Assessment of heavy metals in tannery solid waste from Challawa Industrial Estate, Kano State, Nigeria

Isa Baba Koki¹* and Jimoh W. L. O.²

¹Department of Chemistry, North West University, Kano.
²Department of Pure and Industrial Chemistry, Bayero University, Kano.

ABSTRACT

The determination of heavy metals in tannery solid waste was conducted by flame atomic absorption spectrophotometer (AAS). The samples were analyzed for the presence of Cr, Cu, Cd, Pb, Zn and Fe. The results showed that leather samples and other wastes deposited at the dumping site contain significant amount of some heavy metals. The concentrations ranged from 26.21-2564.21 µg g⁻¹ for chromium, 50.38-380.54 µg g⁻¹ for iron, 0.48-20.17 µg g⁻¹ for lead, 0.19-0.48 µg g⁻¹ for cadmium, 0.23-13.35 µg g⁻¹ for copper and 2.86-121.13 µg g⁻¹ for zinc. Control skin samples revealed low concentrations of Copper and Zinc, while concentration of Iron was high. Chromium, Cadmium and Lead were not detected in the Control skin samples from the tannery and market. The variable concentrations of these metals may be due to the different chemicals and preservatives used in the production of leather. The concentrations of the metals in leather and other solid waste samples analyzed were found to be in the order Cr>Fe>Zn>Cu>Pb>Cd. Findings of this research will assist the government and tanneries in monitoring the dumpsites with regards to disposal arrangement of the tannery waste and environmental assessment.

INTRODUCTION

Solid waste is defined as any useless, unwanted or discarded material that arises from man’s or industrial activities and can not be discarded through a sewer pipe (FEPA, 1995). The most harmful of pollutants of industries come from its effluents and solid waste which may contain heavy metals. Effluents and solid waste not properly disposed or recklessly discharged into the environment can contaminate the environment which consequently leads to pollution (FEPA, 1995). The environment needs to be free from pollution since plants and animals including man depend ultimately upon their environment for the supply of mineral nutrients (Volkanic, 1980). Therefore illness and diseases are caused by the inability of environment to supply these mineral nutrients needed in adequate, safe and non-toxic form to both plants and animals.

Trace metals such as chromium, copper, iron and zinc have cumulative toxic effects (Sindhu, 2002). These trace metals produce their toxicity by forming complexes or ligands with organic compounds which modify the function of the biological molecules (Theodore, 2006). Leaching of solid wastes contaminates surface and ground water (Chandra et al., 2004; Firdaus and Aisha, 2010). Heavy metals are also introduced into the body through industrial stack gas and soil (Karl and Koupelis, 2004).

Tanneries are major sources of highly toxic and hazardous solid waste; they produce animal residues from such operations as cleaning, fleshing, splitting, tanning, shaving and buffing. Each of these operations generates waste products which must be disposed of. Solid waste of animal origin is powerful pollutants in water and soil, and produce odour when they decompose (Naidu et al., 2000). Also the high quantity of different
Chemicals used in tanning operation produces these metals to the environment. Of the heavy metals tanneries have been found to discharge not only chromium, which is an inherent product of tanning process, but also significant amount of Zn, Cu, Mn and Pb are produced and discharged to the environment (Kashem, 1996). Tanning is the transformation of skin using tanning agents to give the resultant leather (German, 1994). Tanning may be divided into vegetable tannage which is divided into pit and accelerated tannage using tannins such as pyrogallol with high sugar content and those with low sugar content known as catechol (Reed, 1969; Heidemann, 1993).

Another set is the mineral tannage which include Iron (Gastellu, 1992), Zirconium (Hock, 1974), Aluminium (Juan and Waldo, 1984), chrome (Willhard, 1984) and Titanium tannage (Swarthy et al., 1984). Other sets of tanning involve the wet-white using Aldehyde and Chamois tannage (German, 1994).

The shift in vegetable tannins to the production of leather are due to the development of synthetic tannins and the potentials of mineral tannage particularly basic chromium salts for the manufacture of leathers (Haslam, 1996). Among the tanning systems chrome has been used commercially and has improved through research (Ramasami et al., 1999). Chromium can be extracted from the leather waste by thermal, chemical or enzymatic method and extract used as tanning agent (Wilford, 1999).

