15 minutes, hydrogen peroxide (8%) was added to the solution and stirred for 2 hours. Water was removed from the sample by filtration by using a 2 mm sieve. The sample was subsequently washed with sodium sulfate solution (10%) for 15 minutes and filtered (with a 2 mm sieve). The washing step was repeated three times after which the sample was then put in a prepared solution of sodium chloride (6%), hydrogen peroxide (0.2%) and sulphuric acid (1%). This mixture was stirred for 30 minutes and then filtered. After filtration, the sample was then washed in a 6% sodium chloride solution for 15 minutes and filtered again. This washing step was repeated twice. The dechromed leather waste was subsequently allowed to air-dry at room temperature. The effect of the oxidation period on the degree of dechroming was investigated for 0.5, 1, 2, 4, 8, 16, 24, 36 and 72 hours of treatment. The dechroming ratio or percentage of the chromium removed from the sample was calculated as follows:

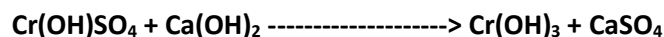
Dechroming ratio (%) = 100 [(Cr_{waste} – Cr_{dec})/Cr_{waste}], where Cr_{waste} and Cr_{dec} are values of concentration of Cr₂O₃ in leather waste before and after the dechroming process, respectively [31].

Dechroming method according to Paul *et al.* (usually known as alkaline hydrolysis) [32]

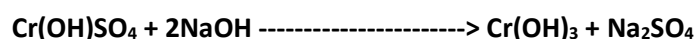
The prepared chrome leather waste was dried at room temperature to a constant weight and then pulverized using an electric mill with a 2 mm mesh size. All the chemicals used were of analytical grade and obtained from OSHO CHEMICALS (K) Ltd.

This method was carried out following the procedure developed by Paul *et al.* [32]. Three samples, each weighing 20 g, were taken from the pulverized leather waste and dechromed as follows:

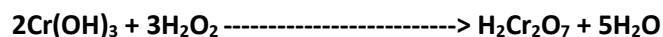
Step 1 – Chrome leather waste (sample) weighing 20 g per 100ml was placed in sodium sulphate (5% w/v) and sodium carbonate (4% w/v) solution for 30 minutes followed by calcium hydroxide (3% w/v) for 1 hour.



Step 2 – sodium hydroxide solution (0.1% w/v) was then added.



Step 3 – Hydrogen peroxide (10% v/v) was added to the solution and stirred for two days.



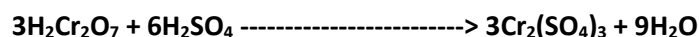
Step 4 – Water was removed by filtration.

Step 5 – The sample was washed three times with sodium sulphate solution (10% w/v) and filtered.

Step 6 – The sample was soaked with sodium chloride (6% w/v) and sulphuric acid solution (1% v/v) for acid steeping for 1 hour and filtered.

Step 7 – The sample was washed twice with sodium sulphate (10% w/v) and sodium chloride (6% w/v) and filtered.

Step 8 – The dechromed leather waste (product) was then allowed to air-dry at room temperature.

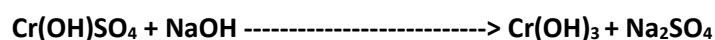


Dechroming method according to Adeoye *et al.* (usually known as modified alkaline hydrolysis) [33]

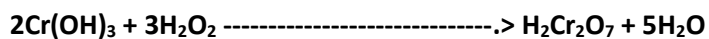
Three other replicated samples, each weighing 20 g, of the pulverized leather waste were also dechromed using the method developed by Adeoye *et al.*, usually known as modified alkaline hydrolysis, for comparison purposes, as described below [33].

Step 1: Chrome leather waste (sample) weighing 20 g per 100 ml was placed in sodium carbonate (5% w/v) solution for 30 minutes.

Step 2: Sodium hydroxide solution (2% w/v) was then added.



Step 3: Hydrogen peroxide (15% v/v) was added to the solution. The reacting medium was kept airtight and the left for 30 minutes for reaction to take place.



Step 4: Water was removed by filtration.

Step 5: The hydrolysed sample was washed three times with sodium sulfate solution (10% w/v) and filtered.

Step 6: The hydrolysed sample was soaked with sodium chloride solution (6% w/v) and sulphuric acid solution (1% v/v) for acid steeping for 1 hour and filtered.

Step 7: The sample was then washed twice with sodium sulfate solution (10% w/v) and sodium chloride (6% w/v) and then filtered.

Step 8: The dechromed leather waste (product) was then allowed to air dry at room temperature.

The newly developed method of decontaminating chrome-tanned leather solid wastes

The new method of decontaminating chrome leather waste samples was carried out following a series of steps, which included detanning, preliminary chromium extraction, further chromium extraction and complexation with potassium oxalate, and finally, hydrolysis of the dechromed samples with phosphoric acid. The respective steps are described below.

