

## CONTAMINATION ROOT CAUSES & ASPECTS AT TANNERIES INDUSTRIES

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**ABSTRACT:** In this study, the authors mostly deal with the issues of handing out different kinds of sewage created by tanneries productions with particular emphasis to chrome tanned sewage, H<sub>2</sub>S/NH<sub>3</sub> emission handling and water conservation at cooling tower. The agents that creates this waste as a potentially harmful is hexa and trivalent chromium, black killer gas (H<sub>2</sub>S) and wastage of water blow-down at cooling tower, the authors show the hazards of unexpected all above three issues and in this contribution, a new retrofit methods of handling tannery waste water, contamination air emission. Tannery dirty water includes a great quantity of chemical mixture containing materials so the efforts were made to categorize physiochemical factor of tannery dirty water and biological treatment.

**Key Words:** Tannery Effluent, Eco-Recovery, toxic effects, methods of treatment.

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### INTRODUCTION

The skin tanning production has been recognized as one of the major causes of ecological and water contamination in Pakistan around sixty thousand tons of raw hides and leather took into procedure each year ammonium salt sulphate, and chloride which discharges a great amount of raw effluent into an open causing air contamination and water bodies [1]. Generally, the tannery dirty waters are fundamental and keep an elevated substance of organic materials that differentiate up to the chemical used.[3]

The uncontrolled discharge of tannery sewage to universal water bodies adds to health dangers for human life and ecological pollution. Effluents from raw hides create wet-blue that contains mixtures of trivalent chrome and sulphide in many of other matters organic and other elements are dependable for a lofty BOD value and represents a huge pollution weight of about three hundred kg chemicals are additional as per ton of hides ( L/A/H/M 1996 ). Central sewage management is essential because of an extensive range of toxic impacts on the atmosphere caused by unprocessed tannery swage and sludge.

**Tabel-1: water consumption in industrial process operation**

| Parameters   | C-Conventional | A-advanced |
|--------------|----------------|------------|
| Soaking      | 7-9            | 2          |
| Liming       | 9-15           | 4.5        |
| Delming      | 7-11           | 2          |
| Tanning      | 3-5            | 0.5        |
| Post-tanning | 7-13           | 3          |
| Finishing    | 1-3            | 0          |
| Total        | 34-56          | 12         |

Technologies of changes are in-house measures at sources, Enzymatic product may take the place of sulphide, surfactants if utilized must be eco-friendly use Pentachlorophenol and it must be let alone, weak acidic may take the place of (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub> in deliming process. Trivalent chromium must be utilized for tanning as an alternative of hexa-valent chromium that is toxic. Dirt water and sludge includes twenty five to thirty percent of total chrome. The straight reprocessing of chrome tanning drift is one of the easy ways to reprocess the chromium in the procedure. After accumulating and enough excellent screening, the drift is reprocessed with the addition of fresh chromium, 1 control of remaining float , 2 the salvage of chrome through precipitation make it able the revitalization of tanning float and effluents form the different post-tanning phases as displayed in figure below- 1.

After assortment, viewing and storage the drifts are precipitated with various kinds of alkalis and base and the sludge is reused behind easy resolve and acidification. Such vegetation for chrome revitalization established in many productions in Pakistan. Tanning manufactured goods that get better exhaustion speed have been accessible which facilitates to a tanning sequence with very little quantities of chrome consumption. These products intend for the whole obsession of the chrome on the protein strands and leaving a minute number of unused chromium in the drift.

The low down loaded stimulate sludge is a established technology for the conduct of tannery dirty water, the end of pipe effluent management in tanneries in any case needs two stages of treatment. The major system of management contains mechanical viewing, Ph Equalization and physiochemical procedures: during this level BOD load decreases ph fluctuation is decreased to a convenient and constant range.

Coagulation and flocculation are affected to take out floating solids at some point in secondary management biological procedure are utilized to get rid

of most of the organic substance from the dirty water by changing it into different gasses and into cell tissues , they are sometime aerobic or anaerobic.

