

# Managing the Quality of Chromium Sulphate during the Recycling From Tanning Waste Water

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**Abstract**— Quality management is a big issue during recovery and recycling process because if desired quality is not received during chromium recovery or recycling process, we may be faced another problem of recycled materials. This also seen that most important that the production processes is useless without taking specific required quality of chromium., in real way about 60%-70% of chromium salt is used as chemical interaction with the hides but 30%-40% of chemical chromium salt is wasted as the solid and liquid form. Therefore, the quality during the recovery process of the chromium sulphate from chromium wastewater that is most important step for controlling environmental pollution with some economical benefits. Recycling of chromium sulphate is possible by using chemical precipitation method for water treatment, two precipitating agents' magnesium oxide and calcium hydroxide plus alum are used for this purpose. Final findings showed that the optimum pH for efficient recovery with required quality was 8 and the Recycling of chromium sulphate was about 99(%) at pH 8 with good sludge with high settling rate. on the Base of these findings an economical production plant can be designed which are useful for quality improvement.

**Keyword**— Economical Recovery, Chromium, Tanning, Chemicals, Recycling.

## I. INTRODUCTION

Two categories of waste are mainly as solid and liquid that is created by the leather manufacturing tanneries. Wet chemical processes in the tannery for leather making are the key source for the generation of wastewater but some mechanical and chemical operations are also contribute to small quantities of tannery waste [1].

The handling of raw skins with adhered dusted salt that is contaminated with dirt, hair, blood and microorganisms which has removed from the skins and then solid waste obtained. Wastes salt is reused partly in the preserving

process of skins and some remaining materials are generally dumped inside the undeveloped land near the tannery industries. Fleshes as an extra part is removed from the limed skins then skins are shaved specially at the neck, tail, legs, and belly parts for giving a smooth and regular shape of the skins and hides but the fleshes and trimmings are basic part of solid waste matter. Chrome tanning of skins or hides is shaved for getting the proper thickness desired and this operation can be produced chrome containing solid waste that known as shavings [2].

In leather manufacturing industry, salted hides and skins of goat, sheep, cow and buffalo are used as raw material for the leather production. Most of the raw material is acquired from local market sources but imported raw materials are also used for production. The peak season that starts every year after Eidul-Adha (a muslim commemoration day) which ranges for 3 days. The processing in leather sector reaches to a high level as compare to the normal production days after three days of Eid but normal production also varies and depending on many conditions including the availability of the raw skins and hides as a raw material source. Variability in the smooth use of raw material can be directly affected of waste generation during the leather productions [3].

A variety of chemicals are used in tanning process as with their effects on increasing the water pollution. in the leather manufacturing process, Different chemicals are applied that depend on the nature and type of raw material with the desired product in finished form. Leather processing chemicals can be divided into four main classes based on as per their use [4].

Chromium sulfate is a greenish solution having characteristics of tanning liquor (basicity of 30%). It can be reused for leather tanning. The recovery process is efficient, relatively simple and cheap, requiring mainly a reliable filter. The recovery of chromium as blue-green pigment, green pigment or basic chromium sulfate can be achieved

on a 96-98% efficiency. In addition, it utilizes lime wastes, also from tanneries, to precipitate chromium [5].

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 the quality in the percent recovery of chromium as  $\text{Cr}_2\text{O}_3$  when lime waste was used instead of analytical grade lime (CaO) [6, 7].

The leather produced using recovered chromium meets standard quality requirements. A comparison of the leather produced from a mixture of 70% fresh chromium and 30% recovered chromium with that produced using 100% fresh chromium shows the leather quality to be equal [8].

The Objective of study is managing the quality during the recovery process and Recovery of chromium from tanning wastewater

## II. MATERIAL AND METHODS

### Wastewater Sampling

The sampling was carried out by dipping the bottle PVC (polyvinyle contained) for 5 Liters. And the container was closed by plastic caps with suitable liner containers were filled 99% of the volumetric capacity. The container were through claim to remove are extremism matter and then rinsed by filling the contained and emptying thrice. The container were washed biodegradable detergents prior to rinsing with the sample water which collected from Siddiq leather industry (pvt) limited.

*Sample transportation:* The stoppers closing the sample containers were fixed in place by adhesive (PVC) tap to prevent leakage. The samples were transported securely without damaging the container or seal.

*Storage:* The samples were stored in a cool (less than  $30^\circ\text{C}$ ) and dry place.

### Chemical Analysis

The analyses were carried out by using standard ASTM methods as follows. Reagent grade chemicals were used in all tests [9].

#### Determination of chromium

Several sample matrices have been identified which produce a yellow-orange complex that interferes with this quantification. When this occurs, it may be remedied by inverting the indicator-buffer sequence. Although each interfere has been reported, most of the common interferences are eliminated by the preservation procedure at the time of collection. The potentially interfering metals are precipitated and the reducing effect of sulfur compounds has been overcome.

