

Toxic Chromium from Tanneries Pollute Water Resources and Soils of Sialkot (Pakistan)

¹UZAIRA RAFIQUE, ¹AISHA ASHRAF, ²ABIDA KALSOOM KHAN, ²SADIA NASREEN,
²REHANA RASHID AND ²QAISAR MAHMOOD*

¹Fatima Jinnah Women University, Rawalpindi, Pakistan.

²COMSATS Institute of Information Technology, University Road, Abbottabad, Pakistan.

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Summary: The present investigation reports the concentrations of total chromium and its species *i.e.* chromium (Cr (III) and Cr (VI)) assessed in soil, drinking water and effluents of tanneries distributed in ten clusters of Sialkot District, Pakistan. 120 samples consisting 40 samples each of topsoil, drinking water, and composite wastewater were collected from the selected tannery clusters. The chelation extraction, and digestion method followed by atomic absorption spectrometer were used to analyze Cr (VI) and total Cr, respectively in soil, wastewater and drinking water at 427 nm and 540 nm, respectively. The concentration of total chromium, Cr (III), and Cr (VI) in wastewater, drinking water, and soil was found to be in range of (Cr) 16.12-36.83 mg/L, 1.0483-3.1824 mg/L, and 3.45-11.43 mg/kg (Cr (III) 0.97-13.25 mg/L, 0-1.05, and 1.56-9.80 mg/kg, and Cr (VI) 11.69-28.61 ppm, 0.83-5.96 ppm, and 2.12-11.85 ppm, respectively. The concentrations of chromium contents are above the National Environmental Standard of Pakistan. It was found that pH above 6 leads to higher concentration of Cr (VI) in the samples due to oxidation behavior. The study recommends the treatment of wastewater before being discharged.

Introduction

Tanning industry is third among the list of principal exporters, which earn foreign exchange in Pakistan [1]. Leather Industry contributes about 35 million US dollars annually to the national economy. About 90% of its products are exported in finished form. Sialkot has become a major industrial town of Pakistan since independence. Every fifth house in the residential area is a factory with all its evils *i.e.* contaminating air, water and soil through the discharge of volumetric hazardous effluents. In Sialkot city there are 250 tanning units, producing more than 65,000 kg of leather per day located in ten different clusters they obtain animal skin from Punjab and Sindh. Leather tanneries in Pakistan produce all three categories of waste: wastewater, solid waste, and air emissions. However, wastewater is by far the most important environmental challenge being faced by Pakistan's tanneries. Heavy discharge of tannery wastewater causes many problems to tanners, the local community and spoils the civic beauty of the area due to these toxic substances and a high concentration of organic and inorganic compounds pollute the water. No factory has independent or combined treatment units and the effluents are discharged into open land, streets, and seepage drains, natural water body and / or the municipal sewer [2].

In leather production, organized sequence of chemical reactions is followed to transform the raw hide into finished leather. Amongst all these, tanning is the fundamental stage, which confers leather its stability and essential characteristics [3-5]. Chromium is an important tanning industry pollutant [6]. Chromium exists in nature in two oxidation states Cr (III), and Cr (VI) [7]. Chromium (VI) is introduced into the environment through industrial discharges from electro plating, leather tanning, glass, ceramic paints, and canning industries [8]. Cr (VI) is very toxic in nature. Due to potential toxic effects of Cr (VI) upon exposure to human beings, plants, animals and as well as ecosystem, its removal from wastewater is imperative [9].

The discharge of industrial pollutants and heavy metals has seriously threatened the sustainability of ecosystems. The toxic heavy metals from industrial units in Pakistan are entering in food chain and drinking water supplies that ultimately pose serious illnesses in human residing near these industrial units. There is no baseline data available in Pakistan that could estimate the potential threats caused by heavy metals from industrial units so as to suggest some treatment options for polluted wastewaters. The objective of this investigation is to

*To whom all correspondence should be addressed.

quantify the amount of Cr in tanneries waste water of Sialkot.

