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Assessment of Pollution Load from Unsafe Chromium Leather Tanneries in India

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Abstract: There are about 2,500 tanneries in our country (India) having an annual processing capacity of 7,00,000 tones of hides and skins in the year 2005. About 80% of the tanneries have used chrome-tanning process. The tannery process consisting of curing, soaking, liming, and unhairing, deliming-bating, deliming-washing, bating-pickling and chrome tanning. Chrome tanning process has used *dichromate, sodium chromate and chromium sulphate having 50% basicity* as raw material. This process has produced tremendous chromium wastes in wastewater. Out of the chromium compounds applied in chrome tanning process, that was about 69,000 tons annually in 1600 tanneries, (i) about 25 to 39% has been spent in waste water. Out of this, there was 45% in the form of Cr^{+6} salts and (ii) 61 to 75 % has been absorbed in the leather. Out of this about 45 % was in the form of Cr^{+6} salts. It is mentioned that about 80% of these leather tanneries have caused *severe water pollution*. This has polluted river bodies. This has caused ground water contamination with *toxic hexavalent* chromium widely spreading all over India. Chromium is a carcinogenic susbstance and acts on human in three ways. (1) Dermatitis, (2) Absorption, (3) Inhalation . Toxic effects are produced by prolonged contacts of chromium and its compounds even in small quantities due their carcinogenecity, mutogenecity . Hence the present paper gives the pollution load due to chromium by leather tanneries in the environment.

Key Words: leather, tanneries, chromium, pollution, contamination

1. Introduction:

Leather Processing Technology

Leather processing is carried out by three methods namely (i) Vegetable tanning, 2) Chrome tanning and (iii) Eco-friendly tanning. 80% of the tannery use chrome-tanning process. In a tannery, these processes are broadly divided into three different operations namely beam house operation, tanning operation (either vegetable or chrome or eco-friendly) and post tanning operation .

2. Animal skin structure

All animal skin consists of three layers. The e*pidermis* (or cuticle) is the layer, which covers the second layer of fatty tissue. The inner most layer is the *corium*. *Leather* is made from corium. The objective of the tanning process is to strip off the two outer layers, subjecting the corium to the action of agents, which converts it from a semi-soluble protein to the tough insoluble mass known as leather. The principal constituent of the corium is the protein *collagen* $C_{102}H_{149}N_{31}O_{38}$ which is kept in contact with warm water for converting into *lyophilize* colloids of gelatin and glue. When subjected into the action of tanning agents, it undergoes a transformation and becomes insoluble leather in water, which is flexible and highly durable.

3. Chrome tanning process

Leather processing using chrome tanning process , a brief description of which is given below ;

Brushing

After receiving raw hides in the tanneries, they are brushed manually to remove as much salt as possible. Then they are sent for soaking.

Soaking

The hides are then soaked for 24 hrs in pits containing water. This effects thorough washing to remove common salt (NaCl), dirt, dung and blood, which are adhering to the raw hide. This process is carried out twice.

Liming

After soaking, the hides are transferred to a pit containing lime and sodium sulfide. They are allowed to remain for two days. *Liming* is done to make the hides swell and loose.

Reliming

The hides are then subjected to *reliming* with lime and caustic soda to remove hair and flesh.

Deliming

Ammonium sulphate and water carry out deliming process.

Chromium tanning

The delimed hides are subjected to pickling, *chrome tanning*, and drying to obtain chrome tanned leather.

Chemicals used for chrome tanning of leather

Some of the leather tanneries situated at Chennai, Calcutta, Kanpur and Calcutta were visited. An extensive study was made on chromium pollution. It is pointed out here that in India most of the tanneries are using sodium chromate, dichromate and impure *basic chromium sulphate (BCS)* for tanning the leather instead of using commercial BCS salts. This generates considerable quantity of pollutants in the environment containing toxic Cr^{+6}, which causes airborne, liquid or solid chromium pollution in their vicinity. Therefore, the information details related to chemicals and their compositions used in tanneries were collected during the visits, which are given below;

Raw material used

Leather of Sheep, Goat and Buffalo.

Chemicals used

Step-I : Soaking the leather of about 900 kg in wetting agent as soap oil of 5 kg . They are kept overnight for 10 hours in the ratio of 1 : 180

Step-II : Liming process : The ingredients used are calcium sulphate, sodium Liquor and soda ash.

Step-III : Flushing process is to remove the flush, enzymes and mass.

Step- IV : Deliming process: The chemical used is 18 kg of ammonium sulphate added in the ratio of 1: 50 and kept for one hour. After one hour, the ingredients added are; ½ % microbate ¼ % bisulphate and 1% soap oil.

Step – V : Pickling process: The chemicals used are 7 % basic common salt, 2 % conc. Sulfuric acid and 1.25 % of 0.01 oxalic acid.

