# PROSPECTS

***Of***

# EM TECHNOLOGY

***In controlling***

# LEATHER INDUSTRY POLLUTION

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## 1. Introduction

In Pakistan the Leather Industry is the 3rd largest export-earning sector with an export income of over US $ 700 million and contributes about Rs. 35 million to the national economy. This is the achieved from the production of more than 750 tanneries, located in clusters of Korangi (160 tanneries), Kasur (238), Sialkot (235), Gujrawanwala-Wazirabad (40), Lahore (26), Sahiwal (6) and Multan (45). For the availability of raw material Pakistan being an agricultural country possesses a well established system of cattle breeding, have large livestock population and produces about 6.1 million hides (2.1 million cow hides and 4.0 million buffalo hides) and 36.5 million skins (22.7 million goat skins and 13.8 million sheep skins) per year [Sialkot Chamber of Commerce & Industry: feasibility study on establishment of tannery zone in Sialkot, August 2002].

## 2. Pollution Magnitude

Pakistan is a developing country. The industries have been installed without any proper planning of pollution control. Pakistan is facing natural resources degradation and pollution problems. The environmental problems such as air pollution, water (natural water bodies and groundwater) pollution, disposal of solid waste have increased manifold. The volume and extent of pollution problem of rivers and groundwater with industrial effluent and sewage water and unplanned dumping of solid wastes of both industries and cities have played havoc because the flow of four rivers (Sutlej, Ravi, Chenab and Jehlum) has been rendered to almost zero with the Indus Water Treaty 1960 and these are now functioning as receivers of sewage and effluents of all the cities and industries. The industrial wastes and effluents contain organic and inorganic salts, pathogenic organisms, toxic material, metal scraps, acids, alkalies, heavy metals and many other pollutants.

The leather processing industry utilizes considerable quantities of organic and inorganic chemical (may be toxic and /or harmful) and over and above large amounts of water. Thus, in the process of leather production considerable quantities of effluent and sludge are generated. Depending upon the production type of tanneries (raw to finish, raw to crust, raw to wet blue, wet blue to crust and wet blue to finish) for one tone of raw skin/hide on an average about 50 to 100 $m^3$ of waste water and 45 to 150 kg dried sludge are produced. Tannery effluent exhibits high values of the environmental pollution parameters i.e. BOD, COD, TSS, TDS, sulphates, sulphide, chloride, sodium and chromium etc. The most dangerous are the sulphide and chromium, which are about 20 to 100 times greater than the requirements (1.0 mg/lit) of National Environmental Quality Standards (NEQS). The parameters of NEQS for various pollutants in the sludge are still to be enforced by the respective organization.

The industrial effluent inclusive of tanneries containing high amounts of all types of toxic salts and sewage water of all the cities are discharged into nearby drains which finally fall into the adjoining river. Many industries are throwing their effluent in low lying areas or on agricultural lands due to the lax of environmental legislation. The chemical composition of pollutants in a typical tannery effluent is enumerated in table –1 and of sludge in table –2. The wastewater sources and their contribution towards pollution parameters are given in table –3.

## 3. Animals skins

The term **hide** is applied to the skins of large animals such as bulls, horses, cows and oxen. The term **skin** refers to skins of goats, sheep, calves, and those of small animals.

Animal skins mainly consist of three layers i.e. the **epidermis**, the **derma or corium** and the **flesh**. The epidermis consists of about 1% of the total skin. It is the outer layer and consists mainly of the protein keratin. The hairs, which grow through both the epidermis and the derma, are also nothing but keratin mainly. This layer is dens and chemically resistant. It allows the epidermis to be readily removed by chemical means. Hot water causes a slow solubilization by hydrolysis of the collagen to produce gelatin. The elastin is not affected by this treatment. The **flesh** is an extraneous layer, mostly adipose tissue, which are necessary to be removed to ensure tannin penetration on both sides of the corium.

## 4. Tanning operations

The tanning operations consist of converting the raw skin, a highly putrescible material, into leather, a stable and mechanically resistant matter, which can be use in the manufacture of a wide range of products (shoes, clothing, bags, furniture and many other items of daily use.

A tanning operation involves a sequence of complex chemical processes and mechanical treatments, of which the fundamental stage is tanning. When coupled to pre-and post-treatments, this confers to the final product specific properties as stability, appearance, water resistance, temperature resistance, elasticity, permeability to perspiration and air, etc.

### 4.1 Preservation/curing of raw hides/skins

Having slaughtered the animals, the skin is taken off carefully so that it is not damaged by sharp knives. The fresh/raw hides or skins are sold to the dealers. Since raw skins decay rapidly, they should be protected from the action of bacteria and consequent disintegration by using some method of preservation. Domestic hides are generally preserved by **brine curing**, in the presence of a bactericide or by **green salt method**.

In **salt curing**, the hides/skins are piled with flesh side-up in alternate layers with salt and these piles/packs are arranged in such a way that a proper drainage is provided to the brine. About 400 kg of salt is applied to one tone of raw hides

**Table-1 Chemical Composition of Tannery Effluent and NEQS Values**

| Parameters | Effluent | NEQS |
|---|---|---|
| pH | 3.5-9.4 | 6-10 |
| Total suspended solids, TSS (mg/l) | 1000-1240 | 150 |
| Total dissolved solids, TDS (mg/l) | 1520-15850 | 3500 |
| Sulphate, $SO_4$ (mg/l) | 1000-1300 | 600 |
| Chloride, Cl (mg/l) | 1200-6500 | 1000 |
| Chromium, Cr (mg/l) | 20-100 | 1.0 |
| Biological Oxygen Demand, $BOD_5$ (mg/l) | 800-1200 | 80 |
| Chemical Oxygen Demand, COD (mg/l) | 1800-2700 | 150 |

