

Appraisal of Chromium Contents from Different Tanneries and Drains of Sialkot

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Abstract. The tanning industry is the major chromium consuming industry. Tanning industries are present throughout Pakistan, but their presence is more concentrated in small industrial city Sialkot. The samples of wastewater were collected from different tanneries and Nullah Aik which are situated in Sialkot and analyzed for the measurement of pollution level. The effluents sample demonstrated high values of temperature (32-42°C), pH (5.1-10.9), biological oxygen demand (335-5818 mg/L), chemical oxygen demand (740-14546 mg/L), total solids (2265-19314 mg/L), total dissolved solids (1313-17467 mg/L), hexavalent chromium (1.8-9.8 mg/L), and total chromium (3.75-16.7 mg/L). The total chromium analyzed by atomic absorption spectrometry and hexavalent chromium determined by UV-Visible Spectrophotometer with DCP. The study focused on the level of pollution in tannery wastewater to estimate the impairment caused by them.

Keywords: chromium, tannery effluents, Sialkot, pollution level analysis

Introduction

Historically, the tanning industry is one of the oldest industries in this world. Archaeological studies have confirmed that the leather materials were being used even in ancient times. In the tanning process of raw hides, the highly decayable material is converted into a stable material called leather which can be conserved for a more extended period and has a crucial marketable significance (Suresh *et al.*, 2001).

The leather goods trade of Sialkot in the year 2015 was two billion US Dollar which is equal to nine percent of the total trades of Pakistan in the same year (Firdousi, 2016). Recently, In Pakistan, there are approximately 2500 tanneries are working, according to Pakistan Tanners Association (Al-Kdasi *et al.*, 2004).

To an estimate, a tannery manufacturing one ton of leather per day needs about 50,000 liters of water. This amount of water is equivalent to the water consumed by approximately 250 persons living in a city at the rate of 200 liters per day. Furthermore, 1000 liters of tannery wastewater can contaminate the same amount of water as 10,000 liters of domestic effluents (Egbu, 2000). Tannery wastewater is frequently used for the irrigation purposes in the areas adjoining cities due to freshwater deficiency. The highly toxic tannery effluents cause contamination of food crops which may cause serious

health problems for consumers (Uba *et al.*, 2009; Khan, 2008; Gumbo, 2005; Adriano, 2001).

Over the past 20 years, it is established that industrial exposure to hazardous chemicals increases the risk of various diseases (McDiarmid and Gehle, 2006). Specifically, environmental pollution and general health are somehow inter-connected (Lee *et al.*, 1989). Hexavalent chromium (Cr⁶⁺) is one such persistent environmental toxicant that trigger neurological and psychiatric disorders, respiratory illness, chromosomal aberrations, skin reactions, allergies, diminution of vision, abortion, corneal opacity, malformation of pregnancy, stunted growth, altered immune responses, mental depression, cancer and other life-threatening conditions (Shrivastava *et al.*, 2002).

The various types of toxic metals transported from the tanning effluents to neighboring rivers, which cause contamination of drinking water. The water thus become unsuitable for consumption and irrigation. One tannery can cause contamination of groundwater within a radius of 7000 to 8000 meters. The tannery effluents holding chromium and sodium composites have polluted more than 135,905 acres of agricultural and nearby waterbodies (Waziri and Ogugbuaja, 2010).

Public health risk increased day by day due to environmental pollution impact on general health (McDiarmid and Gehle, 2006). The chromium has adverse effects on professional tannery workers. The

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dust formed throughout frequent operations particularly buffing of external surfaces during finishing may have an opposing effect on the nose, throat and lungs (Dixit *et al.*, 2015).

Effects of toxic chemicals on plants and environmental impact of tanneries wastewater on the vegetable and animal kingdoms has been investigated. The phytotoxic effect of chromium has been observed in crops such as cabbage, tomatoes, peppers and rice (Upreti, *et al.*, 2004).

In this study, we investigated the concentration of chromium from the effluents of different tanneries and drains running throughout Sialkot city. For this purpose, chelation extraction and digestion method followed by atomic absorption spectrometer have been used to analyze and the results matched with standards of National Environmental Quality Standards (NEQS) for waste liquors.

Materials and Methods

Sample collection. Samples were collected in pre-cleaned polythene bottles and immediately stored in ice and transported to Laboratory and stored in a cool place at 4 °C.

Pollution level analysis. To determine the pollution load in samples, pH, COD, BOD₅, TS, TDS, total Cr and Cr (VI) concentration was tested. These studies were carried out within 24 h after sample collection.

pH. The pH of all tannery waste liquor samples was analyzed by using a portable Cyber Scan pH meter (CyberScan pH 110).

