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SHORT COMMUNICATION

ENVIRONMENTAL IMPACTS OF SHEBA TANNERY (ETHIOPIA) EFFLUENTS ON THE SURROUNDING WATER BODIES

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ABSTRACT. The levels of hexavalent chromium from direct and treated Sheba tannery effluents, downstream river and spring water samples and upstream river water samples were determined spectrophotometrically by the s-diphenylcarbazide method at 540 nm. Temporal and representative samples were collected from the untreated tannery effluent (S_1), sedimentation pond (S_2), chromium oxidation pond (S_3), downstream river (S_4), downstream spring (S_5) and 5 kms upstream river (S_6). The mean levels of hexavalent chromium in S_1, S_2, S_3, S_4, S_5 and S_6 were 10.54, 9.15, 7.82, 0.58, 0.54 and 0.015 mg/L, respectively. The levels of hexavalent chromium in the downstream river and spring water samples exceed the World Health Organization (WHO) permissible limit of total chromium in drinking waters (0.05 mg/L) as opposed to the levels in the upstream waters. The increased concentrations of Cr(VI) in the water samples indicate the possible environmental pollution of the downstream water bodies by the Sheba tannery effluents. In view of the toxicity and related environmental hazards, the levels of hexavalent chromium from the Sheba tannery effluents must be reduced to a permissible limit before discharging into the down stream waters being used for domestic purposes by the nearby communities.

KEY WORDS: Tannery effluents, Hexavalent chromium, s-Diphenycarbazide, Environmental pollution, Ethiopia

INTRODUCTION

Chromium enters the air, water and soil as chromium(III) and chromium(VI) through natural processes and human activities and the leather industry is one of the largest polluters among the various human activities [1-4]. The tanning activity is vital for the leather industry and most tanneries in the world (about 90%) use chromium salts to produce leather, because these salts provide better leather flexibility, better water resistance and a high shrinkage temperature [5]. Unfortunately, chromium salts are not completely fixed by skins and the residual quantity (about 30% of the initial one) remains in the spent tanning liquor [5]. Despite the use of various physicochemical methods such as precipitation by hydroxides, carbonates and sulfides, and adsorption on activated carbon, use of ion exchange resins, and membrane separation processes and bioremediation to remove the heavy metals, the effluents/sludges emerging out of the leather industries are invariably loaded with chromium salts [6]. Hence, large quantities of chromium salts have been discharged into the environment by the leather industries [7-9]. However, it should be noted that chromium salts are not the only wastes from tanneries. Tannery wastes are characterized by strong color, high pH, high biochemical oxygen demand and high dissolved salts.

Although chromium oxidation states range from (–IV) to (+VI), only the (+III) and (+VI) states are stable in the natural environment [10, 11]. The chemical and toxicological behaviors of chromium salts depend on the oxidation state of chromium. Chromium(III) is an essential trace element in human nutrition, required for the maintenance of normal glucose, cholesterol, and fatty acid metabolism. Insufficient dietary intake of chromium(III) leads to increases in risk factors associated with diabetes and cardiovascular disease including elevated circulating insulin, glucose, triglycerides, total cholesterol and impaired immune function. On the other hand, water soluble Cr(VI) is extremely toxic and carcinogenic owing to its ability to oxidize

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*Corresponding author. E-mail: abrishgk@yahoo.com other species and has a significant mobility in the environment because of its high solubility in water and weak sorption onto inorganic surfaces [12]. Although trivalent chromium is considered an essential nutrient for the human body and the toxicity of trivalent chromium is 500–1000 times less to a living cell than hexavalent chromium, exposure to excessive doses of Cr(III) for long periods of time may also cause some adverse health effects. Removal of Cr(VI) from industrial effluents is not only essential because of its toxicity to humans but also because it affects soil fertility by inhibiting biodegradation of organic pollutants due to its ability to inactivating enzymes and precipitating proteins of soil microbial organisms [2].

One of the important features that distinguish heavy metals from other pollutants is that the former are not biodegradable. Once metal ions enter the environment, their chemical form largely determines their potential toxicity. The presence of toxic heavy metal contaminants in aqueous streams, arising from the discharge of untreated metal containing effluents into water bodies, must be one of the most important environmental issues that deserve due consideration [13]. In view of toxicity and related environmental hazards, the level of chromium in wastewaters must be reduced to a permissible limit before discharging into the nearby natural water bodies.

The Sheba tannery from Tigray (Ethiopia) discharges 120 m^3 of waste into the environment on a daily basis. Some of the constituents of the waste are chrome salts, sodium sulfide, sodium hydrogen sulfide, calcium hydroxide, saline and others. But, data on the pollution level of the surrounding waters is nonexistent. Thus, the objective of this study was to determine the concentration of hexavalent chromium in the Sheba tannery effluents entering the surrounding water bodies and assess the severity of environmental pollution in the surrounding water bodies.

