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Determination of the Concentration of Pb, Cu, Cr, Zn and Cd in the Waste Water(Effluent) Discharged from the Ethiopian Tannery

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Abstract

Waste water discharged from the industry were used for irrigation purpose in the vicinity of industrial area of Ethiopia Tannery. The waste water discharged from the tannery industry were examined for its heavy metals (Cu, Zn, Pb, Cd and Cr). For this purpose three samples of waste water from different Sites (Site 1, Site 2 and Site 3) along the channel of the tannery were collected and analyzed by flame atomic absorption spectrophotometry (FAAS). The concentration of heavy metals in waste water discharged from the tannery industry were found that Cu 0.019-0.023, Cd 0.018-0.023, Cr 3.33-7.945, Zn 0.17-0.29 mg/L and Pb below detection limit of the instrumentation.The results are also compared with the levels of metals in the data from previous studies.

Keywords: Tannery, Waste water, Heavy metals, Flame atomic absorption Spectrophotometry,

Introduction

Environmental pollution nowadays is a big concern. Anthropogenic activities have altered the environment significantly throughout the world like mining, industry and agriculture (Wang *et al.* 2008).Environmental contaminants are widely distributed in air, water and soils and, therefore, they will have an effect on the tropic chain (vegetables, animals and men(Tiller 1989).

Disposal of sewage water and industrial wastes is a great problem. Often it is drained to the agricultural lands where it is used for growing crops including vegetables. These sewage effluents are considered not only a rich source of organic matter and other nutrients but also they elevate the level of heavy metals like Fe, Mn, Cu, Zn, Pb, Cr, Ni, Cd and Co in receiving soils (Singh *et al.* 2004).One important dietary uptake pathway could be through crops irrigated with contaminated wastewater. Heavy metals are not easily biodegradable and consequently can be accumulated in human vital organs. This situation causes varying degrees of illness based on acute and chronic exposures (Demirezen and Ahmet 2006).

Typical pollutants (either solid or gaseous) from a tannery include chlorine, formaldehyde, sulfuric acid, glycol ether EB, glycol ether PMA, methyl isobutyl ketone, toluene, xylol, phosphoric acid, methanol, manganese sulfate, chromium III, ethylene glycol, lead, copper, and zinc (U.S. EPA 1993).Pieces of leather (containing 10 to 50% moisture) in various stages of processing, and wastewater treatment sludges constitute the bulk of the process solid waste from tanneries. In order to produce the quality products required by leather consuming industries, tanneries trim off inferior portions of hides at many steps in processing. Smaller pieces of leather wastes are produced in shaving and buffing operations. Approximately 35% of all tannery solid waste is trimmings and shavings of various types (U.S. EPA 1976).Another source of tannery wastes is the finishing department. Finishes are sprayed or rolled onto leather and the residue is considered to be a solid waste since it is land disposed. Finish residues are usually slurries containing 10 to 50% solids. Waste finishes account for about 2% of tannery solid (U.S. EPA 1976).

The characteristics of tannery wastewater vary widely depending on the nature of the adopted tanning process, the amount of water used, the process of hide preservation, the hide processing capacity and the in-plant measures followed to reduce pollution. Treatment of this waste water by conventional biological methods is often inadequate to remove pollutants completely, especially ammonia and tannins, the latter being characterized by low biodegradability, which is common in poly-phenolic compounds. Meanwhile, the biological treatment of wastewaters containing resistant and toxic compounds requires a long duration of time (Szpyrkowicz*et al*. 2005).

One of the major emerging environmental problems in the tanning industry is the disposal of chromium contaminated sludge produced as a by-product of wastewater treatment. Tannery effluents severely affect the mitotic process and reduce seed germination extensively cultivated pulse crops. At high concentrations chromium is toxic, mutagenic, Carcinogenic, and teratogenic. Chromium exists in oxidation states of +2, +3, and +6. The trivalent oxidation state is the most stable form of chromium and is essential to mammals in trace concentration and relatively immobile in the aquatic system due to its low water solubility. The hexavalent chromium is much more toxic to many plants, animals, and bacteria inhabiting aquatic environments (Atlas*et al*. 2008).