**Table 2: Summary of pollution loads released in effluents from creature processing operation.**

| Operation | Technology | SS     | COD     | BOD5  | Cr       | Sulphide | NH3-N | TKN | CL  | SO4 |
|-----------|------------|--------|---------|-------|----------|----------|-------|-----|-----|-----|
| Soaking   | C          | 11-17  | 22-33   | 7-11  | -        | -        | 0.1   | 1   | 85  | 1   |
|           | A          | 11-17  | 20-25   | 7-9   | -        | -        | 0.1   | 1   | 5   | 1   |
| Liming    | C          | 53-97  | 79-122  | 28-45 | -        | 3-9      | 0.4   | 6   | 5   | 1   |
|           | A          | 14-28  | 46-65   | 16-24 | -        | 8-7      | 0.1   | 3   | 1   | 1   |
| D-liming  | C          | 8-12   | 13-20   | 5-9   | -        | 0.4-0.7  | 2.6   | 3   | 2   | 1   |
|           | A          | 8-12   | 13-210  | 5-9   | -        | 0.1-9.3  | 0.2   | 0.6 | 1   | 10  |
| Tanning   | C          | 5-10   | 7-11    | 2-4   | 2-5      | -        | 0.6   | 0.5 | 40  | 30  |
|           | A          | 1-2    | 7-11    | 2-4   | 0.05-0.1 | -        | 0.1   | 0.1 | 20  | 10  |
| Post      | C          | 6-11   | 24-40   | 6-15  | 1-2      | -        | 0.3   | 1   | 5   | 10  |
| Tanning   | A          | 1-2    | 10-12   | 3-0   | 0.1-0.4  | -        | 0.5   | 0.2 | 3   | 4   |
| Finishing | C          | 0-2    | 0.5     | 0-2   | -        | -        | 0.1   |     |     |     |
|           | A          | 0-2    | 0       | 0     | -        | -        | 0.2   |     |     |     |
| Total     | C          | 83-149 | 145-231 | 50-86 | 3-7      | 4-9      | 4     | 12  | 137 | 50  |
|           | A          | 35-61  | 86-183  | 33-51 | 0.15-0.5 | 0.4-0.8  | 0.6   | 5   | 30  | 17  |

Chrome tanning is Wet-blue (Chromium sulphate) and sodium dichromate-salt used to process the leather from hide to finished leather. The effluent was assembled from Z,Y,Z pelt productions Ltd which is situated at fifty kilometer. Effluents models were assembled from individual drainage lines of various operational segments named as A white fix, B black fix, C soaking wet, D batting, E restrictive these models gathered after the ending of every individual function and the color of the models was given name by Colorimeter, temperature was calculated by mercury thermometer divided up 0 to 100 C.

**Quantitative analysis:** TDS/TSS, DO, EC and Salinity of waste matter models were calculated by Hanna mechanism H 19829, PH by ph- sis hundred AQ,BOD/COD settled on by five days BOD Test and Closed reflux, titrimetric technique, Heavy metals ( PB,CU,FE,NA,CR,ZN,NI by atomic amalgamation spectroscopy ( SIMADZU sample-(AA6401FAAS)

Toxicity testing (Tiwari *et al* 2007) aquatic saprophytes plants. To evaluate the toxic effect of tannery effluents. The effluents were kept back in disclosure to the vegetation for a whole 7 days.

The proposed treatment process and NGO Pakistan are on own in Figures 5 BOD/COD. Turbidity, TDS, TSS and chromium (Cr) against the amount of treatment water containing the efficient polluted.

In table-1 method of analysis and value's of physiochemical parameters for tannery effluent values obtained which are too high level as compared to NEQs. So analysis of coagulant dose and setting time for % removal efficiency of pollutants at table-2. This dose are set at 100 mg/L, 150 mg/L and 200 mg/L respectively

against setting (hr) of 12 Hr, 24 Hr. This behavior of pollutants noted as shown in table-2 and below graph.

