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DE-Chroming Chrome Tanned Tannery Solid Waste With *Saccharomycescerevisiae*

[*1]Onukak, I. E.,[2]Nuhu, M. and [1]Oigocho, A. A.
[1]*Department of Research and Development, Nigeria Institute of Leather and Science Technology, Zaria, Nigeria.*
[2]*Department of Chemical Engineering, Ahmadu Bello University, Zaria, Nigeria.*
[*]*Correspondent*

ABSTRACT
Chrome tannage is the most widely adopted tanning process in the leatherindustry besides vegetable and alum tannage. The most commonly used chromium compound in tanneries is Basic Chromium Sulfate (BCS). Chromium (III) is initially trivalent but gets oxidized when left open to atmosphere to hexavalent chromium [Cr(VI)].Cr (VI) is highly carcinogenic and causes damage to health and the environment. In this research, yeast recovered from raffia palm winewas used to treat tannery solid waste (chrome shavings and buffing dust).A buffer solution of Sodium dihydrogen orthophosphate ($NaH_2PO_4.12H_2O$) and disodium hydrogen orthophosphate ($Na_2HPO_4.12H_2O$) was prepared and used to wash the mixture of the waste and yeast followed by 0.2% nitric acid. Both the substrate and filtrate were analyzed using Atomic Adsorption Spectra (AAS). The result from the analysis of chrome shaving filtrate and substrate showed 4589+5 mg/l of and 1861+16 mg/l Cr(III) compound respectively, while that of the buffing dust revealed 3641+4 mg/l and 1783+60 mg/l of Cr(III) both in the filtrate and substrate as well. The yeast, S. cerevisiae, in a non-viable state, is able to adsorb chrome and other metals from the chrome shavings and buffing dust of chrome tanned pilot tannery plant.These level according to literature review falls within tolerance level. The recovered chrome can be reused in leather production.
KEYWORDS: *Tannage, yeast,tannery solid waste, chromium, carcinogenic,substrate, filtrate.*

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I. INTRODUCTION

Leather is the product obtained by tanning skins and hides by either chrome, vegetable or alum tannage. Byconvention, the term ‘hide’ generally refers to the skin-covering of larger animals(cows, steers, horses, buffaloes,etc.), and the term ‘skins’, to those of smaller animals (calves, sheep, goats, pigs, etc.). The tanned skins and hides are used to produce a variety of finished goods such as shoes, bags, clothing, belts, furniture, stuffed animals, puffs, mats, wallets, footballs and a lot of accessories.

More than 70% operating tanneries, adopt chrome tanning process while the remaining tanneries adopt vegetable tanning process [21]. Apart from these two, a few of these industries uses alum tanning. Associated solid waste liberated from the later tanning process contain less chromium but much more aluminum. According to Hazardous Waste (management and handling) Amendment Rule 2003, the sludge and other waste (chrome shavings, buffing dust and trimmings) from tanning industry containing more than 50mg/kg chromium(VI) and 5000mg/kg chromium(III) compounds are considered as hazardous waste.

The most commonly used chromium compound in tanneries is Basic Chromium Sulfate (BCS). Chromium sulfate is initially trivalent but gets oxidized if left open to atmosphere to hexavalent chromium [Cr(VI)]. All forms of chromium are influenced greatly by pH, which affects the solubility and subsequent reactivity of chromium ions. Trivalent chromium is chemically basic and insoluble while hexavalent chromium is acidic and soluble. Chromium as heavy metal has no adverse effect. The trivalent form of chromium [Cr(III)] is considered as essential for normal carbohydrates, lipids and protein metabolism [18]. Little toxic effect is attributed to trivalent chromium when present in large concentrations compared to the hexavalent chromium [4]. Cr(VI) is highly toxic with a large aqueous solubility [14]. Indeed, aqueous Cr(VI) is highly carcinogenic and

causes damage to skin, mucous membrane and respiratory tract. It could also lead to infant mutation causing genetoxic effects such as chromosomal aberrations and sister chromatid exchanges [24].

Chrome can be recovered from these waste and be reused in tanningusing standard qualitative and quantitative methods as described by various authors. In this report, the method proposed by Brady and Duncan (1994) was adopted but modified. They used yeast from the brewery but the yeast employed in this report was recovered from local palm wine.

