Thesis

by Sana Ahad

ANALYSIS OF KASUR TANNERY PRE TREATED WASTEWATER FOR RENDERING IT FIT FOR IRRIGATION

By

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ABSTRACT

Kasur district is famous for leather tanning and its leather products are used worldwide, and thus it contributes significantly to GDP of Pakistan. However, the wastewater generated from the cluster of tanneries of Kasur is highly polluted with obnoxious odor and is also loaded with hazardous pollutants. Thus, Kasur Tannery Waste Management Agency (KTWMA) has installed Common Effluent Pretreatment Plant (CEPTP) that discharges 9000m^3pretreated wastewater per day. The present study is carried out to analyze pretreated tannery wastewater to judge its suitability for irrigation of agricultural soil and propose methods and their subsequent economic evaluation to fit this water for irrigation purposes.

Physicochemical analysis of pre treated tannery wastewater was carried out. The concentrations of various parameters such as pH, EC, TDS, SAR, RSC, SO_4^{2-}, Cl^-, Cr, Cd, Zn, Fe and Cu were computed and compared with the standards of wastewater for irrigation purposes proposed by WWF (2007). The results reveal that the concentrations of heavy metals are in permissible limits except of Cr (0.283mg/L). The concentrations of remaining parameters such as EC (18.6 $dS.m^{-1}$), TDS (13020 mg/L), SAR (91.7), RSC (35.86), SO_4^{2-} (8061.3mg/L) and Cl^- (8930.7mg/L) are much above the permissible limits

The study concludes that the pretreated wastewater is not suitable for irrigation purposes even after mixing it with municipal wastewater on way to Pandoki Drain. The best technology to treat wastewater that may be opted especially from salinity point of view is Reverse Osmosis (RO). However its cost benefit analysis shows that it's not feasible for a country like Pakistan where economic and electricity crisis are at its peak.

Dedication

This research work is dedicated to the memory of my beloved father, (late) Mr. Abdul Ahad Khan, from whom I learnt how to be strong in life and never give up in any situation.

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"In the name of Allah, the Beneficent, the Merciful. All praise is for Allah, the Lord of the Worlds; the Beneficent, the Merciful and Master of the Day of Judgment. Thee do we serve and Thee do we beseech for help. All respect and regards are for the Holy Prophet Mohammad (Peace Be Upon Him), the source of knowledge and torch bearer for whole mankind to illuminate the track that leads to the Ultimate Reality.

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(SANA AHAD)

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List of Acronyms

CEPTP	Common effluent pre treatment plant
Cr	Chromium
Cd	Cadmium
Fe	Iron
Zn	Zinc
Cu	Copper
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
As	Arsenic
NaCl	Sodium Chloride
WDR	World Development Report
B	Boron
Ca	Calcium
Mg	Magnesium
SO_4^{2-}	Sulphate
UNIDO	United nation Industrial Development Organization
UF	Ultra Filtration
RO	Reverse Osmosis
NF	Nano Filtration
EC	Electrical Conductivity
TDS	Total Dissolved Solids

TSS	Total Suspended Solids
SAR	Sodium Absorption Ratio
RSC	Residual Sodium Carbonate
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
CO_2^{-3}	Carbonate
CHO^{3-}	Bicarbonate
PCBs	Poly-Chlorinated Biphenyls
PAHs	Poly-Aromatic Hydrocarbons
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

1.1 Tanning Industry in Pakistan

The leather industry is accepted as one of the highly polluting exclusively with reference to the effluent it liberates in the environment and contains high concentrations of dissolved organic and inorganic compounds and suspended solids that demand high amount of oxygen and also contain potentially harmful metal ions. Unbearable smell released from the decomposing proteinous solid waste is due the chemicals which are used in leather making process such as hydrogen sulphide and volatile organic compounds. Momentous amount of chemicals are added in tanning process is not only used in making leather but also released into the environment in the form of noxious wastewater and solid waste. (Gupta et al., 2007). The wastewater generated from tanneries with special reference to the presence of chromium, is the main concern why most of the developed countries have banned chrome tannin in their countries. Leather being the need of individuals everywhere throughout the world, has the edge that it's fabricate can't be halted. This has provided for some budgetary preference to some creating nations including Pakistan to produce leather and fare it to the developed nations. Pakistan, for example, earns 7% of its foreign exchange from the export of tanning products. To make the accessibility of chromium reasonable distinctive techniques have been created to recoup chromium from the tannery effluents before their seepage in the common water bodies. A couple of samples of these techniques are High Chrome Exhaustion, Direct Recycling of the Spent Tanning Float and Chrome Recovery and Reuse (Khan, 2007).

Due to relatively less expensive cost of labour and materials, over half the world's tanning activity is running in low and middle income countries. Between 1970 and 1995, the percentage of low to middle income countries contributing to the global production of light leather increased from 35% to 56% and of heavy leather materials from 26% to 56%. As indicated by a study directed by Blacksmith Institute approximately something like 75% of chromium sites are spotted in South Asia and of these, almost one third are connected with tannery operations with mining and metallurgy areas also playing its role crucially. In South Asia, concentration of chromium is basically high because of the large number of tanneries in the area. Huge numbers of these tanneries have poor environmental controls (Azom et al., 2012).

The current natural and asset administration laws at the national and provincial level, in the later past, did not sufficiently cover the branches of knowledge and a few were antiquated likewise. Due to the ineffectual execution of administrative control, no contamination control measures are adopted by the tanning units and the risks associated to communities created by the effluents and emanations from tanneries remains an intense issue. High absence of education among tanners and overall population lead to old processing of tanning transforming strategies and poor handling practices have further irritated the contamination issue brought on by the tanneries in Pakistan. (Khwaja, 2000). Roughly 9,000 cubic meters of highly polluted waste water was released without any treatment on consistent schedule, before the Common Effluent Pre-Treatment Plant (CEPTP) was initiated in 1996, ensuing in the development of stagnant pools of waste water enclose an area of 400 acres of land. A lot of solid waste were created and discarded inside the tannery areas because of the unlucky deficiency of a well working strong waste administration framework. Frequently the waste was blazed, making soil and water contamination and a deplorable smell in the territory. The city's underground water was infected and rendered unfit for all living creatures Also, the absence of fitting preparing and defensive apparatus for specialists who took care of risky chemicals implied that tannery managers, laborers and inhabitants in the range were lopsidedly laid open to sicknesses like skin contamination, respiratory issue and stomach-related symptoms. As such, controlling the release of strong waste and water contamination in Kasur was important to enhance living standards inside the city (Malik, 2002).

The tannery wastewater is currently assembled at two pumping stations in the site. They are then pumped into an open channel and stream down to the CEPTP under gravity. After the treatment, waste water passes through 8.4 kilometers of outfall sewer, which has been developed as a component of the task until it is at last released into a neighborhood waterway the Sutlej River. Thus, while the stagnant pools have now been cleared, the water released into Sutlej is still perilous for human wellbeing, accentuating the need to redesign the current treatment plant. The CEPTP has been launched and been in working since 2001 (Thomsen, 2007).

1.2 Environment and Economic Development

The economic development of 21st Century mainly involved the improvement in lifestyle of human being for their present as well for their future. With this objective in mind, man, instead of living in tune with nature by protecting himself and his environment, is out to destroy the very sustenance of life of soil, water, flora and diversified ecosystems. The quantity of waste generated due to household activities and industrialization pose a major problem for worldwide municipalities for its proper and adequate treatment, so that its final disposal may not cause environmental pollution. However, the sludge exhibits wide variations in the physical, chemical and biological composition (Dhamnaskar, 2012). Industrialization is seen as securely attached a share of financial advancement and creating economies are embracing arrangements for change of agro-based underdevelopment areas to industry and trade based evolved countries. General society mindfulness about natural issues radiating from industrialization has swelled altogether and analysts have been attempting to assess the result of contamination through field studies and quantitative investigation. It is currently acknowledged that the profit from industrialization in a locale needs to be analyzed against the apparent expense of expanding contamination and must be precisely concentrated on before permitting any further commercial enterprises to come up in concerned region (Firdous and Majumder, 2010).

Industrialization has significantly expanded all through the entire world. Developed and developing nations much the same now understand that profits of a proper developed industrial environment, with all its benefits, including decreased unemployment and diminished destitution. Each one industry that is evolved contributes a certain level of pollution to the nature. It must be observed that, if contamination is not controlled to the permissible levels, it can cause hazardous impacts on the society as well as on the environment. The degree of contamination differs with the extent of industry, the way of the industrialization, the kind of items utilized and delivered, and so on. Besides everything else, industries not only pollute air, water and soil but also have harmful impact on humankind and numerous different manifestations of ecological debasement (Dlamini and Joubert, 1996).

1.3 Industrial Pollution

Effluents coming from different industrial and commercial establishments are posing serious threat to the environment, particularly to the urban and semi urban areas. They tend to contaminate surface and subsurface water, soil and air. Their proper management and disposal is one of the most important challenges all over the globe (Hossain et al., 2011). Different industries produce different types of wastewater as shown in table 1 (Ijeoma and Achi, 2011).

Table 1.1: Examples of Waste water produced by different Industries

Type of waste	**Type of plant**
Oxygen-consuming	Breweries, Dairies, Distilleries, Packaging houses, Pulp and paper, Tanneries, Textiles.
Highly suspended solids	Breweries, Coal washeries, Iron and steel industries, Distilleries, Pulp and paper mills, Palm oil mills.
Highly dissolved solids	Chemical plants, Tanneries, Water softening.
Oils and greases	Laundries, Metal finishing, Oil fields, Petroleum refineries, Tanneries, Palm oil mills.
Colored	Pulp and paper mills, Tanneries, Textile dye houses, Palm oil mills.
Highly alkaline	Chemical plants, Laundries, Tanneries, Textile finishing mills.

Wastewater from industries are the fundamental source of straight and continuously non-stop input of toxic waste into amphibian ecosystems with long-term implications on environment functioning including changes in nourishment accessibility and an extreme threat to the self-regulating size of the biosphere. These industrial discharges or wastes include heavy metals, pesticides, polychlorinated biphenyls (PCBs), dioxins, poly-aromatic hydrocarbons (PAHs), petrochemicals, phenolic compounds and microorganisms (Nubi et al., 2008). These pollutants are usually drained off into the near water bodies therefore the, cumulative hazardous impact it has on the environment have gained much attention. Industrial wastes generally have high concentration of microbial nutrients would definitely increase an after growth of significantly high coliforms and other microbial types. Some heavy metals are present in these waste waters have been found to be the cause of cancer in human beings, whereas other contaminants are also lethal according to the exposure time and amount of the dosage. Without a doubt, effluents from commercial, industrialized and residential areas released into another environment without any proper monitoring can aggravate the ecological equalization of such an environment (Botkin and Kelly, 1998).

1.4 Metallic Pollution

Heavy metal pollution is a worldwide problem and human activities have become a major process for mobilization of metals in the biosphere. Use of low quality fertilizers, discharge of effluents from industries, metal smelting, mining practices, pesticides and sewage has increased the level of heavy metals in agriculture land above levels consider harmless for food production. A group of trace elements consists of heavy metals such as iron, nickel, copper, chromium, selenium that are essential for cell in trace amounts for different biochemical reactions, however, when present at higher concentrations, they have toxic (Yasin and Faisal, 2012). Metals are universal. They are necessary and beneficial part of our day by day lives. They have many advantages for example; metals have been used for fast developments in human services, data innovation, telecommunication sectors and many other parts of the society (Mamtani et al., 2011). Around different hazardous substances released by industrial activities, heavy metals have been known as a key pillar because they have been studied adequately and frequently in different types of ecosystem. Not all, organic toxic waste that may deteriorate to secondary adverse components as a reaction of biological or chemical processes, metals are not degradable by natural mechanism especially when basic metallic substance is considered. The impact of metal contamination on local surroundings and all forms of life may therefore be significant and permanent in spite of immense remediation efforts. Such as, manganese, copper, lead and cadmium etc have been generally opt as representative metals for which their concentrations in the environment may be used as reliable indices of environmental contamination (Kabir et al., 2012).

Heavy metals which are comparatively rich in the Earth's crust and commonly used in modern techniques or agribusiness are poisonous to people. These metals can build irreversible changes to the biochemical cycles of living bodies (Srivastava and Majumder, 2008). Heavy metals are now present in every kind of waste, especially with reference to waste water, where new modern techniques have been developed to utilize the earth resource in many ways. This makes industries to release their toxic waste water in sewage system or dispose off in near water bodies. Lead, Cadmium and Mercury are the three major heavy metals represent the extreme threat to mankind, whereas Be, Cr and As are particularly associated with the risk of developing cancer. These metals can also generate significant hazard to the amphibians because they are accumulated through the trophic chain and build toxic effect and teratogenic changes in all living creatures. They also remain in the sediments and are gradually discharged into the near water body (Shanab et al., 2012).

Wastewater released from industries particularly from the textile and tanning industry holds a huge concentration of metals especially cadmium, chromium and copper. These effluents discharged on the soil as well as enters in the water body which eventually percolates into ground and leads to contamination due to accumulation of lethal metallic elements and results into a chain of well known problems in living creatures because they cannot be fully degraded (Gangwar, 2010).

1.5 Tanning Industry

Among many industries, tanning industry is specifically known for their consumption of huge amount of water on daily basis that released various kinds of pollutants carrying by effluents; hence its treatment is necessary for the safeguard of nature. The main issue experienced in tanning industry is the strong variance of the flow, load and the excessive concentration of main contaminants (Shafy et al., 2003). However, the tanning industry has particularly been related with high pollution due to the bad odour, organic wastes and lots of water is utilized during conventional manufacturing processes (Ozgunay et al., 2007). Approximately, 90% of leather product is tanned by using chromium salts. In traditional methods of tanning, around 8% of basic chromium sulphate salt is used, because it fastens the collagenous protein to turn into fine leather. During this process, many kinds of pollutants discharged like, Sulfide, pesticides, strong alkalines, sodium chloride, salts of chromium sulphate, dissolved organic and inorganic matter. Chlorinated phenols are important compounds to be studied because of the various mixtures used in the leather industry and their eco toxicity impact (Mwinyihija, 2010).

In various steps of tanning, where hides are converted into leather, large amount of solid and liquid wastes are generated. 200 kilograms of fined leather product is achieved by processing one metric ton of raw animal hides, where as 250 kilograms of non tanned trash, 200 kilogram of tanned trash and 50 kilogram of effluents are generated during this process. Hence, only 20% of raw animal hides are transformed into fine leather product (Kolomaznik et al., 2003). According to the World Bank, around 70% of the solid waste is generated from the soaked mass of animal hides. Hides which are tanned by using chromium salts are low in density and thus hold a large volume. It causes difficulty in the handling of massive wastes generated by tanning industries (Herráez et al., 2012).

1.6 Characteristics of Tanning Wastewater

Multiple kinds of chemicals are used during the transformation of animal hides therefore the treatment of tanning effluents is quite complicated. Due the presence of many toxins like lime, chloride, chromium, dissolved and suspended solids, it poses serious threat to the environment (Durai et al., 2010). Around 300 kilograms of chemicals and different salts are used for the production of one ton of raw hides. Because of the addition of these chemicals, tanning industry is considered one of the most toxic industries worldwide; it has greatest noxious intensity per unit output. The characteristics of effluents released from leather industry are highly complex. 30 to 35 liters of wastewater is produced during the processing of per kilogram of hides with inconstant pH and very excessive amount of chemical oxygen demand, suspended and dissolved solids, chromium and biological oxygen demand (Durai et al., 2011). Due to the highest consumption rate of water and producing large amount of pollutants in the environment, tannery effluents should be carefully considered in the plant designed for its treatment and processing (Lofrano et al., 2006). The major components of the effluent include sulfide, chromium, volatile organic compounds, large quantities of solid waste, suspended solids like animal hair and trimmings. For every kilogram of hides processed, 30 liters of effluent is generated and the total quantity of effluent discharged by Indian industries is about 50,000 m^3 /day (Midha and Dey, 2008).

1.7 Tanning Process

There are mainly 4 stages of production in tanning industry i.e. A) raw skin storage and beamhouse processing B) tanning processing C) post tannin processing and D) finishing processing (GATE, 2002). Sub-processes involved are shown in Fig.1.1 and outlined in the notes given below. The conventional making of leather from raw to wet blue and to crust constitutes the following stages:

- Soaking and Washing – raw animal skins are washed with water to remove dirt from it. These skins are again thoroughly washed by adding wetting agent and preservatives. Then these skins are fit for unhairing processing.
- Liming – Lime and sulfides are utilized along with water in the paddle containing raw skins.
- De-liming and Bating – skins are then added in water drum, where different chemicals are used for de liming. After doing bating, the waste water is discharged from the drum.
- Pickling – for pickling in acidic conditions, skins are de limed by using chemicals and water. Wastewater is then discharged and the skins that are pickled are ready for the treatment of chrome tanning.
- Chrome Tanning – crucial stage in tanning operation where; chemicals are allowed to diffuse through the pores of skins in consequence of which the skins turn into leathers. The tanned skins get the characteristics of leather.
- Neutralization – After performing chroming and re-chroming in acidic conditions in drum, the skins are neutralized using soft alkaline solutions. Then the skins are processed for re-tanning, dyeing and fat-liquoring to produce wet blue. For producing crust and finished leathers, some more steps such as piling, setting, drying, staking, toggling, trimming, buffing and de-dusting etc. are vital (Panda and Rao, 2011).

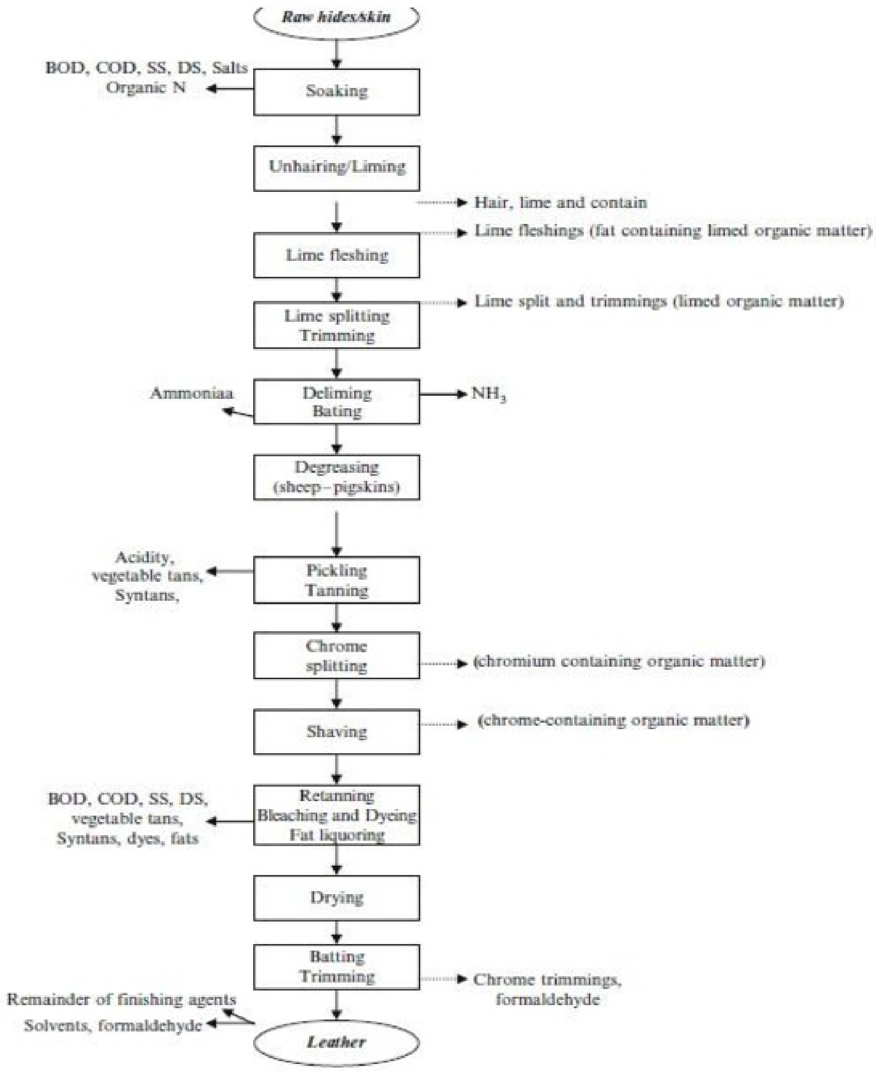

Fig 1.1: Shows the different type of pollutants releasing at different stages of tanning.

