The environment nowadays is facing acute pollution problem with the discharge of various industrial effluents, containing substances varying in characteristics from nutrients to highly toxic substances. Pollution leads to wide spread denaturation of the environment, threatening the very existence of living being in a given habitat. Tannery industry is reputed globally as a major industry and contribute serious environmental problem (UNIDO, 2005). The current pattern of industrial activity alters the natural flow of materials and introduces novel toxic chemicals into the environment (Faisal and Hasnmann, 2004). Heavy metal release to the environment of industrial activities and technological development and poses a significant threat to the environment has been increasing continuously because of industrial activities and technological development and poses a significant threat to the environment, soil and public health. Contamination of agricultural soil with heavy metals is a major problem on industrial and defense related sites all over the world (Parameswari et al., 2010). Tannery industries release effluents directly on the agricultural land or surface of water bodies which eventually leaches to ground water that lead to contamination of toxic metallic component and result in a sense of well documented problem in living beings (Zang and Li., 2011). Chromium exists in many oxidation state of which only Cr (VI) and Cr (III) ions are the most stable under environmental circumstances (Masood and Malik., 2011). Chromium (III) is required in human body, but in very small amounts and relatively immobile, slightly acidic to alkaline and chemically more stable than Cr (VI) and less bio available due to its negligibility and permeable nature to bio membrane. Cr (VI) is highly mobile and water soluble when compare to Cr (III), where as chromium is also used as a pigment.
Hexavalent chromium can be harmful to human health and is toxic, mutagenic and also carcinogenic (APHA, et al., 1998). Chromates in soils have also been found to induce allergic reactions in some individuals. Due to those health and environmental issues, restrictions have been imposed on the use of certain chromium compounds in many countries. Soil is an important system of terrestrial ecosystem. There is a direct impact of pollutants ion minerals, organic matter and microbial community of soil (Nagaraju et al., 2007). The discharged of industrial effluent especially without treatment may have profound influences on physicochemical and biological properties of soils related to soil fertility. A wealth of information on occurrence of changes in properties of soils due to discharge of effluent from other industries is available such as cotton ginning mill (Narasimba et al.,1999), sugar industry (Nagaraju et al., 2007), dairy waste water (David shyam babu, 2010) and dairy industry (Nizamuddin et al.,2008). Effluents from leather processing, a major industry that produces huge volume of waste water normally discharged to irrigate agricultural lands. This tannery waste water contains a very little amount of proteins except for the sludge waste that has nitrogenous compound from hides and skins of animals

The analytical determination of metal ions at low concentration levels has received considerable attention in the last few years (Sarazaninic and Mentasti., 1997). The determination of heavy metals including chromium, has traditionally been carried out by atomic absorption spectrometry (AAS) (EN 1233, 1996) or inductively coupled plasma ICP (ISOLL 885), precise and sensitive but allow determination of total chromium only. The concentration of Cr (VI) is estimated from the difference of total chromium content and Cr (III), which can be analyzed using photometric methods this so called difference method causes in accurate calculated concentration of Cr (VI). In this present investigation atomic absorption spectrometry (AAS) was used to determined total chromium ion from industrial tannery effluent discharge on land fill abatement and control land fill.

MATERIALS AND METHODS

Sampling

The soils samples were collected from Gasau (A1) and Daula (A2) landfills and the Yankusa (A3) control site in Challawa industrial area, Kano State, Nigeria. Four samples were randomly collected from each site making a total of 12 samples. After the removal of surface litter, 20gram of sample was collected from each of twelve sites at a depth between 10 – 15cm using soils auger into clean polythene bags. All the samples were properly labeled (S1 – S12) and transported to National Research Institute for Chemical Technology (NARICT) Basawa Zaria, Nigeria for analysis.

Physicochemical properties of contaminated soil and control landfill

pH: Ten grams of the soil samples was taken and added to twenty five ml of distilled water. The mixture was shaken intermittently for 30 minutes. The pH was then determined by using the pH meter in standard bulb solution (Nag 2007).

Temperature

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

Organic matter

Two and a half grams of dried, sieved soil was taken into a pre-weighed crucible and ignited over a Bunsen burner to a bright red heat, stirring occasionally with a wire loop. The sample was heated for 15 minutes. Then it was allowed to cool in a desiccator and the weight of the soil was taken. The organic carbon content was calculated as follows:

\[
% \text{Organic matter} = \frac{\text{loss in weight X 100}}{\text{Weight of Sample}}
\]

Fawole and Oso, (2004).