Detanning of chrome leather waste samples

The fresh chrome leather waste samples were dried at room temperature for two days and then conditioned to a moisture content of 50%. The samples were thereafter mixed with water (15 litres for every 10 kg of sample) and alkali in plastic containers and the pH adjusted to 12 (lime works best at pH 12). Approximately 350 g of pure lime was used for every 10 kg of the sample at a moisture content of 50%. Mixing in the plastic containers was then allowed to take place for 1 hour; contents were poured into the experimental tannery drum at the Kenya Industrial Research and Development Institute (KIRDI) and the drum was allowed to run for an hour, and thereafter 10 minutes every hour for 12 hours.

After 12 hours, the contents were carefully offloaded into plastic containers ensuring that no liquor was lost. The contents were filtered with a 2 mm sieve and a strainer, and then lime-washed for 30 minutes with 0.2% ammonium sulphate in 200% fresh float (based on the weight of original leather waste sample) to remove excess alkali. This led to a considerable reduction in the quantity of acid used later during the chromium extraction step. Extracted chromium was collected in the filtrate. The filtration process was repeated to ensure complete extraction of chromium from the sample. The amount of chromium extracted was determined using the method developed by Sun *et al.* [31].
 Dechroming ratio (%) = $100 [(Cr_{\text{waste}} - Cr_{\text{dec}})/Cr_{\text{waste}}]$, where Cr_{waste} and Cr_{dec} are values of

concentration of Cr₂O₃ in leather waste before and after the dechroming process, respectively.

Preliminary chromium extraction from detanned leather waste samples

A modified form of the new approach of decontaminating chrome leather waste according to Malek et al. was used [43]. Approximately 200 ml of formic acid (85% purity) was added to 10 kg of detanned leather waste samples in a plastic container containing 100% fresh float, with the pH adjusted to 3. Mixing was allowed to take place for an hour in the horizontal shaker and, thereafter, the contents were transferred to the experimental tannery drum, which was then run intermittently for 10 minutes every hour for a total period of 12 hours. The contents were subsequently filtered using a 2 mm sieve and a strainer. All the filtrate was collected in a plastic container and the volume was measured.

The remaining water was squeezed out mechanically by pressing the samples while ensuring that the water was being collected in another container and its volume noted. The percentage of the chromium extracted was then calculated on the basis of the volume of water collected both after filtration and after mechanical dewatering of the samples following the method described by Sun et al. [31].

Further chromium extraction from detanned leather waste samples and its complexation with potassium oxalate

Further extraction of the remaining chromium was done by using potassium oxalate (250 g of potassium oxalate in 100% fresh float, for every 10 kg of the sample) instead of formic acid. The amount of chromium extracted after this further extraction with potassium oxalate was determined by atomic absorption spectrometry (AAS), Model No. 210 VGP, 115-230 Volts (Bulk Scientific), made in USA, in the Department of Land Resource Management and Agricultural Technology (LARMAT), University of Nairobi. The few traces of chromium remaining in the collagenic material after this final extraction with potassium oxalate were expected to form chromium oxalate complexes, which would be needed in the resultant fertilizer as a nutrient for crop growth. These few traces of chromium (VI) remaining in the collagenic material after final extraction and complexation with potassium oxalate were determined using UV-Vis spectrophotometer U2900 model SP-291 (200V made in Japan) in the Department of Animal Production (University of Nairobi). The samples were prepared for this determination following the procedure described in the official methods of analysis of the society of leather technologists and chemists [44]. The calculation for the residual traces of chromium (VI) content in the final collagen hydrolysate was done using the following formula:

$$\% \text{Cr}^{6+} = \frac{[\text{Absorbance Graph reading} \times \text{Dil. Factor (12.5)} \times \text{Initial Vol. Of sample (100ml)}]}{\text{Weight of sample (300g)} \times 1,000,000} \times 10$$

Hydrolysis of the dechromed leather waste samples

After chromium extraction, the dechromed leather waste samples were pressed and thereafter hydrolysed with phosphoric acid (100ml for every 1kg of sample or 1000ml for every 10kg of sample) at a controlled temperature of 50°C in 300% float for 1hour to avoid dissolution of the collagen. The hydrolysis was carried out in a stainless-steel tannery experimental drum at KIRDI. Mixing was allowed to take place in a closed plastic container for 1 hour before loading the contents to the stainless-steel tannery experimental drum.

After loading the contents to the experimental drum, temperature controls were set at 50 °C and then an extra 1000 ml (1 litre) of orthophosphoric acid added to the 10 kg sample in the drum. The experimental drum was then switched on to run for 1 hour after which it was allowed to rest overnight. The following morning the drum was allowed to run for 30 minutes and then the liquor was drained. Thereafter, the drum contents were offloaded, pressed and squeezed through a strainer while collecting some of the squeezed liquor to be analysed for total chromium by atomic absorption spectrometry (AAS), Model No. 210 VGP, 115-230 Volts (Bulk Scientific), made in USA, in the Department of Land Resource Management and Agricultural Technology (LARMAT), University of Nairobi. The collagenic material was then dried in the laboratory oven at 40 °C until completely dry and ready for the potential use as a fertilizer with a few modifications.