Chemical oxygen demand (COD). COD is the required quantity of oxygen for organic matter to oxidation by utilizing a robust chemical oxidant. COD was tested by a standard method to analysis the degree of pollutant in waste liquor samples (Jirka and Carter, 1975).

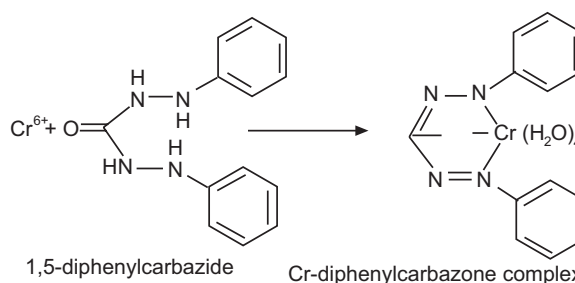
Biological oxygen demand (BOD₅). The sample was taken in the bottle which was airtight and placed it into incubated at a 20 °C temperature for five days. The content of dissolved oxygen of the sample was obtained after and before five days of incubation at 20 °C (Rump and Krist, 1992).

Total solids (TS). A well-mixed effluent sample was transferred into the dish and placed it on the boiling water bath until its contents are evaporated to dryness. At that time the dish placed into the oven at 105 °C for

two hours, followed by cooling in a desiccator for half an hour. It was weighed and again placed in the oven at 105 °C for half an hour and weighed again after cooling in a desiccator for half an hour. Until the constant weight was obtained the same procedure was repeated Howard (1983).

Total dissolved solids (TDS). The filtered wastewater sample transferred into the dish and placed it in the boiling water bath until dryness. In an oven at 105 °C for 2 h the dish was placed, followed by cooling in a desiccator for half an hour. Then it was placed again at 105 °C in an oven for half an hour and weighed again after cooling in a desiccator for half an hour. The same procedure is repeated until the constant weight was obtained (Howard, 1983).

Chromium concentration. The concentration of total chromium in the wastewater samples was determined by Atomic Absorption Spectrophotometric (AAS) method, and hexavalent chromium was determined by the UV-visible Spectrophotometric with DCP method. The reddish violet colour formation was based on the reaction of chromium (VI) with 1,5-diphenylcarbazide (DPC) in an acidic solution, which is shown in scheme 1.



Results and Discussion

To evaluate the toxic waste load in the tannery wastes water Sialkot industrial estate (SIE) and in Nullah Aik, the samples were assessed for several physicochemical parameters, and the results matched with standards of National Environmental Quality Standards (NEQS) for tannery waste liquors.

The temperature of water is very significant indicator for the existence of aquatic life. The temperature values of various tannery waste liquors ranged from 32 to 42 °C and mean value (37.3 °C) is given in Table 1. The highest value was found in the effluents of Gujjar Tannery, Wazirabad road, while lowest in that of Mughal

Table 1. Characteristics of effluents samples

Sample code	Temperature °C	pH	COD	BOD5	TDS	TS
NA-1	34	8.2	740	335	5845	7790
NA-2	42	7.5	7401	3124	5060	6247
NS-3	40	8.5	7654	3421	8425	9886
NMK	41	6.5	4587	1245	9547	11426
SLT	35	8.3	12941	5176	12147	13209
MTM	33	9.4	11807	1201	12242	13217
NTM	34	9.1	8854	4127	9264	11153
ITS	38	8.9	10241	3996	10652	12109
MTS	32	10.2	781	337	6194	7791
ALT	40	5.1	9340	4670	14743	15988
GTW	42	8.5	12754	5101	12976	14148
AYW	41	10.4	14546	5818	8676	10618
HTW	38	6.5	12875	756	17467	19314
TTW	37	9.7	9854	1535	14943	16528
QTW	40	8.2	13254	5097	13413	15164
HTP	32	9.9	1664	697	1313	2265
NTW	37	9.2	987	365	9172	10845
LFT	34	8.4	12645	4215	9898	11785
NTM	39	10.9	9864	3951	12310	13457

Tannery, Marala road. The temperature of waste liquor was within the acceptable limits of NEQS.

The samples pH was seriously varied, and these variations were significant from different tanning sections and dependent upon the various chemicals used in the tanning process. Minimum pH 5.1 was recorded for the effluents of Arshad Leather Tannery Marala road, while maximum pH, 10.9 was recorded for Najam Tannery Marala Road and mean value was of 8.6 (Table 1). In Nullah Aik, Near Kotli Marlanwali point maximum pH was documented 8.5. Comparing with NEQS (6-9) standards, the pH value of the wastewater of Arshad Leather Tannery Marala road was beyond the permissible limit and due to its high acidic nature of effluents may adversely affect the aquatic life. These results are in line with the outcomes of (Qadir *et al.*, 2008; Sinha *et al.*, 2002) and shown in Fig. 1.