Total Nitrogen

One and a half gram of crushed dried soil samples was pour into 300ml Kjelda flask along with 25ml of concentration. H2SO4 and 3g mixed catalyst. The sample was digested using Kjeldahl digestion apparatus until a clear green or whitish color was obtained. The digested solution was then diluted to 100ml with distilled water. Distillation was done adding 20ml of diluted digest into 500ml Kjeldahl flask containing anti – bumping chips and 40ml of 40% NaOH was slowly added by the side of the flask. A conical flask (250ml) containing a mixture of 50ml 2% boric acid and 4 drops of mixed indicator (Cresol/bromthymol) was used to trap the liberated ammonia. The distillate was then titrated with 0.1m HCL. The total nitrogen content was then calculated using

\[
\%N_2 = \frac{14 M V_x V_y}{\text{weight of sample (mg)} \times VS} \times 100
\]

Where

- \( M \): Actual molarity of acid
- \( V \): Titre volume of HCL used
- \( V_x \): Aliquot volume distilled

(Onyeika and Osieji 2003).

Phosphorus

Fifty grams of the dried crushed soil was suspended and filtered through a nylon cloth into a glass beaker. Twenty five ml of the filtrate was heated for 25 minutes with HN03/HCL in a ratio of 3:1 (digestion). The mixture was dilute was diluted to the 100ml mark with distilled water. Fifteen ml of the diluted solution was then pipette into a cuvette and 1ml of the phosphate reagent was added to it and the reading taken using the phosphate meter (Nag, 2007).

Potassium

To determine the potassium content of soil samples fifty grams of the dried soil was suspended in 50ml of distilled water and filtered using nylon cloth. The filtrate (25 ml) was mixed with HNO3, HClO4 in a 2:1 ratio. The beaker containing the mixture was then placed on a hot plate and boiled until the solution became clear. This was then filtered using what man filter paper No.1 in a volumetric flask and the volume of the...
filtrate was made up to 100 ml by the addition of deionized water digested sample was stored in a sterile polyethylene bottle at room temperature for further analysis of the metal using atomic absorption spectrophotometer.

**Calculation**

% Potassium = \( 2 \times 0.005 \)

Where \( R = \) Potassium Concentration (ppm) in the aliquot (Nag, 2007).

**Total Chromium**

Fifty gram of the dried crushed soil was suspended in 50ml distilled water in a beaker and was filtered through nylon cloth. Twenty five of the filtrate was collected in a 400ml beaker and 10ml of concentrated H\(\text{SO}_4\) and 5ml of concentrated H\(\text{NO}_3\) were added to the filtrate in ratio 3/1. The beaker containing the mixture was then placed on a hot plate for boiling until the solution becomes clear and then the solution was transferred by filtration through what man Filter paper No 2 into a volumetric flask. The volume of the filtrate was made up to 50ml by adding deionized water. Digested sample were store in sterile polyethylene bottles at room temperature for further analysis of the metal using flame atomic absorption spectrometry (FAAS) Rani, 2003.

**Statistics**

The data obtained in the study were analyzed by one – way of variance (ANOVA) differences between means of chromium ion were considered significant at values of P < 0.05.

**RESULTS AND DISCUSSION**

In trying to determine the physiochemical characteristics of the soil and the presence of chromium ions in environment due to their toxicity is of great concerned to public health and environment. The data showed the level at which the polluted landfill has been fully devestistated due to the discharged of industrial chemical recipe. The unprecedented discharge of effluent containing chromium ions could be dully mitigated or resuscitated by the abating land through bioremediation process. Soil is a potent system of terrestrial system, and direct discharge of industrial tannery effluent especially that without treatment may have profound influence on physiochemical and biological properties of soil fertility (Narasimba et al., 2011). The colour is usually the first parameter to be recognized in control and polluted land fill due to contaminated waste water that affect the integrity of the land mass. Such colour were observed to be brown, and blue/black in their identity and were symbolized with label (\(S_1, S_2, S_3\) and \(S_4\)), (\(S_5, S_6, S_7\) and \(S_8\)), and (\(S_9, S_{10}, S_{11}\), and \(S_{12}\)) from control sample, contaminated site and deposited site respectively. (Dhungana and Yadav, 2009). WHO reported colourless, dirty dark green and green appearance for tannery effluents in like manner affect the colour, appearance and permeability of the virgin soil when discharge. Obnoxious odour is also perceived and recognized within the affected area of effluent discharge compared with the reference soil sample as shown in table 1. The mean pH values of the contaminated soil at Gasau (5.6) and (5.7) Daula was found to be acidic in comparison with (6.8) Yankusa control site as shown in table 1. Jyoshana and Narasimba (2007) reports show that discharge of effluent from tannery increased the soil pH slightly in comparison with the control soil pH 3.6 – 7.2 and pH 6.8 – 7.2 respectively. Variation in pH values of effluent waste to soils can alter the rate of biological reaction and survival of various microorganisms. Since the control landfill does not contained chemicals recipe. The organisms absolutely, sincerely maintained their level of integrity in terms of improving the soil fertility for their survival as well as the life of plants and animals (Bannats et al., 2008). The varying pH could be attributed to the chemical discharge on landfill due to excessive use of NaOH, H\(\text{2O}_3\) and atomic stabilizer use during finishing processes in tanning and in conjunction with environmental stresses brought about by the contamination (wood and Kellogg, 2007). The soil samples collected from polluted sites were mostly affected by waste water irrigation due to the presence of heavy metal which affects the pH and might likely reduced the population densities of micro flora within a given habitat.