II. LITERATURE REVIEW

2.1 Tanning Operations

Tanning operations is divided into three stage; beam house operations, tanning operation and post tanning operation. The processes involved in beam operation are; soaking,unhairing, liming, fleshing, de-liming, bating and pickling. The next stage is the tanning operation involve in most cases the use of chromium(III)sulfate. The last stage is the post tanning operation involving processessuch asneutralizing, mineral tanning, re-tanning or semi chrome tanning, dyeing, fat liquoring, fixation, staking, buffing and glazing[13][15].

2.2 Tannery solid waste

Different forms of waste in quantity and quality are generated at the various stages of the tanning operations. These wastes differ in composition and nature base on the chemicals and machine used in the processes. From the beam house operation which is the pre-tanning stage where the tanner is concerned with converting the skins and hides to its original state before curing (preservation with brime) and preparing the raw material for tanning, the solid waste generated from the stage are hairs, fleshings, trimmings and salt dust. Chrome shavings, splits, buffing dust and trimmings are generated after the tanning process. The beam house solid waste from reviews and analysis contain little or no chrome and are therefore not relevant in this research. The wastes selected for this work were chrome shavings and buffing dust obtained after the chrome tanning process[13] [15].

2.3 Chemical composition of Tannery Solid Waste

The chemical composition of solid wastes generated from beamhouse operations (fleshings, trimmings, splits) depends mainly on the type and quality of the raw material, treatment type and process conditions. The main components of the waste are organics comprising mainly of proteins and fat, up to 10.5% (w/w) for both groups. Water content is high: moisture amounts to 60%. These wastes contain small amounts of mineral substances, 2-6% (w/w). Chromium compounds are not present in the material [11].

The tanned leather wastes are mainly useless splits, shavings and trimmings. These waste groups differ mostly in size and shape; the chemical composition is comparable for each. They contain 3-6% (w/w) of fat and about 15% (w/w) of mineral components, including 3.5-4.5% (w/w) of chromium as Cr_2O_3. Sludge from wastewater treatment plants contains mostly water (up to 65% (w/w), organic substances (30% (w/w) and chromium (III) compounds (about 2.5% (w/w) [6]. These total chromium values, greater than 3g/kg and below 5%, render these waste types non inert and non-hazardous according to Portuguese law [9].

Some research work on tannery sludge shows that the level of chromium content is 500 mg/kg and this is five folds higher than that should be present in the soil (100 mg/kg). It has moisture content (60.6%), pH (7.4), Organic Carbon (20%), Total kjeldhal nitrogen (1.0) and carbon to nitrogen ratio (20). Due to the low solubility of chromium, only a little (Cr) is bioavailable, which means that even when crops are grown in soils treated with sludge relatively high in Cr, phytotoxicity is rarely observed [1].Chromium(III)sulfate $[Cr(H_2O)_6(SO_4)_3]$ has long been regarded as the most efficient and effective tanning agent. The chromium(III) compound dissolves to give the hexaaquachromium(III) cation, $[Cr(H_2O)_6]^{3+}$, which at a higher pH undergoes process called olation to give polychromium(III) compounds that are activein tanning, being the cross-linking of the collagen subunits[8].

III. METHODOLOGY

The methodology was categorized into four stages; sample collection, sample pre-treatment, yeast recovery, preparation of buffer solution and de-chroming of tannery solid waste.

3.1 Sample Collection

Chrome Shavings and buffing dust from chrome leather tanning process were collected from NILEST mini tannery used for student practical. In all, 60 g of the waste were collected for the research. 25 litres of raffia palm wine was gotten from a retailer in HayanDogo, Samaru, Zaria.

3.2 Sample Pre-treatment

Sample pre-treatment involved, sorting of the sample to remove impurities such as pieces of wood, bone, metal and any other unwanted material, drying at 105 °C in Gallenkamp Oven (model no. OV-010 (9A-122-B9) Leicestershire, UK) to reduce the moisture content (up to 90 % dryness).