Data analysis

Statistical analysis of the experiments was performed through the analysis of variance (ANOVA) to determine statistical significance of the various factors studied in this work. P-Value of < 0.05 was considered significant in all statistical comparisons for amounts of chromium extracted and TKN concentrations in dechromed and hydrolysed leather waste as shown in Table 8 and Table 10, respectively [45]. The factors (variables) that were being correlated in this study were performance (i.e. time taken for the chromium extraction to be completed), efficiency (i.e. amount of chromium extracted per unit time using various methods), and concentrations of TKN in the dechromed collagen hydrolysates using the respective methods.

RESULTS AND DISCUSSION

Estimation of chromic oxide (Cr₂O₃) in raw chrome leather waste samples

Determination of the amount of total chromium in both leather and leather waste samples is very important for a number of reasons. Firstly, basic chromium (III) tanning salts are widely used during the manufacture of shoe upper leather and clothing leather as well as upholstery leather (particularly automotive and furniture upholstery), used mainly for decoration and/or covering purposes [46]. Therefore, the amount of chromic oxide (Cr₂O₃) fixed onto the hide collagen determines the

superiority of the resultant leather and consequently, the final leather product in terms of versatility, hydrothermal stability, flexibility, durability and resistance to microbial degradation. Secondly, before chrome-tanned leather waste could find meaningful use in other applications, the chromium needs to be removed first. Consequently, determination of the total chromium content both in leather and leather waste samples is very important.

It is also worthwhile to note that although chrome tanning is a very important process that provides stability to the skin matrix, we have to deal with the problem of increased use of chromium (III) tanning salts in the tanning industry, which afterwards are released into the environment or remain in and on the leather product [47]. In this regard, therefore, Table 2 shows the average total chromium content (Cr_2O_3) in raw chrome leather waste samples that needed to be extracted in this study, as 3.67%.

Table 2. Estimation of chromic oxide (Cr_2O_3) in raw chrome leather waste samples by the wet oxidation method

Raw chrome leather waste	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Mean
Cr_2O_3 content (%)	3.17	3.77	3.97	3.91	3.34	3.89	3.67

Dechroming and hydrolysis process

The hydrolysis method followed in the various dechroming procedures carried out in this study focused especially on the extraction of chromium from chrome-tanned leather waste. This was particularly so on the newly developed method, which was the subject of this study and, being able to extract 99.89% of chromium from the leather waste (Table 3), became the most suitable method of dechroming leather waste as compared to all the other methods investigated in this study (Table 4).

Table 3. Chemical characterization of chrome leather waste v/s mass of collagen hydrolysate produced and the percent of residual chromium in the resultant collagen hydrolysate after dechroming using the newly developed method

Dechromed Leather Waste	Moisture Content (%)	Total Organic Carbon (%)	pH	Total Ash (%)	TKN (%)	Chromium Extracted (%)	Residual Cr (%)
Mean	12.61	23.27	10.01	12.42	52.89	99.89	0.11

Chrome tanning agents (mostly in the form of basic chromium (III) sulphate) interact with the collagen triple helix and its supramolecular water layer by different interactions, including covalent, hydrogen and van-der-Waals bonding, involving both the acid and the basic group of aspartic and

glutamic acids as shown in Figure 1 [48]. Therefore, the alkaline hydrolysis procedure followed in the various dechroming methods investigated in this study is basically a simple process by which complex molecules are broken down into their simplified constituent building blocks by water (H₂O) in the form of the hydrogen ion (H⁺) and hydroxyl ion (OH⁻) between the atoms of the bonds that hold those building blocks together [33].

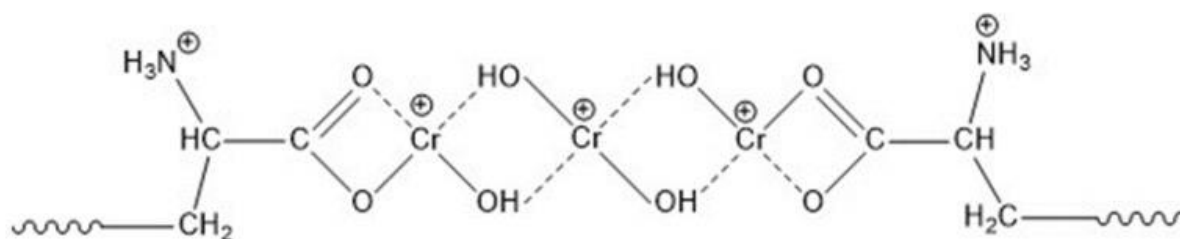


Figure 1. Crosslinking reaction between a chrome-tanning agent and hide collagen [adapted from Ref. 48]

The newly developed dechroming procedure was found to be the most suitable method of extracting chromium from chrome-tanned solid wastes without destroying the collagen tissues. At P-Value of < 0.05, concentrations of both chromium and %TKN extracted from the waste reached up to 99.89% and 52.89%, respectively (Table 3). The levels of total ash and total organic carbon were also relatively high in the resultant collagen hydrolysate (i.e. 12.42% and 23.27%, respectively, as indicated in Table 3).