Results and Discussion

Temperature and pH

Temperature and pH are two important factors that affect the detection of chromium in the wastewater samples. Thus these two parameters were considered in the analysis of various samples. Wastewater, drinking water and soil samples of tanning clusters showed temperature variation of 35-42 °C, 22-29.8 °C, and 26-29.99 °C, respectively. The highest temperature being (42 °C) for wastewater in Naika Pura Cluster was attributed to direct discharge after exothermic reactions in the tanning operation [1]. The average temperature ratio is shown in Table-1. It was noted that temperature of drinking water and soil is comparable. This is due to the fact that source of drinking water in the area is ground water.

Table-1: Temperature and pH values of wastewater, drinking water and soil of the tanneries.

Sample code	Waste water		Drinking water		Soil	
	Temperature	pH	Temperature	pH	Temperature	pH
CHM	37.7	8.55	25.7	7.21	28.1	7.86
CPA	41.0	6.74	26.3	8.56	29.1	8.07
CDR	39.4	6.75	26.8	7.56	28.47	8.27
CWR	38.6	10.2	27.0	7.45	27.6	7.81
CPR	38.8	5.50	25.7	7.55	27.9	8.17
CDS	39.2	7.00	25.5	7.72	27.8	6.62
CKA	40.0	6.25	24.9	7.36	28.2	8.03
CSIE	22.0	9.80	25.2	7.40	28.1	7.24
CNP	40.2	4.70	26.6	7.31	28.3	6.82
CGR	38.1	7.50	26.2	7.3	27.0	7.88
average	39.2	7.29	26.0	7.10	28.0	7.68

The pH of wastewater, drinking water and soil was found to be in the range of strongly acidic to strongly basic (3-14), weakly acidic to weakly basic (6.50-9.70) and strongly acidic to weakly basic (3.91-9.51), respectively. The vast range of wastewater was

observed due to fact that pH is adjusted for enzymatic reactions changes due to chemical reaction during rechroming [2]. It was noted that ten selected tanning clusters vary in pH values, the highest being of Wazirabad Cluster (*i.e.* pH 10.25) (Table-1). It is related to fact that wastewater of tanning process is a mixture of various chemicals [9-10] and dyes, composition of which varying from tannery to tannery, and time to time and running time during a day.

Chromium Concentration in Wastewater Samples

Total chromium concentration varied from tannery cluster to cluster and also from one sampling point to another (Table-2). The variation in minimum and maximum concentrations of total chromium within the same cluster was found to be in the range from 4 µg/L (Gondal Road Cluster, point 4 and 1) to 15 µg/L (Small Industrial State, point 1 and 3). It was found that Cr (III) was oxidized to Cr (VI) by 2, 2, 4, and 6 orders in Daska Road Cluster, Khadim Ali Road Cluster, Head Marala Cluster, and Naika Pura Cluster, respectively (Fig. 1). It was also found that Cr (VI) was reduced to Cr (III) by 1, 2, 5, and 6 orders in Small Industrial States, Daska Road Cluster, Gondal Road Cluster and Wazirabad Road Cluster, respectively. Low availability of Cr (III) for oxidation in these clusters may be due to formation of oxides and hydroxides which binds to solids in the suspension [4]. A value as high as 100% has been reported for Cr (VI)/Cr total as compared to 20% in air. The existence of some metals like iron in the wastewater may cause reduction or oxidation of Cr.

Drinking Water Samples

Insignificant variation in minimum and maximum concentration was found at different sites of the same clusters except for the Cr (VI) in Wazirabad Road Cluster. Oxidation of Cr (III) to Cr

Table-2: Chemical fraction of average total chromium in wastewater, drinking water and soil.