The COD value of various tannery waste liquors ranged from 14546-740 mg/L and mean value (8567 mg/L) given in Table 1. COD of the samples were highly variable ranging from 781 mg/L from Mughal Tannery, Marala road to 14546 mg/L from Ayesha Tannery, Wazirabad road, Sialkot. COD of the sample taken from Nullah Aik also varied, the maximum COD value (7654 mg/L) was recorded at point Nullah Aik, Near Kotli Marlanwali. The effluents had high COD value and were above the permissible limits of NEQS (150 mg/L).

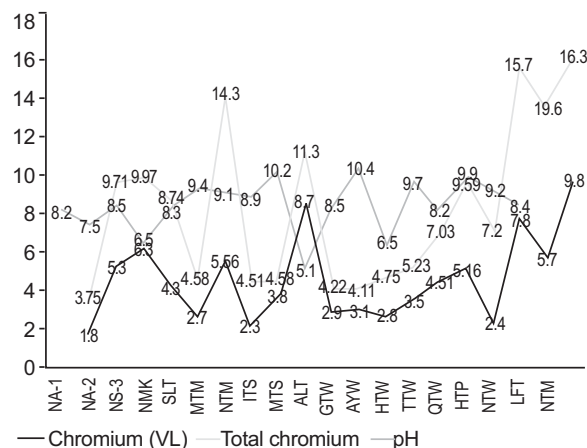


Fig. 1. Effect of pH on the concentration of Cr^{6+} and Total Cr

The highest COD was recorded for the effluents of Mughal Tannery, Marala road, while lowest was for the Ayesha Tannery, Wazirabad road. These results are also supported by those obtaining by Cooman *et al.*, (2003).

The BOD₅ value of various tannery waste liquors ranged from 5818-335 mg/L and mean value (2903 mg/L) given in Table 1. BOD₅ of the samples was also varied and a maximum value (5818 mg/L) was recorded for Ayesha Tannery, Wazirabad road and minimum value (337 mg/L) was recorded for Mughal Tannery, Marala

road. BOD₅ of the sample withdrawn from Nullah Aik at point Nullah Aik, Near Kotli Marlanwali (3421 mg/L) was maximum recorded, and a minimum value of BOD₅ (335 mg/L) was recorded at point Nullah Aik Near Oora. The effluents had high BOD5 value and were above the permissible limits of NEQS (80 mg/L) standard. These results are also in line with those obtained by Haidar *et al.* (2015).

The total solid waste value of various tannery waste liquors ranged from 19314-2265 mg/L and mean value (11733 mg/L) as shown in Table 1. Total solid waste varied from a maximum value (19314 mg/L) for Humayun Tannery, Wazirabad road and minimum (2265 mg/L) was recorded for Hassan Tanneries, Pasrur road. Total solid waste recorded from Nullah Aik was 11426 mg/ L. If discharged into the river or if directly applied to the agricultural field, it will not be suitable for the environment. These results are also supported by those obtained by Bhalli and Khan (2006) and shown in Fig. 2.

Total dissolved solids (TDS) value of various tannery waste liquors ranged from 17467-1313 mg/L and mean value (10225 mg/L) as shown in Table 1. TDS varied from maximum (17467 mg/L) Humayun Tannery, Wazirabad road and minimum (1313 mg/L) from Hassan Tanneries, Pasrur road. Total dissolved solids were recorded from Nullah Aik at point Nullah Aik, Near Kotli Marlanwali (9547 mg/L). Comparing with the NEQS (3500 mg/L) standard, it was observed that the TDS values from all the tannery waste liquors were above the permissible limits. High TDS value of effluents may cause various problems if it discharged to irrigation water. Similar results were also reported by Cooman *et al.* (2003).

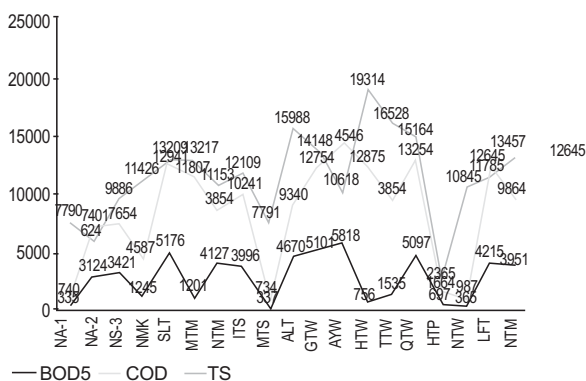


Fig. 2. Effect of TS, BOD₅, and COD.

