ABSTRACT
The tannery waste contain utilizable nutrients and toxic organic compound which might affect soil processes and plants growth, and pathogens which might pose a threat to the local environmental communities. The study was designed to investigate the development of tannery waste collected from Unique leather finishing company Sharada, Kano, Nigeria, to compost Cow manure and Rice bran. Tannery waste was composted with cow manure and rice brand for sixty (60) days to reduce pathogens and toxic organic compounds. The compost was characterized by electric conductivity (EC) of 10.11µs/cm, pH of 7.62 and Carbon-Nitrogen (C: N) ratio of 28.8. The total concentration of Chromium, Lead, Cadmium, Copper, Zinc and Iron as mg/kg were 57.2, 0.92, 12.50, 10.11, 0.45 and 10.10 respectively. No Salmonella sp. and Shigella sp. were detected in the compost, however, total bacterial counts decrease from 8.2 x 10⁶ cfu/g to 1.8 x 10³ cfu/g, the compost characteristics indicated that it was mature, and the germination index of the beans seed was 80% which may suggest the removal of most of the phytotoxic compound.
Key words; Composting, Heavy metals, Organic matter changes, Pathogens, Tannery wastes.

INTRODUCTION
Composting is a process of exothermic biological oxidation of various organic wastes in the presence of air and involving microorganisms. Through microbial decomposition, the organic matter is stabilized, matured and deodorized into a product rich in humic substances that can be used as organic soil conditioner (Ouatmane et al., 2000).

Many organic waste materials are now being investigated and used as soil amendments in the growth of ornamental and some food crops in many communities. These include composts of yard wastes, sewage sludge, and to lesser extent, municipal solid wastes either singularly or in combination (Silva et al., 2009). There is concern, however, about the presence of toxic metals, polychlorinated biphenyls and asbestos (Simujide et al., 2013). Another waste material, which is commonly used in organic fertilizers as a source of nitrogen, is tannery sludge, a by-product of leather manufacturing (Insam and de Bertoldi, 2007).

Chromium is both a toxic and essential element for humans (Sánchez-Monedero et al., 2001) and has long been used in the tanning of leather (Sasaki et al., 2006). The resultant fertilizer products may contain extremely high concentrations of the metals. Apart from organic material, which releases valuable nutrients on decomposition, tannery sludge may contain pathogens and toxic organic components, which pose a serious threat to the environment. Aerobic (composting) or anaerobic (fermentation, biogas digestion) treatments can be applied to reduce pathogens and reduce toxic organic compounds. Composting which is a biological aerobic decomposition in which labile organic matter is degraded to carbon dioxide, water vapor, ammonia, inorganic nutrients and stable organic material containing humic-like substances (Simujide et al., 2013). This phenomenon has been updated to process organic wastes of different origins, such as sewage sludge, animal manure, agro-industrial wastes (Sasaki et al., 2006).

Compost, the generated product, can subsequently be applied to soil to increase soil organic matter content, which will release nutrients upon decomposition, and improve soil structure and cation exchange capacity (Varsha and Apurwa, 2008).
The objective of this study was to compost tannery wastes with cow manure and rice bran to reduce pathogens and toxic organic components, so that the disposal of tannery wastes into the landfill can be limited while generating a product that can be used to improve soil fertility.

**MATERIAL AND METHODS**

**Sampling site**
The dried tannery wastes used in this study was collected from Unique leather industry in Saharada, Kano, Nigeria, as it is the most abundant type of tannery waste produced in Kano. The research was carried out at ecological garden of Bayero university, Kano during the month of September/October, 2017. A unit plan consisting of 27 pits of (1.8 x 1.2 x 0.9)m\(^3\) were excavated on clean grown surface, cover with polyethen bags. The method of Hiraoka, (2002) was adopted.