Sample codes	wastewater drinking water soil		
	18.69	2.14	6.51
CHM			
CPA	19.34	2.27	8.43
CDR	22.66	2.27	7.30
CWR	23.28	2.49	8.93
CPR	24.17	2.01	7.03
CDS	28.81	1.90	9.02
CKA	29.29	2.25	9.12
CSIE	31.87	1.16	5.34
CNP	31.12	2.04	7.00
CGR	28.86	1.29	8.06
Average	25.31	2.42	7.68

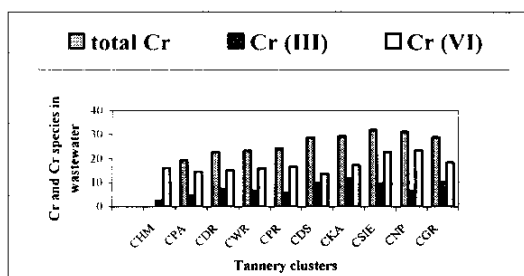


Fig. 1: Redox reaction rate in wastewater of tannery clusters.

(VI) was observed in all drinking water samples of tanneries; however, significantly high oxidation was noted in Wazirabad Road Cluster. The high concentration of Cr (VI) was due to the fact that the high oxidation states are generally found in shallow aquifer [11]. Chromium speciation in ground water depends on redox potential and pH conditions in aquifer [12]. The concentration of total Cr, Cr (III) and Cr (VI) in natural water was found to be in ranges (0.057 $\mu\text{g/L}$ -1.60 $\mu\text{g/L}$) (0.80 $\mu\text{g/L}$ -2.00 $\mu\text{g/L}$), and (0.072 $\mu\text{g/L}$ -1.6 $\mu\text{g/L}$), respectively [13]. In contaminated ground water, the pH is typically 6-8; Cr (VI) species predominates at this pH.

Soil Samples

On contrary to wastewater and drinking water samples, it was observed that on the average, soil samples show reduction of Cr (VI) to Cr (III) in tannery clusters. High concentration of Cr (III) in the soil was attributed to the fact that Cr (III) compounds rapidly eliminate from surface water and binds to sediments [4]. However, individual clusters exhibited oxidation of Cr (III) to Cr (VI) in soil was due to the fact that Cr (III) is present in some soils in unbounded form leading to oxidation reaction [10,15]. It was also reported that soluble Cr (III) in soil can be partial oxidized by MnO_2 at pH higher than 6 (Tables 2-4) (Figs. 1-4).

Several techniques used for the removal of Cr include ion exchange, precipitation, reverse osmosis, evaporation, chemical reduction and electro-dialysis [16]. The toxicity, mobility, and bioavailability of Cr depend fundamentally on its chemical forms, *i.e.* Cr (VI) and Cr (III). Cr (VI) exhibits toxic effects on biological systems and is mobile in soil and water [17]. Cr (VI) was effectively removed by adsorption process using low-cost

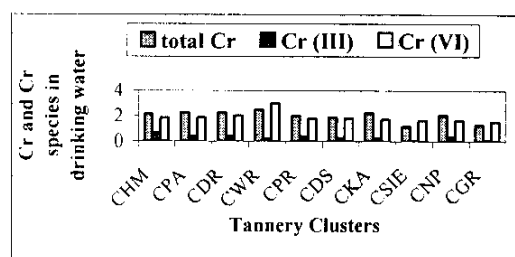


Fig. 2: Redox reaction rate in drinking water of tannery clusters.

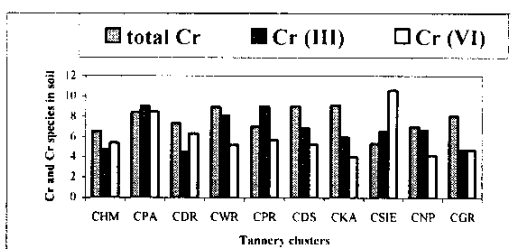


Fig. 3: Redox reaction rate in soil of tannery clusters.

