CHAPTER 1

INTRODUCTION

Pollution from tanneries has a negative long-term impact on the environmental resources, although tanning of animal hides to convert them into leather is an important industrial activity. Liquid waste from tanneries is a dangerous pollutant because it contains organic matter and inorganic pollutants in the solution, suspension and colloidal dispersion. Various workers have done research on the characteristics and treatment of wastewater from vegetable and chrome tanning. Chromium used in the tanning stage is a controversial chemical on account of the persistence and potential toxicity of some of its chemical forms. Depending on its chemical state, it has various levels of impact on humans, aquatic life and terrestrial plants, with some ability to move between media. Chromium is known to be highly toxic to the living aquatic organisms in the hexavalent state and somewhat less toxic in the trivalent form. Hexavalent chromium is carcinogenic, even with a little quantity, 10 mg/L can cause nausea and vomiting. Skin irritation and problems related to respiratory track can cause lung carcinoma due to chromium toxicity. Thus chromium and other toxic substances must be removed from tannery effluent before it is released to render them harmless.

Basically two methods are employed for the recovery of chromium from liquid tannery waste.

(a) By purifying exhausted chrome liquor and reuse as pickling float for further tanning.
(b) By precipitation of chromium from waste chrome liquor.
During chrome tanning, two-thirds of the total base chrome offered was consumed at the end of the tannage and the spent tan liquor discharged after the tannage contained 27% of the chrome and 6% is drained away. Therefore, it was concluded that the spent tan liquors are the largest contributors of chromium in effluents. The easiest possible method to reduce the concentration of chromium (III) in liquors discharged in waste is to combine and mix all the process waste streams.

1.1 TREATMENT PROCESSES

Treatment of tannery effluents involves primary, secondary and tertiary treatments. The primary treatment includes screening (to remove hair, fleshings, fats etc.) and sedimentation. It is reported that about 90% removal of suspended solids is effected in sedimentation tanks. The sludge is dried over sand drying beds and utilized as a manure. Chemical coagulation (using Alum/ferric chloride) and biological treatment are the effective secondary treatment methods. Activated sludge process with acclimatized organisms yield effluents of better quality. Prior removal of chromium is an essential step when the chrome tanning waste is subjected to activated sludge process. 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.

1.2 IMPORTANCE OF PHYSICAL - CHEMICAL PROCESS

There are certain situations where biological methods of waste water treatment are not well suited. These waste contain predominantly inorganic or biodegradable compounds in nature. Treatment of these wastes requires a process that is capable of intermittent operation and starting and stopping on a demand basis and one that is unaffected by inorganic or toxic waste. It is in situations such as these that physical - chemical treatment
1.2.1 Theory of Chemical Precipitation

The equation and stages involved in the recovery of chromium from waste chrome tan liquor are given below.

(i) Precipitation of chromium hydroxide with lime

\[ \text{Cr}_2(\text{SO}_4)_3 + 3 \text{CaO} + 3\text{H}_2\text{O} \rightarrow \text{Cr(OH)}_3 \text{ Sludge} \]

(ii) Separation of precipitated Cr(OH)_3 sludge by settling.

(iii) Concentration of settled sludge through slow sand filtration.

(iv) Recovery of chrome liquor from the concentrated Cr(OH)_3 sludge by redissolving it with conc. H_2SO_4.

\[ 2 \text{Cr(OH)}_3 + 3 \text{H}_2\text{SO}_4 \rightarrow 2 \text{Cr(OH)}_4 \text{SO}_4 + \text{Na}_2\text{SO}_4 + \text{CO}_2 \]

Recovery of chromium from spent chrome tan liquor by chemical precipitation has been reported (Arumugam 1976). It was given that chemical precipitation with lime was efficient in obtaining 98% removal of chromium at an optimum pH of 6.6. A study on the treatment of chrome tanning liquor by chemical precipitation has been conducted (Tomlinson et al 1969) using lime and reported that the maximum removal of chromium from the spent chrome liquor was attained at a pH of 11.5. It was reported that after 4 hours of sedimentation, the supernatant had a total chrome content of 25 mg/L and a COD of about 3000 mg/L.

Studies carried out on chemical treatment of tannery effluent showed that when the different waste fractions are mixed in certain ratios and settled and the supernatant treated with 400 mg/L of alum and further settled for 3 to 5 hours, an overall reduction of 57% in BOD could be obtained (Bose et al 1960). Experiments were conducted on chrome recovery consisting of chemical coagulation and adsorption or activated carbon seems to have greatest potential.
from leather tanning wastewater by raising the pH to 8.7 - 9.0 with 30% NaOH, flocculating with a polymer, and precipitating chromium hydroxide (Daigle et al. 1986). The effluent total chromium was seldom > 0.5 ppm. The recovered Cr(OH)₃ was dewatered by filter press and acidulated and reused.

Studies were conducted on the treatment of tanning wastewater (MaO et al. 1987). Heavily loaded tannery wastewaters are treated separately by physico chemical methods including catalytic oxidation of S²⁻ with MnSO₄, chromium precipitation and decolourization using Fe(II), to obtain maximum reduction of pollutants. Studies on intensification of the recovery of chromium compounds from spent chrome tanning solutions were carried out (Khavroshin et al. 1988). A chromium containing precipitate was obtained from spent tanning solution by using a 10% Na₂CO₃ solution as the precipitating agent followed by dewatering of the precipitate on a filter press. It was reported that less dewatering results were obtained when NH₃ and Ca(OH)₂ solutions were used as the precipitating agents.