Heavy metals could be determined in tannery wastes. The concentration of the metals depends on the quantity of waste employed (Kapel et al., 1979; Carneiro et al., 2003). An analytical method such as iodometric or spectrophotometric method of analysis could be employed to ascertain the level of metal concentration in the sample waste (Balasu and Padmaja, 1997; Milacic et al., 1998). High concentrations of Cr, Cu, Ni, Cd and Zn were found in tannery effluent and soil samples near the tannery (Mohammad et al., 2011). Tannery affected soils enriched in Cd followed by Cr, Pb, Ni, Cu, Co, Zn and Mn were studied (Ali et al., 2015). But these metals can be stabilized to reduce or prevent their mobility, becoming of less threat to environment (Pantazopoulos et al., 2015).

MATERIALS AND METHODS

Study area

The study area is the dump site of tanneries in Challawa industrial Estate in Kumbotso Local Government Area of Kano state. Kumbotso Local Government Area lies between latitudes 11° 50’ S to 12° N and longitude 8° 24’ W to 8° 40’ E. It falls within the Kano settlement zone bordering the south and west by Madobi, Northwest by Rimingado, and North by Gwale and East by Tarauni Local Government Areas respectively. The sampling zone covers an area of 30,072 m² (Figure 1).

The vegetation of the area is savannah and a hot semi-arid climate. The state is 481 meters (or about 1580 feet) above sea level with average of about 690 mm (27.2 in) of precipitation per year, the bulk of which falls from June through September.

Sample source

The animal skin, leather and other solid waste used in this analysis were collected at the dumping site of the tanneries in Challawa Industrial Estate Kano, behind Nigeria Meats and Associated Product Ltd Kano. Control samples were collected from Sabon Gari Market, Rimi Market and abattoir Market in Kano State.

Sampling procedure

Three samples each were collected randomly from the dump site, Sabon Gari market, and Abattoir market. The samples were collected using plastic bags (Ayodele and Gaya, 1998).

Sample treatment

The skin and leather samples were dried to constant weight at 105°C for 2 h in an oven, ESCO Isotherm (DJB Labcare Limited England, ISO 9001:2008), (Garry, 2004).

Dry ashing of skin and leather sample

Five grams (5 g) of dried leather and trimmed skin samples were ashed to a constant weight using porcelain crucibles at a temperature of 550°C (Garry, 2004). The ash obtained was dissolved in 1 moldm⁻³ hydrochloric acid, made up to 25 cm³ mark with the acid, the resulting solution was heated, filtered and analyzed using atomic absorption spectrophotometer model V1200 (Shimadzu Japan) with air acetylene flame (Balasu and Padmaja, 1997).

RESULTS AND DISCUSSION

Different heavy metals Cr, Fe, Cd, Cu, Pb and Zn were analyzed for their concentrations. Metal ions such as Fe, Cr, Zn, Cu and Pb were found to be present in high concentrations, while low Cd ions concentration was detected in few samples, and not detected in some samples.

The presence of toxic metals in skin and leather comes from the chemicals used during the chemical
pretreatment process and up to dyeing which gives different colour to the skin contain significant amount of some heavy metals (Naidu et al., 2000). After the disposal of tannery wastes as sludge, some are used in agricultural production causing more problems due to heavy metal contamination (Gorecki, 1974). Toxic metals are carried by waste water flow from industries to rivers, streams and lakes which are used for irrigation purposes in agriculture. These heavy metals are in turn taken up from the soil by plants roots, and passed to stems and leaves, which are eventually consumed by animals and humans (Folaranmi et al., 2002).

The results of heavy metals analyzed in skin, leather and other solid waste are shown in Table 1.

Chromium, Cadmium and Lead were not detected in five different Control skin samples from markets.

The distribution pattern of Chromium for various samples in Figure 2 shows that dried solid waste from tannery effluent obtained as sediment from water treatment plant of the tannery has the highest concentration of 2564 µgg\(^{-1}\) and the lowest is skin sample from fleshing unit of the tannery with 26.21 µgg\(^{-1}\). This result is similar to that reported by Swati (2005) on Chromium concentration in tannery wastes in Punjab district India.

