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TREATMENT OF TANNERY WASTEWATERS BY ACTIVATED SLUDGE PROCESS

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ABSTRACT

The amenability of tannery wastewater to activated sludge process was investigated using three plexiglass, 8.5-litre bench-scale activated sludge units. A well equalized composite wastewater from Viiala Tannery was used as the basic raw wastewater feed. When a steady or pseudosteady state was verified, two reactors out of the three were given a short-term shock load by changing the composite wastewater feed to segregated chrome tanning process wastewater to one unit and segregated liming process wastewater to an other unit.

It was found that composite tannery wastewater can be treated by activated sludge process with more than 80 % COD removal efficiency. But, segregated process wastewaters such as chrome tanning and liming process wastewaters, can cause upset of the system, which result in high substrate leakage and increased pollutant concentration in the effluent.

The activated sludge unit was observed to recover by itself within few weeks time when the steady feed condition was resumed. It is suggested that a dependable equalization tank should be provided in order to minimize the exposure of the activated sludge unit to shock loads.

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¹ INTRODUCTION

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In many developing countries, where there Is abundant raw material for leather industries, environmental pollution assoclated with the expansion of leather industries is an Inevitable problem.

Tannery discharges are notorlous for their intermittent nature of effluent flow and have a varying composition of pollutants and extreme pH values. In addition to this they form large quantities of sludge when different effluents are mixed. Furthermore, high levels of sulphide contamination with chrome are common In the effluent. Therefore, municipal treatment plants are not willing to accept such discharges which may interfere with their treatment process.

There are many methods that may be applied for the treatment of tannery wastewaters. The choice of the appropriate method is governed by factors such as the nature of the wastewater, the degree of treatment required, the available manpower and the economic consideration.

Many biobogical treatment plants have failed in treating wastewater discharges from small and/or old tanneries. One of the major causes is their exposure to shock loads resulting from:

- 1) Interruption of some processes due to machine breakdown.
- 2) Spillage of strong chemicals to the drains.
- 3) Stoppage of work on week-ends and long holidays.

Due to the above-mentioned reasons, the variations in wastewater characteristice and flow are much higher in the smaller and the older than in the large and the modern tanneries. These variations may severely affect the treatment efficiency and hence create a treatment problem on subsequent municipal treatment 1f the wastewater is supposed to be discharged into the municipal wastewater treatment plant.

In this thesis the amenability of tannery wastewater to activated sludge procees was evaluated by simulating the possible conditions of tannery discharges from the smaller, older tanneries in developing countries as mentioned above.

Bench scale activated sludge process units were used in order to simulate the actual conditions and to study the effect on efficiency of the process.

The efficiency of the system_. was, measured by using The efficiency of the system was measured by using
COD, TOC, BOD, SS, VSS, Cr³⁺, S²⁻ and SVI-values of influent and effluent samples.

In this paper the typical manufacturing processes of tanning industry and the nature of wastewaters resulting from these processes are discussed in chapter 2. This chapter also inciudes a brief discussion of the activated sludge process. The activated sludge process is the type of process used in this particular experiment for the study of tannery wastewater treatment.

In chapter 3 the status of Ethiopian tanneries and
regulations concerning their wastewater disposal are regulations concerning their wastewater disposal discussed. This chapter is included because the writer is of an Ethiopian background and at the same time Ethiopla is one of the developing countries where there is a great potential for expansion of leather industries.

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In chapter 4 the experimental set-up and sampling methods are discussed. The results from this experiment and are discussed. The results from this experiment discussion of the results are presented in chapter 5.

Conclusions and recommendations based on the result of the experiment are presentad in chapter 6.

2 TANNERIES AND ACTIVATED SLUDGE PROCESS

2.1 Tannerles and Their Wastevaters

2.1.1 General

The art and science of tanning of skins has gradually developed from the primitive treatment of rubbing with oil, earth and fruit juices to a series of scientifically controlled operations which involve the usage of chemicals.

The wastewater produced in a tannery is one of the strongest and most difficult to treat. The problem is even worse in developing countries where there are lots of smali—size tanneries which are not as well organized and operated as the larger size tanneries in the developed countries.

Because many developing countries would like to have their own complete tanneries instead of exporting raw hides and sklns or semi—processed products, the pollution from these tndustrles will inevitably grow proportionally with the number and size of tannerles.

The wastewaters discharged from each tannery have their own individual nature. The type of raw materials used and the procees appiled can give a fair Indicatlon of the characteristic of the wastewater.

2.1.2 Manufacturing Proceases and Sourcea of Wastewaters

Leather Is a product of the tannery industry derived from the skin of certain animals. Hide is a name given to the skin of larger animals, such as cow, buffalo, deer and horse. The skin of smaller animals, such as goat and sheep Is referred to as skin. The raw hides and skins have three distinct layers: keratin, corium and adipose tissue. Corlum is the middie layer, whlch is the true skin. The processes in tannery are directed to removing the keratin and the adipose tissue, whlch Is the Inner fleshy layer. The corlum is composed of protein, collagen and elastin which exists as a bundle of fibres connected together. Leather is a highly flexible and durable material which is produced after these fibres are processed and preserved. The following process sequences are typical of leather

industries:

A. Beam house process and vastewaters

The operations In the beam house processing prepare the hide or skin for tanning by removing all undesirable impurities, and leave the collagen in a receptive condition to absorb the tanning agents. The various steps involved in this process are deecribed in the following paragraphs. The wastewaters produced during these operatlons are known as the beam house wastewater. They account for 85 % of the flow and 75 % (or more) of the BOD_5 , COD and SS generated
by typical full process tannery (Rest et al 1982). Typical typical full process tannery (Rest et al 1982). Typical concentratlon ranges of beam house effluent components are shown In Table 1.

Table 1. Typical concentration range of beamhouse effluent components (Bally et al 1983).

i Soaklng

Soaking is the first process in the leather manufacturing where raw hide and skin are rehydrated. Since this process may be carrled out in pit, paddie or drum, the wastewaters from this operation are Intermittent. Dirt, blood and dung removed from the skin and different chemicals used in the process such as sodium hydroxide, sulphide or sulphite,
sodium hypochlorite, wetting agents, emulsifiers and sodium hypochlorlte, wetting agents, emulsiflers and surfactants, may also be present in the wastewaters.

ii LimIng

In this process the hair and wool are loosened by subjecting the hide in the suspension of lime and sodium sulphide blend. The process opens the flbre structure and "plumps" the hide. This operation facilitates the penetration of tanning agents deeper into the hide (Winters 1984).

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The wastewater discharge from this section is intermittent. Although small In volume, these wastewaters constitute the heaviest fraction of the tannery waste (Table 2).

iii Unhalring

After the liming operation, the hides and skins are placed
in machines with roller knives to remove hairs and machines with roller knives to remove hairs epidermis. The cuttings are flushed out In a stream of water, which passes through screens for hair removal. Then, the unhaired hldes are washed in a stream of clean water.

The wastewater flow from these operations is continuous. The volume of wastewaters is large and the waste waters contain fine hair, some epidermal layers and lime. The figures in Table 2 demonstrate that the contribution of the unhairing process to the pollution load is rather high.

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iv Fleshing

In this procesa the adipose tissues are removed from the flesh side of the hide. The wastewater discharge from this process is continuous and it contains the resultant fleshing. It is the most difficult wastewater to handle due to the mucous - like condition of the fleshings which are readily putrescible (Winters 1984).

v Delime

Deliming is a reverse process of liming. Thorough washing in a drum or paddie is followed by the application of neutralizing chemicals. The discharge of delime wastewater is intermittent.

vi Bating

In the bating process some of the undesirable proteins, such as elastin, are hydrolysed and the excess lime absorbed is removed. Prevlously this process was done by placing the limed skin in a warm infusion of dog dung or pigeon droppings. The current practice is to treat It using enzymatic aqueous suspensions in a drum or paddie. The wastewater discharges from this section are infrequent and contain little pollutional material.

vii Pickling

In this operation the pH of the pelt is adjusted, and the skin is sterilized. Pickling with salt and acid helps to prevent chromium precipitation during the tanning process (Winters 1984). The wastewater discharge from this operation is very small. This is because the pickling liquor is reused many times before It is drained.

B. Tanning and tan-yard wastewaters

Tanning is the most important process in leather production. The hide or skin is converted to a non putrescible material and, in addition to this, the tanning gives the necessary chemical and physical characteristics to the leather. Two principal methods are vegetable tanning and chrome tanning. Alum tanning for the production of
white leather is sometimes used. The wastewaters leather is sometimes used. The wastewaters originatIng from the tanning operations are designated as tan—yard wastewaters.

¹ Vegetable tanning

The tanning operation utilizes reagents such as tannings which are of vegetable extracts or synthetic tanning agents such as syntans. Tannings are widely used In tanneries In developing countries. This method is used mostly for the production of sole and saddiery and some speclality leathers. The wastewater discharge from the vegetable tanning operations is intermittent, but the wastewater is very strong due to Its high concentratlon of organic pollutants and colour.

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11 Chrome tanning

In chrome tanning the sklns or hides are placed In rotary drums or fixed vats containing an acidified solution of sodium dichromate along with reducing agents. The wastewater (referred to as tan-yard wastewater) flow from chrome tannery is intermittent, and has a high concentration of chromium and salt.

