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Pollution Level Analysis in Tannery Effluents Collected From Three Different Cities of Punjab, Pakistan

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Abstract: In present study Tanning industries were selected as to evaluate their ability to cause environmental pollution. Tanning industries are present through out Pakistan being more concentrated in Kasur, Karachi, Sialkot and Faisalabad. Effluent samples were collected from 12 different sections of 6 different industries from Sialkot, Kasur and Faisalabad. These samples were tested for pollution level analysis. Parameters adopted to study pollution levels were pH, Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Solids (TS) and Chromium (Cr) Conc. Tanning industry is the major Cr consuming industry. Much of this Cr comes out in effluents rendering them polluted. Cr is highly mutagenic and carcinogenic, therefore effluents containing Cr as a pollutant are the potential mutagenic and carcinogenic agents. Study was focused on the pollution levels in tanning industry effluents to evaluate the damage caused by these effluents.

Key words: Tannery effluents, pollution level analysis, chromium concentration, COD, BOD

INTRODUCTION

It was not until 1970's that the issue of global threat to the environment found recognition in the developing world. Over the last thirty years Pakistan's environment has come under grave stress. The level of pollution in its fields, in streets and in water courses is horrible (Anonymous, 1989).

In Pakistan where industrialization has gone without due consideration to environmental pollution or adequate safety measures for the use and disposal of hazardous chemicals and the absence of environmental pollution laws till the recent past have resulted in gradual deterioration of our environment and consequently generated health hazards of perceptible magnitude (Hanif *et al.*, 1987).

Leather industries use about seventeen different kinds of tanning substances but chromium is the most commonly used tanning agent (Venier *et al.*, 1985). Nearly 90% of all the leather produced is tanned by using chromium (Kathrine and Schwedt, 1994). In chrome tanning process chromium actually cross links the collagen fibers and thus decreases the porosity of the leather (Kathrine and Schwedt, 1994).

Leather tanning business is gaining special attention. Different cities of Pakistan especially Karachi, Kasur and Sialkot are actively involved in this business (Personal Communication). With the increase in the number of

tanning units, this industry is becoming the major cause of pollution in Pakistan. Hazard to the environment caused by the effluents from tanneries is currently an acute problem in the country (Anonymous, 1998).

Kasur district has more than 300 tanning units (Personal communication) where industrial wastes are thrown open in the fields and/r in the water bodies in the area thus causing serious threat not only to the plant and animal life but also to the human population.

The present free style disposal system for discharge of tanneries effluents is polluting air, soil, sub-soil, surface water and underground water as these effluent contain pollutants such as sediments, toxic metallic compounds (including chromium), chemicals, biologically oxidizable and large quantities of putrefying suspended matter. These heavy pollutant load containing effluent, when discharged to water bodies also affect the food chain and ecosystem. In addition these compounds can be converted in nature to other compounds, which can be more toxic than the parent compounds (Kamal *et al.*, 1990).

The damage to the environment by the hazardous tannery effluents is becoming an acute problem in the country. Therefore there is an urgent need to determine the pollution levels in the waste waters from these industries. The present study is a preliminary report on estimating pollution load from tanning industries situated at Sialkot, Kasur and Faisalabad.

Twelve effluent samples collected from different sections of tanneries were tested for pH, Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Solids (TS) and Chromium concentration. The alarming results of the present study suggest that appropriate measures must be carried out to treat tannery effluents before their disposal to the environment.

MATERIALS AND METHODS

Sample collection: Twelve different samples of tannery effluents were collected from the following tanning units of Sialkot, Kasur and Faisalabad

Samples were collected in autoclaved reagent glass bottles and immediately stored in ice and transported in ice to Environmental Biotechnology Division, NIBGE, Faisalabad. In Laboratory, samples were stored in cold room at 4°C.

Pollution level analysis: To determine the pollution load in these effluents pH, COD, BOD, TS and Cr concentration was tested. These studies were carried within 24 h after sample collection.

pH: pH of the effluent samples was checked at the time of sample collection by using portable pH meter (Orion). pH was again checked in laboratory by using CD 660 digital meter by WPA Linton Cambridge, UK.

Chemical oxygen demand: Chemical Oxygen Demand (COD) is the amount of oxygen required for the oxidation of organic matter using a strong chemical oxidant. COD was tested to determine the degree of pollution in effluent samples. For COD determination procedure of Jirka and Carter (1975) was followed.

Biological oxygen demand: Biological Oxygen demand is the amount of oxygen required by the microorganisms to stabilize the biologically decomposable organic matter in wastes under aerobic conditions. This gives the amount of oxygen used up when sample is incubated for 5 days at 20°C. It is called BOD₅ (Rump and Krist, 1992).