Source: *ICTP Environmental Audits Report / PTA.*

**Table-2 Chemical composition of tannery sludge from sedimentation tank.**

| Parameters | | Quantity |
|---|---|---|
| N | % by weight | 5 |
| Sulfide | -do- | Nil |
| Sulfate | -do- | 2.3 |
| Calcium | -do- | 4.63 |
| Lime | -do- | 11.60 |
| Cl | -do- | 22.62 |
| P | -do- | 0.2 |
| K | -do- | 0.063 |
| Organic matter | -do- | 57 |
| Cr | -do- | 5 |
| C/N ratio | -do- | 6 |
| Zn | Ppm | 190-220 |
| Fe | Ppm | 9000-9500 |
| Mn | Ppm | 240-280 |

Source: *PTA /ICTP phase II report.*

**Table –3 Wastewater resources and their contribution towards pollution parameters in leather processing industry**

| Source | Wastewater | Pollution parameters |
|---|---|---|
| Storage | | Salt |
| Soaking | Wastewater | Salt, BOD, COD, SS, DS, preservatives |
| Soak wash | Wastewater | Salt, BOD, COD, SS, DS |
| Liming | Wastewater | BOD, COD, DS, SS, sulphide, hair, epidermis, lime, $H_2S$ |
| Liming wash | Wastewater | BOD, COD, SS, DS, sulphide, hair, epidermis, lime, $H_2S$ |
| Deliming/Bating | Wastewater | BOD, COD, sulphates, SS, DS, sulphide, ammonia |
| Deliming wash | Wastewater | BOD, COD, SS, DS, ammonia |
| Pickling & Tanning | Wastewater | BOD, COD, SS, DS, salts, acids, Cr |
| Wet Back | Wastewater | BOD, COD, SS, DS, Cr |
| Washing | Wastewater | BOD, COD, SS, DS, Cr |
| Re-chroming | Wastewater | BOD, COD, SS, DS, Cr, sulphates |
| Re-chroming wash | Wastewater | BOD, COD, SS, DS, Cr |
| Neutralization | Wastewater | BOD, COD, SS, DS, salts |
| Neutralization wash | Wastewater | BOD, COD, SS, DS, salts |
| Fat: Liq./retanning/dyeing | Wastewater | BOD, COD, SS, DS, retanning, fats & oils, dyes |
| Topping | Wastewater | BOD, COD, SS, DS |
| Wash | Wastewater | BOD, COD, SS, DS |

(40% on weight of raw stock). The curing requires about 3–4 weeks at about 13–15°C, during which the hides/skins lose part of its moisture by dehydration and gain weight through salt absorption. The loss is the greater and the overall difference is known as **shrink**.

The hides and skins are traded in the salt state or many leather processing industries sell the partially tanned (wet blue condition) salted raw hides/skins.

### 4.2 Tanning Processes

Tanning operations include a series of chemical and mechanical treatments, converting a putrescible organic material into a bio-chemically and mechanically stable product. After treatment, the leather appears soft, elastic and resistant to mechanical stress after cross-linking of the long-chain proteic structure of the collagen, the main constituent of the raw hide and skins.

Two main processes are applied for this purpose: chrome tanning and vegetal tanning. The chrome tanning is applied in the majority of cases (70%), while vegetal tanning is applied for specific preparations, e.g. shoe soles manufacturing. Chrome tanning operations include the following main steps.

#### 4.2.1 Inspection of hides/skins

The salted raw hides/skins are stored in piles. The hides/skins are opened, examined and inspected carefully for defects. These are graded into good ones and bad/defective category. Trimming is carried out by cutting off the ears and ends. The hides and skins are graded accordingly.

#### 4.2.2 Raw hides/skins Trimming

Before starting any tannery operation, raw hides/skins are trimmed from the sides cutting off the ears and ends to bring them in proper shapes. This helps in the reduction of weight of hides/skins and subsequently use of chemicals is reduced. Raw hides/skins trimmings can be sold easily to the manufacturer of poultry feed, adhesives and soap. The raw trimmings also reduce the quantity of solid waste thus minimize pollution at source.

#### 4.2.3 De-salting

The hides/skins are cleaned to remove dirt and manure. These are further desalted manually using desalting table or mechanically. About 10–15% of the salt used during curing can be recovered easily and can be reused.

Proper desalting will surely help to prevent the salt from entering the effluent stream at source. This will help in reducing total dissolved solids (TDS) in the effluent. This will reduce effluent pollution with sodium and chloride. This is the ideal step to reduce pollution at source.

### 4.2.4 Reviving or soaking

The reviving step consists of soaking dry partially desalted and trimmed hides/skins in water to remove excess salinity and to soften after rehydration of the natural fibers. Soaking as well as washing of the hides is very important, because if moisture is not restored, the hides/skins will not respond properly to different tanning operations. Soaking is done in vats. Soaking is assisted by sodium tetra sulphide; 1/5 to 2/5 of 1% hastens rehydration and produces more uniform hydration. Soaking can be increased by adding small amounts of sodium poly sulphide and surfactants as accelerators. Disinfectants have also been used in soaking so as to check bacteria present from delayed or inadequate curing. Over soaked hides/skins are generally soft. Properly soaked hides contain about 65% water.

### 4.2.5 Green fleshing

From the well soaked hides flesh is removed manually with the help of blunt iron knives or by a machine equipped with a spiral bladed cylinder, known as beaming. Green fleshing of properly soaked hides is recommended because the fleshing can easily be used in animal feed, soap and glue production as it does not contain any harmful chemical. Green fleshing reduces the time of the next step i.e. liming etc, encourages better penetration of the chemicals and reduces the pollution load in the effluent due to less consumption in the soaking and liming processes.

### 4.2.6 Liming/lime splitting/dehairing

After the step of green fleshing the soaked hides are then treated with a saturated solution of lime in the presence of certain accelerators such as sodium sulphide (0.2–3%) or or sulph–hydrate and dimethylamine for 3 to 7 days. In case of light hides, liming for 24 hours is sufficient.