The mean temperature values of the contaminated and deposited landfills (Gasau and Daula) respectively were (37°C) and (35°C) in comparison with the reference soil sample (30.0°C) Yankusa. The findings are in line with the study conducted by Nandakumar (2008). It appears the values falls within the permissible limit. It might be that at the time the sample were collected at winter season, the reference water sample falls within the ambient temperature and other below. High temperature could be as a result of addition of warm water while low temperature could be attributable for the season of samples collection (winter). Increase in temperature can cause change in the species in a given habitat. It could also reduce solubility of oxygen and amplified odour due to anaerobic and aerobic reaction respectively (Nandakumar, 2008). The electrical conductivity of both contaminated and control soil were (0.57, 0.81) and 1.27\(\mu\)Mhos cm\(^{-1}\)respectively. Higher water holding capacities of the mean values were observed in contaminated soil than control, values were found to be (0.56, 0.5) and 0.31mg/l respectively. Increased water holding capacity and decreased electrical conductivity in contaminated soil may be due to the accumulation of organic wastes such as amino acid residues and alkalis in tannery industries (Alvare Bernal et al., 2006).

Mean soil texture values of (Gasau) contaminated soil, deposited soil (Daula) in comparison with (Yankusa) control reference soil in terms of gram of sand, silt and clay were (52.75, 71.50, and 71.50), (23, 24 and 20.24) and (16.25, 16.50 and 8) respectively. The parameters like organic matter mean values, were observed in contaminated soil than control values at (8.23, 8.20) and 4.44mg/l respectively. This result is in accordance to the report of (Mohammed and Sani, 2006). Soil organic matter comprises of the following: Firstly fresh plant and animal residues capable of rapid decomposition and loss of identity with simultaneouse release of nutrient elements; secondly “Humus” which represents the vast bulk of having high adsorptive capacity for cat ions and capable of improving soil structure. In this current result, the Yankusa control land fill had little quantity of organic matter due to the high adsorptive capacity for cat ion, the synergy role play by the plants and the microbes have well improved the soil structure. On the other hand, where high quantity of organic matter is
Physicochemical Properties of Control and Contaminated landfill