**Table-3: the contrast of the limit of the collected waste water model with the permissible restrictions WHO.**

| S. No        | Parameter | Wastewater | Who   |
|--------------|-----------|------------|-------|
| 1            | DO mg     | 2.72       | 4.5   |
| 2            | TDS       | 21300      | 2100  |
| 3            | TSS       | 1250       | 600   |
| 4            | EC cm     | 42500      | 1200  |
| 5            | BOD L     | 4464       | 30    |
| 6            | COD       | 2840       | 250   |
| 7            | PH        | 8.3        | 5.5-9 |
| 8            | PO3       | 17.1       | 5     |
| 9            | CL        | 13.8       | 1000  |
| HEAVY METALS |           |            |       |
| 10           | Pb        | 0.1818     | 0.1   |
| 11           | Cu        | 0.4112     | 0.1   |
| 12           | Fe        | 14.675     | 10    |
| 13           | Na        | 12996      | Nm    |
| 14           | Cr        | 10.23      | 2     |
| 15           | Cd        | 0.0046     | 2     |
| 16           | Zn        | 1.534      | 1     |
| 17           | Ni        | 0.1513     | 3     |

Gidhamaari *et al* 2012

In gifure-3 the process flow of chrome recovery [8] the regenerate tanning mixer passed through how sieve where. Coder's solids are removed and settled coarse sediments with skin fiber. After holding and primary settling tank, the precipitation agent added at meant section to morose the size of affluent from soluble

to insoluble to increase the efficiency of filtration process. The mother liquor solution reacts with  $H_2SO_4$  where effluents again react do increase the size of pollutants the liquor recycled to precipitation section and filtration to decrease this concentration of pollutant within limit. This solid residue sent to extraction plate and frame filter press. The dry solid lumps packed and sent to manifesting of bricks (concrete blocks). He liquor recycled to sleuthing tanks.

During the Hides Raw preservation in Smoking unit the chemicals are used alkalis, Enzymes surfactants. Bactericides, wills in liming section the sodium supplied and hire hydrated used where toxic gases produced ( $H_2S$ ,  $NH_3$ ). Moreover ammonium sulphate, acids and enzymes added at de-liming unit. For greasy residues solvents and surfactants used. Next and important portion of tanning preparation where chromium salts, chloride and tanning agents pigments, dyes used while is actual cause of environment continuation. Tannery waste water most contamination source. It may cause ecological issues correlated idiots an elevated organic substance, floating solids and chromium causing highly pollutants.

Tannery waste wastes ewe mainly lofty salinity, elevated organic consignment and particular contaminants like as sulfide and chromium (3,5,6 ) prevailing the after consequences of these contaminants. Their discarding to water bodies may cause exhaustion of oxygen biding to damaging impacts on living creature [8,9].

Emerging pollutants can be understood (chemical or micro organism) that is not commonly monitored or regulated with suspected adverse ecological and gunman better effects.

PFOA and PFOS are two researched PFAS classified as emerging contains or contaminants of emerging concern by the EPA. These are cancer or affect the liver, immune system, cholesterol levels and thyroid. These are not listed as (RCRA) resource conservation. Recovery Act or clean air Act regulations. Floropolymer Coating PFAS (Poly fluorinated alkali substances). These are not filtered Brita filter. Teflon (Teflon) called PFAS is found in blood of people 99% of Americans, these chemicals pollute water do not break down and remain in the environment and people for decades (www.cancer.org) (www.ewq.org)

PFOA (Perfluorooctanic acid). (www.ehn.org). DuPont's C8 was not to be fluted into surface waters-but the company did so for decades.

The behavior of all pollutants BOD, COD, EC and water anions phosphate, bicarbonate and chloride, metals like NA, K were tested and treated found within limit. Except Cr, Cu, BP and As heavy metals. As they found beyond the permissible limit in the textile and tanneries waste. (12840, 4464 (mg/L), 42500 mg/L, 17.1, 207.6, 13.8mg/L. The impact of (CR) releases from tanneries has remained a widespread scientific and