Finishing processes

In finishing processes the stiff leather coming from the tanning section is lubricated to make the fibres soft and pliable. Depending on the type and desired quality of leather a series of finishing operations are carried out. The major sources of wastewaters from this section are the bleaching, dying and fat liquoring processes.

The mechanical processes such as rolling, polishing and treatment of oil produce a negligible volume of wastewater. The wastewater discharges from bleaching are intermittent and have substantial colour and organic load. Fat liquoring operatlons contrlbute cobour and oil emulsIons to the wastewater.

2.1.3 Pollutants and Their Environmental Impacts

Chrome and sulphide are the two major toxic pollutants whlch are common In tannery wastewaters. In addition to this nitrogen, phosphorous, chlorides and suspended solide in organic and Inorganic form are found in abundant concentrations. It is estimated that 30 Z by weight of the green salted hide Is disposed as waste in the form of halr, trimmings, fleshings and shavings together with lime whlch is about 10 % by weight of the green salted hide to the waste stream (Redlich 1953).

1 Chrome

The toxic effect of chromium Is dependent on the type of specles exposed, the temperature and pH of the wastewater and the valence of chromium. Chrome in the hexavalent form
is reported to have a toxic effect on aquatic life, is reported to have a toxic effect on aquatic life, especially on fish food organisms and other lower forms of
aquatic life. It is also known to inhibit the growth of aquatic life. It is also known to inhibit the growth algae.

Trivalent chrome, which is common in tannery discharges Is believed to be less toxic. But the studies made by Ryder (1978) show that concentrations as low as 0.04 mg/l chromium can significantly affect the life of Daphnia which are fish food organisms. In the same study it is reported that a concentration of chromium as high as 0.5 mg/l could be treated with no deleterious effect by algae oxidation ponds.

ii Sulphides

Suiphides are hlghly toxic to aquatic life at bower pH values. By lowering the dissolved oxygen (DO) concentration of the water they can affect all forms of aquatic life. In additlon to this they impart unsightly colour and noxlous odour to the recipient waters (Winters 1984).

Dlscharging a tannery wastewater wlth a suiphide content to a lees alkalIne sewage may result In formation of hydrogen sulphide gas. Hydrogen sulphide is extremely fatal to sewer workers even at a very low concentration. In addition to this hydrogen sulphide gas may, condense with a vapour tnside the sewer and can cause serious deterioration to the fabric of sewers (UNIDO 1975 and EPA 1974).

til Organic loads

The effect of an organic load from tannery wastewater on the reclplent water is the lowering of DO concentration of the water. This In turn will adversely affect the survival of the aquatic life. The degree of the effect is dependent on the dilution capacity of the recelving water.

The joint study report of UNIDO/UNEP (1975) as cited by
Winters (1984) shows that a stream flow of 6 $\frac{m}{N}$ /day per kg Winters (1984) shows that a stream flow of 6 $\frac{1}{9}$ day per kg hide processed supports normal fish life, 4 m³/day per kg hide, processed/day creates localized degradation and 2 m³/day per kg hide processed/day demonstrates that the stream will not be able to support any life since It will be completely devoid of oxygen. DilutIon requirements of tannery wastewaters for protection of various beneficial uses of receiving water are presented in Figure 1.

Dilution requirements of tannery wastewaters for Figure 1. protection of various beneficial uses of receiving water (Winters 1984).

iv Nitrogen and phosphorous

Nitrogen and phosphorous from tannery wastewater may encourage the uncontrolled growth of algae and other plant life that may create eutrophication problem in
receiving waters. The eventual effect of eutrophication the $1s$ total destruction of fish life and general lowering оf \mathbf{a} water quality with respect to aesthetic and recreational use (Arceivala 1981).

critical limits of these nutrients have individual **The** nature for each recipient water. Therefore, each problem should be dealt individually.

Chlorides \mathbf{v}

The toxicity concentration of sodium chloride (common salt) is not well established. But highly saline water is known to cause problems of corrosion, of taste and in the quality of the water necessary for industrial or agricultural use.

Colour $v₁$

Colour is one of the difficult problems caused by tannery effluent since it persists even after treatment. The use of water for domestic and industrial purposes from the downstream side of tannery outfail could hardly fuifii water quality criteria.

vii Bacillus anthraces

Anthrax is primarily a disease of animals, but it can be transmitted to man. The spores of bacillus can survive for
long period of time in the soil or on hides. There is long period of time in the soil or on hides. evidence recorded of anthrax been transmitted to human beings through water courses receiving tannery wastewater discharges (Moore 1961).

2.2 Activated Sludge Process

2 • 2 • ¹ Background

Activated siudge process is a process by which nonsettleable substances are converted into bioiogical fiocs. These newiy formed biological flocs, termed sludge, are removed from the system through solids separation. The biological floce are developed in aeration tanks and settied out in final clarifiers (WPCF 1976).

Activated sludge is a heterogeneous microbiai culture composed mostly of bacteria, protozoa, rotifers and fungi. Removal of most of the organic material is mainly done by the bacteria. The role of protozoas and rotifers In this procese is to remove the dispersed bacteria that otherwise would escape in the effluent (Benefield & Randail 1980).

Activated sludge process takes place in two stages. The removal of organic materials from the wastewater by the siudge floc and the aerobic digestion of the materials so removed by the microorganisms in the fioc.

The sludge floc is formed by mutual coagulation of bacteria with other suspended and colioidai materials. The floc gradually increases to a maximum size. This size depends on the extent of the shear resistance of the floc particle. The floc while moving through the aeration tank picks up suspended and colloidal particias by colliding with them.

The studies made by Pavoni et al (1972) describe the mechanism of biological flocculation as a process which is governed by the physiological state in the micro-organisms and which did not occur until the micro-organisms entered into the substrate depleted or endogenous growth phase. Cells are bridged into three-dimensional matrices as a result of physical and electrostatic bonding of exocellular polymer which accumulates at the cell surface during endogenous growth.

The micro-organisme present in and on the floc in addition to forming the floc, by using the material sorbed to the floc for food and, in the process, reopen new sorptive siteg. This aliows more waste material to be trapped by the floc. Thus, the sorptive sites are continuously regenerated by the organisme living there. This sorptive power of activated sludge is the main cause that makes the sludge activated (Pavoni et al 1972).

The success of activated sludge procees is dependent on the separation of excess biomass, which is created as a result of synthesis during substrate utilization and on maintenance of relatively constant mass of micro-organism in the system by recycling sufficient biomass. Fallure to do this means failure of the process. The flow scheme for a typical activated sludge plant Is presented in Figure 2.

Fiqure 2. Flow diagram of the conventional activated sludge process (WPCF 1976).

2.2.2 System Components

i Aeration Tank

Aeration tank is part of the process unit, where oxygen is introduced into the system to provide the organisme with the necessary oxygen and to keep the activated sludge dispersed in the aeration liquor. The engineering design and placement of the aeration equipment limits the oxygen supply available to the activated sludge system.

The bubbie size, the contact time between the bubbie and the liquid and the turbulence in the liquid, determine the rate of oxygen transfer for a given system. Good transfer efficiencies can be achieved by prolonging the contact time, maintaining bubbie size as small as possible, and controlling the turbulence in which it Is possible to hold the bubble in the liquid as long as possible before reaching the surface (WPCF 1976).

ii Final settling tank

The final settling tank separates the activated sludge from the treated wastewater. The operation of final settling tank will be successful if the removal rate of solide copes with the rate they are applied. Otherwise solide will accumulate in the final settling tank and eventually may spill over the effluent weir. Solids removal by pumping or by gravity may turn out to be difficult and

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the sludge blanket may become anaerobic. The capacity of the settling tank will decrease also due to the accumulation of the solide. 1f storage of the solide is desirable for a particular reason, it is better to keep them in the aeration basin, in which the solids may best be used to maintain or improve high quality treatment (WPCF used to maintain or improve high quality treatment 1976).

2.2.3 Process Modifications

Activated sludge process was developed in 1914. Since then, many modifications have been made to develop more efficient aeration, better contact between the sludge and the pollutants, shorter retention time, lower quantities of waste sludge and lower power requirement (Callely et al 1977). Some examples of these modifications are presented in Figures 3-7.

Figure 3. Activated sludge flow diagrams (Eckenfelder and O'Connor 1961).

Figure 4. Schematic diagram process (WPCF 1976). of contact stabilization

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Figure 5. Schematic diagram of completely mixed activated sludge units (WPCF 1976).

Figure 6. Flow diagram of activated sludge procese (WPCF 1976). Kraus modification of the

Figure 7. Schematic figure of (Stensel and Wright Carrousel aeration tank 1978).

2.2.4 Procees Ilnetice

A) Food to microorganiem ratio (F/M)

The F/M ratio is defined as the substrate load applied to the process per unit of biomass in the aeratlon tank per unit of time. Mathematically F/M ratio can be expressed as:

 F QS_o (1) m xv_a where F $---$ = food to microorganism ratio, d^{-1} M 3 S_0 = influent bob of concentration, g/m V_a = aeration tank volume, m^3 Q = influent wastewater flow rate, m^3/d $x =$ concentration of volatile aeration tank $g/m³$ (Metcalf and Eddy 1979).

