Characterization of chrome buffing dust (CBD) generated from NILEST tannery associated with pathogenic fungi

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An attempt was made to monitor the level of chromium from chrome buffing dust waste (CBD) from Nilest tannery through preliminary investigation of the physicochemical characteristic of dried buffing dust (CBD) waste: pH, temperature (°C), alkalinity (mg/L), ash content (%), crude fibre (%) for example, using effluent and reference water sample as (control). Comparative study of the mean values of CBD, effluent and reference water sample were also assessed. Comparative studies of fungal isolates from CBD, effluent and reference water were also assessed in situ. A total of four fungi species were observed from CBD: Aspergillus niger, Penicillium sp., Aspergillus flavus and Aspergillus fumigatus with fungal count of 5.43 × 10³ CFU/ml, followed by effluent sample: A. niger and A. flavus with fungal count of 2.48 × 10³ CFU/ml and none was observed in reference water sample. The study recommended the combination of pyrolysis incineration and bioremediation methods for effective treatment of chrome buffing dust (CBD).

Key words: Buffing dust, physical properties, pathogenic fungi.

INTRODUCTION

Chrome buffing dust (CBD) is a microfined solid particulate impregnated with chromium synthetic fat and oil, tanning agents and dye chemicals (Swarnalatha et al., 2007). Buffing dust from chrome tanned leather is among solid waste generated from the leather industry which is hazardous to human health and environment. Thus, the solid wastes generated from leather industry can be broadly classified into untanned collagenous, tanned collagenous and non pretentious waste. Among the tanned collagenous waste, the one resulting from the finishing operation is called CBD (Swarnalatha et al., 2007).

Land co-disposal and thermal incineration disposal methods are used for treatment involving volume reduction through incineration, gasification and pyrolysis as the means of disposal with the emphasis to recover energy from the waste (Kirk et al., 2002). Thermal incineration is considered as the cheapest alternative method for its simultaneous energy production and volume reduction of solid waste as to avoid health hazards. The thermal

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incineration of tannery solid waste in particular, chrome buffering dust, needs a special attention on the issues such as release of toxic chromium (VI), halogenated organic compounds polyaromatic hydrocarbons etc, into the environment (Aeeta et al., 2005).

The major species formed from Cr$^{3+}$ during thermal incineration of solid wastes are Cr$_2$ (SO$_4$)$_3$Cr OCl$_2$ and CrO$^2$ which later accounts for the path for the formation of Cr$^{6+}$ (Skripsi, et al., 1995). Solid waste composition and oxygen concentration in the incinerator determine the extent of conversion of Cr$^{3+}$ to Cr$^{6+}$. In the present investigation, the CBD generated from a garment leather manufacturing industry was subjected to starved air incineration (SAI) to utilize its maximum calorie value as well as to inhibit the oxidation of Cr$^{3+}$ to Cr$^{6+}$. The process produced bottom-ash containing toxic heavy metal mainly Cr$^{3+}$ and partially burn carbon.

The highly toxic properties of bottom ash prohibit its direct land co-disposal. Therefore, an effective solidification/stabilization of bottom ash was restored to change potentially hazardous solid waste in to less hazardous or non-hazardous solid waste before it is disposed off on land fill (Filibelix, et al., 2000). SAI initially suffered operational problems due to the release of volatile organic compounds and partially converted carbon dioxide in the flue gas. This was controlled by catalytic combustion of flue gas over nickel impregnated ceramic granules of diameter 7 mm of 0.05 g of Ni/g of ceramic granules at 4500°C using air as an oxidant. The flue gas from catalytic converter was scrubbed in a scrubber to remove acidic vapour using alkaline water. Tannery waste brings about multiple problems for tanneries. Its treatment is difficult and there are no methods of its comprehensive utilization. None tanned waste is used as a raw material for glue, gelatin, technical fats, proteins sheaths, even feed and fertilizers. This waste is also suitable as a substrate for biogas production. The tanned leather waste can be used for secondary leather production. Nevertheless, for economic reasons waste remains mostly unutilized and goes to landfills (Cabeza, et al., 2010).