Liming is done for loosening and removing the epidermis and hair from the hide and usually carried out in paddles, drums and pits. The hides are tied or hooked together and kept in the vats containing water containing lime @ 10% of the weight of hide and sodium sulphide @ 2% of the hide weight (accelerator). Other accelerating or sharpening agents used are dimethylamine, cyanide salts and sulph-hydrate etc. The hides are moved ahead daily in a series consisting of 3 – 7 vats, remain in each for one day and then enter in a fresh lime vat.

The epidermis and hair are mainly composed of a protein, known as keratin. The keratin is readily attacked by alkali. Lime thus attacks the disulphide linkage of the keratin of the epidermis and the cortical layer and the hair. As a result hairs are softened and epidermis is removed.

$$R - S - S - CH_2R + H_2O \longrightarrow RSH + RCH_2SOH$$

$$RCH_2SOH \longrightarrow RCHO + H_2S$$

After the above process, hides are usually placed in a vat of warm water, which permits an easier removal of the hair in a dehairing machine. The skins are brought into contact with a roller set with dull knife blades, which run off the loose hair and epidermis.

### 4.2.7 Bating / deliming / skudding, cleaning and neutralization

Bating is the most unpleasant method carried out in a tannery. The old method consisted of placing the limed hides/skins in a warm infusion of the dung of dogs or fowls until the plumpness of the skins disappeared. Later on, organic artificial materials having constituents similar to dung have been used and the process became known as **bating.** The hide undergo bating or deliming process, just before immersion into the tannin liquor, and consists in adding *ammonium sulphates or ammonium chloride* as the deliming agent and addition of proteolytic enzymes for the removal and alteration of certain proteins and for the improvement of the color of the grain. Bating regulates the proper degree to which the skin structure is prepared to make it accessible for uniform absorption of the tanning agents.

Skudding operations are aimed at the removal of residual fats from pores and superficial dermis (the layer of the skin just below the epidermis). This is followed by neutralization and cleaning for residual sulfide and elimination of excess of alkalinity.

### 4.2.8 Falling

Bating is accompanied by falling. The **falling** is the reduction in the degree of swelling of the protein constituent of the limed skin previously swollen.

### 4.2.9 Pickling

Picking is a treatment given to the de-limed hides to prepare them for the tanning process or pickling is used for conditioning hides and skins for subsequent mineral tannage. The pickling process consists in treating bated hides and skins with acidic brines. The acidic brines are prepared with a mixture of formic acid (0.5%) and sulfuric acid (1 – 2%) and sodium chloride salt (6–7 or 10–15%). The hides and skins are treated in an acidified solution having pH 2–3, with a mixture of formic acid and sulfuric acid. This process helps to make deep penetration of tanning agents. To the acidic brine (pickling solution) sodium chloride salt is also added to suppress the hide’s tendency to swell and sodium format (0.5%) as masking agent.

In the pickling step, the structure of collagen is modified for better permeation of chromium into the pores of the leather. Today, recycling of pickling floats is strongly recommended to the tanneries to reduce salt pollution at site. In the pickle recycling the spent liquor is collected in a collection tank, and its acidity i.e. pH is adjusted with the addition of formic acid and sulfuric acid in the laboratory. After readjustment to the initial pH values of 2 – 3, the pickling float is reused for the next batch. With recycling of pickling float, salt savings are about 80% and reduced acid consumption is estimated at 25%, although more formic acid is saved than sulfuric acid, meaning thereby that in the spent pickle float about 80% salt and about 25% acids remains unexhausted.

### 4.2.10 Tanning

More than 90% of the world's production of light leather is chrome–tanned by one-bath process. In chrome tanning, the combination of the chromium salts and hide fibers is very rapid and takes place without any degree of swallowing. Hence chrome leather is much more pliable and loose in structure. In order to impart water resistance properties some fillers are also added. Chrome leather is characterized by high original hide proteins contents, and mineral matter but low water soluble materials. The main chrome tanning mechanisms is co-ordination of chromium to the carbonyl groups of the proteins.

The tanning process per se consists of contact with concentrated solutions of basic chromium sulfate ($CrOHSO_4$ 10%) in large rotating drums (one-bath process) for a contact time of several hours (max. 24 h). In one-bath process, chrome liquor can be prepared by reducing an acidified solution of sodium dichromate by glucose solution or by passing $SO_2$ through the dichromate solution until the reduction is complete.

$$Na_2Cr_2O_7 + 3SO_2 + H_2O \longrightarrow 2Cr\,(OH)\,SO_4 + Na_2SO_4$$

The aim of this operation is the preservation and consolidation of raw materials through cross-linking of the structure of natural collagen.

### 4.2.11 Washing and Pressing

After the tanning operation, the swollen leather is subjected to washing and pressing to remove excess Cr along with water.

### 4.2.12 Finishing

The finishing operations include shaving, coloring, polishing and finishing according to market demand. Leather, if dried rapidly, is quite stiff. The fibers must be lubricated to give them pliability and softness. If the tanned leather is not smooth, it is shaved by a machine with sharp blades. Vegetable tanned leather are sometimes washed, bleached or scoured. The bleaching or washing is carried out in revolving drum containing $Na_2CO_3$, NaOH or $H_2SO_4$ and water. Sodium bisulphite, sulphurous acid, sulphite cellulose solutions and various synthetic tanning agents (syntans) have also been used as bleaching agents.

Stuffing or fat liquoring involves the incorporation of oils and greases. Sulphonated oils blended with raw oils are the most important fat liquors. Dry or wet leather may be stuffed either by hand or in a rotating drum. In order to import desired properties to sole leathers, they are usually loaded with magnesium sulphate and cellulose.

