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De-chromingof 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 the recycling of tannery solid wastes (leather shavings, buffing dust, leather trimmings etc.) has shown that different methods have been developed to convert these wastes to useful products such as fertilizer, animal feed supplement, leather board and soap, production of glue among others [13][12][17] [20][18][14][28]. These methods both serve as chrome recovery processes as well as production of useful potential materials for other industries. Although these methods have economic value, the collagen matrix of the tanned leather is usually destroyed. Methods used in tanned solid waste management include: incineration at 900-1200^{o}C in the presence of abundant air [11][19]; pyrolysis at 300-600^{o}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 (H_2O) 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 known as alkaline hydrolysis. 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/w) solution for 30 minutes followed by calcium hydroxide (3% w/v) for 1 hour.

$$Cr(OH)SO_4 + Ca(OH)_2 \rightarrow Cr(OH)_3 + CaSO_4$$

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

$$Cr(OH)SO_4 + NaOH \rightarrow Cr(OH)_3 + Na_2SO_4$$

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

$$2Cr(OH)_3 + 3\,H_2O_2 \rightarrow H_2\,Cr_2O_7 + 5H_2O$$

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.

$$H_2Cr_2O_7 + 6H_2SO_4 \rightarrow 2Cr_2(SO_4)_3 + 7\,H_2O$$

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.

$$Cr(OH)SO_4 + NaOH \rightarrow Cr(OH)_3 + Na_2SO_4$$

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.

$$2Cr(OH)_3 + 3\,H_2O_2 \rightarrow H_2Cr_2O_7 + 5H_2O$$

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% v/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_2SO_4 solution (5% v/v, taking v = 500ml).

Three samples were washed with NaCl (50w/v, taking v = 500ml) and H_2SO_4 solution (5% v/v, taking v = 500ml).

Three samples were washed with Na_2SO_4 (50w/v, taking v = 500ml) and H_2SO_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

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.

Samples	Concentration (ppm)				
	Trial 1	Trial 2	Trial 3	Mean	SD
1	218.644	218.626	218.662	218.644	0.015
2	55.288	62.910	69.351	62.516	5.750
3	23.527	21.532	19.942	21.667	1.470

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

Samples	Concentration (ppm)				
	Trial 1	Trial 2	Trial 3	Mean	SD
1	218.664	218.626	218.662	218.644	0.015
2	23.527	21.532	19.942	21.667	1.470
3	29.249	26.878	32.760	29.620	2.240
4	34.481	33.494	32.086	33.354	0.670
5	27.103	25.957	29.664	27.575	1.550

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 washed with H_2SO_4 solution.

Sample 4: De-chromed Leather Shavings washed with NaCl and H_2SO_4.

Sample 5:De-chromed Leather Shavings washed with $NaSO_4$ and H_2SO_4.

A. *Discussion of Results*

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 218.644ppm before the de-chroming process. This concentration was reduced by 71.41% to a mean concentration value of 62.516ppm 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 21.667ppm.

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 21.667ppm 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 29.620ppm. With acidified sodium chloride as the washing solution, the mean concentration of chromium reduced by 84.75% to 33.354ppm. Finally, with acidified sodium sulphate as the washing solution, the mean chromium concentration reduced to 27.575ppm, depicting an 87.39% chromium removal from the chrome-tanned leather shavings.

Independent sample t-test was carried out on the result and t-value calculated to be 11.920 and t (tabulated) from statistical table at 95% confidence level is 2.015.The result shows that there is significant difference at 95% confidence interval, since t (calculated)is greater than t (tabulated).

There is also provision for the recycling or recovery of chromium in the effluent of the hydrolysis and washing stages. This is achieved by hydrolyzing the heptaoxodichromate ($H_2Cr_2O_7$) solution with concentrated tetraoxosuphate (iv) acid to give chromium sulphate and water.

$$H_2Cr_2O_7 + 6\ H_2SO_4 \rightarrow 2Cr_2(SO_4)_3 + 7\ H_2O$$

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-chroming 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 recycling process as well as a step for the production of recycled or re-used chromium sulphate.

REFERENCES

[1] J.C.Agunwamba,O.K. Ukpai, and I.C. Onyebueyi, ,Solid waste management in Onitsha, Nigeria. *Journal of Waste Management Research*,Vol. 16, issue 1, pp. 23-31, 1998.

[2] M.Alves dos reis and V.Beleza, Utilization of leather waste - animal feedstuff from chrome shavings: part 1, pilot plant study. *JSLTC*.Vol 75, pp. 15-19, 1991a.