Due to the European waste hierarchy, land filling is the least favoured waste treatment method. Land filling of tannery waste poses serious threats to the environment. The non-tanned waste undergoes biological degradation which may be the source of pathogenic bacteria, fungi and volatile organic compounds emission. The significant disposal of chromium in tannery waste is about 30 thousand Mg per year worldwide (Kanagajeras, et al., 2009). The environmental effects of such proceeding go far beyond the potential contamination of the environment. The reuse of chromium from tannery waste could help save energy and financial expenditure for chromium ore output and processing (Cabeza, et al., 2010).

The waste management hierarchy is an ordered set of preferred practices that can be used to reduce the amount of waste being disposed. The hierarchy has five components, generally ordered in decreasing preference as follows: (i) waste minimization, (ii) reuse, (iii) material recycling, (iv) energy recovery and (v) waste disposal. Therefore, the higher levels of the hierarchy are environmentally benign than the lower level in most cases; with land filling waste in the ground as the least desirable approach to waste management (Bain, et al., 2010).

The present work is undertaken with the view to study the nature of chrome buffering dust, a waste material generated from leather industry and its physicochemical properties for future treatment of solid waste using fungi by bioremediation process.

MATERIALS AND METHODS

Chrome buffering dust (CBD) waste water sample and reference water sample

Chrome buffering dust, waste water and reference water were used in the study collected from Nigerian institute of leather and science technology (NILEST). CBD was dried for a week and utilized for further experiment. The dried CBD was characterized for moisture content, chemical oxygen demand (COD), total organic carbon (TOC), pH, temperature, ash, crude fiber, estimation of total chromium and alkalinity. Waste water samples and reference water samples were collected from the same institute (NILEST). The samples were collected using clean plastic container, well cleaned, with no ionic detergent rinsed with tap water and washed with deionised water prior for usage. While collecting samples contamination of the sample was avoided from any foreign material. Collected samples were brought to the laboratory and stored in the refrigerator at 4°C temperature.

pH

Ten grams of buffing dust samples was taken and added to 25 ml of distilled water. The mixture was shaken thoroughly for 20 min. The pH was determined using the pH meter in standard buffer solution (Nag, 2007).

Temperature

Ten grams of buffing dust sample was taken and added to 25 ml of distilled water. The mixture was shaken thoroughly for 20 min. The temperature was determined using the thermometer in solution (Aneja, 2007).

Moisture

The moisture content of the buffing dust was calculated based on the method described by Aneja (2007). Empty petri dish was weighted and a sample of buffing dust was placed on the dish and weighted. The buffering dust in the petri dish was dried in oven (Fisher, isotherm oven model 175) at 105°C, weighting was done at regular interval until; a constant weight was obtained and the moisture was determined thus:

\[
\text{Percentage moisture} = \frac{\text{Loss in weight of buffing dust}}{\text{Weight of dried buffing dust}} \times 100
\]
Organic carbon

Two and half gram of dried, sieved buffing dust was taken into a pre-weight crucible and ignited over a bunsen burner to a bright red heat, stirred occasionally with a wire loop. The sample was heated for 15 min. Then it was allowed to cool in a desiccators and the weight of buffing dust was taken. The organic carbon content was calculated as follows:

\[
\text{Percentage organic matter} = \frac{\text{Loss in weight}}{\text{Weight of sample}} \times 100
\]

\[
\text{Percentage organic carbon} = \frac{\text{Organic matter}}{1.724}
\]

(Dawole and Oso, 2004).

Determination of ash content

A porcelain crucible was dried in an oven at 100°C for 10 min, cooled in a desiccator and weighed (W1). Two grams of the finely ground sample (buffing dust) was placed into the weighed porcelain crucible and re-weighed (W2). It was then transferred into a furnace, which was set at 550°C. The sample was then left in the furnace for 6 h to ensure proper aching. The crucible containing the ash was then removed and allowed to cool in the desiccator and weighed (W3). The percentage ash content was calculated as:

\[
\% \text{ Ash content} = \frac{W_3 - W_1}{W_2 - W_1} \times 100
\]

Where, \( W_3 \) = weight of crucible and the content after cooling in the desiccator; \( W_2 \) = weight of content and crucible before heating; \( W_1 \) = weight of the crucible (AOAC, 1984).