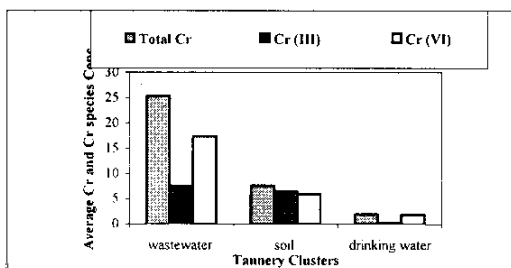


Fig. 4 Average concentration of Chromium and its species in wastewater, drinking water and soil of tannery clusters.

adsorbents such as Abiotic adsorbents include brick kiln ash, fly ash, [15], and Wallastonite [16]. Biotic adsorbent includes peanut hull [18], bidi leaves [19], Chinese reed [20], amla dust [21] and neem leaves [22]. Whereas Cr (III) is considered to be a trace element essential for the proper functioning of living organism [23-24] Some hexavalent chromium such as, chromium trioxide, ammonium and alkali metals (*e.g.* sodium potassium salts of chromic acids are readily soluble in water Most forms of Cr (III) are present in or added to soil are low in solubility and reactivity, indicative of its kinetic inertness in most soils the predominant form of Cr (III) are chromic

Table-3: Chemical fraction of average Cr (III) concentration (mg/L) in wastewater, drinking water, and soil.

Sample codes	wastewater	drinking water	soil
CHM	02.65	0.69	4.74
CPA	04.76	0.38	9.06
CDR	07.53	0.45	4.51
CWR	06.60	0.21	8.07
CPR	05.72	0.38	8.98
CDS	10.08	0.26	6.88
CKA	11.94	0.26	5.95
CSIE	09.73	0.04	6.52
CNP	06.49	0.35	6.66
CGR	10.49	0.09	4.70
Average	07.59	0.30	6.60

Table-4: Chemical fraction of average Cr (VI) concentration (mg/L) in wastewater, drinking water, and soil.

Sample codes	wastewater	drinking water	soil
CHM	16.06	1.85	5.39
CPA	14.58	1.89	8.47
CDR	15.12	2.03	6.30
CWR	15.93	3.00	5.19
CPR	16.60	1.78	5.65
CDS	13.72	1.84	5.26
CKA	17.35	1.73	4.00
CSIE	22.71	1.66	10.59
CNP	23.56	1.63	4.18
CGR	18.44	1.53	4.70
Average	17.41	1.90	5.97

oxide (Cr_2O_3), $\text{Cr}(\text{OH})_3$, or mixed oxides of Fe (III) or Cr (III)[25-26]. Leaves of trees are very versatile natured chemical species as these contain a variety of organic and inorganic compounds. Cellulose, hemicellulose, pectins, and lignin present in the cell wall and chlorophyll, carotene, anthocyanin, and tannin in leaves are the most important sorption sites, the important feature of these compounds is that they contain hydroxyl, carboxylic, carbonyl, amino, and nitro groups which are important sites for metal sorption [27]. At present we are treating chromium containing wastewaters through anaerobic biological processes and will publish our results soon [28-31].

Experimental

Sampling and Analysis

The research was carried out in the heavily industrialized areas of Sialkot located in the eastern part of Pakistan. The 250 tanning units are divided into ten clusters. Four tanneries were selected from each cluster randomly. For the assessment of total chromium and chromium species, 40 samples each of topsoil, drinking water, and composite wastewater were collected from the selected tannery clusters (Table-5)

Table-5: Sample characteristics.

Sample No	Waste Water	Drinking water	Location	Sampling point
1	CHMww	dw-1	Head Marala Road	1-4
2	CPAww	dw-2	Pul Aik Haji Pura	1-4
3	CDRww	dw-3	Defence Road	1-4
4	CWRww	dw-4	Wazirabad road	1-4
5	CPRww	dw-4	Pasror Road	1-4
6	CDSww	dw-5	Daska Road	1-4
7	CKAww	dw-6	Khadim Ali Road	1-4
8	CSIEww	dw-7	Small Industrial Estate	1-4
9	CNPww	dw-8	Naika Pura	1-4
10	CGRww	dw-9	Gondal Road	1-4

