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CHROMIUM IN SEDIMENT OF THE MOVING STREAM OF TANNERY WASTE-WATER, FROM SECTOR 7-A OF KORANGI INDUSTRIAL AREA TO ARABIAN SEA.

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Chrome compounds are included in the category of heavy metal derivatives and thus are part of a group which must be kept out of the environment. Tanneries, located in sector 7-A of Korangi industrial area of Karachi, are discharging their effluent without any treatment. This effluent carries chromium, used in the tanning process, towards the sea. Due to mixing of different streams of tannery waste into the drain, most of the chrominum settles down in sediment and leaves very little chromium in liquid. Samples were collected to check chromium in sediments in the stream of tannery effluent, from the source of discharge, sector 7-A to the sea. It has been found that after some distance the chromium in wastewater become undetectable which shows almost complete settling of chromium into the sediment. Results showed that even at 10 Km away from the source, considerable quantity of chromium was found to be present in the sediment, which reveal that sludge formed during the mixing is travelling toward the sea and contaminating it with chromium.

Key words: Chromium, Tannery waste Water, Pollution.

Introduction

Chromium is one of the most important constituents of tannery waste water. In the tanning process trivalent chromium is used to convert the animal skin into leather. In fact the solubility, environmental mobility and toxicity of chromium exclusively depends on its oxidation state. At physiological environmental pH levels, Cr(VI) compounds are more soluble, more environmentally mobile and more toxic than Cr(III) [1]. However, in a study on effect of trivalent chromium from tannery wastewater on plants, a decrease in growth was observed when large amounts of chrome were first added to the soil. After 6 months to a year this retardation was reversed and soils with the added chrome showed increased yields [2]. Microorganism in soils are effected the same way by Cr(III), a temporary retardation of growth followed by a return to normal growth [3]. Hence, it can be observed that the growth of plants and animals was effected (temporarily) due to the presence of Cr(III) in the soil. Besides, the interconversion of two species of the chromium is also possible [4-6]. Therefore, the build up of chromium, due to indiscriminate discharge of tannery effluent, may effect the environment.

Every stage of tannery processing produces effluent of different characteristics, pH, COD, BOD, Cr, sulphide, total solids, suspended solid, etc. [7]. Presence of settleable matter in these effluents produces considerable quantity of the sludge. This sludge in addition with other contents does also contain chromium in it.

Tanneries located at sector 7-A of Korangi industrial area, Karachi are discharging untreated chromium containing effluent into nearby storm water drain which lead to the Arabian sea. The mixing of the different effluents from different tannery processes takes place in this storm water drain. This mixed effluent attains pH value between 8 and 10. Under this condition, chromium settles down into the sediments of the drain.

The storm drain was made with cement mortar but now the walls have collapsed at many places. Piles of the solids are cleared out occasionally to make the flow continue. Width of storm drain differ at different places, narrow at near to the sector 7-A and becomes wider after some distance. Due to irregularity in structure of storm drain the velocity of the flow of effluent varies point to point. The slope of the storm drain is almost the same as that of the natural slope of the plain, in this area it is one foot to a mile. Hence, the natural flow of storm water leads it through the drain towards the sea. The discharge of tannery effluents, in this drain, is 36000 m^3/day, estimated by IUCN in 1992 [9].

This investigation was undertaken to assess the build up of chromium in the sediments of the stream, from sector 7-A Korangi industrial area to the Arabian Sea. It was also determined if the chromium discharged by the cluster of tanneries located at sector 7-A, settles down into the sediment close to this sector or is moving toward the sea. Settleable matter in effluents of each stage of the tannery process and in composite effluent was also determined.

Materials and Methods

Live effluents, immediately after completion of the processes, soaking, liming/unhairing, reliming,deliming/bating, pickling and chroming, retaining and fatliquoring, were collected from a local tannery producing garment leather from goat skins. Settleable matter was determined with the help of cones of one litre capacity. Readings were noted after 1 hr. and experiments were run in triplicate.

