PROCESS BASED WATER FOOTPRINT ASSESSMENT IN SELECTED LEATHER GOODS MANUFACTURING INDUSTRY OF SIALKOT, PAKISTAN

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ABSTRACT

Sialkot is considered as one of the largest Leather producing city in Pakistan. The manufactured Leather and Leather products are also imported to many countries. There are many researches have done on Leather tanneries in order to identify the health risks, water risks and solution to these problems have proposed. This research work involves the calculation of Water Footprint which tells about the amount of water uses in the reprocessing of wet blue hide which referred as BWF, and also the amount of fresh water required to dilute pollutants in the sludge before discharging it into water body and this is referred as GWF. Water is normally used in five processes which are Wet Wash, Re-chroming, Neutralizing, Re-tanning and Finishing. Finishing processes generally carried out in Spray Plant where further desired dye is given to dry Leather. By using their process chart sheet, input of water for each process has calculated and The BWF was 134.604 liters which was calculated by adding the total DWC i.e; 108.644 liters and virtual water content i.e; 25.96 liters. For GWF, water samples have collected in bottles from the drums. The waste water as a result of those processes was then analyzed for heavy metals i.e As, Cr, Cd, Cu and Pb, BOD and COD. Then GWF has calculated for those pollutants which exceed the permissible limit of NEQs. In the analysis of waste water samples As, BOD, COD and Cr exceeds the permissible limit of NEQs so calculated GWF for As, BOD, COD and Cr was 1mg/l, 113.37mg/l, 100.2mg/l and 100.8380mg/l respectively. GWF tells about the fresh water required for the dilution of those contaminants before discharging it into canal. In addition to extracting fresh/ raw water for re-processing of wet blue hide, fresh water will also have to be extracted to reduce pollutants in the waste water before discharging it into the water body. Blue Water Footprint and Gray Water Footprint have calculated separately to better understand the detailed water consumption on daily basis.

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Al -	Aluminum
As -	Arsenic
ASP -	Activated Sludge Process
BOD -	Biological Oxygen Demand
BWF -	Blue Water Footprint
Cd -	Cadmium
Cr -	Chromium
Cu -	Copper
CEPT-	Common Effluent Treatment Plant
COD -	Chemical Oxygen Demand
DWC -	Direct Water Consumption
GWF -	Gray Water Footprint
KOH-	Potassium Hydroxide
L -	Liter
Mg -	Milligrams
NEQs -	National Environmental Quality standards

Pb -	Lead
Ph -	Negative Log of Hydrogen Ion Concentration
ppm	Part per million
ppt	Part per trillion
Ti -	Titanium
TDS -	Total Dissolved Solvents
TWC -	Total Water Consumption
VWC -	Virtual Water Consumption
VWF -	Virtual Water Footprint
WF -	Water Footprint

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CHAPTER 1

INTRODUCTION

The increasing growth of global population combined with the accelerated rate of economic growth have changed to a significant impact on agricultural and industrial needs, which in turn, has had a number of far reaching consequences, one of which is the increased demand for large quantities of good quality freshwater(Charchousi, Tsoukala, & Papadopoulou, 2012). In the recent years, environmental regulations have been tightened to improve the quality of treated waste water. An extensive variety of technologies for treatment of waste water have been developed for elimination of heavy metals from industrial effluent before being discharge into water body. Although many different methods can be employed to treat wastewater filled with heavy metals, and it is so important to choose the most suitable treatment for waste water contaminated with metals, depending on few elementary parameters such as pH, preliminary metal concentration, the general treatment execution contrasted with different advances, natural effect just as financial aspects boundary, for example, the capital venture and operational expenses (Barakat, 2011). Because of the release of a lot of metal-polluted wastewater, ventures bearing weighty metals, are the most unsafe among the compound serious businesses. Because of high solvency of hefty metals in the oceanic situations, living creatures can retain them and once they enter the evolved way of life, enormous groupings of substantial metals may aggregate in the human body (Barakat, 2011).

Tanneries have been constantly viewed as one of the most fouling businesses described by low innovative degree of its tasks. Leather industries change crude or wet-blue skins into items utilized for shoes assembling, garments and gloves, calfskin products and others. This change requires a progression of synthetic and mechanical medicines. Substance measures are acknowledged in synthetic reactors (tumblers) in which the skins respond with various synthetics (acids, antacids, chromium salts, colors, and so forth.) in watery arrangements (Cassano, Molinari, Romano, & Drioli, 2001).

1.1 Import of Chemicals

The Pakistan Institute of Trade and Development (2012) indicates that 90 %of the dyes and chemicals used are imported which are used in the tanning sector, mainly from Germany, Spain and Italy, while the remaining 10% is from domestic production by international companies mainly, Bayer, BASF and Clariant (Dr Conor Linstead, 2015).

1.2 Leather Goods Industry

Cowhide industry, including calfskin items, is the second biggest fare gaining section after textiles in Pakistan. This area can possibly increase volume of fares with the improvement of value and enhancement in various scope of items, uniquely pieces of clothing and footwear. Cowhide pieces of clothing and footwear is a vocation arranged part giving work to a huge fragment of the general public other than procuring unfamiliar trade for the nation. The calfskin business comprises of six sub-areas in particular, Tanning, Leather Footwear, Leather Garments, Leather Gloves, Leather Shoe Uppers, and Leather Goods. The Tanning business assumes an essential function in the advancement of these sub-divisions by giving the fundamental material for example cowhide. Today, Pakistan is among the main nations in the creation of Leather Garments and Gloves. The cowhide and calfskin made-ups industry assume a noteworthy part in the economy of Pakistan.

In Pakistan there are in excess of 2500 tanneries (registered& Un enrolled) and footwear producing units running in Pakistan. Throughout the long term, the quantity of enlisted tanneries in the nation has expanded from 529 out of 1999 to 600 of every 2003 and to 725 in 2016 (Pakistan Bureau of Statics). These are situated in Karachi, Hyderabad, Lahore, Multan, Kasur, Faisalabad, Gujranwala, Sialkot, Sahiwal, Sheikhupura and Peshawar. The increment in the quantity of tanneries and expanded fare can be ascribed to increment popular of tanned calfskin in the overseas market.

1.3 Tannery Operations under study

The cowhide creation measure is protracted and includes a few stages which must be completed before the real tanning is finished. Each progression is significant and ordinary looks at should be conveyed to guarantee that the best nature of leather is delivered. In tannery leather hides or skins are referred as Wet Blue Hides. Leather hides or skin are treated in the aqueous medium results in discharging the waste water which contain high amount of organic as well as inorganic content. Leather manufacturing industries take wet blue as a raw material and then further process that wet blue according to their requirements. Fig. 1.1 shows the processes flow chart carried out in the leather tannery. In some of the processes water is used which are of main concern in this research and remaining are the drying processes of leather.