In order to understand the role of F/M ratio in activated sludge process a knowledge of microorganisms food utillzation mechanism Is essential.

Bacteria living In activated sludge use the food pacteria iliting in activated siduge use the lood production of energy to support their basic life actlvities, such as movement, production of heat and maintenance of internal and external structures. Second, 1f there is additional food, it allows production of addittonal energy which will be used to produce new cellular material. These processes can occur simultaneously until the organisms reach a certain maximum size if there Is excess food. Then a rapid increase In number by reproductlon happens. This phase Is termed the bog—growth phase. This phase is characterlzed by a high food to mlcroorganism (F/M) ratlo. 1f a system is operating at this phase, since there are not enough bacteria to oxidize the available food, the excess food or waste will be che available loog, the execut loog of wable will be
discharged with the effluent. Also, if a slug of high strength wastewater reaches (shock-load) the plant, there strength wastewater reaches (shock-load) the plant, there
are not sufficient bacteria to sorb and stabilize the organlcs.

As the food is consumed, the number of bacteria will be too much for the available food. Therefore it will take longer to complete reproduction, since the organism use the available food for basic life functions. This slower rate avaiiavie lova for vasie ille funccions, fils slower face
of growth is termed the declining growth phase. Most conventional activated sludge processes are belleved to operate et the end of this phase.

Finally, a stage may be reached where food Is so limited that growth and death reach an equilibrium. At this stage F/M ratio becomes quite low. Organisms fight for survival. They begin to break down the cellular material. This growth phase, during which the bacteria feed on their internal reserves and own body structures, is called endogenous respiratlon. This is the phase of moet complete oxidatlon and effluent Is usually excellent. Extended aeration plants operate in this phase of the food use cycle (WPCF 1977).

Since the activated sludge treatment process is a continuous procesa each plant theoretically operates at one point along the mass time curve. One F/M ratio is maintained for a fixed period of time. But it is impractical to keep the system at single F/M point. The common method In real life is to select a fixed renge of optimum efficiency for each Indlvidual plant. This is done by operating the plant for two to four weeks periods at different activated sludge mixed liquor total suapended solids (MLTSS) concentrations, and establish the range of operating point.

B) Sludge age or mean cell residence time

Average sludge is a measure of the average residence time of the organisme in the system. It can be simply determined by dividing the total amount of solide in the system by the amount leaving the system. In equation form, sludge age would be represented as follows:

$$
0_c = \frac{V_a x + V_c X}{Q_w X_w + Q_e X_e}
$$
 (2)

where

- 0_c = sludge age, days
- v_a = volume or aeration tanks, m 3
- $x = constant relation of, which is generated by the function of $x$$ aeratlon tank, g/m
- $V_c =$ volume of final settling tank, $m³$
- Q_w = waste sludge flow rate, m^3/d
- X_w = concentration of vglatile suspended solids in the waste stream, $g/m³$
- Q_e = flow rate of wastewater leaving plant, m³/d
- X_{α} = concentration of volatile suspended solids in the treated effluent, g/m~

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The showe equation is simplified by acquaing the term Q \bar{Y} ing upove equerion to bimpitited by absuming the term $ve^{\alpha}e^{\alpha}e$ is negligible. This is because the amount of solids in the effluent is small and if the contents of the final settling tank were mixed vigorously, the solId concentration In the settling tank would equal the solid concentration in the aeration tank, x.

$$
Q_C = x \frac{(V_a + V_C)}{Q_w X_w}
$$
 (3)

Further, if the sludge wasting is done from the
tank, **x** could be equal to X_W then the above becomes (WPCF 1976): aeration eciecion
equation

$$
Q_{\rm c} = \frac{V_{\rm a} + V_{\rm c}}{Q_{\rm w}}
$$
 (4)

C) Sludge yield

The quantity of excess sludge that must be wasted on a daily basis can be estimated by the following equation:

$$
P_x = Y_{obs} Q (S_0 - S) x (10^3 g/kg)^{-1}
$$
 (5)

 \sim

where

- $P_{\mathbf{y}}$ — vaste activated sludge produced each day, measured in terms of volatile suspended solids, kg/d
- Y_{obs} = observed yield, g/g
- Q, S_o = influent wastewater flow rate in m
definent ROD or COD concentration is $3/d$ and $\frac{1}{10}$ influent $\frac{1}{200}$ or $\frac{1}{200}$ concentration in α/π^3 . respectively.

The observed yield can be calculated using equation (Metcalf and Eddy 1979):

$$
Y_{obs} = \frac{Y}{1 + k_d(0_c)}
$$
 (6)

in whlch

- Y maximum ratio of the masa of celle formed to the mass of substrate consumed, mass/mass
- k_d = endogenous decay coefficient, time $^{-1}$

D) Sludge volume Index (SVI) and Donaldson Index (SDI)

Sludge volume index (SVI) is an empirical measurement method that can glve an indicatlon of the characterlstics of activated sludge settleability. It is defined as the volume in ml occupied by ¹ g of activated sludge after settllng for 30 min. This test Is routinely used by scitting for 50 min. This test is foutinely used by
traatment plant operators to check the condition of creatment piant operators t
activated sludge (White 1978)

The other most common index used is the Donaldson index (SDI):

MLSS $\frac{2}{3}$ x 100 100 100
------------------ (7) and SVI = ------ $SDI =$ ----------------- (7) and $SVI =$ ------ (8)
 $\frac{7}{2}$ volume occupied SDI % volume occupied by MLSS after 30 minutes settllng

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Interpretation of the index is shown In Table 3.

Table 3. Sludge density index and sludge volume Index (WPCF 1976).

2.2.5 Microbiology of Activated Sludge

Cultivation of a proper microbial population which will remove and assimilate waste material, then agglomerate prior to settling, and will be amenable to concentration and recycle is the main target of activated sludge process operatlon.

Activated sludge is a heterogenous microbial culture composed mostly of bacteria and protozoa sometimes with fungi, rotifers and nematodes.

1 Bacteria

BacterIa are the moet dominant and Important organisme in activated sludge process. By changing soluble BOD Into carbon dioxide and water and cellular mass, flocs, while utilizing the subetrate for their energy requirement, they eliminate pollution and remove non—settleable and colloidal matters. The type of dominant species is influenced by the nature of the organic compounds forming the pollution and by the characteristics of the environment: pH, temperature, dissolved oxygen etc. There are aerobic, anaerobic and facultative types. The majority of the bacteria in activated sludge are facultative, because they can live in either the absence or the presence of molecular oxygen. This is crltical to the survival of activated sludge during periods of low dissolved oxygen concentration. It is belleved that the bulk of the organisme in this system can undergo anaeroblc periode of up to 24 hours without any significant deterioration in viability although solids settleability night suffer (WPCF 1977).

II Fungi

Fungi are multicellular organisms which metabolize soluble organics and which under certain conditions, i.e. a low PH; low oxygen; a deficiency of nitrogen and phosphorus become dominant in the microbial culture. Their presence may not be desirable since some forma of fungi can cause filamentous flocs. These flocs do not settle creating the commonest problem of actlvated sludge, mostly by bacteria, known as bulking. But some studies indicate that these organisme have a higher purlfylng capacity than activated sludge bacteria (Randali et al 1972).

Iii Protozoa

Protozoa play the part of predators on the bacterlal flora. They ere sensitive to variatlons in environmental conditions. For this reason and due to their size (10 to 200 m) they are valuable indicators of the activated sludge condition in an operational sense (WPCF 1977). The majority of the protozoa are strict aerobes and are therefore excellent indicators of an aerobic environment. In addition to this, protozoa are much more sensitive to toxic conditions than are bacteria, and their absence or lack of mobility could indicate that toxicity is a problem.

Figures from 8 through 14 show different specles of protozoa in actlvated sludge.

Aspidisca

This ciliatum can be seen widely distributed in older activated sludges treating effluents of varying origin, moving quite quickly over the surface of the flocs (Degremont 1979).

Flgure 8. Aspidisca lynceus Ehrenberg. A, ventral view; B, diagrammatic cross-section. The right upper arrow indlcates the interior rudiment of the adoral zone (Bick 1972).

Epistylis

An attached ciliatum that forms dense clusters, it is characteristically found in ageing and fairly well oxygenated activated sludge only. It often takes the place of vorticella when the sewage contains a subatantial proportion of various industrial effluents (phenola etc.)

Epistylis sp. Colony of cells. The stalkmuscle is not branched. x 230 (Eikelboom and Van Buijsen 1981). Figure 9.

t

Lionotus

A ciliatum swims and crawis over the surface of flocs. This genus Indicate a fully developed sludge in plante operating under normal loading conditions and dissolved oxygen concentration of greater than ¹ mg/l. It appears just before the attached ciliata.

Figure 10. Lionotus fasciola, right lateral view. Arrows indicate the main features used for identification (Bick 1972).

2.2.6 Operation ManageMent and Procesa Control

The three basic operational requirements to produce an acceptable effluent by activated sludge process are:

- 1) Maintenance of en adequate number of active micro organisms in the system in proportion to the suspended, colloidal, and dissolved organic material in raw wastewater to form final end products of carbondloxide, water, and inert materials.
- 2) Creation of acceptable environment in the aeration tank for the micro-organisms. DO, substrate, and nutrients in the eeration tanks should be sufficient for the required celi growth and energy demand.
- 3) The activated sludge should be separated from the treated wastewater in the final settling tanks.