The tanning industry transforms raw animal skins and hides for many goals. Raw skins are converted into stable fine products by a chain of chemical and mechanical stages. During these stages, tanning is most important. In tanning industry, tanning means the transformation of raw skin into fine leather through different specified stages. Unless the tanning procedure is done, collagen which is made from the protein of raw skin will gradually decay. When this collagen protein is warmed up, it will become gelatin in water. Therefore, tanning is important process for the transformation of the collagens present in natural skin and hides into a stable form, making the product individual longevity by enabling the penetration of different tanning agents with different properties into the structure through mechanical action in floats and by reaction with reactive groups of collagens. Tanning agents are not only used in the tanning stages, but they can also be used in another operation, which is known as re-tanning/retannage, to gain the final features (Basaran et al., 2008).

1.8 Review of Global Water Crisis

Industries are not only responsible for the consumption of natural resources such as water, but they are also responsible for making it polluted. 70% of wastewater from the industries in third world countries is disposes off without any kind of treatment, thereby contaminating the available water resources (WDR, 2003). Water contamination is the major reason of non availability of the suitable water for agricultural lands. Since many industries disposes of their wastewater on open lands due to the huge quotation of dilution and poor treatment facilities. Industries must consider the usage of this wastewater and making it profitable (Shrivastava et al., 2012). During the last ten years, water is the most debatable topic around the world, as we are going towards the water crisis especially with reference to climatically dried parts of the world such as, South Asia and Africa. Thus there is a great need to consider the quality and quantity of the water. Wastewater is one of the best options available to reuse in regions where there is water scarcity (Blumenthal et al, 2000). Numerous urban sites in third world countries is facing the problem of safe water supply, liquid and solid management of wastes and food safety to their expanding populations. Around two third of the effluents which is discharged from the urban areas receives no kind of treatment. In many cases, effluents are directly discharged into near water body such as in stream, sea and oceans (Sally et al., 2001). In many arid and semi arid parts of the world, water is becoming insufficient because of the few resources of fresh water and simultaneously there is a growing demand of fresh water due to the increase of population at high rate. Therefore wastewater can be reused for irrigation purposes, not only fulfilling the need of water but also it can provide essential nutrients for the production of crops by reducing the cost of fertilizers to be applied on land. Treated wastewater can be used in many ways, like it can be used in recreational activities, in golf courts, applied on agricultural lands more over it can be reuse in industrial activities again. Besides, as different industrial and horticultural needs are met by treated waste water, more freshwater could be made accessible for municipal use (FAO and WHO, 2003).

As the world population is increasing, there is a great need of water to be used on agricultural lands. This need can be fulfilled by reusing the treated or untreated wastewater. Currently this approach has been practicing in many regions of the world by using wastewater from municipalities and industries (Ensink et al., 2002). In 50 countries, approximately twenty million hectares of land is irrigated by moderately treated wastewater. The main goals of wastewater used on agricultural lands are that it gives a safe source of water supply to agronomists and has the advantageous feature of adding essential plant nutrients and organic matter to the soil. With careful planning and management, the positive aspects of wastewater irrigation can be exploited to achieve the social objectives narrated above (Ruma and sheikh, 2010).

1.9 Use of Treated Wastewater in Irrigation

Waste water after the treatment has many benefits as compared with the other sources of water. It's not only a good source of nutrients for crops but also lessens the contamination of toxins (Saleem et al., 2000). For irrigation purposes, wastewater is used for centuries in countries like China, Mexico and Vietnam. Now this practice has gained much attention in the world for its benefits and as the freshwater is becoming scare. The reuse of wastewater in agricultural land and for plantation is also practiced in many parts of the Asia and Middle Eastern countries (Al Salem and Abouzaid, 2006). The re-use of waste-water from either municipal or industries is used for irrigation that is a common practice of most urban industrial areas of the world. In Pakistan for example agriculturists are able to grow good quality crops like vegetables with wastewater (Hoek, 2002). The diversion of wastewater from drains and or canals into irrigated fields may result into accumulation of harmful substances in the soil root zone at intensities and levels likely to impair and degrade the soil and result into health hazards. Wastewater when used directly for irrigation can raise the concentration of certain ions and eventually lower the quality of the water for irrigation (Ayers and Westcots, 1985). The major constrains to the use of waste water for agriculture are the issues of environmental pollution, soil degradation and health hazards posed to both the farmers and consumers of the irrigated crops and evidences of many completed researches abound on these issues for many areas of the world.

Reports from many studies have shown that large scale and long term application of wastewater on the soil may lead to danger of insect infestation, pollution of groundwater and built up of heavy metals, salts and other toxicants in the soil (Ishaya et al., 2011). In cities of many arid and semi-arid areas, this is sometimes the only major source of irrigating urban lands being used for food production and fortunately for such areas, there are no prohibitions of disposal of wastewater in urban rivers. Disposal of wastewater in streams has several advantages including maintaining proper environmental flows and boosting the water volume for downstream users. Treated wastewater can be applied on agricultural land under fully monitored examination to minimize the health risks associated with pathogens and toxic pollutants of the agricultural produce, soils, and surface and underground water (Ruma, 2009).

Wastewater provides an excellent source of nutrients to plants; hence the land when irrigated with this wastewater gives a good yield of the crop. When applying this wastewater the fertilizers such as nitrogen and phosphorous should be applied carefully to avoid unnecessary build of nutrients in soil. Therefore, soil should be monitored and its analysis should be carried over a certain period of time to avoid soil sickness and imbalanced nutrients (Kaur et al., 2009). Harmful impact on the soil will occur if certain nutrients start to build up in the soil. Relaying on the specific characteristics, if the land is irrigated by specific wastewater it may cause soil salinity with the unsaturated zones of soil, and accumulate the toxic organic and inorganic components. To keep away from this situation, land should be irrigated by the waste water discharging from domestic regions. Carrying out soil drainage is also important to avoid the soil salinity (Helmer and Hespanhol, 1997). The pollutants and contaminants in waste water and their potential impacts through agricultural use are narrated in Table 1.2.

Table1.2: Pollutants in wastewater and their potential impacts through agricultural use

Pollutants	Parameter	Impacts
Plant food nutrients	N, K, P etc	Excess N: potential to cause nitrogen injury, excessive vegetative growth, delayed growing season and maturity, and potential to cause economic loss to farmer. Excessive amounts of N and P can cause excessive growth of undesirable aquatic species. (Eutrophication) Nitrogen leaching causes groundwater pollution with adverse health and environmental impacts.
Suspended solids	Volatile compounds, settle able, suspended and colloidal impurities	Development of sludge deposits causing anaerobic conditions. Plugging of irrigation equipment and systems such as sprinklers
Pathogens	Viruses, bacteria, helminthes eggs, fecal coliforms etc	Causing communicable diseases.
Biodegradable organics	BOD, COD	Depletion of dissolved oxygen in surface water Development of septic conditions Unsuitable habitat and environment Inhibition of pond-breeding amphibians Fish mortality, humus build-up

"Continued"

Stable organics		Persistence in the environment for long periods Toxicity to environment Making wastewater unsuitable for irrigation	
Dissolved inorganic substances	TDS, EC, Na, Ca, Mg, Cl, B	Causing salinity and associated adverse impacts Phytotoxicity Effect on permeability and soil structure	
Heavy metals	Cd, Pb, Ni, Zn, As, Hg, etc.	Bio-accumulation in aquatic organisms (Fish and planktons) Accumulation in irrigated soils and the environment Toxicity to plants and animals Systemic uptake by plants Subsequent ingestion by humans or animals Possible health impacts Making wastewater unsuitable for irrigation	
Hydrogen ion concentration	pH	Possible adverse impact on plant growth due to acidity or alkalinity Impact sometimes beneficial on soil flora and fauna Especially of concern in industrial wastewater	

"Continued"

Residual chlorine in tertiary treated wastewater	Both free and combined chlorine	Leaf-tip burn, Groundwater, surface water contamination. Carcinogenic effects from organic chlorides formed when chlorine combines with residual organic compounds.

1.10 Irrigation Water Quality

Factors which are used to determine the quality of water used for irrigation purposes and study its effects on crop yield and on the quality of soil are Sodium, and its ratio to Calcium and Magnesium ions, total available salt, such as Chloride, Bicarbonates and Carbonates, Sulphate, Nitrate-Nitrogen and Boron. Besides from these chemical pollutants, other parameters are also included such as heavy metals e.g. Chromium, Copper, Iron and Microbial parameters such as E. coli etc (Bauder et al., 2007).

The major problems which are associated with salt content are the three i.e. 1) salinity, 2) sodicity and 3) toxicity. Salinity is defined as the, total amount of salt in the dissolved form present in the water and soil. When this type of saline water is available to the plant, its growth will be halted because plant can't uptake the essential nutrients from its root and its leads towards the osmotic stress. Same kind of impact that water will not be available to the plant. The term sodicity refer to the when excessive amount of sodium is available in ratio to magnesium and calcium ions. This high concentration of sodium causes the soil salinity and makes the soil like drought. Sodicity term has now replaced the term alkaline when pointing out the excessive sodium in the soil. Toxicity is used for specific kind of ions that have toxic effects on the crop yield or on the soil, such as boron chloride and other trace elements. Woody crops and trees are more sensitive towards these toxic and trace elements (Hoffman, 2012). The quality of water is usually determined by what type of crop it has be irrigated and its tolerance towards the concentration of sodium and other trace elements. The impact of salinity on the osmotic pressure in the un-saturated zone of is one of the most necessary water quality considerations because this has an impact on the availability of water for plant consumption. When sodium is present above the permissible limits in soil, the movement of water will be reduced through the soil, and it will cause damage to the fruits of the tress too. Phototoxic trace elements like heavy metals (Cr, Cd, and Cu), boron, chloride and pesticides may halt the plant growth and make the crop consumption unfit for (WWF, 2007). Fig 1.2 shows the water quality evaluation (George, 2004).

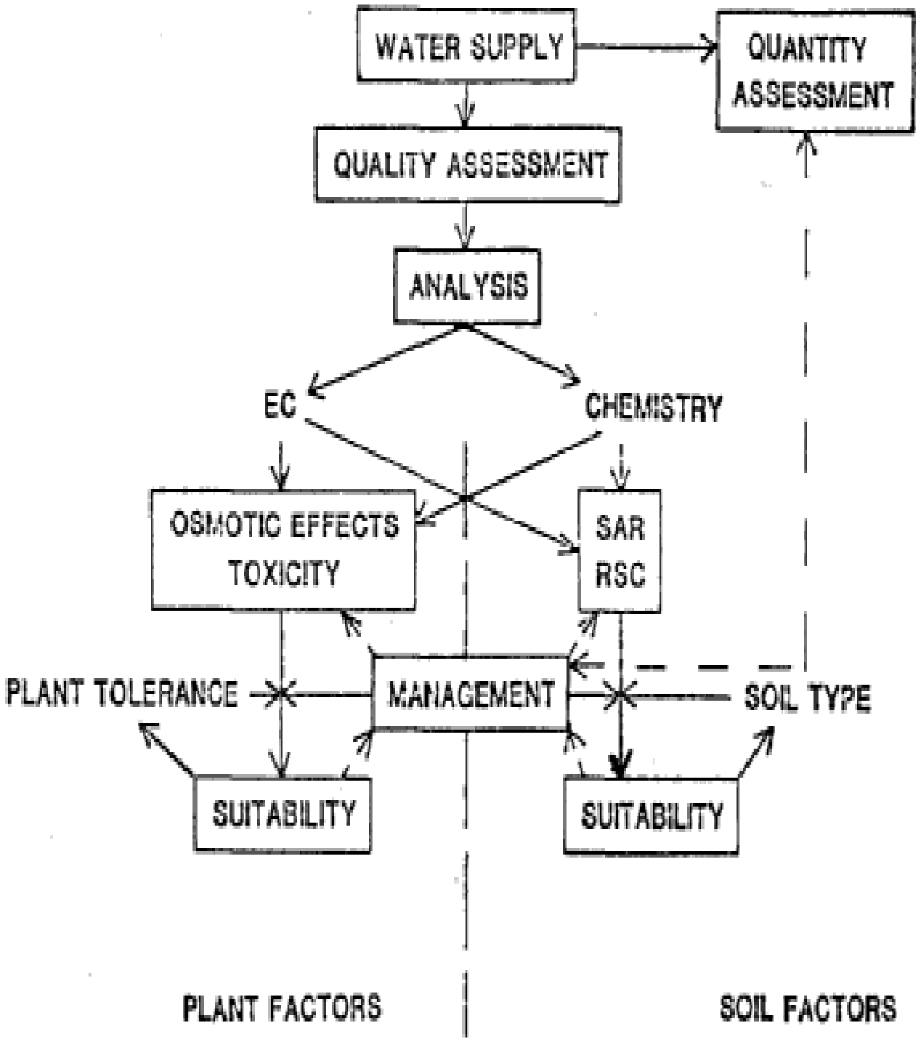

Fig.1.2: Flow diagram for evaluation of water quality

1.11 Heavy Metals Toxicity and its Impact on Ecosystem

Heavy metal wastewater pollution is a serious environmental threat facing by the today's world. The heavy metal concentration is increasing in the environment due to the massive industrialization has happened since the 17th century. Most of the industrial wastewaters carry heavy metals like chromium, zinc, cobalt, lead and cadmium. Along heavy metals chromium is the major pollutant of the leather tanning industry and is toxic to plants and animals in the environment (Smrithi and Usha, 2012). The intemperate aggregation of excessive metals in farming soils through wastewater irrigation system, may bring about soil sullying, as well as lead to raised substantial metal uptake by yields, and along these lines influence the quality of food and safety. Homo sapiens are vulnerable to the dangers lined with utilization of contaminated yields polluted with heavy metals and that is one of the main pathways for the entrance of poisonous substances into the human body. A portion of the unsafe effects on the intake of dangerous metals get obvious just after a few years of exposure. A few studies report that the intake of substantial metal defiled sustenance can drain some necessary supplements from the body that are eventually in charge of diminishing immunological resistances, intrauterine development impediment, weakened psycho-social workforces, incapacities connected with hunger and high pervasiveness of upper gastrointestinal malignancy rates (Srinivasan and Reddy, 2009). Water use proficiency procedures along with traditional resources have been upgraded. Nonetheless, in some parts of the world where fresh water resources are scarce, need to explore new water resources, to reduce the risk of water shortage in their regions. Non traditional resources of water are generated in many ways, such as the treatment of wastewater released by different industries, or primary level treatment of wastewater, can be applied, after taking special consideration according to soil and crop. In water-scarce parts of the world, non traditional kind of water is achieved through the treatment of sea water to remove excessive salt content from it, and extremely brackish ground-water, collecting rainwater in reservoir, and use of partially treated water for irrigation purposes. Partially treated wastewater that can be used for irrigation comprises of wastewater from agricultural lands, and groundwater having distinctive sorts of salts. A large amount of wastewater released by residential, urban, and industrialized areas is used for yield production in non treated or partially treated form in many third world countries (Cirelli et al., 2009).

1.12 Constraints on Reuse of Wastewater in Developing Nations

The fundamental purpose behind the usage of contaminated water in the developing nations is the non accessibility of enough financing to treat contaminated water before applying it on agricultural land. Therefore, it debases the environment and in addition turns a source of water borne diseases. Contaminated water has nutrients that are essential to the growth of plants like organic matter and soluble amounts of salts and heavy metals. Most of the agriculturists use this contaminated wastewater to spare their costs. Hazardous impacts will remain for decades if contaminated water is used on agricultural land, so it can percolate down to the zones of soil as well as has negative impact on under-ground water quality (Ashraf et al., 2011).

In third world countries, the constrained economic and physical assets to treat water, the socio-economic circumstances and the context of expanding cities create the situation for uncontrolled and unplanned wastewater use. A study appointed by the Comprehensive Assessment of Water Management in Agriculture demonstrates that over 53 communities in the third world countries, the principle source of wastewater use for irrigation are a combination of the following aspects:

- Restricted limits of urban communities to treat their wastewater, bringing on contamination of soils, water bodies and conventional irrigation systems
- Absence of option (less expensive, comparatively dependable, accessible or more secure) water sources in the areas.
- Cities food production demand and corporation sector interests' sustenance creation in the vicinity of urban areas, where water sources are contaminated (Sally et al., 2010).

1.13 Leather Industry in Pakistan

Manufacturing of leather products contributes around 5% to GDP and from this sector country gain 7% of its earnings. It is one of the most dynamic sectors of Pakistan after textile. From this sector not only foreign exchange is earned but also many workers are associated with this industry. More than 250,000 laborers are associated with tanning industry. In the world of leather market, contribution of Pakistan is only 1.5% and it is placed at twentieth in number.

As of now, this sector is competing to improve its share of export in the world of leather market. However quality and manufacturing expenses are the two significant difficulties confronted by tanning industry (http://www.nec.com.pk/ECPT.aspx). If consider the consumption and the export rate, leather industry has a good advantage to expand at domestic level. The modern development of the industry is fundamentally because of export of worth included leather products, for example, leather jackets, gloves, foot wear and products of sports goods. The local market of leather is constrained and around 80% of production is sent out. Between the era of 2002-2003, the aggregate gained from the export of leather is 694US$ that is around 7% of the export. More than 80 percent of the units are placed at Karachi and Lahore (Ali, 2004).

At present in Punjab, industries that produce leather are 516, from this 130 industries are developed on large scale, 176 are on medium scale while 210 industries are at small level. Most of these are located in the clusters of Kasur, Multan, Sialkot, Sahiwal and Gujranwala. The untreated stuff for these tanneries is buffalo/cow hide and sheep/goat skins. The industry uses substantial amount of inorganic salt (ammonium chloride, chromium sulphate). A typical chrome tanning salt contains 50% sodium sulfate, dyes may be diluted with an electrolyte) and organic chemicals (e.g. sulphonated mono, di- and tri- nuclear aromatics, sulphonated azoaromatic compounds) that may be hazardous and uses large amounts of water. In the tanning industry, about 25% of the weight of raw hide results in the finished leather where as the remaining 75% becomes as solid waste; of the solid waste about 50% is utilized by the manufacture of poultry feed, gelatin, glue, fish meal and soap, and the remaining 50% is dumped indiscriminately. In the raw hide/skin processing of the offered quantity of chemicals (except chromium) about 15% are consumed and the unconsumed chemicals are either discharged into tannery effluent or as solid waste. In case of chromium about 70% of the used amount is taken up by the hides/skins and about 30% remains unexhausted and goes into effluent waste water as well as into solid waste (EMRO and PTA, 2009). There are 725 tanneries in Pakistan and most of them employ chrome tanning because of the rapid processing, low cost, and better quality of the finished leather products (Bukhari et al., 2012). The characteristics of tannery wastewater change respectably from tannery to tannery relying upon the size of tanning industry, reagents used for a particular processes, amount of water used and type of finished products generated by a tannery. In 1998, Federation of Pakistan Chambers of Commerce and Industry directed a study in Pakistan and find out the physical and chemical characteristics of wastewater from tanneries processing raw goat and sheep skins to finished leather as given in Table 1.3 (Haydar et al., 2007).

Table 1.3: Quantitative analysis of Tannery wastewater

Parameters	Range
pH (unsettled effluent)	7.3-10
BOD_5, mg/L (30 minute settling)	840 – 18,620
COD, mg/L (30 minute settling)	1320 – 54,000
Suspended Solids, mg/L (30 minute settling)	220 – 1610
Settle able Solids, ml/L (30 minute settling)	11 – 40
Total K. Nitrogen, mg/L (unsettled effluent)	236 – 358
Sulfates, mg/L (unsettled effluent)	800 – 6480
Sulfides ,mg/L (at 0 time settling)	800 – 6480
Chromium, mg/L (unsettled effluent)	41 – 133

1.14 Tanning Industries in Kasur

Originally there were about 180 tanneries in Kasur but the figure has now gone up to over 300. As a consequence of tanning practices around 9,000 cubic meter of vigorously polluted waste water is being generated along side the dumping of about 150 tons of solid tannery waste daily basis around the city. The outcome was stagnant pools covering an area of 327 acres on the permanent basis with about 311 acres of fertile land affected during the monsoon period. This brought out about deterioration of the environment of the area presenting consequential threat to the health of human being directly exposed to unhygienic environment, consuming unsafe ground water and indirectly through the impacts of the chemically polluted water used for irrigation for the production of crops, yield output from the animals and their health. The environmental conditions in Kasur hence were detrimental to the health and well being of the inhabitants, the tanneries workers, and the formers. Taking into account the significance of the environmental and health hazards and the occupational health and safety problems in Kasur, UNDP started the Kasur Tanneries Pollution Control Project in cooperation with the Government of Pakistan, Government of Punjab and the owners of tanning industries. The government of Pakistan and United Nations Development Program (UNDP) signed the Kasur Tannery Pollution Control Project document in January 1996 with the United Nations Industrial Development Organization (UNIDO) being the implementing agency for technical assistance. UNDP allocated US$ 2.5 million, whereas the local input was Rs. 199 million. The Project intended to deal and minimize the environmental degradation caused by wastewater produced from tanning industry, to improve the tanner's technical and managerial skills; to promote environmental awareness among the pollution, hence upgrading their standards of living and working conditions and creating an environmentally sustainable tannery industry in Kasur. The program was conceived to deal with stagnant polls evacuation, providing effluent drainage and collection system, constructing common effluent pre treatment plant and sanitary landfill for solid waste disposal, and incorporating in-house waste minimizing measures such as low-waste leather processing, chromium recovery and occupational health improvement (Nawaz, 2011).

