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Study on the Pollution Levels of Trace Metals from Modjo Tannery Effluent in the Surrounding River Water and Soil

Amanial Haile Reda

Department of Chemistry, College of Natural Sciences, Arbaminch University, Arbaminch, Ethiopia

Email address:
amanual.haile@amu.edu.et

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Abstract: This study was conducted to assess the extent of trace metals in Modjo tannery wastewater and their levels of contamination in the vicinity of Modjo river water and agricultural soil. Samples of tannery wastewater, river water and agricultural soils have been analyzed for Cd, Cu, Ni, Pb, Zn and Cr using atomic absorption spectrophotometry (AAS). The result showed that the concentration of Zn and Cr metals in Modjo tannery wastewater as well as Cd, Ni and Cr in the river water sample were above the standard values of FEPA and WHO. But Pb was found below the method detection limit for both wastewater and water samples. Results of one - way ANOVA shows that variations for all selected metals in both wastewater and water samples at different sampling points were statistically significant except Cd in the river water sample. For the agricultural soil sample levels of Cd, Ni, Zn and Cr were above NEQS standard limit value. The metal contamination factor (CF) also shows that the agricultural soil was highly contaminated (CF>6) with Cd and Cr, but moderately contaminated (1<CF<3) with Cu, Ni, Pb and Zn. Very high contamination factor for Cr and Cd was observed in the agricultural soil indicating that both tannery wastewater and river water affects the quality of the soil around the tannery factory.

Keywords: Modjo Tannery Wastewater, Modjo River, Trace Metals, Soil Contamination

1. Introduction

Advanced industrialization processes have provided comforts to human beings on one hand, and on the other, it has resulted in indiscriminate release of gasses and liquids, which polluted the environment of biological system [1].

Of the various sources of pollutants industrial effluents containing heavy metals pose a threat to the ecosystem. Presence of pollutants in effluent is a common environmental hazard since the toxic metal ions dissolved can ultimately reach the top of the food chain and becomes a risk factor for human beings [2].

According to Akan *et al* [3], in tannery various chemicals are used during the soaking, tanning and post tanning processing of hides and skins. It has also been reported by UNIDO [4] that only about 20% of the large number of chemicals used in the tanning process is absorbed by leather, but the rest is released as waste. Tariqu *et al* [5] also stated that effluents from tanning units are discharged indiscriminately into natural water bodies or open lands, resulting in contamination of the surface and ground waters as well as the soil flora and fauna. Discharges of untreated wastewater to the aquatic environment can result in the accumulation of pollutants. The consequence of this accumulation could result in loss of lively hood, loss of biodiversity and degradation of water quality, which in general affects the ecosystem [6]. Tanneries have been found to discharge not only Cr which, is an inherent product of the tanning process, significant amounts of Zn, Mn, Cu Cd, Pb, As, Ni, B, Se, Mo, N and P have also been observed at the main waste disposal points exceeding the toxic range in soils [3,7]. Heavy metals (Pb, Cd, Hg and As) contamination in drinking-water is also seriously threats human health at different levels of diseases [8]. Lead and Copper have no known nutritional and physiological function and they are usually toxic for organisms with a serious cumulative [9, 10]. The toxicity of Cr (VI) is also well documented and is considered a hazard to health of man and animals. The various compounds of chromium are found to be both corrosive to flesh and carcinogenic [11,12]. Even though Copper is an essential element to living organism copper together with cadmium is considered as the most toxic heavy metal to soil microorganisms [13]. Similar to copper small amount of nickel is essential for normal growth and reproduction in some species of animals, plant and micro organisms [14]. But under various conditions could either activate or inhibit several enzymatic reactions, which are considered to be of crucial importance in humans and other animals, and that interference with these reactions could have severe deleterious effects [15].

Therefore; Modjo tannery is one of the 14 tanneries located along Modjo town, Ethiopia in which its untreated wastewater discharge directly into the Modjo River. The tannery is considered as a source of pollution to the environment and has a strong potential to cause soil and water pollution owing to the discharge of untreated effluent. Most adverse of this tannery effluent is polluting the Modjo river in which the wastewater is discharged to it and the agricultural soil in the vicinity of the tannery. In accordance with the unsafe discharge of the tannery effluent into the nearby environment the present study was formulated to assess the levels of trace metals like Cd, Cu, Ni, Pb, Zn and Cr in the tannery wastewater, river water and agricultural soil.