The color and shade of the finished leather are produced by combining dyeing and finishing operations. Dyeing may be done with fat liquoring process or it may be carried out before or after it. Dyeing is usually carried out in revolving drums or vats equipped with rotating paddles and synthetic coal tar derivatives, which have widely when used as dye stuffs. The more common material used in leather finishing are cellulose ethers, waxes, resins, dyes, pigments, lacquer materials, antiseptics, miscellaneous materials such as soaps, perfumes, solvents, metal salts, sulphonated oil, acids, alkalies, plasticizers etc.

Mechanical operations carried out in the finishing leather include staking, glazing, buffing, graining, trimming, rolling, brushing and plating.

[1. *Environmental Separation of Heavy Metals by Arup K. SenGupts.p. 307 –314.*
2. *Industrial Chemistry by B. K. Sharma, 2002, p. 1366–1370*]

## 4. Environmental Pollution

All the above mentioned operations in the leather lead to the formation of liquid and solid wastes. All the wastes are to be disposed of under environmental protection requirements. Efforts have been made to reduce the pollutants in the tannery wastes at Kasur, where more than 230 tanneries exists, by constructing Common Effluent Pre-Treatment Plant (CEPTP) under Kasur Tannery Pollution Control Project (KTPCP) at a cost of Rs. 425 million with an annual running cost of Rs. 20 million. In the effluent $Cr^{3+}$ is said to be reduced by 96–98%, $BOD_5$ by 60–75%, COD by 50–65%, sulphides by 65–75%, TDS by 20–30% and sulphate by 25–35%. Permanent sludge lagoons have been constructed to collect the sludge so that the sludge stays permanently in the sludge lagoons. The CEPTP is functioning since Oct 2001. It is worth mentioning that only very few tanneries have their primary treatment plant to separate sludge from the effluent. These wastes are thrown without any treatment into the environment. It is also to be noted that more than 235 tanneries exist in Sialkot cluster and none of these have any type of treatment plant, thus all these industries throw their wastes without any treatment in to the environment.

# 5. Effective Microorganisms (EM)

## 5.1 Invention and composition of EM

Prof. Dr. Teruo Higa, University of Ryukyus, Okinawa, Japan developed the first batch of Effective Microorganism, which eventually called EM in 1980. EM is an abbreviation of effective microorganisms. It is produced through a natural process of fermentation and neither chemically synthesized nor genetically engineered. EM is a combination of various beneficial, naturally occurring microorganisms mostly used for or found in food. EM is a liquid concentrate. It is produced in vats from cultivations of over 80 varieties of microorganisms. The microorganisms are drawn from 10 genera belonging to 5 different families. The most outstanding characteristic of EM is this that it includes both aerobic and anaerobic species coexisting symbiotically in a most beneficially productive manner. EM contains beneficial tiny anabiotic microorganisms form 3 main genera: phototrophic bacteria, lactic acid bacteria and yeast. These effective microorganisms secrete beneficial substances such as vitamins, organic acids, chelated minerals and antioxidants when in contact with organic matter.

There are aerobic and anaerobic bacteria. The anaerobic microorganisms are lactobacillus bifidis and other various strains of intestinal bacteria, zymogens (zymogenic microorganisms or fermenting bacteria), sulfur / sulfate reducing bacteria, chlorobacteria and brown green photosynthetic bacteria. In the group of aerobic bacteria included are blue green algae, azotobacter, bacillus sp. (bacillus subtiles) acetobacters, methanogens and sulfur bacteria. Lactobacilli and photosynthetic bacteria, which are important components in the EM formula, belong to the anaerobic group. They are now recognized as being effective in the control of diseases.

EM is a living entity containing active microbes. Manufacturing of EM requires good quality water free of pollutants or chemicals. EM can be stored in a closed container for a period up to 6 months if kept in a dark cool place (refrigeration is not required). EM always has a sweet sour smell. One may notice a white film on the surface of EM solution when it is stored. This is yeast and does not cause any harm to the EM.

EM is a versatile product that uses microorganisms found in all ecosystems. The principle of EM is the conversion of a degraded ecosystem full of harmful microbes to one that is productive and contains useful microorganisms. This simple principle is the foundation of EM Technology in agriculture and management of environmental pollution (URL: http//www.embiotech.org).

## 5.2 EM Technology

The application of different types of EM in combination with all other products prepared using EM in proper proportions at definite times and intervals to achieve desired results with respect to decomposition and elimination of pollutants inclusive of heavy metals is named EM Technology. It is a biological tool to minimize and diminish the concentration of pollutants through bioremediation in the wastewater and solid wastes of sewage system and industries. EM Technology controls the propagation of the harmful microorganisms that cause contamination and prevents oxidation effectively with the production of antioxidants. Actually two kinds of effective microorganisms coexist within EM: zymogenic microorganisms and synthesizing microorganisms. Decomposition achieved with Zymogenic microorganisms reduces organic matter to a soluble state. This is the best food for the bacteria in EM and they readily consume it. Large quantities and wide variety of both organic and inorganic acids as well as antioxidizing enzymes are produced. This makes for the EM easy to bring about break down and decomposition of chemical substances, which are a major cause of pollution.

### 5.3 Elimination of odor (deodorization)

EM possesses the capacity to effectively eliminate the unpleasant odor. An admixture of among other things ammonia, hydrogen sulfide, trim ethylamine and methyl mercapton generally causes the offensive odor. These substances are happened to become the substances (substrate) for the microorganisms of EM. Thus, the microorganisms of EM gobble them up and the odor is eliminated because of non-existence of components of odor.