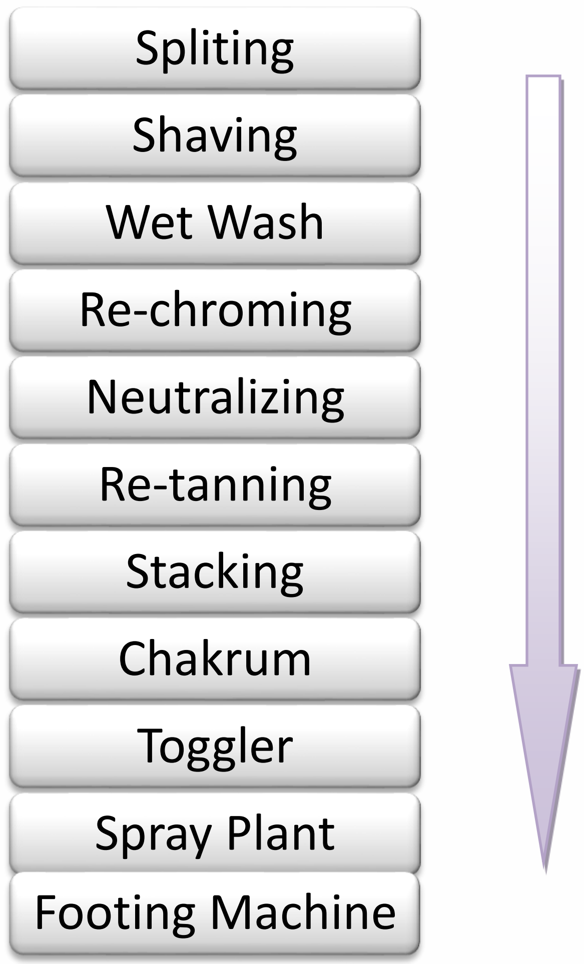

Fig.1.1: Flow chart of processes occur in tannery.

When tannery imports wet blue hides from primary tanneries the process starts with the splitting and shaving of wet blue hide. The processes in which water involved are Wet Wash, Re-chroming, Neutralizing, Re-tanning and finishing.

1.3.1 Splitting

Wet blue hides cut into two horizontal layers through splitting machine in order to get a uniform thickness as shown in Appendix A. The top layer is known as grain side and used to produce fine and even granule leather. The base is used for split cowhide for different employments. When the splitter splits the wet blue hide it also reduces small amount of moisture in it.

1.3.2 Shaving

Split wet blue hide was then send to shaver machine. See image in Appendix B. By passing through this machine unwanted flesh has removed from hide to prepare it for tanning processes. It is important to remove unwanted flesh from the hide so that chemicals can easily penetrate into the hide and give best quality of leather.

1.3.3 Wet Wash

The process of wet wash occurred in a huge drum operated electrically. This process took around 40 minutes. In this drum, wet blue hide was treated with water so that it regains its moisture content and removing extra dirt, excessive chemicals and flesh if present on the hide. Then water had removed from the drum and hide was then piled up for the next process.

1.3 4 Re-chroming

This process was also carried out in a drum. Chromium along with other agents was added to the drum with fresh water so that skins absorb those tannins and retain chromium content. This process took 40-45 minutes so that all the tannins and chromium completely penetrate into the hide. This process also increases the pH level of the hide up to 10. By re-chroming the skin is irreversibly artificially protected and changed over into the leather material. Waste water was then drained out and wet blue hide was piled up.

1.3.5 Neutralizing

The process of neutralizing also carried out in a drum. During re-chroming pH of the hide increases so this process is done to minimize the pH up to 6 to 7. For this water had added to the drum along with few agents which minimized the pH level in the hide so that the tanning reagents can easily penetrate into hide to give it desired color. This process took around 40 to 45 minutes. After draining the waste water, hide was piled up for dying process.

1.3.6 Re-tanning

The process of Re-tanning also occurred in the drum. The image is shown in Appendix C. The purpose of re-tanning is to give desired color to the hide. During this process desired colors added to the wet blue hide along with oils so that it tightened lose grains and filled the gaps. After 40 to 45 minutes the wet blue hide piled up and hanged in the air for drying. And the waste water was drained from the drum. The purpose of drying the leather is to reduce moisture content up to 12% for better quality of leather.

1.3.7 Finishing

Finishing involves different steps and it started with drying of leather. It is important to keep in mind that the leather should not completely dry as drying will reduce moisture content in the leather. For best quality of leather there should be 12% of moisture content in the final leather. Following are the further steps.

- **Stacking**

After drying the leather was pile up and stacked according to the desired product. For manufacturing of garments dried leather is stacked and directly sent to the Toggler to removed wrinkles. And for the manufacturing of gloves dried leather sent to the Chakram.

- **Chakram**

Chakram is a huge drum. Dried leather had put into the drum and processed in order to gain more softness.

- **Toggler**

Stacked leather and leather from Chakram was then sent to the Toggler machine. Toggler is a screen like machine which rotates along the rod. See image in Appendix D Workers locked the leather on the screen and stretched it again and again in order to remove wrinkles from the leather.

- **Spray plant**

After removing wrinkles from the leather, it was then sent to the spray plant. Spray plant is a machine with a rotating spraying nozzle and a burner attached to it. If the leather color faded out, then dyes mixed with various chemicals sprayed on the leather to get the desired color. This spraying introduces moisture in leather, so it is then entered into the burner and where it gets dried. Workers checked the color of leather and sent it to the footing machine.

- **Footing machine**

Footing machine measured the leather width, length and thickness and remove excessive or unwanted corners. Finally, leather is reviewed and stacked for sewing purpose.

Table 1.1: Chemicals used during the processes of leather.

Processes	**Chemicals**
Wet Wash	Bemanol DA
	Oxlic Acid
	Acitic Acid
	Novoil LG
	Acid Bate 7702
Re-chrome	Novoil FST
	Novoil TS
	T 25

	Salt
	Formic Acid
	Sulfuric acid
	Hexatan PMA
	Veshnu Chrome
	Catalix L
	Sod. Formate
	Sodium Bicarbonate
Neutralizing	Tanigan PAK
	Sodium Formate
	Sodium Bicarbonate
	Novoil TS
Dying (1)	Novoil TS
	Novoil FST
	T 25
	Formic acid
Dying (2)	Formic acid
	Green BS
	Brown 1288

1.4 Definitions

1.4.1 Water Footprint

The water footprint is utilized to evaluate water asset net necessities for items and administrations (Hoekstra, Chapagain, Aldaya, & Mekonnen). It may be estimated for a solitary cycle, for example, developing rice, for an item, for example, some pants, for the fuel we put in our vehicle, or for a whole global organization. The water footprint can likewise reveal to us how much water is being devoured by a specific nation – or universally – in a river basin or from a spring. It calculates all the straight and divergent usage of water involved in the products manufacturing or services and incorporates water utilization and contamination all through the full creation cycle from the flexibly chain to the end-client. WF calculation methodology helped to perform evaluation of the trend for restructuring processes for industries and it is obvious that these actions lead to improved water resources management independent the applied calculation methodology (Charchousi et al., 2012).