[3] M.Alves dos reis, and V.Beleza, utilization of leather waste - animal feedstuff from chrome shavings: part 2, A model for the hydrolysis kinetics. *JSLTC*.Vol 75, pp. 45-47, 1991b.

[4] R.W.Andrew, and M.Julie, Environmental Science: the Natural Environment and Human Impact.McGraw Hill international, New York, 1996.

[5] APO, Solid Waste Management: Issues and Challenges in Asia. Report of the APO Survey on Solid Waste Management 2004-2005, published by the Asia Productivity Organization 1-2-10 Hirakawacho Chiyoda-ku, Tokyo 102-0093, Japan, 2007.

[6] W. Aitkenhead, and R.Edmonds, Biochar – a Possibility of Leather Waste Disposal, 2013. Retrieved from www.leathermag.com, 30th August 2014, 5:00pm.

[7] A. Babalola,H.T. Ishaku, I.Busu, and M.M. Rafee, The Practice and Challenges of Solid Waste Management in Damaturu, Yobe State, 2010.

[8] A. Bain, S. Megha, A. Weslynne, M. Chertow, Industrial symbiosis and waste recovery in an Indian industrial area. *Resources, Conservation and Recycling.*Vol 54, pp. 1278-1287, 2010

[9] M. Braungrat, 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. 15, pp. 1337-1348, (2007).

[10] J.H.Bruce, Sustainable Development: the essential element, *Waste Management*, Vol. 4, pp. 32-38, (1998).

[11] J. E. Cartier, An ash stabilization process for the recovery and reuse of chromium from chrome-laden tannery waste and a treatment process for pollution control of tannery waste water. *JALCA.*Vol. 75, pp. 322-330, (1980).

[12] Collivignarelli, C. and Barducci, G. (1984). Waste recovery from the tanning industry.*Waste Management and Research.*Vol. 2, pp. 265-278.

[13] J. Cot, C. Aramon, M., Baucells, G.Lacort, and M.Roura, Waste processing in the tannery: production of gelatin, reconstituted collagen and glue from chrome-tanned leather splits and trimmings subjected to a modified detanningprocess, *JSLTC*, Vol. 70, pp. 69-76, 1986.

[14] Cotance Report – Tannery and Environment. TannerieetEnvironment, EC Tanners Face Environmental Test, *Leather*, October 1991, pp. 122-124.

[15] I. K..Gordon, B. W. Peter, M. W.William,2004. Cited in http://alnmag.com/article, retrieved on 14th August 2014.

[16] T.Hammed, Overview of solid waste management in Nigerian communities, 2006. Cited in http://eziniearticles.com, retrieved on 6th May, 2011.

[17] R. A. Hauck, Some notes on utilization of fleshings and blue shavings. *JALCA*, Vol. 69, pp. 195-204, 1974.

[18] F.A. Johnson-Banks, From tannery to table: an account of gelatin production. *JSLTC, Vol.* 74, pp. 395-403, 1984.

[19] B. H. Jones, Recovery of Chromium from Tannery Wastes. *Leather Manufacturer*, August 1977,pp. 12-28.

[20] V.A. Lipsett, Offal Blue. *JALCA.*Vol. 77, pp. 291-301, 1982.

[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, Philadelphia, PA, USA, 10-13 March 2013. Philadelphia USA: The Journal of Solid Waste Technology and Management, ISSN 1091-8043.

[22] P.S. Phillips, T.Tudor, H. Bird, M. Bates, A critical review of a key waste strategy initiative in England: zero waste places projects 2008-2009, *Resources, Conservation andRecycling*, Vol. 55, issue 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, Gasification of tannery wastes. Posted 3rdSeptember, 2013.Cited in www.cleantechsolutions.com, retrieved on 14th August 2014, 3:30pm.

[25] M. M. Taylor, E.J. Diefendorf, and G.C. Na, Enzymatic treatment of chrome shavings. *JALCA.*Vol. 85, pp. 264-275, 1990.

[26] R.S. Thomson, Chrome tanning in the nineteenth century. *JSLTC*, Vol. 69, pp. 93-98, 1985.

[27] D.Tsotsos, Tanneries: a short survey of the methods applied for waste water treatment. *Water Science and Technology*. 18: 69-76, 1986.

[28] C. Wickliff, V. V. Volk, D. T. Tingey, W.L. Griffis, M. Y. Trunk, and J. L. Witherow, Reactions of chrome tannery sludge with organic and mineral soils. *Water, Air and Soil Pollution.*Vol. 17, pp. 61-74, 1982.

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