1.15 Characteristics of Common Effluent Pre-Treatment Plant (CEPTP)

By considering the environmental protection laws, wastes from any industry should be disposed off according to the standard operating procedures (SOPs). That's why Kasur tannery pollution control project has been launched where the common effluent pre treatment plant has installed. The total budget of this project to establish is 424 million Rs. While the running annual cost is 20 million Rs. After the treatment, it is reported that, Chemical oxygen demand is reduced by 50-65%, trivalent chromium is reduced by 96-98%, and sulphate 25-35%, sulfide 65-75% and total dissolved solids are reduced by 20-30%. This primary level treatment plant is running since the October, 2001. The solid waste produced from the primary treatment is collected as sludge, for the disposal of sludge, lagoons have been made. It is important to consider that just not too many tanneries have primary level of treatment, where sludge is separated from the wastewater. The most of the industries dump their waste in near water body or on open grounds without any kind of treatment (Sangyo, 2008).

The waste water pretreated in Kasur plant has been declared unfit for the irrigation purpose. The central theme of this study is how to render it fit for agriculture.

CHAPTER 2

LITERATURE REVIEW

Tanning in Kasur is a protracted tradition in suburbs of this town. Earlier tanneries were developed in the Dingarh village area on the bank of Rohi nallah and tanning process was carried out manually using natural tanning materials such as babool tree bark. With the passage of time, tanning industry was extended and Kot Molvi, Abdul Qadir, Niaz Nagar and Younus Nagar agglomerations were gradually developed. No significant measures were adopted to handle the tannery wastewater and solid waste. Thus the extension of industry lead to accumulation of tannery waste water in large areas in vicinity of the tannery clusters. The situation became so bad that around 400 acre land turned around a pond that spread obnoxious odorous gases around Kasur. In order to improve the condition of environment, tannery effluent treatment plant was constructed in which screening system separates the coarse material. After the manual screening, mechanical bar screening was carried out to remove suspended solids up to the size of 6 mm, in which 95% of suspended solids are removed. After that, wastewater goes in aeration tank through two drains. There are two aeration tanks; each aeration tank has eight aerators that mean total sixteen aerators are installed having a total volume of 12675 m^3 wastewater. Around 1.6 kg O_2/Watt hours is transferred in aeration tanks. From the aeration tanks wastewater is transferred to two sedimentation tanks with a detention time of five to seven days. Sludge is separated in the tank and transferred to the sludge disposal sites and sludge free water is transferred in lagoons. These lagoons are bedded with rammed clay and geo membrane to avoid the leaching effect. There are overall thirty two lagoons where water is hold for four to five days, where many organic and inorganic reactions take place. This pre treated tannery wastewater is made to join the Pandoki drain which ultimately disposes off in Sutlej River (GOP, 2001; Nawaz, 2011).

With the passage of time, new techniques and methodology have been evolved and many researches were conducted to find the most effective and appropriate methods to treat the tannery wastewater for the betterment of the environment. Some of these techniques and treatments have been discussed below with methods and their results on the basis of which appropriate techniques have been adopted for the treatment of tannery wastewater.

2.1 Tannery Wastewater Characteristics

Tariq et al., (2005) conducted multivariate analysis of selected metals in tannery effluents and related soil in Kasur region. Thirty eight samples of soil and effluent were determined in atomic absorption spectrophotometer and data reported in two media, i.e. metal distribution and metal to metal correlations. Effluent and soil sample analysis showed strong evidence that the Cr in tannery wastewater samples was a source of Cr in Kasur soil.

Ecotoxicological characterization of tannery wastewater in Dhaka, Bangladesh was done by Barreiro et al., in (2009). Chemical analysis showed that chromium was present in high concentration i.e. 47g/L, whereas electrical conductivity, pH and dissolved oxygen ranged 8430 μScm^{-1}, 7.20 and 0.5 mg/L respectively. The microbiological analysis reveled that the sampling area is infected by fecal contamination.

Shakir et al., (2012) investigated the eco toxic potential of tannery wastewater of Kasur and their chromium based components, potassium dichromate and chromium sulfate. Cytotoxicity assay, artemia bioassay and phytotoxicity assay was used to find out the eco toxicological potential of different concentrations of tannery wastewater, potassium dichromate $K_2Cr_2O_7$ and chromium sulfate $H_{24}Cr_2S_3O_{24}$. Results showed that, different concentration of hexavalent chromium caused significantly more damage to vero cell, brine shrimp and germination of maize seeds and thus, concluded that hexavalent chromium and tannery wastewater posed significant eco-damaging potential in Kasur district.

Tariq et al., in (2012) did comparative statistical analysis of chrome and vegetable tanning effluents of Kasur and Mian Channun. Kasur district was reported to have high concentration of heavy metals (Na, K, Ca, Mg, Fe, Cr, Mn, Co, Cd, Ni, Pb and Zn) due to the adoption of chrome tanning then, vegetable tanning. Na showed the highest concentration with a mean level of 15.186 g/L, Cr showed a mean concentration of 505.6 mg/L. The mean concentrations of Ca, Mg and K were 214.0, 178.9 and 72.95 mg/L, respectively. Among other metals, Fe, Co, Pb and Zn also showed relatively higher levels in effluent samples.

2.2 Treatment of Tannery Wastewater by Bioremediation Means

Hussain and Saati (1999) assessed the wastewater quality and its reuse in agriculture. Results showed that use of wastewater not only increased crop production but also reduced the cost of inorganic nitrogen fertilizer if it is present around 40mg/L in wastewater. Treated wastewater could be reused in agriculture if it is monitored by managing practices like suitable crop choice, crop requirements and right amount of fertilizers.

The authors further added that Cr caused oxidative stress that involves the induction of lipid per oxidation in plants that causes severe damage to cell membranes, degradation of photosynthetic pigments leading to decline in growth and can disturb the chloroplast ultra structure thereby interrupt the photosynthetic process (Panda. and Choudhury, 2005).

Aspergillus oryzae was used by Sepehr et al., (2005) for the removal of Cr (III) from tannery effluents. At the pH 5, temperature 30°C and shaking velocity 150 rmp, the biomass growth and chromium removal rate were found as 0.45% and 99.8% respectively. After the detention time of 30 hours, the biomass growth and chromium removal were 0.28% and 97.6% respectively.

Fahim et al., (2006) used the low cost potential absorbent for the removal and recovery of chromium from the tannery wastewater. Three types of activated carbon C1 (waste generated from sugar industry), C2 and C3 were (the commercial granular activated carbon) used as an absorbent. Results reveled that the waste generated form sugar industry with surface area of (520.66m^2/g) and calcium content (333.3 mg/L) showed highest adsorption values for the removal of trivalent chromium.

Tahir and Naseem (2007), selected bentonite clay as a local, cheaper and readily available adsorbent from Kheora region (Punjab) for the removal of trivalent chromium from the tannery wastewater. Adsorption of Cr (III) was studied both by batch and column techniques and it was noted that 93% of Cr (III) was removed using one gram of bentonite at a pH of 2.4–2.5. The negative surface charge on the clay is responsible for the sorption of trivalent chromium. More than 99% of Cr (III) was regenerated from the adsorbent using 50mL of 3M H_2SO_4. Atomic absorption spectrophotometer was used to find out the concentration of Cr (III) before and after adsorption.

Calheiros et al., (2007) conducted a seventeen month study on constructed wetlands received tannery wastewater in which five different plant species (C*anna indica, Typha latifolia, Phragmites australis, Stenotaphrum secundatum and Iris pseudacorus*) were grown. Two different hydraulic rates, 3 and 6 cmd^{1} were monitored. COD was reduced by 41–73% for an inlet organic loading varying between 332 and 1602 kg ha^{-1} and BOD_5 was reduced by 41–58% for an inlet organic loading varying between 218 and 780 kg ha^{-1} d^{-1}. When compared with BOD and COD, nutrient removal was much less. *Phragmites australis* and *Typha latifolia* were the only plants that were able to establish successfully.

Biosorption of trivalent chromium from tannery wastewater by *Pleurotus ostreatus* was done by Javid and Bajwa (2007). Through biotechnology, the fungus was grown on low cost available substrates like rice straw, wheat straw and cotton waste. When *Pleurotus ostreatus* was used for biosorption at pH 4.5 and stirring intensity 150rpm, 55% of biosorption efficiency was obtained for trivalent chromium. Most successful readings were obtained when wheat straw was colonized with *Pleurotus ostreatus*.

Treated tannery wastewater in the Jajmu area (Kanpur) used for irrigation on 35 Rhizobium sp. which were isolated from root nodules of *Trifolium alexandrinum (*Egyptian clover). Results showed that, *Trifolium alexandrinum* roots and leaves accumulated the highest amount of metals. The mean concentrations found in the soil were chromium 1178 μg/g, nickel 51.5 μg/g, zinc 39.86 μg/g, copper 21.3 μg/g, and cadmium 1.09 μg/g. Altaf et al., (2008) found that despite these toxic stresses, the Rhizobium isolates may have evolved resistance mechanisms to deal with metal toxicity that include volatilization, extracellular precipitation and exclusion, binding to cell surface, and intracellular sequestration.

Haydar and Aziz (2009) reported the kinetic co efficient for the biological treatment of tannery wastewater by adopting the activated sludge method. The reactor was operated for 86 days. Kinetic coefficient k (maximum substrate utilization rate, per unit mass of microorganisms, time^{-}1) was 3.125/day, Ks (half velocity constant, mass/unit volume) was 488mg/L, Y (cell yield coefficient) was 0.64/day and Kd (decay coefficient) was 0.035/day were noted. Biological oxygen demand (BOD) was removed at a rate of 1.46/day. This value can be used in the design of aerated lagoons and waste stabilization ponds.

Abdulla et al., (2010) focused on the treatment of tannery wastewater by chemical and biological means. By chemical method, 98% of trivalent chromium was recovered by dissolving 2g/100mL lime, maintain the pH between7.7-8.2 and gave the settling time for about 120 minutes. For biological treatment, 34 actinomycetes isolates were showed to tolerate up to 100mg/L of hexavalent chromium, five of them showed tolerance up to 2500mg/l. Isolate S65 was the most effective isolate to remove 97% of hexavalent chromium over the period of four hours.

Kannan et al., (2012) studied the Cyanobacteria (*Anabaena flos-aquae*) for the bioremediation of chromium in tannery wastewater. Cultures of *Anabaena flos-aquae* were grown in allen and arnon's medium (free of nitrogen). For the remediation, the tannery wastewater was amended with growth medium at different dilutions (1:10, 1:100 and 1:1000). The results indicated that, higher the concentration of chromium (8ppm) greater was the chlorophyll and carotenoid content at 48 hours.

Saeed et al., in (2012) reported the removal of toxics from the tannery wastewater by building a hybrid wetland system. *Phragmites australis* plant species was selected with different media control and followed by three treatment stages (subsurface vertical flow, horizontal flow and vertical flow). The hybrid wetland showed an overall excellent removal of NH_3–N, NO_3–N, BOD, COD, and PO_4 were 86%, 50%, 98%, 98% and 87%, respectively.

Siraj et al., (2012) used Chitosan-charcoal composite as a media to treat tannery effluent. The Chitosan gel was prepared by adding shrimp shells (in powdered form) in oxalic acid and heating the mixture at 40-50°C. Then Chitosan gel (50g) and charcoal (250g) were mixed to get Chitosan charcoal composite and characterized by XRD (X-ray diffraction) and SEM (Scanning Electron Microscope). Adsorption of chromium (Cr) was investigated by varying the contact time between adsorbent and composite, pH of solution and dose of composite. Results revealed that the, maximum Cr was removed at pH 4 and optimum dose and contact time was 40g/L and 250 minutes respectively. The experimental results showed that the chitosan charcoal can be used for the removal of chromium present in tannery effluents.

Sangeetha et al., in (2012) studied the impact of tannery effluents on maize (Zea mays), containing chromium concentration above the permissible limits i.e. 92.32 mg/L. Due to the presence of chromium, the quality of growth deteriorated by exerting oxidative stress in maize seeds. However, when the tannery wastewater was diluted, it showed improved plant yield, if metals and organic compounds were present within the acceptable range.

Chakraborty and Mukherjee (2013) accomplished the removal of chromium from treated tannery wastewater using Pistia plants (water lettuce). Results showed that Pistia was able to accumulate hexavalent chromium from treated tannery wastewater containing soluble hexavalent chromium at reduced level of 2.78mg/L. Accumulation of hexavalent chromium in Pistia root and shoot ranged 17.46µg/g and 4.23µg/g respectively.

2.3 Treatment of Tannery Effluents by Chemical Means

Liberti et al., (2002) conducted a nine month pilot scale (100m^3/h) study for the advance treatment of wastewater for its reuse in irrigation by applying UV disinfection technique to remove parasites. The disinfection by product (DBP) developed during the UV disinfection of clarified (CL) at the dose of 160mWs/cm^2 and clarified filtered (CF) at 100mWs/cm^2, essential for the obtaining the reading of total coliforms bacteria, around 2 CFU/100ml for its reuse in irrigation. 65% of protozoan parasites (*Giardia lamblia* cysts and *Cryptosporidiumvparvum oocysts*) were removed. The nitro phenols and nitro-amines were also analyzed by GC/MS analytical technique, indicating the absence of detectable photochemical reactions at UV dose, used in the disinfection of wastewater.

Ferric chloride and aluminium sulphate were used as a coagulant by Song et al., (2004) for the removal of toxic components from the tannery wastewater. When the results of two coagulants were compared, ferric chloride showed better results than aluminium sulphate. 38-46% removal of suspended solids, 30-37% removal of total COD and 74-99% removal of chromium at dosage of 800mg/L at 7.5 pH. Experiment also revealed that chromium at low concentration and elevated pH showed better result on removal of chromium than larger concentration of chromium at low pH.

Awan (2004) conducted a study on the reduction of chemical oxygen demand (COD) from tannery wastewater by oxidation method. Three oxidant's solutions i.e. hydrogen peroxide, sodium hypochlorite and calcium hypochlorite were used at different temperatures and reaction durations for the oxidation of tannery wastewater having high COD 3413mg/L. Results revealed that the treatment with calcium hypochlorite was the best at temperature around 100°C for 5 minutes and it gave 76% reduction of COD from the tannery wastewater. Calcium hypochlorite is also cost effective when compared to two others oxidants.

Treatment of tannery wastewater by electro coagulation method was performed by Apaydin et al., (2008). Two methods of treatments were tested i.e. electro-coagulation (EC) and electro-Fenton (EF). At anode and cathode iron plates were placed, and 33.3 mAm^{-2} current was passed for the removal of chemical oxygen demand (COD) and sulfide. EC showed better removal results than EF. COD and sulfide were removed 46% at electric consumption of 1.8 kWh/kg and 90% at 27.7 kWh/kg respectively, by EC method. Rema et al., (2010) studied the degradation of syntan used in tanning by ozonation method. Experimental results showed that highest concentration removal of COD, tannin and aromatic compounds was obtained at pH 7 and ozone dosage was 1g/hr.

Coagulation, flocculation, sedimentation technique was applied by Haydar and Aziz (2009) to treat tannery wastewater. Alum when used with cationic and anionic polymers showed better results than the use of alum alone. 5 mg/L cationic polymer C-496 with 100 mg/L alum showed 97% removal of turbidity, 93.5%, 36.2% and 98.4% removal of TSS, COD and Cr respectively. While 5mg/L anionic polymer A-100 with 160mg/L alum indicated 99.7%, 96.3%, 48.3% and 99.7% removal of turbidity, TSS, COD and chromium respectively.

According to Costa and Olivia (2009) concentration of chloride affects the treatment of tannery wastewater by electrochemical process. The higher concentration of chloride, gives the speedy removal of phenolic compounds, total organic carbon

(TOC), COD, conjugated double bonds and color. Higher current efficiencies and lower energy consumptions are also obtained at higher chloride concentrations.

Sundarapandiyan et al., (2010) treated the tannery wastewater by electrochemical method using graphite electrodes. It was revealed that ideal results were achieved at the current density of 0.024 A/cm^2 for a time of 2 hours at pH 9. For the removal of 1kg of TKN and 1kg of COD, 22.45Kwh and 0.80kWh energy were required respectively. This treated wastewater can be reuse thrice in tanning process.

Saleem et al., (2011) carried out laboratory based electro coagulation (EC) experiment to treat the wastewater to achieve the international standards of wastewater reuse. It was observed that by applying the 24.7mA/cm^2 current density with an inter electrode spacing of 5cm gave the 91.8% removal of COD, 77.2% removal of TSS and turbidity 68.5% within the 30 minutes of EC treatment. The values of electrical conductivity, sodium absorption ratio and total dissolved solids were found within the acceptable range for its reuse in irrigation and plantation.

Islam et al., (2011) determined the efficiencies of different coagulants (lime, alum, ferric chloride) by combining them. Results showed that alum as well as the combination of alum and ferric chloride provides the reduction in terms of total dissolved solids, alkalinity, salinity, chloride, biological oxygen demand and chemical oxygen demand. By the use of alum at the dose of 70mg/L, Cl was 423.33, BOD5, COD, and Cr^{6+} were noted at 2460, 1329.33 and 0.53mg/L respectively. And by the use of ferric chloride and alum together, the Chloride, BOD5, COD and Cr^{6+} were noted as 426.67, 710, 1242 and 0.03mg/L respectively.

Banuraman and Meikandaan (2013) conducted a study on the treatment of tannery effluents by using alum, ferric sulphate and their combination. The results revealed that use of alum 80mg/L, gave the removal of TSS, BOD_5, COD and Cr 91%, 89%, 78% and 90% respectively at pH 8. While the use of ferric sulphate at the dosage of 100mg/L showed 87% removal of TSS, 82% of BOD_5, 71% of COD and 78 % of Cr. At optimum dosage of alum (70mg/L) + ferric sulphate showed effective results of removal, i.e. 95% of TSS, 91% of BOD_5, 80% of COD, and 92% of Cr.

2.4 Treatment of Tannery Wastewater Using Membrane Technology

Gotor at al., (2001) used a membrane process for the recovery and reuse of wastewater for an irrigation purpose. A pilot plant was established with reversible electrodialysis (with a production of 100m^3/d), Ultrafiltration (430m^3/d) and reverse osmosis (210m^3/d). The plant had polyamide spiral-wound membranes. It was established that, EDR generates 100-140m^3/d of water with a content of dissolved solids of less than 500mg/L and a hydraulic recovery of 82-90%) was the most suitable treatment of wastewater as it did not remove the essential nutrients required by the plant, while reverse osmosis removes more salinity.

Oron et al., (2006) used the UF (Ultrafiltration) and RO (Reverse Osmosis) membrane treatment for secondary treated wastewater which can be further applied on agricultural fields. At the first stage of treatment, wastewater was treated with UF membrane which removed various organic matters and certain pathogens, after that UF treated wastewater can be used for unconditional irrigation. In the RO stage, dissolved solids were removed successfully from the wastewater. Membrane fouling was controlled by flushing sodium hydroxide solution to prevent the re growth of bacteria.

Aleixandre et al., (2011) adopted the pollution prevention techniques like recycling of unhairing wastewater and nanofiltration (NF) (spiral wounded membrane of 2.5 inches of diameter, temperature maintained at 26°C) to reuse chromium sulphate from the tannery wastewater. The experimental data showed that, by using 50% fresh water and 50% unhairing wastewater can be used to achieve good quality of leather, while by NF, 97% of sulphate were removed from the wastewater, by applying these two techniques together, total 14.82 kg sulphate per ton of hide was removed

Yim et al., (2007) evaluated integrated membrane system (IMS) consisting of microfiltration (MF) spiral wound typed and reverse osmosis (RO) each module has a membrane area of 7.5m^2. Microfiltration (pore size of 0.1 μm) was selected as a pre treatment because it was effective in the removal of small sized particles, followed by reverse osmosis for the treatment dissolved solids. The characteristics of IMS treated wastewater were acceptable except zinc and ammonia.