Name of tannery	Section
Ikaso Leather, Sialkot	Neutralization
Leather Field, Sialkot	Main effluent
Sublime Sports, Sialkot	Dyeing
Nazir Tanneries, Sialkot	Chrome tanning
Nazir Tanneries, Sialkot	Main effluent
Arshad Nazir Tanneries, Kasur	Chrome tanning
Arshad Nazir Tanneries, Kasur	Neutralization
Arshad Nazir Tanneries, Kasur	Liming
Arshad Nazir Tanneries, Kasur	Dyeing
Arshad Nazir Tanneries, Kasur	Main effluent
Saeed Ihsan Tanneries, Faisalabad	Chrome tanning
Saeed Ihsan Tanneries, Faisalabad	Vegetable tanning

Total solids: Total solids were checked from these samples to get an idea for the levels of pollution. Twenty milliliter effluent sample was taken in a pre-weighed Petri plate (without lid). Petri plate was placed in oven at 50°C overnight to let the liquid evaporate. Plate containing completely dry solids was reweighed and the amount of solids was calculated by subtracting the weight of empty Petri plate (Howard, 1983).

Chromium concentration: The concentration of Cr (CR III and CR VI) in the effluent samples was determined by Atomic Absorption Spectrophotometric method on Spectra AA Varian 10/20 computerized spectrophotometer.

RESULTS

pH of the samples was greatly varied. Variation was considerable from section to section. The same sections of different tanneries were having almost similar pH values. Minimum pH (less than 4) was recorded in chrome tanning section sections while liming section was having maximum pH i.e., 11.0 (Table 1).

COD of the samples was highly variable ranging from 15.6 mg L⁻¹ for neutralization section of Arshad Nazir Tanneries, Kasur to 30107 mg L⁻¹ for vegetable tanning section of Saeed Ihsan Tanneries, Faisalabad (Table 1).

BOD of the samples was directly proportional to COD values. BOD of the samples was ranging from 4.7 mg L⁻¹ for neutralization section of Arshad Nazir Tanneries, Kasur to 10500 mg L⁻¹ for vegetable tanning section of Saeed Ihsan Tanneries, Faisalabad (Table 1).

Table 1: Pollution level analysis of effluent samples collected from various sections of different tanneries

Sample	Tannery	pH	COD (mg L ⁻¹)	BOD (mg L ⁻¹)	TS (mg L ⁻¹)	Cr Conc. (mg L ⁻¹)
Neut	ILS	6.6	730	72	5440	4
ME	LFS	7.4	484	51	2265	ND
Dye	SSS	5.5	7403	3127	6240	44
CT	NTS	3.3	11110	5763	12866	600
ME	NTS	7.2	740	335	7790	2
Neut	ANK	8.0	15.6	4.7	2840	ND
Lim	ANK	11.0	11907	1200	125860	ND
CT	ANK	3.4	13149	2210	25520	900
Dye	ANK	5.4	4020	1007	7075	100
ME	ANK	8.2	1660	693	2235	4
CT	SIT	3.7	12042	1980	39630	1600
VT	SIT	6.0	30107	10500	32332	ND

Abbreviations

Tanneries	Samples
ILS	Ikaso Leather Sialkot
LFS	Leather Field Sialkot
SSS	Sublime Sports Sialkot
NTS	Nazir Tanneries Sialkot
ANK	Arshad Nazir Tanneries Kasur
SIT	Saeed Ihsan Tanneries Faisalabad
CT	Chrome Tanning
Neu	Neutralization
Lim	Liming
VT	Vegetable Tanning
ME	Main effluent

Total solids of the samples were varied from section to section and for the same section of different industries. Maximum amount of total solids was observed in liming section of Arshad Nazir Tanneries, Kasur (125860 mg L^{-1}). The main effluents sample of the same tannery was carrying minimum amount of total solids which was 2235 mg L^{-1} (Table 1).

Total chromium was determined in the effluent samples by using Atomic Absorption Spectrophotometer. Chromium concentration differs greatly among different sections. Maximum Cr concentration was 1600 mg L^{-1} , detected in Chrome Tanning section of Saeed Ihsan Tanneries, Faisalabad (Table 1).

DISCUSSION

Tanning industry is among the major consumers of chromium chemicals and the hazards to environment caused by the effluents from tanneries is currently an acute problem in the country. The present study was commenced to seek a possible solution to the problem being created by tanning industry effluents. For this purpose industrial effluents were collected from Sialkot, Kasur and Faisalabad. Samples were subjected for the determination of pollution levels. For this study pH, COD, BOD, TS and chromium concentration was checked in these effluents. These parameters were selected because these factors determine the pollution load in effluent samples coming from different sources.

pH of the samples varied greatly depending upon the kind of the section from which a specific effluent is coming out. This variation in pH was due to different kinds of acidic or basic salts which are used in respective sections of leather tanning. The pH of chrome tanning sections was in the range of 3.3-3.7 because of the use of NaCl, H_2SO_4 , formic acid and salts of Cr-III and Cr-VI (Kathrine and Schwedt, 1994). Khawaja and Nasreen recorded the pH of chrome tanning section as 3.14 from Hayat Tannery, Charsada. pH of vegetable section was observed in this study from Saeed Ihsan Tanneries, Faisalabad was 6.0. pH of vegetable tanning section of Al-Tawakal Tannery, Charsada was 6.4 (Khawaja and Nasreen, 1993). Maximum pH 11.0 was observed in liming section because in this step chalk, Sodium sulfide (Na_2S) and Sodium hydrogen sulfide (NaHS) is used (Kathrine and Schwedt, 1994). As these compounds are basic in nature so they cause an increase in the pH of the effluent of this section. Because samples from different sections are mixed up, so the pH of the main effluent samples was found to be within the desirable limits of 6.0-10.0 as prescribed by the Pakistan National Environmental Quality Standards (The Gazette of Pakistan Environment and Urban Affairs Division, 1999).

