De-chroming of Chrome Tanned Leather Solid Waste using Modified Alkaline Hydrolysis Process

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Abstract - Modern tanning activities generate considerable liquid and solid wastes into the environment. The management of tannery solid waste has been a challenge to the tanning industry for years and a focal point for researches carried out in the tanning industry. This paper reports the study and development of a more efficient de-chroming process for tannery solid wastes in which the recovered collagen tissues are intact. A hydrolytic process was carried out using twenty grammes (20g) each of pulverized chrome tanned leather shavings at two millimeter (2mm) particulate size for both established alkaline and modified alkaline hydrolysis. A triplicate result shows that the modified alkaline hydrolysis method gave a better de-chroming process with minimal chromium concentration when compared with the alkaline hydrolysis method. Also, when the modified alkaline hydrolysis process is used with different washing solutions, results obtained showed that washing with the established method gave an improved washing with minimal chromium concentration when compared with other washing solutions.

Keywords - Waste Management, Tannery Solid Waste, De-chroming, Alkaline Hydrolysis, Modified Alkaline Hydrolysis.

I. INTRODUCTION

Tanning is an age long art that has transcended generations. For centuries, skins of animals such as goats, rams, snakes, crocodile etc. have been converted into useful end products that are used for the manufacture of fashion goods such as shoes, bags, caps, jackets etc., and other household products through the tanning process. The tanning industry has developed over the years to the point where chromium salt is used as a major tanning agent [26]. Leather production is a chain of processes that can be categorized into three stages, namely:

pre-tanning operation which, include flaying and curing; beam-house operations which include soaking, un-hairing, liming, de-liming, bating and pickling; and tanning and post-tanning operations which includes shaving, splitting, washing, neutralization, dyeing, setting out, fat-liquoring, drying and rolling. Tanning activities has been the major cause of some environmental pollution world-wide. The pollutant of most concern is chromium.

A. Tannery waste management

The improper management of municipal wastes is one of the environmental challenges facing urban cities worldwide with particular emphasis to developing countries [5][10]. Little or no attention is given to waste management practices as heaps of wastes are dumped indiscriminately in drainages, vacant plots and open space with overwhelming majority of landfills in Africa been open dumps [23]. This has contributed not only to the spread of communicable diseases in the affected areas; it has also resulted to flooding and the emission of greenhouse gases [7][19].

With recent technological advancements, virtually all industries and the society at large is gravitating toward Zero Waste. The terminology ‘Zero Waste’ implies the elimination of the entire concept of waste and also suggests that whatever waste is generated should be considered as a residual product or a potential resource [22]. Waste is something or any moveable material that is no longer wanted or useful to the owner at a particular point in time [1][4][16]. Zero waste has brought in opportunities such as reduced cost, increased profit and reduced environmental impacts as major benefits to industries. The concept of zero waste usually involves re-designing both products and processes to eliminate harmful properties or components that make for unusable and unimaginable quantities of industrial wastes that overburden the industry and environment [9]. The waste management hierarchy starting from the most preferred has five components and is as followed: (i) waste minimization, (ii) reuse, (iii) material recycling, (iv) energy recovery and (v) waste disposal. The higher levels of the hierarchy are more environmentally benign than the lower level in most cases [8].
With the advent of the use of chromium salt as a tanning agent, researches have been on-going on various ways to convert all effluents generated from tanneries to non-toxic components safe for disposal environmentally and the removal of the toxic component from the solid wastes before disposal or re-use [12][25][27][2][3]. Reviews on removal of the toxic component from the solid wastes include: incineration at 900-1200°C in the presence of abundant air [11][19]; pyrolysis at 300-600°C in a limited oxygen environment [6]; gasification which results in the conversion of the carbon compounds of the solid waste to carbon monoxide, hydrogen and methane gases [24]; and alkaline hydrolysis[21].

B. Alkaline Hydrolysis
Alkaline hydrolysis is a simple process by which complex molecules are broken down into their constituent building blocks by the insertion of water (H₂O) in the form of hydrogen ion (H⁺) and hydroxyl ion (OH⁻) between the atoms of the bonds that hold those building blocks together [15]. Alkaline hydrolysis has been researched on as one of the methods suitable to de-chrome leather solid wastes without destroying the collagen tissues. Paul et al., in their research came up with a tannery solid waste de-chroming method as described below. This process consists of two stages: hydrolysis and washing. The de-chromed leather shavings were used in the production of poultry feed.

II. EXPERIMENTAL

A. Materials
Chrome-tanned Leather Shavings was collected from a major tannery dumpsite in Bumpai, Kano State, Nigeria. The shavings were dried at room temperature to a constant weight. The shavings were pulverized by the use of an electric milling machine with a 2mm mesh size. All the chemicals used in the de-chroming process were of analytical grade obtained from BDH Chemicals Limited, Poole, England; Park Scientific Limited, Northampton, U.K and Qualikem Fine Chemicals Private limited, New Delhi, India.