Settleable matter of composite effluent was determined after mixing the wastewater of each stage of tannery process in a ratio described elsewhere [7], which is 15% soaking, 50% liming and reliming, 20% tanning (chrome), 15% finishing and dyeing. This mixture was stirred gently for half an hr and the settleable matter was determined with the help of an Imhoff cone of one litre capacity. Readings were noted after 1 hr. and experiments were run in triplicate. The settled matter was separated from the liquor and total chrome and solid content were determined.

The settled matter was dried at 110°C for determination of moisture. The chromium in this dried matter was oxidized by heating it with a mixture of concentrated perchloric acid, sulphuric acid and nitric acid. Further procedure was followed as per described in Official Test Method for chromium determination in leather [8]. This method was chosen because settled matter in tannery effluent contains leather fibers which can not be disintegrated easily with other oxidation methods, like potassium permangnet method.

Thirteen sediment and wastewater samples were collected from the storm drain at different distances, samples No 1-5 were collected within 1 km distance from the source of discharge whereas from samples No. 6 to 13 each sample was collected with a difference in distance of approx. 1 Km along the course of stream. Collection points are indicated in Fig. 1, from sector 7-A Korangi industrial area to the point near to the sea (about 9-10 km from the sector 7-A). Samples were collected with the help of plastic jugs, perforated from the bottom, to drain the excess water, and then transferred into plastic bags. Wastewater samples were collected in wide mouth plastic bottles. pH was measured at the time of collection.

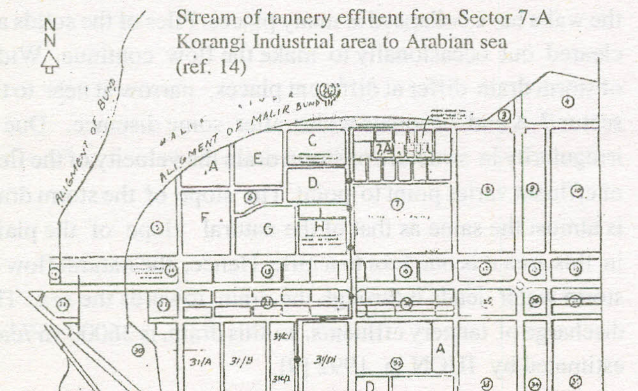

Fig. 1. Sediment samples collection points in stream of tannery effluent.

To determine the chromium content sediment samples were digested in sulphuric acid (1+1) and filtered with ordinary filter paper. Chromium in these digested samples and in filtered wastewater samples was determined as total chromium. As these samples do not contain leather fibrous material therefore the trivalent chromium in these samples were oxidised with $KMnO_4$ as described in "4d" of section 307 B [9] then total chromium was determined with the help of diphenylcarbazide as described in "4e" of the section 307 B, colorimetric method [9]. Distilled water used as blank. Experiments were run in triplicate and average values were quoted.

Results and Discussion

Results show that most of tannery processes contain considerable quantity of settleable matter (Fig.2), exclusively responsible for the presence of sludge in tannery effluent. The Liming/unhairing process contributed higher amount of settleable matter which is 3, 3.5 and 4 times more than produced

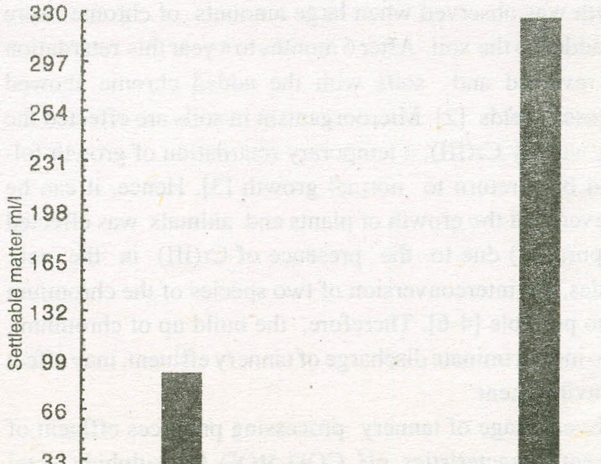

Fig. 2. Settleable matter in effluent of tannery processes.

