

Environmental Pollution Potential of Tannery Sludge from Challawa Industrial Area of Kano State, Nigeria

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Abstract: Tannery sludge waste is currently being used by many farmers for cultivation of vegetable on large scale for human consumption. This study investigated the pH, conductivity, Organic matter and heavy metal contents of ten tannery sludge samples. The analyses showed the tannery sludge samples could support plants growth and all the metals studied were present in the samples, except Cobalt. The highest concentration of the metals analysed by Atomic Absorption ranged from 2071.10 – 10933.20mg/kg Fe, 14.30 - 28.10mg/kg Ni, 1.80 – 14.60mg/kg Cd, 57.70 – 849.00mg/kg Pb, 5.90 – 89.70mg/kg Cu, 1642.20 - 30647.10mg/kg Cr and 139.60 - 5203.0mg/kg Zn. All the metals except Chromium and Lead were below the USEPA acceptable limits. The detrimental effect of Chromium and Lead suggests that the sludge may pose human health risks. Hence measures should be taken on the Industries to treat their effluents to conform regulated standards before discharge into the environment.

Keywords: Heavy metals, Pollution, Sludge, Tannery, Environment.

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I. Introduction

The environment upon which our life depends is under increasing pressure from human activities (Ezike, et al., 2012) for survival and comfort. These activities generate different kind of wastes, which accumulates and alters the natural characteristics of the environment, which creates an increasing number of far reaching consequences in the air, water and land. According to the World Health Organization (WHO, 2007), the environment is considered polluted when it is altered in composition or condition directly as a result of man's activities, so that it becomes less suitable for some or all of the uses for which it would be suitable in its natural state. The Federal Environmental Protection Agency (FEPA, 1990) also defined pollution as a man-made or man-aided alteration of chemical, physical, or biological quality of the environment to the extent that it is detrimental to the environment beyond acceptable limits.

Land pollution is common in urban and peri urban areas as a result of industrial and municipal wastes. Industrial wastes are the major pollutants in the environment and highest quantities are generated by tannery industries (Ademir, et al., 2013; Ezike et al., 2012; FME, 2012), where hides and skin are converted into leather. Kano has several tannery industries in Challawa, Sharada and Bompai industrial estates, only two had functional upgraded primary treatment plant (Akan, et al., 2009). Hence, resolving environmental pollution from these industries have been a challenging issues. Because their operations could generates large amount of organic and inorganic wastes known as Sludge (Varsha and Apurva, 2008). The quantity continually increases because of the high demand in leather materials and its status (as a second non-oil source of foreign exchange) in the nation's economic development (FME, 2012).

Numerous organic compounds are present in tannery Sludge and about 70% of the organic substances have applications as a high-quality fertilizer (Li, et al., 2005). Its richness in organic compound salts and other elements make it serves as a partial replacement for chemical fertilizers, which seems to be expensive to most peasant farmers. Sludge as an organic waste improves Soil physical properties and increase Soil organic matter content (Taek-keun, et al., 2010; Zoubi et al., 2008). However, its land application could presents some hazards due to presence of heavy metals, such as Cd, Cr, Pb, Cu, Zn, Fe, Ni, Co, Hg, etc, whose concentrations is of major health concern all over the World (McBride, 2003). Thus, the characterization of sludge is an important requirement, especially for agricultural activities. The study therefore, determines the concentration of heavy metals in the tannery Sludge samples and compared the concentrations of the metals with allowable requirements in order to ascertain their levels of toxicity and possible implications.

The study Area

The study area is the Challawa industrial estate in Kumbotso local Government area (Figure 1). Kumbotso falls within the Northern part of Kano, Nigeria. It is bordered in the South and West by Madobi local government, in the Southwest by Rimin Gado, in the South by Dala and Gwale, in the East by Kano municipal and Dawakin kudu local government areas.