It was more efficient than the other dechroming methods investigated in this work (shown in Table 4 as method 4) because the hydrolysis part was performed using orthophosphoric acid at a controlled temperature of 50 °C after preliminary extraction of the chromium using formic acid and potassium oxalate.

Table 4. Efficiency of dechroming leather waste using different methods in percentages

Duration	0hr	0.5hr	1hr	2hr	4hr	8hr	16hr	24hr	36hr	72hr
Method 1	0	5.00	7.20	15.20	36.80	68.60	82.90	82.90	82.90	82.90
Method 2	0	2.90	6.80	13.00	22.30	48.20	53.10	62.60	68.20	71.50
Method 3	0	11.30	20.20	28.90	42.70	66.60	72.50	83.40	90.00	90.00
Method 4	0	20.00	28.60	31.80	62.80	77.10	89.40	99.89	99.89	99.89

Key

- Method 1 – Dechroming method according to Sun *et al.*, 82.9% Cr extracted in 16 hours[31].
- Method 2 – Dechroming method according to Paul *et al.*, 71.5% Cr extracted in 36 hours [32].
- Method 3 – Dechroming method according to Adeoye *et al.*, 90.0% Cr extracted in 36 hours [33].
- Method 4 – New method of dechroming developed in this study, 99.9% Cr extracted in 24 hours.

Independent sample t-test on the results indicated in Table 4 gave a calculated $t_{.025}$ -value of 12.62 against the one given in statistical tables of 2.306 at 95% confidence interval with 8 degrees of freedom. This is an indication that there was a significant difference at 95% confidence interval when comparing the efficiency of the various dechroming methods investigated in this study.

Analysis of chromium extracted from chrome-tanned leather waste

The analysis of chromium extracted from chrome-tanned leather waste was done by using atomic absorption spectroscopy (AAS), model No. 210 VGP, 115-230 Volts (Bulk Scientific), from the soil chemistry laboratory, department of Land Resource Management and Agricultural Technology (LARMAT), University of Nairobi. The target of the analysis was to determine the chromium content in the respective samples both prior and after the dechroming process. Results obtained in this study indicate that the mean concentration value of chromium in raw chrome leather waste samples was 218.65 ppm (Table 6, sample A), which was reduced to a mean concentration value of 62.52 ppm after dechroming with the alkaline hydrolysis method developed by Paul *et al.* (Table 6, sample B) [32].

Table 5. Dechroming ratio/percent of chromium extracted from chrome-tanned leather waste using the normal alkaline hydrolysis method

Sample	Trial 1	Trial 2	Trial 3	Mean
	Cr extracted	Cr extracted	Cr extracted	Cr extracted
1	83.5	81.2	84.0	82.9
2	80.6	81.9	83.2	81.9
3	81.6	83.2	83.9	82.9

Table 6. Dechroming ratio/percent of chromium extracted from chrome-tanned leather waste using both alkaline hydrolysis and modified alkaline hydrolysis methods

Sample	Trial 1	Trial 2	Trial 3	Mean
	(concentration – ppm)			
A	218.65	218.63	218.66	218.65
B	69.35	55.29	62.91	62.52
C	19.94	23.53	21.53	21.67

Key

Sample A: Chrome-tanned leather shavings (raw sample)

Sample B: Dechromed leather shavings after using the alkaline hydrolysis method [32]

Sample C: Dechromed leather shavings after using the modified alkaline hydrolysis method [33]

Dechroming using the modified alkaline hydrolysis method developed by Adeoye *et al.* was relatively more efficient in chromium extraction from the leather waste samples as it reduced the mean concentration value to 21.67 ppm (Table 6, sample C) (i.e. by 90.0% as opposed to a 71.5% reduction achieved by the alkaline hydrolysis method described by Paul *et al.* and the commonly used standard method (normal alkaline hydrolysis) according to Sun *et al.* which achieved 82.9% as indicated in Table 5) [31-33]. Results obtained from the AAS analysis of the amount of chromium extracted from leather solid wastes at different intervals with various dechroming methods indicated that the new method was the most efficient compared to all the others investigated in this study (Table 4) as well as from literature values of other dechroming methods carried out [43,49-51]. Atomic absorption spectrometry analysis of residual chrome content in leather waste dechromed with the new dechroming method gave an average value of 0.12% as shown in Table 7. This is a clear indication that the method was very effective.