To fulfil the above mentioned operational requirements, proper food level should be maintained by controlling the amount of biological floc in the aeration tank per kg of BOD load, sufficient DO should be provided to maintain aerobic conditions throughout the aeration tank and
a favourable temperature should be kept for proper a favourable temperature should be kept functioning of the micro—organisme. In addition to this there should be adequate air supply for mixing and for keeping the solide constantly in suspension until they reach the secondary settling tank.

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Better settling may be achieved In the final settling tanks if the arrangement of air supply is designed so that its agitation intensity decreases towards the end of the basin. This helps in reducing floc break-up and encourages the aggregatlon.

Process Control

There are three major process control methods practised in running activated sludge plant. These are (WPCF 1976):

- 1) Control by keeping constant wixed liquor volatlie suspended solide concentratlon (MLVSS) in the aeration tank.
- 2) Control by malntenance of a constant food to micro organism (F/M) ratio.
- 3) Control by maintenance of a constant sludge age. The term sludge age is also referred to as the solide retention time, (SRT) or the mean cell residence time of the activated sludge system.

The first control method, by maintenance of constant MLVSS, Is applicable for systems with stable incoming vaste strength. The limitation in this method is that the importance of F/M ratio Is Ignored. This may lead to process failure in times of high organic overloading which results in high F/M ratio (WPCF 1976).

Control by maintenance of constant F/M ratio would be moet successful if the plant received a waatewater wlth a very predictable variatlons. The MLVSS is adjusted according to incomlng wastewater strength to fali within the optimum F/M ratio range that give the best effluent. This requires a lot of laboratory vork, because It is necessary to know both the amount of food added to, and the mass of organisms in the system. Sometimes the indicative parameters such as BOD, or COD test may be too slow to allow MLVSS adjustment for the sudden varlation in the strength of Incoming vaste. The third method, control by maintenance constant sludge age, is the sImplest system to control. Average sludge age will be simply the total amount of solids in the system divided by the amount leaving the system each day (WPCF 1976).

1f the plant is designed in such a way that wasting of excess sludge is done directly from aeration tanks, a knowledge of only the total combined volume of the aeration tank, the final settling tank and the sludge age required to be maintained, is enough to fix the wasting rate (WPCF 1976).

1f a constant volume of mixed liquor is wasted, as the concentration of the mixed liquor increases, the mass of solids wasted also increases, lowering the MLVSS solide wasted also increases, lowering the MLVSS concentration over a period of time. 1f the MLSS concentration decreases below the level dictated by the selected sludge age, the mass of solids wasted decreases, raising the MLVSS concentration over time. The drawback in this method is the high pumping cost associated with the larger volume of mixed liquor vaste volume than of the return sludge (WPCF 1976).

2.2.7 App].ication of Activated Sludge Procesa **to** Treatment of Tannery Wastewaters

Continuous operations and intermittent discharges in the tannery cause the wastewater to vary in volume and concentration. This nature of the discharge has made blological treatment difficult.

Past studies show the investigations made by different researchers on the possible methods of treatment. For example Eye and Clement (1972) investigated the use of potassium permanganate as a catalyst for oxidation of segregated sulphide-rich tannery wastewater. Also, the use of oxidation ditch (Eggink and Kagei 1971), anaerobic lagoons (McFarlane and Melcer 1978), hydrogen peroxide (O'Neill et al 1978) and RBC and activated carbon treatment method (Rest et al 1982) were investigated on segregated beam house waste. In addition to these, physiochemical treatment by electrocoagulation (Ramirez et al 1977), anaerobic treatment (Baily et al 1983) and flotation system (Roets 1984) have all been studied for the treatment of tannery wastewaters.

Li-Fen Yi and Tian-Min Xie (1987) developed a comprehensive tannery wastewater treatment system based on the recovery of useful materials auch as fatty acids, protein, sulphide and chrome. Activated sludge process in its conventional form and modified version has been also studied and applied in the treatment of tannery discharges by Chakrabarty et al (1967), Kasmiwaya and Yashimoto (1980) and Tomlinson et al (1969). In all reports it is stated that tannery wastewater could be satisfactorily treated by the activated sludge process on the conditions that appropriate loading rates are used. Furthermore, the reports indicate that the tannery wastewater could be successfully treated in combination with municipal wastewater if the ratio of tannery wastewater to total flow does not exceed approximately 25 per cent (Tomlinson et al 1969 and Chakrabarty et al 1967).

As we have observed there are many treatment methods to treat tannery wastewater. But, since each tannery has

individual nature, adaptation of the numerous treatmen methods should be viewed carefully. The type of raw material used, the process and different chemicals employed, the size and location of the industry, the required quality of effluent and disposal method are some
of the factors affecting the selection of treatment of the factors affecting the selection of proceas.

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2.2.8 Shock Loads

Shock loads are loads that can create an abrupt change in the environmental conditions of a treatment proceas. They cause rapid changes in microbial activity and increase the amount of biomass required. Effluent quality deteriorates due to the secondary effecta of the shock loads on the clarifier. A sudden increase in the substrate concentration
is termed as quantitative shock and a sudden change in is termed as quantitative shock and a sudden change nature of substrate Is termed as qualitative shock (Manickam and Gaudy 1978). There are also other types of shocks such as temperature shock and pH shock which are capable of upsetting a treatment system.

In this paper organic shock loads and toxic shock loads are only discussed since they were used in the experiment of this thesis.

Organic shocks are characterized by a rapid increase in microbial growth rate and dissolved oxygen uptaka rate (OUR). Their secondary effects are manifested by:

- 1) A dissolved-oxygen (DO) limitation in the aeration basin which occurs when the OUR of the culture exceeds the oxygen-transfer capabilities of the aeration system.
- 2) Poor solid-liquid separation in the sedimentation basin, resulting from dispersed growth or filamentous bulking. The dispersed growth is caused by growth rate that exceeds the rate of bioflocculation. Filamentous organisme prevent normal floc compression creating settlement problem.
- 3) Clarifier failure caused by excessive growth which results in solids overloading.

Toxic shock loads are characterized by ^a rapid decrease in microbial growth rate, and often in OUR. There are exceptions like sulphides. Sulfide shocks can cause a rapid decrease In microbial growth rate, but due to their high oxygen demarid the OUR will increase instead of decreasing (Gaudy and Engelbrecht).

Many researchers have dealt with the response of activated sludge in different conditions with different types of shock loads. But due to the existence of many possible factors that might affect the response, no one has come up with a clear cut explanation of the mechanisms and factors that govern the response (Komolrit and Gaudy 1966, George and Gaudy 1973, Krishnan and Gaudy 1976, Saleh and Gaudy 1978 and Manickam and Gaudy 1985).

The type of system (batch or continuous) the availability
of adequate nitrogen supply and the type of shock have a adequate nitrogen supply and the type of shock have a significant role on the magnitude of shock bad effect (Komolrit and Gaudy 1966). It is also believed that the sludge age, the biological heterogeneity of the biomass the mean hydraulic retention time and specific growth rate prior to the shock bad play a significant role for the type of response (Krishnan and Gaudy 1976).

Krishnan and Gaudy (1976) came to the conciusion that improvement in the response with regard to amount of subatrate leakage during transient phase at a given shock concentration of substrate, can be achieved by having ^a longer hydraulic retention time. In addition to this, though they are unable to give guidelines regarding limits of shocks, which might be accommodated by activated sludge system, they have an impression that this system can accommodate, with littie or no leakage of substrate, in the transient phase, a 200 per cent increase in concentration of feed.

Manickam and Gaudy (1978) after their study on the combined qualitative and quantitative shock load at constant concentration, conciuded that having higher concentration of cells in the recycle flow to the activated sludge reactor can result in lesser substrate leakage.

A comparison experiment made on different types of shock loads shows that, based on mass leakage rate, a pure hydraulic shock was much more disruptive to effluent quality, both in suspended solids and soluble COD, than was the combined shock and pure quantitative shock at the same mass loading rate (Manickam and Gaudy 1985).

The report made by Thabaraj and Gaudy (1969) states that DO and adequate nitrogen supply may have a role in increasing
the ability of the activated sludge process to accommodate ability of the activated sludge process to accommodate a qualitative Bhock loading.

Biological treatment systems treating wastewaters are always exposed to the danger of being subjected to a quantitative, qualitative, pH or a combination of these shock loads.

The fluctuation in volume and in quality of the wastewater discharge is very high. Unless there is an adequate equalization tank which is capable of dumping these peaks, the frequency of being exposed to shock is inevitable for the treatment system.

As mentioned before the problem is severe in older and/or smaller tanneries, which are common in developing countries. Power failure, machine break-down, interruption of production and ahort working hours are some of the causes that result in additional fluctuation in flow and quality of wastewater discharge.

