Estimation of Chromium in Effluents from Tanneries of Korangi Industrial Area

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ABSTRACT

The samples were collected from the tanneries located in Korangi industrial area, have high chromium concentration exceeding the tolerable limit. The effluents from tanneries are directly disposed off into streams without any treatment or ineffective method are used for treatment. The concentration of chromium was found to be 18.57-.170.12 ppm in residue and 15.20-185.50 ppm in filtrate of korangi industrial effluent in 2011. The conductance varies from 6.7 to 175 S/m which shows the high concentration of ionic species. The pH of samples was found to be mostly alkaline (7.0-8.9) except in T1 of January.

Keywords: tanneries effluents, Chromium (VI) and (III) potential, conductance, pH

1. INTRODUCTION

Chromium (Cr) is an environmentally important metal used in a range of industrial processes[1]. Chromium as an environmental toxin increases in the system by electroplating, metal finishing, chromate preparation, leather tanning etc. The Cr (III) and Cr (VI) are predominant oxidation states of chromium present in the environment. These two main oxidation states significantly differ in biological, geochemical and//toxicological properties[1]. The Cr (VI) is soluble, toxic and carcinogenic[1], while Cr (III) over a narrow concentration range, is considered vital for mammals. The Latter maintain many metabolic processes of glucose, lipid and protein, whereas Cr (VI) is reported to have a toxic effect on humans. It is mutagenic, carcinogen, cause of allergic contact dermatitis[6]. Chromium (III) is characteristically treated by increasing the pH of the industrial effluent through adding chemicals and coagulants such as lime and Fe compounds in order to recover precipitated chromium hydroxide. Numerous studies have reported 99.5% recovery using this method[7-8].

Chromium (III) sulphate salts mostly are used as tanning agent, consequential in severe groundwater contamination around tanneries, which is oxidized into Cr (VI)[9]. The Brazilian environmental legislation states that total Cr in final effluents[10] should not exceed 0.5 mgl^{-1}. The limits of 0.5 and 50 mg l^{-1} for Cr (III) and Cr (VI) were only specified for the domestic supplied water, respectively[11]. Therefore, the determination of total Cr is still very useful, even when speciation is necessary, one formis determinate and the other form is calculated by difference. Iwata et al[12] used photo-reduction method on the surface of titanium oxide (TiO_2) films of dilute Cr(VI) solutions at an adjusted pH 2 for a period of 7 days. It was found that concentration of Cr (VI) ion decreased from 10ppm to 0.03ppm. Three different analytical methods comprising colorimetric method with 1, 5-diphenyl-carbazide, electro-thermal, atomic absorption spectrometry (ET AAS) and flame atomic absorption spectrometry were utilized dy to determine traces of chromium (Cr) in synthetic tannery effluent from laboratory scale treatment process variation[13]. Rajmond[14] use a mixed bed ion exchange column for the simultaneous determination of Cr (III) and Cr (VI) using UV detector from environmental samples such as rainwater and galvanic sediments. The method was conventional from the linearity, limit of detection, limit of quantification, and the influence of sample pH. Similarly, Jen-Fon et al[15] used a reversed-phase ion – pair high-performance liquid chromatographic method for simultaneous determination of Cr (III) and Cr (VI) in an aqueous solution. The Cr (III) was first chelated with ethylenedi-aminetetraacetic acid (EDTA) and separated with C_8 – column using an effluent containing acetonitrile and tetrabutylammonium ion. The separated species were then monitored with a UV – detector at 242nm.

In another work Noroozifar and Khorasani[16] established a method that is very specific, selective, simple and inexpensive for the speciation of Cr (VI) and Cr (III) from spiked natural water samples and effluent samples from leather treatment plant. The method is based on the quantitative extraction of chromate and Cr (III) as tetrabutylammonium – chromate ion-pair in methyl isobutyl ketone (MIBK), and then back extraction and pre-concentration with an acidic diphenylcarbazide (DPC) solution. Whereby Cr (VI) – DPC complex was determined by a spectrophotometer at 548nm.

The present work is to estimate the concentration of chromium in effluents of tanneries in Korangi Industrial Area Karachi. We focused on chromium as it is the major require constituent of tanneries.

2. MATERIAL AND METHOD

The digestion of samples was carried out in Nitric acid (Merck AR Grade) and Perchloric acid (70% Merck AR Grade). Standard solutions of chromium for calibration curve were prepared by Chromium solution 1000μg/ml in 1wt% HCl (Sigma Aldrich, Atomic Absorption Grade).

Samples were collected from various sampling units' sites from outlets of different Tanneries at distance of 5-10 feet in Korangi Industrial Area. The locations of tanneries are reported as GPRS locations [Table-1].These samples were collected and stored in plastic bottle of 50 cm^3, coded and brought to laboratory for chromium analysis.