Determination of crude fiber

Two grams of the finely ground sample was weighed out into a round bottom flask and mixed with 100 ml of 0.25 M H₂SO₄. The solution was thoroughly mixed and boiled under reflux for 30 min. The hot solution was quickly filtered under suction. The insoluble matter was washed several with hot water until it was acid free. This was later transferred into a flask and 100 ml of hot 0.31 M NaOH solution was added and the mixture boiled again under reflux for 30 min and then quickly filtered under suction. The soluble residue was washed with boiling water until it was base free and later dried to a constant weight in the oven at 100°C and finally cooled in a desiccator and weighed (C1). The weighed sample (C2) was then incinerated in a Gallemkamp (80) muffle furnace at 550°C for six hours.

\[
\% \text{ Crude fibre} = \frac{C_1 - C_2}{\text{Wt of sample}} \times 100
\]

(AOAC, 1984).

Chemical oxygen demand (COD)

50 g of dried buffing dust sample was suspended in 50 ml of distilled water in a beaker and filtered using nylon cloth. 25 ml of the filtrate was collected in a beaker and poured into a round bottom flask fitted with a condenser and several anti-bumping granules were added, followed by 30 ml of concentrated sulphuric acid and 10 ml of K₂Cr₂O₇ and digested for 2 h at 150°C using heating mantle (Hitachi, 1987). To the blank, 20 ml of distilled water was taken and treated in the same manner. After 2 h digestion of both sample and distilled water (blank), the mixture was made up to 140 ml and later cooled to room temperature; the solution was titrated with 0.1 N ferrous ammonium sulphate (FAS). After adding 3 drops of ferion indicator in the cooled digested buffing dust, the colour of the solution was changed from blue-green to reddish blue and was noted. The COD was calculated as:

\[
\text{COD mg/l} = \frac{[A - B] \times 8000}{\text{ml sample}}
\]

Where: \( A \) = ml of ferrous ammonium sulphate used for blank; \( B \) = ml of ferrous ammonium sulphate used for sample; \( N \) = normality of ferrous ammonium sulphate solution (Wong, 2009).

Estimation of total chromium

50 g of dried buffing dust was suspended in 50 ml of distilled water in beaker and was filtered through nylon cloth. 25 ml of the filtrate was collected in 400 ml beaker and 10 ml of concentrated H₂SO₄ and 5 ml concentrated HNO₃ were added to the filtrate. The beaker containing the mixture was then placed on a hot plate for boiling until the solution became clear and then the solution was then transferred into a volumetric flask. The volume of the filtrate was made up to 50 ml by adding deionized water. The digested sample was stored in sterilized polyethylene bottle at room temperature and taken to atomic absorption spectrometry (AAS) (Rani, 2003) for chrome analysis.

Alkalinity

100 g of the buffing dust sample was introduced in 100 ml of distilled water in 250 ml Erlenmeyer flask and left over night. The solution was heated in a water bath at 65°C for 45 min. The solution was filtered through a nylon cloth. 50 ml of the filtrate was introduced into 250 ml Erlenmeyer flask followed by addition of 3 drops of phenolphthalein indicator. Upon the development of pink colour, 0.02 N sulphuric acid from a burette was gradually added to the solution until the pink colour just disappear and the amount of acid used was recorded. Three drops of methyl orange indicator was then added to the flask. If the sample became yellow, then 0.02 N sulphuric acid was added until the difference in colour was noted when compared with the distilled water. The alkalinity was then calculated using:

\[
\text{Total alkalinity as CaCO}_3\text{(mg/l)} = \text{Total acid} \times 10
\]

(Nag, 2007).