Diphenylcarbazide indicator solution: 1,5-Diphenylcarbohydrazide (0.25 g) was dissolved in acetone (100 mL) and stored in an amber glass-stoppered flask at  $4^\circ\text{C}$  when not in use. This solution was stable for about one week when kept refrigerated.

Phosphoric acid (1 + 1): Concentrated phosphoric acid, sp gr 1.69, (500 mL) was diluted to 1 L with distilled water.

Four standard solutions containing from 0 to  $0.50\text{ mg L}^{-1}$  of chromium were prepared by diluting measured volumes of the standard chromium solution to 100 mL with water in separate volumetric flasks [10].

#### Determination of sulfate ions [11]

*Sampling:* The samples were collected in accordance with Practice D 1066, Specification D 1192, and Practices D 3370 of ASTM.

Sulfate standard solution ( $1\text{ mL} \equiv 0.100\text{ mg SO}_4^{2-}$ ) — Anhydrous sodium sulfate (0.1479 g) was dissolved in distilled water and diluted with distilled water to 1 L in a volumetric flask.

*Calculation:* The photometer readings obtained with the sample were converted to milligrams per liter sulfate ion ( $\text{SO}_4^{2-}$ ) by use of the calibration curve [12].

#### Determination of hardness [13]

Buffer Solution: The buffer solution was prepared in three steps as follows:

Sodium tetraborate  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  (40 g) was dissolved in 100 mL of water. Sodium hydroxide (10 g), sodium sulfide  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  (10 g) and  $\text{KNaC}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$  (10 g) were dissolved in 100 mL of water. The two solutions were mixed and 1 g of magnesium disodium ethylenediamine tetraacetate, having a magnesium-to-EDTA mole ratio of 1 to 1, was added. The volume was made up to 1 L with distilled water. The solution bottles were kept stoppered when not in use. The reagent was effective for at least 1 month.

Calcium indicator — Hydroxynaphthol blue.

Hardness indicator solution — Chrome Black T<sup>3</sup> (0.5 g) was dissolved in 50 mL of diethanolamine or triethanolamine and stored the solution in a dark-colored bottle. This solution had a storage life of several months.

Hydrochloric Acid (1 + 4) — One volume of concentrated hydrochloric acid (sp gr 1.19) was mixed with 4 volumes of water.

Disodium ethylenediamine tetraacetate ( $\text{Na}_2\text{H}_2\text{EDTA}$ ) standard solution, ( $1\text{ mL} \equiv 1.0\text{ mg CaCO}_3$ ) Disodium ethylenediamine tetraacetate dehydrate (3.8 g) was dissolved in approximately 800 mL of water. The pH of the solution was adjusted to 10.5 with NaOH solution and the procedure given below was used for the sample analysis. The concentration of the EDTA was adjusted so that 1 mL was equivalent to 1.0 mg of  $\text{CaCO}_3$ . The solution was stored in polyethylene bottles and restandardized monthly.

Sodium hydroxide solution ( $50\text{ g L}^{-1}$ ) — Sodium hydroxide (50 g) was dissolved in distilled water and diluted to 1 L.

When the titration required more than 15 mL of the titrating solution, the sample was diluted and the test was repeated.

#### Determination of ammonia nitrogen

Some organic compounds such as ketones, aldehydes, alcohols, and some amines may cause an off color on Nesslerization. Some of these, such as formaldehyde may be eliminated by boiling off at a low pH prior to Nesslerization. Residual chlorine must be removed prior to the ammonia determination by pretreatment of the sample. Turbid samples may be clarified with  $ZnSO_4$  and NaOH solution; the precipitated  $Zn(OH)_2$  is filtered off, discarding the first 25 mL of filtrate, and the ammonia is determined on an aliquot of the remaining clear filtrate by direct Nesslerization. Ammonia can be lost in basic conditions. The procedure is checked with a standard solution [14].

#### Determination of biological oxygen demand (BOD)

Phosphate buffer — 8.5 g  $KH_2PO_4$  + 21.75 g  $K_2HPO_4$  + 33.4 g  $Na_2HPO_4 \cdot 7H_2O$  + 1.7 g  $NH_4Cl$  dissolved in distilled water to make 1 liter. Magnesium sulphate solution —  $MgSO_4 \cdot 7H_2O$  (22.5 g  $L^{-1}$ ). Calcium chloride solution —  $CaCl_2 \cdot 2H_2O$  (27.5 g  $L^{-1}$ ) in distilled water. Ferric chloride solution —  $FeCl_3 \cdot 6H_2O$  (0.25 g  $L^{-1}$ ) in distilled water. Manganese sulphate solution —  $MnSO_4 \cdot H_2O$  (364 g  $L^{-1}$ ) in distilled water. Alkali iodide azide reagent — 500 g of NaOH + 150 g of KI in distilled water to make one liter. To this was added  $NaH_2$  (10 g) dissolved in 40 mL distilled water. Sodium thiosulphate stock solution (0.1N) — Dissolved 24.82 g  $Na_2S_2O_3$  in boiled distilled water and diluted to one liter.