Chemical Oxygen Demand (COD) is the amount of oxygen required for the oxidation of organic matter present in the effluent samples. In this study, it was found that vegetable tanning samples showed highest value for COD (30107 mg L^{-1}). It may be due to the fact that in vegetable tanning different kinds of plant materials which produce tannins are used along with some other chemicals. Tannins are mixtures of different kinds of glucosides of various phenols. Their action is to combine with and between the collagen fibers of the skin. Use of this organic matter results in the increased chemical oxygen demand. Khawaja and Nasreen (1993) found that Al-Tawakal Tannery Charsada had COD value of 14267 mg L^{-1} . In contrast to this neutralization section had very low COD. The reason for this low COD value may be due to the use of neutral salts and this step is just added up for the washing of the chrome tanned hides. Effluents of this section containing low concentration of chemically oxidizable materials. This fact justified the low COD results. The permissible limits for COD set by Pakistan National Environmental Quality Standards (PNEQS) are 150 mg L^{-1} (The Gazette of Pakistan Environment and Urban Affairs Division, 1999). COD of chrome tanning section was in the range of 11000-13000 mg L^{-1} . Khawaja and Nasreen (1993) found the COD value as 22880 mg L^{-1} for chrome tanning section of Hayat tannery, Charsada. The difference may be due to the use of varying concentrations of chromium salts in this process. In this study out of twelve effluent samples tested for COD eleven were having COD values more than the recommended limits. Even main effluent samples of tanneries were having much higher values than those prescribed by NEQS.

Biological oxygen demand is the amount of oxygen required for the biodegradation of organic matter. It is almost directly proportional to the COD values but always less than COD. The maximum permissible limit set by the Govt. of Pakistan for BOD is 80 mg L^{-1} (The Gazette of Pakistan Environment and Urban Affairs Division, 1999). Most of the effluents tested including main effluent were having BOD value much greater than the permissible limits indicating the high levels of pollutants in these effluents.

Maximum limit of total solids allowed in liquid industrial effluents is 3650 mg L^{-1} (The Gazette of Pakistan Environment and Urban Affairs Division, 1999). But in this study most of the effluents examined were having the value greater than the permissible limits. Amount of total solids in liming section was 125860 mg L^{-1} . It may be due to the fact that in this section protein, hairs, skin and emulsified fats are removed from the hides (Kathrine and Schwedt, 1994). Therefore these components result in the increased

weight of total solids in this section. Amount of total solids in chrome tanning section of Saeed Ihsan Tannery, Faisalabad was 39630 mg L⁻¹ whereas Khawaja and Nasreen (1993) reported 51653 mg L⁻¹ of total solids in the same section of Hayat Tannery, Charsada. The amount of total solids in two main effluent samples (Leather Field, Sialkot and Arshad Nazir Tannery, Kasur) and one neutralization section (Arshad Nazir Tanneries, Kasur) was below than the maximum permissible limits (Table 1).

Chromium is the main tanning agent in chrome tanning process (Venier *et al.*, 1985). Chromium and sulfide are among the most hazardous effluent of the tanneries. The use of excessive amount of these chemicals in tanning process gives rise to their high concentrations in the effluents (Kathrine and Schwedt, 1994). Camp *et al.* (1994) have reported that approximately one half of the sulfides used in tannery appear in the plant waste. Chromium VI is known to cause cancer (Kamal *et al.*, 1990). The recommended limit for maximum amount of chromium in the effluent samples is 1.0 mg L⁻¹ (The Gazette of Pakistan Environment and Urban Affairs Division, 1999). For chromium estimation, samples taken directly from chrome tanning drum showed extremely high values of chromium. Samples of other section and main effluent samples showed values much lower than the permissible limits except main effluents of Leather Field Sialkot, Neutralization section of Arshad Nazir Tanneries Kasur, Liming section of Arshad Nazir Tanneries Kasur and Vegetable Tanning section of Saeed Ihsan Tanneries Faisalabad where chromium concentration was not detectable due to extremely low concentration or absence of chromium (Table 1). This may be due to the mixing up of liquid wastes from other processes of the tannery where no chromium is used with effluent from chrome tanning section.

The analytical data on the composition of effluents from these tanneries reveals that these effluents are highly toxic in nature. Some of these may contain DNA damaging agents, so the testing for their mutagenic, carcinogenic nature by using some living systems is also necessary.

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