Isolation of fungi species from wet chrome buffing dust waste

Thirty grams of dried chrome buffing dust waste was dissolved in 50 ml distilled water in 250 ml beaker and left for 3 days aseptically. Ten ml of the wet chrome buffing dust waste extract was transferred in 90 ml of sterile distilled water and aseptically serial dilution was
performed. Ten ml of the buffing dust waste extract was pipetted into 90 ml water blank number 2 to make up 1:00 (10⁻²) and another 10 ml of chrome buffing dust extract was pipette into 90 ml water blank number 3 to make up 1:1000 (10⁻⁶). Further dilutions were repeatedly carried out for 10⁻⁴ to 10⁻⁷, respectively. Aliquots 0.1 ml was aseptically transferred into freshly prepared potato dextrose agar (PDA) medium. Sterile glass spreader was used to aseptically spread the sample on the surface of agar medium. The plates were then incubated at ambient temperature (27 to 32°C) for 3 to 4 days. Emerging fungal colonies were picked and aseptically sub cultural into freshly prepared PDA and incubated to obtain a pure isolates. These pure isolates were then kept on PDA slants at 4°C for further use (Adawiah, 2008). Fungi were also isolated from tannery effluent waste and reference water sample on the same by the same procedure.

Identification of fungal isolates

Smear of the isolated fungi were prepared in lactophenol cotton blue method. Cultural characteristic such as colure, size of colonies of fungal isolates, size and shape of conidiophores/fruiting bodies and conidia were measure and recorded. Fungal isolates were identified by matching these characteristics (Hemanmbika et al., 2011).

RESULTS

The result is focused mainly on the mean values of chrome buffing dust (CBD), effluent waste and reference water sample associated with pathogenic fungi on each respective sample. Pictures were also taken with regard to the practically oriented wet and dry buffing dust as well as incinerated buffing dust in readiness for media formulation by bioremediation. Picture of fungi associated with chrome buffing dust was also noted in situ as seen in (Figure 1, Table 1, Plates 1, 2, 3, 4 and 5, respectively).

There is gradual change in the values of the parameters being compared. Total chrome was the lowest reference sample but exhibited the highest value in chrome buffing dust and effluent water sample, while others exhibited various noticeable changes. Study of the fungi in the chrome buffing dust waste (CBD) and effluent waste are shown in Table 1 shows that fungi were isolated both in CBD and effluent sample. The highest fungi colony count is 5. 43 × 10³ CFU/ml) from CBD, followed by effluent sample 2.48 × 10³ CFU/ml and none was observed in the reference water sample.

DISCUSSION

In trying to determine the physicochemical properties of chrome buffing dust in comparison with those of effluent and reference water sample focus was mainly on leather tanning and finishing. Leather tanning and finishing industry produces unique and complex industrial waste water that result in special problem with regard to treatment; whether discharged directly into receiving water or into publicly owned treatment work. The main source of organic pollution from most tanneries is the chrome waste stream apparent from chromium species. Analysis of chromium species in the chrome buffing and waste water discharge requires special attention for their treatment by biological method. In this discussion, there was a gradual decrease in pH values of the samples from reference water > chrome buffing dust > effluent water, respectively. The pH of the effluent might also be adjusted with acid or alkaline depending upon the nature of leather tanning or finishing. pH is the measurement of intensity of acidity, alkalinity and measures the concentration of hydrogen ion water. Deepali et al. (2009) reported pH of the tannery effluent as 3 to 3.5 which was a very acidic condition whereas Krishnamoorthi et al. (2009) observed pH of tannery as 8 to 9. However, WHO guide line stated a tolerance limit of pH 6 to 7 (Akan et al., 2008). Determination of pH is an important objective in treatment of waste variation in effluent which can affect the rate of biological reactions and survival of various microorganisms. Nearest to neutrality or neutral pH value was recorded from reference water sample as an evidence for fitness in industrial and domestic usage; since there was no chemical recipe added to the naturally existing water bodies. In addition, the discharge of waste water into water bodies may cause a drop or increase in their pH due to the chemicals and activities of microbial population.

Temperature is basically important for its effect in chemical reaction rate, aquatic life and the suitability of water for beneficial use. Temperature values of the samples are within the ranged of ambient temperature (27 to 30°C). Banat et al. (1996) reported that the textile and tannery effluent are produced at relatively high temperature (50 to 60°C). High temperature of waste water is commonly due to addition of warm water from industrial activities. Increase temperature can also cause change in the species of fish that exists in receiving body. The results indicate that some reactions could be speeded up by the discharge of this waste water into stream. It will also reduce solubility of oxygen and amplified dour due to anaerobic reaction (Akan et al., 2008).