Most of the samples analyzed for Chromium has values above (USEPA, 1993) and (UK-Department of Environment, 1987) threshold limits of 1500 and 600 µgg\(^{-1}\), respectively. High concentration of Chromium in the leather and solid waste of the tannery is because of the chrome tanning method employed by the tanneries. Sources of Chromium in tannery wastes are the tanning salts, dyes, pigments and preservatives (Puntener, 1998; Turner, 1994).

The distribution pattern of Iron in various skin and leather samples as shown in Figure 3 shows that Iron is present in all samples analyzed. Wet blue skin has the highest concentration of 380 µgg\(^{-1}\) and skin from fleshing unit of the tannery has the lowest concentration of 188 µgg\(^{-1}\). These values are below the standard limit for waste disposal (Corning, 1979). Sources of Iron in tannery wastes are the tanning agents, dyes, natural

Figure 1. Sampling site at Kumbotso Local Government Area, Kano State.
Figure 2. Distribution of Chromium in various skin, leather and solid waste samples.

Table 1. Concentration (µg g⁻¹) of metals in skin, leather and dried tannery solid waste sampled.

<table>
<thead>
<tr>
<th>Sample tag</th>
<th>Sample code</th>
<th>Cr</th>
<th>Fe</th>
<th>Pb</th>
<th>Cd</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Fleshing skin from tannery</td>
<td>26.21±10.51</td>
<td>188.64±14.16</td>
<td>2.41±0.13</td>
<td>ND</td>
<td>10.18±0.75</td>
<td>15.84±1.08</td>
</tr>
<tr>
<td>B</td>
<td>Fleshing skin from dump site</td>
<td>47.22±11.31</td>
<td>207.35±15.21</td>
<td>1.29±0.17</td>
<td>ND</td>
<td>8.43±0.71</td>
<td>16.49±2.81</td>
</tr>
<tr>
<td>C</td>
<td>Salted raw skin Market 1</td>
<td>ND</td>
<td>336.21±32.18</td>
<td>ND</td>
<td>3.82±0.69</td>
<td>5.28±1.25</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Salted raw skin Market 2</td>
<td>ND</td>
<td>328.62±32.18</td>
<td>ND</td>
<td>2.65±0.69</td>
<td>2.86±1.25</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>Salted raw skin Market 3</td>
<td>ND</td>
<td>278.18±32.18</td>
<td>ND</td>
<td>2.63±0.69</td>
<td>6.33±1.25</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>Roasted skin Market 4</td>
<td>ND</td>
<td>330.87±20.75</td>
<td>ND</td>
<td>2.01±0.13</td>
<td>8.19±0.67</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>Salted raw skin Tannery</td>
<td>ND</td>
<td>260.75±32.18</td>
<td>ND</td>
<td>1.89±0.69</td>
<td>4.75±1.25</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>Wet blue skin from the dump site</td>
<td>1282.31±124.88</td>
<td>380.54±59.83</td>
<td>ND</td>
<td>ND</td>
<td>12.54±11.97</td>
<td>33.57±0.87</td>
</tr>
<tr>
<td>I</td>
<td>White leather from dump site</td>
<td>1132.85±56.88</td>
<td>313.59±6.66</td>
<td>ND</td>
<td>9.78±0.45</td>
<td>23.72±0.96</td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>Black leather from dump site</td>
<td>1762.83±152.11</td>
<td>200.66±6.65</td>
<td>ND</td>
<td>9.56±0.39</td>
<td>54.28±3.02</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>Buffing cake from polished wet blue skin at dump site</td>
<td>1423.43±78.19</td>
<td>288.77±4.35</td>
<td>20.17±1.26</td>
<td>0.19±0.61</td>
<td>13.35±0.61</td>
<td>121.13±9.53</td>
</tr>
<tr>
<td>L</td>
<td>Purple skin dust after paddling</td>
<td>966.15±91.75</td>
<td>108.43±6.47</td>
<td>3.86±0.49</td>
<td>ND</td>
<td>11.46±0.40</td>
<td>35.39±0.99</td>
</tr>
<tr>
<td>M</td>
<td>Dried solid waste from tannery effluent A</td>
<td>2564.21±75.16</td>
<td>52.80±1.21</td>
<td>9.48±4.49</td>
<td>0.48±0.02</td>
<td>0.23±0.31</td>
<td>18.21±1.70</td>
</tr>
<tr>
<td>N</td>
<td>Dried solid waste from tannery effluent B</td>
<td>2413.80±75.16</td>
<td>50.38±1.21</td>
<td>0.48±4.49</td>
<td>ND</td>
<td>0.36±0.31</td>
<td>21.60±1.70</td>
</tr>
</tbody>
</table>

All values are mean values of triplicate determinations. ND, Not detected.
geochemical processes and production process which include fleshing, setting out, shaving, staking and buffing (Tranikaivelan et al., 2000; Loredo et al., 2003).