1.4.2 Green Water Footprint

Green water footprint mentions to the utilization of green water assets i.e rain water, for example evapo-transpiration from agriculture and forest area (Veettil & Mishra, 2016). Water from precipitation put away in the root zone of the dirt and dissipated, happened or consolidated by plants. It is especially applicable for farming, green and ranger service items.

1.4.3 Blue Water Footprint

Blue water footprint is the human water utilization from blue water assets and it may be evaluated dependent on the volume of surface and groundwater devoured because of the creation of a decent or administration (e.g., homegrown, mechanical, power creation, water system, and so forth. (Veettil & Mishra, 2016). Blue water footprint is also referred as total water consumption (TWC).

1.4.4 Grey Water Footprint

The Grey Water Footprint (GWF), is the volume of raw water needed to absorb the heap of poisons released into water (Li, Liu, Yang, & Hao, 2016). It considers point-source contamination released to a freshwater asset straightforwardly through a line or by implication through overflow or filtering from the dirt, impenetrable surfaces, or other diffuse sources.

1.4.5 Virtual Water

Water which is stored or embodied in a product is called virtual water. Water is stored in a virtual sense not in physical sense. The stored water states to the water which is required to produce that particular product and it is stored throughout the life cycle of that product. Virtual water also known as “embedded water”(Hoekstra, 2003).

1.5 Water Footprint for Industries

For industrial systems, blue and grey water footprints are the largest than green water footprint (Mekonnen & Hoekstra, 2012). For many industries and production processes water footprints was calculated to better understand the different water risks and provide specific recommendations to reduce the risk (Gu et al., 2015).

Similar unnatural quickened maturing considers were directed between a cow-like cowhide tanned with eco–accommodating Ti–Al based salts, by another technique, and of a similar calfskin tanned with Cr (III) salts by an old-style strategy. Of the two tanned leathers the differences in photo-stability designs, created by the tanning operators, will be useful in increasing new and more profound information about the tanning specialist calfskin surface science, supplanting wet–blue cowhide with wet–white calfskin and the picking of appropriate photo-stabilizers (Rosu, Varganici, Crudu, Rosu, & Bele, 2018).

Creature creation and utilization assume a significant part in draining and contaminating the world's undermined freshwater assets, so data on the water footprint of creature items will assist us with seeing how economically scant freshwater assets be use (Mekonnen & Hoekstra, 2012).

1.6 Water Footprint in Leather Industry

The water footprint (WF) for finished leather includes the WFs for all raw materials that are used in processing, such as tanning chemicals. Estimating the water footprint for the many complex products used by the tannery sector in Pakistan would be very challenging. However, using information published by others the approximate water footprint figures for the processes involved in the manufacturing of leather have been established by weight and, based on the quantities used, their total contribution to the water footprint of finished textiles has been estimated.

1.7 Purpose of Water Footprint

Improvement in the efficiency of water resource utilization is the key measures to mitigate water shortage problems. For this administration is anticipated to endorse the optimizes distribution of water ration furthermore, support the modern divisions toward low water utilization, additionally empower virtual water utilization by creation to limit the nearby water asset use (Ma, Xian, Zhang, Zhang, & Ouyang, 2015). In order to reduce the WF promote maintainable utilization of water, improve innovation with water usage and collective approaches that focus on various components of natural and assets the board ought to be planned (Tian et al., 2018). The gray water footprint (GWF), measures the amount of raw water needed to weaken the contaminations in industrial sewage. The information yield approach can ascertain immediate and backhanded progressions of materials in conclusive items all through the creation chain, as it has been known as an appropriate device to reflect the main origin of natural effects by every area in the general monetary framework (Li et al., 2016).

1.8 Contaminants in Leather Industry Sewage

Tanning industry is characteristically considered as impurities generated trades that harvest inclusive diversities of noxious elements. It is known a genuine ecological danger because of high synthetic levels including saltiness, natural burden (substance oxygen burden or request, organic oxygen request), inorganic matter, suspended solids, alkali, explicit toxins (sulfide, chromium, chloride, sodium and other salt buildups) and heavy metals and so on. Huge volume of water is utilized for the cycle of calfskin tanning of which 90% of the water is released as slime. During the chrome tanning measure, 40% unused chromium salts are generally released in the last effluents, which is a genuine danger to the earth (Chowdhury, Mostafa, Biswas, & Saha, 2013).

Wastewater coming from different operations from leather tanneries contains high level congregations of non-chemical, manmade constituents and heavy metals triggering important polluting occurrence. Natural contaminations originate from skins or they are presented during the working cycle while Inorganic toxins are surviving from the pre-owned synthetic substances that are not totally fixed by skins because of the low productivity of the activities (Cassano et al., 2001).

The modern effluents contain significant measures of both inorganic and natural synthetic concoctions and their side-effects. Most businesses are in little scope division and are not having any drain lines. Indeed, even today the vast majority of them don't have appropriate wastewater treatment plants and they release modern effluents in unlined channels and streams accordingly causing tremendous tainting of air, water and soil (Bougherira et al., 2014).In the leather industry, chromium ions are released into rivers by waste water after chromium contamination. The presence of chromium is a problem not only for human health, but also for the environment(Rezić & Zeiner, 2009)

1.9 Effects on Human Health

The 21st century opened with one of the most vital issue of human's access to basic water services. In the developing world billion of individuals don't approach safe drinking water and suitable sanitation systems needed to minimize revelation to diseases caused by polluted water. Nearly one-half of the people in the developing world suffer from the water related diseases such as; cholera, typhoid, diarrheal diseases (Gleick, 1998).

Because of the release of a lot of metal-polluted wastewater, enterprises bearing heavy metals, are the most dangerous among the substance concentrated businesses. Because of high dissolvability of heavy metals in the amphibian conditions, living creatures can assimilate them and once they enter the evolved way of life, enormous convergences of heavy metals may gather in the human body (Barakat, 2011).

The direct release of modern effluents may have immense effect on physico-concoction and natural properties of soil identified with soil richness. Effluents from cowhide handling, a significant industry that produces colossal volume of waste water typically released to inundate rural terrains. As a result of leather processing, tannery waste water contains some proteinous waste, salts and chromium (Cr), that may influence soil cycles and yield creation (Narasimha & Reddi, 2012).

1.10 Study Objectives

- To evaluate the water consumption footprint (WCF) in Leather manufacturing industries.
- To analyze the contaminants in the effluent in order to find the gray water footprint.

CHAPTER 2
MATERIAL AND METHODS

2.1 Study Area

Sialkot is Pakistan 12th most populous city located in north-east Punjab. The geographic coordinates of Sialkot are 32.4945° N, 74.5229° E. In this research water footprint had been calculated for the JMS Tradewell International pvt ltd. It is located at the 13km Wazirabad road, Sahowala, Sialkot, Pakistan. It is a national export award winning company specialized in the Tanning of leather for fashion and motorcycle garments, shoe upper and lining, bags along with Denim garments, gloves and accessories.

