Characterisation of Various Stage Effluent In Tannery Industry and Efficiency of Combined Effluent Treatment After Chromium Recovery

By

Thilagavathy P.

A DISSERTATION SUBMITTED TO THE AVINASHILINGAM INSTITUTE FOR HOME SCIENCE AND
HIGHER EDUCATION FOR WOMEN - DEEMED UNIVERSITY, COIMBATORE - 641 043
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE IN APPLIED CHEMISTRY

APRIL - 1998

CHARACTERISATION OF VARIOUS STAGE EFFLUENT IN TANNERY INDUSTRY AND EFFICIENCY OF COMBINED EFFLUENT TREATMENT AFTER CHROMIUM RECOVERY

BY

THILAGAVATHY . P

A Dissertation submitted to

Avinashilingam Institute for Home Science
And Higher Education
For Women, (Deemed University),
Coimbatore - 641 043.

In Partial Fulfilment of the Requirements for

THE DEGREE OF MASTER OF SCIENCE
IN APPLIED CHEMISTRY
APRIL 1998

Certified as Bonafide Research Work.

S. Sivakamasundari
30.4.98
Signature of the
Head of the Department

S. Bhanumathy
30.4.98
Signature of the
Guide

Acknowledgement

ACKNOWLEDGEMENT

The author is grateful to ***Hon. Col. Dr. (Tmt). Rajammal. P. Devadas,*** M.A., M.Sc., Ph.D., (Ohio State), D.Sc., (C.Azad university, Kanpur), Chancellor, Avinashilingam Institute for Home Science and Higher Education for Women (Deemed University), Coimbatore, for the facilities provided to her by the institution, to make this study possible.

She owes her special thanks to ***Dr. (Tmt.) Lakshmi Santa Rajagopal***, M.Sc.,(Tennesse), Ph.D., Vice Chancellor, Avinashilingam Institute for Home Science and Higher Education for Women (Deemed University), Coimbatore , for providing all facilities necessary for the study.

Her special debt of gratitude goes to ***Dr. (Tmt.) Saroja Prabakaran***, M.A., Dip in Ed. Ph.D., (Madras), Registrar, Avinashilingam Institute for Home Science and Higher Education for Women (Deemed University), Coimbatore, for providing adequate help required to carry out the work.

She acknowledges ***Dr. C. V. R. Indira,*** M.Sc., Ph.D., (Madras), Dean, Faculty of Science, Avinashilingam Institute for Home Science and Higher Education for Women (Deemed University), Coimbatore, for granting permission to conduct the study.

Her overwhelming gratitude goes to ***Dr. (Tmt.) S. Sivakamasundari*** M.Sc., M.Phil., Ph.D., (Madras), Head of the Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women (Deemed University), Coimbatore, for her meticulous care, patience, help, encouragement and motivation right from the selection of the topic to the compilation of this work.

The author is very grateful to her guide ***(Tmt.) S. Bhanumathi***, M.Sc., Dip. Ed., (Madras)., M.Phil., (Bharathiar), for her ardent guidance, support and help throughout the completion of this work.

She also wishes to grant all the staff of the Chemistry Department, Avinashilingam Institute for Home Science and Higher Education for Women (Deemed University), Coimbatore, who rendered their help whenever required.

The author wishes to spell her heart felt gratitude to ***Mr. Abdul Rafiq***, M.D., K.K.S.K. Leathers Pvt. Ltd., Erode, for permitting her to carry out the project work in their R&D Laboratory.

The author profusely thanks A.O. ***Mr. Manohar***, the lab chemist and the working staff K.K.S.K. Leathers Pvt. Ltd. for their timely help.

She is forever grateful to ***Mr. S. Dhanabal*** for his untiring help throughout the study and her family who helped her complete the study.

Contents

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

Introduction

1. INTRODUCTION

Owing to an increase in population, urbanisation and industrialisation are inevitable and infact has increased the life style of common man. However, the impact of waste in the form of effluent and sludge on the soil, water and living organisms have been studied . Steps have been taken to curtain the problem of pollution and treatment methods have been implemented resulting either zero pollution or zero discharge from the industry.

Pollution is the change in the environment due to a particular species. Pollution is defined as the deterioration in the physical,chemical and biological properties of the environment..

Water is considered to be polluted when its quality degenerates due to industrial effluent, sewage, degradation of proteinaceous materials and surface run off water containing pesticides, herbicides, fertilizers etc..

Every human society, be it rural, urban, industrial or more technologically advanced, disposes off certain kinds of by-products and waste products which when injected into the biosphere in great quantities affect the normal functioning of ecosystems and have an adverse effect on plants, animals and man. These are collectively called pollutants (Smith 1977).

Industrial effluents are the major pollutants which pollute water bodies. Most of the Indian rivers and fresh water streams are seriously polluted by them. The chemicals of industrial wastes are toxic and may cause lethal or sublethal effects on aquatic fauna and flora and on cultivated plants(Seth and Bhaskaran,Ghoush and Basu).

The Ganga river system faces major pollution due to the presence of various industries on its banks. The Ganga at Kanpur is affected by the discharge of wastes from

Tanneries, Textiles, Wollen and Jute mills, Chemical and Pharmaceutical industries and Sewage (Ray and David, 1996).

Most of the rivers in India are polluted by industries. In Tamilnadu, the Cauvery receives various wastes from chemical, textile processing and bleaching, paper and pulp industries, distilleries and tanneries along its course. The effect of industrial effluent on the quality of water and also the fauna and flora of the river Cauvery and Bhavani was investigated thoroughly (Sreenevasan and Sounder Raj, 1967, Sreenevasan. et.al ,1978, 1979).

Among the industrial wastes, tannery effluent pollutes the environment to a considerable extent. In Tamilnadu there are about 600 tanneries of which nearly 275 are located in and around Erode (Subramaniam, 1988). Tanneries in general, discharge about 3000 litres of waste water per 100 kgs of hides processed in a day (Mahadevan & Muthu Kumar, 1980).

In Tamilnadu, the entire Palar river basin had been affected by the tannery discharges from Vaniambadi, Walajahbad, Pemembet and Ranipet. Goat and sheep skins were selectively processed by vegetable tanning at Ranipet.

The Pollution of the River Cauvery by tannery effluents is studied and therefore pretreatment of effluents before discharging into the river is recommended. (Dhanabal and Sivakumar, 1988).

Since tannery is a major polluting industry, its processing and treatment of the effluent are to be considered. Hence it becomes essential to the study the characteristics of tannery effluent and the different methods adopted for the treatment of tannery effluent.

The industry under consideration of this study is treating the effluent separately in each stage. The combined effluent from all processes may lead to the formation of complex compounds which makes the treatment tedious and less efficient. But when treated in each stage separately, the efficiency will be more, the treatment will be easier and also the waste is minimised by recycling.

In this method, Chromium is recovered and can be reused, Liming effluent is recycled and the liquor is used for soaking. Hence the objectives of this study.

OBJECTIVES:

- To study the characteristics of tannery effluent at various stages.
- To find the efficiency of the treatment systems prevailing.
- To discuss the chromium recovery and combined effluent treatment after Chromium recovery.
- To discuss about each parameter before and after treatment of effluent in each stage.
- To assess the pollution load of the effluent from each stage of process.
- To discuss suitable method of effluent treatment with merits and demerits.

Review of Literature

2. REVIEW OF LITERATURE

One of the major problems of rapid industrial growth is water pollution which is threatening all life forms. Tanning is one of the industrial process which causes pollution to a greater extent.

2.1. TANNING:

Tanning is a process of converting animal skins and hides into non-putrescible and tough material known as leather by certain tanning agents. Vegetable tannins predominate in their use but Aluminium and Chromium salts, Picrates, Oxidisable oils and Aldehydes are also used. (G.V. James, Manivasakam).

2.2. TANNERY INDUSTRY:

Leather industry occupies an important position in the natural economy of our country. India occupies a predominant position in the world production of hides and skin and stands amongst the five top export oriented industries. It is estimated that about 58.31 million hides and skins or 314 million kg of hides are processed annually in India.

About 70% of the total exports of leather and leather products are from Tamilnadu. (Senthil Kumar, 1993).

Dr. Kareem observed that in Tamilnadu alone there are 1,008 small scale Tannery units and 75 large scale tanneries functioning accounting for 6% of the world leather production. (The Hindu, Feb 3, 1998).

2.3. LEATHER PROCESSING:

The process of manufacturing leather is an art than science, since by utilising the same raw materials and tanning agents, one can either get a very soft leather or a rough and hard leather. Mere change of the conditions of processing alone is involved. Leather making involves processing of a natural fabric, skin into a well preserved and aesthetically appealing product. The operations prior to tanning aim at cleaning the skin of unwanted matter, hair, flesh, pigments, fats and other debris.

The tanning processes are broadly classified as

i) Beam house processing and

ii) Tan yard processing

2.3.1. BEAM HOUSE PROCESSING:

The dry matter of the skin is almost protein, reported to be about 85%. The skin also contains lipids, albumin, carbohydrates and globulin in minor amounts. In beam house processes, all the impurities are removed & collagen of the skin is made ready to absorb the tannin or chromium.

The Beam house processes are

i) **Soaking :**

The cured hides and skin are weighed and soaked in water for a period of one to two days. This removes dust, dirt, soluble matter including salt used in curing. Some antiseptic agent such as formalin is added to prevent bacterial growth. Surface active (wetting) agents are used to facilitate water absorption. (Shukla, Pandey & Manivasakam).

ii) **Liming :**

After soaking, the hides are washed with water and treated with milk of lime suspension. This treatment swells the hides and hydrolyses the collagen. The hair bundles are loosened and the fat is hydrolysed due to soaking in a pit containing lime and sodium sulphide (8:1). The hides and skins become attractive and more amenable for the removal of trace protein impurities. The hairs and flesh of these limed hides are completely removed by mechanical means and washed well with a fresh supply of water.

In liming process, Sodium sulphite, lime cell and a preservative are added and left for 2-3 days. The hide is given to fleshing section where gelatin is removed and pelt washing is done for 40 mins and weighed.

iii) Deliming and Bating:

The deliming is usually done with diluted acids or their salts. The hides are then bated or delimed using Ammonium Sulphate or Chloride as deliming agent. This regulates the pH to about 8-9. After deliming the stock is sent for tanning.