Generally, the hazardous chemicals typically discharged from tanneries were summarized as indicated in table 1. (EPA, 1976)

Waste source	Pollutant	Concentration range (mg/Kg	Disposal method
Chrome trimming and shavings	Cr^{+3}	2,200-21,000	Land fill
Chrome fleshing	Cr^{+3}	4000	Land fill
Unfinished chrome leather	Cr^{+3} Cu Pb Zn	4,600-37,000 2.3-468 2.5-476 9.1-156	Land fill
Buffing dust	Cr^{+3} Cu Pb Zn	9-12,000 29-1,900 2-924 160	Land fill
finishing residue	Cr^{+3} Cu Pb Zn	0.45-12,000 0.35-208 2.5-69,200 14-876	Dewater
Sludge	Cr^{+3} Cu Pb Zn	0.33 - 19,400 0.12 - 8,400 0.75 - 240 1.2 - 147	Land fill

Comprehensive studies related to the analyses of waste water (effluent) and vegetables around the particular industrial area of tannerywere only a few in the country even though Ethiopia is one of the top country which process and export the skin and hide on the world. Therefore, the present study has been undertaken to assess the extent of heavy metal contamination in the waste water discharged from the Tannery (Ethiopian tannery) which is found in the East Shoa, Oromia regional state, Ethiopia.

2. Materials and Methods

2.1. Description of the Study area

Ethiopia Tannery Share Company is a public enterprise, located in Koka near Modjo town about 90 km from Addis Ababa. The tannery was established and started production in 1976. Today the company has 722 permanent and 244 contract employees. The tannery is fully equipped with modern technology for production up to finished stage. The tannery has a modern wastewater treatment plant.

Ethiopia Tannery Share Company, a tannery, engages in manufacturing and exporting sheepskin, goatskin, and cattle hide products in Ethiopia and internationally. Its products include crust and finished sheep skins, goat skins, and hide products for gloves, shoe uppers, garments, and linings, as well as cow side products for leather goods.

2.2. Chemicals and instruments

Stock standard solution of 1000 mg/L in 2 % nitric acid of the metals Cu, Pb, Cr, Cd, Zn, (scientific venture) were used for preparation of calibration standards and in the spiking experiments.Working standard solution for the construction of calibration curves were prepared by appropriate dilution of intermediate standard solutions of 1000 mg/L of the metals Cu, Pb, Cr, Cd, Zn, Ca and Mg with deionized water. Nitric acid (Uni-chem 69-72 % v/v) hydrochloric acid (Uni-chem 35.4 % v/v) and hydrogen peroxide (Uni-chem 30% v/v) were used for digestion of samples. Deionized (<1µs/cm) water was used throughout this work.

A heating bath was used to heat waste water during open digestion. A 50 ml of volumetric flask was used to dilute digested sample solutions and for the preparation of standard solutions. A refrigetor (LEC LR 1602) was used to keep the digested sample until analysis. (Buck scientific 210VGP AAS, Este Norwaik, U.S.A) atomic absorption Spectrophotometry equipped with deuterium background correctors was used for the analysis of the analyte metals (Cu, Pb, Cr, Cd and Zn,) using air-acetylene flame.

2.3. Waste water sample collection and preparation

Treated waste water samples were collected at discharge point, 200 m from discharge point and at irrigated land. Since the treated waste water discharged from the tannery is continuous flow in order to find out the representative sample, the treated waste water were sampled by difference of 6 hr for each sampling points. Finally treated waste water was collected in prepared highland bottles and were brought laboratory for analysis

(APHA, 1998).