2.3 **Treatment** of **Tannery** Wastewater by Activated Sludge **Procesa** — **Case History**

The tannery used for this case history study was Vilala Tannery. This tannery is bocated 30 km south of Tampere. It is the largest tannery in Finland. The factory processes 40 000 \mathfrak{g}^2 of hides each day. Its average water consumption $1s$ 50 m³/ton of raw hide. The 200 000 m³ of average annual process water requirement is met by pumping raw water from the adjacent river. Municipal water is used for social activitles inside the factory. A schematic presentation of the water balance is shown in Figure 11.

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Figure 11. Viiala Tannery water balance and sewer lines (Ehder 1987).

The wastewater from this tannery is discharged back to the same river after it is treated by the activated sludge process. The treatment plant consists of course screen, equallzation basin with aeration facllity, aeratlon basin and sedimentation tank. There is also a sludge dewatering unit for further treatment of excess sludge. The arrangement of the treatment plant is shown in Figure 12.

Figure 12. Schematic diagram of Vliala Tannery's activated sludge treatment process (Ehder 1987).

The activated sludge process in this plant has MLSS concentration of $9000 - 11000$ mg/l and hydrauli retention time of one day. The mixed liquor, before it is allowed to settie in the sedimentatlon tank, is mixed wlth cationic polymer solution in order to have larger and stronger flocs which readily settle. Nutrient deficiency is overcome by addition of sodlum hexametaphoaphate into the system.

The procedure followed in the treatment system is simple. The wastewaters from different processes are collected into one large equalization tank after passing through a coarse screen. The equalization tank is useful for neutralizing the extreme pHs of some proceas wastewaters and regulating the flow to the aeration basin. The wastewater Is aerated while it Is in the equalization basin to keep the solide In suspenslon and at the same time oxidize the suiphide. After the equalization basin the waatewater Is pumped Into the aeration where the major biological degradation of the oxidable matter is taking place. Then the liquid is allowed to settle in the sedimentation basin aided by cationic polymer solution.

The clear water from this tank is discharged directly to the river. The sludge is recycled back to the aeration basin, and the excess sludge is pumped to the dewatering unit.

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The Water Pollution Control Federation inspection team's reports made on three different days in 1984, on the quality of the factory's wastewater discharge, show that tannery wastewaters could be satisfactorily treated using
activated sludge process. The results of the treatment
plant influent and effluent samples analysis data are shown in Table 4.

Table 4. Characteristics of influent and effluent during 1.8. - 31.12.1984 at Viiala treatment plant (Ehder 1987).

However, the treatment plant has some problems such as siltation of suspended solids in the equalization basin, excessive scum formation and sudden rising of sludge volumes.

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3 TANNERIES IN ETHIOPIA AND REGULATIONS CONCERNING THEIR WASTEWATER DISPOSAL

3.1 Status of Ethiopian Tanneries and Their EnvironRental Inpact

Ethiopla is among the large producers of hides and skins in Africa. Due to the few numbers of leather industries available in the country, moet of the production is exported unprocessed. But, there exists a large potential for future expanslon of leather Industry in order to exploit this abundant resource.

At this moment there are only eight tannerles throughout the country. These are located as follows:

² in Asmara

3 in Addis Abeba

- 2 around Addis Abeba within 90 km radius
- ¹ in Comboicha

Their total annual production amounts USD 46.000.000 (July 1986 — June 1987) (NLSC 1987).

According to a survey made in 1974 all new tanneries and some of the older ones have reasonable effluent treatment facilities. But all tanneries in Asmara and some old tanneries in Addis Ababa discharge their wastewater to the recelving river directly without any treatment (UNIDO 1975).

The situation is now even worse. Most of the biological treatment plants are not functioning well. The rate of flow of the receiving rivers is lower than it used to be in many places. This is due to the increasing consumption of the waters upstream of the tanneries, and the general drought situation. Less flow rate means lower capacity of dilution. Thus the impact of environmental pollution from industrial discharges in general and tannery discharges in particular is becoming more and more pronounced.

There is no available data that shows the proportion of pollutlon contribution to these receiving waters from the tannery discharges. There exists a pollution contribution from other industries, municipal discharges and human and animal excreta along the bank of the rivers. But, due to its strength and potentional to increase, the ecological impact from the tannery is moet feared. Table 5 shows the laboratory analysls report of the year 1980 on the characteristica of tannery discharges from different tanneries In Ethiopia. The characteristics are simllar to typical "non—environmentally sound" tannery effluent shown in Table 6.

Table 5. National Leather and Shoe Corporation laboratory analysis of composite wastewater samples $(NLSC 1987)$.

Note this analysis was done in 1980 by Sancon Engineering

Table 6. Composition of typical "non-environmentally sound" tannery effluent (UNIDO 1975).

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A laboratory test was carried out in the Water and
Environmental Laboratory of the Tampere University of rechnology on grab samples brought from different process
sections in Awash Tannery. The results of this test are presented in Table 7. As can be seen from these results, if a discharge from one of the strongest processes reaches the
treatment plant without being diluted or equalized, there will be manifold quantitative shock loads in the system.

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Parameters/ Process	SS	VSS $g/1$ $g/1$	COD $mg/1$ mg/l	Cr^-	S^2 - Total SO_4 $mg/1$ mg/1
Pickling			0.67 0.36 5 400 0.19		7 300
Liming - hide – skin			39.75 21.80 123.000 20.40 15.75 80.900		1 530
Soak			0.72 0.43 3 700 < 0.03		170
Batting 0.79 0.69 15 800					29
Chrome Tanning - hide - skin			4.05 1.75 18 000 3 700 2.10 1.15 16 700	2 700	
Deliming			9 400	0.82	3 100

Table 7. Test result of wastewater characteristics from different processes of Awash Tannery.

3 • **2 Regulation** Concerning Industrial Wastewater **Disposal**

Industrial wastewaters are an avoidable by-product of moet industrial processes. They are becoming increasingly complex and a threat to the environment as chemical technology develops with the invention of new chemicals. Many governments have already set rules and regulations,
through their responsible authorities, on limits of their responsible authorities, on limits of hazardous wastewaters disposal. One of the few disposal alternatives available is to discharge them into municipal sewerage system for combined treatment. But industrial discharges to municipal facilities are routinely identified as the source of significant environmental problems. One of the most notorious discharges comes from tanneries.

The three common problems that might be encountered from industrial discharges in general and tannery wastewaters in particular are as followa:

- Inhibition or interference with normal plant operation due to slug discharges and high concentrations of certain pollutante. This generally results In inadequate treatment of normal domestic wastewater and industrial wastewaters.
- Some pollutant might "pass through" untreated in quantities and concentrations that are harmful to the environment.
- Sludge from the treatment plant might be contaminated and might turn out to be unacceptable for direct disposal and thus increase the cost of sludge disposal (Wright et al 1978).

Due to the above mentioned reasons it is appropriate to have a pretreatment standard regulation in order to protect the municipal treatment plants and thus the environment.

The reguletion should neither be too stringent so as to discourage development of Lndustrles, nor too lenient, on the pretext of encouraging industrial development.

Currently there is no clear idea of the best option to handle sludge which is contaminated with toxic pollutants. Some believe that the burden of toxic sludges should not be placed on municipalities contending that toxics should be handled at their source, with emphasis on recycling and recovery techniques. While others believe that since, municipal treatment plants are more experienced at sludge management than industries, sludges are more appropriately handled at a central (municipal plant) location (Wright et al 1978).

In Ethlopia there are only provlsional effluent standarde proposed by a committee for liquid wastes, eet under the Ethiopian Standards Institute in 1974. The standards proposed are shown In Table 8.

Table 8. Provisional effluent standards (UNIDO 1975).

The idee of pretreatment standard can not be applied because there are no municipal treatmept plants. Currently the city of Addis Ababa Is provided with a conventional sewerage system and a treatment plant with oxidation pond system. The sewer pipe passes abong many of the Industries and especially all tanneries in Addis Ababa. This will
attract many of the industries to connect their discharges attract many of the industries to connect their discharges to the system. This in turn might create a big dilemma from the Sewerage Authority side whether to accept the connection or not.

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The cause of this possible dilemma could be

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- 1) There are no prepared guidelines that limit the volume and concentration of pollutants which could be concentration of pollutants which acceptable for the new sewer system and treatment plant.
- 2) The Authority is unlikely to get sufficient statistical data concerning the amount of flow and physical and chemical characteristics of wastewater from each characteristics of wastewater from industry.
- 3) The capacity and efficiency of the new treatment plant is not yet established.
- 4) The river that is receiving untreated industrial discharges is also being heavily polluted by human and animal excreta along the bank of the river.

All the above mentioned conditions will deprive of any substantial reference to base the most reasonable limits because the limits should be acceptable and economically achievable to both parties for the existing local to both parties for the existing local condition.

Therefore, a study system must be developed to idetermine two conditions. The first is to establish the capacity of the receiving waters to dilute the load to be discharged in concentration and volume/time. The second is the limits of pollutants to be discharged in concentration and pollutants to be discharged in concentration and
volume/time. Based on these studies a control of
incompatible pollutants can be-developed by establishing incompatible pollutants can be developed by the maximum mass emission rates (kg/day) permit for each discharge. According to Dietz and Dietz (1978) thts kind of method will encourage conservation of water as well as allow for the management of the mass of incompatible pollutanta entering a treatment system.