Starch indicator, Dissolved 2 g starch powder + 0.2 g salicylic acid as a preservative in 100 ml boiled distilled water.

*Procedure:* A dilution water was prepared by aerating the required volume of distilled water in a container by bubbling compressed air to attain saturation. To this was added 1 mL each of phosphate buffer,  $MgSO_4$ ,  $CaCl_2$ ,  $FeCl_3$  solutions for each liter of dilution water.

One sample bottle was kept for initial dissolved oxygen (DO) and the other bottle was incubated at 20°C for 5 days [15].

#### Determination of chemical oxygen demand (COD)

Chloride ion is quantitatively oxidized by dichromate in acid solution. (1.0 mg  $L^{-1}$  of chloride is equivalent to 0.226 mg  $L^{-1}$  of COD.) As the COD test is not intended to measure this demand, concern for chloride oxidation is eliminated up to 1000 mg  $L^{-1}$  of chloride by complexing with mercuric sulfate. Oxidizable inorganic ions, such as ferrous, nitrite, sulfite, and sulfides are oxidized and measured as well as organic constituents.

*Sampling:* The samples were collected in accordance with Practices D 3370 of ASTM. The samples were preserved by cooling to 4°C if analyzed within 24 h after sampling, or preserved for up to 28 days at 4°C and at pH < 2 by addition of concentrated sulfuric acid. The addition of 2 mL of concentrated sulfuric acid per litre at the time of collection generally achieves this requirement. The actual holding time

possible without significant change in the COD is less than 28 days, especially when easily oxidizable substances are present.

*Sampling:* The samples were collected in accordance with Practices D 3370 of ASTM in plastic bottles filled completely and capped tightly. The biologically active samples were analyzed as soon as possible after collection. The samples were stored up to 28 days by adjusting the pH to 2 or less with sulfuric acid (about 2mL per liter) and storing at 4°C.

The sample (0.50 mL) was transferred to a reagent-filled COD tube. In case of samples over 1000 mg  $L^{-1}$  COD, a smaller aliquot of homogenized sample was diluted as described above. Reagent water (0.5 mL) and any standard were transferred to their respective COD tubes. The reagent blank and standards were subjected to the procedure along with the sample. The screw-top tubes were capped, mixed well and the sample, standard(s) and the reagent blank were placed in the heating block preheated to 165°C. It was heated at 165°C for two hours, removed from block and cooled to room temperature.

The photometric cell was filled with reagent water, the prepared sample for COD and measurements were made against the reagent water filled cell at 510 nm. The prepared reagent blank served as a quality control only, and was not used to zero the instrument. The cell was inverted several times prior to reading in order to ensure that the filter disc and any undigested suspended solids do not settle, so that they do not interfere with photometric readings.

*Calculation:* COD values (mg  $L^{-1}$ ) were calculated from the calibration curve [16].

#### Determination of solids

*Procedure:*

*Total solids:* The unfiltered thoroughly shaken sample (100 mL) was evaporated to dryness in a pre-weighed platinum dish on a steam or water bath. The residue was dried at 103°C for one hour.

*Dissolved solids:* The sample was filtered to reduce its turbidity to less than 1 unit. The clear sample (100 mL) was taken in a pre-weighed platinum dish and evaporated to dryness. The residue was dried at 103°C for one hour.

*Suspended solids:* The water sample (2 L) was filtered through a pre-weighed Gooch crucible having an asbestos mat, dried for one hour at 103°C, cooled in a desiccator to a constant weight [17].

#### Determination of phosphate ( $PO_4^{3-}$ )

Preparation of sample — The samples (20 mL) were taken in 50-mL measuring flasks separately and then 5mL of sodium molybdate solution and 2 mL of hydrazine sulphate solution were added to each flask. The volume of all the flasks was made up to the mark with double-distilled water. Then all the flasks were heated at about 80°C on water bath for about 10 min. The absorbance was measured at 823 nm.

Preparation of blank, In 50-mL measuring flask 5 mL of sodium molybdate solution and 2 mL of hydrazinium sulfate were added and the flask was filled upto the mark with double-distilled water. Then the flask was heated at 80°C for about 10 minutes in a water bath and absorbance was measured at 823 nm [18].

#### Determination of sodium

Then calibration standards (2.0, 4.0, 8.0, 10 mg L<sup>-1</sup>) were prepared from this. Absorbance was measured by the flame photometer using the sodium filter. The calibration curve was constructed from this data. The concentration was determined from the curve [19].

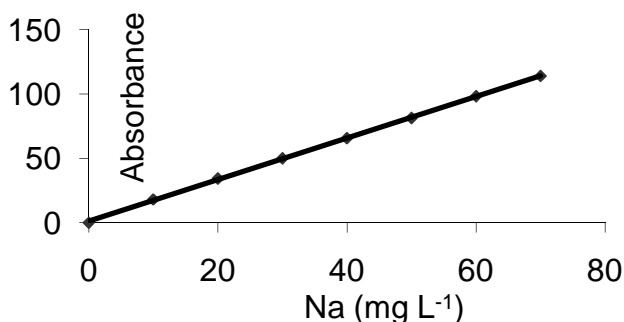


Fig.1: Graph between Sodium concentration and absorbance

#### Determination of potassium

It was determined flame photometrically by using KCl as standard and potassium filter. The procedure was as described for determination of sodium [20].