### 5.4 Dissemination of EM Technology

EM Research Organization was founded in 1994 in Okinawa, Japan to promote and disseminate EM Technology all over the world through its regional branch/ liaison offices, joint venture companies, NGO, NPO affiliates and local governments. EM Research Organization has a team of over 100 researchers around the globe conducting research in different fields to uncover viable solutions for existing environmental and health problems in 23 countries inclusive of USA, China, Germany, Korea, Thailand, Netherlands, Australia, and many others. EM is being manufactured and used in 45 countries, and use of EM is in progress in 71 countries. EM Research Organization, Okinawa, Japan holds international conferences, seminars and workshops annually in various countries in order to pool the achievements / work done relating to EM in the field of agriculture and environments. EM has shown its worth where chemicals have failed to work.

#### 5.4.1 Establishment of EM Pakistan

EM Pakistan is a private entity and is responsible for carrying out research in the field of agriculture and environments.

## 6. Collaboration with PTA in research

### 6.1 Treatment of tannery sludge at Eastern Leather Company

EM Pakistan is collaborating with Pakistan Tanners Association (PTA) for carrying out research in the leather industry. During February 2002 EMRO & PTA initiated research on “Tannery Sludge Bioremediation using EM Technology” in the premises of Eastern Leather Company (ELC), Muridkey. ELC was not equipped with Cr removal plant and the sludge was containing 5% Cr. The sludge was just like flacks of 1.0 to 1.5 cm thickness, very hard to break with hands, can be broken with hammer into small pieces of various dimensions. The experiments was conducted on crushed sludge and non-crushed sludge. The sludge was treated with EM Technology products, mixed thoroughly with the sludge, covered with a plastic sheet for anaerobic conditions and left for 40 days for the microbial activity. The sludge changed into a powdery like material giving a nice fermenting smell.

The analytical data the original pure sludge and crushed biosludge and non-crushed biosludge are given in table -4. The microbial activity reduced the Cr content from 50,000 ppm to 312 – 620ppm in the non-crushed and crushed sludge.


Experiment in progress | EM treated Sludge

**Table 4: Analysis of original sludge crushed biosludge and non-crushed biosludge**

| Parameter | Original | Crushed Bio-Sludge | Non crushed Bio-sludge |
|---|---|---|---|
| N % | 4.6 | 0.68 | 0.76 |
| P % | 0.2 | 0.052 | 0.039 |
| K % | 0.063 | 0.39 | 0.35 |
| C % | 22.0 | 8.2 | 7.6 |
| C: N | 4.8:1 | 12:1 | 10:1 |
| Organic matter % | 38.0 | 14.1 | 13.1 |
| pH | 8.3 | 7.6 | 7.4 |
| EC ms/cm | 14.2 | 13.9 | 13.0 |
| $CO_3$ me/l | Nil | Nil | Nil |
| $HCO_3$ me/l | 4.4 | 60 | 50 |
| Cl me/l | 192.5 | 100 | 90 |
| Na me/l | 34.38 | 28.2 | 36.9 |
| Ca % | 4.63 | 0.64 | 0.23 |
| $SO_4$ % | 2.30 | 0.23 | 0.26 |
| Zn ppm | 195 | 44 | 33 |
| Cu ppm | ---- | 8.8 | 3.8 |
| Fe ppm | 9400 | 9825 | 11563 |
| Mn ppm | 248 | 132 | 128 |
| Cr | 5 % | 620 ppm | 312 ppm |

### 6.1.1 Application of EM Treated sludge (biosludge) in agriculture

An experiment was designed using ELC labor in the premises ELC. The area was divided into 4 equal plots for the conventional fertilization (C–1), original pure non-crushed tannery sludge (C–2), crushed biosludge with EM extended irrigations and EM spraying (T–1), and non-crushed biosludge with EM extended irrigation and EM spraying (T–2).

The soil samples from 0–15 cm (plough layer) of the original soil were taken before the start of the experiment on 14th May 2002 and on 23rd October 2002 from the plots of 4 treatments at earring stage. It was got analyzed (table–5). The Cr concentration was nil in the original soil and it ranged from 0.24 to 0.05 ppm, maximum being in T–2 and minimum in T–1.

**Table 5: Analysis of soil before and after the application of bio-sludge and EM-irrigations & sprayings**

| Parameters | Original | After the application of bio-sludge & EM-irrigation | | | |
|---|---|---|---|---|---|
| | | C-1 | C-2 | T-1 | T-2 |
| N % | 0.028 | -- | ---- | ---- | --- |
| P (available) ppm | 2.280 | 4.3 | 7.8 | 5.1 | 4.3 |
| K ppm | 67.25 | 173 | 133 | 140 | 158 |
| $SO_4$ ppm | 88.00 | 7.4 | 32.4 | 26.1 | 2.1 |
| Mg ppm | 98.3 | 77 | 75 | 75 | 76 |
| Zn ppm | 2.33 | 0.61 | 6.0 | 0.25 | 4.0 |
| Cr ppm | Nil | 0.08 | 0.08 | 0.05 | 0.24 |
| Cu ppm | ND | 1.84 | 2.0 | 1.7 | 1.82 |
| Fe ppm | 14.25 | 32.5 | 38.6 | 27.2 | 29.5 |
| Mn ppm | 5.50 | 8.9 | 8.9 | 10.3 | 9.7 |
| B ppm | 0.933 | 1.45 | Nil | 1.16 | 2.0 |
| Cd ppm | | 175 | 175 | 178 | 162 |
| O.M % | 0.473 | 0.28 | 1.1 | 1.1 | 1.1 |
| Na mg/l | 3.70 | 0.6 | 0.46 | 0.49 | 0.31 |
| Ca+Mg mg/l | 4.55 | 1.11 | 0.73 | 0.34 | 0.52 |
| $CO_3$ mg/l | Nil | 27.7 | 25.5 | 25.55 | 26.2 |
| $HCO_3$ mg/l | 0.167 | 2.9 | 3.4 | 2.8 | 2.7 |
| Cl mg/l | 1.833 | 0.81 | 0.75 | 0.64 | 0.79 |
| EC dS/m | 0.667 | 0.6 | 0.4 | 0.4 | 0.5 |
| pH | 7.900 | 8.1 | 8.1 | 8.1 | 8.1 |
| Water saturation % | 36.67 | 32 | 32 | 32 | 32 |
| Textural class | Loam | Loam | Loam | Loam | Loam |

The plant samples from all the treatments were also taken at the time of harvesting on 13th–14th November 2002. The concentration of Cr ranged from nil to 0.02 ppm (table–6).