**Composting**
An in vessel (pit) type of compost was used and consisted of approximately 5000 kg of material with ratio of 1:3:1 of tannery wastes, rice bran, and cow manure respectively, and the initial moisture content of the composition was 60%. The composting cycle lasted for sixty days. The pit were turned after every five days to maintain adequate aeration and to prevent odors. Subsequently, samples were then systematically taken at the end of every ten days of the composting process. Each sample was air-dried for a period of ten days. The dried sample was ground down into a fine powder as described by Mahdi et al., (2007).

**Physicochemical analysis**
The temperature was measured in triplicate using the method described by Taiwo and Oso, (2004), during mesophilic, thermophilic and maturation phases of composting using mercury in glass thermometer. The moisture content of composts was determined after oven-drying (105°C) of samples (10g, fresh weight) for 24h as described by Bruce et al., (2009). Total carbon was determined by dry combustion at 550°C and total N content (TN) by the Kjeldahl digestion analysis as described by Eno et al., (2009). pH and electrical conductivity (EC) were measured in aqueous extracts (1:10, w/v) using a pH meter (HD8602, Italy) and a conductivity meter (CC401 ELMEIRON, Poland), respectively. Samples were analysed in triplicate. Micro nutrients and heavy metals were analysed by Atomic Absorption Spectrometry (AASPE 403).

**Microbiological Analysis**

**Enumeration of Bacteria in Compost Material**
The bacteria were isolated from the compost by serial dilution method by plating 1ml of diluted suspension from each phase (the mesophile (30 and 35°C), thermophile (40 and 70°C), maturation and cooling phase (35 and 30°C) samples) were spread plated on nutrient agar (NA). The plates were incubated at 30°C, 35°C, 40°C and 70°C for 24h. Colonies were counted and populations were expressed in term of cfu/g. Morphologically, different colonies were purified on NA plates. All isolates were preserved on slants at 4°C (Mahdi et al., 2000).

**Isolation and Identification of some Bacteria from Compost Materials**
Nutrients agar was used for the growth of bacteria then sub-cultured using other selective media, identification of the bacteria was carried out using colony morphology, Gram staining and biochemical tests which includes; catalase, coagulase and Imvic as described by Cheesebrough, (2006).

**Compost Maturity Test**
The most widely used physical and chemical method of compost maturity/stability test were adopted. This include color changes by visual observations, odour through olfactory judgment, texture sensing coarseness CN ratio using chemical method, germination index and temperature production as described by European Union of Compost Maturity, (2013). Compost maturity is the measure of completeness of composting (Boutler et al., 2001) maturity is not described by a single method that has been universally applied to all kinds of composting system. Maturity is best assessed by measuring two or more parameters like physical, chemical, plant and microbial activity assay (Wu, 2000). For this research four different parameters of maturity test were used, which include (i) color (ii) odour (iii) CN ratio (iv) germination index.

**Determination of Germination index**
Germination index was determined using the method adopted by Gomez-brandon et al., (2008)

**Determination of Total Nitrogen**
Total nitrogen (N) was determined by micro-kjeldahl method as described by Eno et al., (2009).
Carbon Nitrogen Ratio (C/N)
Carbon nitrogen ratio is a test for organically bounded carbon and for total nitrogen and one of the most important characteristics that determines the extent and degree of composting maturity, irrespective of material used for composting. Organic carbon content was determined using the method adopted by Eno et al., (2009). While, color changes was accessed by visual observations and odour through olfactory judgment as adopted by Pan and Sen, (2013).

Statistical Analysis
Analysis of variance was carried out using SPSS version 20 for the Physicochemical Properties of the Raw Materials (Tannery Sludge, Rice Bran, Cow Manure) used for Composting

RESULTS AND DISCUSSION
Physicochemical properties of the raw materials used for composting
The results of the physicochemical properties of the raw biomass (tannery sludge, rice bran and cow manure) used for composting are presented in (Table 1). The cow manure showed that it was lowest in C/N ratio (25.96) then rice bran and tannery sludge with CN ratio of 59.14 and 28.81 respectively. The EC of the substrate were (10.11, 8.00 and 6.950)µs/cm. The tannery wastes showed that the level of chromium was high (52.20 mg kg) and below the maximum level which should be present in the soil (100 mg kg). The pH of cow manure and rice bran were acidic, 5.71 and 6.90 respectively, while that of tannery wastes was alkaline with the value of 7.62.