technical argument. (Cr-6) compounds are answerable for the bulk of the human issues, agriculture and live stock. The residents and workers have been the victims of this pollution, which has led to severe ailments such as eye diseases, skin, and kidney failure. The acceptable limit by WHO for (Cr) is 0.05 mg/L while in ground water supplied to Lahore region at 165 meters depth noted 5 time more i.e. 10 mg/L for direct discharge into stream bodies and 1-50 mg on meandering releases into the sewage system [5]. The traditional chrome tanning procedure engages water washing ratio is 3-5m<sup>3</sup>/t of raw hides which includes chrome, chloride and sulphates are the main pollutants. The sophisticated chrome tanning techniques aim at dropping the pollution weight of chrome in this methods the tanning mediators used are changed to Enhanced rupture up to ninety percent. Use of shorter floats (20-30%) in closed system. Use of higher temperature (40-42 Co) and ph (4-5). Use of chrome tanning mediators. (Powder)

The lofty exhaustion and chrome fixing bring regarding a reduction in chrome release and an increase in chrome usage. In an unlock organization float quantity increase throughout recycling mean number of rotation is not incomplete and needs controlling of the comparative amount of float mixtures ph and salt subsequent to three cycles, the result reaches convinced constancy because of increases height of fat and ferrous ions. Recycling methods mostly utilized in traditional tanning procedures. The increase in chrome usage from seventy percent up to ninety five percent and decrease in chrome release from two to five kilogram to 0.1-0.25 kilogram raw hide. The recycling system also decrease sulphate load in affluent 30-55 kg/ton 10-22 Kg/t rallied.

**Table- 4 The assessment of chrome release and usage in traditional and sophisticated tanning with an elevated exhaustion and chrome fixing [4].**

| Chrome Amount<br>kg Raw hide | Technology     |                 |
|------------------------------|----------------|-----------------|
|                              | Conversational | High exhaustion |
| Offer                        | 15             | 10              |
| Tanning Float                | 3.2            | 0.03-0.05       |
| Draining & Water             | 0.6            | 0.02-0.05       |
| Post Tanning                 | 0.7            | 01-0.4          |
| Total Discharge              | 4.5            | 0.15-0.50       |
| Utilization                  | 70             | 95-98           |

[3]

These meandering arrangements are rooted in the precipitation of chrome having effluents with alkalis Mgo, Ca(OH) NaOH [3] Protrude / GTZ, (1995) "Ecology and Environment in the leather industry". Technical Hand book Ashburn.

Due to lack of supervisory environmental agencies the release of industrial effluents into receiving waters. Industries should look to properly treat their effluents and to achieve efficient removal

contaminations. The producers are responsible of liquid effluents with concentration of pollutants.

In recent technologies changes it is necessary to now and analyze behavior of tannery effluents. This may be used to plan and design unit operation in waste water treatments plants. This paper in order to contribute to this purpose the test results of the parameters for containments for each type of tanneries is discussed.

Globally by (UNEP) industrial dector tores up an average of twenty two percent of the water. Water utilization strength is important to all business whose sustainability will depend on its accessibility, price tag and superiority. Properties of waste water are interrelated affect the large quantity species composition, reliability and an organic situation of aquatic provision.

The pollution impending of waste water is directly relative to the pollutants absorption. After preliminary physical treatment the effluents go to chemical by adding aluminum sulphate or ferric chloride to form flocks and cages (Sathih *et al* 2013), (Kurt *et al* 2007). The biological treatment aerobic is activated sludge by (Micro organisms)

## RESULTS AND DISCUSSION

In this present research efforts were made to treat the effluents in an organic method and that way is more ecological, friendly, easy and very cheap.

Some particular parameters are analyzed by authors and summarized in table-3 and table-4. The results for four of the tanneries accessed in this work. It is evident that the big contribution to waste water contamination is made by tanneries 1 & 2 due to high levels of the pollution parameters.