Reagents

Analytical grade reagents and distilled water were used throughout. Ammonium pyrrolidine dithiocarbamate solution (APDC) solution was prepared by dissolving 1.0 g of APDC in one liter of distilled water. Bromophenol blue indicator solution was prepared by dissolving 0.1 g in 100 mL of 50% ethanol. For chromium standard solutions, 0.2829 g of pure dried $\text{K}_2\text{Cr}_2\text{O}_7$ was dissolved in 1000 mL of distilled water and further diluted. (1.0 mL=100 μg Cr) [32]. The following working solutions were used: Hydrochloric Acid (HCl), 0.1M; Perchloric Acid (HClO_4), 0.1M; Nitric Acid (HNO_3), 0.1M; Sulfuric Acid (H_2SO_4), 0.2N; Sodium Hydroxide Solution (NaOH), 1M; Methyl Isobutyl Ketone (MIBK); S-Diphenyl Carbazide Solution, 0.25%.

Extraction Procedure

Cr (VI) was determined in wastewater and drinking water samples by chelation extraction method [22]. The samples were adjusted at pH 8.0, refrigerated till further analysis. 5 ml of ammonium pyrrolodine dithiocarbamate solution (APDC) and 10 mL of methyl isobutyl ketone (MIBK) was added to the samples and pH adjusted to 2.8. The mixture was shaken in a separating funnel. The upper organic layer (ketone) was aspirated in AAS at 357.9 nm.

Cr (III) and Cr (VI) in the soil samples were determined by UV- Visible Spectrometer at 427 nm and 540 nm, respectively [21], and a standard curve was plotted as function of wavelength. The samples were digested and oxidized with drop wise addition of 5 ml each of nitric acid and perchloric acid on hot plate. The solution was diluted to 50 mL with distilled water. After cooling, reaction mixture undergoes complexation reaction with 1 mL of 1,5-diphenyl carbazide to intense violet color.

Total chromium was determined in wastewater, drinking water, and soil samples by AAS at 357.9 nm. Soil samples were digested by HCl, filtered and filtrate was aspirated at 357.9nm in AAS [33-35].

Conclusions

The following conclusions are drawn:

1. Tannery wastewater is highly polluted in nature and is being discharged without any treatment into canals and municipals sewerage system to eventually reach the rivers of Pakistan.
2. The concentration of total chromium varies in wastewater from tannery to tannery and also from one sampling point to another depending on amount, quality and use of tanning agents. In Pakistan a great problem in tanning technology is lack of information and difficulty in procuring chemicals. The wastewater of all samples has highest Cr (VI) as compared to Cr (III) due to oxidizing behavior of samples.
3. On average soil samples are showing reducing a behavior in all tanning clusters because Cr (III) compounds rapidly bind to sediments.
4. The wastewater is directly affecting soil and indirectly to drinking water of the area through

leaching into the water table. The drinking water of the area is highly contaminated, as Cr (III) concentration is very low as compared to soluble Cr (VI) that is very carcinogenic in nature. The concentration of Cr (VI) in ground water decreases as the distance from the tanneries increases.

5. The pH value above 6 leads to higher concentration of Cr (VI) than Cr (III) in the samples and species of chromium are exchangeable, oxidizeable, acido-soluble, reducible and residual in nature.