Gisi et al., (2009) conducted the feasibility of the reuse of treated tannery effluents in industrial process. For this, activate sludge was used as a pretreatment followed by RO (reverse osmosis) with plane membrane due to the salinity content in the treated tannery effluent. Active sludge treatment showed reduction of chemical oxygen demand by 67% at the retention time in aeration tank was thirty hours and DO (dissolved oxygen) was around 5mg/L. after the biological treatment, RO was used. The COD removal percentage for a TMP (transmembrane pressure) of 90 bars was 97.4%. Ammonium substances removal (not sufficiently removed by the activated sludge treatment) was 96.1% and 98.5%, respectively for ammonia and nitrate. While, in relation to salts, chloride and sulphate removal was 98.8% and 99.8%, respectively.

Roger et al., (2007) evaluated combination of filtration, Ultrafiltration and reverse osmosis as treatment for the physical-chemically treated wastewater. Ultrafiltration was not effective to remove the soluble COD, concentrations were found high around 2000mg/L in all tested UF membranes (3, 10, 30 and 100kDa). For RO, polyethersulfone membrane with cut-off of 30 kD was selected. Permeate fluxes of the reverse osmosis membrane reached 40 l/(m2h) at 30 bar. Due to the high chloride concentration of the tannery wastewater, a reverse osmosis process was necessary for water reuse in the factory.

Krishanamoorthi et al., (2009) treated the tannery wastewater by embedded system for its reuse. Ultrafiltration with an effective membrane area of $0.009m^2$ and four polyetersulphone (PES) membranes of different cut off (3,10,30100 kDa) were experimented at different transmembrane pressures (1,2 and 3 bar) at 25°C and1.3m/s, temperature and velocity respectively. For reverse osmosis, spiral viral wounded membranes with an effective area of $2.8m^2$ with three transmembrane pressures (20,25, and 30 bar) at a rate of 500/h was tested. Results indicate that, reverse osmosis is obligatory, for the reuse of wastewater in leather industry, when chloride concentration was quite low. While the Ultrafiltration (UF) with the combination of physico-chemical treatment showed that, the removal of soluble chemical oxygen demand (COD) was not effective from the tannery wastewater.

Bolzonella et al., (2010) studied the effectiveness of conventional activated sludge and membrane bioreactor with particular reference for the removal of pollutants. The studies proved that the MBR provides solid free, high quality permeate, most nutrients, heavy metals and persistent organic pollutants were removed, particularly, dioxins, furans, and poly chlorinated biphenyls. This treated wastewater can further be used in agriculture, where water is scarce now.

Goals and Objectives

The goal of the study will be the complete physicochemical analysis of the wastewater pretreated by the installation of Common Effluent Pre treatment Plant (CEPTP) declared unfit for use in irrigation of land for growth of agricultural crops by the international consultants and subsequent identification of certain measures to render pretreated wastewater fit for agricultural growth and its conservation under the concept of sustainable development instead of polluting Sutlej River in which it is finally drained. The objectives will be as follows:

1. Sampling of the pretreated wastewater after its passing through CEPTP at Kasur till the end where it disposes off in River Sutlej.
2. Physico-chemical analysis of wastewater for toxic ingredients particularly salt content that is most hazardous for irrigation purposes.
3. Indentifying the changes when pre treated wastewater drains off in Pandoki drain.
4. Notifying the chemical composition of pretreated wastewater as it runs off.
5. Proposing methods of treatment for rendering pretreated wastewater fit for agriculture and techno-economic evaluation of proposed methods and recommendation of suitable measures for elimination of the negative impact components from pretreated wastewater.

Research Questions:

1. What is the chemical composition of pretreated tannery wastewater along the length of the drain?
2. How does it compare with the standard composition of water requisite for normal irrigation?
3. How it can be rendered fit for irrigation?

CHAPTER 3

MATERIALS AND METHODS

The present study deals with the pre treated tannery wastewater in Kasur district. The common effluent pre treatment plant (CEPTP) was installed to treat tannery wastewater at primary level that started functioning in 2001. Standard methods are applied to treat tannery wastewater produced by a cluster of 230 tanneries of Kasur. The wastewater from tanning clusters is collected through open channels under the flow of gravity. The wastewater is first screened manually then mechanically with 6mm mesh size screens. The tannery effluent is then transferred to equalization tanks where it is subjected to mechanical aeration. The aerated effluent is pumped to sludge separation tanks, where sludge settles down due to its difference in density. The wastewater is then transferred to and allowed to stand in natural aeration lagoons for 4 to 5 days. In the last, this pre treated tannery wastewater is drained out through a "green channel" to the Pandoki drain, which ultimately disposes off in the river Sutlej. The map of the Kasur tannery control project is shown in Figure 3.1.

3.1 Samples Collection

3.1.1 Sampling plan

The sampling was planned with the collaboration of Soil Testing laboratory near thokar niaz baig and Environmental Protection Department (EPD) Government of the Punjab near qaddaffi Stadium Lahore in the month of June 2013. Total sixteen numbers of samples were collected from the selected sites. Grab sampling technique was used to carried out sampling.

3.1.2 Sampling Points

The pretreated wastewater samples were collected from sixteen different points. Green channel (1.7Km) originates from the CEPTP leads to the Pandoki drain where it finally disposes off in River Sutlej. Each wastewater sample was collected by a distance of 2Km. Table 3.1 demonstrates the sampling points, where the samples have been collected for analysis. Figure 3.2-3.7 shows the sampling sites.

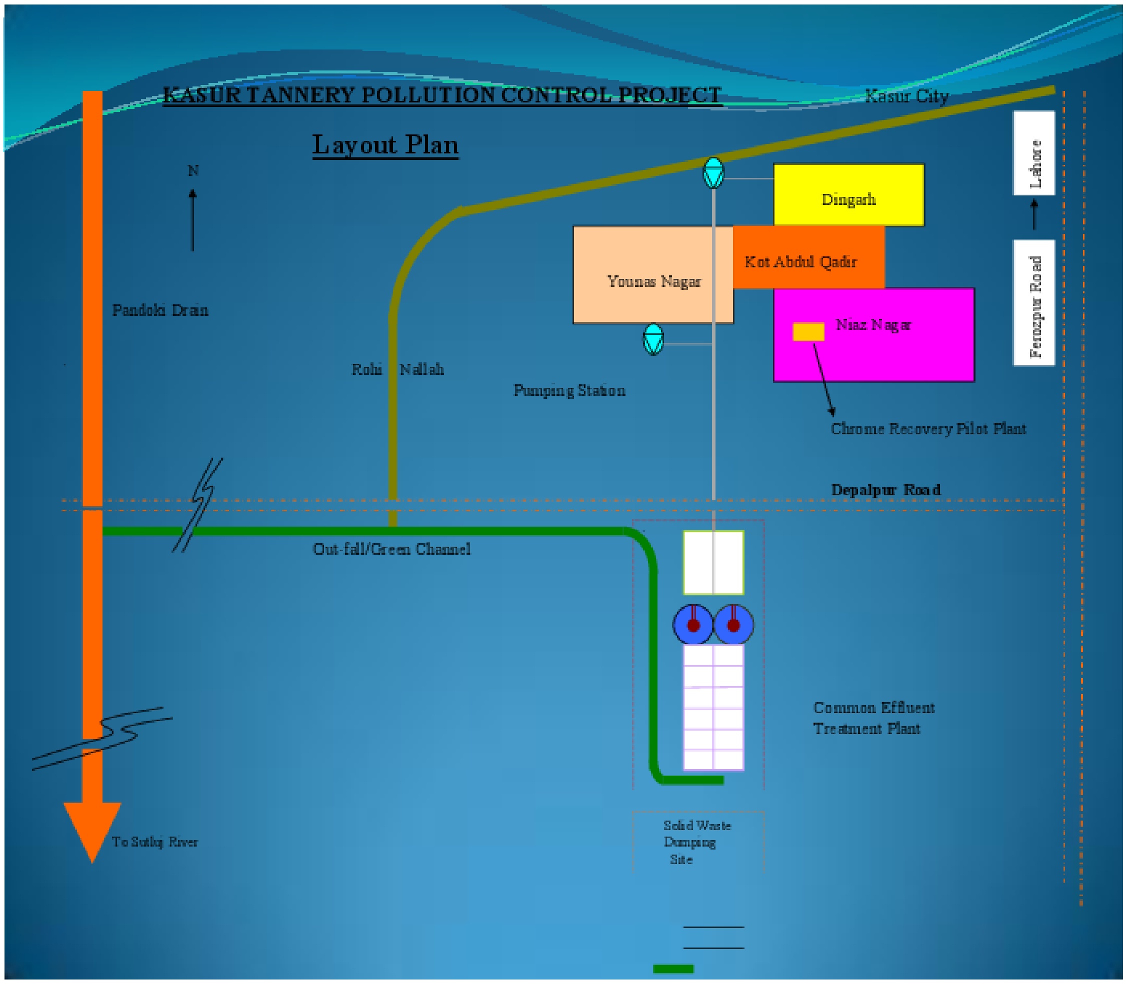

Fig.3.1: Map of the Kasur tannery pollution control project.

Table 3.1: Shows the samples collected with their designated numbers and collection point/Area

Serial No. of Sample	Designated as	Collection Point/ Area	
1	S_1	After settling tank	
2	S_2	Lagoon no. 15	
3	S_3	Green channel	
4	S_4	Main hole (at a distance of 2km)	
5	S_5	Main hole (at a distance of 2km from the previous point)	
6	S_6	Before mixing in Pandoki drain	
7	S_7	Tannery wastewater enters in Pandoki drain	
8	S_8	Pandoki drain	
9	S_9	Pandoki drain	Upper stream
10	S_{10}	Pandoki drain	
11	S_{11}	Pandoki drain	
12	S_{12}	Pandoki drain	Lower stream
13	S_{13}	Pandoki drain	
14	S_{14}	Pandoki drain before mixing in the Sutlej river	
15	S_{15}	Sutlej river	
16	S_{16}	Sutlej river	

Fig.3.2: Tannery wastewater after the settling tank.

Fig.3.3: Lagoon no. 15

Fig.3.4: Open green channel/Outfall drain.

Fig.3.5: The main hole

Fig.3.6: Tannery wastewater entrance in Pandoki drain.

Fig.3.7: Pandoki drain at upper stream.

3.2 Parameters measured

The selected parameters for the physicochemical analysis of pretreated tannery wastewater samples after its discharge from CEPTP were pH, temperature, electrical conductivity (EC), total dissolved solids (TDS), sulphate (SO_4^{2-}), chloride (Cl^-), sodium absorption ratio (SAR), residual sodium carbonate (RSC) and heavy metals i.e. Chromium (Cr), Cadmium (Cd), Zinc (Z) and Copper (Cu). The selected parameters are shown in table 3.2.

3.3 Sampling Procedures

Samples were collected according to the standard methods for water and wastewater (APHA, 2005). Standard sampling techniques were followed in each sampling site to ensure the integrity of the samples. The samples were collected in accordance with the required and established methods. Extreme care was taken during sampling, sample handling, sample preservation, identification, transportation and storage. The procedure followed was as under:

- Polyethylene bottles were used for the wastewater sampling. The bottles were air tight to avoid any kind of contamination.
- Manual sampling procedures were carried out for the collection of pre treated tannery wastewater samples.
- As a general rule, it is best to analyze samples as soon as possible after collection. However, samples were preserved in an ice box at or near 4°C temperature.
- The samples could become contaminated if they were to come in contact with human flesh; therefore protective gloves were worn during sample collection and preservation.
- Each sample bottle was given an identification number immediately after the collection of sample. Following information was attached to each sample bottle. Sample identification number
    i. Sample origin
    ii. Sample conditions (pH, temperature, etc)
    iii. Sample type (Composite, grab)

iv. Sample date and time

v. Sample preservation

vi. Analysis required

vii. Sample integrity

viii. Sample transportation time

- Soon after sampling, the samples were brought to the Lahore School of Economics (LSE) and Soil & Water Testing Laboratory, Thokar Niaz Baig Lahore, for Laboratory analysis.

3.3.1 Preservation of samples

Samples were collected and handled carefully to avoid contamination before they reached the laboratory. They were stored in appropriate containers to maintain the integrity of the samples. To obtain the reliable results, the samples were analyzed as soon as possible.

Following steps were followed for sample preservation:.

i. The samples were preserved in sterilized bottles to maintain the integrity of the samples collected.
ii. Samples were protected from sunlight which may initiate photo degradation of sample components.
iii. The preservatives were added to avoid any contamination and retardation of chemical compounds in the samples.

For the analysis of different parameters, pre treated tannery wastewater samples were preserved according to the analysis required. Table 3.3 shows the recommended containers, preservatives and holding time for the collection and storage of samples.

Table 3.2: Selected parameters for the analysis of wastewater samples from the drain

Sr. No.	Parameters
1	Temperature
2	pH
3	EC
4	SAR
5	RSC
6	TDS
7	Sulphate
8	Chloride
9	Cadmium
10	Copper
11	Chromium
12	Zinc
13	Iron

Table 3.3: Recommended containers, sample preservation, storage and holding time collection of wastewater samples (APHA, 2005)

Sr. No.	Parameters	Containers	Preservatives	Maximum holding time
1	Temperature	Plastic, Glass	Nil	Analyze immediately
2	pH	Plastic, Glass	Nil	Analyze immediately
3	Hardeners	Plastic, Glass	HNO_3 or H_2SO_4 to pH < 2	6 months
4	Electrical Conductivity	Plastic, Glass	Cool, 4°C	Analyze immediately
5	TDS	Plastic, Glass	Cool, 4°C	28 days
6	Sulphate	Plastic, Glass	Cool, 4°C	28 days
7	Chloride	Plastic, Glass	Nil	28 days
8	Metals	Plastic, Glass	For dissolved metals filter then add HNO_3 to pH < 2	6 months
9	Sodium	Plastic, Glass	Cool, 4°C	14 days

3.4 Laboratory analysis

3.4.1 pH

pH of the sample was determined by HI 2210 pH meter (company HANNA instruments). The electrode of the pH meter was first rinsed carefully with distilled water before immersing its probe in the sample. The readings were noted by pressing the ON button on pH meter.

3.4.2 Electrical Conductivity and Total Dissolved Solids

Electrical conductivity of wastewater samples was measured by Conductivity meter (HANNA HI8633). Its electrodes were also rinsed with distilled water before immersing in the sample. The readings were noted in µs/cm.

3.4.3 Total Dissolved Salts

To obtain the readings for total dissolved solids in ppm, the EC readings were multiplied by factor 0.7.

3.4.4 Sulphate

Sulphates were measured by gravimetric method (4500-C APHA/AWWA, 2005).

Procedure

100 mL filtered sample was taken in a flask and 1.5 mL of HCl was added and the mixture was boiled on hot plate.. Then about 30 mL of barium chloride (10%) also boiled on hot plate was added into the sample at boiling state. The sample was placed for overnight and filtered using Whatman filter paper No. 42 pre-weighed initially to obtain precipitates of barium sulphate after filtration. The filter paper was then placed in an oven for drying at 103°C. After drying, the filter paper was placed in desiccators for cooling. After cooling, filter paper was weighed finally.

Calculations

Final weight of precipitate – Initial weight of filter paper = A

$A \times 411.6 \div \text{mL of sample} = SO_4^{2-}$ mg/L

3.4.5 Chloride

Chlorides were determined by Argentometric Method (4500-B APHA/AWWA, 2005).

Procedure

10 mL filtered sample was taken in a flask and 40 mL of distilled water was added in it. Then 2 to 3 drops of K_2CrO_4 were added in it. After that, sample was titrated against $AgNO_3$ (0.05N). End point was noted, when the sample color turned from yellow to pinkish. Same procedure was repeated with distilled water, to obtain blank reading.

Calculations

$(A - B) \times N \times$ Equivalent weight of $Cl^- \times 1000 \div$ mL of sample = mg/L Cl^-

Where

A= mL titration for sample

B= mL titration for blank

N= normality of $AgNO_3$

3.4.6 Residual Sodium Carbonate (RSC)

Residual Sodium Carbonate (RSC) was calculated applying the following formula:

RSC (mEq/liter) = $(CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+})$

Carbonates and bicarbonates

Carbonates and bicarbonates were determined by acidimetric titration:

Carbonates:

50 mL of filtrated samples was taken in a porcelain dish and few drops of Phenolphthalein indicator was added until it turned pinkish in color. Then the sample

was titrated against 0.1N of H_2SO_4. End point was noted, when pink color disappeared.

Calculation:

2 (Volume of H_2SO_4 used) × Normality of H_2SO_4 × 1000 ÷ mL of sample = CO_3^{2-} mEq/liter

Bicarbonates:

To the same sample after carbonates titration, few drop of methyl orange was added as an indicator and titrated against standardized 0.1N H_2SO_4. The end point was noted when the color changed from golden yellow to light pink or light orange.

Calculation:

Volume of H_2SO_4 used for HCO_3^- - Volume of H_2SO_4 used for CO_3^{2-} × Normality of H_2SO_4 × 1000 ÷ mL of sample taken = HCO^{3-} mEq/liter

3.4.7 Calcium and Magnesium

Ca and Mg were determined by EDTA method:

10 mL filtrated sample was taken in a porcelain dish, few drops of ammonium chloride (NH_4Cl) + ammonium hydroxide (NH_4OH) buffer solution was added. Few drops of Eriochrome black – T (EBT) was used as an indicator. The sample was then titrated against standardized 0.01N EDTA solution until the color changed from wine red to blue/green.

Calculation: Volume of EDTA used × Normality of EDTA × 1000 ÷ mL of sample = Ca^{2+} + Mg^{2+} (mEq/liter)

3.4.8 Sodium Adsorption Ratio (SAR)

SAR was calculated by the following formula:

$$SAR = \frac{Na^+}{\left(\frac{Ca^{2+} + Mg^{2+}}{2}\right)^{1/2}}$$

Sodium was measured using flame photometer. The Flame Photometer was standardized with 100ppm, 50ppm and 10ppm Sodium standards. Then the water samples were fed into Flame Photometer and Sodium contents were recorded in ppm. Dilutions of samples were made as and when required.

3.4.9 Inductively coupled plasma mass spectrometry (ICP-MS)

Five heavy metals i.e. cadmium (Cd), chromium (Cr), copper (Cu), zinc (Z) and iron (Fe) were analyzed on ICP-MS (Inductively Coupled Plasma Mass Spectrometry). Filtered samples were used to run on the machine. Table 3.4 shows the standard methods and equipment used for physicochemical analysis of wastewater.

3.5 Data analysis and interpretation

After the completion of sampling and analysis, the data was compared with international standards for wastewater irrigation. The data was presented in the form of graphs and tables for which mean and standard deviation were also calculated. One way Anova (Analysis of Variance) and correlation is also applied.

Fig.3.8: Collected tannery wastewater samples in Polyethylene bottles.

Fig.3.9: Flame spectrophotometer was used for the analysis of Sodium (Na).

Table 3.4: Standard methods and Equipment used for physicochemical analysis of wastewater samples

Serial No.	Parameters	Standard specification/ Techniques/ Equipment used
1.	pH	pH meter
2.	Temperature	Calculated from thermometer
3.	Electrical conductivity	EC meter
4.	TDS	By multiplication factor
5.	SAR	By SAR formula
6.	RSC	Ca^{2+}+Mg^{2+} by EDTA method $CO3^{2-}$ + HCO^{3-} by Acidimetric method.
7.	Sulphate	4500-SO_4^{2-}-C Gravimetric Method AWWA/APHA, 2005.
8.	Chloride	4500-Cl^--B Argentometric Method AWWA/APHA, 2005.
9.	Heavy metals (Cd, Cr, Cu, Z, Fe)	ICP-MS

CHAPTER 4

RESULTS

The results of the analysis of pretreated tannery wastewater samples are presented below in the form of graphs. The physicochemical analysis was carried out for pH, temperature, electrical conductivity (EC), total dissolved solids (TDS), sulphate (SO_4^{2-}), chloride (Cl^-), sodium absorption ratio (SAR), residual sodium carbonate (RSC) and heavy metals (Cr, Cu, Z, Fe, Cd). Mean and standard deviation (± SD) is calculated for each parameter. The values of the each parameter are compared with the international standards of wastewater for irrigation proposed by World Wide for Nature (WWF) Pakistan. The bivariate correlation coefficient of the mean value of each parameter is computed and the significance is tested against 5% level. To test the difference in the mean value of each parameter across different sites one way ANOVA is also applied at the significance level of 0.05.