The Challawa Industrial estate, is bounded by latitude of $11^{\circ} 54'N$ and longitude of $8^{\circ} 28'E$ at an elevation of about 430 meters above sea level. Tanneries are the dominant industries in the area and they include Fata tannery represented (TSA), Mamuda (TSB), Mario-Jose (TSC), Muhaza (TSD), Multitan (TSE), Globus (TSF), GB-Tannery (TSG), Mefela (TSH), Kanotan (TSI) and Fine Leather processing (TSJ). The T and S are acronyms for Tannery Sludge while the A, B, C, etc are meant to identify the tannery from which the sludge is obtained. All the industries located in the area dumps their solid wastes in the waste disposal site (about $30.072m^2$) located behind Kano Coca – Cola industry. The distance between the area and Challawa River is about 6.0 km and there are also constituted portions of land and few village settlements in between. Farmers' uses the sludge from the area as fertilizer.

II. Materials And Methods

Sampling collection and sample preparation

Sludge samples were collected from the tanneries in the study area. Each sludge sample was collected before disposal in separate and labeled polythene bags. The samples were air- dried and gently crushed with mortar and pestle separately. Each was sieved using 2mm plastic sieve and stored in a labeled container for analysis. Some of the physicochemical parameters of the tannery samples analysed are pH, conductivity, organic matter and heavy metals.

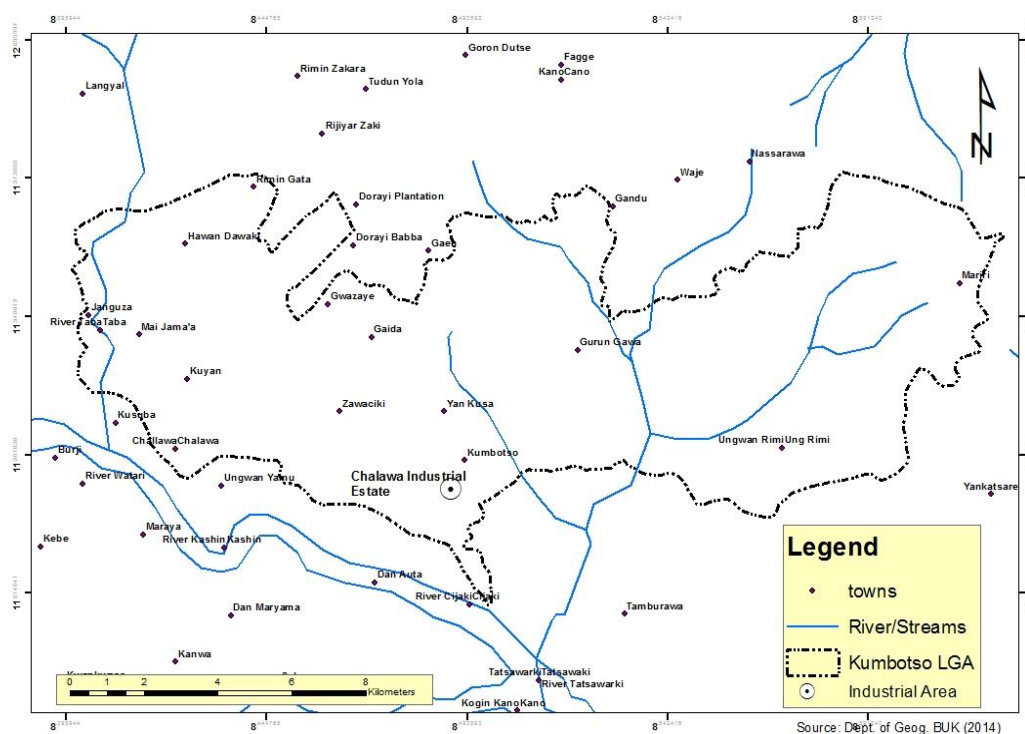


Figure1: Map of Kumbotso Local Government Area showing Challawa industrial Area

pH and Conductivity measurements: The sludge pH was measured on sludge suspension using deionized water at 1:5 (w/v). All pH measurements were made with pH meter Jenway 3510 and all weighing were done on Mettler Toledo PB 203 weighing balance. Similarly, Electrical conductivity (EC) was measured using Jenway 4010 Conductivity meter.