**Table 6: Plant Analysis**

| Parameters | Concentrations of Nutrients | | | |
|---|---|---|---|---|
| | **C-1** | **C-2** | **T-1** | **T-2** |
| N % | 1.1 | 1.1 | 1.1 | 1.8 |
| P2O5 % | .2 | 0.14 | .22 | 0.23 |
| K % | 0.63 | 0.62 | 0.64 | 0.56 |
| Ca % | 0.27 | 0.18 | 0.25 | 0.24 |
| Mg % | 0.29 | 0.26 | 0.27 | 0.26 |
| Na % | 0.69 | 0.90 | 0.60 | 1.01 |
| Zn ppm | 39.0 | 33.0 | 94.0 | 58.0 |
| Cu ppm | 7.9 | 17.9 | 11.1 | 4.8 |
| Fe ppm | 154 | 101 | 217 | 194 |
| B ppm | 2.9 | 13.1 | 21.8 | 6.5 |
| Mn ppm | 129 | 332 | 99 | 206 |
| Cr ppm | Nil | 0.01 | 0.02 | 0.01 |

## 6.2 Deodorization at Siddiq Leather Works

For deodorization EM extended was sprinkler on the effluent in the equalization tank (71.25 $m^2$) with the help of sprinkler and dozing unit. These were run for about 10 hours daily. The sprinkling of EM did help in the elimination of odor over the equalization tank as only one sprinkler was used that too had to be fix reverse with the iron beam placed on the equalization tank (photo).

Preparation of EM Extended

Sprinkling of EM in the equalization tank

## 6.3 Treatment of tannery effluent

During this experiment (3rd to 11th Feb) a total quantity of 15m$^3$ EM extended, prepared in installments as per requirements, was applied to the effluent.

To start with 1m$^3$ EM extended was applied immediately to the effluent at a point in the medium size drain, where it has just reached after screening through the fine sieve, before entry into the equalization tank. After which a suitable quantity of EM extended was continued to be dripped daily from 09:00 to 22:00 hours at the same point in the medium size drain (photo).

Application of EM

### 6.3.1 Reaction place and period for EM

The useful microorganisms were propagated in the EM extended prepared already 2 to 3 days before the application / dripping. The application of 1 m$^3$ EM extended in the beginning provided basic doze of effective microorganisms to start and to boost bio remediation process. The continuous daily dripping of EM extended helped to continue, maintain and propagate the useful bacteria for the treatment of the effluent and to reduce the pollutants in the equalization tank because this is the first bio remediation place in the SLW. The aerators in the equalization tank are run for 16 hours a day. Thus, 16 hours is the maximum reaction period between effective microorganisms and the pollutants in the effluents and are closed for 8 hours at night.

The effluent containing solid particles had to be pumped into the sedimentation tank as and when its quantity increases in the equalization tank. The useful microorganisms not only reacted with the pollutants in the equalization tank but also continued its working in the sedimentation tank, which retains slurry for maximum period. In the sedimentation tank the effluent remains at quiescent state. The sludge settles down slowly and the supernatant liquid is continuously drained out and thrown into the nearby open drain, which carries it to the river Ravi.

### 6.4 Results and Discussion

The success of EM to reduce pollutants in the effluent and in the sludge can only be judged with analysis of the treated effluent and sludge at various stages and at the final stage. For this purpose SLW did the sampling of the effluent and sludge at different stages of the experiment.

#### 6.4.1 Results of EM treated effluent

The sampling of the raw effluent and EM treated effluent was made by SLW-Chemist on 3rd, 4th, & 6th February from two points i.e. one from the point where effluent enters the equalization tank and the other from the point where clear effluent overflows from the sedimentation tank and enters into the main drain. The samples were analyzed by the Chemist of SLW laboratory. The results are given in table -7.

**Table -7 EM efficacy in eliminating pollutants in SLW effluent**
(Analysis carried out by SLW laboratory)

| Sampling point & date | | pH | TSS mg/l | TDS mg/l | Cl mg/l | S mg/l | $SO_4$ mg/l | Cr mg/l |
|---|---|---|---|---|---|---|---|---|
| 3.2.03 | a | 8.0 | 400 | 5600 | 142 | 92 | 1600 | 210 |
| | b | 7.5 | 200 | 5600 | 135 | 37 | 400 | 0.27 |
| 6.2.03 | a | 10.0 | 900 | 5900 | 57 | 320 | 1150 | 110 |
| | b | 9.0 | 300 | 4100 | 43 | 128 | 400 | 0.195 |
| 4.2.03 | a | 7.5 | 2400 | 4000 | 895 | 80 | 2000 | 178 |
| | b | 7.5 | 3600 | 2800 | 1065 | 26 | 700 | 0.346 |

a = sample taken at the entry point into the equalization tank (raw / untreated effluent)
b = sample taken from the point where the effluent overflows from the sedimentation tank and enters into the main drain (after treatment with EM)

The perusal of the data shows that on 3rd & 6th February, TSS (33 to 50%), $SO_4$ (25 to 35%), S (40%), Cl (75 to 95%) were reduced after treatment with EM products. Cr was minimized from 210 mg/l to 0.27mg/l on 3rd February and from 110mg/l to 0.195mg/l on 6th February.