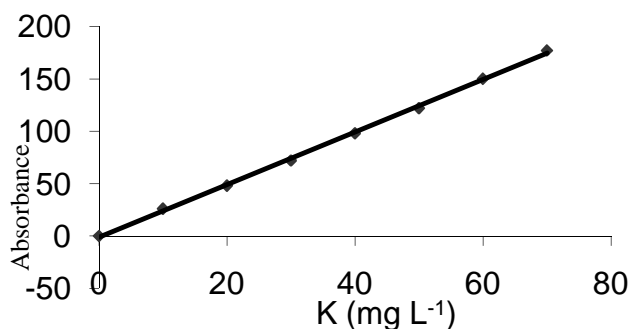


Fig.2: Graph between Potassium concentration and absorbance

#### Determination of phenol

The estimation of phenol in tannery effluents was done by the colorimetric method.

*Working standard solutions:* This solution was freshly prepared every day before use. This solution was further diluted to prepare 10 mg L<sup>-1</sup> solution. This solution was used to prepare standard solutions for calibration.

*Amino-4-antipyrine solution:* 4-Amino antipyrine (2.0 g) was dissolved in 100 ml of distilled water to make 2% solution. This solution was prepared before use.

*Potassium ferricyanide solution:* 34 g of ammonium ferricyanide – 235 ml of Ammonium ferricyanide solution 200 g of potassium sodium tartarate were dissolved in small amount of deionized water and the volume was made up to the mark (1000 ml).

*Phosphoric acid solution:* Phosphoric acid (10 mL) was dissolved in distilled water to make 1 L.

*Copper sulphate solution:* Copper sulfate (10 g) was dissolved in distilled water to make 100 mL.

*Methods:* There are two methods for colorimetric determination of phenols which were used as follows:

*Aqueous method* – From standard solution of phenol 10, 20, 30, 40, 50 mL were taken in six beakers. Each of the solution was diluted with 100 mL distilled water. The pH of the solution was adjusted to 10 with the buffer. To this amino-4-antipyrine (20 mL) and K<sub>3</sub>Fe(CN)<sub>6</sub> (2.0 mL) solutions were added. The mixture was mixed thoroughly and allowed to stand for 15 min. The red colored developed. It was diluted with distilled water and absorbance of each solution was recorded at 510 nm. The calibration curve was constructed from this data [21].

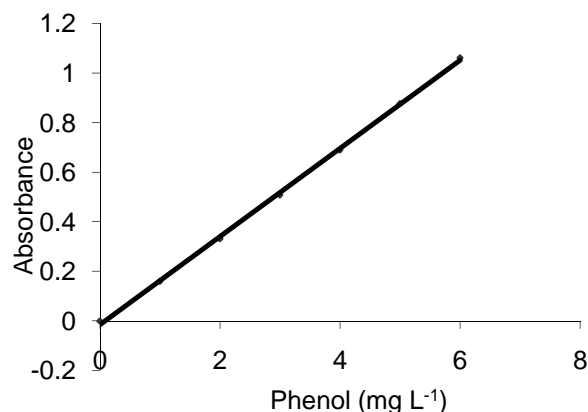


Fig.3: Graph between Phenol concentration and absorbance in organic medium

#### Recovery of chromium from wastewater [22]

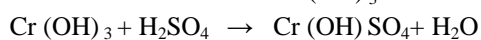
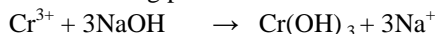
##### The process

The chromium was removed from the wastewater by using CaO + alum and MgO as the precipitating agent. The procedure is given as follows:

To the wastewater (500 mL) an appropriate amount of lime solution with 0.1% alum or MgO 10% solution was add so as to bring the pH to 8±1 with constant stirring by a mechanical stirrer (90 rpm) for 20 min. The mixture was allowed to settle for 4 h. The precipitated chromium was separated by filtration through ordinary filter paper. The optimum amounts of CaO, alum and MgO used were determined by varying the doses of these solutions. The efficiency was measured by analyzing Cr in the supernatant by atomic absorption spectrometry.



**Preparation of basic chromium sulphate:** The chromium (III) present in tannery waste water was recycled and it is reused in tanning operation. For this purpose, the chromium containing waste water was treated with 10% NaOH which produced the precipitates of chromium (III) hydroxide. The precipitates of chromium hydroxide was collected and dissolved in 2N sulfuric acid. The resulting solution was the basic chromium sulfate. This basic chromium sulfate was used in one both tanning process.



Basic chromium sulfate (solid) is obtained by evaporating the solution of Cr(OH)<sub>3</sub>.