Organic carbon measurement: organic matter was determined by the modified Walkley – Black method as described by Bruce and Schulte (2009) using $10cm^3$ of 0.167M potassium dichromate ($K_2Cr_2O_7$), $10cm^3$ of concentrated H_2SO_4 , $10cm^3$ of ortho- phosphoric acid (30% H_3PO_4) and titrated with 0.5M Ferrous ammonium sulphate; $(Fe(NH_4)_2(SO_4).6H_2O)$ using Ferroin indicator.

Heavy metals determination: The samples were digested in Nitric acid (HNO₃), Hydrochloric acid (HCl) and Hydrogen peroxide (30% H₂O₂) as described by Akin & Guven, (2011). The procedure was repeated for the blank sample. The elements Pb, Cr, Zn, Fe, Cd, Ni, Co and Cu were measured by Atomic Absorption Spectrophotometry (AAS), using Variant spectra Atomic Absorption Spectrophotometer, Agilent Technology model. All determinations were done in triplicates.

III. Results And Discussion

The results of the analysis are shown in figure 2 below. The pH of the tanneries samples analysed showed slight differences among the sampling sites. The pH value ranged from 7.9 - 8.4, with TSC sampling site having the least pH (7.9 ± 0.071), while TSI (8.4 ± 0.099) and TSD (8.4 ± 0.021) sampling sites have the highest values. The values were in agreement with the pH of the tannery sludge samples reported by Tudunwada, (2007), as well as pH of 7.4 and a range of 7.7 - 11.8 reported by Mahdi, Azni and Omar, (2007) and Gupta, Rohit, Sarita and Byeong-kyu, (2010) respectively. One way analysis of variance indicated insignificant differences ($p = 0.1228 > 0.05$) in the sludge pH across the various sampling sites. Although high pH were observed in all the tanneries analysed, but it's still within the acceptable range (6.5 - 9.0) recommended by FEPA, (1991) and UNIDO, (2000). This indicates that, the pH is not alarming. pH is an important factor in determining the fate of metals in the sludge (Olowu, et al., 2012), when the sludge is deposited in the environment as a source of cheap fertilizer. The observed pH were found to be alkaline and ranged between 7.9 ± 0.071 to 8.4 ± 0.099. The values may be attributed to the various chemicals such as sodium salts used in tanning.

Conductivity is a measure of salinity (soluble salts) and the sludge analysed showed a conductivity range from 3.66 - 30.45mS/cm for the samples, with the lowest value observed in TSB (3.66 ± 0.494mS/cm) and highest in TSC (30.45 ± 0.071mS/cm) sampling site (fig.2). The higher conductivity value observed may be attributed to the high salts content of the sludge added from the additives and chemicals used during skin/hide processing. As a general guideline however, a good soil electrical conductivity (EC) is somewhere above 200 - 1200µS/cm (1.2mS/cm). Means any soil with EC below 1.2mS/cm doesn't have enough nutrients to support plant and could perhaps show a sterile soil with little microbial activity (Rehm, et al., 2001). However, according to Oliveira, et al., (2002) conductivity value higher than 3mS/cm indicates saline soils. Thus, the study, showed EC values ranged from 3.66 - 30.45mS/cm. It therefore indicates that, the sludge may increase soil salinity after its amendment with soil as also reported in other studies (Ademir et al., 2013). Hence, continuous use of this sludge on land will be detrimental to the soil.