Temperature changes
In this study, three different temperature phases were observed for the different composting pits. An initial mesophilic phase (25-40°C) which lasted for 4 days for TRC and TR respectively, but 24 days for T only. Thermophilic phase (40-70°C) which lasted for 28 and 22 days for TRC and TR but 10 days for T respectively. Maturation phase which lasted for 20, 24 and 14 days for the TRC, TR and T respectively. However significant differences were evident in the temperature changes among the three different composition (Figure 1). The long thermophilic phase which lasted for 26 and 22 days could be as a result of higher microbial activity and availability of easily degradable organic materials. Nurul Ain et al., (2014) reported that, the rise in temperature during composting is due to intense microbial activity that favours the higher concentration of easily decomposable organic molecule. The results of the present study suggests that co-composting of tannery sludge with the rice bran and cow manure accelerated the composting processes as reported by Diaz et al. (2002). These findings are also in agreement with those of Boultere-bitzer et al. (2006), which produced 4 compost from mixture of different feedstucks (husk, chicken and paunch manure, bone meal ash, nark mix, soya bean meal and milogranite), reported increase in temperature within the first 10 days from ambient to 55-70°C, and a second increase in temperature after 31 days prior to cooling phase.

pH changes
The pH values recorded in each composition were within the range of 6.9 - 8.5 during the composting processes (Fig. 2). The difference in value of pH may be due to the different starting material and different treatment used for the research Zhu et al. (2007). The pH value of different compost piles increased minimally at the start of the experiment to more alkaline values at thermophilic stage. Specifically, this pH rise from mesophilic to thermophilic was more pronounced for Pit three (tannery sludge only) than for the two co-composted piles P = 0.00001, probably due to the production of more ammonia during ammonification and mineralization of organic nitrogen in tannery sludge. Between thermophilic and maturation phase, pH values were found to decrease minimally. Such increase in pH over composting phase can be attributed to a release of ammonia associated with protein degradation, and its subsequent decrease to a volatilisation of ammoniacal nitrogen and H+ release resulting from a microbial nitrification process (Gómez-Brandón et al., 2008). The presence of volatile fatty acids may also influence the pH development in the compost pit, as shown in previous studies (Beck-Friis et al., 2001). The dynamics of fatty acid formation and decomposition seem to be important in controlling biological activity and in turn, the gaseous emissions during the composting process. Fekedu et al., (2014), observed that, when the thermophilic phase began in the self-heated household waste compost, fatty acids were decomposed followed by a rapid increase in pH and NH3 emissions.
**Table 1:** The Physicochemical Properties of the Raw Materials (Tannery Sludge, Rice Bran, Cow Manure) used for Composting

| Characteristics | Tannery sludge | Cow manure | Rice bran |
|-----------------|----------------|------------|-----------|
| pH              | 7.62±0.1<sup>a</sup> | 5.71±0.026<sup>b</sup> | 6.90±0.01<sup>c</sup> |
| E.C (µs/cm)     | 10.11±0.1<sup>a</sup> | 69.50±0.021<sup>b</sup> | 8.00±0.02<sup>c</sup> |
| C:N             | 28.81±0.2<sup>a</sup> | 25.96±0.62<sup>b</sup> | 59.14±0.03<sup>c</sup> |
| **Heavy metals**|                |            |           |
| Fe (mg/kg)      | 1101.00±0.65<sup>a</sup> | 620.20±0.56<sup>b</sup> | 140.00±3.03<sup>c</sup> |
| Cu (mg/kg)      | 60.50±0.09<sup>a</sup> | 20.10±0.04<sup>b</sup> | 22.47±2.01<sup>c</sup> |
| Pb (mg/kg)      | 0.92±0.01<sup>a</sup> | 2.4±0.05<sup>b</sup> | 9.50±0.09<sup>c</sup> |
| Cd (mg/kg)      | 12.50±0.02<sup>a</sup> | 1.50±0.01<sup>b</sup> | 0.7±0.01<sup>c</sup> |
| Mn (mg/kg)      | 82.40±0.67<sup>a</sup> | 13.60±0.02<sup>b</sup> | 27.30±0.02<sup>c</sup> |
| Zn (mg/kg)      | 130.60±0.29<sup>a</sup> | 126.50±0.02<sup>b</sup> | 40.00±0.03<sup>c</sup> |
| Cr (mg/kg)      | 57.20±0.36<sup>a</sup> | 2.60±0.02<sup>b</sup> | 5.82±0.01<sup>c</sup> |