1. Soaking, 2. Liming/unhairing, 3. Reliming, 4. Deliming/bating, 5. Tanning, 6. Degreasing, 7. Fatliquoring, 8. Composite effluent

by the effluent of soaking, deliming/bating, and degreasing or pickling processes respectively. The higher amount of settleable matter in effluent of liming/unhairing is due to the presence of lime which has low solubility. Beside, due to the coagulating effect of lime other suspended or colloidal matter also settles down with the lime.

The amount of the settleable matter (Fig.2) in composite effluent was four times higher than that of effluent of the liming/unhairing process, which contains, the highest settleable matter among the effluent of other processes. Mixing of effluents from each stage of tannery processing resulted in the formation of a large amount of floc particles, which appeared immediately on mixing of the tanning (chrome) effluent with the effluent of other processes (i.e. beam house). Change in pH of the resultant mixed effluent is the most important factor.

The Beam house process has a pH value 11-12 and contains protein, fats and lime as major constituents. Effluent of the tanning process has a pH of 3-4. Chromium as the major constituent remains in soluble form at this pH. When two effluents combine, the change in pH of the resultant mixture make most of the content, organic and inorganic including chromium, of these two streams insoluble. Coagulating effect due to lime, present in the effluent helps in the settling of this insoluble matter. The settled matter has a large volume about 1/3rd, i.e. 334 ml, of the total volume (One litre). Whereas, this settled matter contains 6% solid content. Hence one litre of the mixed effluent produced about 20 gm dried sludge. The chromium content in this sludge was found to be 175 mg/Kg (3.5 mg/20 gm sludge). Whereas, the chromium in supernatant liquor (filtered) was undetectable. As mentioned above in mixed effluent the ratio of chrome tanning effluent was 20%. Therefore, one litre of mixed effluent contained 200 ml of chrome tanning effluent in which chromium content was 4 mg. As shown above 3.5mg (85% of the total chromium) was settled down in the sludge of mixed effluent. It is suspected that remaining 0.5 mg (15% of the total chromium) was retained in mixed effluent in the form of colloidal/suspended particles. This mass balance make it evident that the mixing of effluents of different tannery processes resulted the settling of chromium in the sludge.

The production of the sludge in mixed tannery effluent exclusively depends on the quantity of lime used in liming process, presence of organic matter and quantity of chromium left in the spent chrome liquor. Therefore, it is most probable that the quantity of the sludge in the effluent generated from garment leather processing may be higher as compared to the effluent from shoe upper leather processing. Since the former uses more lime as compared to the later.

In sector 7-A tanneries are producing different kind of leather. Hence, it is difficult to calculate actual quantity of sludge per litre of effluent discharged by this sector. Nevertheless, on the basis of sludge quantity (20 gm/1), found in above mentioned laboratory study, and estimated volume of effluent i.e., 36000 m^3/day [9], being discharged in storm drain by sector 7-A, a crude estimation shows 720 tonnes per day sludge (dry) production in this drain. This may be a main reason for the repeated blockage of this storm drain.

Since the volume of chrome tanning affluent of this sector, being discharged with other effluents in the storm

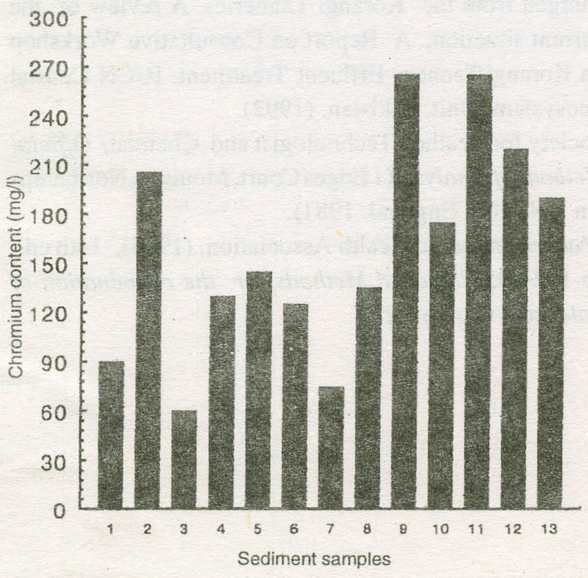

Fig. 3. Chromium content in sediment samples collected from the stream of tannery wastewater from sector 7-A Korangi to Arabian sea.