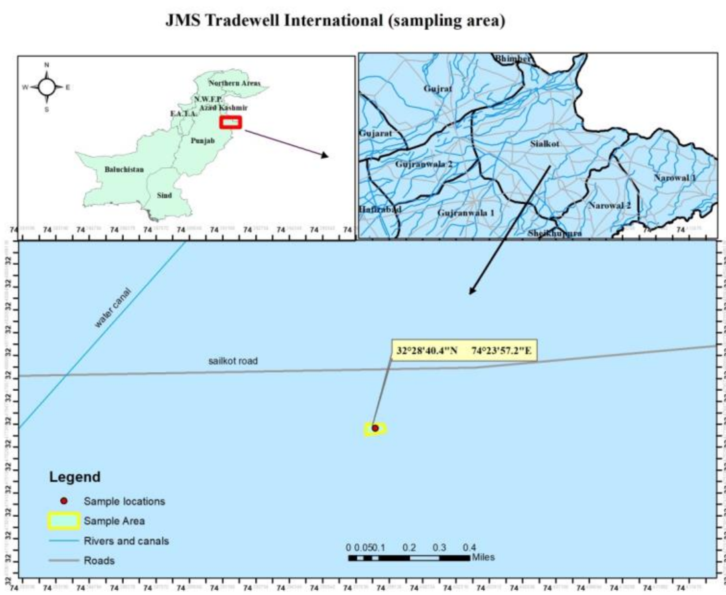

Fig: 2.1: Map of the area under study.

2.2 Sampling Type

Purposive non-probability sampling technique has been used for this study. As this research is about the total water consumption in the leather manufacturing industry and five processes which are Wet wash, Re-chroming, Neutralizing, Re-tanning and Finishing have been observed. For these five tannery processes water had used. Volume of raw water used in the reprocessing of leather had been noted by using hide chart sheet of the tannery. After the calculation of volume of raw water, samples of waste water from the drums as a result of different tannery processes i.e. Wet wash, Re-chroming, Neutralizing, Re-tanning and finishing were collected in the propylene bottles and stored at 3.85-4C until analysis.

2.3 Analysis

2.3.1 Chain Summation Approach

Two techniques can be utilized to figure water footprint: the chain summation approach and the stepwise accumulative methodology. Chain summation approach is for the most part utilized for such creation frameworks which just produce one item yield. The water footprint co-related with the few stages in the creation framework can be totally credited to the item that outcomes from a framework. Though the stepwise accumulative approach is the overall water footprint estimation process. This approach is builded on the water footprint of ending process or step in the manufacture of desired or last product (Gu et al., 2015). The processes chain of leather manufacturing industry includes Wet Wash, Re-chroming, Neutralizing, Re-tanning, drying processes of leather and Fat-liquoring. Fig.2.1 shows the processes involved in the lather industry. In this research Chain summation approach has used because there was a single product output which is leather.

2.3.2 Blue Water Footprint

BWF or water consumption footprint was calculated by using given equation;

$$WCF=DWF+VWF \qquad 1$$

In the above equation WCF is the water consumption footprint, DCF is the direct water footprint and VCF is the virtual water footprint.

2.3.3 Direct Water Footprint

Direct WF was calculated by using given equation,

$$DWF= WF\ (obtained) – WF\ (discharge) – WF\ (loss) \qquad 2$$

Here, WF (obtained) is the quantity of water attained, WF (discharge) is the volume of direct water ejection and WF (loss) is the loss of water due to evaporation, water embedded during the processes.

Direct water footprint has been calculated for each of the process; Wet wash, Re-chroming, Neutralizing and Re-tanning involved in the reprocessing of blue hide. For this input and output of the water has been noted.

2.3.4 Virtual Water

Virtual water was defined as the final moisture content or stored water in the product which is embedded for the duration of the existence pattern of an item. After drying the leather moisture content in the dried leather should be 12%. if moisture content reduces below 12% then water is again introduced in the leather in order to produce best quality of leather. as this 12% of moisture content is present throughout the life cycle of leather so it is considered as the virtual water for leather.

2.3.5 Gray Water Footprint

This research also focused on the estimation of gray water footprint and it includes trade manure managing. In the estimation of the grey water footprint of industrial slop, sewage from reprocessing of leather was collected, calculating the water required to dilute that pollutants meeting the National Environmental Quality Standards for Surface Water what's more, treated before being released. The measure of dilution water required (Yi) depends on fulfilling the Environmental Quality Guidelines for Surface Water of Pakistan or the Seawater Quality Standard of Pakistan.

Yi has calculated by using the following equation;

$$Yi = Xi/ Qi \qquad 3$$

Where, Xi is the calculated average value of pollutant concentration of the sewage sample and Qi is the National Environmental Water Quality Standard of wastewater discharge for pollutant i. MAX [Yi] was the final grey water footprint. The above equations has been used to measure the water footprint in leather manufacturing industries (Gu et al., 2015).

2.4 Parametric Analysis

Other physiochemical parameters includes pH, Biological Oxygen Demand, chemical oxygen demand, total dissolved solids, salinity, and conductivity and five heavy metals i.e Cadmium (Cd), Arsenic (As), Chromium (Cr), Copper (Cu), and Lead (Pb),were also calculated.

2.4.1 Biological Oxygen Demand (BOD)

In waste water microorganisms used dissolved oxygen during the oxidation of concentrated constituents and the measurement of that dissolved oxygen is known as BOD. Readily biodegradable carbonaceous and nitrogenous substances are the main sources of BOD as these are the most common materials or by-products of animal and plants wastes and also domestic and industrial wastes. Though there are standardized methods for the measurement of BOD in waste water which are remain unchanged for years but in this research APHA 22^{nd} Edition has used as reference method for BOD and for the quantification of BOD Lovibond BOD Tintometer had used.

2.4.2 Chemical Oxygen Demand (COD)

COD is the quantity of dissolved oxygen which is mandatory to source oxidation of the organic substantial in water. It is commonly measured in mg/L.BOD and COD, both are important indicators of the environmental health of a surface water supply. It is commonly measured in waste water treatment(Patil, Sawant, & Deshmukh, 2012). In this research COD has calculated using COD reactor and APHA 22^{nd} Edition had used as reference method.

2.5 Instruments

The assessment of heavy metals has been done using the AA-7000 and AAS Vario 6. BOD had assessed by Lovibond BOD Tintometer and COD had assessed by using COD reactor (Hach model 45600). APHA ^{22nd} Edition had used as a reference method for As, BOD and COD. Results were then compared against the National Environmental Quality Standards for Municipal and Liquid Industrial Effluent, 1999. pH meter has been used for the physicochemical parameters. Before analysis meter was first regulated. By dipping the probe of the meter into waste water samples, readings were recorded.

- **pH meter**

A portable pH meter was used to determine the pH of the samples right after the samples had been collected from the drum where the leather processes had been carried out. But before this pH meter was calibrated with buffer solution of pH for better results. The samples were poured into 250ml ml beaker one by one and probe of the pH meter dipped into samples and readings for each samples were recorded. The same pH meter was used to determine conductivity, salinity and total dissolved solvent (TDS) in the samples of waste water.