2. Materials and Methods

Study area

Modjo tanning industry, which is found in Modjo town is located 80 Kms South of Addis Ababa the capital city of Ethiopia and is a medium-sized leather industry with installed capacity of processing 844,000 and 1, 656,000 sheep and goatskins, respectively, per annum [16]. The Plant is sited near the Modjo River and channels its effluents directly to the river course. The volume of wastewater discharged into the Modjo River varies between 3500-5500 cubic meters per day [17]. Apart from its unfortunate use as open waste disposal site the river is also used as a source of drinking and irrigation for the rural population living around the Modjo River.

2.1. Sampling and Sample Pre-Treatments

Tannery wastewater and river water sampling

Tannery wastewater (effluent) samples were collected with 1 L-capacity polyethylene bottles at different distance along the wastewater channel. River water samples from which the tannery wastewater discharged to it were also collected from downstream site of the river at different distance. In a similar way another river water sample was also collected from the upstream site of the river to obtain a background or control sample and is believed free of the Modjo tannery wastewater. All river water samples were collected from the main flow of the stream at 3-5 cm depth. After collection 500 mL of each of wastewater and water samples were acidified to pH < 2 with concentrated nitric acid for metal analysis to prevent the precipitation of metals and finally stored in icebox and transported in to the Hawassa University chemistry department laboratory.

Soil sampling: A composite soil sample was collected from the agricultural area in the vicinity of the tannery from the depth of 0-15 cm. In a similarly way another soil sample was collected from remote areas of the tannery which served as control (background). After the soil samples were transferred to polyethylene plastic bags the samples were stored in icebox until they were transported to the Hawassa University laboratory.

Figure 1. *Drain (channel) where Modjo tannery wastewater travels from the source.*

2.2. Digestion of Samples

Digestion of wastewater and water samples: 100 mL of each wastewater and water sample was transferred into separate beakers and 2 mL of concentrated HNO_3 and 5 mL of concentrated HCl were added to each beaker and covered with a ribbed watch glass. The beaker was heated on a hot plate at 90 to 95^{o}C until the volume has been reduced to 15-20 mL. After cooling the beaker wall and watch glass were washed with distilled water and the sample was filtered to remove any insoluble materials that could clog the atomizer. Finally the volume was adjusted to 100 mL with reagent water [18] and measurement was done using AAS.

Digestion of soil sample: The soil sample was air-dried, homogenized and ground into fine powder using pestle and mortar and passed through 1 mm sieve. Finally, 1.0 g of soil sample was transferred to 250 mL Griffin beaker and 10 mL of 1:1 HNO_3 was added and heated to 95 ^{0}C and refluxed for 15 minutes. After cooling, 5 mL concentrated HNO_3 was added and then heated to 95 ^{0}C, and refluxed for 30 minutes until no brown fumes was given off by the sample. The mixture was refluxed again to approximately 5 mL at 95 ^{0}C without boiling for two hours. After cooling, 2mL of water and 3 mL of 30% H_2O_2 were added heated until effervescence subsides. Further, 1-mL of 30% H_2O_2 was added until the general sample appearance was unchanged and digested until the volume has been reduced to approximately 5 mL without boiling for two hours. Finally, 10 mL concentrated HCl was added and refluxed at 95 ^{0}C for 15 minutes and then the sample was filtered and diluted to 100 mL volumetric flask [19]. Measurement for the trace metal was done using AAS.

Statistical analysis: The significance of variation within sample and between samples has been studied using one-way analysis of variance (ANOVA) for effluent (wastewater) and water samples. The least significant difference (LSD) method was applied to test the mean differences at the 5% level of significance. Two sided t-test was also used for soil samples. All statistical data analysis was carried out using stastical package for social studies (SPSS) software version 16.0.