Fig. 4.1 exhibits the graph showing the values of pH for samples as compared with the proposed standards of wastewater for irrigation by WWF. The international standard of pH for wastewater for irrigation is 6.5-8.4 (2007). Within these limits the pH value is safe. The maximum averaged pH value with standard deviation (SD) was recorded for sample No.S_2 is 8.48± 0.05568 and averaged minimum value is measured as ± SD; 8± 0.03215 in sample No. S_5. The pH is in acceptable range in all samples, except sample No.S_2. The results of the ANOVA table indicated that the mean pH value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 4a).

Fig. 4.2 presents the graph showing the values of temperature for samples as compared with the proposed standards of wastewater for irrigation by WWF. The optimum temperature range suggested for wastewater for irrigation is 20-26°C (2007). The maximum averaged value of temperature is measured with ± SD for sample No.S_2 and S_6 are the same i.e. 35.6°C± 0.57735. While the minimum averaged value of temperature is measured as ±SD; 29.3± 0.333 for sample No.S_{16}. The temperature range is decreasing at the end of sampling points. The results of the ANOVA table indicated that the mean temperature value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 4b).

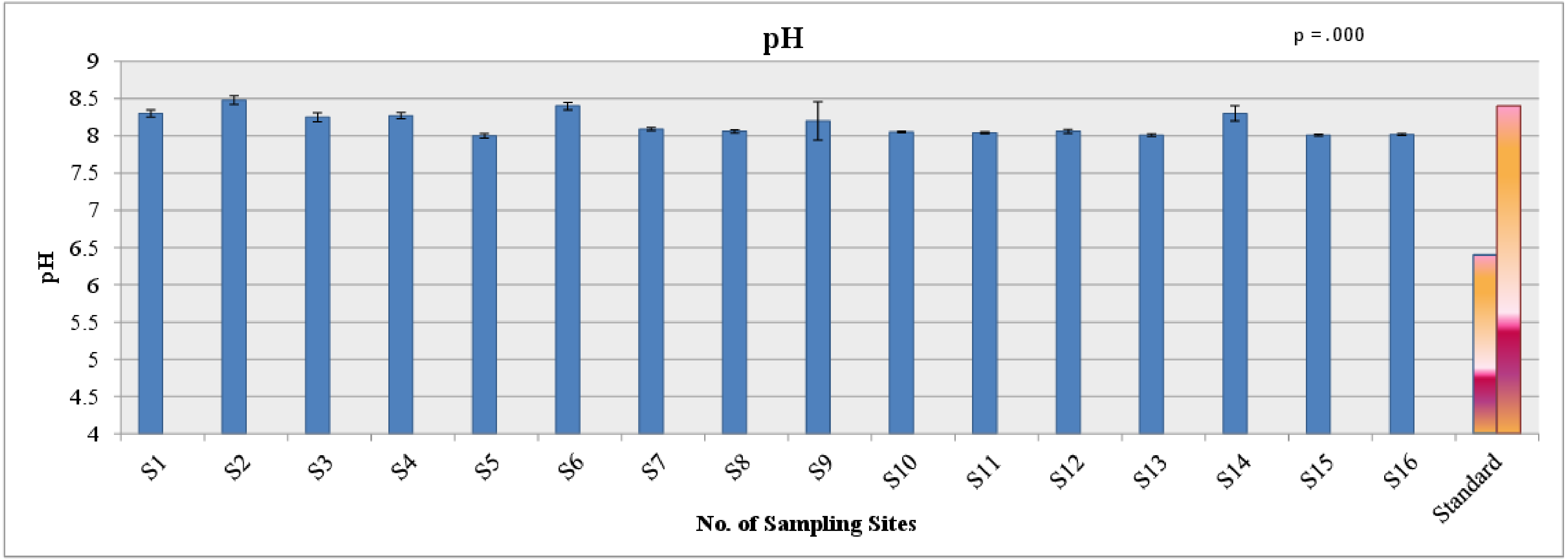

Fig. 4.1: Graph showing the averaged values of pH for samples and their comparison with the proposed standard of wastewater for irrigation by WWF.

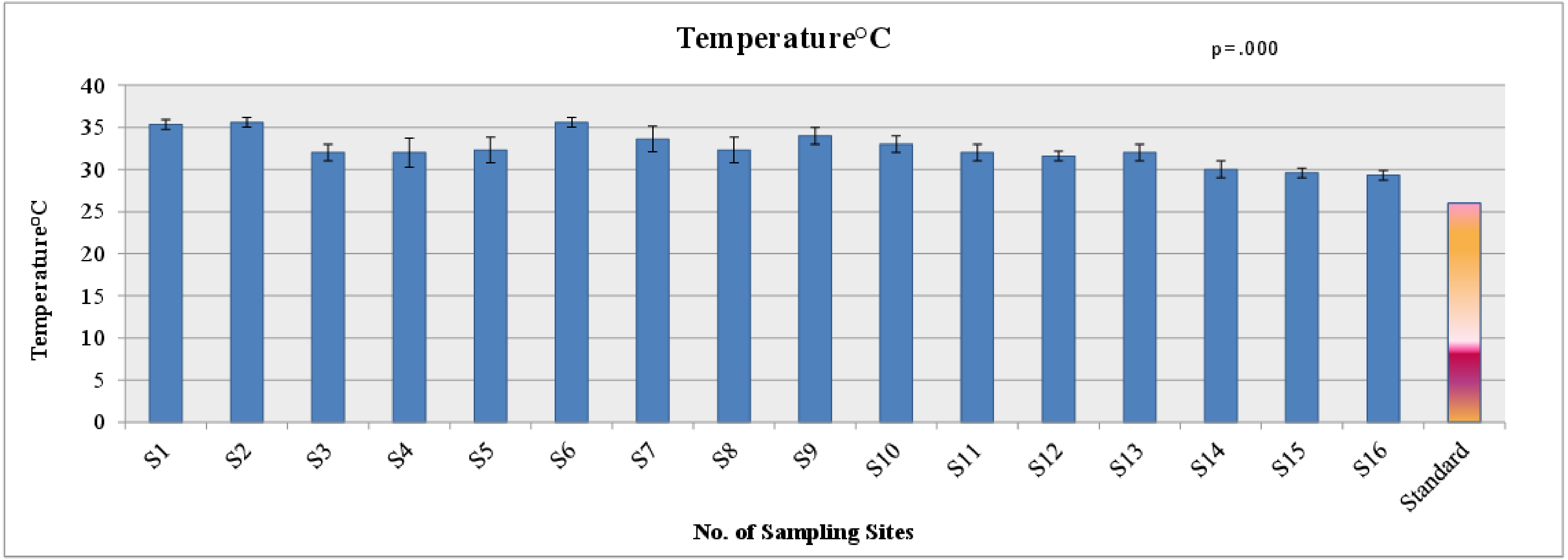

Fig. 4.2: Graph showing the averaged values of temperature for samples and their comparison with the proposed standard of wastewater for irrigation by WWF.

Fig. 4.3 delineates the graph showing the values of electrical conductivity (EC dS/m) for samples and compared with the proposed standards of wastewater for irrigation by WWF. Electrical conductivity (EC) is an important parameter to test the quality of wastewater especially when it is used for irrigation purposes. The international standard for electrical conductivity is 1.5 dS/m (2007). Results indicates maximum averaged value of electrical conductivity with ±SD is for sample No.S_2 i.e. 18.8±0.25166 dS/m and the minimum averaged value is indicated for sample No.S_{16} with ± SD i.e. 0.316±0.01528 dS/m. The results indicate that, trend is decreasing gradually at the end of sampling sites. The results of the ANOVA table indicated that the mean EC value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 4c).

Fig. 4.4 illustrates the graph showing the values of total dissolved solids (TDS mg/L) for samples as compared with the proposed standards of wastewater for irrigation by WWF. Total dissolved solids (TDS) are the sum of the cations and anions which are present in the dissolved form in water. In international standards of wastewater for irrigation, permissible value of total dissolved solid is 1000 mg/L (2007). While the averaged maximum value of TDS as ± SD is for sample No.S_2 i.e. 13020±176.1628 mg/L and the averaged minimum value is recorded for sample No.S_{16} as ± SD i.e. 221.2±10.69268 mg/L. The concentration of TDS is decreasing as the No. of sampling sites goes towards Sutlej River. The results of the ANOVA table indicated that the mean TDS value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 4d).

Fig. 4.5 represents the graph showing the values of sulphate ($SO4^{2-}$mg/L) for samples as compared with the proposed standards of wastewater for irrigation by WWF. The permissible limit for sulphate (SO_4^{2-}) in the international standard of wastewater for irrigation is 600 mg/L (2007). The maximum averaged value of sulphate with ±SD is calculated for sample No.S_2 i.e. 8061.3±9.11976 mg/L and the minimum averaged value with SD is calculated for sample No.S_{16} i.e. 435.6± 6.02771 mg/L. The value of SO_4^{2-} is decreasing as move towards the end of sampling sites. The results of the ANOVA table indicated that the mean SO_4^{2-}value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 4e).

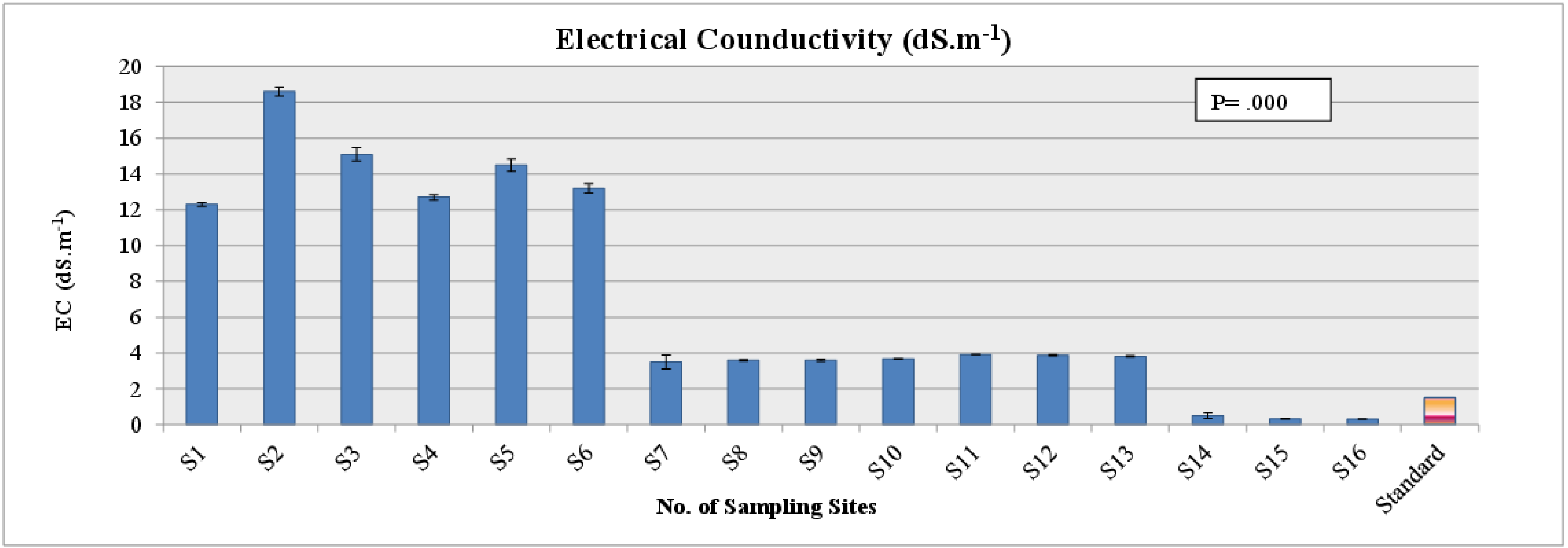

Fig. 4.3: Graph showing the averaged values of electrical conductivity for samples and their comparison with the proposed standard of wastewater for irrigation by WWF.

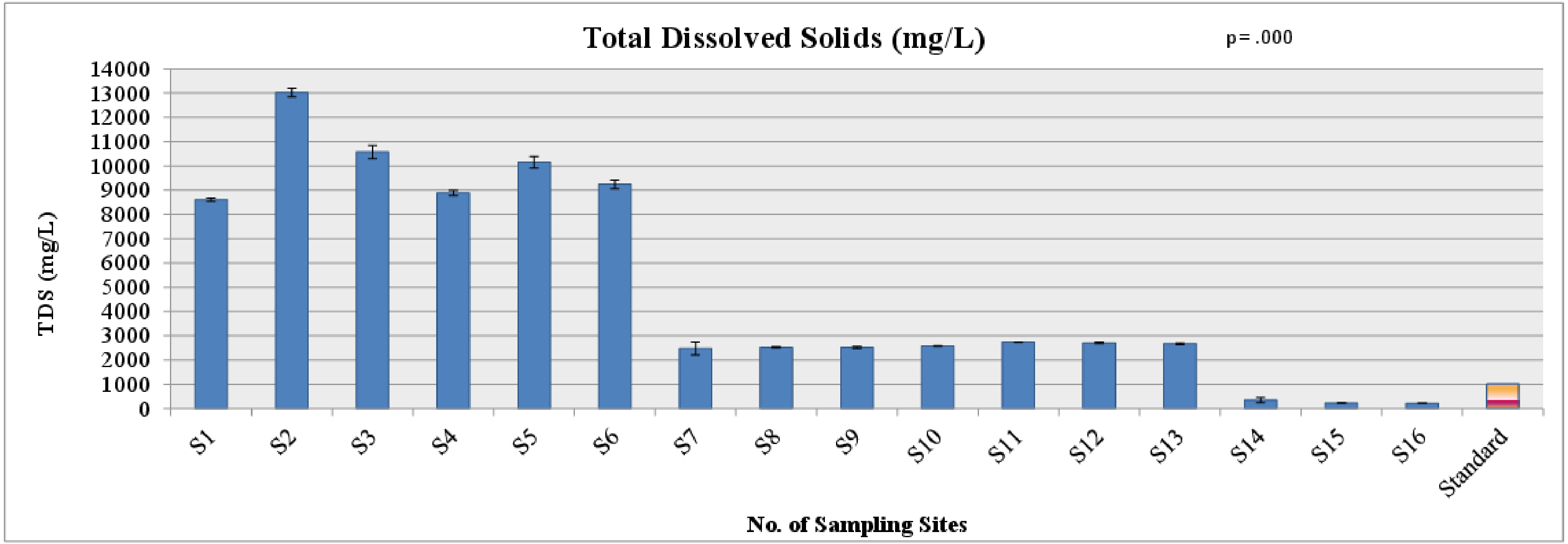

Fig. 4.4: Graph showing the averaged values of total dissolved solids for samples and their comparison with the proposed standard of wastewater for irrigation by WWF.

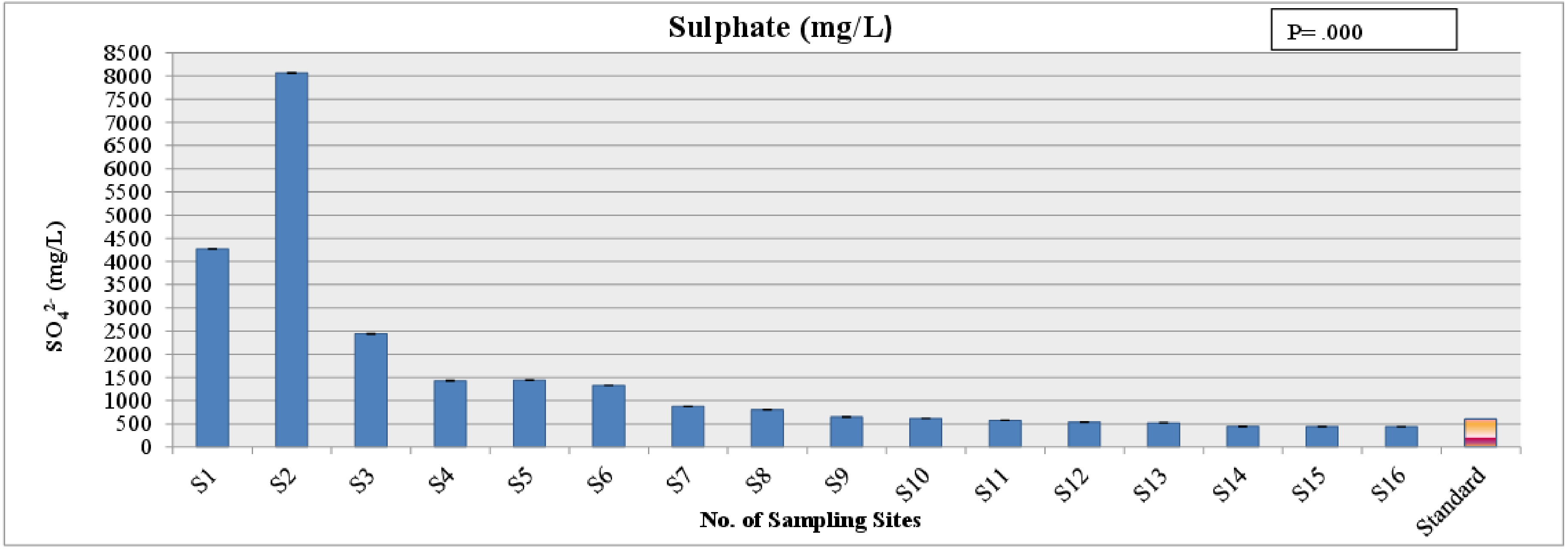

Fig. 4.5: Graph showing the averaged values of sulphate for samples and their comparison with the proposed standard of wastewater for irrigation by WWF.

Fig. 4.6 exhibits the graph showing the values of Chloride (Cl^- mg/L) for samples as compared with the proposed standard of wastewater for irrigation by WWF. Chloride (Cl^-) contributes to salinity in irrigation water, and it can be toxic to plants when concentrations are high. The acceptable limit for chloride is 100 mg/L in the international standards of wastewater for irrigation (2007). The maximum averaged value of chloride is measured with ± SD is for sample No.S_2 i.e. 8930.7± 26.867 mg/L. While the minimum averaged value as ± SD is measured for sample No.S_{16} i.e. 36.1±0.67484 mg/L. The concentration of chloride decreases as the water run off towards the Sutlej River. The results of the ANOVA table indicated that the mean Cl^-value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 4f).

Fig. 4.7 depicts the graph showing the values of residual sodium carbonate (RSC mEq/L) for samples as compared with the proposed standard of wastewater for irrigation by WWF. Residual sodium carbonate (RSC mEq/L) is used to assess the sodium permeability hazard, and takes into account the bicarbonate/carbonate and calcium/magnesium concentrations in irrigation water. The permissible value of residual sodium carbonate is 1.25mEq/L for the wastewater used in irrigation (2007). The maximum averaged value of residual sodium carbonate (RSC) with ±SD is calculated for sample No.S_1 i.e. 35.86±0.80208 mEq/L and the minimum averaged value as ± SD is calculated for sample No.S_{16} i.e. 1.11±0.01 mEq/L. The value of RSC decreases as the water runoff towards the last sampling point. The results of the ANOVA table indicated that the mean RSC value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 4g).

Fig. 4.8 illustrates the graph showing the values of sodium absorption ratio (SAR mEq/L) for samples as compared with the proposed standard of wastewater for irrigation by WWF. Sodium absorption ratio (SAR) is the relative concentrations of sodium, calcium, and magnesium which are important determinants of irrigation water quality. In international standards of wastewater for irrigation, the sodium absorption ratio is acceptable at 5mEq/L (2007). The maximum averaged value of SAR is recorded for sample No.S_2 with ±SD i.e. 91.7±1.03944 mEq/L and the minimum averaged value is recorded for sample No.S_{15} with ±SD i.e. 0.97 ±0.02 mEq/L. The value of SAR decreases at the end of sampling sites. The results of the ANOVA table indicated that the mean Cl^-value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 4h).