Fig 2.2: pH meter to determine pH, TDS, conductivity and salinity.

- **AA-7000**

For the determination of heavy metals atomic absorption equipments, AA-7000 and AAS Vario 6 had used. This series accents high sensitivity analysis. The sample was first filtered using syringe filter sartorius CA 0.2µm. See image in Appendix E.

The equipment was first calibrated with blank sample for better results. The filtered water samples were then poured into the 250ml beaker individually and with the help of nebulizer the tests were brought into the molecule cell where it is first desolvated and afterward atomized. The analyte molecules so framed at that point quantitatively assimilate light in a manner that is relative to the grouping of the iotas of the analyte in the cell. The light, which is at the particular frequency, is then secluded from different frequencies that might be produced by the molecule cell and afterward distinguished.

Fig 2.3: Instrument used to detect heavy metals in waste water samples.

- **COD reactor (Hach model 45600)**

COD in the waste water samples of wet wash, Re-chroming, Neutralizing, Re-tanning and finishing had measured by Hach COD reactor. Dichromate Digestion method had used for the determination of COD. Before the analysis all the waste water samples were filtered by using syringe filter so that all the micro fibers should be removed.

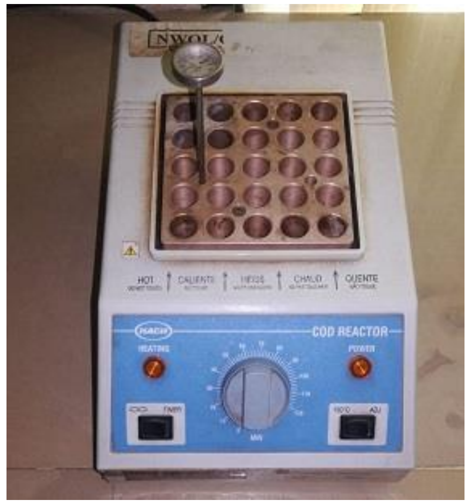

Fig 2.4: Equipment used for the measurement of COD in waste water samples.

Before analysis, samples had homogenized simply by stirring system or shaking with hand. According to the location of the samples range of COD vial and volume of samples had selected. The COD reactor had turned on and adjusted at the 150^{o}C temperature and the whole batch was heated for 120 minutes. Then the vessels were allowed to cool to 12^{o}C or fewer. Separately vessel was overturned few times and sited in a stand till it come to the room temperature then COD was measured by selecting saved program on colorimeter. COD adapter was fixed into the cell. After cleaning, the reference tube had inserted in adaptor and covered with instrument cap and pressed ZERO. This displayed 0 mg/l COD. Now clean outside of the sample tube and placed in the adaptor properly and covered tightly with instrument cap and pressed READ and readings were noted for each sample.

- **Lovibond BOD Tintometer**

BOD in the waste water samples had measured by Manometric Pressure Measurement method by using Lovibond BOD Tintometer.

Fig 2.5: Thermostat cabinet used for the measurement of BOD.

Before the analysis Bod containers and blending poles were cleaned with teepol and flushed with hot water and afterward at long last cleaned with de-ionized water. The temperature of the thermostat was set at 20^o C. Before analysis, pretreatment which was filtering of the samples were carried out. The filtration of the samples had done by syringe filter in order to remove micro fibers. Then the extent series for the samples was evaluated and the size of the samples was carefully chosen. By using overflow measurement flask, the volume of the samples was measured exactly and transferred to BOD bottles. At that point the cleaned attractive blending poles were embedded in the BOD bottles. 3-4 drops of potassium hydroxide (KOH) solution were set into the fixed gasket and afterward embedded the gasket in the bottle rack. The BOD sensors were firmly screwed to test bottles and put appropriately in the container rack. To start the measuring unit “ESC” had pressed. The incubation time of unit was for 5 days. After pressing START the READ button was pressed to record BOD measurements.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Water footprint of leather industry

3.1.1 Direct Water Consumption

In this study JMS Tradewell International pvt ltd in Sialkot, Pakistan was used as a case. This industry offers production processes for leather and leather products using wet blue hide (cow hides). The industry produces about 2500 to 30000 square feet per day leather based on demand using approximately 40 tons of water. According to general system investigation method, the DWF of the industry was 108.644 liters shown in the table given below, within 4-5% error, considering 2% water loss by evaporation, infiltration. This means 98% water is consumed for reprocessing of wet blue hide in the industry.

Table 3.1: Measured or calculated values of blue water footprint using Direct water consumption (DWC) and virtual water consumption (VWC) in liters.

Processes	DWC (L)	TOTAL DWC (L)	VWC (L)	TWC (L)
Wet Wash	103.97	108.644	25.96	134.604
Re-chrome	2.17			

Neutralizing	1.884			
Washing	0.22			
Dying 1	0.2			
Dying 2	0.2			

Table 3.1 shows the amount of fresh water used in different tannery processes i.e, Wet wash, Re-chrome, Neutralizing, Re-tanning and dying was 103.97 liters, 2.17 liters, 1.884 liters, 0.22 liters, 0.2 liters and 0.2 liters respectively which is represented as direct water consumption (DWC). Sum of all the DWC was 108.644 liters which was referred as total DWC. As defined that VWC is the final moisture content in the dried leather which was 12% and 25.96 after converted into liters. TWC was calculated by adding total DWC and VWC which was 134.604 liters. TWC is representing blue water footprint for the industry showing the estimated amount of fresh water used by the industry for the reprocessing of wet blue hide.

3.1.2 Virtual water

Virtual water is distinct as embedded water in product. For the best quality there has to be 12% of moisture content in the finished leather which remains in the leather and its products for the entire life cycle of leather product. That moisture content is virtual water of leather. So, there was about 25.96 liters of virtual water as shown in the table 3.1.

3.2 Gray Water Footprints

As a result of different tannery processes i.e, Wet wash, Re-chrome, Neutralizing, Re-tanning and Finishing, waste water from the drums had collected in bottles in order to measure heavy metals, which were As, Cd, Cr, Cu and Pb and BOD and COD. The observed values for As, Cd, Cr, Cu and Pb and BOD and COD are given in table 3.2. As highest values were measured for As, Cr, BOD and COD so gray water had calculated for these four contaminants using equation 3.

Table 3.2: Measured or calculated values for gray water indicators in mg/L.

Processes	As	Cd	Cr	Cu	Pb	BOD	COD
Wet Wash	0.0689	0.0065	6.68	0.4664	N.D	880	1580
Re- chrome	0.1025	0.0228	100.8380	0.9064	0.0103	9070	15030
Neutralizing	0.0498	0.0214	100.4427	0.4770	N.D	7900	1470
Re-tanning	1	0.0269	49.5438	0.5721	0.2376	9020	14080
Finishing	BDL	0.0053	0.8093	0.1459	N.D	725	1395
NEQs	1.0	0.1	1.0	1.0	0.5	80	150

Table 3.2 tells about the results of five heavy metal i.e, As, Cd, Cr, CU and Pb, BOD and COD in the waste water samples from different tannery processes, Wet Wash, Re-chroming, Neutralizing, Re-tanning and Finishing. NEQs for municipal and industrial effluent are also presented in the table to show the permissible limit for each of the contaminant. These results were further used for the calculation of GWF which is discussed below.