Values are mean ± S.D, values with different letters within the same row are considered significantly different (P < 0.05), using SPSS version 20.

**Key:**
- Canadian Std. of Biosolid = Canadian Standard of Biosolid

**Figure 1:** Temperature Changes during Composting Treatment One (Aeration plus Effective Microorganism). Key; AE – Aeration + Effective Microorganisms, AN – Aeration only, NN – No Aeration No Effective Microorganisms
Figure 2: pH Changes at Mesophilic, Thermophilic and Maturation of the Biomass (TRC, TR and T) with Different Treatment

Keys; Meso – Mesophilic temperature, Thermo – Thermophilic temperature

Changes in Electric Conductivity
Electric conductivity (EC), an indirect measurement of soluble salt of a sample, is used as chemical indicator of the composting status. EC increased significantly in all treatment from the start of the experiment $P = 0.00001$, probably due to the release of ions, such as phosphate, ammonium and potassium throughout the composting process (Fig. 3). Bernal et al., (2009) reported increase in EC during mesophilic phase and decreased after mesophilic and maturation phase, composts had EC values suitable for soil application (threshold value of 3 mS cm$^{-1}$; Gómez-(Brandón et al., 2008). Compost treatment using cow manure showed higher trend of electric conductivity values compared to the treatment without cow manure, this is because microbial biodegradation of the organic manure releases salt from the manure. The results obtained are in agreement with Irshad et al., (2013), which showed increase in level of EC for goat manure composting around 10.4 ds/m to 10.6 ds/m, during manure composting. Nurul Ain et al. (2011) reported that compost treatment using goat manure showed higher trend of EC values compared to the treatment without goat manure.

Changes in Carbon Nitrogen Ratios (CN)
The CN ratio decreased significantly over the phases, of composting especially in the co-composted piles $P = 0.00001$ (Fig. 4), as Carbon was lost in the form of CO$_2$ through microbial respiration and N nitrogen was recycled (Ryckeboer et al., 2003). A much low CN ratio and high offensive odor at the end of the composting process for the tannery sludge compost (T) was found, this indicates rapid biodegradation process in this compost. The addition of cow manure and rice bran to tannery sludge, however, significantly contributed to the decomposition of the ligno-cellulosic compounds of the rice bran, resulting in decrease N losses; in these mixed composts, this is in agreement with the finding of Sánchez-Monedero et al. (2001).

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Figure 3: E.C ($\mu$Scm$^{-1}$) Changes at Mesophilic, Thermophilic and Maturation of the Biomass (TRC, TR and T) with Different Treatment

Figure 4: Carbon Nitrogen Ratio Changes at Mesophilic, Thermophilic and Maturation of the Biomass (TRC, TR and T) with Different Treatment
Changes in Bacterial Population during Composting