### Optimization of process

Six beakers were used for each stage and 500 mL of wastewater was added to each beaker. Precipitating agents were added to each sample separately and pH was maintained at 6 to 12 using 0.1M nitric acid. The samples were mixed for one minute at 90 rpm as the first step. In the next step samples were mixed for 20 min at 30 rpm. After this the samples were allowed to settle. In the last stage, after 5 h settling time, a sample was taken from the supernatant. The chromium concentration was determined in the supernatant after filtrations.

The effect of each factor on the three precipitation processes was measured by fixing the value of other variables [23].

## III. RESULTS

### Analysis of samples

The results are given in Table-1, it is showing the chemical analysis of wastewater samples that tannery wastewater is highly quality polluted as seen parameters like COD, BOD, settleable solids, suspended solids, conductivity, total Kjeldhal nitrogen, sulfide, sulfate and chromium metal. The parameters values (given in table-1) are very extraordinary as compared to values given by National Environmental Quality Standards (NEQS) as per fixed by the federal government of Pakistan.

Leather wastewater that coming from different industrial chemical process having different types of pollutants and even pH value varies from 3.3 to 4.1. Similarly, it can be seen a large variation that exists in parameters like COD, BOD, sulphate, chloride, Total Dissolved Solids, Total Suspended Solids and settle able matter. In addition to this the parameters are showing clearly that the wastewater has highly considerable quantities of chromium metal which presents in wastewater. The pollutants of wastewater coming out of tanneries are given in Table 1.

Table.1: Analytical data of samples

Parameter	Siddiq Leather Works	
	Mean	Range
pH	3.74	3.1 - 4.2
BOD (mgL <sup>-1</sup> )	5376.2	4587 - 6547
COD (mgL <sup>-1</sup> )	4345.6	3654 - 5000
SO <sub>4</sub> <sup>2-</sup> (mgL <sup>-1</sup> )	800.2	698 - 874
PO <sub>4</sub> <sup>3-</sup> (mgL <sup>-1</sup> )	707.6	583 - 784
TDS (mgL <sup>-1</sup> )	622.8	412 - 874
TSS (mgL <sup>-1</sup> )	546.8	456 - 654
TS (mgL <sup>-1</sup> )	1558.2	1147 - 2547
S <sup>2-</sup> (mgL <sup>-1</sup> )	166	104 - 246
Cr (mgL <sup>-1</sup> )	5335	4587 - 5478
Phenol (mgL <sup>-1</sup> )	53.2	25 - 89
Ca (mgL <sup>-1</sup> )	497	399 - 596
Na (mgL <sup>-1</sup> )	716.6	587 - 874
K (mgL <sup>-1</sup> )	311.6	154 - 587
NH <sub>3</sub> (mgL <sup>-1</sup> )	2368.4	1254 - 3210

### Effect of settling rate on supernatant due to precipitants

The change in pH was rapid in case of magnesium oxide as observed by comparison of the graphs given in Fig. 4. Similarly it was observed that the settling rate in case of magnesium oxide was higher than that for calcium hydroxide as indicated by the height of the supernatant. A lot of experiments are conducted on determination of the optimum pH at which maximum chromium recovery from chrome containing wastewater. The limitation of this study are showing in fig. 4 as in pH range of 2.0 – 10.0.

Sulphides are discharged from the de-hairing process of leather manufacturing then hydrogen sulphide gas is released at a pH 8.4 and this gas has an unkind smell even in small quantities as it is highly toxic for any life forms. If observe in the higher concentrations as 9 mg L<sup>-1</sup>, fish can die in common case. In case of public health, this gas can create a pose structural problem. Due to corrosion by sulfuric acid is produced after microbial action on hydrogen sulphide gas. Sewage wastewater contains sulphide with the range of 16-21 mg L<sup>-1</sup> as compare to tannery wastewater contains about 290 mg L<sup>-1</sup> but NEQS maximum level is 1.0 mg L<sup>-1</sup> in wastewater.

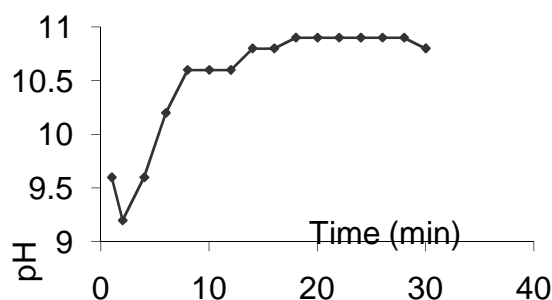


Fig.4: Graph showing change of pH (by use of MgO) with time

### Effect of pH on recovery of chromium

Series of experiments were conducted to determine optimum pH for maximum chromium removals from tannery wastewater. It is shown in Fig. 5 that at pH 7.0 – 7.5 about 112 – 228 mg L<sup>-1</sup> chromium was present in the treated effluent which is not acceptable for further treatment. It is clearly seen from the results that when pH increases from acidic to basic the recovery of chromium increases. In fig. 5, the results of the present study is showed that high quality settling rate, high sludge of chromium and low volume of MgO sludge is obtained by a limited use of Magnesium Oxide. Chromium removals (99.7%) is observed at pH 8.0 and at above pH 8.0 as significant increase in efficiency of chromium recovery as observed in Fig 5. After Applying this method, the treated effluent contains 0.5-1 mg L<sup>-1</sup> of chromium that will be acceptable for usual water flowing body.