Toxic materials in various forms of solid, liquid and gaseous contamination an 1991 selm *et al* 17 analyzed that among all the wastes, tannery effluents are the top ranked toxic releases. A significant part of the chemicals used is not actually absorbed or lack of proper reaction timing and Lience it is discharged in the environment. Liquid effluents comprise 10 to 100 mg/L of organic matter. {2}

An overview of tanning industries consists of input (Rew lides, chemicals, water, fleshlier) the output (products) wet-blue, crust, finished leather, (effluent) for treatment of water. Air pollution. Solid wastes (processing & disposal)

The removal of biodegradables organics materials possible to treat using conventional treatment such as activated sludge or trickling fitters. Raw water sent to Aeration tank where fresh air added and mixer sent to clarifier-setter where waste sludge and treated water separated.

Chromium present in tannery effluent is removed with the use of chromium salt, chromium

chloride as adsorbent and cement tined dust that is wasted by white cement manufacturing as adsorbent.

**Tabel-5: Typical characteristics of tannery waste water.**

|    |                  |       |
|----|------------------|-------|
| 1. | Ph               | 8-9   |
| 2. | Al Kalinity mg/L | 2700  |
| 3. | Total BoD        | 3100  |
| 4. | Soluble BoD      | 2600  |
| 5. | Totla CoD        | 7500  |
| 6. | Soluble CoD      | 37000 |
| 7. | Clilorine        | 15000 |
| 8. | Sulphatis        | 3300  |
| 9. | Chromium         | 300   |

Advance treatment include, mf 10 em, 50 lim, UF MF25 Um, MF5Um, UF, NF, Ro, Thuse are all tertiary stage includes certon fluews also. IRF, Acc (Activated carbon column) Iron removal fitter.

The chrome water in reactor contains Ph3. Mgo added to increase Ph 6-7 the chrome settled as sludge (Givisl *et al* 2011).

The word tanning is derived from tannin meaning acidic chemical compound UNIC. www.unic.itum,(2013)

Chemicals used at each steps are preservation (sodium chloride. Pcp) soaking (Sodium sulphid caustic soda, surfactants) Deliming (Ammonium chloride, ammonium sulphate). Degreasing (Alkyl phenyl ethoxylate). Pre-tanning (Basic chrome salphate), tanning (mineral tannages) Finishing (Cadmium, lead chrome pigment).

**Table-6:**

| Parameter             | Austria Sewer | Clina Sewer | Pakistan Sewer |      |
|-----------------------|---------------|-------------|----------------|------|
| Chrome 3 mg/l         | 1.6           | 1.5         | 1.7            |      |
| Chrome 6              | 0.1           | 0.5         | 0.6            |      |
| Total chrome          | 3.1           | 1.5         | 2.5            |      |
| Oil & grease          | 100           | 100         | 100            |      |
| Phenol                | 20            | 21          | 22             |      |
| Detergent             |               |             |                |      |
| Parameter             | Bangladesh    | Lagos       | Pakistan       | Who  |
| DO                    |               |             |                | 4.5  |
| Sodium                | 367           | 12006       | 12000          | nm   |
| Electric conductivity | 3487          | 42500       | 43000          | -    |
| TDS                   | 3072          | 21300       | 22000          | 1200 |
| Ph                    | 5.7           | 8.3         | 8.5            | 5-9  |
| Cr                    | 1.33          | 10.35       | 11             | 2    |
| Sulfate               | 270           | 280         | 275            | -    |
| Nitrates              | 170           | 190         | 185            | -    |
| Chlorides             | 13.8          | 50          | 44             | 1000 |

| Bangladesh    |      |          |
|---------------|------|----------|
| Ph            | 7.67 | 7.80     |
| Phosphorus    | 50   | 18       |
| Sulfur        | 170  | 27       |
| Chromium mg/L | 9800 | 0.05–0.1 |

40–50m<sup>3</sup> of liquid waste contains COD 175Kg, BOD 60Kg, TSS 125Kgs chromium-3 6Kg, Sulphides 6Kg manages sulfate added for fast reaction as a catalyst for sulphids oxidation to reduce the soluble and suspended organic matter in effluents into carbon dioxides & mineral trio logical treatments methods used: (Bubble aeration systems, Lagoon Systems, Sequencing Batch biofilm reactor (SBBR) ozone is used).

