Analysis of Heavy Metals Concentration in Effluents, Groundwater and Top Soil at Textile and Tanneries Waste Dumped Site Located in Challawa Industrial Estate Kano-State, Nigeria.

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Abstract
Industrial solid wastes and discharges from tanneries and textile during the process of converting raw hides/skin into leather and raw cotton into garments that were being dumped in open place situated at Challawa industrial estate Kano-state, Nigeria. A field survey was conducted to assess the level of contamination of the effluents on groundwater and soil by heavy metals as a result of percolation and leaching. Groundwater and soil samples were collected for physico-chemical parameters and heavy metals analysis using atomic absorption spectrophotometer (AAS).The groundwater and soil samples were collected at a depth of (0-20 cm).The physico-chemical parameters and heavy metals determined were: P^H, Electrical Conductivity (EC), Phosphate (PO_4^{2-}), Sulphate (SO_4^{2-}), Chlorides (Cl^-),Nitrate (NO^-_3) and for heavy metals vizly: $Cd^{+,}$ Cr^{6+}, Cu^{2+}, Fe^{2+}, Pb^{2+},Zn^{2+},Ca^{2+},Mg^{2+},Na^+,and K^+,. The concentration of physico-chemical parameters and heavy metals in the collected samples were in the range of effluent >groundwater>soil. These result showed that all physico-chemical parameters (P^H=6.4-7.24), (EC=760.00-886.00), (PO_4^{2-}=87.83-111.82),(SO_4^{2-}=6.00-15.30),(Cl^-=17.50-53.20),(NO^-_3=135.03-373.55) and heavy metals (Cd=10.00-30.00),(Cr=19.21-33.16), (Cu=8.62-16.55), (Fe=22.15-58.14), (Pb=9.42-13.31),(Zn=10.14-16.52),(Ca=2.66-58.14),(Mg=1.65-64.88),(Na=0.36-253.30) and (K=0.48-639.60) analyzed in the samples were found to have beyond the threshold limit as recommended by British Indian Standard (BIS),Federal Ministry of Environment(FMENV,NIGERIA) and World Health Organisation (WHO) except calcium, magnesium, sodium and potassium in soil.

Key words: *Contamination, groundwater, heavy metals, soil, leaching, and percolation.*

1. Introduction

Metals play an important role in chemical, biological, biochemical, metabolic, catabolic, enzymatic reactions in the living cell of plants, animals, human beings and in the life processes of microbes. Some metals such as chromium (Cr), calcium (Ca), magnesium (Mg), manganese (Mn), copper (Cu), sodium (Na), nickel (Ni) and zinc (Zn) are essential as micronutrients for various metabolic functions and for redox functions. Other metals have no biological role e.g.

cadmium (Cd), lead (Pb), mercury (Hg), aluminium (Al), gold (Au) and silver (Ag). They are non-essential and potentially toxic to soil microbes. Some of them e.g. Cd^{2+}, Ag^{2+}, Hg^{2+} tend to bind the SH groups of enzymes and inhibit their activity [26,29].Groundwater and Soil contamination by heavy metals may repress or even killed parts of microbial community in the soil. Interactions of metals with cellular proteins/enzymes are more commonly implicated in causing toxicity than interaction with membranes. Binding affects the structure and function of proteins/enzymes.

Heavy metals are defined as metals having density more than 5 g/cm^3 and the group are about 65. Some heavy metals, such as cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni) & zinc (Zn) are essential and serve as micronutrients for plants like calcium (Ca), potassium (K), magnesium (Mg), manganese (Mn), iron (Fe) and sodium (Na). They are used for redox-processes, as components of various enzymes and for regulation of osmotic pressure in cells [29]. Heavy metals are one of significant category of the industrial pollutants which are unique being selectively toxic, persistent and non-biodegradable. At high concentrations, both essential and non-essential metals can damage cell membrane, alter enzyme specificity, disrupt cellular function, damage the structure of DNA and their solubility in water is considered as imbalanced of the major environmental issues. They have been linked to birth defects, cancer, skin lesions, retardation leading to disabilities, kidney & liver damage and several other health problems [25, 33].