2.3.2 TAN YARD PROCESSING :

The two types of tanning processes are

1. Vegetable tanning
2. Chrome tanning

1. Vegetable Tanning :

This type of tanning produces heavy leathers which are less affected by changes in humidity and body perspiration. This process includes Tanning, Myrobing, Oiling and Drying. (Manivasakam).

2. Chrome Tanning :

It is applied to prepare light and more resistant leather. It involves more operation than vegetable tanning, but the duration is much less. In chrome tanning operations, time, temperature, concentrations of liquor, speed of agitation and protein to liquor ratio, determines the quality of the product.

i.Bating :

Bating is the treatment given to the delimed materials with a bating agent which reduces the pH and swelling, peptizes the fibers and removes the protein degradation products. It renders the grain, silky and slippery, smoother and porous nature, diminishes wrinkles and increases width.

ii.Pickling :

It is done to prevent precipitation of chromium salts on the skin fibers and involves pickling in sulphuric acid and common salt for one day. The amount of chemicals and timing varies according to the material (Normally 6 - 10%).

iii.Tanning :

After pickling, they are tanned by soaking in chrome tan liquor containing basic chromium sulphate for 6 hrs (Pickling and tanning are done in the same drum). After tanning, Sodium carbonate is added to the drum to fix the chrome. It is left for 24 hrs for complete after taking out of the drum. A preservative fungicide is added.

iv.Dyeing :

The tanned leather is rechromed for better fixation and then washed, neutralised and dyed with different types of dyes (commonly basic dyestuffs are employed).

Bleaching is done using Potassium permanganate commonly. The compounds added are fat liquor for flexibility, fish oil, sulphite or sulfates and synthetic oils. Fixing is done using formic acid. pH changes to 3.5. A washing is given and a preservative is added.

v.Fat liquoring :

To the leather is then applied an emulsion of sulphonated oil to make it soft and pliable. The schematic diagram of the process that is carried out in chrome Tanning Industry is shown (Refer Figure 1).

2.4 TANNERY EFFLUENT :

Waste waters produced in leather industry originate from the processes by which animal skins are converted into leather.

The processing of hides and skins into leather is carried out in an aqueous medium and hence the discharged water from pits, drums or paddles containing several solubles and insolubles constitute the effluent from the tannery. (Sarkar, 1991).

Tanners normally use 3000-7000 litres of water for processing 100kg wet salted hides and skins (Average - 5000 liters per 100 kgs). (Sarkar, 1991).

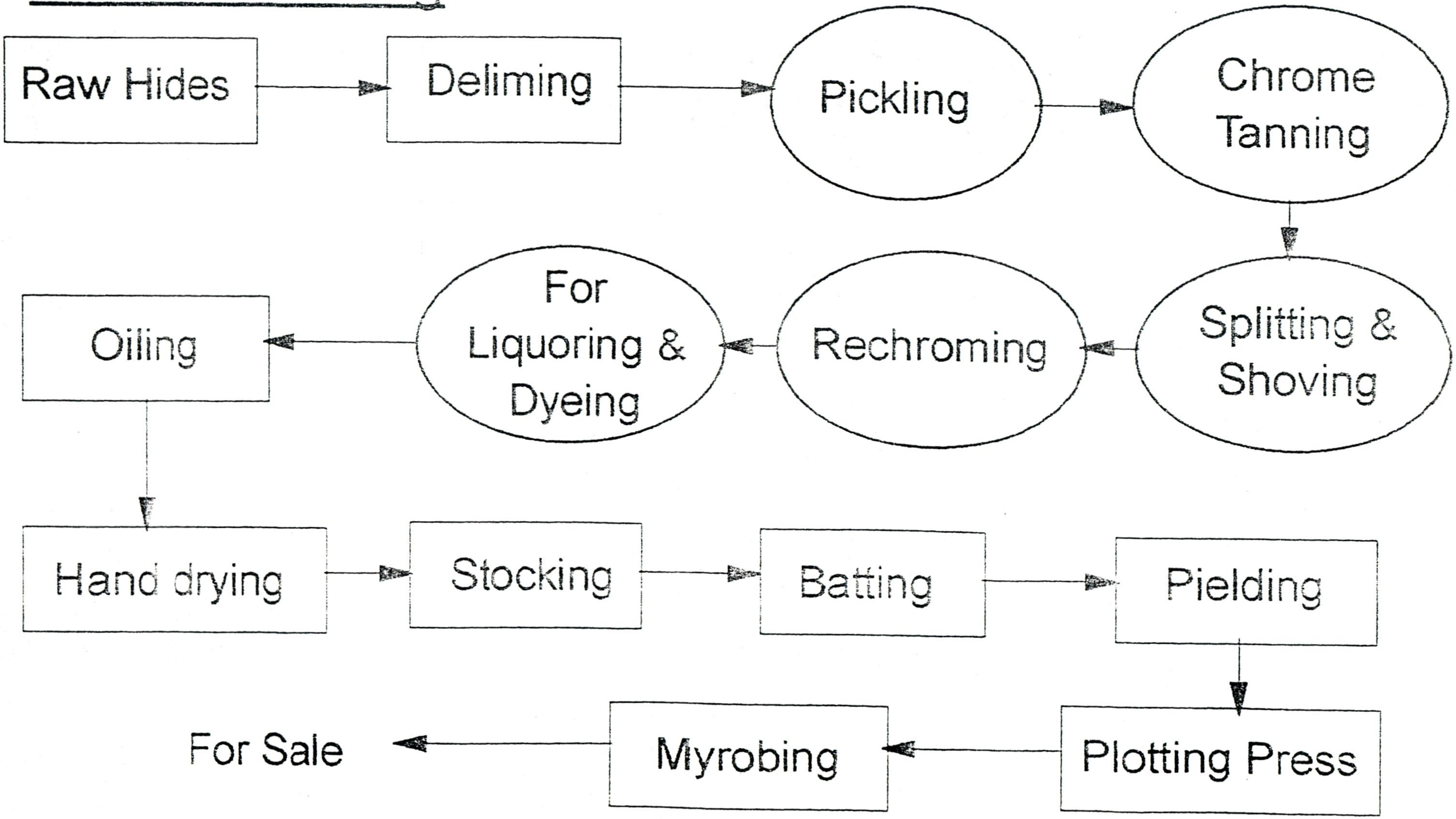
The effluent from deliming, washing operations account for about one fifth of total discharge. 80% of the total volume of waste was produced in the preparation of skins and 20% from tanning and finishing process. (Refer Table I).

The effluent produced in chrome tanning is about 10 gallons per pound of hide.(Laverick & Hammond).

FIGURE I

TANNING PROCESS

Chrome Tanning



2.5 POLLUTION DUE TO TANNERY EFFLUENT :

The tannery refuse is highly polluting containing suspended matter, total dissolved solids (mineral and organic matter), sulphides, sodium chloride, phenol, oil and grease in small quantities, chromium (trivalent) in chrome tanning effluent, tannin in vegetable tanning and sulphates. In addition it swarms with bacteria. (G.V. James).

Sodium chloride used for curing and preservation of hides and skins, Calcium hydroxide used in liming operation,sulphides and hydrosulphides used for unhairing and chromium salt used in chrome tanning are the most abundantly available constituents in the tannery effluent. (Sarkar, 1991).

The major pollution comes from beam house operation from soaking to tanning which consumes 80% of the water used in leather processing. Salt, Sodiumsulphide, Lime and Chrome liquor used in leather processing contribute to the pollution of water. All these chemicals greatly increase Chemical Oxygen Demand.

It was studied that the effluent causes high pollution due to high Chemical Oxygen Demand, high Biochemical Oxygen Demand and high concentration of Chromium(Raj.et.al;,1996).

2.6 .CHARACTERISTICS OF TANNERY EFFLUENT:

The characteristics of waste water from tanneries were studied in Kanpur by Arrora.et.al;(1972). The tannery effluent which contain chiefly salts of Sodium,Calcium,Potassium and Chromium when discharged into rivers, greatly affect the aquatic life and thereby pose a threat to aquatic ecosystem(Eye and Lawrence,1971). Sastry and Madhavakrishna(1984) reported that the discharge of untreated tannery effluent into the streams may affect the physicochemical and biological characteristic of water and deplete Dissolved Oxygen. A high degree of pollution by tannery effluent at Chennasamudram reservoir in North Arcot District was recorded by Guruprasada Rao and Nandakumar(1981). Due to the discharge of tannery effluent planktonic population decreased in Kalingarayan canal, near Erode(Ranjithakani,1983).

Tannery wastes are usually alkaline, hot and of high Biochemical Oxygen Demand. It is highly coloured by the tanning extract and dyes used in tannery and act as a barrier for the penetration of sunlight into the water. The temperature of effluent is also high when stagnated in sunlight due to infrared absorption(Sarkar,1991).

The initial wash water may have a high concentration of Sodium chloride(20,000-30,000 mg/l) its volume being 10-15% of the total waste water. The major portion of the inorganic settleable solids and sulphides come from the lime liquors.(Virendrakumar,1983).

The chrome tan liquor is acidic(Its pH is 3.1-6.0), greenish and contains trivalent chromium(1000-2200mg/l). In tanning leather from raw to finish, about 80-90% of organic impurities come from beam house treatments. Of the total effluent, these organic pollutants comprise about 40%.

The chemicals used in each stage of the process and the characteristics of effluent produced is given in table Ia.