3. Results and Discussion

3.1. Levels of Trace Metals Along the Wastewater Channel

Table 1. *Average concentration (mean ± SD, n = 3, mgL^{-1}) of metals in Modjo tannery wastewater channel.*

Metal	Sampling sites		
	E1	E2	E3
	Mean ± SD	Mean ± SD	Mean ± SD
Cd	0.081±0.003	0.043±0.002	0.040±0.002
Cu	0.31±0.02	0.22±0.01	0.17±0.01
Ni	0.85±0.06	0.75±0.04	0.64±0.07
Pb	ND	ND	ND
Zn	2.81±0.001	2.30±0.07	1.99±0.24
Cr	282.59±20.42	174.64±25.55	132.03±13.22

ND: Concentration of the tested metal below the method detection limit

The concentrations of the metals studied along the wastewater channel showed a decrease in concentration from the point source (E1) up to 800 m (E3), in the order of E1>E2>E3 (table 1) and this might be due to adsorption of the metal within the wall of discharged channel soil. Analysis of variance (ANOVA) indicated that variation among points were statistically significant ($p<0.05$) except Pb. But the level of Pb was below the method detection limit (0.05mgL^{-1}); hence no appreciable amount of Pb was detected at all sampling points of the wastewater channel. The mean concentrations of Zn and Cr at all sampling points along the wastewater channel were higher than the standard limits for industrial effluents to be discharged to water bodies set by WHO [20] and FEPA [16] which is 1 mgL^{-1}. Especially the concentration Cr was found elevated by about an average of 196 times the standard value of WHO. The high value of Cr mentioned above is due to the fact that Cr is a compound of tannery effluent emanating from the use of chromium salt. Continuous discharge of chromium in low concentration has been reported to be toxic to aquatic life and has been shown to disrupt the aquatic food chain [2].

3.2. Levels of Trace Metals in Water Samples of River

Table 2. *Average concentration (mean ± SD, n = 3, mgL^{-1}) of selected metals in water sample.*

Metal	Sampling sites		
	W1	W2	Wup (control)
	Mean ± SD	Mean ± SD	Mean ± SD
Cd	0.023±0.002	0.021±0.002	0.011±0.001
Cu	0.12±0.002	0.038±0.003	0.030±0.003
Ni	0.24±0.002	0.064±0.003	0.04±0.001
Pb	ND	ND	ND
Zn	1.22±0.002	0.49±0.01	0.20±0.003
Cr	72.14±3.8	9.99±1.89	1.2±0.09

ND: Concentration of the tested metal below the method detection limit.

The average concentration of Cd, Cu, Ni, Zn and Cr except Pb shows a decrease in their concentration from W1 to W2 in the downstream site of the river (table 2). This indicated that the distribution of metals becomes less as the distance increases downstream and thus decrease in concentration might be due to dilution and adsorption of the metal by sediments and organic matters present in the river water. Akan *et al* [3] also stated that metal adsorbs strongly to sediments and organic matters. One way ANOVA also showed that variations among the different sampling points were statistically significant ($p<0.05$) for all metals except Cd. But the concentration of Pb was below the method detection limit at all the sampling points.

The levels of Cd, Ni and Cr in both sampling sites of the river W1and W2 were higher than the guide line value of water quality set by WHO [21] which is 0.003 mgL^{-1}, 0.02 mgL^{-1} and 0.05 mgL^{-1} respectively. High concentration of these metals in W1 and W2 were also recorded as compared to values obtained in the Wup which is up steam site of the river used as control (table 2). This indicated that the high concentrations of these metals in the downstream site of the river are due to the direct discharge of tannery wastewater to the river water and the river is polluted by these trace metals. Whereas the mean concentrations of Cu and Zn in the downstream site of the river W1 and W2 were within the guide line values of water quality set by WHO which is 1.0 mgL^{-1} and 5.0 mgL^{-1} respectively. The concentrations of these metals in the downstream site of the river W1 and W2 were also above the values obtained from the upstream site of the river Wup used as control (Table 2). This indicated that an increased in the levels of these metals in the downstream site of the river is due to the discharged tannery effluent. Even though the current concentrations of these metals were within the standard values of WHO but till there is an increase in concentration of these metals and thus might also increase the accumulation of these metals on the sediments and organic matters present in the river.