3.2.1 GWF for Arsenic (As)

The concentration of the As in the waste water samples was determined by using APHA 22nd Edition for Wet wash, Re-chroming, Neutralizing, Re-tanning and Finishing processes. The determined values for As are given in the table 3.2. The concentration of As in waste water samples of Wet wash, Re-chroming and Neutralizing were 0.0689 mg/l, 0.1025 mg/l and 0.0498 mg/l respectively. In Re-tanning concentration of As were equivalent to the permissible limit that is 1 mg/l and in the water samples of Finishing process the concentration was below detection limit. During Re-tanning of leather different dyes, oils and chemical like formic acid were mixed with water to give leather a desired color. These increases the As concentration in the waste water. So, Max Yi for As was 1, which means 1 mg/l of fresh water is required to dilute As in waste water samples before discharging effluent in stream (Gu et al., 2015). It is important to dilute As in the waste water because of its chronic exposure to drinking water causes a variety of skin lacerations such as melanosis, leuko-melanosis and keratosis. More demonstrations consist of blood vessels, including neurological effects, maternal problems, hypertension, diabetes mellitus, respiratory illnesses and cardiovascular sicknesses, and most commonly skin, lung and bladder cancers. It looks as if that the skin is comparatively sensitive to the effects of As(Rahman, Ng, & Naidu, 2009).

3.2.2 GWF for Cadmium (Cd)

For determination of concentration of Cd in waste water samples, samples were tested against AA-7000. The concentration of Cd in water samples of Wet wash, Re-chroming, Neutralizing, Re-tanning and Finishing was 0.0065 mg/l, 0.0228 mg/l, 0.0214 mg/l and 0.053 mg/l correspondingly. According to national environmental quality standard for municipal and industrial discharge, the defined limit of Cd in waste water samples is 0.1 mg/l, and the concentration of Cd was below the permissible limit in each sample of water. So, no fresh water is required to dilute the concentration of Cd in effluent.

3.2.3 GWF for Chromium (Cr)

In order to measure the concentration of Cr in waste water samples, AA 7000 instrument has used, and the results are shown in table 3.2. For different tannery processes i.e, Wet wash, Re-chroming, Neutralizing, Re-tanning and Finishing the concentration of chromium was 6.68 mg/l, 100.8380 mg/l, 100.4427 mg/l, 49.5438 mg/l and 0.8093 mg/l correspondingly. It has noted that concentration of Cr was much higher in the samples of Re-chroming and Neutralizing processes while in the sample of Finishing process the concentration of Cr was much lower. During the process of Re- chrome, the addition of Chromium along with other chemicals and water, increases the chromium content in the waste water and when re-chromed wet blue hide is processes to retain the pH in leather in neutralizing process it also increases the content of Cr in waste water of neutralizing process because wet blue hide has soaked that chromium and chemicals.

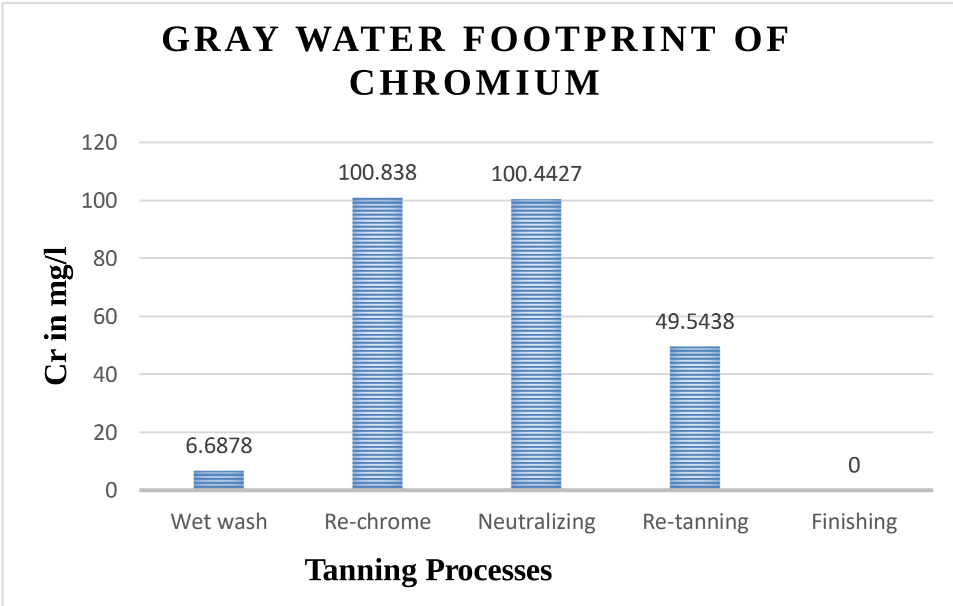

Figure 3.1: Graphical representation of gray water footprint of chromium.

Figure 3.1 shows the calculated gray water footprint of Cr for processes Wet wash, Re-chrome, Neutralizing, Re-tanning and Finishing which are 6.6878 mg/l, 100.838 mg/l, 100.4427 mg/l and 49.5438 mg/l respectively. The calculated Max Yi for Cr was 100.8380 mg/l, which shows that 100.8380 mg/l fresh water is required to dilute Cr in the waste water before discharging it into Upper Chenab Canal through drainage pipelines/system(Gu et al., 2015).

If polluted water is directly discharged to the water body, it will be dangerous not only for aquatic life but also for humans. A definite amount of Cr is important for the proper functioning of organisms but when its concentration increases it may cause serious health issues.

3.2.4 GWF for Copper (Cu)

The concentration of Cu in waste water samples from different tannery processes was also calculated using AA 7000 and values were compared with the permissible limit defined in NEQs for Municipal and Industrial Liquid Effluent, 1999, given in table 3.2. The concentration of Cu in samples of five tannery processes, Wet Wash, Re-chroming, Neutralizing, Re-tanning and Finishing, was 0.4664 mg/l, 0.9064 mg/l, 0.4770 mg/l, 0.5721 mg/l and 0.1459 mg/l respectively. The concentration of Cu in each water sample was below the limit as per defined in NEQs for Municipal and Industrial Liquid Effluent, 1999, i.e, 1 mg/l, so no fresh water was required for dilution of Cu.

3.2.5 GWF for Lead (Pb)

To determine the concentration of Pb, waste water samples were tested in AA 7000. The concentration of Pb in water sample from different tannery processes is given in table 3.2. in the water samples of Wet wash, Neutralizing and Finishing the concentration of Pd was below the Detection limit while in Re-chrome and Re-tanning processes water samples, the measured value of Pd was 0.0103 mg/l and 0.2376 mg/l. as per defined limit of Pb in the NEQs of municipal and industrial discharge in land water the measured concentration of Pb in each sample of water was within the defined limit so GWF had not calculated for Pb.