TABLE Ia

CHEMICALS USED AND CHARACTERISTICS OF EFFLUENT GENERATED IN EACH STAGE

PROCESS	CHEMICALS USED	CHARACTERISTICS OF EFFLUENT GENERATED
Soaking	Sodium chloride	Sodium chloride - 7000 to 20,000 mg./l BOD - 800 to 2500 mg./l pH - Neutral
Liming	Sodium Sulphide, Lime	pH - Alkaline BOD - 4000 to 9000 mg./l
Deliming	Ammonium chloride or sulphate	pH - Acidic BOD - 1000 to 2000 mg./l
Batting	Proteolytic Enzymes	High Nitrogen content
Pickling	Sulphuric acid and Sodium chloride	pH - Acidic BOD - 500 to 1000 mg./l
Chrome Tanning	Basic Chromium sulphate Sodium carbonate	Chromium III - 2000 to 5000 mg./l pH - Acidic BOD - 1000 mg./l
Dyeing	Dyes	Highly coloured
Fat Liquoring		Excess oil and grease

TABLE - I

QUANTITY OF EFFLUENT GENERATED / Kg OF HIDE PROCESSED

PROCESS STAGE	VOLUME OF WATER USED IN Lits.
SOAKING	2.5 – 4.5
LIMING	3.5 – 9.0
DELIMING	2.6 – 8.0
BATTING	2.0 – 3.0
PICKLING	1.0 – 2.0
CHROME TANNING	10 gallons / pound
FAT LIQUORING & DYEING	Small volumes.

2.7 . TREATMENT OF TANNERY EFFLUENT:

Many of the tanneries in India do not appear to have proper treatment facilities. Whenever treatment of effluent is practiced, it includes settling and exposure to sunlight and atmospheric oxygen. This necessitates a very large open land(Senthilkumar,1993).

The liquors produced in a tannery are of such widely differing character that no method has come into general use for treatment of tannery wastes to produce an effluent capable of being discharged to surface water. At best partial treatment is adopted followed by entry to sewers(Sarkar,1991).

Sanitary authorities usually permit tannery discharge to be treated with public sewage, but on account of the very high oxygen absorption, it is not done so. Alum or other coagulant effects a great improvement. Other percolating filters and then sand filters will be needed to produce a good effluent.

The tannery waste is biodegradable and activated sludge units have been studied, but they require long aeration time and cost(Virendrakumar).

Freundup(1970) states that biological oxidation of tannery waste waters on their own is difficult owing to the slow decomposition of hide protein. Consequently they are best treated in ad-mixture with sewage. Treatment at the factory is more effectively given to the segregated liquor before mixing and dilution with the other wastes.

Collection and storage of the liquors in a mixing and balancing tank can in itself result in a considerable reduction in strength due to the mutual precipitation of various substances such as spent tans, lime protein and chromium.

Neutralisation may also be achieved resulting in economy in chemicals for final pH adjustment. Ideally, the balancing tank should have a capacity equal to one whole day's production. This should be followed by an upward flow sedimentation tank with provision for desludging under hydrostatic head.

Sulphide can be removed from spent lime yard liquors by fine bubble aeration at the rate of 0.005cub.m air/sqm of tank. Secondly, in a tank 5-6m deep in presence of 100mg Mn/l as Manganous chloride with the addition of an anti foaming agent(Bailey and Humphreys,1966)

Bailey.et.al,(1972) showed that there are no inherent difficulties in the biological oxidation of mixed waste waters from a chrome side leather tannery. After mixing, pH adjustment with Sulphuric acid followed by sedimentation, the crude liquor had 500-900mg/l of Biochemical Oxygen Demand, 1000-3000mg/l of Suspended solids, 5-33mg/lof Chromium and sulphide of less than 100mg/l.

43% removal of Biochemical Oxygen Demand in a 4m deep "flocor" plastic filter at an average loading of 4kg BOD/cub.m/day was reported(Laverick and Hammond). Chandra Babu said that enzyme assisted dehairing process could produce Chemical Oxygen Demand by 20-30%. Except in the case of pit liming methods, the enzyme assisted process can help in reducing the sulphur used in liming by about 50%.

Treatment of tannery effluent involves primary, secondary and tertiary treatments.The primary treatment includes screening and sedimentation.Chemical coagulation and biological treatment are the effective secondary treatments.Activated sludge process yield effluents of better quality.

Plain sedimentation can be used as a pretreatment before secondary or combined treatment with municipal wastes as it removes 70-80% of suspended solids.The sludge from this unit is easily drainable and can be used as manure.(Virendra kumar,1983).

Chromium is removed by precipitation with lime at a pH of about 6.5.Oxidation pond and anaerobic lagoon are also recommended for small and solated tanneries.Chromium precipitated as hydroxide dissolved in Sulphuric acid has been reused to tan leather.The use of spent or tanning solutions for preparing pickle liquor for subsequent hides was investigated.(Davis and Scroggie,1973).

The effluent from the secondary treatment contains chloride,the most hazardous ion in excess concentration which makes the disposal of the effluent very difficult.Segregation of spent soak liquor and spent pickling liquor and solar evaporation are the recommended treatments.(Manivasakam). The analytical limits of discharged effluents after chemical treatment and biological purification may have the standards as in Table Ib.

2.7.2. TREATMENT PREVAILING IN THE INDUSTRY UNDER STUDY:

The industry treats the effluent by segregation in each stage. The lime liquor is aerated in aeration ponds for a day and then alum settling is done. The recycled lime liquor is used for soaking process. The sludge is disposed off. The deliming liquor is led separately to the Neutralisation pond(fig.IIa).

The chrome liquor is collected in a tank, treated with Magnesium oxide and Sulphuric acid, the basic chromium sulphate is recovered and the effluent is used for deliming.

The dyeing liquor is highly acidic and is led to the neutralisation pond for the neutralisation with the alkaline deliming liquor. This after neutralisation, is led to a series of primary settling tanks for sedimentation. After sedimentation the effluent is led into a 13 meter deep lagoon and is left for anaerobic oxidation. The sludge from sedimentation tank is removed off periodically.

From the lagoon, the effluent is led to a series of five aerobic ponds which are aerated by diffusion aerators. (Ref Phase II, Figure II b).

The effluent from the fifth aeration pond of Phase II is led to an agitator where it is mixed with alum and is left to settle in secondary settling tanks, the sludge being removed regularly.

The effluent from the secondary settling tank overflows into a series of nine secondary aerobic ponds. (Ref Phase III, Figure II c). The effluent then passes through a carbon filter and flows into pond 15 of phase III.

The water from treated effluent holding tank (Pond 15, Phase III,Figure II c) is led for irrigation and flora and fauna are grown. (Eichhornia and Fish).

The soak liquor is treated separately in evaporation ponds (Five in Number) where the liquor is led for natural evaporation. A small solar evaporation tank is also set and the efficiency is under study. The scheme of the treatment plant is given in Figure II.

2.8 DISPOSAL OF SLUDGE :

Disposal of sludge from treatment is reported as one of the major problems. It does not dewater well and clogs the vacuum filters. High concentration of inorganic ions tends to hamper separate anaerobic disposal of the sludge. (Virendra Kumar, 1983).

After treatment the effluent is either disposed off into stream or to municipal sewers. Land application has also been discussed but it is to be mentioned that they need large area of land. After drying the sludge is incinerated or used for land filling. It is used for manure also. (Chakraborthy.et.al, Eye and Lin, Parker. et. al.).

TABLE Ib

ANALYTICAL LIMITS OF DISCHARGED EFFLUENTS AFTER CHEMICAL TREATMENT AND BIOLOGICAL PURIFICATION

Parameters	Mg. / Litre except pH
pH	6.5 - 9.0
Total Suspended Solids	400
Sulphide	2
Chromium III	2
BOD	80 - 100
COD	300