Step – VI : Chromium tanning **:** The chemicals used are 7 % BCS - 63 kg, 0.5 % sodium pharmate – 4.5 kg, 0.35 % magnesium oxide –2.25 kg, 1 % bicarbonate – 9 kg. Soaking is done for 2 hrs.

4. Description of chrome tanning process

Chrome tanning is essentially the reaction of *chromic ion* (Cr^{+6}) or its complex with the protein in the hide substance to obtain good quality of leather.

$$Na_2Cr_2O_7 + H_2SO_4 \rightarrow Na_2SO_4 + H_2Cr_2O_2$$

The sulphurous acid reduces the chromic acid. Cr^{+3} and Cr^{+6} compounds are formed inside the skin, which tan the latter.

The following reactions take place during the reduction of chromic acid.

$Cr_4O_7 + 2\ H_2SO_4 + 3\ Na_2S_2O_2 \rightarrow$
$2\ Cr(OH)SO_4 + 3\ Na_2SO_4 + 3\ S + 2\ H_2O$
$4\ H_2Cr_2O_7 + 5\ H_2SO_4 + 3\ Na_2S_2O_3 \rightarrow$
$8\ Cr(OH)SO_4 + 3\ Na_2SO_4 + 5\ H_2O$
$H_2Cr_2O_7 + 5\ H_2SO_4 + 6\ Na_2S_2O_3 \rightarrow$
$2\ Cr\ (OH)\ SO_4 + 3\ Na_2SO_4 + 3\ Na_2S_4O_6 + 5\ H_2O$

In the "one-bath" method, the pickled skins are charged into the drums containing a solution of BCS or chromic chloride, produced by the addition of reducing agents to acidified solution of sodium dichromate. Salts such as sodium chloride or sodium sulphate are present to promote the penetration of a tanning solution containing *trivalent chromium* salt. Hides are treated in revolving wooden drums with BCS solution of 7 % pelt weight for about 13 hours. At the end of this period, the solution is discharged. The hexavalent chromium changes to trivalent chromium form during the process of tanning .

The size of the molecules of Cr^{+6} is small and hence it can penetrate easily into the skins/hides. Once the necessary amount of penetration has been achieved, basification is done by adding 1 % soda ash or 1.5 % sodium bicarbonate to convert the Cr^{+6} to Cr^{+3}. Since, the size of the Cr^{+3} molecules being larger and cannot come out from the skin/hide, these molecules get fixed in leather. Tanning involves skill for proper basification to achieve desired tan leather. Improper basification causes fixing Cr^{+6} to fill in the skin and gets remained without converting into Cr^{+3} therefore rubbery feel is obtained. Proper basification causes Cr^{+6} to fill in all the voids of corium and converts Cr^{+6} to Cr^{+3} therefore a ruggy feel of leather is obtained. For easy penetration and to maintain rubbery feel, many tanneries use sodium chromate and dichromate, the leather is fixed with Cr^{+6}. The waste generated by using this method is much larger than the waste generated by using BCS (Barnhart, B.J., 1978).

In the "two-bath", chromium salt namely dichromate and chromic acid are used for chrome tanning. At first, Cr^{+3} and Cr^{+6} salts made to enter through the pores of the leather. Subsequently the basicity is increased to fix up the Cr^{+6} and Cr^{+3} in the voids. The trivalent chromium cannot penetrate the hides, unless it is in the Cr^{+6} form. Thus, Cr^{+6} compounds penetrated inside the pelt get fixed as Cr^{+3} in the leather leaving some portion as Cr^{+6}. For complete conversion into Cr^{+3}, the strength of salts being maintained at 33% basicity with proper basification. The hides are kept in the floating condition for 6 hours, after which it attains a bluish colour .

All the types of chromium compounds cannot tan protein collagen. For this particular property, the chromium compounds must have hydroxyl group in complex form that is directly attached to the chromium compounds. The basicity increases with more and more percentage of chromium valence attached to hydroxyl group. Therefore, the tanning power of chromium compounds increase with basicity and vice versa .

With the amount of acid or alkali present in the liquor or added from outside, the tanning behavior of chrome liquor is increased. Therefore, the quality of the leather produced is of rubbery feel. The alkali is added to chrome liquor causing the molecules of chromium salts to become larger size. This increases the size and reduces the rate of penetration of chromium into the skin in which over tannage risk is there as grain size is increased. Free acid presents in the chrome liquor penetrating the skin more readily than BCS. This causes the chrome liquor to become more basic and colloidal due to hydrolysis. If the pelt is pickled, the acid from the pelt diffuses out into the chrome liquor first. This decreases the basicity of external chrome liquor decreases such that the risk of overtannage of the grain is removed .