Heavy metals occur naturally in soils as a result of diverse geological processes such as chemical reaction and erosion of underground geological materials [30]. Beside these natural sources, industrial activities can supply a considerable quantity of metals to soil [36]. A large number of industrial activities produce wastes and contaminants that reach the soil through direct disposal, spills, leaks, atmospheric deposition from air, and other pathways [21]. Hence, enhanced metal levels (e.g., Cu, Zn, Pb, Co, Ni, Cd, As, and others) in soil media have been reported from in and around several industrial sites. As one of the dominant transportation routes of heavy elements, atmospheric emissions have commonly been designated as the main route of metallic accumulation in surface soils via their subsequent deposition; along with other transport routes like waste water discharge [11].

Industrial effluents which discharged from the textile and tannery contains a higher amount of metals especially chromium, copper and cadmium. These effluents released on the agricultural field as well as dumped in to the surface water which ultimately leaches to ground water and lead to contamination due to accumulation of toxic metallic components and resulted in a series of well documented problems in living beings because they cannot be completely degraded (Malarkodi et. al. 2007). The presence of heavy metals in industrial effluents offer a wide scope of environmental problems and health hazards are becoming more complex and critical.

In this work, particular emphasis is placed on the status of metals in effluents of tannery and textile industries and related soil. A variety of reagents is used in tanning and textile industries along with large quantities of water which are released as effluents and contain huge bulk of liquid, solid waste, substantial quantities of Cr and other heavy toxics metals, organic matter, lime and sulfide [19, 28]. Different forms of waste emanate in quantity and quality during transformation of raw hides and skin into leather, raw cotton into garment from primitive to modern all over the world. However, tanning and textile industries have been commonly associated with high pollution due to bad odour, organic wastes and surplus volume of water consumption during manufacturing processes (Taylor M.M, 1998).All these metals in effluents cause serious health hazards due to unsafe disposal on soil and into water.

Therefore, it is important to bear in mind that tanning and textile industries are the major source of pollution and contributors of metals to the environment. Hence, there is a dire need to examine and redress the present status of toxic trace metal concentration in tanning industries with associated soil so that evaluation could be made upon the relationship between the levels of the metals in the area in terms of origin and mutual dependence.

2. Materials and Methods

2.1 Description of the study sites

Challawa Industrial Estate (Lat.11^{o}52' 41''N,Long.08^o 28' 09''E) 515m above sea level is located in Kumbotso Local Government area of Kano (Lat.11^{o}59' 18.3'' N, Long.08^{o}32' 05.8''E) 418m above sea level. Industrially; it is one of the predominant areas in Kano-State which encompasses many industrial activities such as Nigerian bottling company, cosmetics, plastics, and rice mill etc, meanwhile tanneries and textile are the common industries.

2.2 Sample preparation and analysis

The samples were taken on 11th August 2015 by10:00 a.m, effluents, groundwater and soil (0-20 cm depth) were collected from the dumped site of both industries wastes and all the collected samples were analyzed for physico-chemical parameters and heavy metals. Effluents and groundwater samples were collected and stored in a clean polythene bottles that had been pre-washed with 10% nitric acid and thoroughly rinsed with de-ionized water. Soil sample was collected in fresh polythene bags. Standard methods were used for collection and analysis [1].

2.3 Metals in effluents and groundwater

Suitable volume of effluents and groundwater samples were taken, filtered through What man No: 42 filter paper and then acidified with concentrated HNO_3 to bring down the pH up to 2.0, 100 ml of sample was taken and added 5ml concentrated HNO_3, and then digested in a closed chamber, within 30 minutes digestion was completed and make up the volume to 100 ml with distilled water. Digested samples were analyzed for physico-chemical parameters and heavy metals concentrations by atomic absorption spectrophotometer (Perkin Elmer 3110). The Cr (VI) concentrations in samples were determined calorimetrically by using spectrophotometer at 540 nm by diphenyl carbazide (DPC) method [1].