FIGURE II a

EFFLUENT TREATMENT PLANT
PHASE – I

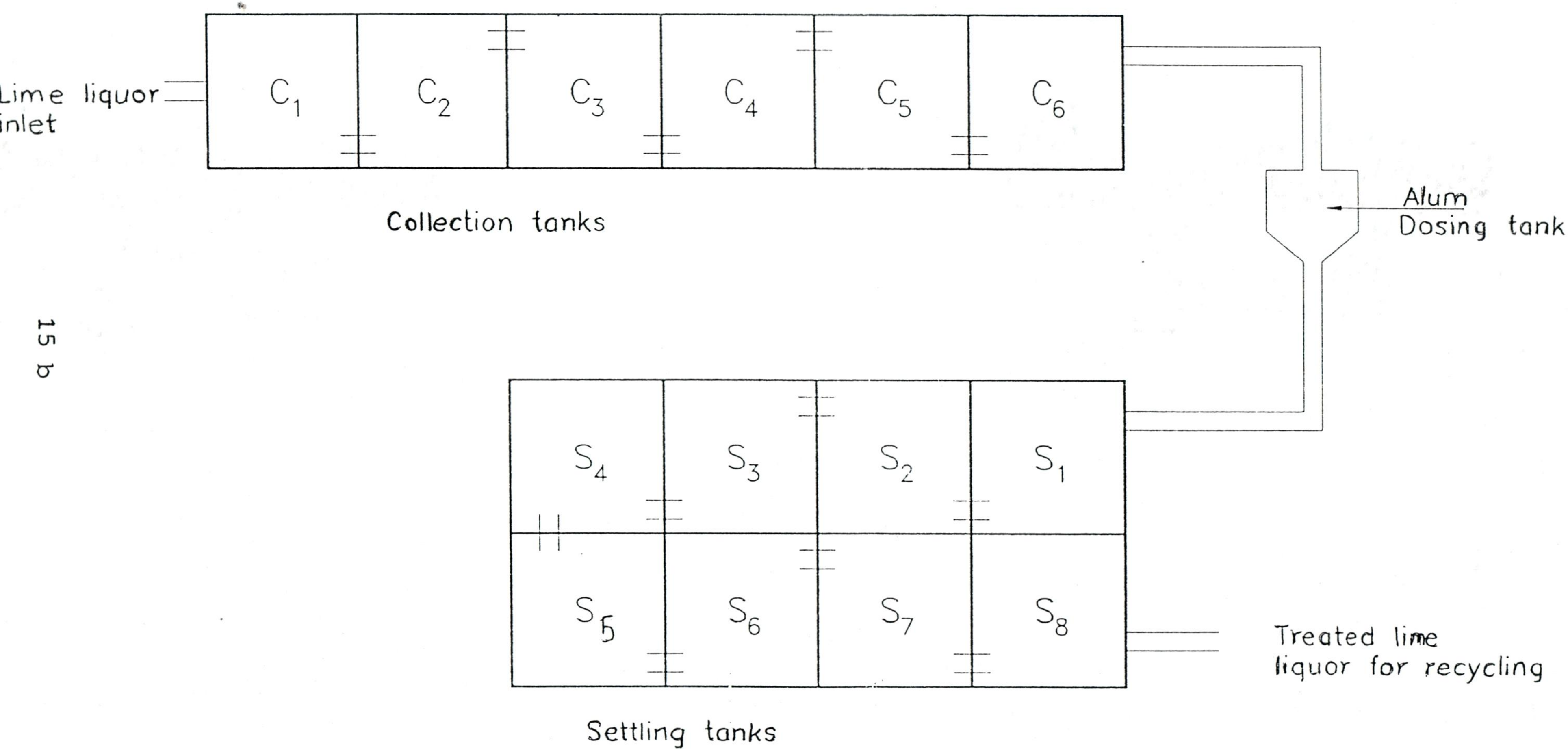


FIGURE II b

EFFLUENT TREATMENT PLANT
PHASE II

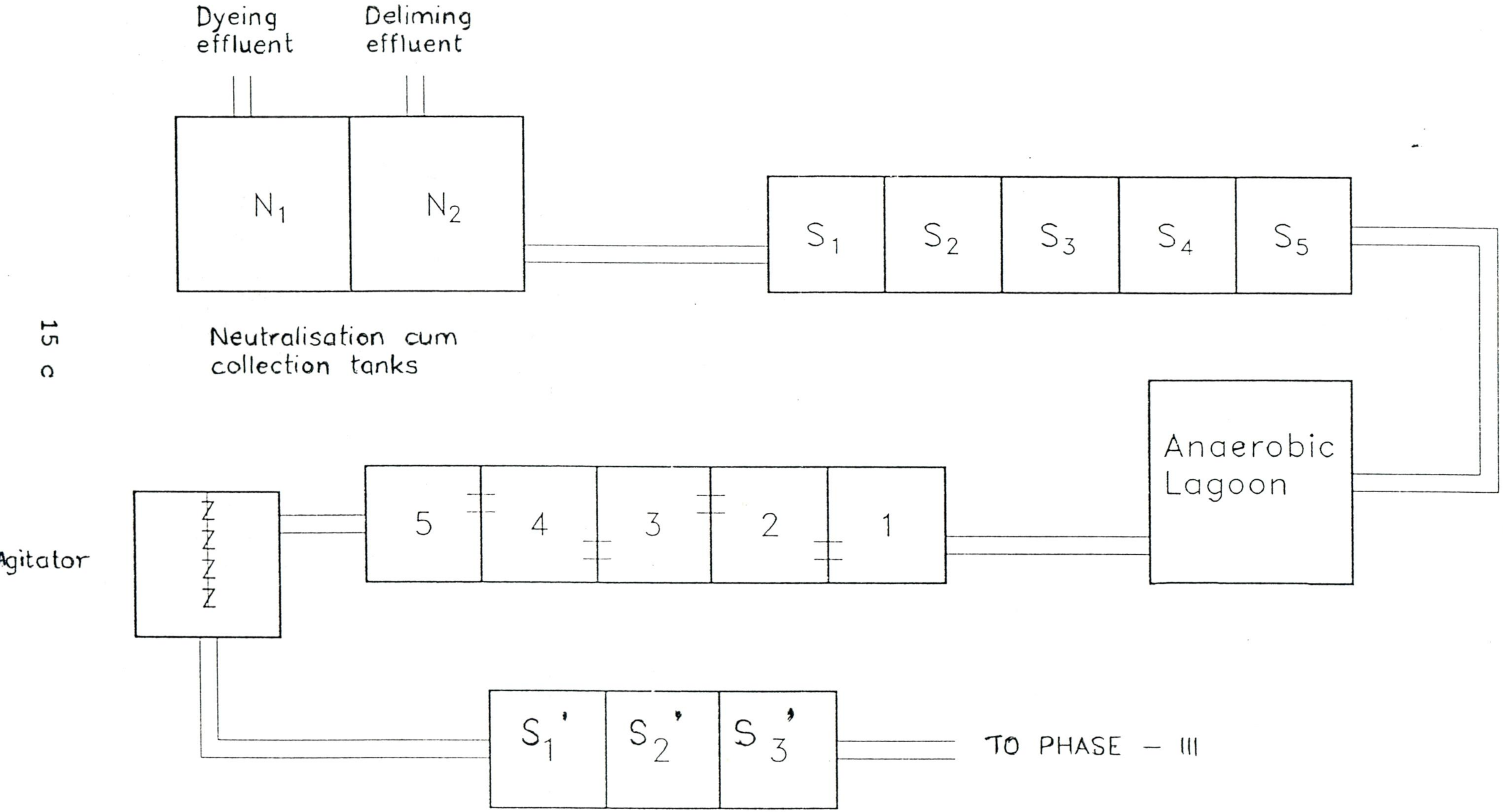


FIGURE II c

EFFLUENT TREATMENT PLANT
PHASE – III

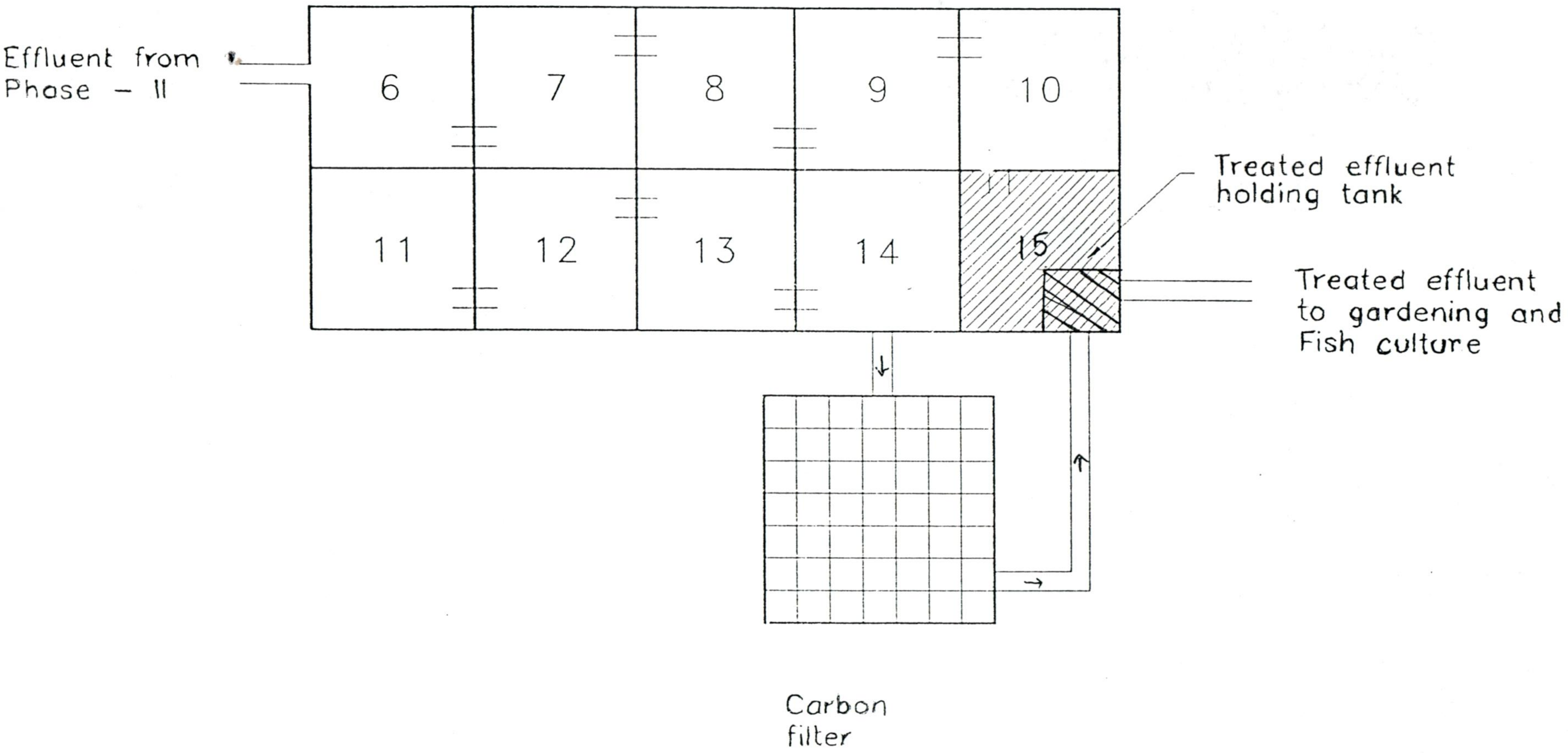
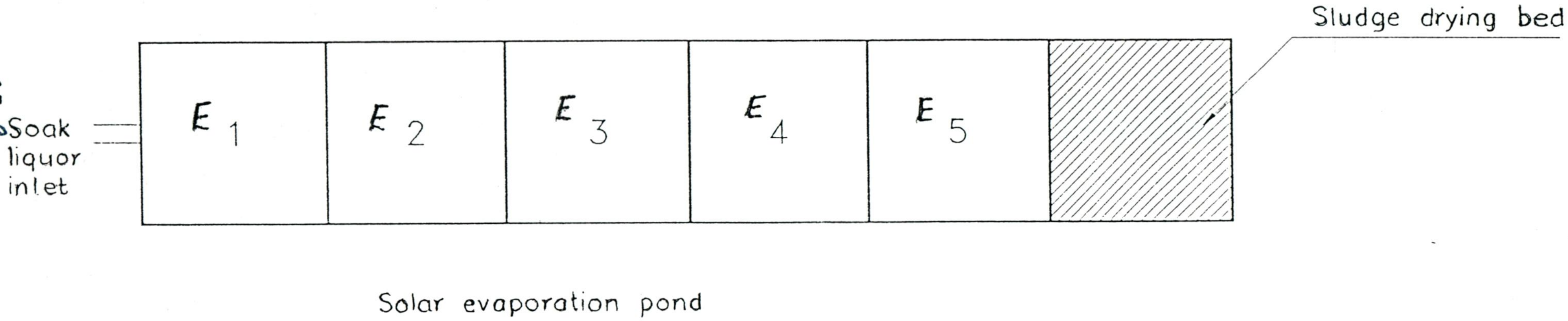