Table 7. Atomic absorption spectrometry analysis of residual chrome content in leather waste dechromed with the new dechroming method

Dechromed leather waste	Percent residual Cr content	Percent Cr extracted
Mean	0.12	99.89

After subjecting the resultant data to ANOVA to determine statistical significance of all factors considered on concentrations of chromium extracted using the new method as a comparison, there was a positive significant effect at P-Value of < 0.05 (Table 8).

Table 8. ANOVA table showing positive significant effect (P<0.05) of all factors on concentrations of chromium extracted from leather waste using the new dechroming method as a comparison

Sample	Sum of squares	Degrees of freedom (x 10 ⁻⁵)	Means of squares (x 10 ⁻⁵)	Sample Variance	F _{ratio}
1	0.09990	1	0.01665	0.00072	0.04320
2	0.09968	1	0.01661	0.00050	0.03010
3	0.09942	1	0.01660	0.00648	0.03480
4	0.09992	1	0.01665	0.00098	0.05890
5	0.09984	1	0.01665	0.00018	0.01080
6	0.09972	1	0.01663	0.00010	0.00600

Analysis of collagen hydrolysate obtained from dechromed leather waste

Tanned leather waste constitutes mainly of collagen, which is responsible for the formation of leather by combination with tanning agents [52]. This combination involves several simultaneous chemical reactions between chromium (III) and the carbonyl side chains of aspartic and glutamic acid on hide collagen making the resultant material with high hydrothermal stability [53,54].

Collagen fibres in the leather waste are normally found enclosed in a connective tissue known as sarcolemma, where under conditions of ordinary temperature, they are insoluble in water and in diluted solutions of acids and alkalis as well as in organic solvents [55]. Due to the steric configuration of the collagen triple helix, the Hyp ring normally points outwards in the sarcolemma sheath constituting an aggregation point for water molecules, which use hydrogen bonding to bond with the prolyl hydroxyl group, leading to the formation of a solvating cylinder of supramolecular water by nucleation at the Hyp sites, as shown in Figure 2 [56].

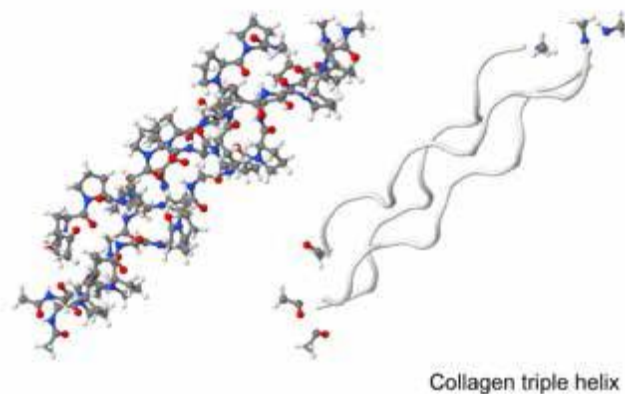


Figure 2. Collagen triple helix with Hyp rings (red) pointing outwards in the sarcolemma sheath [adapted from Ref. 56]

Since this is the region where tanning reactions occur, it has been found that most of the residual chromium in the conventional dechroming methods remained trapped within the collagen hydrolysate fibres in form of chromate ions even after final washing. However, in the new method (developed in this study), the residual chromium was complexed with potassium oxalate as part of the dechroming process leading to the formation of potassium chromate complexes and some traces of chromium oxalate. Due to its high solubility in water, potassium chromate could easily be washed away from the dechromed leather waste after final washing step, whereas the few traces of chromium oxalate remaining in the collagen hydrolysate have been suggested in literature to play an essential role in the growth of food crops [57]. This is an added value to the resultant collagen hydrolysate, which is intended to be used as fertilizer. It has already been established that the nitrogen content in hydrolysed tannery solid wastes with less than 0.5% chrome content, as is the case in this study (Table 7), is quickly and decomposed to a very high extent due to a high presence

of organic matter in such wastes [58]. This results on the one hand in a very good fertilizing effect and on the other hand in the need to restrict the amount applied to the needs of individual plants. Investigation of residual traces of chromium (VI) in the final collagen hydrolysate obtained after complexation with potassium oxalate using the 1, 5 Diphenyl carbazide method [44] gave the results indicated in Table 9 after measuring the absorbance at 540 nm with UV/Vis spectrophotometer (U2900 200V model SP-191 made in Japan).