2.4 Metals in soil

The collected soil samples were air-dried and sieved into coarse and fine fractions. Well-mixed samples of 2 g each were taken in 250 ml glass beakers and digested with 8mL of aqua regia i.e. HCl and HNO_3 in a ratio of 4:2 on a sand bath for 2 hours. After evaporation to near dryness, the samples were dissolved with 10mL of 2% nitric acid, filtered and then diluted to 50mL with distilled water. Heavy metal concentrations of each fraction was analysed by Atomic Absorption Spectrophotometer [4, 5] pH and electrical conductivity (EC) were analyzed by Digital pH and electrical conductivity meter.

3. Results and discussion.

This study aimed to examine the concentration of physico-chemical parameters and heavy metals in effluents, groundwater and their contamination in associated soil. Generally, concentrations of heavy metals in environment occur due to continuous disposal of untreated industrial effluents and wastes generated during operational phase of industries. Among various industries, tanning and textile industries are major producer of metals like hexavalent chromium, iron, manganese, copper, lead, cadmium and nickel etc. Hence, all the collected samples were analyzed for physico-chemical parameters and heavy metals.

3.1 Metals in effluents and groundwater

The data of physico-chemical parameters and heavy metals concentration in effluents and groundwater is represented in Table 3. Analytical results revealed that the average concentration of physico-chemical parameters $(EC > NO^-_3 > PO_4^{2-} > Cl^- > SO_4^{2-} > P^H)$ and heavy metals (*K>Ca>Na>Mg>Fe>Cr>Cd>Cu>Zn>Mn*) in effluent while in groundwater were $(EC > NO^-_3 > PO_4^{2-} > Cl^- > SO_4^{2-} > P^H)$ and (*K>Ca>Na>Mg>Fe>Cr>Zn>Cd>Cu>Mn*).Electrical conductivity is a measure of water capacity to convey electric current and simplifies the quantity of total dissolved salts [7].High EC values indicated high amount of dissolved inorganic substances in ionized form. Groundwater can be contaminated due to sewage and waste disposal that are rich in nitrates. Groundwater accumulates nitrate as a result of leaching and percolation of water. Phosphate is present in groundwater due to partial treatment of effluent and industrial waste water. Sulphate occur naturally in water as a result of leaching from gypsum and some common minerals, discharge of industrial waste and domestic sewage tends to increase the concentration of sulphate in groundwater. The concentration of chloride serves as an indicator of pollution by sewage, high chloride in water can result to severe illness [7].The predominant source of potassium, sodium, magnesium and calcium in groundwater is weathering of rocks but the quantities rise due to industrial effluent [31]. Higher iron content may produce undesirable effects such as astringent taste, discoloration, turbidity, deposits, and growth of iron bacteria in pipes affecting the acceptability of water for domestic use [8]. Present study reflects that the average concentration of manganese in groundwater and effluent were 9.22 mg/l and 11.46 mg/l (Table 3). On the contrary, higher value of manganese was reported by some workers in effluent of textile industries in Nigeria, which was 65.46% higher, as compared to the value of present study [37]. Depending upon the exposure route, manganese may be among the least toxic of the trace elements if ingested [32] but if inhaled, can enter the brain in two ways: by olfactory (nasal airway) that provide a direct path to brain tissue, and by lung uptake that could provide a source of continuing exposure [34]. The average concentration of copper was found to be 8.65 mg/l in groundwater and 16.55 mg/l in effluent. Copper is an essential element in mammalian nutrition as a component of metallo-enzymes in which it acts as an electron donor or acceptor. Conversely, exposure to high levels of copper can result in a number of adverse health effects [6]. As revealed by analytical results (Table 3) cadmium content in effluent was 30.00 mg/l and 10.00 mg/l in groundwater. Long term exposure to lower levels of cadmium in air, food, or water leads to a build up of cadmium in the kidneys and possible kidney disease. Other potential long-term effects are lung damage and fragile bones [2]. The values of lead observed in effluent and groundwater were 13.31mg/l and 9.42 mg/l. In excess amount, lead affects central nervous system, particularly in children and also damages kidneys and the immune.