Akalinity is the measurement of waste water due to the presence of hydroxyl (OH⁻), carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) used during buffing process. Alkalinity of the sample was very low. Similar findings were reported by indira and ravindra (2010) of high alkaline content (1210 mg/L) and (500 mg/L), respectively. In this current investigation, the level of alkalinity is very much lower than the values obtained by indira and ravindra (2010). Low alkalinity is attributed to the fact that there was little or no (OH⁻) or (CO₃²⁻) present in the natural existing water bodies and life is assured of safety for animals, humans, microorganisms as well as plants.
Figure 1. Comparative Study of mean values (parameters) of: (a) chrome buffing dust (CBD), (b) effluent sample and (c) reference water sample.
Table 1. Comparative study of fungal isolates from chrome buffing dust (CBD), effluent and reference water.

| Chrome buffing dust (CBD) | Effluent Sample | Reference water sample |
|---------------------------|-----------------|------------------------|
| Aspergillus niger         | Aspergillus niger | -                      |
| Penicillium sp            | Penicillium sp   | -                      |
| Aspergillus flavus        | -               | -                      |
| Aspergillus fumigatus     | -               | -                      |
| Fungal count $5.43 \times 10^3$ CFU/ml | $2.4 \times 10^3$ CFU/ml | -                      |

Plate 1. Flayed raw skin (sheep).

Plate 2. Dried buffing dust.
The moisture content is measured with the amount of water lost from materials upon drying to a constant weight. It is directly affected by physical and chemical properties of material which enable it to absorb the exiting waste in the environment. High moisture content was observed in chrome buffing dust and none was observed on those of effluent and reference water samples as seen Figure 1. Similar finding was conducted on solid waste by Rajendra (2002) and found the values within the range of 14 to 40%. In this current investigation, the value was a bit higher than Rajendra report. To this effect, high amount of moisture added to solid waste beyond its holding capacity constitutes the danger of leachate produced from the waste. The knowledge of moisture holding potential of solid waste is important to estimate the amount of moisture to be added in a landfill before any leachate is produced and drained off through the bottom (Rajendra, 2002).

Ash content of waste is the non-combustible residue left after waste is burnt. This represents the natural
substances after carbon, oxygen, sulfur and water. Kalanatarifard and Go (2012) recorded high percentage of ash content in fruit husk, rubber and leather with 27 and 22%, respectively, dominating in the ash content percentage. In this current investigation, low or moderate percentage of ash content is an evident that favoured the activity fungi in solution or medium.

Organic carbon is defined by carbon found in the material which is left after volatile test. Organic carbon is determined by removing the mass of volatile from the original mass of the sample. Organic carbon is the carbon remaining on surface as charcoal. The high percentage of the organic carbon in waste materials such as metals (74%) shows that this element requires a longer detention time on the surface of the furnace to achieve complete combustion compared to paper waste, food waste or even textile that has been reported by Kalanatarifard and Go (2012). In this study, the result obtained due to low organic content in chrome buffing dust agreed with the report of Kalanatarifard and Go (2012). Possible explanation could be related to ash contents on fungi.

Chemical oxygen demand (COD) is the amount of oxygen required by organic matter for its oxidation by strong COD substance in water. The COD is a test which is used to measure pollution of domestic and industrial waste. The waste is measured in terms of equality of oxygen required for oxidation of organic matter to produce CO$_2$ and water. There was significance difference between the concentrations of COD at different treatment. The lowest was found in reference water followed by effluent water and buffing dust, respectively as seen Figure 1. It has been reported by Nourissepehr et al. (2005) that the range of COD in tannery waste water is 1200 to 1300 mg/L. Similar finding regarding high COD (1230 mg/L) of effluent discharges from a diary effluent (Kolhe et al., 2008). In other words, a high degree of discharge of effluent in combination with buffing dust into soil or streams may cause eutrophication of water bodies (Gbolagunte et al., 2003).