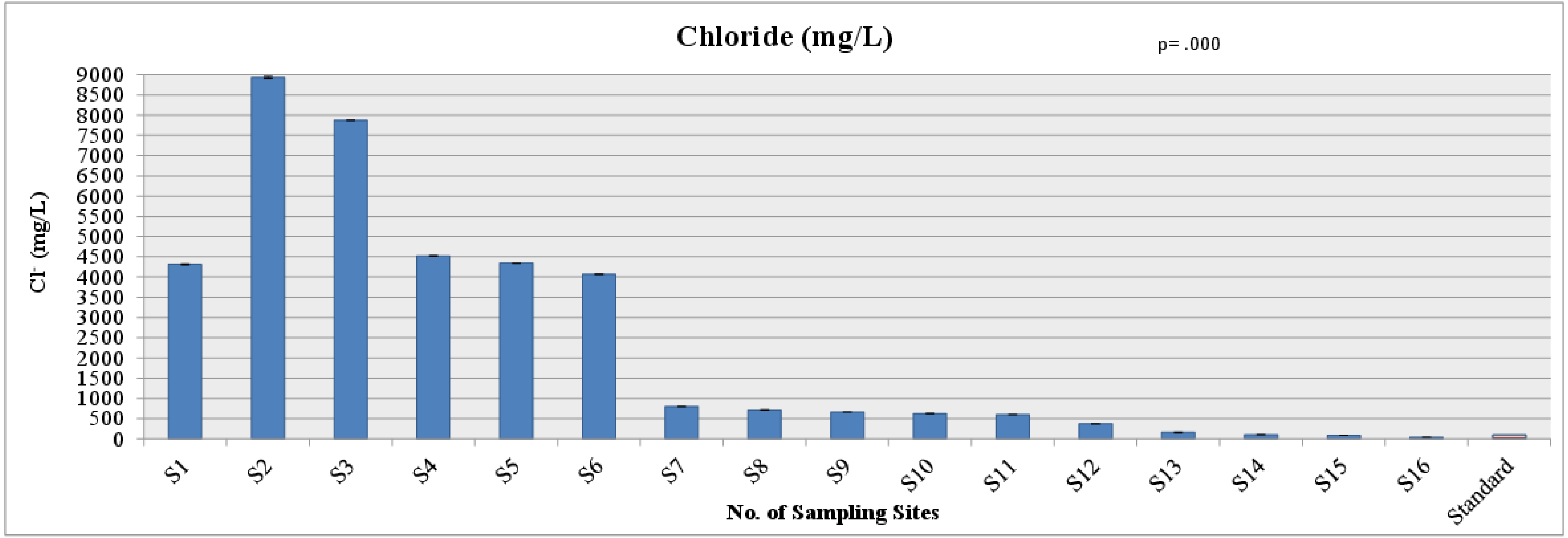

Fig. 4.6: Graph showing the averaged values of chloride for samples and their comparison with the proposed standard of wastewater for irrigation by WWF.

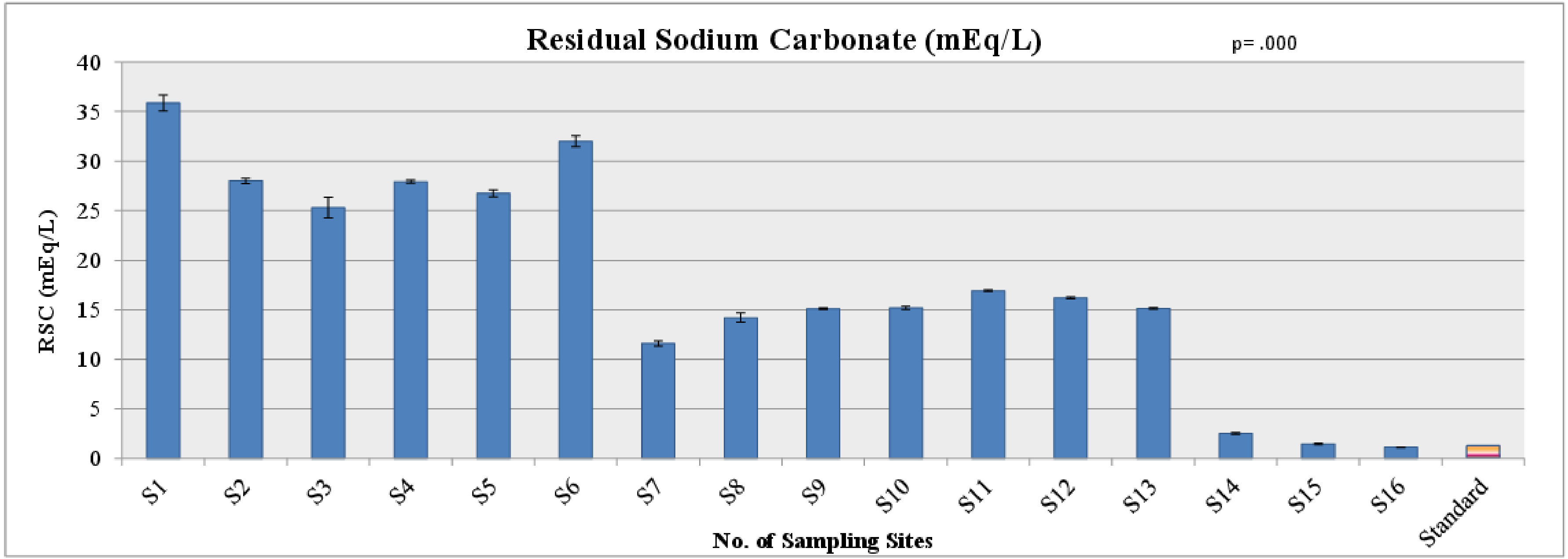

Fig. 4.7: Graph showing the averaged values of residual sodium carbonate for samples and their comparison with the proposed standard of wastewater for irrigation by WWF.

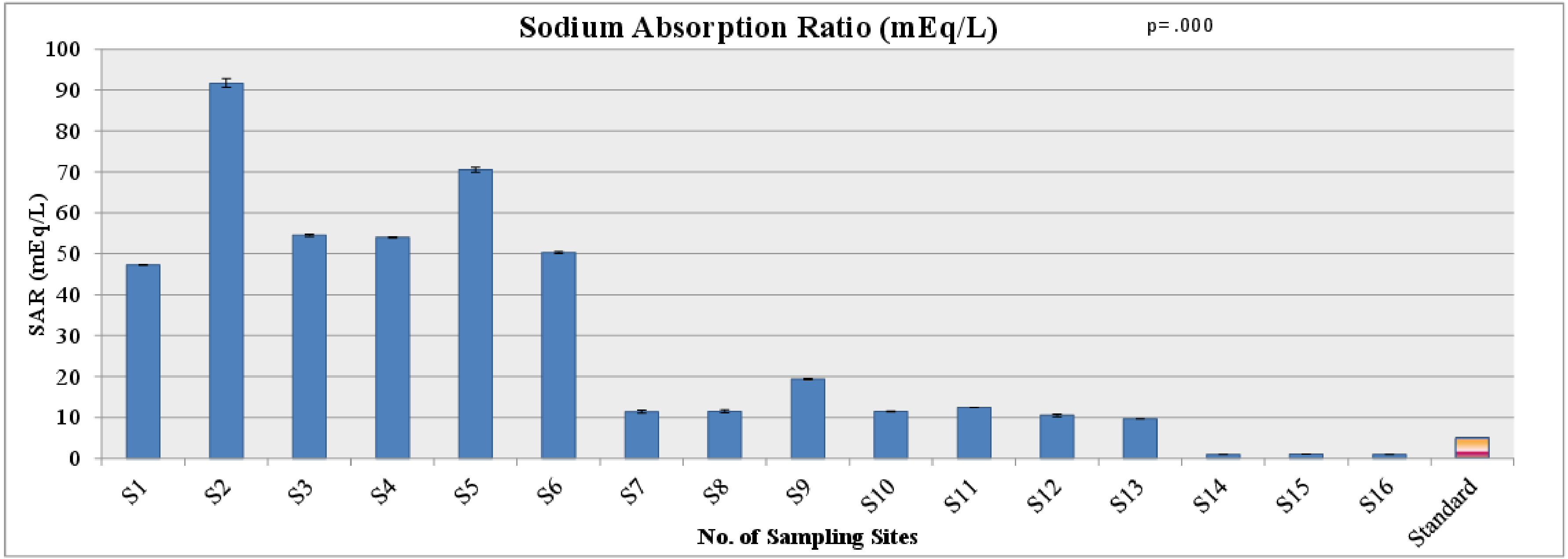

Fig. 4.8: Graph showing the averaged values of sodium absorption ratio for samples and their comparison with the proposed standard of wastewater for irrigation by WWF.

For EC, TDS, SO_4^{2-} Cl^-, RSC and SAR decreasing trends are observed downstream from the beginning to the end of the sampling points, whereas pH remains alkaline in all samples without showing any significant difference.

Fig. 4.9 delineates the graph showing the values of Chromium (Cr mg/L) for samples and compared with the proposed standard of wastewater for irrigation by WWF. The permissible limit for chromium (Cr) in wastewater used for irrigation purposes is 0.01 mg/L (2007). The maximum averaged concentration of chromium is observed for sample No.S_9 with ± SD i.e. 0.283±0.003 mg/L while the minimum averaged value is observed for sample No.S_7 with ± SD i.e. 0.002±0.001 mg/L. The high concentration of chromium is observed at the starting point of drain, which decreases with the run off. The results of the ANOVA table indicated that the mean Cr value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 4i). For chromium maximum reading was observed in sample.S_9 i.e. 0.283mg/L. This is due to the heterogeneous character of the channel carrying wastewater that is closed up to S_7 and is open onward up to S_{16}. Thus former is not in contact with soil while latter passes through the reclaimed soil contaminated with toxic metals particularly chromium at S_9. Thus the wastewater dissolves Cr from the reclaimed soil that translates into higher values of chromium. Moreover, these metals have been accumulated over a period of time thus showing a maximum value in sample no. S_9. Afterwards gradual decreasing pattern is observed in chromium because the soil in contact is not contaminated reclaimed soil.

Fig. 4.10 displays the graph showing the values of cadmium (Cd mg/L) for samples as compared with the proposed standard of wastewater for irrigation by WWF. Cadmium is acceptable at range in 0.01mg/L for wastewater used in irrigation (2007). The maximum averaged concentration of cadmium (Cd mg/L) with ±SD is calculated for sample No.S_{10} to S_{16} is 0.001±0 mg/L. While zero cadmium concentration is found from sample No.S_1 to S_9. The value of cadmium concentration is observed towards the point where Pandoki drain wastewater mixes with pre treated tannery wastewater. The results of the ANOVA table indicated that the mean Cd value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 4j).

Fig. 4.11 depicts the graph showing the values of copper (Cu mg/L) for samples as compared with the proposed standard of wastewater for irrigation by WWF. In international standards of wastewater for irrigation, the permissible limit for copper (Cu mg/L) is 0.2 (2007). While the results indicate that copper is present in acceptable range in all samples. The maximum averaged value of copper (Cu) is observed with ± SD for sample No.S_9 i.e. 0.02± 0.00351 mg/L, while the minimum averaged value for copper is observed with ± SD for sample No.S_7 i.e. 0.004± 0.00115 mg/L. The concentration of copper slightly increases where the pre treated tannery wastewater joins the Pandoki drain then gradually decreases at the end of sampling sites. The results of the ANOVA table indicated that the mean Cu value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 4k).

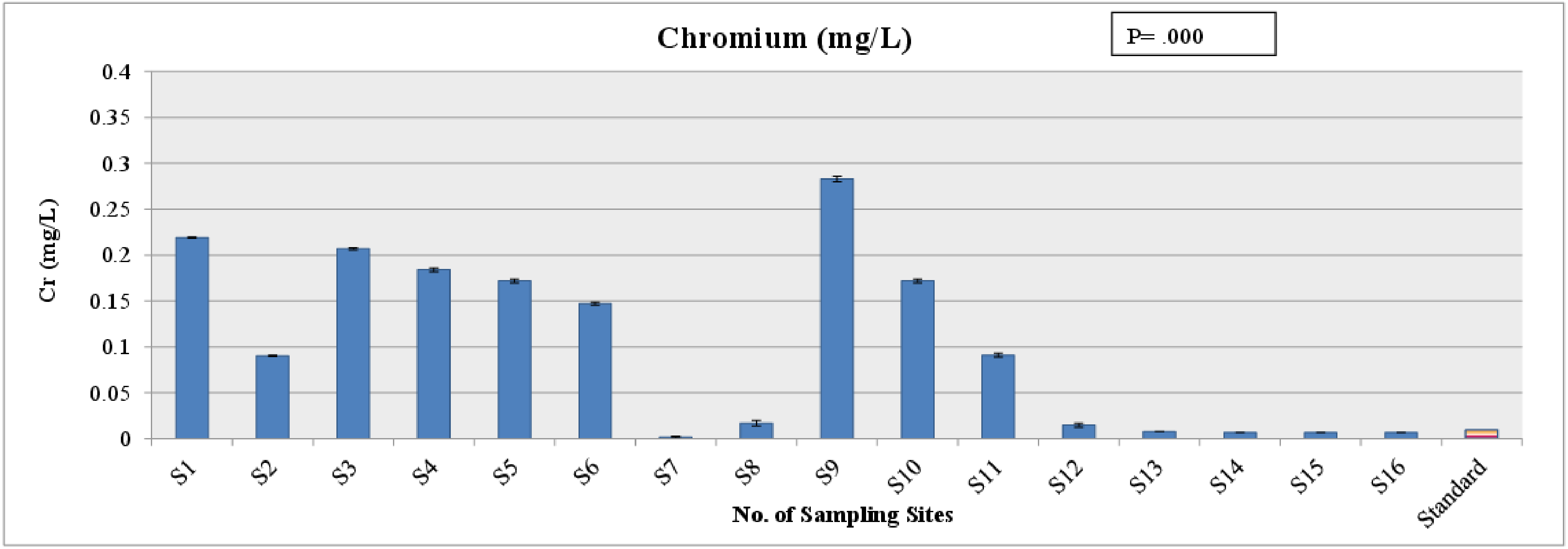

Fig. 4.9: Graph showing the averaged values of chromium for samples and their comparison with the proposed standard of wastewater for irrigation by WWF.

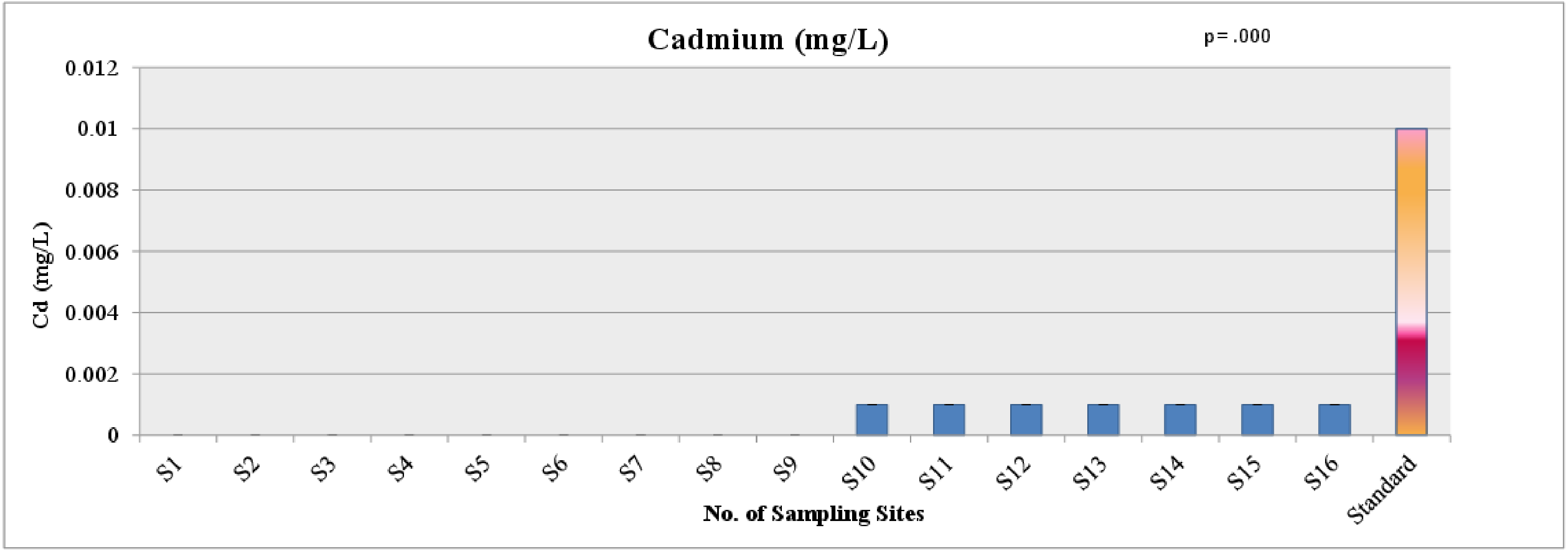

Fig. 4.10: Graph showing the averaged values of cadmium for samples and their comparison with the proposed standard of wastewater for irrigation by WWF.

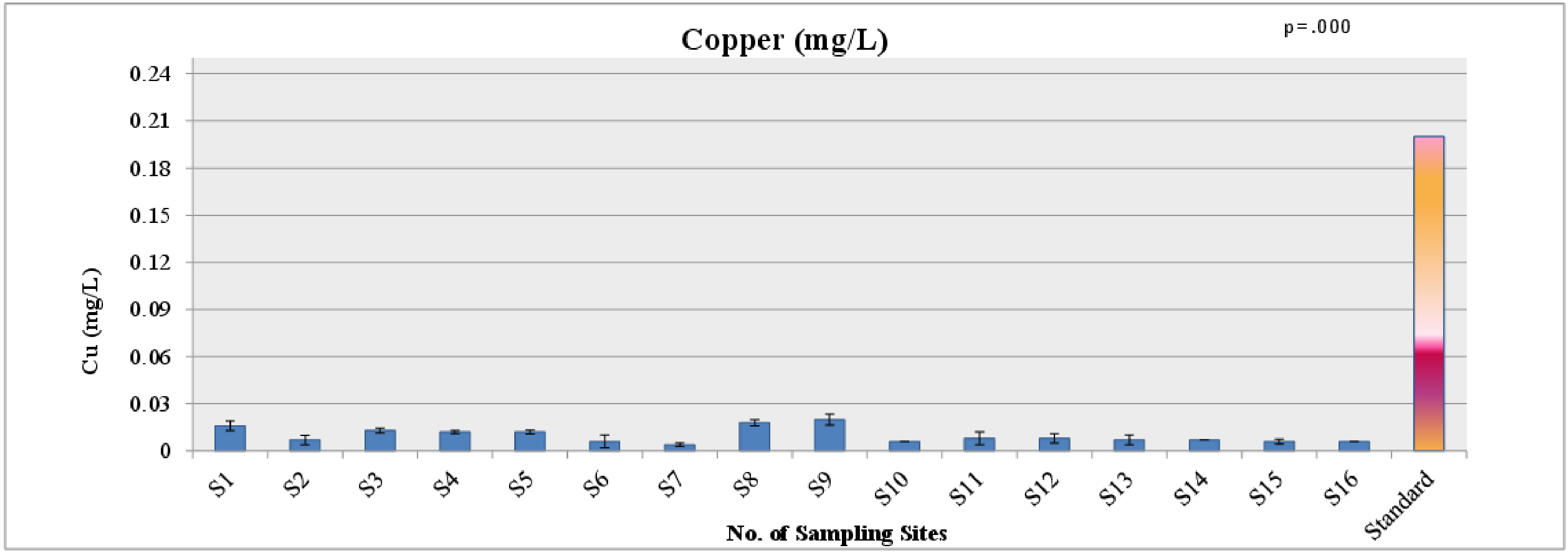

Fig. 4.11: Graph showing the averaged values of copper for samples and their comparison with the proposed standard of wastewater for irrigation by WWF.

Fig. 4.12 represents the graph showing the values of iron (Fe mg/L) for samples and compared with the proposed standard of wastewater for irrigation by WWF. The maximum concentration of iron (Fe) is observed in sample No.S_{14} with ± SD i.e. 3.531± 0.03001 mg/L while the minimum concentration of iron is observed in sample No.S_{11} with ± SD is 0.197±0.002 mg/L. According to standard of wastewater for irrigation, iron (Fe) is acceptable at the range of 5mg/L (2007). Iron was present in acceptable range in all samples of wastewater collected. The results of the ANOVA table indicated that the mean Fe value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 4l). The range of iron from S_1 to S_{13}, is between 0.2 -2.3mg/L, then there is a sudden increase in the concentration of Fe, from S_{14} to S_{16} i.e. 3.3-3.5mg/L. That is because of the accumulation of iron overtime at the end of the downward steam due to much slower movement of wastewater. Even so this range is within the permissible limits of wastewater for irrigation i.e. 5mg/L. Water pH, water aeration, reactions with organic matter and plant adaptation influences the availability of iron.