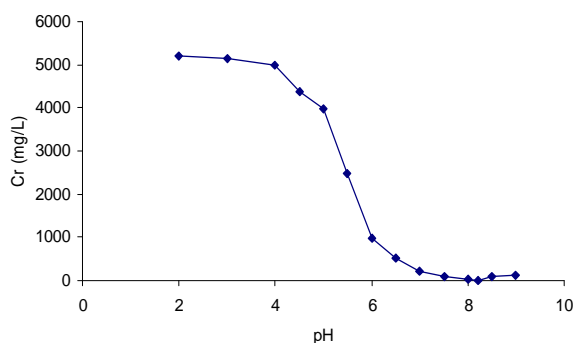


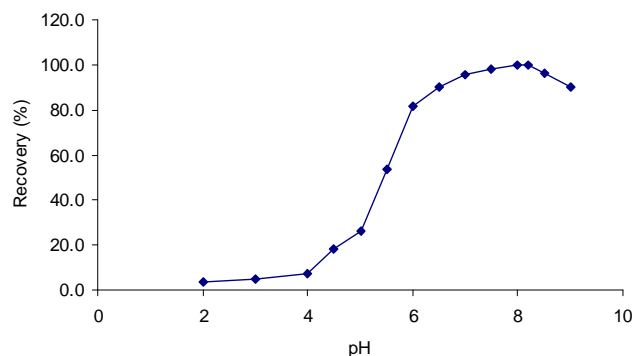
Fig.5: Graph between pH and concentration of chromium

### Effect of chromium concentration on recovery

In the present studies an attempt has been made to recover economically chromium from tannery waste. In fig. 6, quality of chrome recovery at pH 8.5 is 92 % which is great achievement by experiments. The pH value of directly discharged tannery wastewater is varied from 3.5 to 13.5 which is against NEQS level. By nature, Water with a low pH is acted as corrosive for water-carrying systems. But in unfavorable circumstances situation can be led to the dissolving of heavy metals in the wastewater environment. Usually, the pH high value in tannery effluent is caused by lime using in excess quantities but this causes bad effects. A large variation in pH can exert the stress on aquatic environment that may be killed some plants and animals sensitive species.

Chromium recovery is very feasible at pH 8 as seen in fig. 6, but chromium (III) much less toxic than hexavalent chromium chemically. The toxicity of chromium salts is variable for plant and animal life but Algae have been shown as very sensitive, particularly. It has been assessed that wastewater of chrome tanning process carries about 2 % of the total chromium in the wastewater of a tannery that means it have 6050 - 7040 mg L<sup>-1</sup> of chromium metal [16].

Fig 6. Graph between pH and recovery of chromium



### IV. DISCUSSION

Suspended solids have a bad effect when they settle down in aquatic environment because the layers are formed on the bottom of the stream that can cover the natural fauna where the aquatic life exists. It can lead to a depletion of oxygen supplies in the bottom of the waters bodies but a secondary effect is the less of light penetration which make the consequential reduction in photosynthesis due to high turbidity of polluted water source. Tanneries are the discharged wastewater that has 450 – 895 mg L<sup>-1</sup> of suspended solids as reported, similarly Karachi sewage wastewater contains 550-950 mg L<sup>-1</sup>, against the NEQS limit of 150 mg L<sup>-1</sup> [24].

The Large proteins quantities and its degraded products can change into hazard form of ammonia in the effluent and they can affect the environment that can be expressed by two complex parameters like suspended solids and BOD. BOD is defined as a measuring of the oxygen consuming capacity of water with organic matter if protein like material is dissolved. It is already reported that in tannery wastewater have high BOD values due to dissolving of proteins of leather. But organic matter does not cause as direct harm for the aquatic environment but it can be exerted an indirect effect by miserable dissolved the oxygen in the water body. The oxygen content of water is a critical part of water quality as parameter and its reduction can create a serious cause as stress on ecosystem, naturally. As an example, the total deficiency of dissolved oxygen is a result of high BOD that can kill all the natural life around the affected area, mentioned in literature survey. Discharged wastewater from tanneries with high BOD value as usually in the range of 1750-10050 mg L<sup>-1</sup> which is against the normal value of 80 mg L<sup>-1</sup> under NEQS. As result, the BOD value of tannery effluent is existed in range of 4-20 times higher than sewage wastewater [25].