3.2.6 GWF for Biological Oxygen Demand (BOD)

Biological Oxygen Demand (BOD) is the amount of the dissolved oxygen used by the microorganisms during the oxidation of concentrated constituents. In this research BOD was calculated by using Lovibond BOD Tintometer. The concentration of BOD in samples of waste water from different tannery processes are given in the table 3.2. It was noted that the maximum values of BOD were measured for the process's Re-chrome, Neutralizing and Re-tanning that are 9070 mg/l, 7900 mg/l and 9020 mg/l respectively. During the reprocessing of wet blue hide different chemicals, oils and dyes mixed in water and wet blue hide is treated with that water to get the desired quality of leather. This addition of chemicals, oils and dyes increases the BOD of water and make it toxic for marine life if discharged without treating that water.

While comparing the obtained values with the permissible limit defined in NEQs for Municipal and Industrial Liquid Effluent, 1999, it was noted that in the waste water samples from different processes of tannery; Wet Wash, Re-chroming, Neutralizing, Re-tanning and Finishing, indicated the BOD values higher than the defined limit i.e 80mg/l in land. The presence of higher organic matter content will enhance the anaerobic action that primes to the accumulation of toxic composites in bodies of water. The present result agrees with the studies of liquid water from tanneries (Islam et al., 2014).

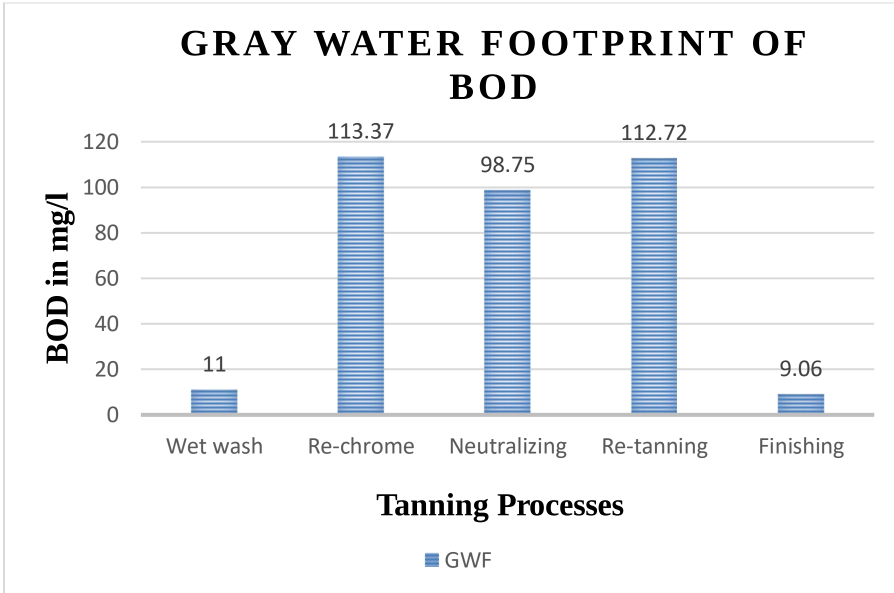

Figure 3.2: Graphical representation of gray water footprint for Biological Oxygen Demand.

Figure 3.2 shows that the calculated GWF of BOD for five tannery processes, Wet wash, Re-chrome, Neutralizing, Re-tanning and Finishing were 11 mg/l, 113.37 mg/l, 98.75 mg/l, 112.72 mg/l and 9.06 mg/l respectively. The Max Yi for the BOD was 113.37 mg/l which shows before discharging waste water into drainage pipe 113.37mg/l of the fresh is required to minimize BOD. It is necessary to treat BOD contaminated water because such polluted water can cause water quality problems and discharge of that waste water into huge water bodies could be harmful for marine life (Penn, Pauer, & Mihelcic, 2009).

3.2.7 GWF for Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) is the estimation of the amount of oxygen required for the oxidation of natural considerable in water. It was calculated by using COD reactor. The measured values of COD in the samples of waste water from five tannery processes is given in table 3.2. The concentration of COD in the samples of waste water from tannery processes, Wet wash, Re-chroming, Neutralizing, Re-tanning and Finishing were 1580 mg/l, 15030 mg/l, 1470 mg/l, 14080 mg/l and 1395 mg/l correspondingly. The results, showed COD content much higher than the permissible limit defined in NEQs i.e 105mg/l. The reason for such high concentration of COD in waste water samples was the chemicals, dyes and oil used for the reprocessing of wet blue hide. This decreases the amount of oxygen essential for the oxidation of biological substantial in water.

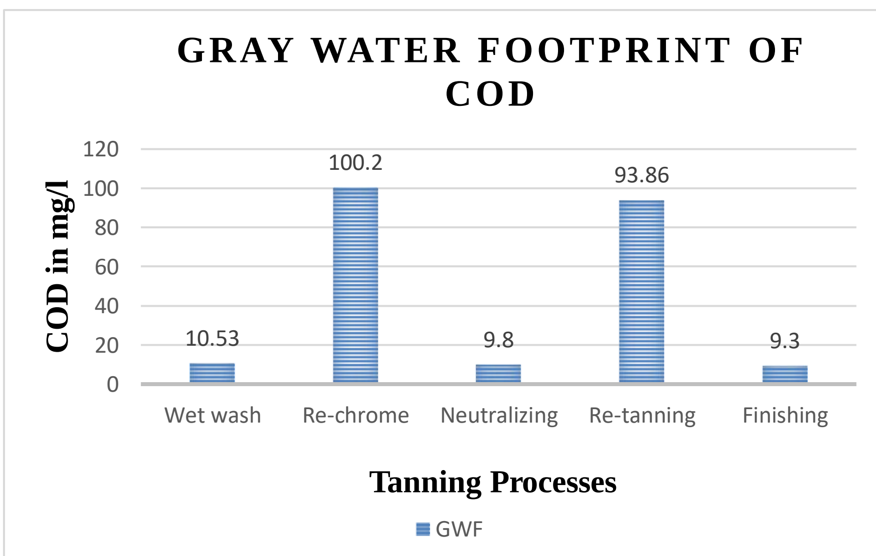

Figure 3.3: Graphical representation of GWF of chemical oxygen demand.

Figure 3.3 represents the calculated gray water footprint of COD which is 10.53 mg/l for Wet wash, 100.2 mg/l for Re-chroming, 9.8 mg/l for Neutralizing, 93.86 mg/l for Re-tanning and 9.3 mg/l for Finishing process. The calculated Max Yi value of COD was

100.2 mg/l which was referred as GWF of COD. This showed that 100.2mg/l fresh water required to thin this pollutant in waste water before discharging it into water body. This illustrated that due to devaluation in the dissolved content, the waste water/ sludge is not suitable for the presence of marine organisms (Islam et al., 2014).

Table 3.3: gray water footprint had calculated for five heavy metals, BOD and COD in Wet wash, Re-chroming, Neutralizing, Re-tanning and Finishing process waste water samples.