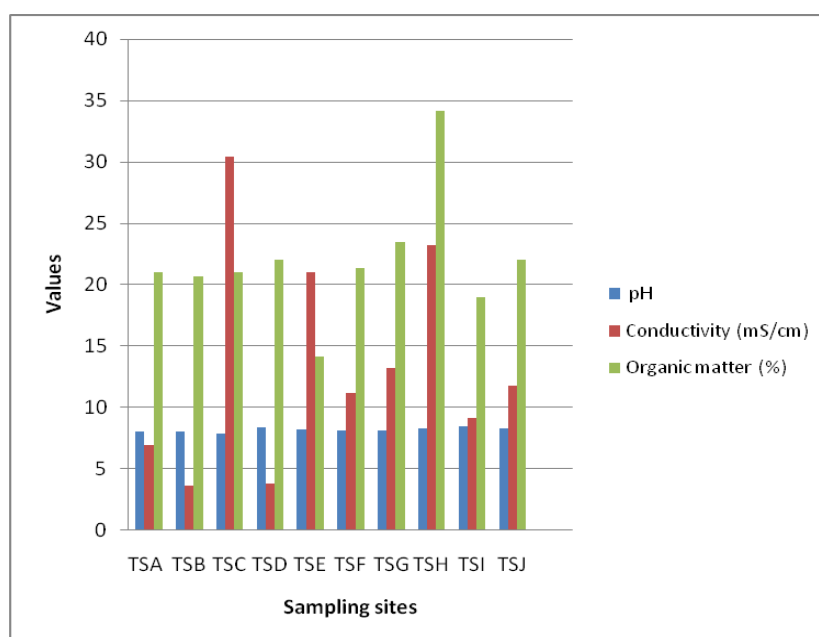


Figure 2: Mean pH, EC and OM content of the sludge sampling sites

Also, higher Organic matter content ranging from 14.14 - 34.15% was observed across the samples. These ranges compared with the guidelines for Organic matter content indicates that, the organic matter content of the sludge was adequate (George and John, 2013), and may be attributed to the animal leather residues. High organic matter content contributes to the structural stability of the soil and resistance to erosion (Ortiz and Alcaniz, 2006) as well as improving soil aeration, water holding capacity and aggregate stability of the soil

(Gupta, et al., 2010). This makes the sludge preferable to synthetic fertilizers which have no or little organic matter content and reveals its potential to support agriculture and enhance soil fertility.

Heavy metal concentrations

Heavy metals in sludge are undoubtedly the most serious problem, especially when the sludge is for agricultural purposes. The concentrations of the metals investigated in the sludge are presented in Tables 1 and 2 below. The concentrations of iron across the sampling sites ranged from 2071.10 – 10933.20mg/kg with the highest value observed in TSC (10933.20±0.839mg/kg) and the Lowest value noticed at TSG (2071.10 ±0.476mg/kg).

Table 1: Mean heavy metal concentrations (mg/kg) in the sludge samples

Sludge Sites	Heavy metals concentrations			
	Fe	Ni	Cd	Pb
TSA	2344.7±0.865	14.3±0.084	10.5±0.654	617.1±0.047
TSB	2662.2±0.567	15.1±0.090	10.7±0.054	849.0±0.074
TSC	10933.2±0.732	28.1±0.245	14.6±0.012	278.3±0.098
TSD	2675.3±0.839	15.1±0.987	2.0±0.710	69.6±0.050
TSE	3104.6±0.987	18.3±1.250	2.0±0.258	202.9±0.574
TSF	2197.2±0.058	15.1±0.321	2.0±0.325	69.4±0.250
TSG	2071.1±0.476	14.5±0.075	2.4±0.562	59.5±0.140
TSH	2153.6±0.041	15.6±0.065	1.8±0.321	57.9±0.104
TSI	2728.8±0.013	16.8±0.082	6.9±0.369	369.4±0.780
TSJ	2827.5±0.529	17.0±0.031	1.9±0.245	79.6±0.541
Range	2071.10 – 10933.20	14.30 - 28.10	1.80 – 14. 60	57.70 – 849.00
Maximum allowable limits				
USEPA	NA	420	39	300
EU	NA	NA	20 – 40	750 – 1200
SouthAfrica	NA	NA	15.5	50.5