Fig. 4.13 delineates the graph showing the values of □inc (Zn mg/L) for samples as compared with the standard of wastewater for irrigation. Zinc (Zn) is another important heavy metal. In international standard of wastewater for irrigation the acceptable range of □inc in 2.0mg/L (2007). The maximum concentration of □inc is noted for sample No.S_{11} with ± SD i.e. 0.028± 0.00902 mg/L and the minimum concentration of □inc is noted for sample No.S_4 with ± SD i.e. 0.005± 0.00252 mg/L. Analysis of all wastewater samples collected showed the concentration of □inc in acceptable limits. The results of the ANOVA table indicated that the mean Zn value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 4m).

Correlation among different parameters is also analy□ed as shown in table 4.1. As concluded from the Table 4.1 among all 16 samples taken from multiple sites, the EC and TDS are perfectly correlated with p = .000 (r=1.000). Moreover, EC and TDS were found highly correlated with SAR with p =.000 (r=.981). Cl^- is found highly significantly correlated with EC and TDS with p = .000 (r=.954) and p = .000 (r=0.939). RSC is found significantly correlated with EC and TDS i.e. p= .000 (r=.889) and SAR (r=.828). In contrast, metallic and non metallic parameters are not correlated. There is significant correlation between Cr and SAR i.e. p = .032 (r=.537). Cu and Cr are moderately correlated with p=.014 (r=.598).

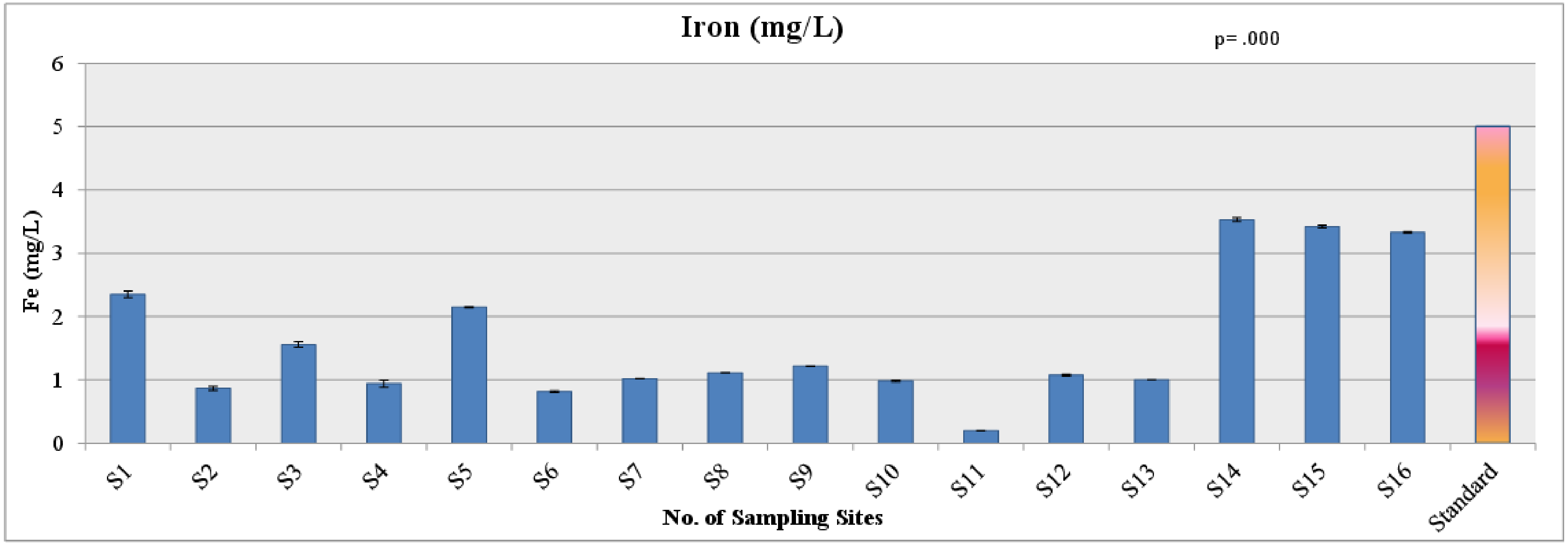

Fig. 4.12: Graph showing the averaged values of iron for samples and their comparison with the proposed standard of wastewater for irrigation by WWF.

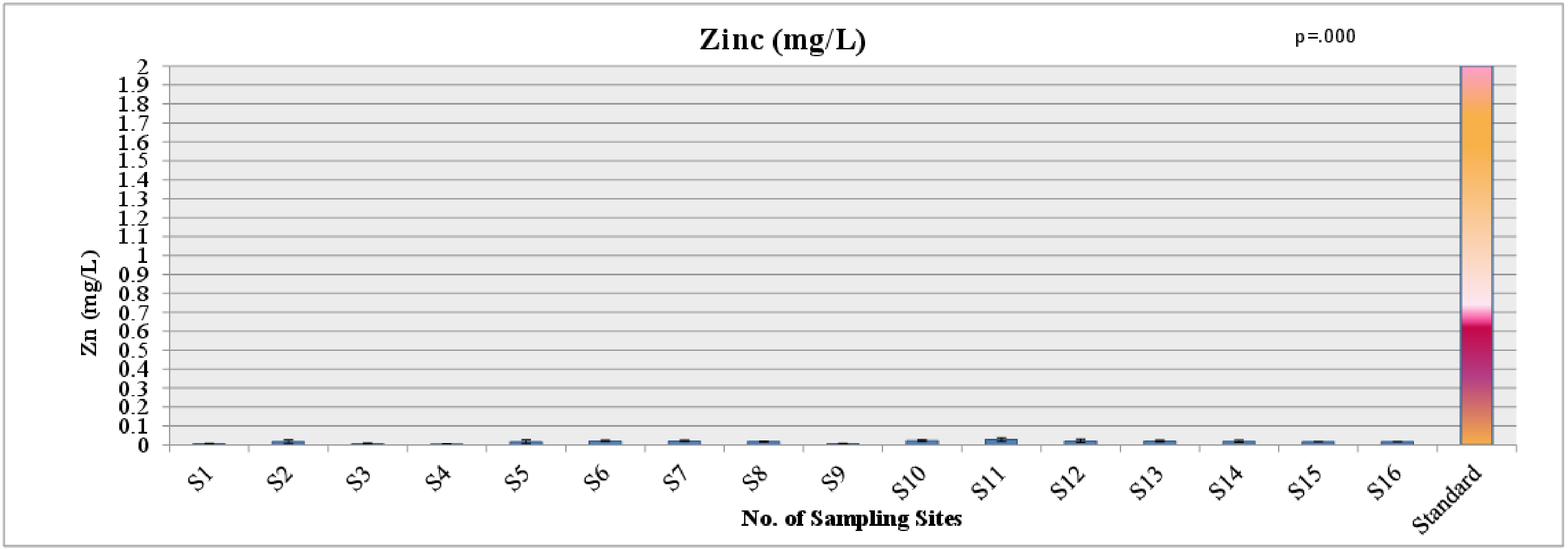

Fig. 4.13: Graph showing the averaged values of zinc for samples and their comparison with the proposed standard of wastewater for irrigation by WWF.

Table 4.1 shows the correlation among different selected parameters.

Correlations

		pH	Temperature	EC	TDS	SAR	Sulphate	RSC	Chloride	Cr	Fe	Zn	Cu	Cd
pH	Pearson Correlation	1												
	Sig. (2-tailed)													
	N	16												
Temperature	Pearson Correlation	.606*	1											
	Sig. (2-tailed)	.013												
	N	16	16											
EC	Pearson Correlation	.637**	.637**	1										
	Sig. (2-tailed)	.008	.008											
	N	16	16	16										
TDS	Pearson Correlation	.637**	.637**	1.000**	1									
	Sig. (2-tailed)	.008	.008	.000										
	N	16	16	16	16									
SAR	Pearson Correlation	.628**	.617*	.981**	.981**	1								
	Sig. (2-tailed)	.009	.011	.000	.000									
	N	16	16	16	16	16								
Sulphate	Pearson Correlation	.691**	.609*	.744**	.744**	.782**	1							
	Sig. (2-tailed)	.003	.012	.001	.001	.000								
	N	16	16	16	16	16	16							
RSC	Pearson Correlation	.553*	.782**	.889**	.889**	.828**	.582*	1						
	Sig. (2-tailed)	.026	.000	.000	.000	.000	.018							
	N	16	16	16	16	16	16	16						
Chloride	Pearson Correlation	.690**	.531*	.954**	.954**	.939**	.813**	.753**	1					
	Sig. (2-tailed)	.003	.034	.000	.000	.000	.000	.001						
	N	16	16	16	16	16	16	16	16					
Cr	Pearson Correlation	.377	.529*	.557*	.557*	.537*	.252	.658**	.488	1				
	Sig. (2-tailed)	.149	.035	.025	.025	.032	.347	.006	.055					
	N	16	16	16	16	16	16	16	16	16				
Fe	Pearson Correlation	-.113	-.586*	-.322	-.322	-.270	-.143	-.500*	-.209	-.252	1			
	Sig. (2-tailed)	.677	.017	.224	.224	.312	.598	.048	.437	.346				
	N	16	16	16	16	16	16	16	16	16	16			
Zn	Pearson Correlation	-.382	-.143	-.407	-.407	-.393	-.260	-.370	-.458	-.658**	-.183	1		
	Sig. (2-tailed)	.145	.597	.118	.118	.132	.331	.158	.075	.006	.497			
	N	16	16	16	16	16	16	16	16	16	16	16		
Cu	Pearson Correlation	.104	.235	.205	.205	.204	.082	.340	.168	.598*	-.089	-.677**	1	
	Sig. (2-tailed)	.701	.381	.445	.446	.449	.762	.198	.534	.014	.743	.004		
	N	16	16	16	16	16	16	16	16	16	16	16	16	
Cd	Pearson Correlation	-.520*	-.670**	-.706**	-.707**	-.702**	-.475	-.683**	-.657**	-.552*	.295	.562*	-.545*	1
	Sig. (2-tailed)	.039	.005	.002	.002	.002	.063	.004	.006	.027	.267	.023	.029	
	N	16	16	16	16	16	16	16	16	16	16	16	16	16

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Chapter 5

DISCUSSION

The present study has been carried out for the assessment of pre treated tannery wastewater for its reuse and rendering it fit for irrigation purposes in Kasur district. This is to be followed by a discussion on how to treat the pre treated tannery wastewater for making it suitable for agriculture purposes.

Fig. 4.1 shows that the pH of the pre-treated tannery wastewater is alkaline that when compared to the WWF standards (2007). It indicates the presence of abnormal salt content in wastewater due to the addition of ammonium salts, chloride and lime, etc, in leather tanning operation. The uncontrolled usage of salts in leather tanning renders the pH of wastewater alkaline. The alkaline pH of tannery pre-treated wastewater being reported here is in tune with the results of the physicochemical analysis of treated tannery effluent from common effluent treatment plant (CETP) in India reported by Bhatnagar et al., (2013) as 8.4. Low pH or high pH makes water unfit for irrigation and the soil over large area becomes alkaline resulting in poor crop, growth and yield (Mythili and Karthikeyan, 2011).

The values of electrical conductivity, total dissolved solids, sulphate, chlorides, residual sodium carbonate and sodium absorption ratio are much higher than the permissible limits in pre treated tannery wastewater samples i.e. 18.6 dS/m, 13,020mg/L, 8930.7mg/L, 8061.3mg/L, 91.7mEq/L and 35.86mEq/L respectively, as shown in Fig. 4.3, 4.4, 4.5, 4.6, 4.7, 4.8. Basically 30 to 50% of sodium chloride is used in beamhouse operation for the treatment and preservation of hides and skin; after that considerable amount of salt is also used at the pickling and tanning stage. Sulphate in tannery wastewater appears from the chemicals having sulphate ion like sodium sulphate. Ammonium sulphate is utilized in deliming and bating where sulphuric acid and chromium sulphate are used in pickling and tanning stages (Pelckmans and Page, 2010). The characteristics of pretreated tannery wastewater reported here were also compared with those reported by different researchers. Awan, et al., (2003) reported that the tannery wastewater samples collected from the Sialkot region exhibits total dissolved solids, electrical conductivity and sodium as 91972mg/L, 43.7mS/cm and 127.6 mg/L respectively. Banuraman and Meikandaan

(2013) reported the results of tannery wastewater samples from the Chennai leather industry reported the range of pH, chloride, total dissolved solids as 6.2, 1136mg/L, and 4950mg/L respectively. Physico-chemical characteristics of the leather wastewater from the Tensift river of Morocco reported by Mandi et al.,(2009) are electrical conductivity and chloride is 119ms/cm and 207mg/L respectively. In India common effluent treatment plant for tanning industries were assessed, the analysis of wastewater from CETP has shown the results of pH, total dissolved solids, chloride and sulphate concentrations as 7.0-8-1, 5500-8300mg/L, 1000-2000mg/L and 40-50mg/L respectively (Vasudevan et al., 2012). Huge load of industrial and domestic waste is discharged on daily basis in river Yamuna situated in the city of Agra, India. Analysis of wastewater samples from the river revealed the results of pH and total dissolved solids as 7.8 and 16.782 mg/L respectively (Shrivastava et al., 2012).

Total dissolved solids have been considered one of the most important parameter of tannery wastewater in several parts of the world. Different countries have set different permissible limits of salts in tannery wastewater after treatment: example, South Africa (1350mg/L of total dissolved solids), Italy (1200mg/L of chloride, 1000mg/L of sulphate), India (2100mg/L of total dissolved solids, 1000mg/L of chloride, 1000 mg/L of sulphate), Sometimes the value of total dissolved solids goes high up to the 7000mg/L and in some cases more than 10,000mg/L. The concentration of total dissolved solids will be higher in wastewater, if less amount of water is used (IUE, 2001).

In Bangladesh, tannery wastewater showed the results of analysis; pH 3.94, TDS (13360.0mg/L), EC (60.7mS/cm) and Cl^- (18800.8 mg/L) (Sabur et al., 2013). The chloride in tannery effluents comes from the common salt (sodium chloride) which is used in skin and hides preservation or in the pickling process. Due to the nature of its highly solubility and stability in water, chloride remains unchanged by most of the wastewater treatment processes. Chloride stops plant and bacterial growth whereas its high concentration causes the breakage of cell structure. If the chloride is present in irrigation water, it increases the soil salinity due to water evaporation which damages the crop yield (Bosnic et al., 2000).

Another most important parameter from irrigation point of view is the sodium absorption ratio (SAR) because the presence of high sodium concentration causes the dispersion and swelling of clay mineral, reduces permeability of the soil and decreases the infiltration rates and the formation of hard clay crust (Margane and Steinel, 2011). Residual sodium carbonate (RSC) is the excess sum of carbonate and bicarbonate over the sum of calcium and magnesium making the wastewater unfit for irrigation purposes. Wastewaters with high RSC have alkaline pH and if the soil irrigated with this water, renders the color of the soil black (Alobaidy et al., 2010). The analysis of wastewater reported in this study show the values of RSC and SAR above the permissible limits which are not suitable for irrigation purposes (Fig. 4.7, 4.8).

The analysis of the surface wastewater quality in India indicated the values of SAR, EC and RSC as 0.39mEq/L, 7430μmohs/cm and 12.99mEq/L respectively. From these values it can be concluded that if a piece of land is irrigated with this wastewater, the soil will be subject to salinity hazards (Sinica, 2013). Analysis of wastewater used for irrigation purposes reports its parameters as SAR (4.8mEq/L), RSC (2.54mEq/L), TDS (733mg/L), Cl^- (350mg/L) and SO_4^{2-} (60.4mg/L) (Jan et al., 2008). EC (4.75±20.mS/cm) and pH (6.90±0.27) (Matsuno et al., 2001). SAR (38.5mEq/L), RSC (22.8mEq/L), Cl^- (2500mg/L), TDS (4600mg/L), SO_4^{2-} (1400mg/L) and EC (4.2μS/L) (Kakar et al., 2010).

The major threat to the environment from the leather tanning industry 90 % of which is using chromium in the form of chromium sulphate its carcinogenic activity .The analysis of the pre treated tannery wastewater samples done here indicates that iron (Fe), zinc (Zn), cadmium (Cd) and copper (Cu) are present in permissible limits except chromium (Cr) as shown in Fig. 4.9, 4.10, 4.11, 4.12, 4.13. The results are compared with the reported concentration of heavy metals in tannery wastewater by different authors. From the total chromium used in tanning industry only 60-70% is utilized while rest of the chromium present in wastewater. The analysis of different studies show the chromium in tannery effluents is 0.01-0.02mg/L in common effluent treatment plant India (Vasudevan et al., 2014). (Awan et al., 2003) reported Cr, Zn, Cu, Fe, and Cd concentrations around 220mg/L, 1.021-0.105mg/L, 0.49-0.397mg/L, 0.786-1.404mg/L and 0.262-0.296mg/L respectively. Barreiro et al., (2008) report the results of heavy metals in tannery effluents as. Cr (13mg/L), Cd (0.6mg/L), Zn and Cu (0 mg/L). Chakraborty and Mukherjee (2013) have shown the Cr (0.48mg/L).

Sangeetha et al., (2012) conducted the analysis of tannery effluents and reported Cr concentration as 92.32mg/L and Zn concentration 0.198mg/L in tannery wastewater samples. Sadia et al., (2005) reported the analysis from Kasur tannery wastewater samples for heavy metals i.e. Fe (4.4mg/L), Cr (391mg/L), Cd (0.056mg/L) and Zinc (0.684mg/L).

According to a case study from Iran, analysis of wastewater stabilization ponds shows that the heavy metals concentrations such as cadmium (1.14µg/L), arsenic (11.7µg/L), chromium (71.6µg/L), copper (36.9µg/L), lead (7.8µg/L), zinc (50.3µg/L) and mercury (5.0µg/L) are within the limits of international guidelines for wastewater used for irrigation purpose. Thus the wastewater can be used for short term or long term irrigation with regard to heavy metals (Mansouri and Ebrahimpour, 2011).

Chromium is not only vital for the metabolism of insulin in human beings but is also important for the animals; however for plants its importance is still unknown. Hexavalent chromium is more dangerous to the invertebrate species like polychaete worms, insects and crustaceans than vertebrate species such as fish, etc. The fatal dose for chromium is 0.05mg/L for aquatic and terrestrial invertebrates. Copper is also present in wastewater where electroplating is done or where electric circuit boards are manufactured. When copper enters the soil through wastewater, it firmly binds with the organic matter and nutrients presents in the soil. In wastewater copper moves as a free ion or either suspended on sludge particles (Baysal et al., 2013). From the present study it is concluded that, chromium is present above the permissible limits in wastewater, which cannot be used for irrigation purposes and it can also be a threat to the aquatic ecosystem.

Table 5.1: Shows the reading of present study compared with tannery wastewater India and Bangladesh.

Serial No.	Selected parameters	Readings of Kasur tannery pre-treated wastewater	Readings observed in India	Readings observed in Bangladesh	Safe limits
1	pH	8-8.48	6.2	3.94	6.5-8.4
2	EC dS/m	0.316-18.8	7430 µmohs/cm	60.7mS/cm	1.5 dS/m
3	TDS mg/L	221.2-13020	4950mg/L	13360mg/L	1000 mg/L
4	SO_4^{2-}	435.6-8061.3	1000-2000 mg/L	-	600 mg/L
5	Cl^-	36.1-8930.7	1136mg/L	18800.8mg/L	100 mg/L
6	RSC	1.11-35.86	12.99mEq/L	-	1.25 mEq/L
7	SAR	0.97-91.7	0.39mEq/L	-	5 mEq/L
8	Cr	0.002-0.283	0.48mg/L	-	0.01 mg/L
9	Cd	0-0.001	-	-	0.01 mg/L
10	Cu	0.004-0.02	0 mg/L	-	0.2 mg/L
11	Fe	0.197-3.531	-	-	5 mg/L
12	Zn	0.005-0.028	0 mg/L	-	2.0 mg/L

5.1 Proposed Treatment of Kasur Pretreated Tannery Wastewater for Its Reuse in Agriculture

From the present study it is clear that, one of the major problems in pretreated wastewater is the TDS which includes salts like chloride, sulphate, carbonates, bicarbonates, calcium, magnesium and sodium above acceptable limits. Many technologies have been developed to remove the excessive salt content from water which is hazardous to the soil and crops. For the removal of TDS from tannery effluents one of the most effective technology is Reverse Osmosis (RO).