4 EXPKRIMENTAL SET-UP AND SANPLING

4.1 Equipment

Reactors

Three reactore made up of transparent plexy-glaas were used for the bench-scale activated sludge process study. All reactors had equal capacity and dimensions. Each reactor had an aeration chamber and a clarifier chamber which were separated by a baffle wall. The net useful volumes of the separated by a baffle wall. The net useful volumes of aeration chamber and the clarifier chamber were ⁶ litres and 2.5 litres, respectively. For identification purposes each reactor was given number name 00, 77 and 88. Reactors 00 and 88 were the units which ware used for chrome tanning process waste shock and liming process waste shock studies, respectively. On the other hand, reactor 77 was used as a control unit by keeping a steady feed condition throughout the experiment. An illustration of the type of reactors used and details of dimensions are shown in Figure 13.

Legend **¹ PnfIu.nt storage** container **2 Fe.d pump 3 A.rator**

4 Aeration basin 5 Clarifier

6 Efftuent overftow

7 EffIuent cotiection container

Aerators

Each reactor was provided with one bubble aerator device
which was made up of polvacryl glass having nine, 1 mm which was made up of polyacryl glass having nine, 1 nozzles. During the experiment when the dissolved oxygen concentration in unit 88 dropped, one additional, fine bubbie stone aerator was provided to this unit.

Pumps

At the beginning of the experiment two peristaltic pumpa, which could be set to discharge at a definite rate were
used. This arrangement was supposed to use one pump for This arrangement was supposed to use one pump contlnuous and steady sludge wasting from the aeration basin, and the other pump for feeding the raw wastewater. But due to the required very low flow, clogging of suction and delivery tubes makes wasting mixed liquor from aeration pump using this pump impractical. Therefore one pump was used throughout the experiment as a feed pump. Usage of these kind of pumps requires very close attention.

Refrigerators

Two small fridges ware used for storing feed containers and effluent collection containers. Due to shortage of space other raw waste containers and samples were stored in large fridgea. 100 ml samples from each kind of test made, were also stored in a deep—freezer in case a re-testing of a certain sample arises. The whole aim of storing in these fridges was to prevent significant biological action between the sampling and testing time.

4.2 Wastewater Collection and Sampling

All wastewaters used throughout this experiment were brought from Viiala Tannery. 60 to 80 litres of wastewater were transported by using 10 litres plastic containers twice a week.

The composite tannery wastewaters which were used for the steady feed condition ware taken from the tannery's wastewater equalization baain outflow. Other wastewaters which were used for administration of shock loads were taken directly from the chrome tanning vat and the liming vat.

At the beginning of the experiment influent samples ware taken just before the containers ware put into the feed system. But later, samples ware taken from the mouth of the feed tube by increasing the pump discharge rate. Effluent samples were taken from the collection containers before they ware emptied. Samples for the determination of mixedliquor suspended solide (MLSS) and mixed-liquor volatile suspended solide (MLVSS) wera directly taken from the aeration chamber before sludge wastage was done. 30 minutes settlement tests for sludge volume index (SVI) determination were done using the sludge to be wasted. Samples for sulphide test ware preserved by adding ¹ ml of Zn (CH₃COO)₂ and 1 ml of NaOR solution to a 100 ml of sample.

4.3 Experiinental Procedure

The three reactors were operated on a continuous flow basis starting from October l9th up to December 2Oth in 1987. The process was started in all reactors at the same time using the tannery wastewater acclimated mixed-liquor from Viiala activated sludge procesa. This was done to avold the period required to acclimate municipal activated sludge mixed lIquor to tannery wastewater.

A composite wastewater from Viiala wastewater equalization tank was fed continuously at ⁵ ml/min rate to each unit. Air was supplied by regulating the pressure high enough for mixing, but not too high to create turbulence in the clarifier. The concentration of dissolved oxygen (DO) was The concentration of dissolved oxygen (DO) was checked from time to time using YSI oxygen meter in order to take action 1f the DO level drops below 2 mg/l.

When the first arrangement of pumping sludge to be wasted directly from the aeration tank failed due to clogging problem, a manual wasting method was adopted. This was done by gently transferring the contents in the aeration and the clarifier basin to a wide mouthed container and mixing it by stirring until the solids content was homogenized. Then one litre of sludge was wasted. To keep the level of liquid In the reactor at the same level as before, one litre of tap water was added. The liquid was put back into the reactor and re-started with low pressure air supply. Starting with low pressure was required due to the foaming problem each time the operation was interrupted and restarted. Sludge wastage was done every two days. This gave a constant sludge age of 17 days (i.e. volume of liquid in the reactor divided by volume of sludge wasted per day).

The effluent from each reactor was continuously collected by gravity into three separate containers which ware placed inside the refrigerator.

Due to the shortage of space inside the small refrigerator, there was a need to replace the empty feed containers by full ones twice a day. Each time a new container was placed a sample was taken for analysls. The aame appiled to effluent collection. After sampling and volume measurement the contante of the effluent collection container were dumped into the building's drainage system, and collection was re-started.

Visual examination, DO measurement, pH measurement, ³⁰ minute settlement test and microscopic examination were used to follow the performance of the system.

When a nearly steady-condition was verified the first shock loads ware applied to units 00 and 88. This was done by changing the composite wastewater feed to chrome tanning procesa wastewater for unit "YROO" and liming process wastewater for unit "YR88". The periods of shock loads appilcation were one hour for unit 00 and 44 hours for unit 88. The volumes that reached the reactors were 150 ml of chrome exhaust wastewater and 8.5 1 of liming process wastewater, respectively. Both type of wastewater used for

shock bad application were brought from Awash Tannery (Ethiopia) process wastewater. Then the second shock load application was done using segregated chrome tanning and liming process wastes from Viiala. The composite wastewater feed was replaced for 44 hours by chrome tanning process wastewater and liming procese wastewater for reactor "YROO" and reactor "YR88", respectively. The pump discharge was adjusted to 1.5 nl/min rate for all reactors. But no change in the type of feed was made for reactor "YR77". Then, feeding of the composite wastewater was resumed.

While running the system, laboratory tests of COD, TOC, BOD, SS, VSS and OUR were carried out in parallel. Samples for chrome and suiphide tests ware sent to the laboratory of Kokemaenjoki Water Pollution Control Federation.

4.4 Analysis

The collected samples were analysed to determine the different parameters described below.

- COD HACH Company
Chemical oxygen demand test procedure oxidation with dichromate method was used.
- SS and VSS Method for analysis of suspended solids and volatile susperided solide is as deecribed in the Finnish Standard SF8 3037. The method involves vacuum filtration of samples using GF/A (10 um) glass microfiber filters.
- BOD7 Method used to measure BOD is as described in the Finnish Standard SFS 3019. The method involves incubation of the wastewater samples with sewage seeded and inhibitory reagent containing dilution water, and measurement of
initial and seven-day dissolved oxygen initial and saven-day dissolved oxygeni concentration. The type of reagents used were
** PO = FeCT = 6H.O = MgSO = 7H.O + (NH) KH_2PO_4 , FeCl_3 . OH_2O , MG_4 . H_2O + (NH_4) ;
SO . CaCl and O 1 MoNaOH . 1 ml/l was adoc SO_4 , CaCl₂ and 0.1 MgNaOH. 1 ml/1 was added from each type to the dilution water.
- TOC Total organic carbon was measured using carbon analyser.
- Chromium Trivalent chrome analysis was performed in accordance with methode described in Standard Methode... (1980) Sta VH73 and AA475.
- SulphIde Sulphide analysis was also performed in accordance with Standard Methods... (1980) Sta
427D **427D.**

The OUR test could not be carried out due to the high
sulphide content of the wastewater which results in sulphide content of the wastewater which results misleading data.

5 RESULTS AND DISCUSSION

5.1 Reactor "TR77"

Reactor YR77 was used as a control unit by keeping a steady feed of composite tannery wastewater. The maximum and minimum characteristics of the influent, effluent and mixed liquor are shown in Table 9.

Tabla 9. Maximum and minimum values of experimental results of reactor "YR77".

5.1.1 Suspended Solide (83) and **Volatile** Suspended **Solide (VSS)**

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All experimental resuits on 11.11.1987 of SS and VSS samples were omitted while plotting the results (Figures 14 and 15). This is because on the 11.11.1987 a change in the influent sampling point from the feed container to the mouth of discharging tube was made, and at the same time the pump discharga was increased for the sample collection period. This resulted in washing of solids accumulated on the inner wall of the delivery tube, thus giving the inner wall of the delivery tube, thus giving misleading information on the nature of the wastewater.

Figure 14. Suspended Solide (SS) concentration of reactor "YR77" 'S Influent and effluent samples.

Figure 15. Volatile Suspended Solids (VSS) concentration of reactor "YR77" 's influent and effluen samples.

The reduction in SS and VSS in this reactor was found to be satisfactory. As the sludge age was increased with the progress of the experiment a general improvement in SS and VSS reduction was observad.