Table 9. Measurement of absorbance at 540nm for residual Cr⁶⁺ in collagen hydrolysate using UV/Vis spectrophotometer (U2900 200V model SP-191)

Collagen hydrolysate samples	Average graph reading (Absorbance at 540nm) (mg/l)	Average residual Cr ⁶⁺ present in a sample (%)
A ₁	1.97	0.0008
A ₂	2.01	0.0008
B ₁	8.51	0.0035
B ₂	8.72	0.0036
C ₁	1.99	0.0008
C ₂	10.45	0.0043
D ₁	10.55	0.0044
D ₂	10.51	0.0044
Average residual Cr⁶⁺ present in sample (%)		0.0028

Key

Sample A₁ and A₂ – Collagen hydrolysate sample concentration (50mg/l)

Sample B₁ and B₂ – Collagen hydrolysate sample concentration (100mg/l)

Sample C₁ and C₂ – Collagen hydrolysate sample concentration (150mg/l)

Sample D₁ and D₂ – Collagen hydrolysate sample concentration (200mg/l)

The collagen hydrolysate obtained after dechroming and the hydrolysis of leather waste using the new method was found to contain a mean value of 0.12% residual chromium, as indicated in Table 7. Further analysis of the collagen hydrolysate to determine traces of residual chromium (VI) remaining after complexation with potassium oxalate gave an average negligible quantity of only 0.0028% Cr⁶⁺ (Table 9) which must have been washed away as Cr⁶⁺ is highly soluble in water. This residual chromium content was the lowest compared to all the other dechroming and hydrolysis methods investigated in this study. The total protein content (TKN) in the collagen hydrolysate obtained using the new method was the highest compared to the other methods studied in this work as well as from literature values, regardless of the time taken for the dechroming and hydrolysis process in the respective methods that were investigated [14,59]. This is indicated in Table 11 where the ratio of TKN to residual chromium after extraction using the new method was found to be 1,238.80 (sample

D), which was the highest compared to the rest. P-Value of < 0.05 was considered significant in all statistical comparisons for TKN concentrations in dechromed and hydrolysed leather waste as shown in Table 10.

Table 10. ANOVA for TKN concentrations in dechromed and modified leather waste (P<0.05) using the new dechroming method as a comparison

Sample	Sum of squares	Degrees of freedom (x 10 ⁻⁵)	Means of squares (x 10 ⁻⁵)	Sample Variance	F _{ratio}
1	0.0222	1	0.0037	6.7512	0.0230
2	0.0273	1	0.0046	0.0769	0.0002
3	0.0272	1	0.0045	3.7152	0.0070
4	0.0271	1	0.0045	0.1479	0.0003
5	0.0312	1	0.0052	1.7880	0.0038
6	0.0280	1	0.0047	0.0000	0.0000

Table 11. Percent chromic oxide (Cr₂O₃) in the original chrome leather waste v/s dechroming ratio and TKN/residual chromium ratio

Sample	Percent Cr ₂ O ₃ content	Dechroming ratio/ percent chromium extracted	TKN/Residual chromium ratio
A	3.17	218.65	960.80
B	3.77	62.52	326.70
C	3.97	21.67	197.20
D	3.91	Negligible	1,238.80

Key

Sample A: Chrome-tanned leather waste (raw sample)

Sample B: Leather waste dechromed using alkaline hydrolysis method [32]

Sample C: Leather waste dechromed using modified alkaline hydrolysis method [33]

Sample D: Leather waste dechromed using the new method (formic acid with potassium oxalate dechroming and orthophosphoric acid hydrolysis)

Strengths of the new dechroming and hydrolysis method compared to other procedures investigated in this study

The new method of dechroming and hydrolysing chrome-tanned leather waste developed in this study achieved 99.89% chromium removal from such waste (within 24 hours) with minimum input of chemicals, energy, and without digesting the collagen fibre structure as no enzymes, strong acids or strong alkalis were used in the chromium extraction process step. This makes the new method more environmentally friendly, cost effective and sustainable, and also the most efficient method of extracting chromium from chrome-tanned leather waste compared to the existing methods. Comparisons of the various dechroming methods investigated in this study in terms of both

efficiency (amount of chromium extracted per unit time) and performance (time taken for the chromium extraction to be completed) are illustrated in Figure 3.