The aerobic mesophilic counts of bacteria in the three different compost piles indicated significant variations in relation to temperature changes during the composting process (Figure 5). At the mesophilic phase of the process, high numbers of bacteria were found in pit one (TRC) (log8.91cfu/g) and Pit two (log7.71cfu /g). Yet, both piles were found to contain significantly lower numbers of bacteria (log5.30 and log4.58cfu/g) during the thermophilic phase of composting as the temperatures peaked. Bacterial numbers increased again in the maturation phase (log6.26 and log3.20cfu/g). These imply that addition of, cow manure, and rice bran were able to improve the degradation process by facilitating the microbial diversity present in the compost throughout the entire composting process. The result agrees with the finding of Liu et al. (2011) that suggests microbial communities in compost changes greatly after meeting with the microbial inoculum. These findings were also in agreement with findings of Hassen et al. (2001). In contrast, bacterial population in pit three (T) differed slightly for the three temperature phases, mesophilic, thermophilic and maturation phase (log4.90, log4.23, 4.54cfu/g) respectively, thereby resulting in a significant interaction between compost pit and phase P < 0.001. Because in (T) there was no bulking agent, cow manure and rice bran that will facilitate microbial biodegradation. Pan and Sen, (2013) reported similar population changes when studying the composting process of wheat straw.

The Heavy Metal Concentration (mg/kg) at 60 days of composting

The heavy metal concentration at 60 days of composting of the biomass are presented in figure 6. The order of the total metal content in the final composted biomass (TRC, TR and T) were Fe > Zn > Mn > Cu > Cr > Pb > Cd. All are within the USEPA standard limit of biosolid. During composting total heavy metal content decreased as reported by Mahdi et al. (2007), this is as result of leaching in the course of composting during thermophilic phase and could be related to the metal released from decomposed organic matter, an increase in moisture from 58.4% to 73.5%, a change in other oxidizing and ionic conditions in the medium and therefore increasing the solubility of metals. Some authors suggest that were the potential toxic metal concentration of compost are higher the leachibility of metal associated with compost is concern. It should consider the role of composting as important environmental sink to illuminate the most liable fraction of metals, mainly during active decomposition phase, indeed, after stabilization phase, metal total concentration is steady indicating that leachibility is stopped, this demonstrates the interest of land application of matured compost. It is also important to allow compost to mature due to the fact that, as compost matures over time, the solubility of heavy metals deceases with a subsequent decease in bioavailability in the environment. The metals become bound to humic compounds, metals oxides and phosphates in the compost when mixed with the soil (Williams et al., 2003).
**Compost Maturity/Stability**

From the results of maturity test at 60 days of composting of different biomasses with different treatment it showed that: Tannery sludge, rice bran and cow manure (TRC) were positive for all the parameters assessed, when compared with European standard of compost maturity. Then followed by tannery sludge, rice bran treatment one (TR AE), then tannery sludge, rice bran, cow manure (TRC), this indicates that co-substrating of tannery sludge with rice bran and cow manure plus aeration enhanced the biodegradation of the biomass in the compost system, this finding agrees with that of Fekedu et al., (2014), and Nurul Ain et al., (2011) who reported reduction in the maturation period from twenty one days to eight days.

**Fig. 6. The Heavy Metal Concentration (mg/kg) at 60 days of composting**

Keys; TRCAE – Tannery sludge Rice bran and Cow manure Aeration plus Effective microorganisms, TRCAN – Tannery sludge Rice bran and Cow manure Aeration, TRCNN - Tannery sludge Rice bran and Cow manure No treatment.

| Substrate combination/ Treatment | C:N | Odour | Colour | Germ index (%) |
|----------------------------------|-----|-------|--------|----------------|
| TRC                             | 13  | Earthly smell | Dark chocolate brown | 80  |
| TR                              | 10  | Earthly smell | Dark chocolate brown | 80  |
| T                               | 6   | High offensive odour | Dark brown | 10  |
| EU.ST                           | 13  | Earthly smell | Dark chocolate brown | 80 - 100  |

Key: EU = European Standard of Compost Maturity

**CONCLUSION**

It can be concluded from the research, that tannery wastes can be developed through composting into a humus-like substances (dark chocolate brown), tannery sludge rice brand cow manure with aeration and effective microorganisms are the best combination that can be applied to enhanced soil fertility, the compost characteristic indicated that it was mature, and the germination index of beans seed was 80% which may suggest the removal of most of the phototoxic compounds.

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