#### 6.4.2 Shutdown of agitators and aeration system

On 4th February there occurred a defect in the aeration system and aeration was blocked, thus the system had to be stopped at about 11:45 hours. The trial was continued to see the effectiveness of EM products under non-aeration. The data show that there was considerable decrease in the concentration of S (32%), $SO_4$ (35%), TDS (70%) but TSS & Cl concentration increased. It may be due to closing of aeration in the equalization tank. Cr was reduced from 178 mg/l to 0.346 mg/l.

This trial did prove the effectiveness and efficacy of EM products meaning thereby that tannery effluent can be treated with EM to achieve the minimum concentration of pollutants with adjustment of quantity of EM corresponding to carrying load of pollutants in the effluents at various stages of production.

### 6.4.3 Results of increased reaction period between EM & effluent on the reduction of pollutants

During the experiments it was thought that enough time is not being provided to the effective microorganisms to react with the pollutants in the equalization tank as the effluent is to be pumped out into the sedimentation tank to accommodate the peak period effluent. To provide more time to EM for reaction with pollutants, two plastic tanks of 1 ton capacity each were placed near the sedimentation tank. These were filled with the effluent that was being thrown into the out going drain. The 1st tank was filled on 6th Feb and the 2nd tank was filled on 9th Feb. These were kept for few days. On 12th Feb the supernatant liquid from the 2nd tank was transferred into the 3rd plastic tank and was kept for few days. It is pointed out that no EM was added into these tanks. The samples from these 3 tanks were taken on 17th and 22nd Feb and were got analyzed (table -8).

**Table –8. EM efficacy in eliminating pollutants in SLW effluent with increased reaction period**

(Analysis carried by laboratory of environmental sciences)

| **Parameters** | | **Date February** | **Tank –1** | **Tank –2** | **Tank –3** | **NEQS** |
|---|---|---|---|---|---|---|
| $BOD_5$ | mg/l | 17th | 300 | 525 | 465 | 80 |
| | | 22nd | 225 | 480 | 457 | |
| COD | mg/l | 17th | 1595 | 1662 | 1638 | 150 |
| | | 22nd | 1388 | 1549 | 1536 | |
| Cl | mg/l | 17th | 712 | 2295 | 2273 | 1000 |
| | | 22nd | 696 | 2249 | 2329 | |
| $SO_4$ | mg/l | 17th | 970 | 866 | 804 | 600 |
| | | 22nd | 920 | 728 | 710 | |
| S | mg/l | 17th | .24 | 3.5 | 6.0 | 1 |
| | | 22nd | .22 | .32 | 7.74 | |
| Cr | mg/l | 17th | 8.6 | 7.74 | 8.6 | 1 |
| | | 22nd | 9.5 | 6.9 | 5.2 | |
| TDS | mg/l | 17th | 3090 | 5810 | 6060 | 3500 |
| | | 22nd | 2600 | 5660 | 5850 | |
| TSS | mg/l | 17th | 360 | 20 | 50 | 200 |
| | | 22nd | 310 | 80 | 50 | |
| Oil & grease | mg/l | 17th | 167 | 143 | 77 | 10 |
| | | 22nd | 70 | 130 | 113 | |
| pH | | 17th | 8.1 | 8.5 | 8.5 | 6-10 |
| | | 22nd | 8.3 | 8.6 | 8.7 | |

The perusal of the data shows that the concentration of all the pollutants has decreased to various degrees when compared for 17th & 22nd in each tank. pH remained unaffected.

### 6.5 Treatment of tannery's sludge with EM products

On 2nd February 100 liters EM extended solution was prepared in a plastic drum. It was made air tight and kept for the treatment of sludge.

On 4th February the weight of 1 square foot sludge was determined with electronic balance. Thus, the area required to weigh 1 ton of sludge was calculated. Accordingly one ton of sludge was removed from the sludge lagoon by four laborers. It was placed on a plastic sheet spread on the brick floor, mixed well with 500 Kg sand; 80 liters EM extended solution and 70 Kg Bokashi manually. A heap was made and it was covered with a plastic sheet to create anaerobic conditions. The EM treated sludge was examined every week and the moisture contents were maintained at 30% with EM solution in order to provide sufficient moisture to the microorganisms for working.

On 14th March the sludge was thoroughly examined by the experts of EM and PTA. It was found that it has been completely fermented as it was giving a nice fermenting smell. The original cohesive nature of the sludge was changed to just powdery type. It was still not dry and was having about 10% moisture. The upper plastic sheet was removed and the sludge was allowed to dry in the natural sunshine.

The bio sludge was finally examined on 28th March by the PTA experts and a sample was taken for analysis. On 29th March the bio sludge was examined by the experts of EMRO. It was found that the sludge was converted into a bio fertilizer. The laborers were asked to store the bio sludge / bio fertilizer in the bags for further use in agriculture and floriculture.

Sludge lagoon

Mixing of EM

Anaerobic conditions

Activity of EM

Biosludge

### 6.5.1 Results of raw sludge and EM treated sludge

The samples from the raw sludge and from the bio sludge were taken by the SLW laboratory in-charge and by the PTA experts on 4th Feb and 14th & 28th March respectively. The samples were analyzed in the SLW Laboratory, Soil and Water Testing Laboratory, Agriculture Department and in the Environmental Sciences Laboratory. The results are given in table -9.

**Table -9. EM efficacy in eliminating Cr in sludge**

| Sr. # | Analyzed by | Cr concentration (%) | |
|---|---|---|---|
| | | raw sludge | EM treated sludge |
| 1 | SLW laboratory | 5 | 3 |
| 2 | Environmental Sciences laboratory | 5 | 1.054 |
| 3 | Soil & water testing laboratory | 5 | Nil |

The effectiveness of EM to reduce Cr concentration varies as per analysis data given by the respective laboratory. Cr concentration in the EM treated sludge varies from nil to 3.0%. This indicates the authenticity of the results of the laboratory and with that the efficacy of EM.

