Abstract—The provided data given by the Tanneries Association, the normalwaste on everyday basis from all the leather industries in district Kasur is assessed above 193 tons as wet salted weight, including 9,000 skins of buffaloes and cattle, and 11,050 to 16,000 hides of goat and sheep processed every day.

A mutual wastewater treatment plant may be a large or a complex factory for collecting on every day basis about 16,000 m$^2$ of high contaminated waste water as processing tifor the producing clean water for the discharging into a water body with 10 of tons of semi-solid sludge is disposed with a suitable manner. It is estimated that 160 tones per annum of chromium in terms of basic chromium sulfate (BCS) is discharged as waste in the effluent. This can be recovered and recycled. For this purposes, precipitation technique is used for separation of chromium from tannery wastewater. In this process, precipitants agent is lime as best one and 97% chromium recovery with help it.

Economics cost of process is very low as Rs. 10. It is very attractive way to install the chromium recovery plant.

Keywords—Chromium Recovery, Chemical Plant, Process Economics, Precipitation.

I. INTRODUCTION

In the leather sector, a variety of finished leather is prepared including upper, lining, and garments from salted raw hides. After bating processing the hides are ready for tanning. Two principal methods of tanning are used according to the related tanning agents: chrome tanning and vegetable tanning. The chrome tanning has been widely used for the preparing the finished form leather. The tanning method is a combination of chrome and vegetable tanning are also used in past in which a series of processes and operations are involved for the production of finished and soft leather goods. A range of chemicals that are used in tanning process with their effects are a great cause of the water pollution source. Differently types of chemicals are used in leather manufacturing process which dependson the type of raw material for getting the desired end product of leather. These chemicals are further divided into four major classes as described below [1].

Chrome tanning: This operation (pickling) helps the better absorption of the chrome salts into the pores and tissues of the skins. After pickling, the hides are kept in contact with the tanning solution. The effluents contain high concentrations of chromium salts [2].

Pre-tanning chemicals, these chemicals are not fully reacting with the skins or fiber and finally they are not retained by the skins of leather. Pre-tanning chemicals after performing their functions are discharged into the wastewater with high rate of pollution rate [3].

Tanning chemicals are reacted with the collagen fiber protein of the skin and then convert it into leather finished form. As these chemicals are reacting with the fiber, a considerable quantity is retained by the skin of leather. But a significant remaining amount is unused and discharged it as in form of the wastewater containing tanning chemicals [4].

BCS as used in leather tanning processes is not wholly taken up by the skins. Its uptake is limited to 55–70% and the remaining portion is discharged as waste. After tanning a series of operations known as finishing process is carried out to produce different types of leather (oilining, dyeing etc.) [5].

Finishing chemicals are used to creating a certain properties in finished leather like appearance, flexibility, softness, strength, colour which are the requirement of import products of leather. Finishing chemicals also react with the proteins of collagen fiber of tanned leather and these chemicals are mixed in side of the leather skins. But due to limited absorbing of chemicals in leather, some quantity go to the waste and making waste water [6].

The present studies an attempt has been made to economically chromium recovery plant from tannery waste with Assessment of the present situation.

II. MATERIAL AND METHODS

The tanneries sampled were collected from three different industrial units (Data Enterprises (Pvt) Ltd, Lahore) of equal capacity for leather production.

The samples were labeled properly with following information.

1. Sample Number
2. Date and Time of Sampling
3. Source of Sampling
4. Point of Sampling (To collect a second sample from the identical spot from which first sample was taken)
5. Temperature of sample
6. Signature of the sample

The Chemical analyses were carried out by using standard ASTM methods as follows. Reagent grade chemicals were used in all tests [6].

Determination of chromium

Apparatus: Spectrophotometer (UV-1700 Shimadzu) equipped with a cell having a path length of 10 mm.
Calibration: Four standard solutions containing from 0 to 0.50 mg L\(^{-1}\) of chromium were prepared by diluting measured volumes of the standard chromium solution to 100 mL with water in separate volumetric flasks.