3.3. Levels of Trace Metals in Soil Samples

The average concentrations of Cd, Ni, Zn and Cr in the agricultural soil sample Ss were 3.14, 31.8, 241.6 and 2017.24 mgkg^{-1} respectively (table 3). All these values were above the values given in the National Environmental Quality Standards (NEQS) of soil which is 0.5, 20, 60 and 20 mgkg^{-1} respectively. In addition to this the levels of these metals in the agricultural soil in the vicinity of the tannery were also above the value obtained from the control soil sample Sb which is collected from the remote areas of the tannery (table 2). t-test also showed that mean concentrations of Cd, Ni, Zn and Cr in both Ss and Sb were statistically significant ($p<0.05$). Thus result indicated that there is a pollution and accumulation of these trace metals in the agricultural soil as a result of the river water used for irrigation purpose. Whereas the average concentrations of Cu and Pb in the agricultural soil Ss were 22.89 and 9.56 mgkg^{-1} and both values were within the standard values given by NEQS which is 100 mgkg^{-1} and 25 mgkg^{-1} respectively. But the concentrations of both Cu and Pb in Ss were higher as compared to the values obtained from the Sb which is used as control. t-test also showed that mean concentrations of Cu and Pb in Ss and Sb were statistically significant ($p<0.05$). Thus might be due to the gradual accumulation of these trace metals as a result of the river water used for irrigation.

Soil contamination factor (CF) was also calculated using equation given by [22]. Where CF < 1 refers to low contamination; 1 ≤ CF < 3 means moderate contamination; 3 ≤ CF ≤ 6 indicates considerable contamination and CF > 6 indicates very high contamination. The CF values of Cd and Cr were 6.41 and 364.12 and this shows that the agricultural soil is very high contaminated with Cd and Cr but moderately contaminated with Cu, Ni, Pb and Zn with their CF values of 1.48, 2.12, 1.35 and 1.39 respectively.

Table 3. *Average concentrations (mean ± SD, n = 3, mgKg^{-1}) of selected metals in soil samples.*

Metal	Sampling sites	
	Ss	Sb (control)
	Mean ± SD	Mean ± SD
Cd	3.14±0.06	0.49±0.01
Cu	22.89±0.39	15.51±0.27
Ni	31.8±1.1	15.03±0.71
Pb	9.56±0.43	7.09±0.19
Zn	241.6±1.1	173.88±1.37
Cr	2017.24±2.01	5.54±1.03

4. Conclusion

Thus study showed that concentrations of Cd, Cu Ni, Zn and Cr decreased with distance from point source in both the wastewater channel and river water. Analysis of variance also showed that variations among sampling points were statistically significant except Cd in the river water sample. The levels of Zn and Cr along the tannery wastewater channel were above the international standard values set by FEPA and WHO for tannery effluents to be discharged into water bodies. In the river water concentrations of Cd, Ni and Cr were above the WHO guide line of water quality. In downstream site of the river where the tannery wastewater travels through the levels of Cd, Cu Ni, Zn and Cr were also higher as compared to the values obtained in the upstream site of the river which is used as control and is expected free of the Modjo tannery wastewater. In the agricultural soil the levels of Cd, Ni, Zn and Cr were much greater compared to background (control) soil sample and international standard values set by NEQS of soil quality. This indicated that the soil around the tannery is polluted with Cd, Ni, Zn and Cr from the tannery wastewater and river water. In general the tannery wastewater has a large contribution for the pollution of the river water and agricultural soil. Consequently, over time, excessive metal accumulation in soil and water might affect the quality of the natural resources around the tannery.

Recommendation

In general, the release of untreated wastewater from Modjo tannery influenced the receiving water body and surrounding soil. Therefore, it is recommended that the treatment of wastewater is not only desirable but also necessary to correct wastewater characteristics so that its use or final disposal of the treated effluents can take place without causing an adverse impact on the receiving water body and surrounding soil. In addition to this further work on the impact of tannery wastewater on sediments of the river and in the surrounding growing crop and cultivated vegetation is necessary to assess the impact of tannery wastewater in the surrounding environments.

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