5.1.2 Mixed Liquor Suspended **Solide** (MLSS) and Mixed Liquor **Volati].e** Suapended **Solide (MLVSS)**

The experiment was started using already acclimated
tannery waste sludge from Viiala Tannery wastewater from Viiala Tannery wastewater treatment plant. The plant usually keeps its mixed liquor
concentration within 9,000 mg/l to 11,000 mg/l range. The concentration within 9000 mg/l to 11 000 mg/l range. attempt to keep the mixed liquor density within a specified range in the reactor has failed due to practical problems. This was because the thick mixed liquor required high pressure for complete mixing. The high pressure caused turbulance and foaming which in turn causad the liquid to spill in significant amount. Therefore a range between
3 000 mg/l to 4 000 mg/l was selected to avoid the 3 000 $mg/1$ to 4 000 $mg/1$ was selected practical problems encountered in this particular condition (Figures 16 and 17). The sharp drops in MLSS and MLVSS concentration shown on these figures are caused by a clogging problem (which happened a few hours before the sampling of mixed liquor on 3.11.1987) on the aerator tube. The mixed liquor solide settied at the bottom of the reactor and the thin mixed liquor layer separated in the upper part of the reactor.

Figure 16. Mixed Liquor Suspended Solide (MLSS) concentration curve of reactor "YR77".

Figure 17. Mixed Liquor Volatile Suapended Solide (MLVSS) concantration of reactor "YR77".

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5.1.3 Food **to** Microorganisa Ratio **(P/M)**

The F/M ratio calculation for this reactor was made by an indirect way, using the volume of the effluent collected per time to determine the amount of inflow that reached the reactor.

But this flow rate does not include some of the liquid losses, such as evaporation losses and spills when such as evaporation losses and spills excesaive foaming was occuring. The fluctuation in the flow rate may have an adverse effect on the combination resuits of the changes in F/M ratio. Figure 19 shows the variation of the F/M ratio during the experiment period.

Figure 19. Food to microorganisms ratio (BOD load/MLVSS) of reactor "YR77".

5.1.4 Biochemical Oxygen Demand (BOD₇)

The average seven day BOD of the influent wastewater was within 2 300 mg/l and 2 500 mg/l. The effluent BOD was
observed to reduce below 100 mg/l as the sludge age was to reduce below 100 mg/1 as the sludge age was (Figure 20). This test is too slow to any increased (Figure 20). This test is too slow to adjustment that might be required in case of sudden change either in the influent or effluent characteristics. This is because It requires ⁷ days to get the test resuits of the samples taken at any time.

Figure 20. Biochemical Oxygen Demand (BOD₇) concentration
of reactor "YR77" 's influent and effluent "YR77" 's influent and effluent samples.

⁵ • **¹** • **⁵** Cheaical Oxygen Deinand (COD) and Total **Organic** Carbon (TOC)

The result of COD and TOC of the influent and effluent
samples are plotted in Figure 21 and 22 respectively. The samples are plotted in Figure 21 and 22 respectively. The
influent COD, ranges, between 3,400 - 6,000 mg/l, with an influent COD ranges between 3 400 - 6 000 mg/l with an arithmetic average of ⁴ 470 mg/l. The effluent COD was between 470 - ¹ 600 mg/l with an arithmetic avarage of 820 mg/l. On the other hand, the range of the TOC concentration of the influent was between $620 - 1300$ mg/l and the effluent $130 - 530$ mg/l.

(COD) curve of influen Figure 21. Chemical Oxygen Demand (COD) curve of influe
and effluent samples from reactor "YR77".

Figure 22. Total Organic Carbon (TOC) curve of influent and effluent samples from reactor "YR77". samples from

The performance of the reactor can be best seen from the COD removal efficiency curve (Figure 23).

Figure 23. COD removal efficiency curve of reactor "YR77".

As could be seen from Figure 23, except at the beginning and towards the end of the experiment, more than 80 % removal efficiency was attained. The cause of the low efficiency at the beginning of the experiment was the high pressure air supply which caused some of the solide to leak with the effluent. But towards the end of the experiment the sudden decline in efficlency was caused by the pump break down on the 7. and 8.12.1987, and the consecutive drainage problem that resulted in solide wash-out when the effluent was suddenly released.

5.2 Reactor "YROO"

This reactor was used for the study of the effects of toxic shock bad from the chrome tanning procese on the activated sludge process. The maximum and minimum of the influent, effluent and mixed liquor characteristics are tabulated in Table 10.

Table 10. Maximum and minimum of experimental resulte of reactor "YROO".

5.2.1 Suspended **Solide (85) and Volatile** Suspended Solide (VSS)

The experimental results on 11.11.1987 of SS and VSS were
omitted while plotting Figures 24 and 25 due to the same omitted while plotting Figures 24 and 25 due to the reason mentioned in section 5.1.1.

The sudden increase in SS and VSS concentration in the effluent does not significantly affect the effluent quality with respect to SS and VSS concentration. But towards the end of the experiment a deterioration of the effluent guality was observed.

Figure 25. Volatile Suspenaea boilde (VSS) concentration of influent and effluent samples from reactor "YROO"

5.2.2 Mixed Liquor Suapended Solide (MLSS) and **Mixed Liquor Volatile** Suepended **Solide (MLVSS)**

The MLSS and MLVSS concentrations were intentionally lowered to avoid the practical problems mentioned in section 5.1.2. It was very difficult to keep the concentration within a specified range (Figures ²⁶ and 27). This was because of the unpredictable Infiow concentration and the sludge wasting procedure used.

Figure 26. Mixed Liquor Suspended Solids (MLSS) concentration curve of reactor "YROO".

Figure 27. Mixed Liquor Volatile Suspended Solide (MLVSS) concentration curve of reactor "YROO".

5.2.3 **Total Chro.e Concentration**

Chrome tanning process wastewater was used as shock load
due to its high toxic concentration. The shock load due to its high toxic concentration. The shock appilcation on this reactor was supposed to be done twice. The first shock bad appilcation could not be performed because of the mechanical pump failure. Although the
characteristics of this wastewater appeared in every characteristics of this wastewater appeared in parameter, it could not have a significant effect because of the negligible volume of the wastewater that reached the system. But the second wastewater which was brought from Viiala Tannery chrome tanning vat, was succesfully applied. The total chromme concentrations in reactor "YROO" influent end effluent samples are shown on Figure 28.

Figure 28. Curve showing Total Chrome concentration in influent and effluent samples from reactor "YROO".

Chrome tests made on mixed llquor samples of this unit, taken on 27.11.1987 and 4.12.1987 show a concentration of 640 mg/1 and 170 mg/1 respectively. This means that most of the chrome was retained in the mixed liquor and was gradually wasted wlth the waste sludge.

5.2.4 Checical Oxygen Demand (COD)

The average COD concentration of the influent sample ranges between $\bar{4}$ 000 - 4 500 mg/1, the highest concentration obeerved was ⁷ 000 mg/l in the first shock bad appilcation (Figure 29). But this wastewater did not reach the system

sudden increase in the effluent COD concentration could not be seen from Figure 29 because the influent COD just before due to concentration failure. The reason for the the daterioration of the effluent quality was low.

The performance of this reactor is best seen in the efficiency curve of COD removal (Figure 30). After the efficiency curve of COD removal (Figure 30). mechanical problems at the beginning of the experiment were solved, this unit attained an average of 85 % COD removal efficiency. But on the transient state of shock bad the efficiency sharply dropped. After the composite waatewater feed was resumed the proceas showed recovery. This took a littie more than a week.

Figure 30. Curve showing the COD removal efficiency from reactor **"YROO".**

5.2.5 Total Organic Carbon (TOC)

The Total Organic Carbon (TOC) concentrations of influent and effluent samples are shown in Figure 31. response of the system to the shock bad is shown by sudden rise of TOC concentration in the effluent sample. the The the

Figure 31. Total Organic Carbon (TOC) concentration of
influent and effluent samples of reactor "YROO".

5.2.6 Biocheaical Oxygen Deaand (BOD7)

The Biochemical Oxygen Demand (BOD₇) concentration curve of this reactor does not show the performance of this reactor. This is because important records are missing from the curve due to laboratory test failures of critical samples curve due to laboratory test failures of critical samples taken in transient shock bad period. Figura 32 shows the partial performance of reactor "YROO".

Figure 32. Curve showing Biochemical Oxygen Demand (BOD₇) of influent and effluent samples from reactor "YROO"

5.2.7 Microecopic Examination

Microscopic examination showed that the media that was becoming predominated by epistylis species just a few days before the shock bad application was lacking any kind of higher order organisme. As the higher order organisme are known to be sensitive to a toxic environment, the observation confirmed the toxicity of the applied wastewater.

5.3 Reactor "YR88"

Reactor "YR88" was used to study the effect of combined pH and organic shock bad on the activated sludge proceas. One of the leather manufacturing process wastewaters which has a high pH and organic concentration is liming process
wastewater. Therefore, a segregated liming process a segregated wastewater was applied as a shock bad.

This wastewater has a very high sulphide content. The high sulphide content made the dissolved oxygen up-take rate test uselese in showing the microbial growth condition. The reason for this is that the suiphide exhibits and chemical oxygen demand though the microbial growth is suffering rapid decrease.

The maximum values of experimental resulta are tabulated in Table 11.

Table 11. Maximum and minimum of experimental results of reactor "YR88".

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5.3.1 Suspended Solide (85) and **Volatile** Suspended **Solide** (VSS)

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The experimental results on the 11.11.1987 of the SS and
VSS were omitted while plotting Figures 33 and 34 due to VSS were omitted while plotting Figures 33 and 34 the same reason mentioned in section 5.1.1.