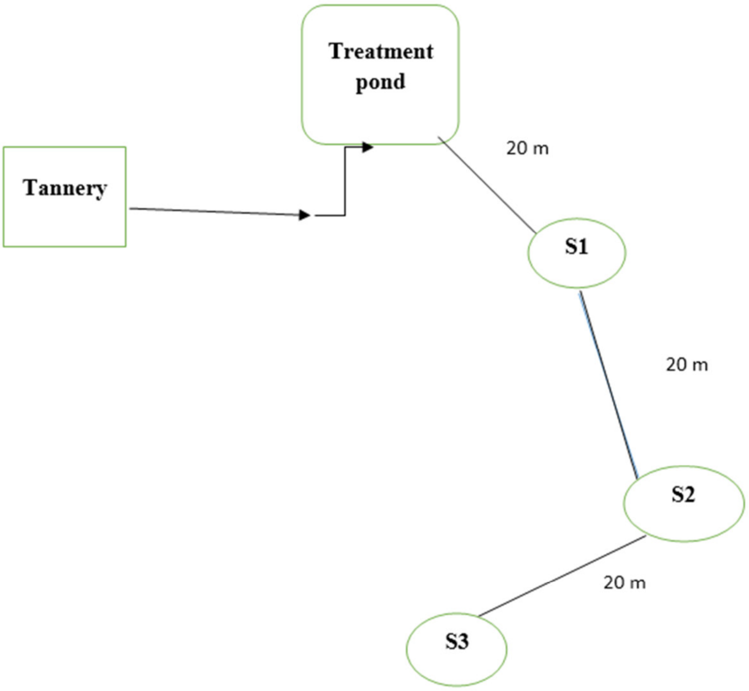


Figure 1:Description of sampling sites

2.5. Digestion of waste water

A 100 mL of treated waste water was transferred into the beaker and 2 mL of concentrated nitric acid and 5 mL of concentrated hydrochloric acid were added to the beaker. The sample was covered with watch glass and heated on a hotplate at 95 ^{0}C until the volume has been reduced to 20 mL. The beaker was removed and allowed to cool. Finally the mixture was filtered through a Whatman No.41 filter paper into 50 mL volumetric flask and made up to the mark with deionized water (Rohrbough, W. (1986).

2.5.1. Determination of metals in the waste water (effluents)

For `the determination of metals in the effluent or the waste water dischargedfrom the tannery a series of four working standard solutions were prepared from the 10 mg/L of intermediate solution of their respective metals, which were prepared by diluting the stock standard solutions of the metals with deionized water. Optimum acetylene and air flow rates were chosen to obtain suitable flame conditions. Other conditions such as slit width, wave length, and lamp current were selected for each hallow cathode lamp according to the manufacture‟s recommendation.

Table 2.Instrumental operating conditions for the determination of metals in vegetable, soil and waste water sample solutions by FAAS

Elements	Parameters				
	Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Sample energy (KJ)	Instrumental detection limit)
Cu	324.7	0.7	1.5	3.854	0.005
Pb	217	0.7	3	2.504	0.04
Cd	228.9	0.7	2	3.267	0.01
Cr	357.9	0.7	2	3.556	0.04
Zn	213.9	0.7	2	3.083	0.005

2.5.2. Determination of percentage Recovery

The efficiency of the standard digestion method was checked by adding known concentration of each metal in all samples and digested by following the same digestion procedure of the corresponding sample due to the absence of certified reference material. 200 µL of (1 mg/L of Cu and Cd) were used to spike 100 mL of effluent in a beaker and then the samples were digested as used for original sample. Similarly 500 µL of (2 mg/L of Zn and Cr) of standard solution were used to spike the same sample and then the samples were digested as used in original sample. Then the digest were transferred into 50 mL volumetric flask and diluted the mark with deionized water. In the same way50 µL of (0.1 mg/L) Pb was used to spike 100 mL of effluent in a beaker and then the same digestion procedure as sample was followed. Then the digest were collected into 100 ml volumetric flask and diluted to the mark with deionized water.

2.5.3. Method detection limit

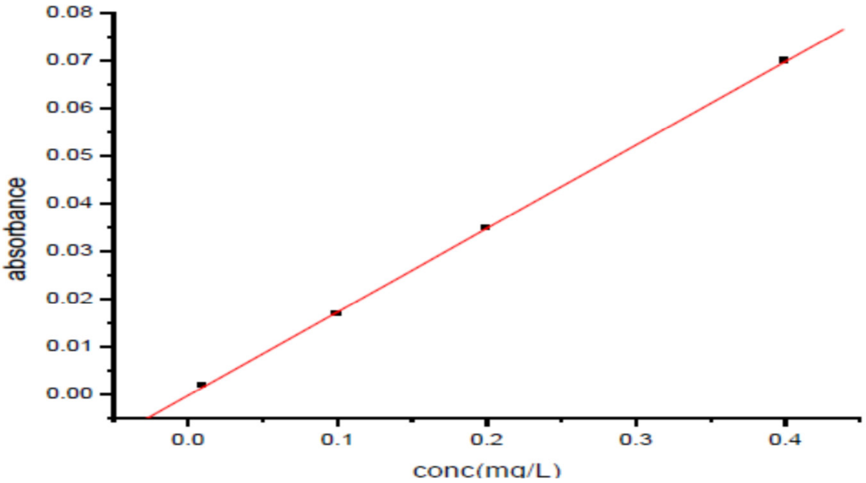
Limit of detection is the smallest mass of analyte that can be distinguished from statically fluctuation in a blank, which is usually corresponding to the standard deviation of the blank solution times a constant. Three reagent blank (deionized water, HNO_3, HCl) samples were digested for influents following the same procedure as the respective samples and each of samples were determined for the elements of interest (Cu, Pb, Cr, Cd and Zn) by atomic absorption Spectrophotometry. The pooled standard deviation for each element was calculated from the reagent blank measurements to determine method detection limit.