Total chromium in the tannery waste liquors was analyzed by using Atomic Absorption Spectrophotometer. Cr concentration varied between different waste liquor samples from 3.75 to 16.3 mg/L and the mean value was 8.34 mg/L (as shown in Table 2). This difference of concentration of Cr in different tannery waste liquors may be due to sampling timing, whereas sample was withdrawn immediately after the tanning process. Maximum total chromium concentration was 16.3 mg/L detected for Najam Tannery, Marala road and minimum 4.11 mg/L for Gujjar Tannery, Wazirabad road. The maximum concentration of Total chromium (9.97 mg/L) for Nullah Aik, Near Kotli Marlanwali point and minimum (3.75 mg/L) for Nullah Aik, Near Oora recorded. Results showed that the levels of chromium were above the permitted limits compared with NEQS (1.0 mg/L) standards. These results reported by the early work of Rafique *et al.* (2010).

Hexavalent chromium was determined by UV-Visible Spectroscopy. Cr (VI) values of various effluents ranged from 1.8 to 9.8mg/L and mean value (4.6 mg/L) as shown in Table 2. The maximum concentration of Cr (VI) 9.8 mg/L detected from Najam Tannery, Marala

Table 2. Concentration of chromium in effluent samples

Sample code	UV-Visible spectroscopy		
	Chromium (VI)	Total chromium	*Chromium (III)
NA-1	1.8	3.75	1.95
NA-2	5.3	9.71	4.41
NS-3	6.3	9.97	3.67
NMK	4.3	8.74	4.44
SLT	2.7	4.58	1.88
MTM	5.56	14.3	8.74
NTM	2.3	4.61	2.31
ITS	3.8	4.58	0.78
MTS	8.7	11.3	2.6
ALT	2.9	4.22	1.32
GTW	3.1	4.11	1.01
AYW	2.8	4.75	1.95
HTW	3.5	5.23	1.73
TTW	4.51	7.03	2.52
QTW	5.16	9.69	4.53
HTP	2.4	7.2	4.8
NTW	7.8	15.7	7.9
LFT	5.7	13.6	7.9
NTM	9.8	16.3	6.5
Range	9.8-1.8	16.3-3.75	8.74-0.78
Average	4.6	8.38	3.7

*Chromium (III)= Total chromium– chromium(VI); *All parameters are in (mg/L), except pH and temperature

Road, and minimum concentration was recorded from 2.3 mg/L Nazir Tannery, Marala road. The maximum hexavalent Chromium concentration (6.3 mg/L) was recorded from Nullah Aik, Near Kotli Marlanwali. These results confirmed the early work of Rafique *et al.* (2010).

Conclusions

The following conclusions are drawn:

- In the routine procedure of leather production, the hide is carried out in an aqueous medium, hence the huge quantity of tannery waste liquor is discharged from tanneries which contain various soluble and insoluble substances. High BOD₅ values in tannery wastewater indicate that a huge amount of organic contents and need of biological treatment.
- A mean COD/BOD₅ value of 2.9 for effluents of the tannery, indicated that a significant portion of organic matter was non-biodegradable or very slowly bio-degradable.
- Tannery waste liquor (TWL) is heavily polluted and are being discharged into the municipal sewage system and canals untreated.
- The total chromium concentration in the effluent varies from the tannery to the tannery and also from one sampling point to the other according to the quantity, quality and use of the tanning agents.
- The method of Cr (VI)-DCP complex is suitable for determination of Cr (VI) in wastewater. The hexavalent chromium develops a red-violet coloured complex with DCP in the pH range of 1 to 2, which is suitable for spectrophotometer measurement.
- If the pH of the sample exceeds 6, it results in a higher concentration of hexavalent chromium than trivalent chromium, because chromium species are oxidizable.
- The analytical results of the samples show that tanneries generate highly polluted wastewater which has a high concentration of solid waste which is hazardous for aquatic life.
- All values Cr, Cr (VI), TDS, TS, BOD₅, and COD, were above the permissible limits of National Environmental Quality Standards (NEQS).
- The results of this study show that all the stakeholders, industrialists, workers, the general public, both municipal and provincial authorities, should be made aware of the environmental problems caused by tanneries and other industries.

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Conflict of Interest. The authors declare no conflict of interest

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