3.4 Recovery of Yeast from Palm Wine

The yeast was recovered by centrifuging 5 ml of fresh palm wine in sterile centrifuge bottles (Hettich Universal Centrifuge, Model no. 32R, Germany) Centrifuge at 50 rpm for 5 minutes. 1ml of the sediment was inoculated by streaking on plates of glucose yeast agar (GYA) and incubated at 28 ^{0}C for 24 hours [Gallenkamp (illuminated Cooled Incubator) Model no. OC- 225J, UK]. Chloramphenicol was added to 0.005 mg/ml to discourage bacteria growth. The yeast colonies developed were isolated and purified by subsequently washing in ultra-pure water three times. Standard methods for yeast identification were employed[3].

3.5Preparation of Buffer Solution

3.12 g of Sodium dihydrogen orthophosphate ($NaH_2PO_4.12H_2O$) was dissolved in 100 cm^3 of distilled water to get 0.1 mole of $NaH_2PO_4.12H_2O$. 7.17 g of disodium hydrogen orthophosphate ($Na_2HPO_4.12H_2O$) was also dissolved in 100 cm^3 of distilled water to get 0.1 mole of $Na_2HPO_4.12H_2O$. 36.7 cm^3 of $NaH_2PO_4.2H_2O$ was added to 13.2 cm^3 of $Na_2HPO_4.12H_2O$ to get a pH of 6.5.

3.6 De-chroming of the Waste Sample

250 ml of distilled water was added to 2 g of the recovered yeast and 5 g of the pre-treated sample in an Erlenmyer flask and suspended in a shaker (Stuart Flask Shaker Model no. 420, UK,) at 110 rpm for 1hr. 50 ml of the mixture was withdrawn using a 10 ml syringe and transferred to a filtration apparatus (Edwards High Vacuum Pump Model no. E2M2, West Sussex, UK) using a 25 mm diameter membrane filter paper. The substrate was then washed twice in a 5ml buffer solution (pH 6.5) of sodium dihydrogen orthophosphate and disodium hydrogen orthophosphate. 0.2 ml of 20 % nitric acid was used to wash the substrate. The substrate in a glass centrifuge test tube was placed in a water bath for an hour after adding 4 ml of distilled water, in order to release any metal ions associated to cells. The biomass substrate obtained was finally washed in 20 ml distilled water and dried overnight at 70 ^{0}C in an oven [5]. Analyses of both the raw samples, filtrates and the substrates were performed by flame atomic absorption spectra (AAS) for metal content[5].

IV. RESULTSAND DISCUSSION

The result from the analysis of chrome shavings filtrate and substrate showed 4589+5 mg/l of Cr(III) compound in the filtrate and 1861+16 mg/l in the substrate. The result for buffing dust analysis revealed that the 3641+4 mg/l of Cr(III) compound has been reduced to 1783+60 mg/l as evident in the concentration of the Cr^{3+} in the filtrate and substrate respectively. A total chromium value, greater than 3 g/kg and below 5 g/kg, render these waste as non-inert and non-hazardous according to Portuguese law[9].

According to [12], a wide range of organisms has the ability to grow in the presence of high metal concentrations and may be the result of intrinsic or induced features, including specific mechanism(s) of resistance and/or environmental factors that may reduce or eliminate toxicity, for example pH, inorganic anions, cations, particulate and soluble organic matter, clay minerals and salinity. Further investigations demonstrated that yeasts are capable of accumulating other cations such as copper, iron, Zinc and manganese are superior metal accumulators compared to certain bacteria [16][17]. The fact that waste brewery's yeast can accumulate heavy metals has been proven with great success by a number of researchers [12] [6][7] [20][23] [25] [22] [19][2]. This is also feasible for raffia palm wine base on the result shown in Table 1.

Table 1:AAS Result for Raw and Treated Tannery Waste Samples.

	Concentration mg/l					
Elements	CS	BD	CSF	CSS	BDF	BDS
Na_2^+	6562±70	3054±9	786±80	-	23±10	-
Mg^{2+}	-	-	103±20	-	5±20	-
Al_2^{3+}	2129±10	9612±90	121±80	-	13±70	-
K_2^+	-	-	28±80	6±36	3±20	511±10
Ca^{2+}	31440±21	650±26	286±60	29±8	4±30	373±10
Cr^{3+}	6647±80	5605±10	4589±5	1861±16	3641±4	1783±60
Mn_2^{3+}	-	58±10	226±80	5±10	20±90	553±10
Fe_2^{3+}	903±57	836±50	722±40	454±6	26±80	2378±60
Zn^{2+}	33±40	29±30	39±50	-	0.2±10	23±10

NB: CSF and BDF are filtrate of Chrome Shavings and Buffing Dust respectively while CSS and BDS are their substrate. – indicate that elements were beyond detection limits.