Procedure: Transfer 50 mL of each prepared standard solution to separate 125-mL Erlenmeyer flasks and proceed as follows:

- Diphenylcarbazide solution (2.0 mL) was added to each solution and swirled to mix. The absorbance was recorded within 30 min after the addition of the diphenylcarbazide solution at 540 nm with a cell having a minimum path length of 10 mm. Milligrams per liter of chromium as Cr\(^{+6}\) in the sample was determined by referring the absorbance to the prepared calibration curve [7].

Determination of pH

Measuring the pH value using the digital pH meter, first of all calibration of meter under standard method of calibration is taken, and then three pH values are recorded of wastewater samples [8].

Conceptual Steps of Process Flow Diagram

The following diagram (Fig. 1) is used for recovery process of chromium sulphate from wastewater. This chemical process flow diagram is very useful for clearing the research concept [9].

![Fig.1: Flow diagram of chromium recovery process developed](image)

III. RESULTS

Chemical analysis of Chromium and pH

Wastewater from each process contains different types of pollutants. The pH value varies from 3.7 to 4.9 in industrial unit 1 to 3 as shown in table 1. This is also cause of increasing the pollutants existing parameters like BOD, COD, Total Dissolved Solids, Total Suspended Solids and settle able matter etc due to presence of other organic materials. Similarly concentration of chromium is very high as shown in table 1 and results suggested to recover and reuse of it in proper way. Chemical analysis suggested that Vanadium, titanium, or irons present at concentration of 5 mg L\(^{-1}\) yield a 10 to 30 % reduction in recovery of chromium. Copper at 100 mg L\(^{-1}\) yields a 20 to 30% reduction in recovery in the presence of sulfate. Mercury gives a blue-purple color, but the reaction is not very sensitive at the pH employed for the test. Nitrite concentrations in excess of 10 mg L\(^{-1}\) as NO\(_2\) yield low test results [11].

Sulfamic acid may be added (~10.1 g) prior to the addition of diphenylcarbazide solution to minimize nitrite interference if present. Excess sulfamic acid itself creates a slightly positive interference. Sulfide and sulfite reduce chromate in an acid medium to give low results.

Comparison of Efficiency of two precipitating agents for rising pH values

Chromium recovery from acidic spent chrome liquor is a chemical treatment where an alkali is added to precipitate chromium as chromium hydroxide. The precipitated chromium can be separated from the liquor by settling and filtering. The filtered liquor is almost free of chromium while the washed precipitate can be processed to produce

| Parameter | Unit 1 | Unit 2 | Unit 3 |
|-----------|--------|--------|--------|
| pH        | Mean: 4.42 | Range: 4.0 - 4.8 | Mean: 3.74 | Range: 3.1 - 4.2 | Mean: 5.12 | Range: 4.9 - 5.3 |
| Cr (mgL\(^{-1}\)) | 3636 | 3187 - 3987 | 5335 | 4587 - 5478 | 4635.6 | 3570 - 5874 |

Table.1: Analytical data of sample

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basic chromium sulfate liquor, blue-green chromium hydroxide, or chromium (III) oxide (Cr₂O₃) green pigment. Some of the precipitating alkalis that can be used are sodium hydroxide, sodium carbonate, sodium bicarbonate, magnesium oxide, calcium sulfate and lime. In this experiments results showed that MgO is best one for rapid increasing pH value as seen in table -2. Although one of the most successfully adopted precipitants is magnesium oxide, this research focuses on tannery spent lime waste as the precipitating agent. As illustrated in the table-2, tannery lime waste is filtered and used to precipitate chromium hydroxide from chrome spent liquor. The filtered lime waste is thoroughly mixed with chrome spent liquor in a reaction vessel until the pH reaches 7.5 ± 0.5, after which the solids produced are allowed to settle overnight. A filter medium is then used to separate the solids from the liquor. The recovered chromium hydroxide solid is subsequently washed with water to remove impurities.