3. Results and Discussion

3.1 Calibration of the instrument

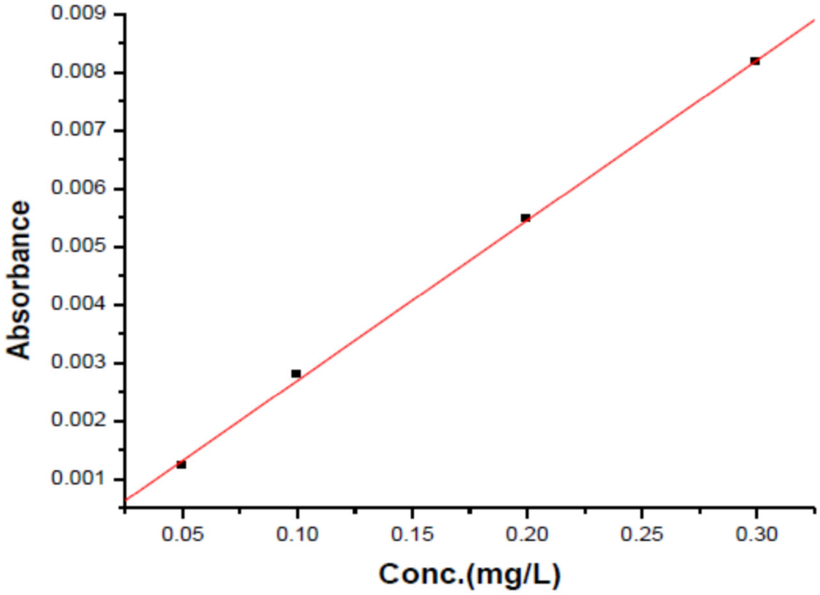
Calibration curves were prepared to determine the concentration of metals in the samples solution. A series of standard working solution were prepared from the 10 mg/L intermediate standard solutions of their respective metals and the solutions were aspirated into the atomizer and absorbance were recorded. Concentration of the working standards and values of correlation coefficient of the calibration graph for each metal are listed in table (3).

The calibration graph and the correlation coefficient of each of the elements were determined by plotting working standard concentration versus their corresponding absorbance as given in Fig 3a to Fig 3g.



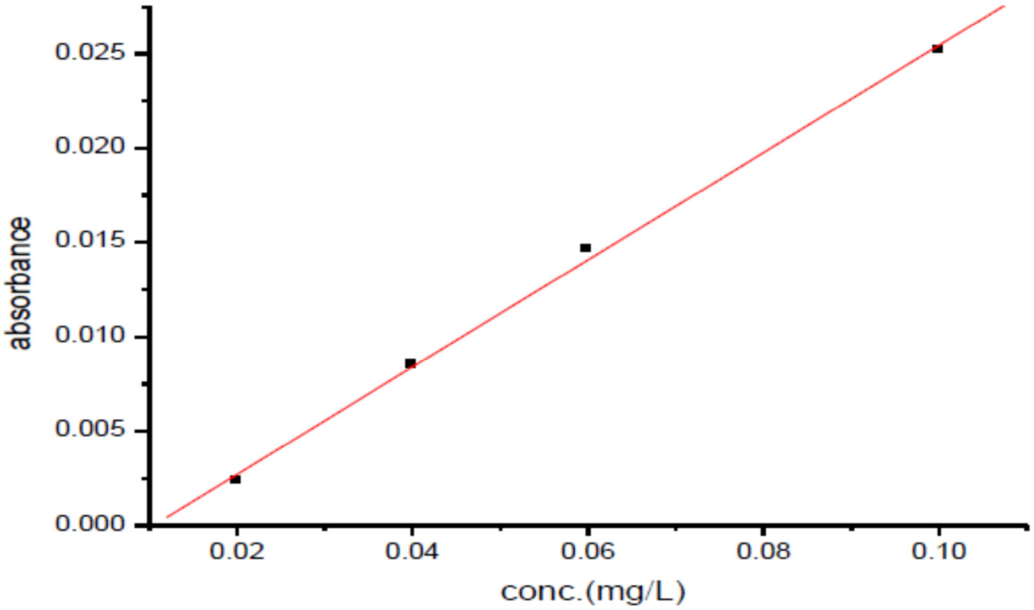
Y= -2.65706E-4 +0.17511X, **R**(correlation coefficient) = **0.9993**