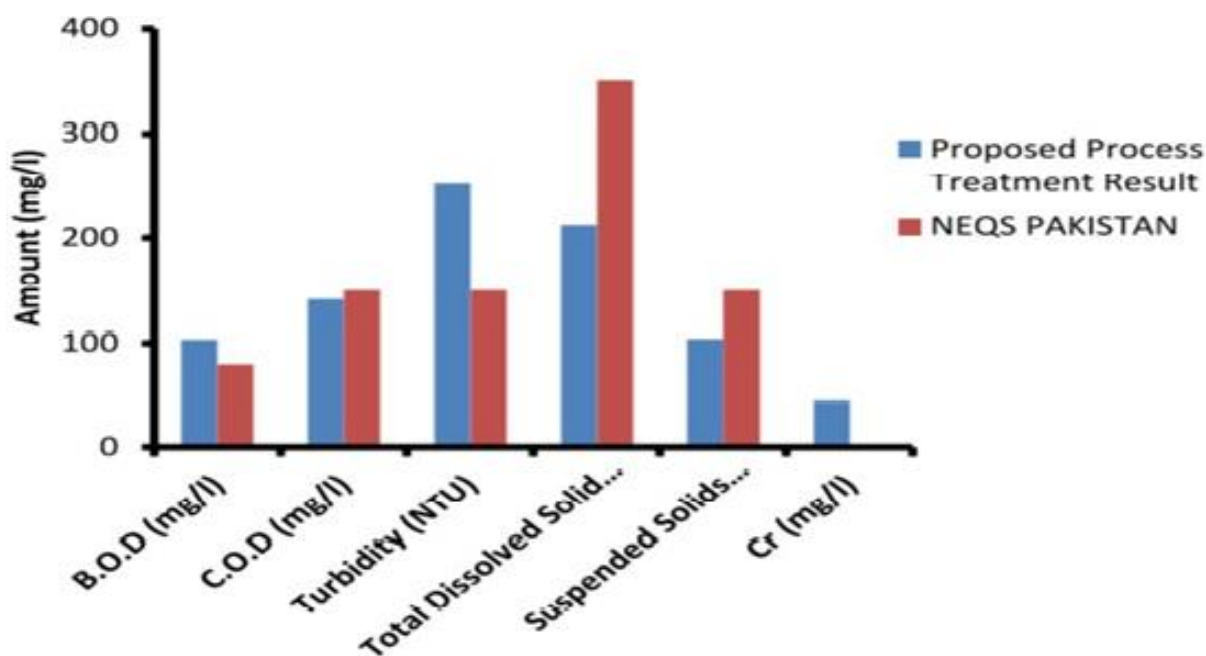
**Other innovative methods are:** (Used activated days in the removal of dyes and surfactants, Use of electro chemical process as alternative biological process. i.e. reformation/ denitrification for removal of pollutants).

**Primary stage:** (Equalization, Neutralization, Sedimentation)

**Secondary Stage:** (Aerobic process, ASP activated sludge process, Aerated lagoons, Trickling)

**Tabel-7 method of analysis by physic-chemical parameters for tannery effluents).**

| S. No | Parameters | Methods of Analysis Used   | Values of Tannery Effluent |
|-------|------------|----------------------------|----------------------------|
| 1     | Chromium   | Colorimetric Method        | 721 mg/L                   |
| 2     | TDS        | Gravimetric Method         | 8672                       |
| 3     | TSS        | Gravimetric Method         | 2295                       |
| 4     | Turbidity  | Digital Nephelometer       | 1550 NTU                   |
| 5     | BOD5       | Microbiological Titration  | 730 mg/L                   |
| 6     | COD        | Closed Reflux Colorimetric | 1155                       |
| 7     | PH         |                            | 6-9                        |