Lead was found to be present in few skins and leather samples as shown in Figure 4 buffing cake has the highest concentration of 20.17 µgg⁻¹. This value is higher than 5.00 µgg⁻¹ for lead in the environment (Bowen, 1979). The lowest is skin from fleshing unit of the tannery with concentration of 1.286 µgg⁻¹.

Lead was not found in skin samples from the market (Control). Cadmium was found to be present in solid waste derived from tannery effluent and buffing cake as shown in Figure 5. Highest concentration of 0.48 µgg⁻¹ was obtained in dry solid waste from tannery effluent, and the lowest concentration of 0.190 µgg⁻¹ was obtained from buffing cake. Cadmium was not found in skin samples from the market and tannery (Control). The concentration of 0.4 µgg⁻¹ in the sample is higher than the naturally occurring cadmium concentration of 0.03 to 0.30 µgg⁻¹ (Bowen, 1979).

The distribution pattern for copper as shown in Figure 6 indicate that buffing cake has the highest concentration of 13,347 µgg⁻¹ and skin from market has the lowest concentration of 2.005 µgg⁻¹. These values are below the limit for waste disposal (Corning, 1979). Sources of copper are the preservative, dyes and polyphenolic tanning agents (Haslam, 1996; Puntener, 1998). Low concentration of copper in the waste could enhance plant growth and development, but its bio-accumulation in the body due to inhalation of the fumes from the burnt waste could lead to health problems (Comings, 1965; Sindhu, 2002).

Zinc concentration as shown in Figure 7 indicates that buffing cake has the highest concentration of 121.126 µgg⁻¹. And lowest concentration of 2.86 µgg⁻¹ was for salted raw skin from abattoir. Zinc concentrations for all the samples are within the natural range of 1.00µgg⁻¹ to 900 µgg⁻¹ in the environment (Bowen, 1979).

**Significance of results**

Based on the result of this study, it is evident that Cr, Pb and Cd in most of the samples analyzed were found to be above the natural occurring values. These metals will find their way directly into the environment due to indiscriminate burning of the waste at the dump site (Jones 1977). Chromium may enter drinking water from the burnt fumes of the leather product (Corning, 1984; Tavani and Volzone, 1997).

The high concentration of chromium in the waste may lead to its bio accumulation by the surrounding and hence a threat to human health (Sezgin et al., 2004). There is increased toxicity of iron during the dry season when the leather wastes are burnt resulting in fumes causing poor visibility (Sezgin et al., 2004) with related health problems. This is because iron bio accumulate and does not degrade naturally even if organic complexes break down by hydrolysis, fresh unreactive inorganic complexes are formed (Corning, 1984).

Zinc is toxic above 15 mg/day; concentration due to bio accumulation of the fumes from the burnt tannery wastes...
Figure 4. Distribution of Lead in various skin, leather and solid waste samples.

Figure 5. Distribution of Cadmium in various skin, leather and solid waste samples.
Figure 6. Distribution of Copper in various skin, leather and solid waste samples.

Figure 7. Distribution of Zinc in various skin, leather and solid waste samples.
into the body through inhalation could lead to nausea and disorder of the immune system (Ottaway, 1978; John, 1986).

Conclusion

Leather and other solid wastes from the tannery contained increased concentration of heavy metal above naturally occurring concentrations which results in pollution of the environment by heavy metals. These metals may reach toxic level in humans through the food chain. The presence of heavy metals in leather and tannery wastes has been traced to many chemicals used for the tanning operations (Naidu et al., 2000).

The tannery wastes disposed at the dump sites needs to be analyzed before their disposal. Thus there is need for adequate attention to the chemical composition of wastes before they are finally disposed.

REFERENCES