Portion of sample of about 40 ml filtered through whatman 40. Physical measurements have been done by the parameters such as pH, conductivity and potential of the filtered effluent samples. The pH of the samples was measured with Jenway 3320 pH meter. Conductivity values were determined by the use of Jenway 4010 conductivity meter.

Table-1: Locations of samples sites

Sites	Degree	Feet	Inch	Direction
T1	24°	5.7'	19.18"	North
	67°	07'	07.07"	East
T2	24°	51'	19.69"	North
	67°	07'	9.79"	East
T3	24°	51'	13.44"	North
	67°	7'	15.37	East
T4	24°	51'	9.82"	North
	67°	7'	11.13"	East
T5	24°	51'	18.02"	North
	67°	7'	11.66"	East
T6	24°	7'	14.80"	North
	67°	7'	14.80"	East

For chromium analysis atomic absorption spectrophotometer was used (Model: Perkin - Elmer AA3100).

Nitric acid and Percholric acid were used as oxidizing agents to destroy matrix. 40 ml of sample solution was filtered through Whatman's 40 filter paper.10 ml nitric acid (60%) was added to the filtrate and heated until got a clear solution. Finally the volume of the filtrate was made up to the mark in 50.0 ml volumetric flask with double distill de-ionized water.

Residue collected on the Whatman´s 40 filter paper, was dried in oven and digested in 10 ml nitric acid (60%) and heated to frothing. Subsequently, 3 ml Percholric acid (70%) was added to dissolve residue completely. Then 1:1 ratio of HCl and water was used to make up the volume up to 50 ml of solution.

3. RESULTS AND DISCUSSION

The major sources of chromium in sea water are effluents from industries. The different sources of chromium are reported by Ismail et al[17].

The concentration of chromium was found to be 18.75-170.12 ppm in residue and 15.2- 185.5 ppm in filtrate of Korangi Industrial effluent in 2011 [Table-2]. This variation of concentration is found according to the availability of raw material. The lowest concentration in filtrate and residue found in tannery coded as T1 15.02±0.76 ppm in January and T1 (18.57±0.21ppm) in March respectively [Table-2]. The highest value of chromium concentration estimated in filtrate of T4 (185.75±1.03 ppm) and residue of T6 (170±1.30ppm) in November [Table-2].The highest concentration of chromium was observed in month after Eid Qurban, when the highest amount of raw material is available. The mean concentration of chromium in the water is higher than the limit (0.05mg/l) recommended by the World Health Organization (WHO) (1989) in drinking water. The levels of chromium in effluents below than 1 mg/l as recommended by the Federal Ministry of Environment (FMENV, 1991)[18].The level of chromium in the collected effluents is much higher than recommended value indicated by Federal Ministry of Environment. In tanneries, oxide of Cr(VI) is used for softening and oxidation process. The minimum pH for removing chromium from the tannery wastewater by sodium hydroxide, calcium hydroxide and magnesium oxide as precipitating agent is pH 8-9[19].The pH variation is found to be 7 to 8.7.

In the pH range of 7, hexavalent chromium exists as CrO_4^{2-}, $HCrO_4^{1-}$ and $Cr_2O_7^{2-}$ ions. These ions are relatively soluble and therefore mobile in the environment. In basic pH tetrahedral, yellow CrO_4^{2-} chromate ion is the prevailing specie formed by CrO_3, while the orange-red $Cr_2O_7^{2-}$ ions are in equilibrium with $HCrO_4^{1-}$ in the pH range of 2 - 6[20]. Mostly the pH range of samples is basic; therefore the most likely form of the hexavalent chromium in the effluent is CrO_4^{2-} as the pH of samples are mostly basic.

The reason of a T1 in January having acidic pH might be due to accidentally matching the time of sample collection with the time when the acid were drain off during the tanning process.

More obvious reason for this high level of industrial pollution shows effluent are dispose off directly to the stream without any treatment. The other reason of high concentration of chromium is the use of already polluted ground water in different industries. This is actually due to leaching from dump sites, poor sanitation and industrial activities[21]. As its concentration is diluted by distance from source to sea but still its level is harmful to aquatic biota and Mangroves along the coastal areas[22]. Conductance of the samples varied between 6.7 to 179 S/m. The

conductance may be attributed to the presence of Na^+, Cl^- and other metal ions. As NaCl salt is extensively used in tanneries for leather preservation.

The values of the potential varied between -90 to +709 mV of different industrial effluent. All tanneries in different months have high positive potential, except T1 in July and T3 in March and May samples have negative potential. Potential can also give us idea about dominating oxidation state of chromium.