Table.2: The value of pH (Mean ± SD)under time with two precipitating agents

| Firm              | Time (Min)  | pH                      |
|-------------------|-------------|-------------------------|
|                   |             | Ca(OH)2 | MgO            |
|                   |             | Mean ± SD | Range         | Mean ± SD | Range         |
| Industrial Unit 1 | 1 -30 (Interval = 2) | 9.59 ± 0.29 | 8.70 - 10.00 | 10.37 ± 0.58 | 8.70 - 11.00 |
| Industrial Unit 2 | 9.08 ± 0.28 | 8.35 - 9.60 | 9.95 ± 0.57   | 8.40 - 10.6 |
| Industrial Unit 3 | 8.57 ± 028  | 7.70 - 8.95 | 9.27 ± 0.57   | 7.70 - 9.70 |

Effect of precipitants on chromium settling
As far as the recovery of chromium concerned studies about the determine and effectiveness of water treatment processes for removing of chromium from aqueous medium have the first step as the conversion of Cr(VI) to Cr(III) by using the reducing agents as alkali or basic nature of chemicals. In these studies, alum coagulation, lime softening, and iron coagulation (using ferric sulfate) have been found as efficient for removing of Cr(III) from wastewater. This research has focused on time limitations that depend on pH values as shown in table-2 which is very useful in chromium recovery.

The UV/TiO₂ photocatalysis can reduce Cr(VI) to Cr(III), which in turn can be removed by co-precipitation technique. In tables 3&4, we can view that supernatant and sludge formation of limes and MgO which showed solubility power of two alkali agents and most powerful agent is MgO. This is only a secure way to control on potential toxicity of some forms of chromium that are environmental regulatory standards specify for the levels of chromium in wastewaters. The discharging of the industrial wastewaters in different countries has the specific permissible concentrations of chromium (in the range of 0.3-1 ppm) which is achieved by this precipitating method with fixed pH values.

Table.3: Height of supernatant with time

| Firm              | Time (Min)  | Height of supernatant (mL) |
|-------------------|-------------|-----------------------------|
|                   |             | Ca(OH)2 | MgO            |
|                   |             | Mean ± SD | Range         | Mean ± SD | Range         |
| Industrial Unit 1 | 30 – 300 (Interval = 30) | 90.61 ± 33.63 | 20 – 129       | 366.67 ± 45.17 | 235 - 394    |
| Industrial Unit 2 | 83.90 ± 33.20 | 12 -123 | 360.00 ± 44.55 | 227 - 388    |
| Industrial Unit 3 | 84.70 ± 33.32 | 10 – 125 | 360.80 ± 44.64 | 225 - 390    |

Table.4: Sludge volume of two precipitants

| Firm              | Sludge volume (mL) |
|-------------------|--------------------|
|                   | Ca(OH)2 | MgO            |
|                   | Mean ± SD | Range         | Mean ± SD | Range         |
| Industrial Unit 1 | 382.60 ± 4.77 | 377 – 389       | 162.60 ± 4.77 | 157 - 169     |
| Industrial Unit 2 | 383.20 ± 6.90 | 376 – 393       | 163.20 ± 6.90 | 156 - 173     |
| Industrial Unit 3 | 427.00 ± 17.73 | 401 – 444       | 207.00 ± 17.73 | 181 - 224     |

Effect of Chromium recovery at pH 8
The precipitate can now be processed to produce blue-green chromium hydroxide, Cr₂O₃ green pigment, or chromium sulfate liquor, depending on the desired function for reuse. Subjecting the precipitate to oven drying at 130°C for an hour produces the blue-green chromium hydroxide. In tab 5, maximum chromium recovery is seen in industrial unit 3 as 99% at pH 8 due to using MgO agent as alkali. Drying this in a furnace at 350°C for 3 hours will remove the hydroxide and produce a more stable Cr₂O₃ green pigment. Meanwhile, basic chromium sulfate liquor can be produced by dissolving the precipitate through slow addition of 5 Normal (N), commercial grade, sulfuric acid to the wet chromium hydroxide then adjusting the pH to 5 with 10% caustic soda (NaOH). The blue-green pigment, Cr₂O(OH)₄ or Cr₂O₃·2H₂O, is soluble in either alkali hydroxide or acid when newly precipitated from solution. This can be utilized
as blue-green, grayish-blue, or blue-gray-green tint in concrete. When further purified, this can be utilized as a pigment for cosmetics. The green pigment (Cr₂O₃) can be used as pigment for paints, concrete and ceramics due to its more stable form. It can also be used in tinting glasses as it combines with silicates.