B. Method

Experiment 1: Effect of Modified Hydrolysis on De-chroming of Leather Shavings
Three samples each of 20g of the pulverized shavings were weighed and they were all de-chromed using the alkaline hydrolysis method as described by Paul et al. The de-chroming steps are as stated below:

Step 1: Chrome shavings (sample) weighing 20g per100ml is 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.

Cr(OH)SO₄ + Ca(OH)₂ → Cr(OH)₃ + CaSO₄

Step 2: Sodium hydroxide solution (0.1% w/v) is then added.

Cr(OH)SO₄ + NaOH → Cr(OH)₃ + Na₂SO₄

Step 3: Hydrogen peroxide (10% v/v) is added to the solution and stirred for 2 days.

2Cr(OH)₃ + 3 H₂O₂ → H₂Cr₂O₇ + 5H₂O

Step 4: Water is removed by filtration.

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

Step 6: The sample is 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 is washed twice with sodium sulphate solution (10% w/v) and sodium chloride (6% w/v) and filtered.

Step 8: The de-chromed leather shavings (product) is then allowed to air dry at room temperature.

H₂Cr₂O₇ + 6H₂SO₄ → 2Cr₂(SO₄)₃ + 7 H₂O

C. Modified Alkaline Hydrolysis Method

Three samples each of 20g of the pulverized shavings were weighed and they were all de-chromed using the modified alkaline hydrolysis method as described below.

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

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

Cr(OH)SO₄ + NaOH → Cr(OH)₃ + Na₂SO₄

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

2Cr(OH)₃ + 3 H₂O₂ → H₂Cr₂O₇ + 5H₂O

Step 4: Water is removed by filtration.

Step 5: The hydrolyzed leather shavings is washed three times with sodium sulphate solution (10% w/v) and filtered.

Step 6: The hydrolyzed leather shavings is soaked with sodium chloride solution (6%w/v) and sulphuric acid solution (1% w/v) for acid steeping for 1 hour and filtered.

Step 7: The hydrolyzed leather shavings is washed twice with sodium sulphate solution (10% w/v) and sodium chloride (6% w/v) and filtered.

Step 8: The de-chromed leather shavings (product) is then allowed to air dry at room temperature.

Experiment 2: Effect of Washing on Chromium Content of De-chromed Leather Shavings

Hydrolysis stage
The modified alkaline hydrolysis method developed in Experiment 1 above is further used in the second stage of this research work. Twelve samples each of 20g of the pulverized shavings were weighed and they were all de-
chromed following the hydrolysis stage of the modified alkaline hydrolysis method (this represents steps 1 to 4 in experiment 1).

**Washing Stage**
Step 5: Three samples were washed using established method. Three samples were washed four times each with H\textsubscript{2}SO\textsubscript{4} solution (5% v/v, taking v = 500ml). Three samples were washed with NaCl (50w/v, taking v = 500ml) and H\textsubscript{2}SO\textsubscript{4} solution (5% v/v, taking v = 500ml). Three samples were washed with Na\textsubscript{2}SO\textsubscript{4} (50w/v, taking v = 500ml) and H\textsubscript{2}SO\textsubscript{4} solution (5% v/v, taking v = 500ml).

Step 6: The de-chromed leather shavings were then allowed to air dry at room temperature.

### III. RESULTS

An elemental analysis was carried out on both the chrome tanned and the de-chromed shavings using alkaline and modified alkaline hydrolysis methods. The analysis was done using the Atomic Absorption Spectroscopy (AAS) from the Multi-user Laboratory, Chemistry Department of the Ahmadu Bello University, Zaria-Kaduna State, Nigeria. This analysis was targeted to investigate the chromium content of the de-chromed leather shavings from each sample. The result is as shown in Tables 1 and 2.

**TABLE 1: EFFECT OF MODIFIED HYDROLYSIS ON DE-CHROMING OF LEATHER SHAVINGS**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Concentration (ppm)</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trial 1</td>
<td>218.644 218.626 218.662</td>
<td>218.644</td>
<td>0.015</td>
</tr>
<tr>
<td>Trial 2</td>
<td>55.288 62.910 69.351</td>
<td>62.516</td>
<td>5.750</td>
</tr>
<tr>
<td>Trial 3</td>
<td>23.527 21.532 19.942</td>
<td>21.667</td>
<td>1.470</td>
</tr>
</tbody>
</table>

**TABLE 2: EFFECT OF WASHING ON CHROMIUM CONTENT OF DE-CHROMED LEATHER SHAVINGS**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Concentration (ppm)</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trial 1</td>
<td>218.664 218.626 218.662</td>
<td>218.644</td>
<td>0.015</td>
</tr>
<tr>
<td>Trial 3</td>
<td>29.249 26.878 32.760</td>
<td>32.086</td>
<td>2.240</td>
</tr>
<tr>
<td>Mean</td>
<td>34.481 33.494 32.086</td>
<td>32.757</td>
<td>1.550</td>
</tr>
</tbody>
</table>

**LEGEND**

Sample 1: Chrome Tanned Leather Shavings (raw sample).
Sample 2: De-chromed Leather Shavings using Alkaline Hydrolysis Method (Paul et al., 2013).
Sample 3: De-chromed Leather Shavings using Modified Alkaline Hydrolysis Method.