RO technology is used in many parts of the world to reduce TDS and recover quality water for its re-use. It is one of the highest technological solutions which require huge investment and running costs. However it provides the possibility of recovering 70-80% of the initial float and TDS is reduced from the range of 8000 to 15000 mg/L to less than 500 mg/L. Proper tertiary treatment is necessary to achieve good results in RO treatment (IUE, 2008). A conventional treatment process cannot overcome the hazards of TDS especially of the salt content in treated tannery wastewater. The salts from these tannery effluents can be eliminated only by using sophisticated high-tech membrane technology i.e. Reverse osmosis (UNIDO, 2000). The main components of the RO are as shown in Fig. 5.1.and sub-processes illustrated below with the help of notes taking the example of sea water that contains very high concentration of salt.

Pretreatment: Suspended solids from the wastewater are removed by filtration through specially made membranes under pressure after adjustment of its pH. Pressure on the wastewater is adjusted according to the membrane toleration capacity.

Separation: Dissolved solids are separated by the membrane with application of pressure allowing the salt free water to pass through. The brine reject is discharged without passing through the membrane.

Stabilization: The pH of water treated with membrane technology is adjusted and it is degasified before using it for any special purpose.

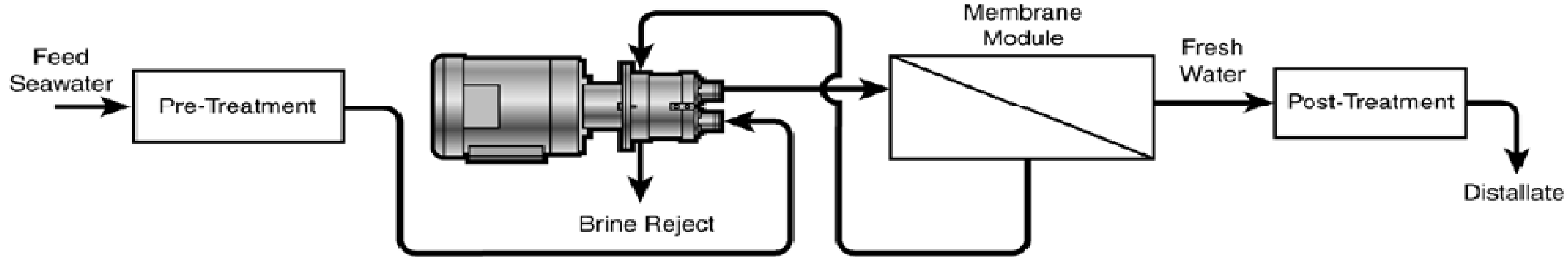

Fig. 5.1 Schematic diagram for RO operation.

The operation and maintenance cost of the treatment plant with RO per cubic meter is calculated by Ranganathan and Kabadgi (2011) as below:

Chemical cost	PKR 14 -17 m^{-3}
Power cost	PKR 5 –7 m^{-3}
Sludge handling	PKR 1.5 –3.5 m^{-3}
Manpower	PKR 3.5 –5 m^{-3}
Filters and cartridges (spares)	PKR 10 –20 m^{-3}
RO/NF membrane maintenance	PKR 34 – 42 m^{-3}
Principal and interest paid on the loan	PKR 67 –84 m^{-3}

The overall cost of treatment of tannery wastewater with RO technology including its operation and maintenance thus comes out to be 135-178.5 m^{-3}. As the pre treated wastewater generated from the CEPTP of Kasur is 9000 m^{-3}per day the total cost of treatment will be 1,215,000-1,606,500 per day, 36,450,000- 48,195,000 per month and 437.400.000,- 578.340.000, per annum. Thus the total expenditure calculated with RO technology to treat pretreated wastewater for Kasur being very high is not affordable for a developing country like Pakistan.

A new technology emerging these days is Periodic Biofilters (PERBIOF) technology, which uses submerged biofilters in which all biological treatments are accomplished in the same tank. Aerobic granules biomass is used; act as a large number of microorganisms grow in granules results the production of sludge in low density as compared to conventional processes. Treated tannery wastewater shows the highest removal of pollutants when a dosage of ozone (150g O_3/m^3) is introduced in the plant. This type of treatment plant is 3 times more compact and produces 1/30th sludge. However, as tanning industry uses hundreds of chemicals in its operations, it is not feasible for a developing country like Pakistan, to adopt this treatment design, which costs 624,784 Euros. That is why it is strictly limited to the developed countries (Layman's Report, 2008).

From present study it is observed that, the salinity of pretreated tannery wastewater in the course of its flow to Pandoki drain decreases but not under the permissible limit, until it reaches at the end of sampling points (S_{14}, S_{15}, and S_{16}) where wastewater disposes off in river Sutlej. After mixing with municipal wastewater of Pandoki drain, the concentration of Cl^-, SO_4^{2-}, SAR and RSC decreases but still not safe for its reuse in irrigation land. Thus before entering in Sutlej River, wastewater is not useable for irrigation purposes because of its high salinity. It should get further treatment to remove its salinity hazards. As described above, the sophisticated RO technology is not cost beneficial for Pakistan to render it suitable for agriculture, to reduce salinity hazards from wastewater following recommendations is made.

RECOMMENDATIONS

There are cleaner options available to reduce hazardous impact on the environment generated by the leather tannery industry. Such as:

I. For preservation of hides common salts may be replaced by enzyme and cold preservation techniques. These techniques may not only reduce TDS in wastewater but also conserve the water in tanning operation.

II. The consumption of lime may be reduced. Alternatively good quality of lime may be used as that can decrease the load of salts in wastewater.

III. Ammonium salts may be substituted by carbon dioxide in de-liming process. This substitution can also leads to less pollution load in wastewater.

IV. Water which is used for soaking purposes in last tank may be used again in the first soaking process.

V. Tannins associated with leather after tanning process may be washed in closed drums instead of washing under running water that ultimate goes into open drains and thus is hazardous for the local population.

CONCLUSION

From the foregoing discussion it may be concluded that pretreated tannery wastewater of Kasur is not suitable for irrigation purposes even after mixing with municipal wastewater of Pandoki drain. The major threat from wastewater is its high salt content i.e. RSC, SAR, Cl^- and SO_4^{2-} which cause soil salinity and contribute to crop damage and halting of growth. All the selected parameters when compared with international standards of wastewater for irrigation purposes proposed by WWF (2007), suggest that, this water is not usable without proper treatment. Selected heavy metals (Cd, Zn, Fe and Cu) are present within the permissible limits except Cr which is a major contributor of pollution in tanning industry. The economic and electricity crisis of the country is not in favor of expending huge expenditures on the RO technology, which is the best option to remove salinity hazards from the wastewater.

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APPENDIXES

APPENDIX: 1 (a)

CHEMICALS USED IN SULPHATE ANALYSIS:

1. Barium chloride.

100 g barium chloride was taken and dissolved in 1 liter distilled water.

2. HCl

50 mL concentrated HCl was added in 50 mL distilled water.

APPENDIX: 1 (b)

CHEMICALS USED IN CHLORIDE ANALYSIS.

1. $AgNO_3$ (0.0141N)

2.395 g of $AgNO_3$ was dissolved in 1 liter distilled water.

2. K_2CrO_4 (Indicator)

50 g K_2CrO_4 was dissolved in 1 liter distilled water.

APPENDIX: 1 (c)

CHMICALS USED IN CALCIUM AND MAGNESIUM ANALYSIS

1. EDTA (0.01N)
   EDTA solution was prepared by dissolving 2.0 gram of disodium salt in distilled water. The 0.05 gram of magnesium chloride was added and diluted with one liter of distilled water. This solution was then standardized against 0.01N of calcium chloride solution. Calcium chloride solution was prepared by adding 0.500 gram of $CaCO_3$ and dissolved in diluted hydrochloride solution and diluted with one liter of distilled water.
2. Ammonium Chloride – Ammonium hydroxide buffer

67.5 gram of ammonium chloride was dissolved in 570 mL of conc. Ammonium hydroxide and volume was made up to one liter at pH 10.

3. EBT indicator:

0.5 gram of EBT and 4.5 gram of hydroxylamine hydrochloride was dissolved in 100 ml of (95%) ethyl alcohol.

APPENDIX: 1(d)

CHEMICALS USED IN CARBONATES AND BICARBONATES ANALYSIS:

1. Phenolphthalein indicator

0.25 (%) solution was added in 60 (%) of ethyl alcohol.

2. Methyl orange indicator:

0.5 (%) solution was added in 95 (%) of alcohol.

APPENDIX: 2

Shows international standards of wastewater for irrigation purposes proposed by WWF Pakistan (2007).

Serial No.	Parameters	Permissible limit
1.	pH	6.4-8.4
2.	Temperature	26°C
3.	TDS	1000
4.	SAR	5
5.	RSC	1.25
6.	EC	1.5
7.	Sulphate	600
8.	Chloride	100
9.	Cr	0.01
10.	Zn	2
11.	Cu	0.20
12.	Fe	5
13.	Cd	0.01

APPENDIX: 3 (a)

STATISTICAL DATA INTERPRETATION OF THE SAMPLE COLLECTED FOR pH.

Variables	N	Mean	Std. Deviation
S1	3	8.3	0.04726
S2	3	8.48	0.05568
S3	3	8.25	0.06028
S4	3	8.27	0.04359
S5	3	8	0.03215
S6	3	8.4	0.05132
S7	3	8.09	0.02082
S8	3	8.06	0.02082
S9	3	8.2	0.25716
S10	3	8.05	0.01
S11	3	8.04	0.01
S12	3	8.06	0.02517
S13	3	8.01	0.01732
S14	3	8.3	0.1
S15	3	8.01	0.01528
S16	3	8.02	0.01528

APPENDIX: 3 (b)

STATISTICAL DATA INTERPRETATION OF THE SAMPLE COLLECTED FOR TEMPERATURE.

Variables	N	Mean	Std. Deviation
S1	3	35.33333333	0.57735
S2	3	35.6	0.57735
S3	3	32	1
S4	3	32	1.73205
S5	3	32.3	1.52753
S6	3	35.6	0.57735
S7	3	33.6	1.52753
S8	3	32.3	1.52753
S9	3	34	1
S10	3	33	1
S11	3	32	1
S12	3	31.6	0.57735
S13	3	32	1
S14	3	30	1
S15	3	29.6	0.57735
S16	3	29.3	0.57735

APPENDIX: 3 (c)

STATISTICAL DATA INTERPRETATION OF THE SAMPLE COLLECTED FOR EC.

Variables	N	Mean	Std. Deviation
S1	3	12.3	0.1
S2	3	18.6	0.25166
S3	3	15.1	0.37859
S4	3	12.7	0.15275
S5	3	14.5	0.35119
S6	3	13.2	0.25166
S7	3	3.5	0.37859
S8	3	3.6	0.03215
S9	3	3.6	0.0611
S10	3	3.68	0.02082
S11	3	3.91	0.01
S12	3	3.87	0.02517
S13	3	3.81	0.02887
S14	3	0.5	0.15275
S15	3	0.33	0.02082
S16	3	0.316	0.01528

APPENDIX: 3 (d)

STATISTICAL DATA INTERPRETATION OF THE SAMPLE COLLECTED FOR TDS.

Variables	N	Mean	Std. Deviation
S1	3	8610	70
S2	3	13,020	176.1628
S3	3	10,570	265.01572
S4	3	8,890	106.92677
S5	3	10,150	245.83192
S6	3	9240	176.1628
S7	3	2473	265.01572
S8	3	2520	22.50185
S9	3	2520	42.77071
S10	3	2578	14.57166
S11	3	2737	7
S12	3	2709	30.51229
S13	3	2667	35
S14	3	350	106.92677
S15	3	231	14.57166
S16	3	221.2	10.69268

APPENDIX: 3 (e)

STATISTICAL DATA INTERPRETATION OF THE SAMPLE COLLECTED FOR SO_4^{2-} .

Variables	N	Mean	Std. Deviation
S1	3	4267.6	8.02081
S2	3	8061.3	9.11976
S3	3	2439.7	13.781
S4	3	1426.9	10.92261
S5	3	1438.5	7.33066
S6	3	1328.8	2.08167
S7	3	874	3.81881
S8	3	805	3.65559
S9	3	647	6.4291
S10	3	615.9	2.92062
S11	3	572.5	3.23471
S12	3	536.8	5.10539
S13	3	521	5.56776
S14	3	443.3	12.34787
S15	3	439.5	7.98686
S16	3	435.6	6.02771

APPENDIX: 3 (f)

STATISTICAL DATA INTERPRETATION OF THE SAMPLE COLLECTED FOR Cl^-.

Variables	N	Mean	Std. Deviation
S1	3	4313.3	15.27525
S2	3	8930.7	26.86751
S3	3	7875.4	4.70886
S4	3	4520	10
S5	3	4347.5	4.04269
S6	3	4072.16	7.56127
S7	3	796.8	3.61156
S8	3	712.6	3.46458
S9	3	660.8	1.31149
S10	3	622.8	2.73008
S11	3	596.7	2.65141
S12	3	371.3	2.08167
S13	3	162.2	2.48261
S14	3	107.7	5.0856
S15	3	88.9	0.3
S16	3	36.1	0.67484

APPENDIX: 3 (g)

STATISTICAL DATA INTERPRETATION OF THE SAMPLE COLLECTED FOR RSC.

Variables	N	Mean	Std. Deviation
S1	3	35.86	0.80208
S2	3	28	0.26458
S3	3	25.32	1.04902
S4	3	27.92	0.16166
S5	3	26.75	0.34429
S6	3	32	0.56048
S7	3	11.6	0.27099
S8	3	14.2	0.47258
S9	3	15.1	0.07506
S10	3	15.2	0.16773
S11	3	16.9	0.09018
S12	3	16.19	0.10017
S13	3	15.14	0.09849
S14	3	2.5	0.1
S15	3	1.45	0.09539
S16	3	1.11	0.80208

APPENDIX: 3 (h)

STATISTICAL DATA INTERPRETATION OF THE SAMPLE COLLECTED FOR SAR.

Variables	N	Mean	Std. Deviation
S1	3	47.3	0.07234
S2	3	91.7	1.03944
S3	3	54.5	0.2442
S4	3	54	0.07506
S5	3	70.5	0.60277
S6	3	50.3	0.24664
S7	3	11.4	0.36474
S8	3	11.5	0.36056
S9	3	19.31	0.16823
S10	3	11.45	0.05568
S11	3	12.48	0.01528
S12	3	10.5	0.30551
S13	3	9.7	0.01528
S14	3	0.97	0.02
S15	3	1.074	0.00451
S16	3	1	0.01

APPENDIX: 3 (i)

STATISTICAL DATA INTERPRETATION OF THE SAMPLE COLLECTED FOR Cr.

Variables	N	Mean	Std. Deviation
S1	3	0.219	0.000333333
S2	3	0.09033	0.000333333
S3	3	0.207	0.00057735
S4	3	0.184	0.001154701
S5	3	0.172	0.00120185
S6	3	0.147	0.000881917
S7	3	0.002	0.00057735
S8	3	0.017	0.001732051
S9	3	0.283	0.001732051
S10	3	0.172	0.001154701
S11	3	0.091	0.00120185
S12	3	0.015	0.0012
S13	3	0.008	0
S14	3	0.007	0
S15	3	0.007	0
S16	3	0.007	0

APPENDIX: 3 (j)

STATISTICAL DATA INTERPRETATION OF THE SAMPLE COLLECTED FOR Cd.

Variables	N	Mean	Std. Deviation
S1	3	0	0
S2	3	0	0
S3	3	0	0
S4	3	0	0
S5	3	0	0
S6	3	0	0
S7	3	0	0
S8	3	0	0
S9	3	0	0
S10	3	0.001	0
S11	3	0.001	0
S12	3	0.001	0
S13	3	0.001	0
S14	3	0.001	0
S15	3	0.001	0
S16	3	0.001	0

APPENDIX: 3 (k)

STATISTICAL DATA INTERPRETATION OF THE SAMPLE COLLECTED FOR Cu.

Variables	N	Mean	Std. Deviation
S1	3	0.016	0.00306
S2	3	0.007	0.003
S3	3	0.013	0.00153
S4	3	0.012	0.001
S5	3	0.012	0.00115
S6	3	0.006	0.00404
S7	3	0.004	0.00115
S8	3	0.018	0.002
S9	3	0.02	0.00351
S10	3	0.006	0
S11	3	0.008	0.004
S12	3	0.008	0.003
S13	3	0.007	0.00306
S14	3	0.007	0
S15	3	0.006	0.00153
S16	3	0.006	0

APPENDIX: 3 (l)

STATISTICAL DATA INTERPRETATION OF THE SAMPLE COLLECTED FOR Fe.

Variables	N	Mean	Std. Deviation
S1	3	2.349	0.05
S2	3	0.867	0.0325
S3	3	1.556	0.044
S4	3	0.938	0.06
S5	3	2.146	0.00802
S6	3	0.813	0.015
S7	3	1.019	0.00208
S8	3	1.108	0.003
S9	3	1.214	0.00503
S10	3	0.982	0.01501
S11	3	0.197	0.002
S12	3	1.073	0.0115
S13	3	1	0.00153
S14	3	3.531	0.03001
S15	3	3.421	0.021
S16	3	3.327	0.013

APPENDIX: 3 (m)

STATISTICAL DATA INTERPRETATION OF THE SAMPLE COLLECTED FOR Zn.

Variables	N	Mean	Std. Deviation
S1	3	0.007	0.001
S2	3	0.018	0.00902
S3	3	0.006	0.004
S4	3	0.005	0.00252
S5	3	0.017	0.00902
S6	3	0.022	0.003
S7	3	0.022	0.002
S8	3	0.019	0.003
S9	3	0.006	0.003
S10	3	0.023	0.00404
S11	3	0.028	0.00902
S12	3	0.022	0.00751
S13	3	0.021	0.00351
S14	3	0.019	0.005
S15	3	0.018	0
S16	3	0.018	0

APPENDIX: 4 ONE WAY ANOVA APPLIED ON SELECTED PARAMETERS

Appendix 4(a): anova calculated for pH

ANOVA

pH

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1.110	15	.074	12.718	.000
Within Groups	.186	32	.006		
Total	1.297	47			

Appendix 4(b): anova calculated for temperature

ANOVA

Temperature

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	173.917	15	11.594	10.306	.000
Within Groups	36.000	32	1.125		
Total	209.917	47			

Appendix 4(c): anova calculated for EC

ANOVA

EC

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1692.784	15	112.852	3005.553	.000
Within Groups	1.202	32	.038		
Total	1693.985	47			

Appendix 4(d): anova calculated for TDS

ANOVA

TDS

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	8.296E8	15	5.531E7	2991.405	.000
Within Groups	591626.000	32	18488.313		
Total	8.302E8	47			

Appendix 4(e): anova calculated for Sulphate

ANOVA

Sulpahte

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1.803E8	15	1.202E7	210674.133	.000
Within Groups	1825.452	32	57.045		
Total	1.803E8	47			

Appendix 4(f): anova calculated for Chloride

ANOVA

score

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	3.826E8	15	2.551E7	332726.197	.000
Within Groups	2453.093	32	76.659		
Total	3.826E8	47			

Appendix 4(g): anova calculated for RSC

ANOVA

RSC

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	5183.169	15	345.545	2086.176	.000
Within Groups	5.300	32	.166		
Total	5188.470	47			

Appendix 4(h): anova calculated for SAR

ANOVA

SAR

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	36264.785	15	2417.652	19697.210	.000
Within Groups	3.928	32	.123		
Total	36268.713	47			

Appendix 4(i): anova calculated for Cr

ANOVA

Cr

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.411	15	.027	9967.874	.000
Within Groups	.000	32	.000		
Total	.411	47			

Appendix 4(j): anova calculated for Cd

ANOVA

Cd

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.000	15	.000	.	.
Within Groups	.000	32	.000		
Total	.000	47			

Appendix 4(k): anova calculated for Cu

ANOVA

Cu

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.001	15	.000	12.090	.000
Within Groups	.000	32	.000		
Total	.001	47			

Appendix 4(l): anova calculated for Fe

ANOVA

Fe

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	48.581	15	3.239	4587.667	.000
Within Groups	.023	32	.001		
Total	48.603	47			

Appendix 4(m): anova calculated for Zn

ANOVA

Zn

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.002	15	.000	6.024	.000
Within Groups	.001	32	.000		
Total	.003	47			

Thesis

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