EXPERIMENTAL

Sample collection and treatment. Seven rounds of temporal samples were collected from six different sample collection sites around the Sheba tannery from Wukro, Tigray (Ethiopia). A total of 42 samples were collected from the direct Sheba tannery effluents, downstream and upstream nearby water bodies between March and April 2007. The direct effluent samples were collected manually from the effluent prior to treatment (S_1), chromium oxidation pond (S_2) and sedimentation tank (S_3). The samples from the surrounding water bodies were collected from downstream running river water (S_4) and spring water (S_5). The upstream river water (S_6) samples were collected at a distance of 5 km from the tannery for comparison purposes. Every possible precautionary measure was taken to obtain a representative sub-sample and avoid temporal variations of the samples. Thus, samples were collected at various distances from the tannery, different depths and similar times of the day at around 4:30 PM when the amount of sulfide is at its minimum. Sulfides reduce Cr(VI) to Cr(III) and hence prior to sample collection, the amount of sulfides in the effluents was checked to make sure that the sulfide levels were as low as possible. Collected samples were then transported to the laboratory at the Chemistry Department of Mekelle University in polyethylene plastic bottles. Once arrived in the laboratory, samples were refrigerated at 4 ± 2 ^{o}C for a maximum of 24 h. Because chromium is ubiquitous in nature, care was taken to avoid sample contamination during collection, preparation and analysis. The use of analytical grade reagents, distilled and deionized water, use of acid washed sample containers and cleaning of sample containers before use by soaking in 1:1 concentrated sulfuric and nitric solutions and then rinsing with water thoroughly were some of the precautionary methods employed to avoid contamination.

Apparatus. Model 752 UV-VIS Grating Spectrometer, England, was used for absorbance measurements.

Reagents. Reagents used throughout the experiment were of analytical grade. Glassware were washed with 1:1 mixture of concentrated sulfuric and nitric acids before use. 1000 mg/L $K_2Cr_2O_7$ stock solution was prepared by carefully weighing 0.282 g of $K_2Cr_2O_7$ using a four digit analytical balance and diluted to 100 mL with distilled and de-ionized water. Diphenylcarbazide solution was prepared by dissolving 500 mg of s-diphenylcarbazide and 8 g of phthalic anhydride in 200 mL of 95% ethanol. The solution was refrigerated and kept in amber bottle until use. 9 M sulfuric acid solution was prepared by dissolving 49.4 mL of concentrated sulfuric acid (assay - 97% and specific gravity – 1.84) to make a 100 mL solution.

Principle of the method. Under acidic conditions hexavalent chromium reacts with s-diphenylcarbazide (DPC) to form a reddish violet colored complex resulting from the reaction of hexavalent chromium with s-diphenylcarbazide. The chromate oxidizes DPC to diphenylcarbazone (DPCO). The determination of chromium with the derivatizing agent, DPC, enables the speciation of chromium without a previous separation step, because this reaction is selective for Cr(VI). The absorbance of the reddish violet colored complex was then measured spectrophotometrically at 540 nm [14]. Acid solutions of potassium dichromate are colored and the intensity of this color is proportional to the concentration of the dichromate anion in solution. For purposes of comparison, the absorbance of Cr(VI) in the unknown acidified sample solutions was measured at 440 nm in the absence of the chromophoric reagent, s-diphenylcarbazide [14]. This method, however, is less sensitive than the s-diphenylcarbazide.

Preparation of standard solutions. 0.0, 20.0, 50.0 and 100 mg/L $K_2Cr_2O_7$ standard solutions were prepared by pipetting 0, 2, 5 and 10 mL of the $K_2Cr_2O_7$ stock solution into four different 100 mL volumetric flasks. To each of the volumetric flasks, 3 mL of 9 M sulfuric acid solution (50 % v/v) was added and diluted to 100 mL with distilled and de-ionized water. To each of four test tubes containing 10 mL of the four standard solutions, 0.5 mL of s-diphenylcarbazide was added and absorbance measured at 540 nm. The absorbance readings of the standard solutions were used to construct a calibration curve. Similar steps except the addition of 0.5 mL s-diphenylcarbazide were followed to prepare the standard solutions for the analysis of hexavalent chromium in the absence of the s-diphenylcarbazide and the absorbance was measured at 440 nm [14].