### 6.5.2 Nutrients status of EM treated sludge (bio sludge / bio fertilizer)

Soil and Water Testing Laboratory, Agriculture Department, Government of the Punjab provided complete analysis covering all the nutrients in the bio sludge. The results are tabulated in table–10.

**Table -10. Nutrients status of EM treated sludge (bio sludge / bio fertilizer)**

| pH | EC mS/cm | $CO_3$ ppm | $HCO_3$ ppm | Cl ppm | Fe ppm | Zn ppm | Mn ppm | Cu ppm |
|---|---|---|---|---|---|---|---|---|
| 7.7 | 14.6 | Nil | 73 | 305 | 70 | 1200 | 60 | Nil |

| Ca % | N % | P % | K % | Cr % | OM % | C % | $SO_4$ % |
|---|---|---|---|---|---|---|---|
| 0.12 | 0.11 | 0.07 | 0.20 | Nil | 12.1 | 7.0 | 17.4 |

The perusal of the data shows that the bio sludge / bio fertilizer is rich in micronutrients (Fe, Zn & Mn), which are essential for plant growth. The concentration of macronutrients (NPK) is more as compared to the concentration of these in the farmyard manure. The $SO_4$ contents are enough to react with Na to reduce alkalinity of the land. Organic matter is sufficient to maintain the release of nutrients as per requirements of the crop and to improve the physical properties of the soil.

The most dangerous constituent of sludge of the leather industry is Cr, which is dangerous for human as well as animal health. World Health Organization has prescribed limits of various heavy metals in the drinking water. According to the

WHO standards for drinking water Cr is 0.05ppm. At least 5-10 litters / day of drinking water is the requirement of each person. This means it will add 0.25 to 0.5 mg of Cr daily to the human body. Now if 500 kg of bio sludge is applied to 1 acre of land and mixed with the upper 9 inches soil, the concentration of sludge will be 11gm / $ft^2$ (1 acre = 220 ft x 198 ft = 43560 $ft^2$) meaning thereby that Cr contents, if $3^{\%}$ Cr concentration is taken in the sludge as given in table –10, will be 0.33gm / $ft^2$ or 0.33gm of Cr will be mixed with 27kg of soil (weight of $ft^2$ ploughed land). The crop grown will take up the nutrients along with Cr from 12mg Cr mixed with one kg soil. In this way the Cr contents in the eatable part will be the least and will have almost no effect on the human health. This needs long-term experiments on various types of soils and crops under arid and semi-arid climate of Pakistan.

## 7. Mechanism of bioremediation

The application of biological methods for pollution reduction is referred to as bioremediation. Bioremediation repertoire is growing. Recently the most significant breakthrough has been its success in treating tannery effluent and tannery sludge and elimination of obnoxious tannery odor using Effective Microorganisms Technology. The useful microorganisms are known and definite quantities of EM products can be estimated to treat different kinds of tannery effluent and sludge for their safe disposal into the environment. The obnoxious tannery odor can also be eliminated with the application of EM Technology.

In our daily life we see many complex chemical reactions, which are brought about by the agency of living organisms. Examples are, souring and curdling of milk, putrefaction of meat, production of indigo dye from the compound present in the food, curing in the tobacco, the development of benzaldehyde or oil of bitter almonds from the amygdalin contained in the almond seed, conversion of fruit juices into wines etc. In these fermentation processes the complex organic material is broken down into smaller substances and decomposition is brought about by the action of living organisms, which secrete the enzymes catalyst suitable to the process. Now the microorganisms like yeasts, bacteria and moulds are being used for the production of large number of chemicals, such as alcohol, acetone, acetic acid, lactic acid, citric acid and many antibiotics which are of great synthetic as well as industrial importance. It has been established that the living organisms secrete a living matter, which itself devoid of life, called **enzyme**. It is complex protein molecule. The biological changes are brought by these enzymes. Enzymes are usually soluble in water or dilute alcohol and are active between 20–50$^{o}$c. a small quantity of enzymes can bring about the decomposition of large amount of the substrate. Enzymes bring about many complex reactions, e.g. oxidation, reduction, hydrolysis etc.

EM is made up of three main genera: phototrophic bacteria, lactic acid bacteria and yeasts. These Effective Microorganisms secrete beneficial substances such as vitamins, organic acid, chelated minerals and antioxidant when in contact with organic matter. Thousand million enzymes suitable to the environment are evolved by these Effective Microorganisms.

The Effective Microorganisms cause biological oxidation of organic and some inorganic substances using the impurities as a nutritive substrate and forming harmless oxidation products such as water, carbon dioxide, nitrate & sulphate ions, and also biological matters (activated sludge). Simply speaking biological purification consists in destroying organic and some inorganic pollutants present in the wastes of tannery (effluent & sludge) with the help of enzymes and secretions produced by the Effective Microorganisms. EM comprised of aerobic as well as anaerobic bacteria. Thus, maximum rate of biological purification processes and maximum efficiency of impurity decontamination is ensured. The composition of tannery effluent and tannery sludge (reasonably high NPK & organic matter) completely covers the demand for these biogenic elements and helps to increase multiplication of biological activity of these microorganisms tremendously at the prevailing temperature of 30–40$^{o}$C. This is the reason that tannery effluent and tannery sludge was purified in terms of reduction / minimization of pollutants. The most dangerous heavy metal Cr was reduced drastically both in the effluent as well as sludge.

## 8. Conclusion

EM Technology is really successful in minimizing the pollutants, especially Cr, in the sludge and effluent. With the application of EM Technology, even in the existing primary treatment system as in case of SLW, the wastes of tannery can be disposed off safely into the environment, the effluent can be drained into the existing drainage system without any danger and the sludge can be used in floriculture or in reclamation of saline alkali soils in the Punjab Province and Sindh Province, where these soils exist at a large area.