3.2 Metals in soils

The heavy metals concentration in soil samples of tanneries and textile solids waste dumped site are recorded and pooled in Table 3. Iron (Fe) is an important element in human body metabolism which acts as catalyst and is present in greater quantity than any other trace metals. Iron function as a component of a number of proteins, including enzymes and haemoglobin but in high level of human being can cause gastrointestinal distress [12].Chromium (Cr) is an essential element especially in metallurgical/steel or pigments industry. Both of its oxidation forms (+3 and +6) in the chemical are used primarily in pigments, metal finishing and wood preservatives [3].The main source of Cr pollution is considered to be from dyestuffs and leather tanning when waste are discharged directly into streams. Zinc (Zn) is an essential micronutrient and catalyzes enzyme activity which contribute to protein structure and regulates gene expression [12].Although consequences of zinc deficiency have been recorded many years but it can be toxic when exposure exceeded physiological needs [24].The adverse effect of Zn intake are acute gastrointestinal, headaches, impaired immune function, changes in lipoprotein, cholesterol level, reduction of copper status and zinc-iron interaction [13]. Cadmium (Cd) is an element that occur naturally in the earth crust's and in ocean water 98.It is an element of concern due to its toxicity point of view and its exposure can resulted to chronic and acute effects in living organisms. Copper (Cu) is an important element and is always present in food and animal liver which are the contributors to dietary [12, 26].Copper acts as a reductant in the enzymes superoxide dismutase, cytochrome oxidase, lysyl oxidase, dopamine hydroxylase and several other oxidases that reduces molecular oxygen, high level of copper concentration in soil can cause bioaccumulation in plants especially the soil which is irrigated by the waste water or which sewage sludge is applied. Lead (Pb) exposure in children and adults can cause a wide spectrum of health problems ranging from small effects on metabolism and intelligence to convulsions, coma, renal failure and death [23].Lead enter the environment at any stage from its mining to its final use and it contaminate crops, soil, water, food, air and dust [17].Manganese (Mn) is widely distributed in nature and is found in animals, plants and soil. Large amount of manganese is released to the atmosphere due to natural as well as anthropogenic activities including fossil fuel consumption, industrial production (mining, smelting, refining) tannery usages. Human exposure to manganese results from Mn contaminated food ingestion, water, inhalation and percutaneous absorption [18].However, in this present study the level of heavy metals in the soil sample is beyond the recommended standard.

4. Conclusion

Solid and liquid waste emanating from tanning and textile industries are known to contain various toxic metal. Tannery and textile waste are directly discharged to nearby land where they adversely affect the quality of both soil and groundwater. According to this research work heavy metals (either essential or toxic) it pose a serious threat to the environment and it needs adequate consideration of toxicity from excessive exposure.

Recommendation.

In this research work conducted, it is necessary to apply an effective remediating technology to treat the waste water before discharging to the environment and proper waste management plan. If waste management planning and remediating technology were not taken into consideration there is possibility of future outbreak of environmental health hazard. Further work needs to be conducted to achieve the control of environmental degradation caused by industrial sectors.

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TABLE 1. NISDWQ, FMENV, BIS AND WHO STANDARD FOR PHYSICO-CHEMICAL PARAMETERS AND HEAVY METALS OF PORTABLE WATER.