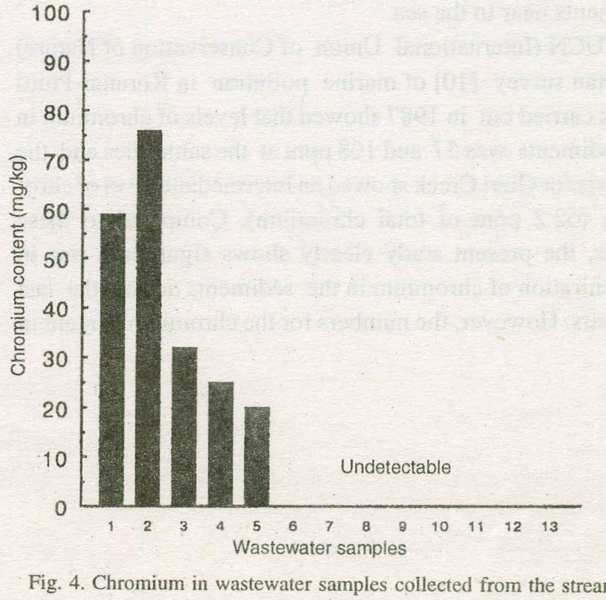

Fig. 4. Chromium in wastewater samples collected from the stream of tannery wastewater from Sector 7-A Korangi, Karachi to Arabian sea. (pH of the samples = 7.5-8.5)

drain, and also the quantity of chromium in it was not known therefore total chromium content in the sludge (720 tonnes/ day) can not be estimated exactly. However, if it is supposed that every kg of this sludge contains the chromium content same as detected in laboratory study (175 mg/Kg) then it is estimated that 126 kg/day chromium being wasted by this sector. The samples of sediment and wastewater were collected from the downstream of the tannery discharge. Results (Fig. 3) show chromium in sediment samples, on dry basis, ranges from 60 mg/kg to 265 mg/kg. In wastewater (filtered) samples chromium (20 to 76 mg/1) was found to be present only in those five samples which were collected within a distance of 1 Km from the source, along the course of the drain (Fig.4). About 1 Km away from the source, wastewater contained no chromium in soluble form. This profile of chromium content along the course of drain shows almost complete sedimentation of chromium, which confirms the above mentioned laboratory study (mixing of effluents of different tannery processes resulted the settling of chromium). It is also evident that the settling of chromium was taking place near (within 1 km) to the point of tannery effluent discharge. On the other hand, results (Fig.3) show that all 13 sediment samples contained chromium in considerable quantity. Even samples Nos.11, 12 and 13, collected about 9 to 10 km away from the source near to the sea, from the source of discharge, contained chromium in quantity 192, 222 and 264 mg/kg respectively. The presence of chromium in these (11-13) sediment samples indicates that the some quantity of the sludge, containing chromium, formed in the sector 7-A of Korangi industrial area Karachi is also travelling with wastewater towards the sea. This may be a reason for the presence of chromium in the sediments near to the sea.

IUCN (International Union of Conservation of Nature) Pakistan survey [10] of marine pollution in Korangi-Phitti Creek carried out in 1987 showed that levels of chromium in the sediments was 57 and 108 ppm at the same sites and the analysis for Gizri Creek showed an intermediate level of chromium (52.2 ppm of total chromium). Compared to these results, the present study clearly shows significant rise in concentration of chromium in the sediments during the last six years. However, the numbers for the chromium content in sediment samples of present study are still low for environmental concern but it indicates an increasing trend in concentration of chromium in Creek areas.

In present study it is infered that settleable matter of tannery effluents contain considerable quantities of chromium which settles down at the sediment of the pathway. Indiscriminate discharge of chromium containing tannery wastewater builds up chromium in the sediments of Creeks area. Due to this, aquatic life near to the shore of Arabian sea can be effected.

It is, therefore recommended that in each tannery of the sector 7-A primary treatment system i.e., mixing, pH equalization followed by coagulation/flocculation must be installed which will be helpful to eliminate most of the chromium from tannery wastewater.

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