Table-2: The concentration of chromium in korangi Industrial are in different months form different tanneries

Sample	Month	pH	Conductance (S/m)	Potential (mV)	Cr in filtrate (ppm)	Cr in residue (ppm)
			T1			
1	January	3.57	132	158	15.20±0.76	36.39± 0.56
2	March	7.96	134	10	53.12± 0.85	18.57± 0.21
3	May	7.92	122	155.9	59.52±0.68	36.15± 0.13
4	July	8.50	102	-50.6	89.25±0.85	78.72 ± 1.00
5	Sept	7.95	95	92	72.89± 0.978	59.12± 0.85
6	Nov	7.85	94	33.7	181.11±0.94	147.83±0.23
			T2			
1	January	8.16	64.6	125	49.35± 0.75	33.65± 0.85
2	March	8.05	54.4	135	40.12± 0.73	42.45±0.35
3	May	8.01	40.5	110	58.50± 0.56	36.13±0.85
4	July	8.72	37.2	157	75.75±0.95	42.83±0.86
5	Sep	8.41	49.7	159	78.50±1.1	40.89±0.92
6	Nov	8.70	44.6	110	96.25± 1.6	122.13±1.20
			T3			
1	January	7.94	89.5	152.5	33.51± 0.66	24.15±0.52
2	March	8.01	75	-90	35.25± 0.74	36.14± 0.23
3	May	8.09	9.6	-89	41.75± 0.56	22.35± 0.34
4	July	7.58	17.6	138	90.75±0.75	82.89± 0.93
5	Sep	7.52	20.1	130	77.50±0.95	62.13± 0.76
6	Nov	7.96	20.9	140	162.25±0.85	136.12±1.00
			T4			
1	January	8.63	6.9	234	52.59± 0.87	43.41± 0.65
2	March	8.68	6.7	709	63.75± 0.95	34.59± 0.55
3	May	8.71	6.8	222	58.25± 0.72	22.48± 0.75
4	July	7.44	39.8	268	102.75± 0.97	89.15±0.86
5	Sep	7.01	39.6	254	109.82±0.75	71.25±0.83
6	Nov	7.96	40.8	266	185.50±1.03	150.95±0.75
			T5			
1	January	8.43	31.42	150	37.25± 0.83	47.25±0.95
2	March	7.99	11.51	178	51.25± 0.45	48.92± 0.81
3	May	7.9	26.8	169	70.51± 0.65	49.78± 0.35
4	July	7.44	39.8	268	103.23±1.1	95.75±0.76
5	Sep	7.01	39.6	254	99.52± 0.87	83.78±0.95
6	Nov	7.96	40.8	266	158.61±0.87	142.10± 0.89
			T6			
1	January	7.07	27.90	177	70.20± 0.53	52.14± 0.56
2	March	7.09	17.5	180	85.35± 0.89	49.13± 074
3	May	7.21	115	169	73.31± 0.45	50.12± 0.98
4	July	7.07	179	235	102.03±0.76	92.45±0.86
5	Sep	7.09	75.5	290	93.45±0.95	99.89± 0.92
6	Nov	7.21	125	211	162.15±0.98	170.12±1.30

The reduction reaction of chromium +6 to chromium +3 occurs at -170 mV. No clear picture can be obtained from these redox potential values, as different redox couple may also exist. Mayer et al[22] used redox potential data to control effluent the concentration of ammonia[23].The Two way ANOVA by Minitab software was applied to the data. There is a significant difference found with respect to month both in residue and filtrate, Fcal=77.55, 36.19 respectively. Whereas insignificant difference between sites was observed for filtrate Fcal =2.693 while it is significant for residue Fcal 5.12 shown in Table 3 and 4.

Table-3: Two-way Anova for Filtrate

Sources of Variances	Sum of Square	Degree of Freedom	Mean Square	Fcrit
Sites	2738.251279	5	547.6502558	**2.639641278**
Months	37551.39877	5	7510.279754	**36.19909648**
Residuals	5186.786746	25	207.4714698	
Total	45476.4368	35		

Chromium toxic effects are associated with long term low level exposure to pollutants common in our environment: air, water, food and numerous consumer products[23-24]. Exposure to chromium is associated with many chronic diseases such as dermatitis, ulcers and perforation of the nasal septum and respiratory illness as well as increased lung and nasal cancer[25].The adsorption methods is developed in the optimized conditions like pH, shaking time and amount of adsorbent. The concentration of Cr after removal was determined by atomic absorption spectrophotometer[26].

Table-4: Two-wayAnova for residue

Sources of Variances	Sumof Square	Degree of Freedom	Mean Square	Fcrit
Sites	2084.685946	5	416.9371892	**5.126618057**
Months	31538.21992	5	6307.643984	**77.55816076**
Residuals	2033.198029	25	81.32792117	
Total	35656.1039	35		

4.CONCLUSION

Keeping in view the toxic effect as chromium as pollutant from tanning industries, it was found that all the samples from the tanneries located in Korangi industrial had high chromium values greater than the tolerable limit.They were introduced into streams directly, due to lake of disposal regulation and non-availability of treatment. The public are unaware about the water quality in Pakistan. This problem is increasing day by day. Efforts have been made and new methods have been suggested for controlling these problems, but yet not are successful as due to expensive or not completely effective to remove all the pollutants including chromium.

Government authorities must be strict against the law violating industries and people's awareness program must have to be started otherwise we have to pay the consequences.

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