Sample analysis. Each sample was filtered with Whatman filter paper (0.45 μm of pore size). One mL of each filtered sample was added into six different 100 mL capacity volumetric flasks. To each of these volumetric flasks, 3 mL of 9 M sulfuric acid was added and finally diluted to 100 mL with distilled water. Ten mL aliquots of each of the diluted samples were taken and added into six different 20 mL test tubes labelled as S_1, S_2, S_3, S_4, S_5 and S_6. To each of the six test tubes, 0.5 mL s-diphenylcarbazide was added and the absorbance of the red violet complex was read at 540 nm. Similar steps were followed for sample analysis in the absence of s-diphenylcarbazide except the wavelength of absorbance measurement at 440 nm [14].

RESULTS AND DISCUSSION

Several analytical techniques are suitable for the determination of chromium at various levels of concentrations. In this study, colorimetric method has been employed. The colorimetric determination is based on the formation of a complex resulting from the reaction of hexavalent chromium with s-diphenylcarbazide. The absorbance of the complex was measured spectrophotometrically at 540 nm. For quality control purposes, the concentration of hexavalent chromium was also determined spectrophotometrically in the absence of s-diphenylcarbazide at

440 nm. Acidified solutions of potassium dichromate are colored. The intensity of this color is proportional to the concentration of the dichromate anion in solution. However, similar concentrations of hexavalent chromium was found in the paired samples as determined by the two methods (Table 1).

Table 1. Concentration (mg/L) of hexavalent chromium in the untreated and treated tannery effluents and nearby water bodies as determined by the two methods at 540 nm and 440 nm.

Sampling date	S_1		S_2		S_3		S_4		S_5		S_6	
	With[a]	Without[b]	With[a]	Without[b]	With[a]	Without[b]	With[a]	Without[b]	With[a]	Without[b]	With[a]	Without[b]
24/03/07	10.82	10.20	08.99	8.67	8.05	7.57	0.60	0.60	0.55	0.52	0.021	0.031
27/03/07	10.65	09.90	8.85	8.85	7.98	7.26	0.59	0.54	0.54	0.53	0.021	0.052
09/04/07	10.77	10.24	8.95	8.92	7.48	7.74	0.56	0.54	0.55	0.53	0.014	0.052
10/04/07	10.70	09.61	9.17	8.71	7.45	7.45	0.60	0.53	0.55	0.50	0.028	0.041
11/04/07	10.41	10.33	9.02	8.90	7.95	7.63	0.58	0.55	0.54	0.53	0.007	0.024
19/04/07	10.29	10.51	9.40	9.10	7.89	8.23	0.58	0.58	0.54	0.55	0.006	0.034
22/04/07	10.03	10.61	9.29	9.06	7.80	8.80	0.57	0.58	0.53	0.54	0.006	0.029
Mean (mg/L)	10.54	10.20	9.15	8.89	7.82	7.81	0.58	0.56	0.54	0.53	0.015	0.037
SD	0.291	0.347	0.198	0.161	0.242	0.53	0.015	0.026	0.008	0.016	0.009	0.011

[a] Concentrations of Cr(VI) as analyzed using 1,5-diphenyl carbazide (DPC).
[b] Concentrations of Cr(VI) as analyzed in the absence of s-diphenylcarbazide (DPC).

Temporal samples have been collected from identical sites at different times but same time of the day. Though the gap between the sampling seasons was not that long, we have found no temporal variation. The concentrations of hexavalent chromium remain insignificantly different regardless of the time of the sample collection (Table 2). The coefficient of variation, which was used as a measure of reproducibility (precision) for the replicate measurements, varied between 4.8 and 7.7%, illustrating a smaller variability associated with the replicate measurements. The results revealed a significant pollution of the nearby water bodies by the Sheba tannery effluents.

Table 2. Paired t-test results for the temporal variation of hexavalent chromium in the Sheba tannery effluents and nearby water bodies (significance set at $p< 0.05$).

Comparison	At 540 nm (with diphenylcarbazide)		At 440 nm (without diphenylcarbazide)	
	t value	p	t value	p
24/03/07 vs. 27/03/07	2.22	0.0766	0.97	0.3777
27/03/07 vs. 09/04/07	0.55	0.6061	-1.74	0.1430
09/04/07 vs. 10/04/07	-0.7	0.5130	1.99	0.1034
10/04/07 vs. 11/04/07	-0.01	0.9896	-1.67	0.1564
11/04/07 vs. 19/04/07	-0.46	0.6647	-1.89	0.1180
19/04/07 vs. 22/04/07	1.97	0.1063	-1.07	0.3322

We have observed a significant difference in the concentration of hexavalent chromium among the untreated and treated effluents and surrounding water bodies. As expected, the highest concentration of hexavalent chromium was found in the direct/untreated tannery effluents (mean value of 10.54 mg/L). The amount of hexavalent chromium in the treated effluents (S_2 and S_3) was significantly lower than in the direct/untreated (S_1) tannery effluents (see Table 1). Moreover, the amount of chromium in the sedimentation tank, S_2 ($n = 7$, mean = 9.15 mg/L) is significantly higher than in the chromium oxidation pond, S_3 ($n = 7$, mean = 7.82 mg/L) ($p = <0.0001$). This means that oxidizing the chromium salts is the preferred strategy than sedimentation to remove hexavalent chromium from the tannery effluents.