Figure 1(a): calibration graph of Cu standard solution

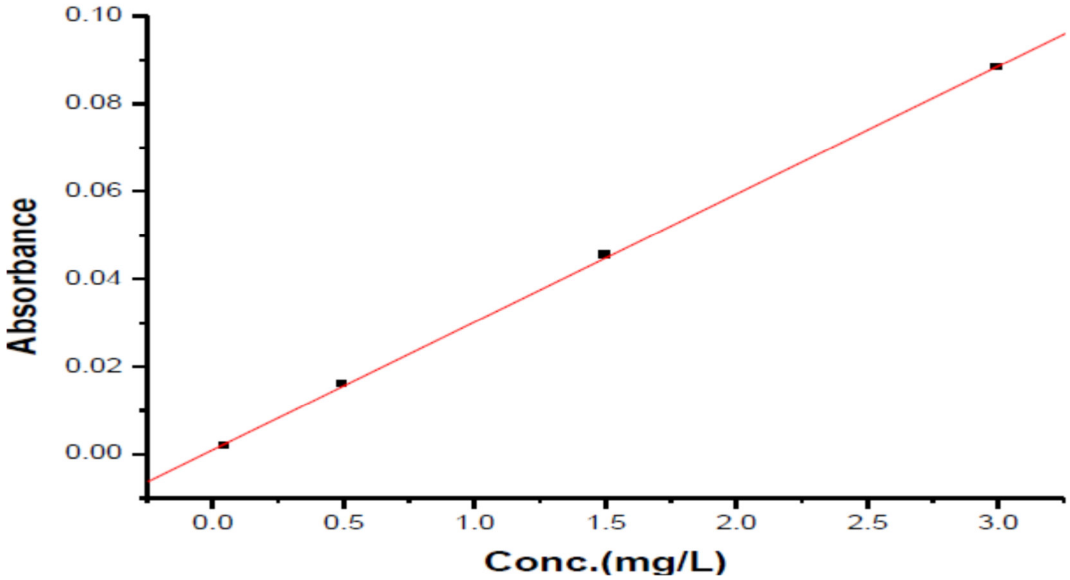


Y= -6.0339E-5 +0.02756X **R**(correlation coefficient) = **0.9996**

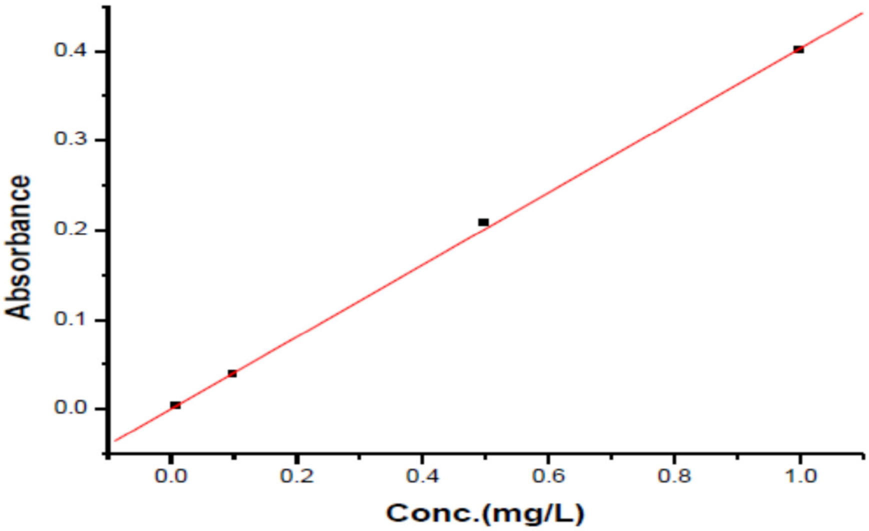
Figure 1(b): calibration graph of Pb standard solution



Y= -0.0036 + 0.28839X **R** (correlation coefficient) = **0.9994**
Figure 1 (c): calibration graph of Cd standard solution