Subjecting the precipitate to oven drying at 130°C for an hour produces the blue-green chromium hydroxide. Drying this in a furnace at 350°C for 3 hours will remove the hydroxide and produce a more stable Cr₂O₃ green pigment. Meanwhile, basic chromium sulfate liquor can be produced by dissolving the precipitate through slow addition of 5 Normal (N), commercial grade, sulfuric acid to the wet chromium hydroxide then adjusting the pH to 5 with 10% caustic soda (NaOH).

| Firm            | Total Chromium (mg mL⁻¹) | Chromium in the supernatant (mg mL⁻¹) | Chromium removed (%) |
|-----------------|--------------------------|---------------------------------------|----------------------|
|                 | Mean ± SD                | Range                                 | Mean ± SD            | Range                           | Mean ± SD | Range |
| Industrial Unit 1 | 2726.967 ± 1698.14       | 108 – 5467                            | 2661.80 ± 686.99     | 98.60 - 5434.18                 | 96.41 ± 2.73 | 90.06 – 99.60 |
| Industrial Unit 2 | 2858.53 ± 1727.53        | 148.49 - 563.97                      | 2750.24 ± 1705.86    | 148.49 - 5563.97                | 94.82 ± 2.40 | 90.20 - 98.99 |
| Industrial Unit 3 | 2750.26 ± 1723.75        | 96.00 - 5690.00                      | 18.69 ±9.36          | 1.5636 - 38.56                  | 99.13 ±0.34 | 98.30 - 99.70 |

Cost Analysis

For initial concentration of 5400 mg L⁻¹ of chromium in spent chrome tan wastewater, the recovery is worth Rs.3970.00 (approx.) against the cost of only Rs 1050.00 (approx.) as shown in table-6. Thus it appears that the recovery of chromium, by the newly developed method, will make the tanning process highly economical resulting in a profitable business and clean environment. From fig. 1, if produce 28 liter solution of chromium sulphate from developed recovery process for tanning process we just need this idea with Rs. 1050.

**Proposed Design of chromium recovery plant**

1. **The purpose of pilot plant**
   - To recover chromium from tannery waste water.
   - To check the quality of chrome achieved for tanning.
   - To convey information for recovery of chromium to tanners.
   - To remove chromium pollution from chromium waste water.

3. **Benefits of chrome recovery pilot plant**
   - We can get 99% chromium from tannery waste by the chrome recovery pilot plant.
   - This plant has reduced water pollution.
   - The recovered chromium has similar properties to that of fresh (powdered) chromium.
   - We can get to save 50% of expenditure of chromium salt for tanning process by chrome recovery pilot plant.

4. This plant requires only three persons to operate.
In order to realize the environmental impact of tanning industry, it is important to discuss about the various processes that involved in tanning process. A skin or hide can divide into three different parts by structure as the epidermis, the hypodermis and the dermis. The epidermis mainly consists of keratin and hair. The dermis part of skin that is normally understood to be skin which is then later transferred into leather finished form. The important leather making component is the protein that is consist of collagen and keratin (a constituent of hair), horn, epidermal structures and wool. Discharging of tannery waste are two types of tannery wastes as the solid and liquid. It is expected that if processing the averaging 11,000 kg of skins per day that can produce the total of about 5,700 kg of solid waste per day in kasure according to previous research analysis. The amount of tannery pollution load is reported as wastewaters discharged per annum have 5,000 tons of biological oxygen demand (BOD) and 11,000 tons of chemical oxygen demand (COD). Tannery wastewaters also have 10,000 tons of suspended solids (SS), 165 tons of chromium, and 407 tons of sulfides which are calculated on basis of 13,000 m³ per day [12].