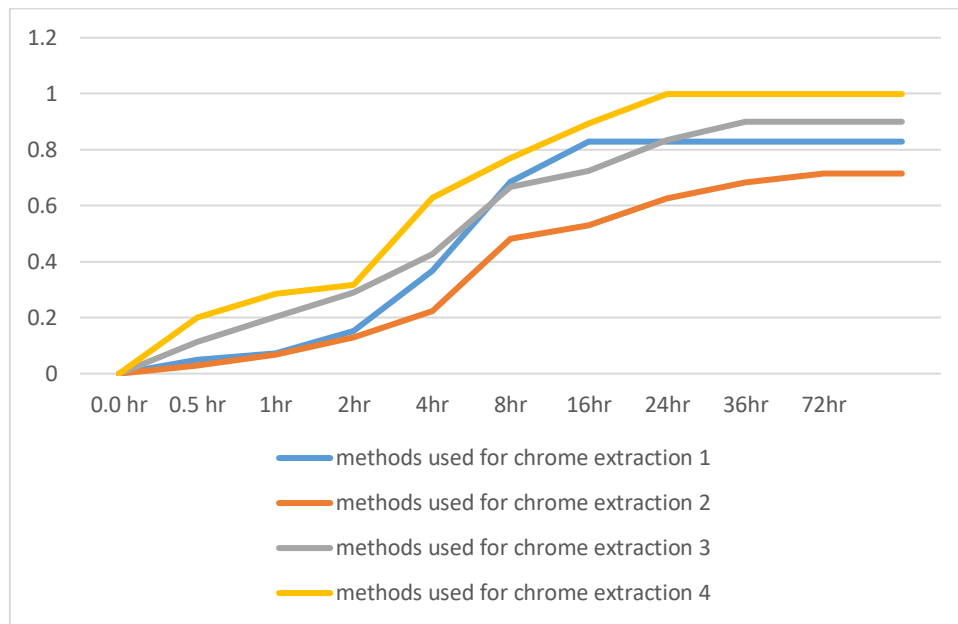


Figure 3. Comparisons of both efficiency and performance of various dechroming methods

Key

Method 1 – Dechroming method according to Sun *et al.*, 82.9% Cr extracted in 16 hours [31].

Method 2 – Dechroming method according to Paul *et al.*, 71.5% Cr extracted in 36 hours [32].

Method 3 – Dechroming method according to Adeoye *et al.*, 90.0% Cr extracted in 36 hours [33].

Method 4 – New method of dechroming developed in this study; 99.9% Cr extracted in 24 hours.

The most commonly used method of extracting chromium from tanned leather waste (normal alkaline hydrolysis), the one developed by Sun *et al.* achieved only 82.6% chromium removal from chrome leather waste after 16 hours, as opposed to the method followed by Catalina *et al.*, which achieved 96% of dechroming after 72 hours of treatment with hydrogen peroxide [31,50]. Decontamination of chrome-tanned leather waste using potassium tartrate as described by Malek *et al.* achieved 95% of chromium removal [43]. This level of achievement was the same as that found in the method developed by Taylor *et al.* where the dechroming process was carried out through enzyme hydrolysis in around 36 hours [49]. The dechroming method according to Paul *et al.* only managed 71.5% of chromium removal in 36 hours [32]. However, the modified alkaline hydrolysis developed by Adeoye *et al.* was able to extract 90% of chromium from the chrome-tanned leather waste in the same number of hours [33].

The new method of dechroming leather waste (developed in this study) was also more efficient than the one performed by Ding *et al.* where at least some degree of hydrolysis of the collagen was witnessed due to the use of sodium hydroxide and sulfuric acid (strong alkali and strong acid, respectively) [51]. It achieved slightly more than 97% of chromium removal from the chromium-containing leather waste. This amount of chromium removal was slightly lower than the amount removed with the new method. In the new method developed in this study, there was no need for cumbersome procedures to be undertaken such as lyophilization or micronizing into a micronizer prior to the dechroming process. Also, there was no need for the use of ultrasound techniques and costly extracting solutions such as in the case of the recently developed method by Ariana *et al.* which achieved slightly more than 98% of Cr extraction from residual tannery leather [60].

Environmental impact of chemical reagents used in various dechroming methods

Sodium sulphate (used in dechroming methods 1, 2 and 3)

A study carried out by Samadhi established that the influence of atmosphere and reducing agents can cause the decomposition of sodium sulphate leading to SO_x and particulate matter emissions [61]. Sulphate particles are usually acidic and when dissolved in water they form sulphuric acid. Deposition of the sulphuric acid is usually through acid rain and snow, which can cause serious damages to a variety of ecosystems and materials.

Disposal of sulphate-containing tailings into the environment (from industrial sources) is especially problematic as the sulphate may enter surface and underground water [49]. A considerable proportion of sulphate in water combines with iron and manganese to form black ooze and wad, which is responsible for the black colour of most marine sediments [62].

Sodium carbonate (used in dechroming methods 1, 2 and 3)

Sodium carbonate is not known to have any adverse effects on the environment. In water, sodium carbonate dissociates into sodium and carbonate and both ions are not expected to adsorb significantly to the sediment [63]. However, in aquatic systems the estimated acceptable limits of sodium carbonate range between 2 and 20 mg/l (depending on the buffer capacity of the aquatic ecosystem) [63]. These limits are unlikely to be exceeded under normal circumstances as sodium carbonate reacts with water leading to an increase in alkalinity and, hence, a tendency to raise the pH value. The carbonate ions will react with water to produce bicarbonate and hydroxide, until equilibrium is reached.

Hydrogen peroxide (used only in dechroming methods 1 and 3)

Presence of hydrogen peroxide in the lower layer of the atmosphere (troposphere) promotes the oxidation of SO₂ to SO₃ causing secondary pollution problems [64,65].