Y= 0.00102 + 0.02918X **R** (correlation coefficient) = **0.9999**
Figure 1 (d): calibration graph of Cr standard solution



Y= 2.2202E-4 + 0.4028X **R**(correlation coefficient) = **0.9997**
Figure 1(e): calibration graph of Zn standard solution

3.2. Method of Validation

3.2.1 Method of detection limit

Method of validation for this work where determined by using method detection limit which is defined as the minimum concentration of the analyte that can be measured by the analytical method with a given confidence limit (WHO 2002).In this work after digestion of three blank solutions for effluent (deionized water, HNO_3 and HCl), three readings were obtained for each blanks. Then the pooled standard deviation of blank reagent was calculated. The method of detection limit of each element was obtained by multiplying the pooled standard deviation of the reagent blank by three (3σ).

Table (4) Method of detection limit of elements in treated waste water (n=9 and in mg/L)

Metal	Method detection limit (mg/L)	Instrumental detection limit (mg/L)
Cu	0.010	0.005
Pb	0.042	0.040
Cd	0.015	0.010
Cr	0.040	0.040
Zn	0.010	0.005

3.2.2. Validation of the digestion procedure

Method validation is the process of providing that the analytical method is acceptable for its intended purpose. Therefore analysts are increasingly encouraged to validate analytical procedures and to estimate the uncertainty associated to the results. Since there is no certified reference material for effluent samples in our laboratory, the validity of the digestion procedure for the samplewas checked by carrying out with lower traceability, such as spiked samples. As shown in tables (5) the percentage recovery ranges 94-110 % effluent.

Table 5: Recovery test for effluent samples

Metal	Conc. In sample (mg/L)	Amount added (mg/L)	Conc. in spiked (mg/ L)	% Recovery
Cu	0.023±0.003	0.1	0.133 ± 0.002	110.00
Cd	0.018 ± 0.005	0.1	0.116 ±0.002	97.50
Cr	7.948 ± 0.300	2	9.824 ± 0.240	94.38
Zn	0.270 ± 0.001	2	2.320 ± 0.015	102.50

3.3. Concentration of heavy metals in irrigated waste water

In table 6 the result show that Cr was determined to give,**7.945 ± 0.30, 3.33 ± 0.20, 6.40 ± 0.20** mg/L at sampling site 1, 2, and 3 respectively which the highest concentration of metals at all sampling sites. Zinc was found higher next to Cr with values **0.27 ± 0.001, 0.17 ± 0.03** and **0.29 ± 0.04** mg/L at site 1, 2 and 3 respectively. Cd was found to be the least of all. The trends suggests that the concentration of chromium and Zinc at sampling site two is less than sampling sites of one and three. The trend for metals concentration in the waste water was found to be Cr > Zn > Cu > Cd. The results were compared to the values recommended by FAO/WHO, FEPA and

NEQS. The concentration of Cu is much less than the required and hence deficiency is expected.

Table 2: The level of heavy metals (mean ± SD) (mg/L) in treated waste water samples.

Elements	Sampling sites			Guide lines		
	Site 1	Site 2	Site 3	WHO (mg/L)	FEPA (mg/L)	NEQS (mg/L)
Cu	0.023 ± 0.003	0.027 ± 0.005	0.019 ± 0.008	1.5	1	1
Pb	ND	ND	ND	1.5	1	0.1
Cd	0.018 ± 0.005	0.023 ± 0.008	0.020± 0.005	1.5	1	0.1
Cr	7.498± 0.3	3.330 ± 0.2	6.400 ± 0.2	1.5	1	1
Zn	0.270 ± 0.001	0.170 ± 0.003	0.290 ± 0.004	1.5	1	5

FEPA= federal environmental protection agency (Nigeria) WHO = world health organization
NEQS = national environment quality standards (Pakistan) Where ND is not detected

4. Conclusion

In this study waste water discharged from the tannery were analyzed for their contents of Cu, Pb, Cd, Cr, and Zn.The standard digestion method for waste water was found effective for all of the elements under the study and as it was evaluated through percentage recovery experiments. Good recovery percentage was obtained (94.5 -110)for all heavy metals examined in the waste water sample.The concentration of chromium was found higher in the waste water along the channel of sampling sites than the concentration of othermetals analyzed, which suggests that the waste water discharged from the tannery is contaminated with chromium. This is due to the fact that almost all Ethiopian tannery industries in general and this Tannery in particular uses chrome tanning or any other chrome related activities in the tannery.

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