Parameters	**Gray Water Footprint (Yi)**					**Max Yi**
	Processes					
	Wet Wash	**Re-chroming**	**Neutralizing**	**Re-tanning**	**Finishing**	
As	N.D	N.D	N.D	1	N.D	1
Cd	N.D	N.D	N.D	N.D	N.D	
Cr	6.6878	100.8380	100.4427	49.5438	N.D	100.8380
Cu	N.D	N.D	N.D	N.D	N.D	
Pb	N.D	N.D	N.D	N.D	N.D	
BOD	11	113.37	98.75	112.72	9.06	113.37
COD	10.53	100.2	9.8	93.86	9.3	100.2

In Table 3.3, GWF had calculated for contaminants which exceeded the defined limit which were, As, Cr, BOD and COD. The calculated values were then compared with each other and maximum or the highest value of that contaminant was considered as GWF.

The highest values of Y(As), Y(Cr), Y(BOD) and Y(COD) were 1 mg/l, 100.8380 mg/l, 113.37 mg/l and 100.2 mg/l respectively.

3.3 Physico-chemical Properties of Wastewater

Some physiochemical parameters were also measured in this research.

3.3.1 pH

The pH of the samples was determined soon after the collection of samples using pH meter by dipping the probe of the meter into the samples. From table 3.4 the measured pH values for Wet wash, Re-chrome, Neutralizing, Re-tanning and Finishing were 4.38, 5.55, 6.55, 6.59 and 7.3 respectively. During the Re-chroming process, different chemicals added to the drum along with chromium. This decreases the pH level not in wet blue hide but also in the waste water of that drum up to 3.5 to 5.5. To produce the best quality of leather it is important to maintain the pH level in leather. But discharging untreated waste water into water body not only will effect the aquatic biota but also has a toxic effect on soil fauna.

3.3.2 Conductivity

The conductivity of the samples was also determined soon after the collection of samples using the same pH meter. Samples were poured into a beaker and by dipping the probe of the meter into the sample's conductivity had measured. Conductivity for the samples for five processes of tannery, Wet wash, Re-chrome, Neutralizing, Re-tanning and Finishing were 14.49, 5.98, 6.79, 6.99 and 3.35 respectively. The observed values of conductivity are given in table 3.4.

3.3.3 Salinity

After the collection of samples, salinity of the samples was calculated using the same pH meter. It is measured in parts per million (ppm). Different salts and chemicals are used to preserve wet blue hide before processing it for manufacturing of leather. During the process of Wet Wash, wet blue hide was treated or washed with water and those salts dissolved into water and thus waste water of that drum carry dissolved salts in it. The measured salinity for Wet wash, Re-chrome, Neutralizing, Re-tanning and Finishing were 9.22 ppm, 3.53 ppm, 4.07 ppm, 4.15 ppm and 1.92 ppm correspondingly as shown in table 3.4.

3.3.4 Total Dissolved Solvent (TDS)

Total Dissolved Solvent (TDS) is the measurement of the minerals, organic content and salts which are dissolved in the water. It is measured in parts per trillion (ppt). By dipping the probe of the pH meter into each samples and values were noted. Table 3.4 shows measured values of TDS for Wet wash, Re-chrome, Neutralizing, Re-tanning and Finishing which are o ppt, 4.23 ppt, 4.82 ppt, 4.84 ppt and 2.39 ppt correspondingly. In the tannery effluent the composition of solids depends on the nature and quality of wet blue hide used for the tanning purpose.

Table 3.4: Measured or observed values for pH, Conductivity. Salinity (ppm) and TDS (ppt) content in water samples of Wet wash, Re-chroming, Neutralizing and Finishing.

Processes	**pH**	**Conductivity**	**Salinity (ppm)**	**TDS (ppt)**
Wet wash	4.38	14.49	9.22	0
Re-chroming	5.55	5.98	3.53	4.23
Neutralizing	6.55	6.79	4.07	4.82
Re-tanning	6.59	6.99	4.15	4.84
Finishing	7.3	3.35	1.92	2.39

So, in this research total amount of fresh water used in the tannery for the reprocessing of wet blue hide had calculated. This was the one-time calculation of fresh water as at a time one process was carried out in drum. Also waste water as a result of those processes was collected in the bottles for the analysis for heavy metals, BOD and COD and some phsico-chemical parameters. By using readings of heavy metals, BOD and COD, gray water footprint (GWF) had calculated for each of the pollutant which exceeds the permissible limit. By the help of GWF it was estimated that how much fresh water is required to dilute such pollutants in wastewater before discharging that sludge in to the canal. If wastewater with higher BOD and COD content and Cr content will directly discharge into the water body, it will not only pollute aquatic environment and make it unsuitable for aquatic biota but also will have a toxic impact on the land adjacent to the Upper Chenab canal.

CONCLUSIONS

For the selected leather industry, firstly BWF had calculated. The BWF which is also referred as total water consumption (TWC) was 134.604 liters, which showed nearly 135 liters of fresh water is required for the processing of about 215.8 kgs wet blue hide on daily bases.

Since leather skins and hides are treated with water sources, the water discharged from wells, drums and pallets is composed of many soluble and insoluble substances. The second purpose of the study was to measure heavy metals (As, Cd, Cr, Cu, Pb) BOD and COD in the wastewater samples. The measured values were much higher for Cr, BOD and COD that is 100.8380 mg/l, 113.37 mg/l and 100.2 mg/l respectively as compared to other heavy metals, so GWF had calculated for Cr, BOD and COD i.e. 100.8380 mg/l, 113.37 mg/l and 100.2 mg/l correspondingly. The results show apart from reprocessing of wet blue hide raw water is also required to dilute pollutants in wastewater.

RECOMMENDATIONS

This work is expected for evaluation of the movement for restructuring the processes for industry and this will lead to recover water resources management. As for the best quality of leather water cannot be reused for the processes in which chemicals are used like Re-chroming, Re-tanning and in Finishing process. But for processes like Wet-wash and Neutralizing, water can be use twice. This will ultimately put less pressure on water body.

As the industry extract enough amount of water for the reprocessing of wet blue hide and to maintain the quality of leather, industry cannot minimize the amount of chemicals which are used for the reprocessing of wet blue hide, nor reuse the processed water for more processes, it is suggested that industry should adopt pretreatment methods like Sedimentation of tannery waste water to minimize the load of pollutants in the sludge. Other ways to treat tannery waste water are through biological and chemical processes. Aerobic and Anaerobic Biological treatment methods are useful for the removal of biological oxygen demand and chemical oxygen demand in the tannery waste water.

Another ultimate way to treat pollutants in tannery waste water is the installation of water treatment plant in the premises of tannery so that waste water will properly be treated and reused for the processing of leather. But unfortunately, this is economically, not suitable for all the tanneries in Sialkot.

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Appendix A

Machine used for the splitting of wet blue hide

Appendix B

Shaving machine to remove unwanted flesh on wet blue hide

Appendix C

Drums used for the reprocessing of wet blue hide.

Appendix D

Toggler machine to remove wrinkles from leather.

Appendix E

Syringe and filter used to filter waste water