References

1. S. Kazmi, *Decline In Leather Exports" Pakistan & Gulf Economist*, 36-37(1994).
2. State Bank of Pakistan, *Annual Report*, Pakistan (2002).
3. N. A. Kabbashi, A. H. Nour, S. A. Muyibi, and I. S. Qudsieh, *Journal of Chemical Technology*, **1**, 44 (2009).
4. M. K. Aroua, F. M. Zuli, and N. M.Sulaiman, *Journal of Hazardous Materials*, **147**, 752 (2007).
5. P. Venkateswarlu, M. V. Ratnam, D. S. Rao, and M. V. A. Rao, *Journal of Physical Science*, **3**, 305 (2007).
6. Y. C. Sharma, *Indian Journal of Chemical Technology*, **8**, 191 (2001).
7. F. J. Wie, S. Y. Being, Z. Zheng, Z. J. Biao, L. Shu, and T. Y. Chun, *Journal of Environmental Sciences*, **19**, 1409 (2007).
8. T. S. Anirudhan, P. G. Radhakrishnan, *Journal of Colloidal and Interference Science*, **316**, 268 (2007).
9. P. Brown, I. Jefcoat, A. Parrish, G. Dana, S. Sarah, and E. Graham, *Journal of Advances in Environmental Research*, **4**, 19 (2000).
10. J. Hu, G. Chen, and I. M. C. Lo, *Water Research*, **39**, 4236 (2005).
11. R. A. Shawabkeh, *Journal of Colloidal and Interference Science*, **299**, 530 (2006).
12. R. K. Shrivastava, A. K. Ayachi, and M. Mora, *Pollution Research*, **20**, 639 (2001).
13. C. Namasivayam, and W. H. Holl, *Holz Roh-Werkst*, **62**, 74 (2004).
14. M. A. Hossain, M. Kumita, Y. Michigami, and S. Mori, *Adsorption*, **11**, 561 (2005).
15. K. Anbalagan, and J. C. Juliet, *Indian Journal of Chemical Technology*, **43**, 45 (2004).

16. M. A. Hossain, M. Kumita, Y. Michigami, and S. Mori, *Adsorption*, **11**, 561 (2005).
17. K. Nikhel, *Journal of Industrial Pollution Contamination*, **12**, 225 (2005).
18. A. K. Rai, and K. Surendra, *Indian Journal of Environmental Health*, **41**, 65(1999).
19. Y. C. Sharma, *Indian Journal of Chemical Technology*, **8**, 191 (2001).
20. P. Brown, I. Jefcoat, A. Parrish, G. Dana, S. Sarah, and E. Graham, *Advances in Environmental Research*, **4**, 19 (2000).
21. A. Sharma, and D. Bhattacharya, *Indian Journal of Environmental Chemistry*, **12**, 285 (2005).
22. C. S. C. Calheiros, A. O. S. S. Rangel, P. M. L. Castro, *Journal of Water Research*, **41**, 1790 (2007).
23. C. R. Costa, C. M. R. Botta, E. L. G. Espindola, and P. Olivi, *Journal of Hazardous Materials*, **148**, 410 (2007).
24. R. K. Shrivastava, A. K. Ayachi, and M. Mora, *Journal of Pollution Research*, **20**, 639 (2000).
25. C. Namasivayam, and W. H. Holl, *Holz Roh-Werkst*, **62**, 74 (2004).
26. R. W. Gaikwad, and D. V. Gupta, *Journal of Applied Ecology and Environmental Research*, **6**, 81 (2008).
27. L. S. Clesceri, A. E. Greenberg, and A. D. Eaton, *Standard Methods of Examination of Water and Wastewater*, United Book Press, Inc., Baltimore (1998).
28. B. Volesky, *Hydrometallurgy*, **71**, 179 (2003).
29. R. A. Shawabkeh, *Journal of Colloidal and Interface Science*, **299**, 530 (2006).
30. I. Zongo, J.-P. Leclerc, H. A. Maiga, J. Wéthé and F. Lopicque, *Separation and Purification Technology*, **66**, 159 (2009).
31. I. Heidmann, and W. Calmano, *Journal of Hazardous Materials*, **152**, 934 (2008).
32. N. Vivek Narayanan, and M. Ganesan, *Journal of Hazardous Materials*, **161**, 575 (2009).
33. F. Rodríguez-Valadez, C. Ortiz-Éxiga, J. G. Ibanez, A. Alatorre-Ordaz, and S. Gutiérrez-Granados, *Environmental Science and Technology*, **39**, 1875 (2005).
34. D. Park, S.-R. Lim, H. W. Lee, and J. M. Park, *Hydrometallurgy*, **93**, 72 (2008).