The amount of chromic oxide uptake by collagen is dependent on concentration. The chromium fixation by the hide protein increases with the increase of liquor concentration up to a limit after which the chromium fixation decreases with the increase of concentration (Moore, J.N., et.al., 1990).

From the above points, it is clear that at the commencement of chrome tanning especially to tan light leather, too much concentrated or diluted chrome liquors should not be used. It is always required to use correct concentration of chrome liquor and controlled by the adjustment of basicity or by the use of masking salts.

The literature survey emphasizes about the conditions of chrome tanned leather. It explains that 50 % of chromium is remained in the leather as Cr^{+6} form to maintain rubbery feel.

5. Chromium Pollution Load from Tannery

The tannery process has consisted upon the following unit operations namely curing, washing, soaking, liming-unhairing, deliming - bating, washing after deliming-washing, bating, deliming-washing, bating-pickling and chrome tanning. All the processes have produced wastes which contained organic compounds to a smaller or greater extent except chrome tanning process waste. This process has contained chromium waste . The concentration of Cr^{+6} was varied between 2000-5000 mg/1 in waste water coming from chrome tanning process. The concentration of Cr^{+6} in chrome tanned leather was 1000-4000 mg/kg, (ppm) and that of total chromium between 8000-11000 ppm and 13000-30000 ppm respectively . The dust-producing, grinding CCLC leather washers and rollers used in ginnery have contained this level of chromium concentration, which was hazardous to human health. The following table 1 gives the details of average pollution loads in tannery wastewater discharged and dust-producing grinding CCLC leather in ginnery (dry).

Table-1
Comparative Analysis of Pollution Load from Tannery

Sl.No.	DESCRIPTION	CONV.CHROME TANNING	IMP. CHROME TANNING
1.	Pelt weight	700 kg	700 kg
2.	Quantity of chromium applied	14.98 kg	14.98 kg
3.	Chromium content in spent liquor	4,714 mg/l	5,244 mg/l
4	Quantity of total Cr discharged in waste chrome liquor	5.77 kg	3.68 kg
5	Hexavalent Cr in the water coming from chrome tanning process	3100 mg/l	3800 mg/l
6	Chromium uptake by the hides	61%	75.43%
7	Quantity of chromium in wet blue	9.21 kg	11.3 kg

8	Total chromium content in the leather	13157 ppm	16142 ppm
9	Hexavalent chromium in rollers	2000-5000 ppm	3000-7000 ppm
	First sampling tannery waste water Cr^{+3}	8289 mg/l	8650 mg/l
	II sampling tannery Cr^{+6}	2590 mg/l	2410 mg/l

6. Pollution load of tannery waste water

Table 2 shows average pollution load discharged per ton for processing raw hides and skins to the finished leather. The data given in total chromium.

Table 2 Average pollution Load Discharged Per Ton of Hides/Skins Processed for Raw to Finished Leather (as total chromium)

Soaking operation	Nil
Beam house operation	Nil
Tan yard operation	5 kg of total chromium/ton of hide/skin
Post tanning and wet processing	1.5 kg of total chromium/ton of hide
Total pollution load	6.5 kg of total chromium/ton of leather
	0.0065 kg/kg= 6.5 g/kg
∴ 1 litre	6500 ppm in the tannery water

∴ 1 litre = 0.001 m^3

∴ One litre of tannery waste water = One kg of tannery waste water

As per environmental protection rules, 1986, the effluent for disposal by cotton textile industries / tanneries should not exceed 2 mg/l as total chromium.

	Case study-I	**Case study-II**
Quantity of chromium in wet blue as Cr_2O_3	9.21- 11.3 kg	: 40.8 kg
Quantity of Cr applied as Cr_2O_3	14.98 kg	: 68 kg
Pelt weight	700 kg	: 900 kg
Total chromium in ppm	13157-16142	: 45333.3
Pelt weight	700 kg	
Quantity of total chromium discharged	3.68-5.77 kg	
Chromium percent in spent waste water in waste liquor per 700 kg	25-39%	

Quantity of total chromium discharged in waste water per ton of processed leather	5.25-8.24 kg of total chromium 5250-8240 ppm or mg/l

Table-3
Chromium Pollution Load Analysis

Sl.No. Description	Indian Leather Survey	Present Analysis
1.Total Cr in chrome leather	13157-16142 ppm	45333.3 ppm
2.Total Cr in waste water	5250-8240	23111.1
3.Quantity of chromium applied/kg pelt	21.4 kg/1000 kg	68 kg/1000 kg
4.In terms of total Cr	21400	68000-68444
5.Total chromium in composite waste	8000-11000	14000-20000
6.Cr^{+6} in ppm or mg/l in waste water coming from chrome tanning process (hexavalent chromium impurity content)	2000-5000	3500-5000
7.Chromium content in roller gin rollers	13200-30000	20000-40000
Cr^{+6} impurity content in roller	6000-8000	10000-12000