Chromium, a heavy metal, was detected to be high in chrome buffing dust, effluent water except in reference water sample as seen in Figure 1. A possible explanation for its high level is as a result of the used chromium salt during tanning. This could be disastrous to the concept of a clean environment. It may also enter the food chain through plants, animals as well as water source. Once it gets into food chains, biomagnifications and bioaccumulation of the metal in various living systems may take place. This result was in conformity with that of khan (2006) in which they reported that bioaccumulation and biomagnifications could lead to toxic level of these metals in organism, even if exposure level is low. This could also cause disruption in the ecological balance when in abundance. However, the said permissible limit for total chromium discharge in the stream or river for irrigation and domestic used should not exceed 0.05 mg/L (WHO, 2004). Then it could be that the rural dwellers that leave within that vicinity are not guaranteed of safety.

High concentration of chromium ion in drinking water can cause skin, allergic reactions, carcinogenic and

**Plate 5.** Mixed culture of fungal isolates from chrome buffing dust. (A) Aspergillus fumigates; (B) Old culture of Aspergillus niger; (C) Aspergillus fumigates; (D) Penicillium sp; (E) Aspergillus flavus, Aspergillus niger, Aspergillus fumigates.
mutagenic allergic effect to humans (Matin and Griswold, 2009).

Study of the fungi in the chrome buffing dust waste (CBD) and effluent waste are shown in Table 1 and it shows that fungi were isolated both in CBD and effluent sample. The highest fungi colony count is \(5.43 \times 10^3\) CFU/ml from CBD, followed by effluent sample \(2.48 \times 10^3\) CFU/ml and none was observed in the reference water sample. The existence of these fungi in CBD and the effluent also could be attributable to the nutrient in the hides and skins shaving; hence, serving as a source of nutrient for the survival of fungi (Gbolagunte et al., 2003). The presence of truck load of pathogenic fungi associated with chrome buffing dust could be disastrous to humans and causes asthma. Several results were obtained on the survey conducted with regard to the numerous tannery industries located in Challawa industrial estate Kano state of Nigeria. The unprecedented discharge of chrome buffing dust in land fill abatement is quiet uncalled for and it is usually used as fertilizer by rural dwellers, which is not the true picture with regard to one’s health. It was also confirmed that 20 to 40% of young and elderly rural dwellers who engage themselves in irrigational farming in dry season were acutely affected by the disease called asthma due to inhalation of dust associated with these pathogens. *Aspergillus fumigatus* is a causative agent of asthma (Gbolagunte et al., 2003).

**Conclusion**

In this current study, the overall results of physicochemical properties from Nilest tannery is characterized by the following pH, temperature (°C), alkalinity (mg/L), moisture content (%), organic carbon (%), crude fiber (%) except chromium content which was high and had high contaminants of fungi species from chrome buffing dust followed by effluent water sample greater than 0.05 and 2 mg/L, as recommended standard of World Health Organization (WHO, 2004) and International Monitoring Regulatory Agency, respectively. This might likely pose health hazard to the tannery workers as well as public health in general. The use of fungi to ameliorate the environmental impact of chrome buffing dust waste and other tannery waste would ultimately be a solution to environmental co-friendly. Nilest leather industry must design excellent sustainability environmental initiative that would allow it to control, monitor and if possible bioremediation processes in order to meet the national and international regulation on control and prevention of pollution. Further, bioremediation of the chrome buffing dust would ultimately be a solution to riverside and landfill abatement. Thus, the process is cheaper and affordable. This study may open new areas for remediation of buffing dust waste using low cost biological method.

**RECOMMENDATION**

Tannery industries have to be advised to use proper means for the treatment of chrome buffing dust waste for disposal into environment. At present (Nilest), tannery is characterized by low levels of technology and the production of low grade leather from low grade raw hides and skins, system innovation and enhancement in industrial efficiency are necessary for quality improvement as well as reduction in pollution. In the present situation, to introduce cleaner technology, it is necessary to build an experimental tannery with the necessary equipment for research and development studies. This could be used to demonstrate new method and test chemical recipes. In addition to this, there is a need for technical expertise in this tannery.

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**Conflict of Interests**

The author(s) have not declared any conflict of interests.

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