Figure 33. Curve showing concentration of Suspended Solids (SS) of influent and effluent samples from reactor "YR88".

Figure 34. Curve showing concentration of Volatile Suspended Solids (VSS) of influent and effluent samples from reactor "YR88".

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Prior to shock load application there was a satisfactory
reduction in SS and VSS concentration in this reactor. But reduction in SS and VSS concentration in this reactor. But
the system responded with a sharp increase in SS and VSS the system responded with a sharp increase in SS and concentration in the effluent sample for each shock bad applied. The system showed a fast recovery after the composite wastewater feeding was resumed.

5.3.2 Mixed Liquor Suepended Solid (MLSS) and Mixed **Liquor Volatile** Suepended **Solide** (MLVSS)

The attempt to keep a certain constant MLSS and MLVSS concentration in this reactor has failed due to fluctuation of f10w and solid concentration of the incoming wastewater.

The flow problem was created because of the pump failures and the cloggings of the supply tube. The test results of min the energy and the engage of the energy and the extended in Figure 35.

The infiow rates determined from the collected effluent quantity are shown In Figure 36. The high fluctuation In flow might have its own shock effect on the system 1f the combined effect with the content of flow create a high fluctuation in F/M ratio.

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Figure 36. Curve showing the inflow eate of raw wastewater to reactor "YR88" based **on** measured volume of collected effluent.

5.3.3 Sulphide (S^2) and Total Chrome (Cr)

The chrome test resuits tend to suggest that there is a reasonable reduction of these pollutants. But most of the reasonable reduction of these pollutants. But most of the
chrome is retained in the mixed liquor and wasted with the chrome is retained in the mixed liquor and wasted with the sludge. Therefore Figure 37 tells little about what is
happening to the total chrome.

Figure 37. Curve showing total chrome contente of Infinent Curve showing total chrome conter
and effluent from reactor "YR88"

When the change of composite tannery wastewater feed to liming process wastewater was done, the sulphide (S^2^-) liming process wastewater was done, the sulphide content of the Influent was extremely high. But the effect on the effluent quallty could not be seen since all the suiphide was oxidised **by** the excess air suppiled for mixing suiphide was oxidised by the excess air supplied for mixing
purpose. Figure 38 shows the sulphide content of the purpose. Figure 38 shows the sulphid
influent and effluent of reactor "YPR8".

Figure 38. Curve showing sulphide (S^2^-) concentration of
influent and effluent samples of reactor "YR88".

5.3.4 Biochemical Oxygen Demand (BOD 7)

After a steady composite tannery wastewater feeding the
cudden chances in the BOD of the influent shoulthe sheek sudden changes in the BOD₇ of the influent show the shock
load (Figure 39), But due to the laboratery test, fotlunes load (Figure 39). But due to the laboratory test failures
in chosing the right dilution, the BOD₇ of the effluent in chosing the right dilution, the BOD₇ of the samples in the transient period of the shock load could not be recorded. Therefore Figure ³⁹ does not show the response of the system to the applied shock load.

Figure 39. Curve showing Biochemical Oxygen Demand (BOD7) of Influent and effluent samples from reactor "YR88".

5.3.5 Total Organic Carbon (TOC)

Records of laboratory test resuits of TOC concentration of effluent samples collected from reactor "TR88" are presented in Figure 40. The sudden rise in TOC concentration of the effluent towards the end of the experiment is due to the disruption of the system by the applied toxic chock load.

Figure 40. Curve showing Total Organic Carbon (TOC) concentration of Influent and effluent samples from reactor "YR88".

5.3.6 Chealcal **Oxygen Decand (COD)**

The Chemical Oxygen Demand (COD) test in this experiment was the best result to show the performance of this reactor under the steady load and the shock load applications.

The system was performing very well until the first shock load was applied. The first shock load created a complete disruption of the system. When the system was seen to recover, the normal composite wastewater feeding was resumed. The second shock load was applied after the system was believed to be in stable condition. The effect was the same but not as strong as in the first case (Figure 41).

Figure 41. Curve showing Chemical Oxygen Demand (COD) of influent and effluent samples from reactor "YR88".

The COD removal efficiency curve gives a better idea of the performance of this reactor. Over 70 % removal efficienc was attained when composite wastewater was fed. The ups and downs in the efficiency curve (Figure 42) are due to the shock load and recovery conditions of the system.

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Figure 42. Curve showing reactor "YR88". the COD removal efficiency of

5.3.7 Reaulte of microscopic examination

microscopic examination made before the shock load
bolication showed that the number of higher order application showed that the number of higher order
organisms was constantly increasing. These organisms organisms was constantly increasing. These disappeared in the transient phase of the first shock. The
increase in pH and the decrease in Dissolved Oxygen (DO) Increase in pH and the decrease In Dissolved Oxygen (DO) $concentration$ of the mixed liquor might have created unfavourable environment for these organisme. But when the system was recovering ^a gradual increase In number of the higher order organisme was observed. The condition In the transient state of the second shock load was different. Besides the lack of higher order organisms, the microbial solide are a dispersed type instead of being the usual flocculated microbial solide.

5.3.8 Test resulta of 30 minutes settiement

The resuits of the 30 minutes settlement test gave a very different clue to what was happening in the system when the shock load was applied. According to this test observation, the effect of the second shock seemed to be worse than the first shock load. This was manifested in the unique mode of settiement observed whlle carrying out the 30 minute settlement test. The solids were observed settling abruptly within the first few minutes of the time the liquid was allowed to stand. Furthermore, the solide are not the usual type of floc seen in the previous tests of the sludge from this reactor. They are like mineral, forming a dense sediment at the bottom of the test cylinder.

5.4 Operational Problems Encountered

There have been some operational problems encountered which inight have a significant influence **on** the experimental results. Ainong these pumping, excess sludge removal, foaming and scum formatlon are discussed more detailed.

5.4.1 Pumping

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Maintaining a continuous flow at a certain desired constant
discharge grate was the most important part of the discharge rate was the most important part of operation. However, because of mechanical pump failures and
tube clogging. interruptions of flow were common. The tube clogging, Interruptions of flow were common. The clogging problem could have been minimized if containers were provided wlth a mixing device.

Since the F/M ratio is directly related to the amount of flow, the fluctuation in flow combined with the high fluctuation In substrate concentration might cause an unintentional shock to the system.

5.4.2 Excesa sludge removal

The manual sludge removal adopted in this particular experiment had the following drawbacks:

- a) Each time the reactor was dismantied and re—agsembied the system suffered from disturbance.
- b) Since the air pressure was adjusted by trial and error It was difficult to keep the dissolved oxygen level within the required optimum range.

5.4.3 Foaming

Foaming was a problem which was moet of the time associated with the high air pressure suppiled. Especlally after the manual sludge removal operation. When the system was restarted the sudden change from the qulet condition to a turbulence resulted foaming. The problem was overcome by using an anti—foam agent.

Sometimes excesslve foaming caused spillage of the reactor content and coated the upper part of the reactor with scum. This could significantly affect the solids balance calculatlon and derivation of the volume of wastewater that reached the reactor from the effluent collected.

5.4.4 Scum foraation

There were two occaslons where a sudden scum formation was observed. In both cases the scum blocked the reactor's drainage system. The cause of these scum formations might be the large proportion of the fat-liquoring process wastewater in those particular composite wastewaters whlch were fed to the system.

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6 CONCLUSIONS AND RECOMMENDATIONS

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Based on the results of the study, the following conclusions may be drawn:

- 1. Activated sludge treatment process may be suitable for pretreatment of tannery wastewaters in order to discharge It to municipal sewerage system. In excess of 80 % COD removal were routinely obtained under pseudo-
steady conditions in all reactors. In addition the steady conditions in all reactors. In addition chrome and sulphide content of the effluent was **80** bow that it can be discharged to municipal wastewater treatment systems.
- 2. 1f unequalized chrome tanning proceas wastewater or liming procees wastewater reach the activated sludge process, It can Induce toxic or organic shock bad combined wIth pH shock. This will result in upset of the procese rendering the effluent not acceptable for discharge into municipal treatment plants. Therefore, an activated sludge plant which is treating tannery wastewater should be provided wlth an equalization basin.
- 3. Activated eludge process may recover from disruption of the process caused by short-term shock loads within a few weeks 1f the normal operation and steady feed is resumed.
- 4. Disposal method of excess activated sludge contaminated wlth chrome, should be chosen in such a way that the method does not allow chrome accumulation that may have an adverse effect on the transferred environment such as surface water, groundwater and agricultural land.

Recommendations:

- 1. Since this experiment was carried out for only two montha period further study for bonger periode, i.e. ⁶ monthe to ¹ year, Is recommended.
- 2. It **¹⁸** recommended to investigate the possible means of speeding-up the recovery of activated sludge process after upset caused by shock loads.
- 3. It is also recommended to study the cause of sudden scum formation in activated sludge process plant treating tannery wastewaters.

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APPENDIX ¹ REACTOR "fl77" INFLUEKT DATA

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APPENDIX 2 REACTOR "YR77" EFFLUENT DATA

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APPENDIX 9 REACTOR "YR88" MIXED—LIQUOR DATA

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