From the result obtained from the analysis carried out on the products from the two de-chroming processes (i.e. alkaline hydrolysis and modified alkaline hydrolysis), the raw sample (chrome-tanned leather shavings) had a mean chromium concentration value of 218.64ppm before the de-chroming process. This concentration was reduced by 71.41% to a mean concentration value of 62.51ppm after the alkaline hydrolysis reaction. Also, after the modified alkaline hydrolysis reaction, the concentration of chromium in the raw sample reduced by 90% to a mean concentration value of 21.67ppm.

Also, from the research on the effect of washing on the de-chroming process, the concentration of chromium in the leather shaving reduced by 90% to a mean concentration of 21.67ppm when the washing method described by Paul et al., 2013 was used. When acidified water was used as the washing solution, the mean chromium concentration in the product was reduced by 86.45% to 29.62ppm. With acidified sodium chloride as the washing solution, the mean concentration of chromium reduced by 84.75% to 33.35ppm. Finally, with acidified sodium sulphate as the washing solution, the mean chromium concentration reduced to 27.57ppm, depicting an 87.39% chromium removal from the chrome-tanned leather shavings.

**IV. CONCLUSION**

The challenge of recycling solid chromed leather wastes is gradually fizzling out as more and more solutions are emerging everyday on de-chroming and recycling these hazardous wastes. From the work done, it can be concluded that modified alkaline hydrolysis method of de-chroming accompanied by washing with Paul et al. method gave the best de-chroming process. The remaining three washing solutions (acidified sodium sulphate, acidified...
water and acidified sodium chloride) gave decreasing de-
chriming efficiency respectively as evident in the
concentration of the chromium in the products obtained
from their washing processes.

The de-chromed leather shavings (collagen fiber) produced
from the experimental procedure above can be put to use in
the agricultural sector as a source of amino acid in the
compounding of poultry feed, as fertilizer and research into
other sectors where this material can be useful.

From the effluents generated from the modified alkaline
hydrolysis process, chromium can be recovered. The
recovery of chromium sulphate used in tanning serves as a
step for the production of recycled or re-used chromium sulphate.

REFERENCES

management in Onitsha, Nigeria. Journal of Waste Management

feedstuff from chrome shavings: part 1, pilot plant study.

feedstuff from chrome shavings: part 2, A model for the hydrolysis

Environment and Human Impact.McGraw Hill international, New
York, 1996.

Report of the APO Survey on Solid Waste Management 2004-
2005, published by the Asia Productivity Organization 1-2-10

August 2014, 5:00pm.

Challenges of Solid Waste Management in Damaturu, Yobe State.
2010.

and waste recovery in an Indian industrial area. Resources,

[9] M. Braunegrat, W. McDonough, A. Bollinger, Cradle-to cradle
design: creating healthy emissions- a strategy for eco-effective
product and system design, Journal of Cleaner Production, Vol.


of chromium from chrome-laden tannery waste and a treatment
process for pollution control of tannery waste water. JALCA,Vol.

265-278.

processing in the tannery: production of gelatin, reconstituted
collagen and glue from chrome-tanned leather splits and trimmings
subjected to a modified detanning process, JSLTC, Vol. 70, pp. 69-76,
1986.

[14] Cotance Report – Tannery and Environment. TanneerietEnvironment, EC Tanners Face Environmental Test,


[16] T.Hammed, Overview of solid waste management in Nigerian
6th May, 2011.


[18] F.A. Johnson-Banks, From tannery to table: an account of gelatin


[21] H. Paul, A. P. M.Antunes, A. D. Covington, P. Evans, and P. S.
Phillips, Towards Zero Solid Waste: utilizing tannery waste as a
protein source for poultry feed. Paper Presented to28th International
Conference on Solid Waste Technology andManagement,

waste strategy initiative in England: zero waste places projects
1, pp. 335-343, 2011.

[23] R. J. Palczynski, Study on solid waste management options for
poverty Africa. Project report for African development bank
sustainable development & reduction unit. 2002.

[24] Z. Salmar, Gasiification of tannery wastes. Posted 3rd September,
2013.Cited in www.cleantechsolutions.com, retrieved on 14th
August 2014, 3:30pm.


[26] R.S. Thomson, Chrome tanning in the nineteenth century. JSLTC

[27] D.Tsotos, Tanneries: a short survey of the methods applied for

[28] C. Wicklliff, V. V. Voik, D. T. Tinge, W.L. Griffith, M. Y. Trunk,
and J. L. Witherox, Reactions of chrome tannery shudge with organic

[29] D.C. Wilson, O.A. Adesibi, C. Kaine, and C.R. Cheeseman,
Building Recycles rates through the Informal Sector. Waste
Management