PARAMETERS	WHO (DESIRABLE)	WHO (MAX.PERMISSIBLE)	NISDWQ	BIS (DESIRABLE)	BIS (MAX.PERMISSIBLE)	FMENV	UNITS
P^H	7.0-8.5	6.5-9.2	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5	
ELECTRICAL CONDUCTIVITY	5	50	1000	NS	NS	NS	ųs/cm
CHLORIDE (Cl^-)	250	600	250	250	1000	600	Mg/l
NITRATE (NO_3^-)	250	600	250	45	45	20	Mg/l
SULPHATE (SO_4^{2-})	200	400	100	250	400	500	Mg/l
PHOSPHATE (PO_4^{3-})	NS	5	3.5	NS	NS	NS	Mg/l
AMMONIUM (NH_4^+)	0.3	17	NS	NS	NS	NS	Mg/l
CALCIUM (Ca^{2+})	100	200	180	75	200	NS	Mg/l
MANGANESE (Mn^{2+})	0.05	0.05	0.05	0.05	0.05	0.05	Mg/l
MAGNESSIUM (Mg^{2+})	NS	150	40	30	100	NS	Mg/l
POTASSIUM (K^+)	NS	200	50	NS	NS	NS	Mg/l
SODIUM (Na^+)	NS	200	200	NS	NS	NS	Mg/l
CHROMIUM (Cr^{6+})	0.05	0.05	0.05	0.05	0.05	0.05	Mg/l
ZINC (Zn^{2+})	NS	1.0	3.0	3.0	3.0	3.0	Mg/l
COPPER (Cu^{2+})	NS	1.5	1.0	1.0	1.0	1.0	Mg/l
LEAD (Pb^{2+})	0.05	0.05	0.05	0.05	0.05	0.05	Mg/l
CADMIUM (Cd^+)	NS	0.01	NS	NS	NS	NS	Mg/l
IRON (Fe^{3+}/Fe^{2+})	0.1	1.0	0.3	0.3	0.3	0.3	Mg/l

TABLE 2. MAXIMUM ALLOWABLE LIMIT OF HEAVY METALS IN SOIL AS RECOMMENDED BY DUTCH, WHO, FAO AND DPR.

HEAVY METALS	DUTCH STANDARD	WHO	FAO	DPR
As	-	20	20	-
Cd	2	3	3	0.8
Co	-	50	50	-
Cr	100	100	100	100
Cu	35	100	100	36
Fe	-	50,000	50,000	-
Mn	-	2,000	2,000	-
Ni	60	50	50	36
Pb	50	100	100	85
Se	-	10	10	-
Zn	120	300	300	140
Hg	0.49	-	-	-

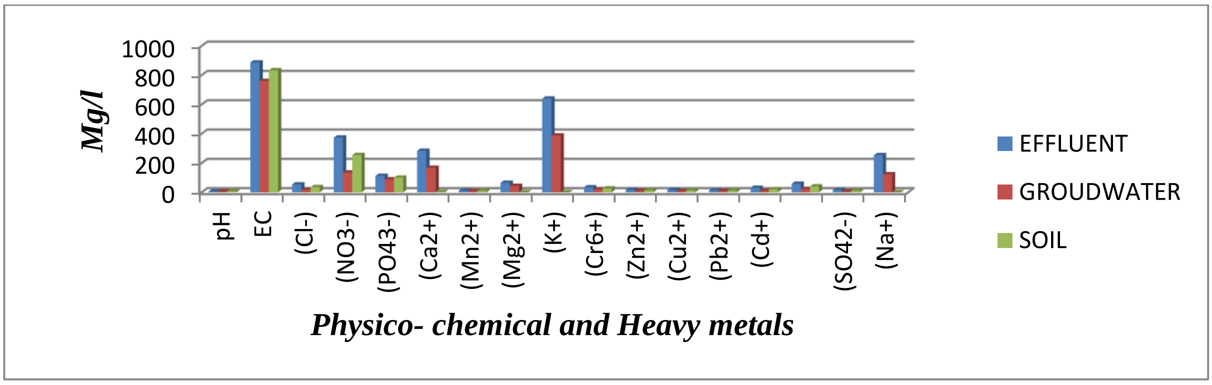

Fig.1.Physico-chemical and Heavy metals of sample