After chromium recovery process, the COD has very low value because concentration of chromium with low values and can be understood as it is a measure of oxygen equivalent to that portion of the chemical matter present in a

sample that is liable to oxidation. It is a most important that rapidly measured parameter for stream and industrial wastewater can help for controlling the pollutants of wastewater. The organic compounds immediately available in tannery wastewater, it is related with the biological compounds which are a part of immediate biochemical load on the oxygen assets. Complex wastewater from tanning industry are usually possesses a COD value in the range of 3800-41300 mg L<sup>-1</sup> (against the normal value of 150 mg L<sup>-1</sup> [26].

It is used the sodium chloride in the tannery that produces no effect when discharged into water body but its effects can appears in fresh water life due to it gives high values of COD and cannot be recycled due to high economical cost. When its concentration in a stream or lake is too high, aquatic life may be damaged rapidly. This is reported that it is no economically viable way for the removing salt from the tannery wastewater. A similar problem is also existed for sulphate that uses as the chrome tanning chemical salt, Sulphate can cause of corrosion of concrete structures. The chloride content of tanneries wastewater has ranged from 5720 to 14360 and sulfate has value from 870 to 1819 mg L<sup>-1</sup>. Vapors of finishing chemicals that used in pre-tanning process like formaldehyde, acetic acid, glycol ethylene, etc. are very hazardous and can effect on the health of labors, severely [27].

## V. CONCLUSIONS

It is concluded that chromium recovery depend on the chromium concentration present in tanning wastewater as well as precipitating agents. The efficiency of the magnesium oxide is much greater than lime for recycling of chromium from waste water. The new developed method is a highly profitable and economical for treatment of wastewater as chromium recovery with best quality in tanning industry. One important suggestions is that here need to improve the mechanical quality of wastewater and recovery plants for its only efficiency.

## REFERENCES

- [1] Vienna JD and DS Kim.. Preliminary IHLW Formulation Algorithm Description. 24590-HLWRPT-RT-05-001, Rev. 1, River Protection Project, Hanford Tank Waste Treatment and Immobilization Plant, Richland, Washington. Weber WJ. 2014. "Radiation and Thermal Ageing of Nuclear Waste Glass." *Procedia Materials Science*, vol. 7, pp. 237-246, 2014.
- [2] Brown SJ. 2010. "Caustic Side Solvent Extraction At the Savannah River Site: Operating Experience and Lessons Learned - 10105." In WM2010 Conference Proceedings, March 7-11, 2010, Phoenix, Arizona.
- [3] Daniel RC, JM Billing, RL Russell, RW Shimskey, HD Smith, and RA Peterson. "Integrated Pore Blockage-Cake Filtration Model for Crossflow Filtration." *Chemical Engineering Research and Design*, vol. 89, no. 7, pp.1094-1103, 2011.
- [4] Dresel PE, MJ Truex, and K Cantrell. 2008. *Remediation of Deep Vadose Zone Radionuclide and Metal Contamination: Status and Issues*. PNNL-18114, Pacific Northwest National Laboratory, Richland, Washington.
- [5] Dunn K and M Louthan. "Evidence of Corrosive Gas Formed by Radiolysis of Chloride Salts in Plutonium-Bearing Materials." *Journal of Nuclear Materials Management*, vol. 38, no. 3, pp. 82-95, 2010.
- [6] EPA - US Environmental Protection Agency. 2011. *Environmental Cleanup Best Management Practices*.
- [7] Fox KM, DK Peeler, JM Pareizs, CL Crawford, and TB Edwards. 2014. *Evaluation of Defense Waste Processing Facility (DWPF) Glass Samples After an Extended Melter Outage*. SRNL-STI-2014-00302, Savannah River National Laboratory, Aiken, South Carolina.
- [8] Gin S, A Abdelouas, LJ Criscenti, WL Ebert, K Ferrand, T Geisler, MT Harrison, Y Inagaki, S Mitsui, KT Mueller, JC Marra, CG Pantano, EM Pierce, JV Ryan, JM Schofield, CI Steefel, and JD Vienna. "An International Initiative on Long Term Behavior of High Level Nuclear Waste Glass." *Materials Today*, vol. 16, no. 6, pp. 243-248, 2013.
- [9] Herman D, M Poirier, M Fowley, M Keefer, T Huff, W Greene, and J Gilmour. 2011. "Testing of the Second Generation SpinTek Rotary Filter." In WM2011 Conference Proceedings, March 7-11, 2011, Phoenix, Arizona.
- [10] Hobbs DT, MJ Barnes, RL Pulmano, KM Marshall, TB Edwards, MG Bronikowski, and SD Fink. "Strontium and Actinide Separations from High Level Nuclear Waste Solutions using Monosodium Titanate 1. Simulant Testing." *Separation Science and Technology*, vol. 40, no. 15, pp. 3093-3111, 2005.
- [11] Hoffman EN, PE Zapp, BJ Wiersma, and TB Edwards. 2010. "Probability-Based Corrosion Control for High Level Waste Tanks." Presented at CORROSION 2010, March 14-18, 2010, NACE International, San Antonio, Texas.
- [12] Jenkins KD, YN Deng, and SL Orcutt. 2012. *2012 WTP Tank Utilization Assessment*. 24590-WTP-RPTPE-12-001, Rev. 0, River Protection Project, Hanford Tank Waste Treatment and Immobilization Plant, Richland, Washington.
- [13] Kim DS, DK Peeler, and P Hrma. "Effects of Crystallization on the Chemical Durability of Nuclear Waste Glasses," *Ceramic Transactions Series*, vol. 61, no. 177-185, 1995.