FIGURE II d

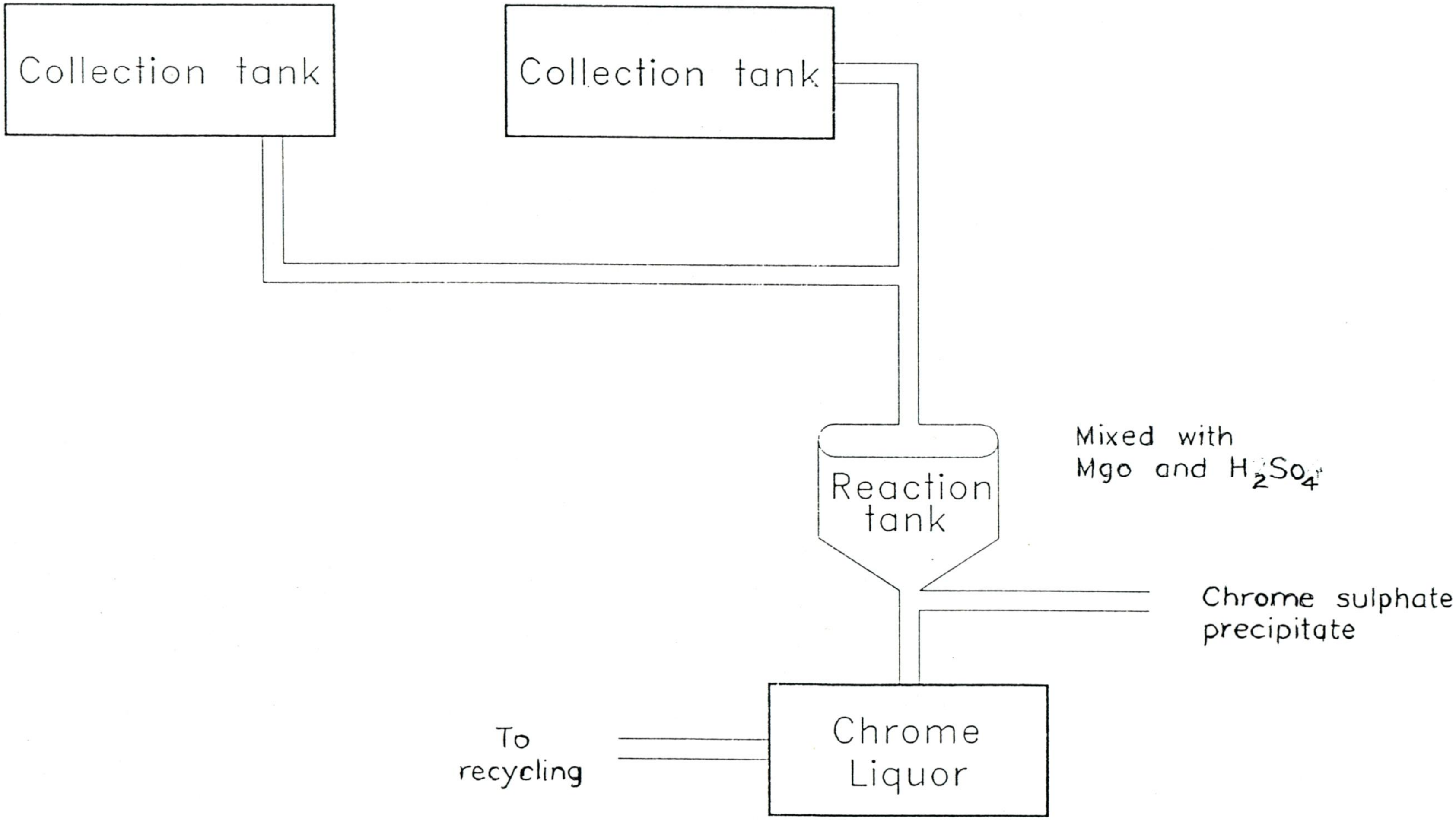
EFFLUENT TREATMENT PLANT

PHASE – IV



EFFLUENT TREATMENT PLANT
CHROME RECOVERY PLANT

FIGURE II e



Materials and Methods

3. MATERIALS AND METHODS :

The present study is carried out with the tannery effluent collected in each stage of the tanning process. All the reagents used for the analysis were of Analytical Reagent grade.

3.1. Selection of the sample :

The increase in demand for leather products necessitates a large number of tanneries, in several parts of the country. Tamil Nadu is one among the major states associated with tanneries which are the most polluting industries. Since pollution is the talk of the time, to study the pollution due to these industries is the need of the hour.

The tannery industry under study is located 12 km. away from Erode. The treated effluent is being utilised by the industry for irrigation purposes.

3.2. Sampling:

The effluent was collected from the industry on a day when the industry was active and functional. The untreated and treated samples were collected from the inlets and outlets of the effluent treatment plants respectively. Effluent samples were collected one at a time in each stage before and after treatment and stored at 4^oC. This grab sample was used for the analysis.

The entire process was done 5 times to ascertain the characteristics of the effluents.The results shown are the average values of the 5 samples of all the stages of the process.

3.3. METHODS OF ANALYSIS:

3.3.1. Physical parameters:

i. pH:

pH of the sample was read using a pH meter which consists of an electrochemical cell.First the instrument was set using buffer solution of pH 9.2, 4 and 7. When the cell is dipped in the filtered sample, the pH meter reads the pH of the sample. pH gives an idea whether the sample is acidic or alkaline. Normally pH should be around 7.

ii. Odour:

Odour is a physical property. Odour was felt when the sample was taken. It was identified as Objectionable or Unobjectionable.

iii.Colour:

The colour of the sample was noted visually when the sample was taken.

3.3.2Chemical Parameters:

i. Total Dissolved Solids:

A well mixed sample was filtered through a standard glass fiber filter and the filtrate was evaporated to dryness in a weighed dish and dried to constant weight at 180^{o}C. The increase in dish weight represented the Total Dissolved Solids.(Appendix I).

ii. Total Suspended Solids:

A well mixed sample was filtered through a weighed standard glass fiber and the residue retained on the filter was dried to a constant weight at 103-105^{o} C.The increase in weight of the filter represented the Total Suspended Solids.(Appendix II).

iii. Chloride:

Chloride was estimated as Silver chloride, argentometrically using Silver nitrate titrant and Potassium chromate indicator. (Appendix III)

iv. Sulphate :

Sulphate was estimated as Barium sulphate by Turbidimetric method using Barium chloride. The estimation was done using systronics spectrophotometer after calibrating the instrument. (Appendix IV).

v. Sulphide :

Sulphide was determined iodimetrically using Sodium thiosulphate titrant and starch indicator. (Appendix V).

vi. Sodium and Potassium :

Sodium and Potassium were estimated using direct reading systronics Flame Photometer. The instrument has been calibrated by feeding a series of standard solutions of known concentrations. The sample was filtered and fed and the readings were obtained in parts per million. (Appendix VI).

vii. Chromium :

Chromium was estimated colorimetrically using systronics spectrophotometer. Chromium III was converted to Chromium VI by oxidising and then estimated using Diphenyl carbazide reagent. (Appendix VII).

viii. Chemical Oxygen Demand : (COD).

The chemical oxygen demand is used as a measure of oxygen equivalent of organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. COD was estimated by reflux method (i.e.) refluxing with dichromate and estimating excess dichromate using Ferrous Ammonium Sulphate titrant and Ferroin indicator. (Appendix VIII).

Results And Discussion

4. RESULTS AND DISCUSSION

4.1. pH :

pH of the samples vary indifferently, from 6.7 to 11.0. Lime liquor being more alkaline has pH 11.0 and the carbon filter outlet which is the final treated effluent has pH 6.7. The most acidic sample is the chrome liquor, soak liquor being almost neutral before and after evaporation.Being acidic in nature,the chrome liquor is used in Neutralisation tank for neutralising the lime liquor. This leads to the minimisation of neutralising agent and easy handling of acidic effluent.(Refer TableII).

4.2. Colour and odour :

Almost all the samples have objectionable odour, except the effluent let out from carbon filter. The colour varies widely.(Refer TableII).

4.3. Total Dissolved Solids :

Total Dissolved Solids, an overall constituent of dissolved solids is high in all the samples, having very high values in chrome liquor and soak liquor before treatment.After treatment the Total Dissolved Solids ranges an average 948 mg/l, which achieves the Pollution Control Norms (Refer TableIII)

4.4. Chloride :

Chloride was found in large quantities only after alum settlement.This may be due to the usage of Ammonium chloride in deliming process. The high values of chloride in the untreated effluent is due to the pretreatment of raw hides,that is, in the Tanning process, the raw hide is treated with large amount of common salt as curing agent (Refer TableIII).The largest quantity was present in soak liquor before treatment (60,359 mg/l).This was reduced to 143mg/l by evaporation method,which is well below the standard values. This shows the high efficiency of Effluent Treatment Plant. (Refer Table V)

In the phase III of the treatment plant,(FigureII c) the reduction of both Chloride and Total Dissolved Solids, nearly 50% and 89% efficiency is achieved respectively, by alum dosage followed by aeration.

4.5. Sulphate :

Sulphate was found to be very high in chrome liquor due to the use of basic Chromium sulphate in chrome tanning and Ammonium sulphate in deliming. The amount of sulphate was reduced by 8-9 times after treatment. The reduction of sulphate value is due to the Chromium salt as basic Chromium sulphate by chrome recovery method(Refer TableIII).

4.6. Sulphide :

Sulphide was found to be 38 mg. per litre in lime liquor and it was found in minimum quantitites in phase II and phase III samples. It was below the detactable level in carbon filter outlet. Soak liquor was found to contain 2 mg. per litre of sulphide.

The presence of sulphide in lime liquor is due to the conversion of sodium sulphite which is used in the liming process to sulphide. Soak liquor contains some sulphide due to the usage of lime recycled liquor for soaking. This was found to be almost removed by the evaporation technique.

4.7. Total Chromium :

Total Chromium was found to be 4000 mg. per litre in chrome liquor. After recovery it has been reduced to 1090 mg. per litre. This shows 73% efficiency of the chrome recovery plant.