<table>
<thead>
<tr>
<th>Properties</th>
<th>Site 1</th>
<th>Site 2</th>
<th>Site 3</th>
<th>Site 4</th>
<th>Site 5</th>
<th>Site 6</th>
<th>Site 7</th>
<th>Site 8</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Colour</strong></td>
<td>Br</td>
<td>Br</td>
<td>Br</td>
<td>Br</td>
<td>Br</td>
<td>Br</td>
<td>Br</td>
<td>Br</td>
</tr>
<tr>
<td><strong>Odour</strong></td>
<td>Nor</td>
<td>Nor</td>
<td>Nor</td>
<td>Nor</td>
<td>Fou</td>
<td>Fou</td>
<td>Fou</td>
<td>Fou</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>7.2</td>
<td>6.8</td>
<td>6.4</td>
<td>6.6</td>
<td>5.6</td>
<td>5.3</td>
<td>5.7</td>
<td>3.9</td>
</tr>
<tr>
<td><strong>Tem°C</strong></td>
<td>35</td>
<td>37</td>
<td>33</td>
<td>33</td>
<td>37</td>
<td>36</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td><strong>Electric conductivity (Mho/cm²)</strong></td>
<td>1.23</td>
<td>1.29</td>
<td>1.30</td>
<td>1.25</td>
<td>0.62</td>
<td>0.72</td>
<td>0.68</td>
<td>0.58</td>
</tr>
<tr>
<td><strong>Water holding capacity(m/g) of soil</strong></td>
<td>0.30</td>
<td>0.29</td>
<td>0.31</td>
<td>0.32</td>
<td>0.62</td>
<td>0.52</td>
<td>0.51</td>
<td>0.60</td>
</tr>
<tr>
<td><strong>Texture</strong></td>
<td>Sand(g)</td>
<td>74</td>
<td>75</td>
<td>76</td>
<td>73</td>
<td>54</td>
<td>52</td>
<td>49</td>
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<tr>
<td><strong>Silt(g)</strong></td>
<td>21</td>
<td>20</td>
<td>19</td>
<td>21</td>
<td>23</td>
<td>24</td>
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<tr>
<td><strong>Clay(g)</strong></td>
<td>9</td>
<td>8</td>
<td>7</td>
<td>8</td>
<td>15</td>
<td>17</td>
<td>16</td>
<td>17</td>
</tr>
<tr>
<td><strong>Organic matter (%)</strong></td>
<td>4.35</td>
<td>4.42</td>
<td>4.20</td>
<td>4.80</td>
<td>8.1</td>
<td>8.4</td>
<td>8.1</td>
<td>8.3</td>
</tr>
<tr>
<td><strong>Chromium ions(mg/l)</strong></td>
<td>2.18</td>
<td>4.15</td>
<td>1.32</td>
<td>1.28</td>
<td>8.36</td>
<td>107.99</td>
<td>67.25</td>
<td>81.52</td>
</tr>
<tr>
<td><strong>Total nitrogen (%)</strong></td>
<td>0.140</td>
<td>0.09</td>
<td>0.019</td>
<td>0.19</td>
<td>0.24</td>
<td>0.23</td>
<td>1.03</td>
<td>1.37</td>
</tr>
<tr>
<td><strong>Potassium (%)</strong></td>
<td>0.610</td>
<td>1.16</td>
<td>1.16</td>
<td>1.24</td>
<td>0.05</td>
<td>0.16</td>
<td>0.26</td>
<td>0.07</td>
</tr>
<tr>
<td><strong>Phosphorus(%)</strong></td>
<td>0.025</td>
<td>0.057</td>
<td>0.012</td>
<td>0.156</td>
<td>1.201</td>
<td>0.233</td>
<td>0.013</td>
<td>0.011</td>
</tr>
</tbody>
</table>

Yankusa Control Site   Gasau Dump Site   Daula Deposited site

KEY: Br=Brown; Nor= Normal; Fou= Foul; FFou= Fairly foul

**TESTING OF HYPOTHESIS**

**Table 2. Analysis of variance of total chromium on reference control soil (Yankusa)**

<table>
<thead>
<tr>
<th>Sources % Variation</th>
<th>Degree of freedom</th>
<th>Sum of squares</th>
<th>Mean squares</th>
<th>FCal</th>
<th>FTab</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>3</td>
<td>1336.503012</td>
<td>445.501004</td>
<td>2.32</td>
<td>3.13</td>
</tr>
<tr>
<td>Errors</td>
<td>19</td>
<td>3646.612652</td>
<td>191.926917</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>22</td>
<td>4983.115664</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The calculated values is less than the F. Tabulated, this depicts that null hypothesis is rejected.

**Table 3. Analysis of variance of total chromium on contaminated land fill (Gusau)**

<table>
<thead>
<tr>
<th>Sources % Variation</th>
<th>Degree of freedom</th>
<th>Sum of squares</th>
<th>Mean squares</th>
<th>FCal</th>
<th>FTab</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>3</td>
<td>828.4206772</td>
<td>276.1402257</td>
<td>0.27</td>
<td>3.13</td>
</tr>
<tr>
<td>Errors</td>
<td>19</td>
<td>19592.95777</td>
<td>1031.208304</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>22</td>
<td>20321.37845</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The F Calculated value is less than the F tabulated. This depicts that the null hypothesis is rejected.

**Table 4. Analysis of variance of total chromium on deposited site (Daula)**

<table>
<thead>
<tr>
<th>Sources % Variation</th>
<th>Degree of freedom</th>
<th>Sum of squares</th>
<th>Mean squares</th>
<th>FCal</th>
<th>FTab</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>3</td>
<td>1336.503012</td>
<td>445.501004</td>
<td>2.32</td>
<td>3.13</td>
</tr>
<tr>
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<td>19</td>
<td>3646.612652</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>22</td>
<td>4983.115664</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The F Calculated values are less than the F tabulated. This depicts that the null hypothesis is rejected.