Thus,



Sodium chloride (used in dechroming methods 1, 2 and 3)

Industrial waters usually contain a large amount of difficult-to-treat wastewater high in salt with compact components which cause great damage to the environment [66]. The chloride ion (Cl⁻) in the industrial wastewaters, though essential for biological function of aquatic organisms, can, in large concentrations, disrupt ion balance in those organisms and can alter the physical structure of soil when exposed to sodium ions (Na⁺) [67].

Sulphuric acid (used in dechroming methods 1, 2 and 3)

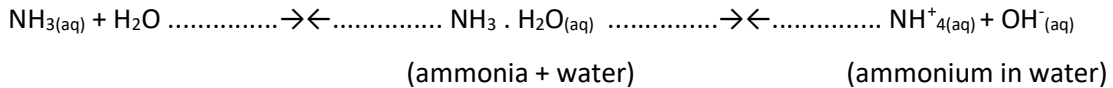
Sulphuric acid discharged to the environment from industrial processes normally exists in the form of droplets in the atmosphere, which may dissolve in clouds, fog, rain, dew, or snow, resulting in very dilute acid solutions. Sulphuric acid has a moderate chronic (long-term) toxicity to aquatic life [68].

Calcium hydroxide (used only in dechroming methods 2 and 4)

Calcium hydroxide is generally not considered to be problematic for environmental quality. However, human exposure to alkaline wastes has adverse health effects which include severe burns to the skin, mouth, throat or eyes depending on the exposed area [69].

Ammonium sulphate (used only in dechroming method 4)

The ammonium ion (NH₄⁺) is non-toxic as opposed to 'unionised ammonia' (NH₃). There exists an equilibrium in water between the toxic ammonia (NH₃) and non-toxic ammonium (NH₄⁺), shifting back and forth depending upon existing or introduced environmental changes (temperature and pH); thus,



At a pH of 6 the ratio of ammonia to ammonium is 1 to 3000 but decreases to 1 to 30 when the pH rises to 8 [70].

According to ARKEMA GPS Safety Summary, ammonium sulphate is harmful to fish but not to the aquatic invertebrates and algae. It is not harmful to aquatic organisms upon long-term exposure in

water. Once exposed to the environment, ammonium sulphate immediately dissociates into its ionic constituents (which are normally present in the environment) [70].

Formic acid (used only in dechroming method 4)

Generally, formic acid is an environmentally friendly and highly efficient organic acid; it evaporates without leaving any residue [71].

Potassium oxalate (used only in dechroming method 4)

Potassium oxalate (laboratory grade) is non-reactive under normal conditions, but should not be released into the environment as it has some bioaccumulation potential [72]. However, it doesn't pose a threat in terms of acute toxicity, chrome toxicity, or corrosion irritation. It also does not show any possible hazardous reactions under normal industrial processing [72].

Phosphoric acid (used only in dechroming method 4)

If phosphoric acid (also known as orthophosphoric acid) is released in small quantities into the environment it will be neutralised, forming harmless phosphate salts, or it will be diluted to harmless levels [73]. However, large quantities of phosphoric acid entering the environment can acidify soils and water bodies [73].

CONCLUSION

This work has demonstrated that it is possible to extract nearly all the chromium in chrome-tanned leather solid wastes constituting of chrome shavings, trimmings and useless splits by using simple technology, which is environmentally sound and sustainable. A careful balance and controlled use of formic acid and potassium oxalate in the dechroming process step was very successful in chromium extraction from the leather solid wastes reaching up to approximately 99.9% in just 24 hours without digesting the collagen fibres. In addition, part of the remaining traces of chromium, usually in the form of chromate ions trapped within the collagenic hydrolysate fibres, was converted into potassium chromate and eventually washed away due to its high solubility in water. However, part of the remaining traces of chromium was complexed to chromium oxalate, which is an essential plant nutrient used for the growth of food crops. Other methods investigated in this study were unable to remove all the chromium in chrome-tanned solid wastes.

All the reagents used in the dechroming and the hydrolysis process in the new method did not show any hazardous reactions, even potassium oxalate which is known to have some bioaccumulation potential when released to the environment. The reagents were used in relatively small quantities

compared to the ones used in existing methods and were found to be very effective in the removal of chromium from leather solid wastes.

Availability of Data and Materials

All data needed to evaluate the conclusions reached in this study are present in the paper.

Authors' contributions

Conceptualization – Mwonda JM, Ombui JN and Kironchi G; methodology – Mwonda JM; formal analysis – Mwonda JM and Onyuka A; investigation – Mwonda JM and Onyuka A; resources – Ombui JN and Kironchi G; writing, original draft preparation – Mwonda JM; writing, review and editing; Mwonda JM and Ombui JN. All authors have read and agreed to the published version of the manuscript.

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Conflicts of interest

The authors declare that they have no conflict of interest, financial or otherwise.

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