4.8. Sodium and Potassium :

High values of Sodium was found in all the samples.When compared with Sodium,Potassium values are very low.The high values of sodium is due to the presence of Sodium chloride as main constituent of the effluent.The least values of potassium comes from the usage of Potassium permanganate for bleaching.(ReferTableIII).

4.9. Chemical Oxygen Demand :

Chemical Oxygen Demand is a measure of pollution load due to the presence of chemical as well as biological matter in the effluent.Since chrome tanning involves chemicals in all the processes, COD value is very high.But after the treatments, the combined effluent after chromium removal and alum settling, when filtered through carbon filter, the COD value was only 58mg/l.The reduction of COD values of about 94% is achieved by the recovery of chromium and sulphate as basic Chromium sulphate which is the most common and successful method of COD and Sulphate removal (88%).The alum dosing, followed by aeration and then filtration was found to reduce 87% COD.

4.10 : The efficiency of stage by stage treatment was assessed and is presented in TableIV.

(i) The alum settling of lime liquor is found to be less efficient.

(ii) In chromium recovery plant, 73% chromium is recovered as basic Chromium sulphate.

(iii) Alum settling along with aeration by diffusion method was 87-89% efficient. Diffusion type of aeration is found to be more suitable because of its efficiency, that is it supplies more oxygen/cub.m than any other aeration methods.

(iv) Evaporation is the most suitable method in controlling the pollution load. It's efficiency is 99%.But it requires more area and time, sludge handling and disposal is also difficult. In this method the quantity of recycled water obtained is low,even though it is cheaper than many other techniques, as it requires less man power and does not require any mechanical techniques.

From the above points we can draw an idea that all the values are minimum in the sample taken from carbon filter outlet, which is used for irrigation and for growing flora and fauna.The effluent can be let out for irrigation when its parameters fall well within the standards as per Pollution Control Board Norms. The tolerance limits for the discharge of trade effluents is given in table VI.

TABLE II

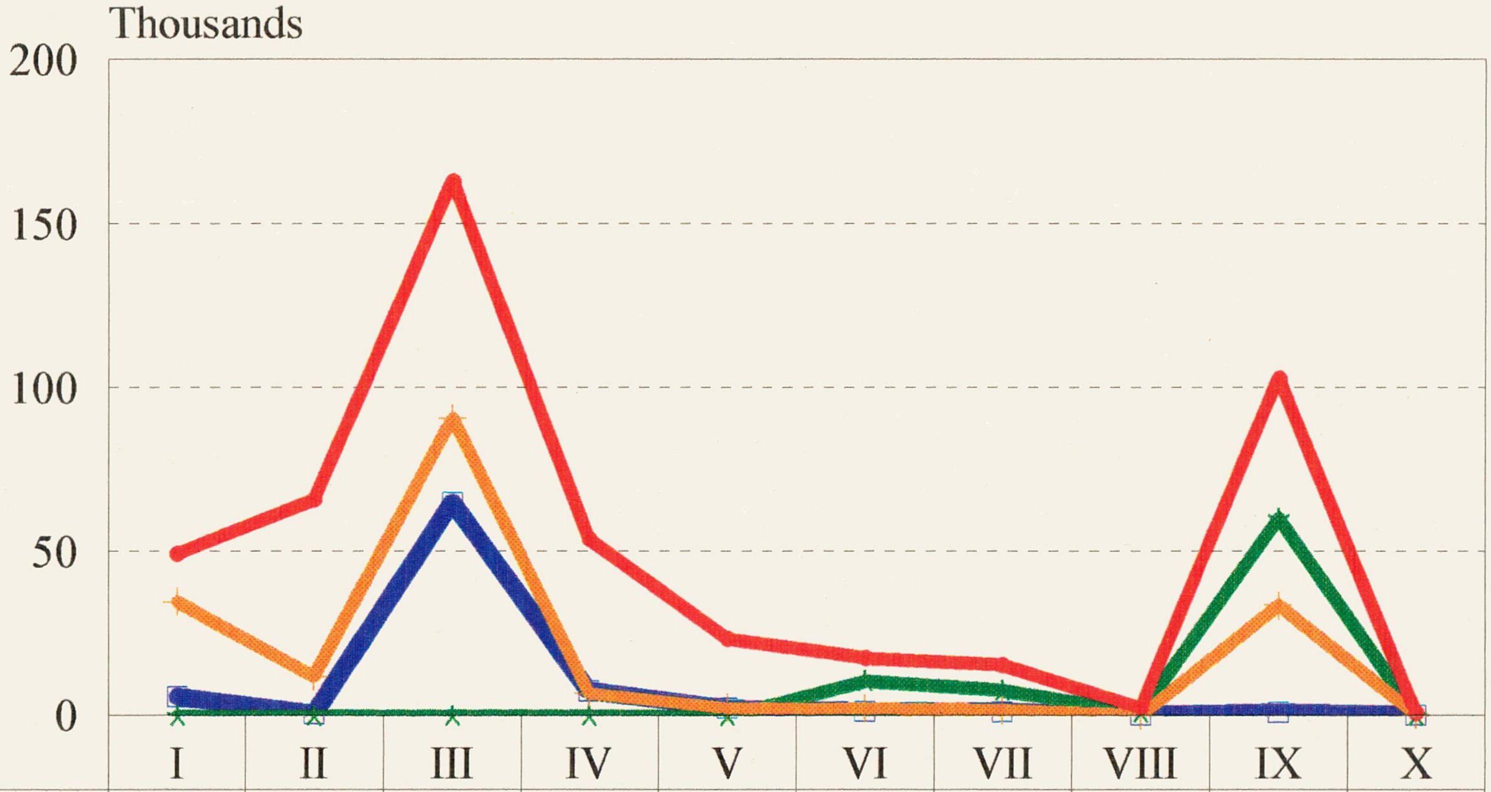
PHYSICAL PARAMETERS

SAMPLE	COLOUR	ODOUR	pH
LIME LIQUOR	PALE GREEN	OBJECTIONABLE	11.0
LIME RECYCLED LIQUOR	GREENISH WHITE	OBJECTIONABLE	10.2
CHROME LIQUOR	BLUISH GREEN	OBJECTIONABLE	2.0
CHROME LIQUOR AFTER RECOVERY	BLUE & CLEAR	OBJECTIONABLE	3.6
LAGOON OUTLET	PALE GREEN	OBJECTIONABLE	9.0
POND - 5	SLIGHTLY GREENISH	OBJECTIONABLE	8.3
POND - 15	PALE PINK	UN OBJECTIONABLE	8.1
CARBON FILTER OUTLET	CLEAR	UN OBJECTIONABLE	6.7
SOAK LIQUOR	YELLOWISH	OBJECTIONABLE	7.6
SOAK LIQUOR AFTER EVAPORATION	CLEAR	UN OBJECTIONABLE	7.3

FIGURE III

COMPARITIVE CHART

Vs TDS, TSS, CHLORIDE, SULPHATE

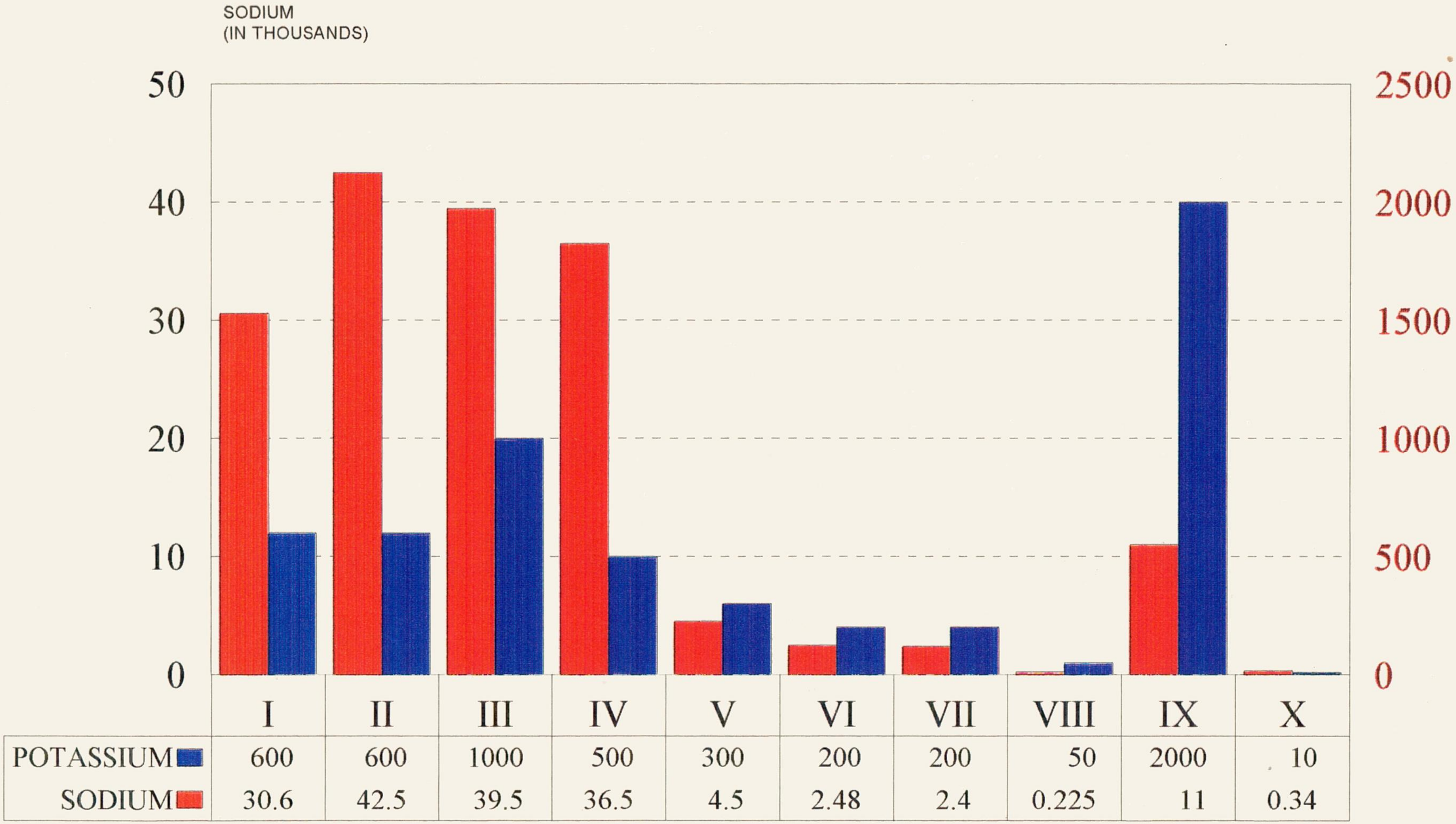


	I	II	III	IV	V	VI	VII	VIII	IX	X
TDS	49.6	66.14	163.2	54	23.57	17.75	15.59	2.51	103.08	0.948
TSS	34.8	11.98	90.8	6.98	2.55	2.19	1.83	0.068	33.8	0.36
CHLORIDE	0	0	0	0	0	10.746	7.797	0.897	60.359	0.143
SULPHATE	6.003	0.666	65.08	7.647	2.347	1.455	1.244	0.272	1.124	0.243