observed, it could be attributed to high concentration of chromium ions that affects the diversity of microbial activity in a given habitat. Some of these less tolerant microorganisms could as well die in the process of struggling for survival. The dead of the organisms could be the reason for high quantity of organic matter in Gasau and Daula contaminated and deposited agricultural landfill; hence, there was no microbial activity within the catchment area of chromium ions disposal as seen in plate 1, 2 and 3. Total nitrogen, phosphorus and potassium (NPK) in percentages were higher in all ramifications from contaminated land fill than the control soil except potassium content. The properties of contaminated soil sample were (0.460, 0.293) and 0.100%); (0.385, 0.040) and 0.063%; (0.385, 0.973 and 1.043%). respectively. However, this could be possibly explain that surface run-offs from agriculturally fertilized and neighboring lands, microbial interaction and synergy role play by the plants and the microbes in converting inorganic to organic compound (mineralization).This might have contributed significantly to the lesser amount of phosphate and nitrogen percentage present in the Yankusa control land fill in comparison with contaminated and deposited soil Gasau and Daula respectively i.e. the lower area of agricultural activities. This is a plus? Except potassium. On the other hand of the essential elements, one could have expected the assimilation to be in this order N>P>K but instead N<P>K. This might be related to the possible use of high amount of fertilizers during such periods by the neighboring farmers. In additions, surface runoffs could have added these nutrients during heavy rains as this is the peak rainy season period in the area under study. Thus, there seems to be a low content of phosphate than nitrates. This might also be related to the fact that some aquatic photosynthetic microorganisms utilized phosphate while oxygen-depleted photosynthetic means of energy generation (Isabelle and Walter, 1979). The order of this trench N>P>K, nitrate might seem to be less abundant than
Plate 1. Yankusa Control Land Fill

Plate 2. Gasau Dumpsite

Plate 3. Daula Sugar cane Plantation deposited site
phosphate, for which reason it may therefore be that nitrate could be said to be a limiting nutrient in the productivity of Challawa land fill. The total chromium content of the contaminated soil were also much higher than that of the control as observed in table 1 with varying values ranging between (1.289 – 4.15mg/l) from Yankusa control land full, (8.36 – 107.99 mg/l) from Gasau dumpsite and (1.93 – 67.08mg/l) Daula dumpsite respectively. The study is in line with the result conducted earlier by (Ugoji and Aboaba, 2004). Total chromium implies chromium (II), chromium (III), chromate ion and chromium (VI) ion present in natural water or contaminated soil. Their present in a given habitat depend on interaction with microbes that led to the significantly differ in biological, geo chemical and toxicological properties (Sule and Ingle, 1996). Cr (III) over a narrow concentration range is considered essential for mammals, maintenance of glucose essential for mammals, lipid and protein metabolism at minimal level. Whereas Cr (VI) is reported to have a toxic effect in human (Cotton et al., 1999). In this current investigation, tannery effluent discharged directly on land fill are usually found to contain higher values of chromium in comparison with the control land. According to Ugoji Aboaba, (2004), chromium ion in polluted land had higher concentration 89.30% against the lower values of 0.255mg/l in the control land. However, 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 by 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 very 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 use should not exceed 0.05mg/l by (WHO, 1985). Then it could be that the rural dwellers that leave within that vicinity are not guarantee of safety. High concentrations of chromium in drinking water can cause skin ulcer, allergic reactions, carcinogenic and mutagenic effect to humans (Mat and Ginswold, 2009). One way ANOVA revealed significant variation, the mean level of pollution between sampling sites Gasau and Daula landfill compared to reference soil samples Yankusa with F calculated values less than the F Tabulated (0.27/3.13, 0.27/3.13 and 2.32/3.13) respectively as indicated in the result obtained. In this present investigation, there is a high level of pollution by chromium ion in Gasau and Daula contaminated landfill with reference to control landfill Yankusa. This may be linked to the fact that the two contaminated sites exceeded the stipulated level of 0.05mg/l (WHO 1985) as shown in table 1 of the Cr ion analysis.

Conclusion

This present investigation atomic absorption spectrometry (AAS) was used to determined total chromium ion from industrial tannery effluent discharge on land fill abatement and control land fill. The analytical determination of metal ions at low concentration levels has received considerable attention in the last few years (Sarazaninic and Mentasti., 1997). The determination of heavy metals including chromium, has traditionally been carried out by atomic absorption spectrometry (AAS) (EN 1233, 1996) or inductively coupled plasma ICP (ISOLL 885), precise and sensitive but allow determination of total chromium only. The concentration of Cr (VI) is estimated from the difference of total chromium content and Cr (III), which can be analyzed using photometric methods this so called difference method causes in accurate calculated concentration of Cr (VI). In this present investigation, the above parameters measured from control and polluted land fill are potential for profound effect on the contaminated soil itself, resident of microorganism, aquatic life and for further research work that will be done regarding to bioremediation process on land fill abatement.

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