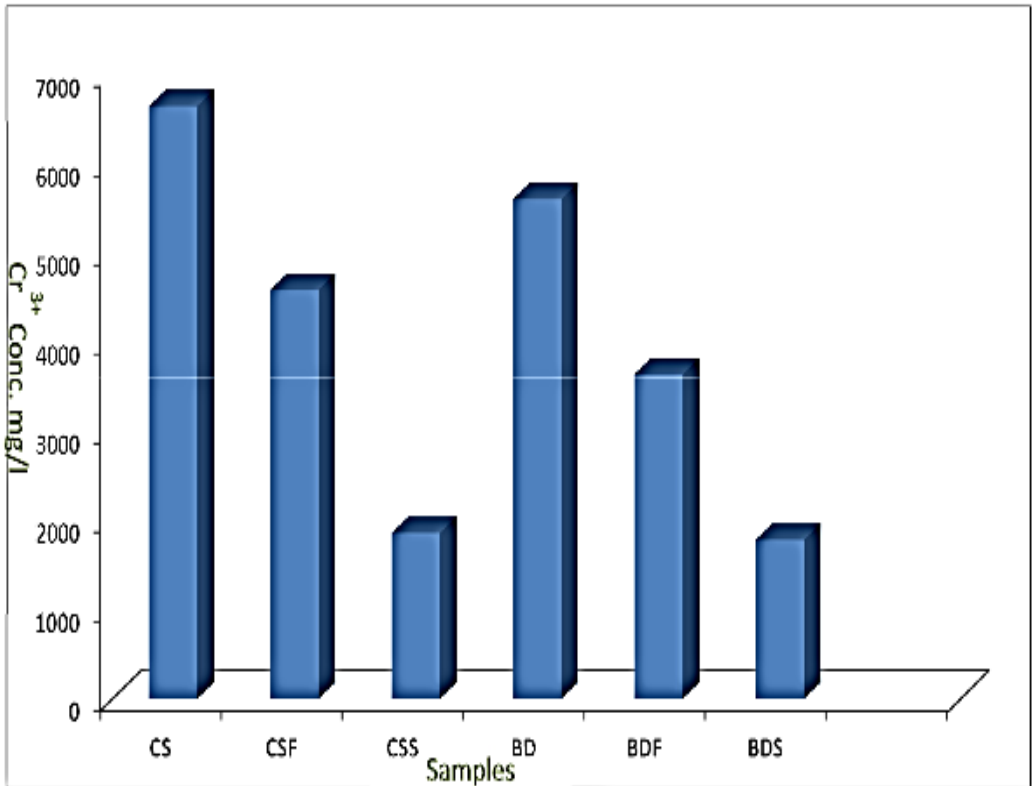

Figure 1: Bar chart for the adsorption of chrome from CS and BD samples

Looking at Figure 1, a total percentage removal of 28% $Cr^{3+}$from the chrome shavings (CS) and 32% removal was observed from the chrome shavings (CS) and buffing dust (BD) samples respectively. The yeast biomass was able to adsorb $Cr^{3+}$from the tannery waste generated.

V. CONCLUSION

The result from the analysis of chrome shaving filtrate and substrate showed 4589+5 mg/l of and 1861+16 mg/l Cr(III) compound respectively, while that of the buffing dust revealed 3641+4 mg/l and 1783+60 mg/l of Cr(III) both in the filtrate and substrate as well. The yeast, S. cerevisiae, in a non-viable state, is able to adsorb chrome and other metals from the chrome shavings and buffing dust of chrome tanned pilot tannery plant.These level according to literature review falls within tolerance levels [9].

The yeast Saccharomyces Cerevisiae (S.Cerevisiae) was a good source for bioremediation of chromium in chrome shavings and buffing dust. The concentration of yeast and acid needs to be increased proportionally in the treatment of chrome shavings having more content of Cr^{3+}.

Adsorption of chrome in buffing dust is 4% higher than that of chrome shavings. This study indicates the application of raffia palm wine yeast for biosorption of chrome from buffing dust and chrome shavings tannery waste generated.

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