The hides are first washed in Beam-House Processinorder to remove dirt and blood, and then soaked for the removal of salt and for softening. The wastewater from this process may contain a high organic load (BOD) due to dirt and blood along with a high concentration of salt. The next step is the removal of muscle and fatty tissue adhering to the corium layer by means of revolving knives while a continuous stream of water carries away the produced waste. The wastewaters from this process usually contain fat and fleshy particles. Liming is done to swell the hides for the better penetration of the tanning agents and for the hair removal. The hides are placed in vats containing a lime suspension. Small quantities of sodium sulfide are added for the acceleration of the dehairing process. These waters are heavily polluted with high concentrations of sodium sulfide, lime, and organic matter. The dehairing of the hides is accomplished mechanically by means of rolling knives. Large amounts of water are used to flush out loosened hairs and excess lime. The related wastewaters contain fine hair epidermal particles and lime. The hides are washed and then subjected to a process known as bating. During this process some proteins, such as elastin, are hydrolyzed [13].

As far as the current disposal practices are discussed as follows. Tannery waste widely used in Poultry feed manufacturing due to the presence of protein content of the solid waste like protein fleshing, chrome shaving, raw trimming, buffing dust and dry trimming but the main problem is presence of some chrome content as one of its constituent. As a reported that chrome content in wastes ranges from 15 to 27 g kg⁻¹ but the tanned chrome waste have chromium as trivalent form that is less toxic as linked to the hexavalent form of chromium and it is classified as carcinogenic agents. Chrome containing solid waste uses in different parts of the country but in Punjab tannery solid waste is used commonly in making the leather board but it is used for making poultry feed in Karachi. Another study is conducted on of solid waste management that is carried out in Korangi as Industrial Area by Pakistan Tanners Association organization. The poultry feed with trivalent chromium has to contain hexavalent chromium but during the poultry feed preparation; a trivalent chromium may be changed into its hexavalent form as mentioned in previous study [14].

In past, biological treatment is the mostly and widely used process as aerobic fermentation but anaerobic process is also used for this type of water treatment. The selection of the wastewater treatment technology depends on many factors like principal cost, availability of land, efficiency of the process, operation and maintenance cost etc. [15]. Subjecting the precipitate to oven drying at 130°C for an hour produces the blue-green chromium hydroxide. Drying this in a furnace at 350°C for 3 hours will remove the hydroxide and produce a more stable Cr₂O₃ green pigment. Meanwhile, basic chromium sulfate liquor can be produced by dissolving the precipitate through slow addition of 5 Normal (N), commercial grade, sulfuric acid to the wet chromium hydroxide then adjusting the pH to 5 with 10% caustic soda (NaOH). The blue-green pigment, Cr₂O₃(OH)₂ or Cr₂O₃·2H₂O, is soluble in either alkali hydroxide or acid when newly precipitated from solution. This can be utilized as blue-green, greyish-blue, or blue-gray-green tint in concrete. When further purified, this can be utilized as a pigment for cosmetics. The green pigment (Cr₂O₃) can be used as pigment for paints, concrete and ceramics due to its more stable form. It can also be used in tinting glasses as it combines with silicates [16]. Now, it is a common practice to use the oils and fats for the chromium (III) tanning process that convert into soft and flexible leathers. In these cases MgO based recovery systems can give the results in the formation of magnesium soaps that are adversely affect the recycling and reuse processes of chromium. In addition, it utilizes lime wastes, also from tanneries, to precipitate chromium. This eliminates the use of fresh alkali chemicals for precipitation, and also recycles the waste. In a study conducted by ITDI, no significant difference was observed in the percent recovery of chromium as Cr₂O₃ when lime waste was used instead of analytical grade lime (CaO) [17].

V. CONCLUSION
It is final result from this research that a common effluent treatment plant needs for treatment of wastewater containing chromium which are hazard for natural and aquatic environmental. This can be recovered and recycled using simple precipitation method. For this purposes, precipitation techniques is used for separation of chromium from tannery wastewater. In this process, precipitants agent is lime as best one and can remove 97% chromium as recovered and again recycled for same production process of leather and cost of process is very low as recordable in short time within two years. It is very attractive for industrial operations units.
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