Source: USEPA, (1994); EU and South Africa (Olowa, et al., 2012)

These concentrations were above 50.38 - 380.54mg/kg reported (Koki and Jimoh, 2013) in the tannery dumping site and 10933.20mg/kg reported by the source might be attributed to the tanning agents, dyes and other leather production processes as reported by Thanikaivelan, et al., (2000) and Verhegen, et al., (1996). Nickel concentrations ranged from 14.30 - 28.10, with TSA (14.30 ± 0.084mg/kg) having the least concentration and the highest concentration was found in TSC (28.10± 0.245mg/kg), followed by TSE(18.30±0.1.250mg/kg) and TSJ(17.00±0.031mg/kg) samples. The results were relatively higher compared to other studies reported (Admir, et al., 2013 and Andre, et al., 2012), but lower than the USEPA, (1994) limits. Thus indicates that the sludge is not contaminated with Ni. Therefore, its use in soil amendment would cause no health effect of Nickel in the environment.

Cadmium is a very hazardous metal to man and other living organisms especially when present in the aqueous medium (Olowu, et al., 2012). In this study, the highest concentration (14.60±0.012mg/kg) was observed in TSA (Table 1), but it is interesting to note that the levels are below the allowable limit (39mg/kg) set as the maximum concentration of Cadmium allowed in Biosolids for land application by USEPA, (1994). While Lead concentrations in the sludge ranged from 57.70 – 849.00mg/kg with highest concentration recorded in TSB (849.0±0.014mg/kg) and lowest at TSH(57.90±0.104mg/kg). The concentrations have exceeded the range (0.48 – 20.17µg/g) reported from Challawa tannery wastes dumping site (Koki and Jimoh, 2013) as well as 40.31mg/kg reported by Admir, et al., (2013).

Lead concentration in the samples analysed were below the European Union (EU) maximum standards, but samples especially, TSA, TSB and TSI have exceeded the limit set by USEPA, (1994). These higher concentrations may be related to the treatment processes and emission from exhaust pipes of the generating plants. The sludge samples may be a source of lead if finally disposed in the environment. And when lead is released into the environment, it has a long residual time compared with most other pollutants (ATSDR, 1999). It mimics the metabolic behavior of Ca and inhibits many enzymes system and accumulates mainly in the skeleton (Mengel and Kirkby, 1987). Its bioaccumulation in human body interferes with proper functioning of the Mitochondria thereby impairing respiration as well as causing constipation, swelling of brain, paralysis and could eventually lead to death (Oluyemi, et al., 2008).

However, Copper is essential to human life. It's only toxic when the concentration exceeded 250mg/day. It causes anemia, liver, kidney damage, stomach and intestinal irritation, hypertension, sporadic fever and coma and its acceptable limit for human consumption is 10ppm (Nair, et al., 1997). The chemistry of the Cu shows that, Copper is specifically adsorbed or fixed in soils. Sludge is capable of substantially increasing the soil levels of Cu (Synman and Vandar-waals, 2004). In this study however, Copper concentrations ranged from 5.90 – 89.70mg/kg and were lower than the limits set by the European Union and USEPA. However, the

samples showed high concentration of Chromium in all the sites. The lowest concentration was obtained in TSI (1642.20 ±0.056mg/kg) and the highest at TSB (30647.10± 0.140mg/kg) and the concentrations were above the allowable limits recommended for land application (Table 2). The relative higher concentration might be attributed to the facts that all the tanneries constantly use Chromium salts as the major tanning agents. The variation in the level of metals concentration among the tanneries may be related to the treatments carried out in the industries. This can be confirmed from the report of Akan et al, (2009) which stated the poor conditions of the primary treatment plants of the tanneries. Thus, sludge from these tanneries may be a source of Chromium contamination if deposited on soil, as high concentration above normal range are highly unsafe and pose health risks to the environment (Olowu et al., 2012). Higher exposure of Chromium above the established critical limits of 0.5 - 10µg/g in plants and 200mg/day in human beings causes toxicity (WHO/FAO, 2007). Some side effects of high doses include irregular heartbeat, upset stomach, itching, kidney, and liver damage (Paul, et al., 2012). Sludge exhibits a wide range of Zn concentrations, which are generally higher than the background level found in soils. Though, Zinc in the tannery samples analysed showed concentrations above recommended standards only in two tanneries (Table 2), it may also be associated with suspended solids and is partitioned into the sludge during treatment (Stainislaw and Krystyna, 2011). Zinc oxide, known as Zinc white or Chinese white, is used as a pigment or