The extent of pollution in the surrounding down stream water bodies was quite significant. The mean hexavalent chromium concentration in the downstream river (S_4) and spring (S_5) were 0.58 and 0.54 mg/L, respectively. The river water contained higher levels of hexavalent chromium than the spring and this difference was statistically significant ($p = 0.0003$). The higher chromium level on the river than in the spring could be explained by the direct discharge of the treated effluents into the river water body. Pollution of the upstream water bodies was not evident from this study. The amount of the hexavalent chromium in the upstream water bodies, included for comparison purposes, was below the WHO permissible limit (0.05 mg/L) and much lower than in the other samples, S_1, S_2, S_3, S_4 and S_5. This observation indirectly proved that the source of the higher concentration of hexavalent chromium in the downstream water bodies is the discharge of chromium salts from the Sheba tannery effluents into the surrounding water bodies. As the hexavalent chromium is extremely toxic and carcinogenic owing to its ability to oxidize other species and has a significant mobility in the environment [12], the Sheba tannery should design some more efficient preventing mechanisms such as bioremediations, stabilization ponds and/or recycling methods. This is by no means a complete list of all the methods used to remove chromium from tannery effluents but it might indicate the importance assigned to the treatment prior to its release into the surrounding environment so that harmful effluents are transformed into harmless substances.

CONCLUSION

This study revealed significant contamination of the surrounding downstream water bodies indicating that the treatment process of the tannery was not able to remove the chromium detected in the downstream surrounding water bodies. As the hexavalent chromium is a hazardous metal to the environment, the Sheba tannery (Ethiopia) should design some more efficient preventing mechanisms so as to create an environmentally benign tannery. The release of significant amount of hexavalent chromium into the environment may pose a potential hazard and hence its impact on human or animal health warrants further investigation. The main constituents of the wastes from Sheba tannery are not only chrome salts but also sodium sulfide, sodium hydrogen sulfide, calcium hydroxide, saline and others. The decomposition of the sodium sulfide or its reaction with acid components of the chemical mix used by the tannery might be causing pollution of the surrounding air with hydrogen sulfide, which also warrants further investigation.

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REFERENCES

1. Rathinamara, V.; Balaraman, M.; Jonnalagadda, R.; Rao, B.; Unni, N.; Thirumalachari, R. *Environ. Sci. Technol.* **2004**, 38, 300.
2. Kanagaraj, J.; Chandra Babu, N.B.; Mandal, A.B. *J. Clean Prod.* **2008**, 16, 1807.
3. Tania, F.; Daut, V.; Ilirian, M**.** *Desalination* **2007**, 213, 56.
4. Oral, R.; Meric, S.; De Nicola, E.; Petruzzellid, D.; Rocca, C.D.; Pagano, G. *Desalination* **2007**, 211, 48.
5. Alfredo C.; Leondina, D.P.; Enrico, D. *Ind. Eng. Chem. Res.* **2007**, 46, 6825.

6. Srivastava, S.; Indu, S.T. *Soil Biology & Biochemistry* **2006**, 38, 1904.
7. Srivastava, S.; Ahmad, A.H.; Indu, S.T. *Bioresour. Technol.* ***2007**, 98, 1128.*
8. Alvarez-Bernal, D.; Contreras-Ramos, S.M.; Trujillo-Tapia, N.; Olalde-Portugal, V.; Frı´as-Herna´ndez, J.T.; Dendooven, L. *Applied Soil Ecology* **2006**, 33, 269.
9. Vikrant, S.; Pant, K. *Bioresour. Technol.* **2006**, 97, 15.
10. Gonul, D.; Nur, K. *Process Biochemistry* **2005**, 40, 2493.
11. Namasivayam, C.; Sureshkumar, M.V. *Bioresour. Technol*. **2007**.
12. Latif, E.; Aslihan, A.; Kartal, A.; Mustafa, S. *J. Hazard. Mater.* **2007.**
13. Rajender, K.; Narsi, R.; Bishnoi, G.; Kiran, B. *Chemical Engineering J.* **2008**, 135, 202
14. Thomas, G.C. *Qualitative and Instrumental Analysis of Environmentally Significant Elements*, John Wiley and Sons: New York; **1993**; p 43.