FIGURE IV

COMPARITIVE BAR DIAGRAM

Vs SODIUM, POTASSIUM



	I	II	III	IV	V	VI	VII	VIII	IX	X
POTASSIUM 🟦	600	600	1000	500	300	200	200	50	2000	10
SODIUM 🟥	30.6	42.5	39.5	36.5	4.5	2.48	2.4	0.225	11	0.34

TABLE III

CHEMICAL PARAMETERS

PARAMETER	I	II	III	IV	V	VI	VII	VIII	IX	X
(mg / l)	SETTLING		RECOVERY		ANAEROBIC LAGOON	AEROBIC POND - 5	AEROBIC POND - 15	` C ' FILTER OUTLET	SOAK LIQUOR	EVAPORATOR TANK
	BEFORE	AFTER	BEFORE	AFTER						
TOTAL SUSPENDED SOLIDS	34800	11,980	90,800	6,980	2,550	2,190	1,830	68	33,800	360
TOTAL DISSOLVED SOLIDS	49,600	66,140	1,63,200	54,000	23,570	17,750	15,590	2,510	1,03,080	948
CHLORIDE	-	-	-	-	-	10,746	7,797	897	60,359	143
SULPHATE	6,003	666	65,080	7,647	2,347	1,455	1,244	272	1,124	243
SODIUM	30,600	42,500	39,500	36,500	4,500	2,480	2,400	225	11,000	340
POTASSIUM	600	600	1,000	500	300	200	200	50	2,000	10
SULPHIDE	38	24	12	6	4	2	BDL	BDL	-2-	-
CHEMICAL OXYGEN DEMAND	18,600	13,424	45,943	2,892	2,525	1,553	462	58	2,788	96

TABLE IV

EFFICIENCY OF TREATMENT PLANT (PARAMETER WISE)

SAMPLE NATURE	EFFICIENCY IN %			TREATMENT STAGE
	TDS	COD	Cr	
LIME LIQUOR	25	28	-	ALUM SETTLING
CHROME LIQUOR	67	93	73	H_2SO_4 AND Mg 0 TREATMENT.
PHASE III	89	87	-	AERATION AND ALUM SETTLING.
SOAK LIQUOR	98	99	-	EVAPORATION.

TABLE V

STANDARD LEVEL AND TOLERANCE LIMITS

PARAMETERS (mg / l except pH)	USPH Standard.	ISI Standard.	SPECIFIC TOLERANCE	CHARACTERISTICS OF COMBINED EFFLUENT
pH	6.0 - 8.5	6.0 - 9.0	5.5 - 9.0	8.5
TOTAL DISSOLVED SOLIDS	500	-	-	11,650
TOTAL SUSPENDED SOLIDS	5.0	-	-	5,990
CHLORIDE	250	600	1000	6700
SULPHATE	250	1000	-	360
CHROMIUM (VI)	0.05	0.05	0.1	-
BIOLOGICAL OXYGEN DEMAND	-	-	30	1200

TABLE VI

TOLERANCE LIMITS FOR DISCHARGE OF TRADE EFFLUENTS

S.No.	CHARECTERISTICS	INLAND SURFACE WATER	PUBLIC SEWERS	ON LAND FOR IRRIGATION
1	TOTAL SUSPENDED SOLIDS	100	600	200
2	TOTAL DISSOLVED SOLIDS	2100	2100	2100
3	pH	5.5 - 9.0	5.5 - 9.0	5.5 - 9.0
4	OIL & GREASE	10	10	10
5	BOD	30	350	100
6	COD	250	-	-
7	HEXAVALENT CHROMIUM	0.10	2.0	1,0
8	TOTAL CHROMIUM	2.0	2.0	2.0
9	CHLORIDE	1000	1000	600
10	SULPHATE	1000	1000	1000
11	SULPHIDE	2	-	2

Summary and Conclusion

5.SUMMARY AND CONCLUSION

From the determination of the parameters before and after treatment of the effluent in each stage and the results obtained, it can be concluded as follows;

(i) Alum dosing along with diffusion type aeration is a cheaper and better method of treatment than any other techniques for the removal of the pollutants.

(ii) The carbon filter is the most suitable system for reducing the pollution load.

(iii) The evaporation technique executed for the treatment of soak liquor is quiet efficient(99%-Refer TableIV),in the removal of the pollutants.

(iv) Chrome liquor when treated with Magnesium oxide and Sulphuric acid, 72-75% of Chromium sulphate is recovered. This method leads to the economic usage of basic Chromium sulphate in chrome tanning.

Finally, it can be concluded that the treatment of tannery effluent in each stage is a must. The pollution due to tannery industries can be minimised when a combined system of the treatment plant, the chromium recovery, alum settlement, diffusion type aeration,filtration through carbon filter and evaporation is employed.

Bibliography

BIBLIOGRAPHY

- **Dr. Abdul Kareem**, Workshop on Money motivates chromium Recovery, HINDU, Feb 4.
- **APHA**, American Public Health Association, 1993, Standard methods for the examination of water and waste water
- **Arrora. H.C., Chattopadhyaya. S.L., and Sharma. V.P.**, 1972, Characteristics of waste from Tanneries in Kanpur. In V.S. Krishnamurthy, C.A. Sastry and R. Baskaran [Edn.] Treatment and disposal of tannery and slaughter house waste CLRI, Madras.: 18-26.
- **Bailey D.A, and Humphreys F.E**, 1966, J. Soc. Leather Trade Chemists, 51:154.
- **Bailey D.A, Robinson K.S, Stella Collins and Clarke**, 1972, J. Nat. Leather, water pollution control : 202.
- **Bailey D.A, Leafe M.K, Robinson K.S and Stella Collins,** 1972, J. Soc. Leather Trade Chemists : 200
- **Chakrabarty R.N, Saxena K.L, and Chattopadhyaya S.N**, 1967 Primary treatment of Tannery wastes - A laboratory and field study at Kanpur. E.N.V. Health, 9 : 162.
- **Dhanabal.S and Sivakumar A.A**, 1988, Effect of Tannery effluents on the water quality of the river Cauvery, J. Env. Zoology : 142 -145.
- **Eye J.D and Lin .L**, 1969, Clarification of lime bearing wastes from a sole leather tannery. (24) : 349.
- **Eye J.D and Lawrence .L**, 1971, Treatment of wastes from a sole leather tannery, J. Wat. Pol control federation, 43 : 2291 - 2303.

- **Freundup .W**, 1970, Int. Cong. Ind. waste waters, Stockholm.
- **Ghoush B.B and Basu .A.K**, 1968, Observation on Estuarine pollution of Hooghly by the effluent from a chemical factory, W.B, Env. Health : 206.
- **Guruprasada Rao .M and Nanda kumar .N.V**, 1981, Analysis of irrigation reservoir contaminated by tannery effluent, Ind. Env. Health (23) : 239 - 241.
- **Huber C.V and Jnes .G.E**, 1974, Combined treatment of Leather tanning and Municipal wastes at Ground Haven, Ind. Waste Conf. : 608.
- **James G.V**, Water treatment - A guide to the treatment of water and effluent purification (3) : 224.
- **Laverick Bert and Hammond**, 1974, Industrial pollution control Year book, Fuel and Met. J. : 124 - 126.
- **Mahadevan .A and Muthu Kumar .G**, 1980, Aquatic Microbiology with reference to Tannin - Degradation hydrobiology : 74 - 75.
- **Manivasakam .N**, 1984, Physico-Chemical examination of water, sewage and industrial effluents, Pragasham, Meerut.
- **Manivasakam .N**, 1984, Chrome tanning - Indl. eff. origin, Characteristics and effects, analysis and treatment.
- **Parker. R.R**, 1967, Disposal of tannery wastes, Ind. Waste Con.: 36.
- **Raj E.M., Sankaran .D.P, Sreenath .S, Kumaran .S and Mohan .N**, 1996, Studies on treated effluent characteristics of a few tanneries at Chrompet, Ind. J. Env. protection, (60) : 252 - 254.
- **Ranjithakani .P**, 1983, Effect of Tannery waste on the Phytoplankton of a stream at Erode.

- **Ray .P and David .A**, 1966, Effects of Industrial wastes and sewage upon the chemical and biological composition and fisheries of river Ganga at Kanpur, Env. Health : 312 - 324.
- **Sarkar .K.T**, 1991, Theory and Practice of Leather Manufacture, First revised edition.
- **Sastry .C.A and Madhava Krishna .W**, 1984, Pollution problem in Leather industries in India, Dept. of Env. Govt. of India : 34 - 35.
- **Senthil Kumar .S**, 1993, Treatment of Tannery waste water using waste Fe III / Cr III hydroxide.
- **Seth .G.K and Bhaskaran .T.R**, 1950, Effects of Industrial waste disposal on the Sanitary conditions of the Hooghly River around Calcutta, Ind. J. Med. Research.
- **Shukla .S.D and Panday .G.N**, A text book of Chemical Technology, (2) : 368-377.
- **Smith .R**, 1977, Elements of Ecology and Field Biology, Harper and Row publishers, New York.
- **Sreenevasan .A and Sounder Raj .R**, 1967, Effects of certain wastes on the water quality and fisheries of River Cauvery and Bhavani, Env. Health : 13 - 21.
- **Sreenevasan .A , Ananthanarayanan .R, Sampath .V and Paramasivam .M**, 1979, Limnological Survey of Cauvery river system with particular reference to pollution indicators Man and Biosphere, Final report.
- **Subramanian .M.K**, 1981, Erode tanneries - A survey.
- **Virendra Kumar**, 1983, Tannery waste Treatment, J. Env. Engg., (63) : 674-676.