7. Discussions on chrome and leather chemistry

Chromium compounds like dichromate, sodium chromate and sulphate have *30% to 60% basicity* were used in the tanning industries. The impure chromates have hexavalent form of chromium salts mixed with chromium sulfate of *50% basicity* were used for making semi-finished leather. This has been used for making ginning rollers by the locally made indigenous manufacturers in Kanpur, Ahmedabad, Chrompet and Chennai. The chromium percent contained in leather was approximately 3 to 4 by weight basis. About 66% of the total chromium compounds applied were absorbed in leather during the tanning process and rest was discharged to effluent The reaction of chromium compounds in tanning solution with hide collagen have been studied extensively. It was firmly established that cross-linking was accomplished by bonding of various chrome species with free carboxyl groups in the collagen side chains. It is mentioned that BCS having 33% basicity contains Cr^{+3} form as 9% of total chromium. A brief outline on chromium and leather chemistry is given below;

1. Chromium salts were used in tanning materials either in Cr^{+3} and Cr^{+6} salts or mixed condition.
2. The experiment results have showed that out of chromium used in tanneries, the leather has been absorbed 66% and effluent as 33%. The analysis has showed that dry leather contained 3% to 4% as total chromium or 30,783 ppm that was 30,783 mg of total chromium / kg of CCLC.

3. The analysis has expressed that traces of Cr^{+6} were found even in analar grade Cr^{+3} compounds and complications have raised due to the reducibility nature of these traces of Cr^{+6} that affected the organic tissues in the body. These regenerating effects occurred rapidly and were dependent upon the doze.
4. Water consumption in tanning operation was 74 m^3 per ton of raw material.
5. Composition of total waste from polish chrome tanneries as total chromium was 11
   to 3,226 mg/l.
6. Average composition of total waste from ten Russian tanneries was 0-300 mg/l.
7. Characteristics of effluents from tan yard operations of tanneries processing hides by chrome tanning during tanning operation was 2,500-5,000 mg/l as total chromium and during re-chroming operation was 700-1,600 mg/l as total chromium. Chrome tanning was done in wooden drums with a processing capacity of 1-1.25 ton of pickled pelts per batch. In the conventional chrome tanning process, the leather on an average has absorbed 60% of the chromium compounds namely sodium chromate, dichromate or basic chromium sulphate applied and the balance was discharged to the effluent. According to 2000-2001 estimate about 65,000 tons of sodium chromate, dichromate and BCS was used for chrome tanning of leather in India. Out of this quantity, about 26,000 tons of chromium was discharged into effluent stream. The proportional ratio of chromium compounds were 55% as Cr^{+3} and 45 % as Cr^{+6}. The impurity content of hexavalent chromium in the leather was 45%. Total pollution load as total chromium was 6.5 kg in tannery wastewater discharged for one ton of hides/skins processed from raw to finished leather that was 6,500 ppm. The chromium uptake to leather was 8,500 ppm. Cr^{+6} impurity content of this compound was 45% on the chromium leather.

Chromium content as Cr_2O_3 in the spent liquor was 4,714-5,244 mg/l (ppm) (with hexavalent chromium as impurity content of 3100-3800 mg/l (ppm). *Neosyn BG 96* and *Neosyn EB* were the specialty chemicals used for chrome tanning to enable greater uptake, exhaustion of chrome and self-basifying characteristics. *Gloden chrome, star chrome* and *TANASCO, Chrome Syntan* were the locally made indigenous chemicals used by the local tanners in India.

8. Conclusions

The above information details have provided us about the *chromium pollution load* in the environment. The studies have provided percentage composition of chromium element including Cr^{+3} and Cr^{+6} .There were about 2,000 tanneries in our country having an annual processing capacity of 7,00,000 tones of hides and skins in the year 2000. About 80% of the tanneries have used chrome-tanning process. The tannery process consisting of curing, soaking, liming, and unhairing, deliming-bating, deliming-washing, bating-pickling and chrome tanning. Chrome tanning process has used *dichromate, sodium chromate and chromium sulphate having 50% basicity* as raw material. This process has produced tremendous chromium wastes in wastewater. Out of the chromium compounds applied in chrome tanning process, that was about 69,000 tons annually in 1600 tanneries, (i) about 25 to 39% has been spent in waste water. Out of this, there was 45% in the form of Cr^{+6} salts and (ii) 61 to 75 % has been absorbed in the leather. Out of this about 45 % was in the form of Cr^{+6} salts. In this about 20 to 25 % chromium has been confined with the CCLC roller element. It is mentioned that about 80% of these leather tanneries have caused *severe water pollution*. This has polluted river bodies. This has caused ground water contamination with *toxic hexavalent* chromium widely spreading all over India.

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