- [14] Kim D, MJ Schweiger, CP Rodriguez, WC Lepry, JB Lang, JV Crum, JD Vienna, FC Johnson, JC Marra, and DK Peeler. 2011. Formulation and Characterization of Waste Glasses with Varying Processing Temperature. PNNL-20774 (EMSP-RPT-009), Pacific Northwest National Laboratory, Richland, Washington.
- [15] Kim DS, MJ Schweiger, WC Buchmiller, and J Matyas. 2012. Laboratory-Scale Melter for Determination of Melting Rate of Waste Glass Feeds. PNNL-21005, Pacific Northwest National Laboratory, Richland, Washington.
- [16] Kim DS and JD Vienna. 2012. Preliminary ILAW Formulation Algorithm Description. 24590-LAWRPT-RT-04-0003, Rev. 1, ORP-56321, River Protection Project, Hanford Tank Waste Treatment and Immobilization Plant, Richland, Washington.
- Michalske T. 2014, July 15. Presentation on behalf of the National Laboratory Director's Council Task Force to the Secretary of Energy Advisory Board.
- [17] Oji LN, DP Diprete, CJ Coleman, MS Hay, and EP Shine. 2014. Tank 16H Residual Sample Analysis Report. SRNL-STI-2014-00321, Rev. 1, Savannah River National Laboratory, Aiken, South Carolina.
- [18] Peters TB, MJ Barnes, DT Hobbs, DD Walker, FF Fondeur, MA Norato, and SD Fink. "Strontium and Actinide Separations from High Level Nuclear Waste Solutions using Monosodium Titanate 2. Actual Waste Testing." *Separation Science and Technology*, vol. 41, no. 11, pp. 2409–2427, 2006.
- [19] Peters TB, MR Poirier, and SD Fink. "Processing Macrobatches 2 at the Savannah River Site Integrated Salt Disposition Process." *Separation Science and Technology*, vol. 45, pp. 1801–1806, 2010.
- [20] Reed S and J James. 2010. Environmental Restoration Overview - Mountain Creek Industrial Center. Naval Facilities Engineering Command Southeast, Jacksonville, Florida.
- [21] Russell RL, JM Billing, HD Smith, and RA Peterson. "Validation of Ultrafilter Performance Model Based on Systematic Simulant Evaluation." *Industrial & Engineering Chemistry Research*, vol. 48, no. 22, pp. 10077–10086, 2009.
- [22] Schonewill PP, RC Daniel, RR Russell, RW Shimskey, CA Burns, JM Billing, BM Rapko, and RA Peterson. "Development of an S-Saltcake Simulant Using Crossflow Filtration as a Validation Technique." *Separation Science and Technology, Special Issue: Seventeenth Symposium on Separation Science and Technology for Energy Applications*, vol. 47, no. 14-15, pp. 2098–2107, 2012.
- [23] Thomas S and G Dickert. 2013. "Regulatory Framework for Salt Waste Disposal and Tank Closure at the Savannah River Site." In *WM2013 Conference Proceedings*, February 24–28, 2013, Phoenix, Arizona.
- [24] Thorson M. 2008. Basis of Recommendation for Use of Spherical Resorcinol Formaldehyde Resin as the Primary Cesium Ion Exchange Resin in the WTP. 24590-WTP-RPT-RT-07-005, Bechtel Waste Treatment Plant, Richland, Washington.
- [25] Van Iseghem P, M Aertsens, K Lemmens, S Gin, D Deneele, B Grambow, P McGrail, D Strachan, and G Wicks. 2007. A Critical Evaluation of the Dissolution Mechanisms of High Level Waste Glasses in Conditions of Relevance for Geological Disposal (GLAMOR). EUR 23097, European Atomic Energy Commission, Brussels, Belgium.
- [26] Van Iseghem P, M Aertsens, S Gin, D Deneele, B Grambow, D Strachan, P McGrail, and G Wicks. "GLAMOR – Or How We Achieved a Common Understanding on the Decrease of Glass Dissolution Kinetics." *Environmental Issues and Waste Management Technologies in the Materials and Nuclear Industries XII*, eds. A Cozzi and T Ohji, John Wiley & Sons, Inc., Hoboken, New Jersey.
- [27] Vienna JD, JV Ryan, S Gin, and Y Inagaki. "Current Understanding and Remaining Challenges in Modeling Long-Term Degradation of Borosilicate Nuclear Waste Glasses." *International Journal of Applied Glass Science*, vol. 4, no. 4, pp. 283–294, 2013