Appendices

APPENDIX I

Total Dissolved Solids :

Procedure :

Filtered a measured volume of well mixed sample through a glass fiber filter, washed with 5ml of distilled water and continued suction for one minute after filtration was complete. Transferred filtrate to a weighed evaporating dish and evaporated to dryness in an oven at 180± 2^oC. Cooled in a dessicator and weighed.

Calculation :

Mg. total dissolved solids per litre = (B-A) X 1000 / Sample volume, ml.

where B = weight of dried residue and dish, Mg.

A = weight of dish, Mg.

APPENDIX II

Total Suspended Solids :

Procedure :

Filtered a measured volume of well mixed sample through a pre weighed glass fiber filter, washed with 5ml. of distilled water and continued suction for one minute after filtration was complete. Removed the filter and transferred to a glass planchet provided with lid. Dried in an oven at 103 to 105 ^oC. Cooled in a dessicator and weighed.

Calculation :

Mg. total suspended solids per litre = (B-A) X 1000 / Sample volume, ml.

where B = weight of filter, dried residue, mg.

A = weight of filter, mg.

APPENDIX III

Estimation of Chloride :(Argento Metric Method).

Principle :

In a neutral or slightly alkaline solution, Chromate can indicate the end point of the Silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed.

Reagents :

A). Chromate Indicator solution :

Dissolved 50 gms. of Potassium chromate in a little distilled water. Added Silver nitrate solution until a red definite precipitate was formed. Let it stand for 12 hours. Filtered and diluted to one litre with distilled water.

B). Standard Silver Nitrate Titrant (0.0141N) :

Dissolved 2.395 gms. of Silver nitrate in distilled water and diluted to 1000 ml.. Standardised against 0.0141N Sodium chloride (1.00 ml. = 500 µg cl) stored in brown bottle.

C). Standard Sodium Chloride Solution (0.0141N) :

Dissolved 824 mg. Sodium chloride in distilled water and diluted to 1000ml..

D). Sulphuric Acid - 1N .

E). Sodium Hydroxide - 1N.

Procedure :

The Silver nitrate solution was standardised using standard Sodium chloride. Adjusted sample pH to 7 - 10 with sulphuric acid or Sodium hydroxide. Titrated against standardised Silver nitrate titrant using Potassium chromate indicator. The end point was the appearance of red precipitate.

Calculation :

Chloride, mg per litre = Titre value X normality X 1000 / Volume of sample, ml.

APPENDIX IV

Estimation of Sulphate :

Principle :

Sulphate ion is precipitated in an acidic medium with Barium chloride so as to form Barium sulphate crystals of uniform size. Light absorbance of Barium sulphate suspension is measured by a photometer and the sulphate ion concentration is determined by comparison of the reading with a standard curve.

Reagents :

A). Buffer solution:

Dissolved 30gms. Magnesium Chloride, 5gms Sodium acetate, 10gms. Potassium nitrate and 20ml. acetic acid (99%) in 500 ml. distilled water and made up to 1000ml.

B). Barium Chloride Crystals :

Procedure :

Measured a portion of the sample and made up to 100ml.. Added 20ml buffer solution and mixed well. Added a spatula of Barium chloride crystals and shaken well. Taken absorbance after 5 minutes in a spectrophotometer at 420 nm. Compared the absorbance with the standard curve and the concentration obtained.

Calculation :

. Sulphate,mg per litre = mg. sulphate X 1000 / Volume of sample, ml.

APPENDIX V

Estimation of Sulphide :

Principle :

Iodine reacts with Sulphide in acid solution, oxidising it to Sulphur. This is estimated using thio titrant iodimetrically.

Reagents :

A). Hydrochloric Acid - 6 N

B). Zinc Acetate

Dissolved 220 gms. zinc acetate dihydrate in 870 ml. water and made upto 1 litre.

C). Sodium Hydroxide - 6 N

D). Standard Thio Sulphate solution - 0.025 N

E). Potassium iodide

Procedure :

Sulphide was precipitated as Zinc sulphide by adding Zinc acetate and Sodium hydroxide to the sample. The precipitate was filtered and taken in a 250ml flask. To this added 100ml. of distilled water, 5ml. of Potassium iodide and 2ml. of concentrated Hydrochloric acid and titrated against standard Sodium thiosulphate solution using starch indicator.

Calculation :

Concentration of Sulphide, mg. / ltr. = Titre value X 16 X 1000 X 0.025 /

Volume of sample, ml.

APPENDIX VI

Estimation of Sodium and Potassium:

Flame Emission Photo metric Method:

Principle:

The sample is sprayed into a gas flame and excitation is carried out under controlled and reproducible conditions. The desired spectral line is isolated by the use of interference filters. The intensity of light is measured by a photo tube potentiometer or other appropriate circuit.

Trace amounts of sodium can be determined by flame emission photometry at a wavelength of 589nm. The intensity of light at 589nm is approximately proportional to the concentration of the element.

Trace amounts of Potassium can be determined at a wavelength of 766.5nm.

Reagents:

A)Deionised Distilled Water:

B)Stock Sodium Solution:

Dissolved 2.542g Sodium chloride dried at 140°C and diluted to 1000ml with water(1.00ml=1000mg Na).

C)Intermediate Sodium chloride solution:

Diluted 10.0ml Stock solution with 100ml water.(1.00ml=100mg Na).

D)Standard Sodium solution:

Diluted 10.0ml intermediate sodium solution with water to 100ml.(1.00ml=10mg Na).

E)Stock Potassium Solution:

Dissolved 1.907g Kcl dried at 100°C and diluted to 1000ml with water.(1ml=1.00mg K).

F)Intermediate Potassium solution:

Diluted 10.0ml stock Potassium solution with water to 100ml(1.00ml=0.100mg K).

G)Standard Potassium solution:

Diluted 10.0ml intermediate potassium solution with water to 100ml (1.00ml=0.010mg K).

Procedure:

Sodium and Potassium were determined in parts per million using flame emission photometer making use of the respective filters.Fuel and air were adjusted and then ignited. The instrument was calibrated first with double distilled water to set zero.The standards were fed to adjust 100 ppm each of Sodium and Potassium.The sample was filtered and fed.When it exceeded the range of the instrument, diluted accordingly.Readings were obtained directly in ppm.

Calculation:

Sodium or Potassium = ppm X Dilution factor.

APPENDIX VII

Estimation of Chromium:

Principle:

This procedure measures only hexavalent chromium.Therefore, to determine total chromium convert all the chromium to the hexavalent state by oxidation with Potassium permanganate. The hexavalent chromium is determined colorimetrically by reaction with diphenyl carbazide in acid solution. A red-violet colour of unknown composition is produced. The reaction is very sensitive, the molar absorbtivity based on chromium being 4000 ug/cm, at 540 nm. To determine total chromium digest the sample with a sulphuric-nitric acid mixure and then oxidise with Potassium permanganate before reacting with the diphenyl carbazide.

Reagents:

Double distilled water was used for the preparation of reagents.

i] Stock chromium solution :

Dissolved 141.4 mg Potassium dichromate in water and diluted to 1000 ml (1.00ml = 50 µg Cr.)

ii] Standard Chromium solution :

Diluted 10.0ml stock Chromium solution to 100 ml (1.00ml = 5.0 µg Chromium)

iii] Diphenyl carbazide solution:

250mg of 1:5 Diphenyl carbazide in 50ml Acetone. Stored in a brown bottle.

iv] Phosphoric acid concentrated :

v] Sulphuric acid : 0.2 N

8ml of concentrated Sulphuric acid was diluted to 1000ml with water.

Procedure:

The calibration curve was drawn taking a series of standard Chromium solutions in the working range. A portion of the digested sample was taken and made upto 100ml in the standard flask, after adding 1ml of 0.2 N Sulphuric acid. Added 2ml of Diphenyl carbazide solution. After 15 minutes the reddish violet colour developed was read at 540 nm. Using the reagent blank, absorbance was corrected to zero.

From the corrected absorbance , Chromium in the sample was determined with reference to the calibration curve.

APPENDIX VIII

Chemical Oxygen Demand : Open reflux method

Principle:

A sample is refluxed in strongly acidic solution with a known excess of Potassium dichromate. After digestion, the remaining unreduced Potassium dichromate consumed and the oxidisable organic matter is calculated in terms of oxygen equivalent.

Reagents :

A) Standard Potassium dichromate solution :(0.0417M)

Dissolved 12.259g of Potassium dichromate, primary standard grade, previously dried at 103°*C* for two hours, in distilled water and diluted to 1000ml.

B) Sulphuric acid reagent:

Added Silver sulphate reagent to concentrated Sulphuric acid at the rate of 5.5 g Silver sulphate per kg Sulphuric acid. Let it stand for 1 to 2 days to dissolve Silver sulphate.

C) Standard Ferrous Ammonium Sulphate titrant(0.25 M)

Dissolved 98 gm Ferrous Ammonium Sulphate in distilled water. Added 20ml concentrated Sulphuric acid, cooled and diluted to 1000ml. Standardised this solution against standard Potassium dichromate solution.

D) Ferroin indicator:

E) Mercuric Sulphate:

Procedure:

The sample was diluted and a portion of it was pipetted into a round bottomed flask. Added 10 ml of standard Potassium dichromate solution, half a spatula of Mercuric sulphate and 30ml of Sulphuric acid reagent. Heated under reflux conditions for 2 hours, cooled and titrated against standardised Ferrous Ammonium sulphate titrant using Ferroin indicator. A blank was also conducted with distilled water.

Calculation:

C.O.D as mg oxygen / l = (A-B) X M X 8000 / Volume of sample, ml

where

A= FAS used for blank , ml

B= FAS used for sample and

M = Molarity of FAS..