Table 2: Mean heavy metal concentration (mg/kg) in the sludge samples

Sludge Sites	Heavy metals concentrations			Zn
	Cu	Co	Cr	
TSA	38.1±0.042	ND	24587.9±0.441	2446.1±0.082
TSB	41.0±0.653	ND	30647.1±0.601	3188.9±0.070
TSC	89.7±0.210	ND	29456.0±0.087	5203.0±0.064
TSD	16.5±0.250	ND	14919.7±0.140	470.7±0.021
TSE	17.1±0.897	ND	26427.3±0.330	259.6±0.025
TSF	33.9±0.648	ND	23264.3±0.258	430.5±0.014
TSG	5.9±0.148	ND	3915.6±0.349	139.6±0.036
TSH	11.9±0.258	ND	2214.9±0.254	220.2±0.087
TSI	16.1±0.140	ND	1642.9±0.056	321.0±0.044
TSJ	17.6±0.125	ND	3247.7±0.022	367.5±0.077
Range	5.90 – 89.70	-	1642.2- 30647.10	139.60 - 5203.0
Maximum allowable limits				
USEPA	1500	NA	1200	2800
EU	1000 – 1750		200 – 1200	NA
South Africa	50.5	100	1750	NA

Source: USEPA, (1994); EU and South Africa (Olowu, et al., 2012)

Dyes for leather industries. Many Zinc compounds are used in manufacture of paints, dye-stuffs and its sulphate is used in preserving hides (Satya, et al., 2008). It is an important micronutrient for plant growth, and its presence in soil is beneficial for plants and animals (Synman and vandar waals, 2004). The application of sludge has been documented to be a major input of Zn to agricultural soils (Alloway, 1995; Wong, et al., 2001). Excessive uptake of Zn by plants causes stunting of shoot, curling and rolling of young leaves, death of leaf taps and chlorosis (Rout and Das, 2003). Studies in animals have shown that zinc deficiency during pregnancy may lead to developmental disorders in the offspring (Rabia, et al., 2012). It is involved in metabolic functions; tissue repairs and wound healing (Audu and Lawal, 2006; Madan and Tuli, 2012). Although the daily intake of Zinc is 7 -16.3mg Zn/day, the recommended dietary is 15mg Zn/day for men and 12mg Zn/day for women (ATSDR, 1999). However, its high intake could cause vomiting, loss of appetite, abdominal cramps, diarrhea, headache (Jeffery, 2012). Acute toxicity of Zn may result in sweet-taste, throat dryness, cough, weakness, general aching, fever, nausea, and vomiting (Kanawade and Gaikwad, 2011).

IV. Conclusion

The tannery sludge samples analysed were alkaline in nature and showed high Conductivity and Organic matter contents. Also, all metals except Chromium and lead were at an acceptable level set by USEPA, While Co was not detected. The most abundant metals in the tanneries was Chromium. Highest concentrations of Iron, Nickel, Cadmium, Copper and Zinc were observed in TSC sludge, while Lead and Chromium were highest in TSB sludge respectively. Though, the entire physicochemical parameters suggested that tannery sludge are highly fertile and could support plants growth, but the heavy metals presence pose a major threat to the human health. It's therefore recommended that, measures should be taken on the Industries to treat their effluents, especially for Chromium and Lead to conform to regulated standards before discharge into the environment to save the environment.

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