**Figure-1 Comparison parameters by hybrid treatment and NEQS**

**Tabel-8 pollutants removal Efficiency % by coagulant dose and settling time.**

| Dose mg/L | Settling time (hr) | Pollutants Removal Efficiency % |     |     |           |      |     |
|-----------|--------------------|---------------------------------|-----|-----|-----------|------|-----|
|           |                    | Cr                              | TDS | TSS | Turbidity | BOD5 | COD |
| 100       | 12                 | 68                              | 59  | 89  | 49        | 50   | 61  |
| 100       | 24                 | 75                              | 60  | 93  | 48        | 58   | 65  |
| 150       | 12                 | 89                              | 72  | 98  | 70        | 75   | 85  |
| 150       | 24                 | 90                              | 70  | 97  | 75        | 85   | 87  |
| 200       | 12                 | 80                              | 65  | 94  | 69        | 60   | 76  |
| 200       | 24                 | 85                              | 70  | 95  | 67        | 65   | 74  |

Table-9 Design Data Water Consumption.

| Item | Description                                           | Cooling Tower Power plant |
|------|-------------------------------------------------------|---------------------------|
| 1    | H <sub>2</sub> O circulation rate (GPM)               | 35000m <sup>3</sup> /h    |
| 2    | Hot-water temperature (C)                             | 40                        |
| 3    | Cold-water temperature (C)                            | 32                        |
| 4    | Wet-bulb temperature (C)                              | 30                        |
| 5    | Drift loss (%design circulation) (m <sup>3</sup> /hr) | 110m <sup>3</sup> /h      |
| 6    | No of fans                                            | 06                        |
| 7    | Evaporation loss (m <sup>3</sup> /hr)                 | 746                       |
| 8    | Bleed(BD) (m <sup>3</sup> /hr)                        | 746                       |
| 9    | Make up water (m <sup>3</sup> /hr)                    | 1492                      |
| 10   | Price/Loss m <sup>3</sup> /hr                         | 3.9                       |
| 11   | Range                                                 | 8                         |
| 12   | Approach                                              | 2                         |

Table-10 Advance ECO approach Makeup water Savings at TPS.

| Sr. No. | COC | Evaporation | Blow Down | Makeup Advance | Makeup Proposed | Saving |
|---------|-----|-------------|-----------|----------------|-----------------|--------|
| 1       | 2   | 475.5       | 475.5     | 951            | 1919            | 968    |
| 2       | 3   | 475.5       | 238       | 713            | 1427            | 713    |
| 3       | 4   | 475.5       | 158       | 634            | 1268            | 594    |
| 4       | 5   | 475.5       | 118       | 594            | 1189            | 596    |
| 5       | 6   | 475.5       | 95        | 570            | 1141            | 570    |
| 6       | 7   | 475.5       | 79        | 555            | 1109            | 555    |
| 7       | 8   | 475.5       | 68        | 543            | 1087            | 544    |
| 8       | 9   | 475.5       | 59        | 535            | 1069            | 535    |
| 9       | 10  | 475.5       | 53        | 528            | 1056            | 528    |

The Water Conservation from current to propose and then Advanced is the outcome of Researcher Research and by Experiment, the physically, theoretically evidence proof has been achieved in above tables, a handsome amount of water conserved for environment Sustainability, Ref Author previous impact factor research papers at Refinery and Fertilizer cooling tower water Lagging performance Indicators and Thermal Power Plant water conservation targets achieved and performance assurance verified.

**Conclusions:** The values of the characteristic parameters of tannery waste water vary widely and depend. On the raw materials and chemical products used as well as the processing steps. Due to growing environmental concerns and worldwide fresh water shortage, clean technologies and water re-use, Nitrogen removal and advanced treatment system are being developed and adopted in order to avoid water.

**Recommendation:** Dirty water is one of the most serious environmental challenges that the people of Pakistan and also global leather sectors are facing at a very large level. This is the main concern area for ecological amelioration in this area. This area needs main focal point and calls for instant attention and asset. It is recommended that in residence development be undertaken instantly. This has

possible to decrease the pollutants as well as the hydraulic weight to a degree where end-of-pipe tools may then be able to bring it downward, furthermore to level close to the NEQS. The management of sulphide having effluent will be kept disconnect and Ph high above nine because low ph lesser than nine the configuration of toxic H<sub>2</sub>S gas may happen, NEQS level of sulphide is 2 mg.

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