Removal of chromium and sulphide from tannery effluents and the chromium removal efficiency of conventional chrome precipitating agents such as MgO and lime were carried out and compared with that of Magadi soda (Mbuthia et al. 1989). It was observed that maximum removal of 99% Cr was possible in the pH range 9.3 to 9.7. Studies on chromium recovery methods were conducted (Kannan and Vijayaraghavan 1992). It was reported that chemical precipitation with lime results in 87% removal of chromium at pH 9.6 with a dose of 8g lime/litre. Experiment has been conducted on recovery of chromium (Hikmet Toprak 1994) and reported that by the incineration method, chromium is recovered from chromium tanned leather wastewater treatment plant sludges as hexavalent form which is directly used in tanning.

Experiment conducted on the chemical precipitation (Archana Shukla and Shukla 1994) revealed that on an average of 4.7% reduction/°C
rise of the temperature was observed in the case of lime whereas only 4% reduction °C was observed in NaOH and the mixture. Properties of chromium sludge from chrome tan wastewater was studied (Pathe et al 1995) and it was reported that the sludge volume increased with increased lime dose upto 3500 mg/L. Adsorption of chromium (III) on a smectite from a tanning wastewater was studied (Volzone and Tavani 1996). They have reported that maximum adsorptions of chromium (III) and sodium were 0.81 and 0.30 mmole/g of smectite respectively.

1.3 OBJECTIVES OF BIOLOGICAL TREATMENT

After preliminary and physical - chemical treatment, the liquid effluent is not yet to be assimilated by the environment, mainly because of dissolved organic matter. Design, operation and efficiency of the biological step which follows will depend on the quality of former treatments. The objectives of the biological treatment of effluent are to coagulate and remove the non-settleable colloidal solids and to stabilize the organic matter. For domestic wastewater the major objective is to reduce the organic content and in many cases, the nutrients such as nitrogen and phosphorus. In many locations, the removal of trace organic compounds that may be toxic is also an important treatment objective. For agricultural return wastewater, the objective is to remove the nutrients, specifically nitrogen and phosphorus, that are capable of stimulating the growth of aquatic plants. For industrial wastewater, the objective is to remove or reduce the concentration of organic and inorganic compounds.

1.3.1 Theory of Bio-chemical Processes

Anaerobic digestion is one of the oldest processes used for the stabilization of sludge. It involves the decomposition of organic and inorganic matter in the absence of molecular oxygen. The major applications
have been, in the stabilization of concentrated sludge produced from the treatment of wastewater and in the treatment of some industrial wastes.

In the anaerobic digestion process, the organic material in mixtures of primary settled and biological sludge is converted biologically under anaerobic conditions, to a variety of end products, including methane and CO₂. The process is carried out in an air tight reactor. Sludge, introduced continuously or intermittently is retained in the reactor for varying periods of time. The stabilized sludge, withdrawn continuously or intermittently from the reactor, is reduced in organic and pathogen content and is nonputrescible.

1.3.2 Mechanism of Biological Reactions

The biological conversion of the organic matter treatment plant sludge is thought to occur in three steps. The first step in the process involves the enzyme mediated transformation (hydrolysis) of higher molecular mass compounds into compounds suitable for use as a source of energy and cell carbon. The second step (acidogenesis) involves the bacterial conversion of the compounds resulting from the first step into identifiable lower molecular mass intermediate compounds. The third step (methanogenesis) involves the bacterial conversion of the intermediate compounds into simpler end products, principally methane and carbon dioxide.

In a digester, a consortium of anaerobic organisms work together to bring about the conversion of organic sludge and wastes. One group of organisms is responsible for hydrolysing organic polymers and lipids to basic structural building blocks such as monosaccharides, amino acids and related compounds. A second group of anaerobic bacteria ferments the breakdown products to simple organic acids, the most common of which in an anaerobic digester is acetic acid. This group of microorganisms, described as
nonmethanogenic, consists of facultative and obligate anaerobic bacteria. Among the nonmethanogenic bacteria that have been isolated from anaerobic digester are clostridium spp., peptococcus anaerobes, lactobacillus, Actinomyces, staphylococcus etc.

A third group of microorganisms convert the hydrogen and acetic acid formed by the acid formers to CH₄ gas and CO₂. The bacteria responsible for this conversion are strictly anaerobic and are called methanogenic. The most important bacteria of the methanogenic group are the ones that utilize hydrogen and acetic acid. They have very slow growth rates, as a result and their metabolism is usually considered rate limiting. Methane gas is highly insoluble and its departure from solution represents actual waste stabilization.

1.3.3 Aerobic Digestion Process

The aerobic digestion of biological sludge is nothing more than a continuation of the activated sludge process. When a culture of aerobic heterotrophs is placed in an environment containing a source of organic material, the microorganism will remove and utilize most of this material. A fraction of the organic material removed will be utilized in the synthesis function, resulting in an increase in biomass. The remaining material will be channelled into energy metabolism and oxidized into CO₂, water and soluble inert material to provide energy for both synthesis and maintenance (life support) functions. Once the external source of organic material has been exhausted, however, the microorganism will enter into endogeneous respiration where cellular material is oxidized to satisfy the energy of maintenance. If this condition is continued over an extended period of time, the total quantity of biomass will be considerably reduced, and furthermore, that portion remaining will exist at such a low energy state that it can be considered biologically stable and suitable for disposal in the environment.
When mixtures of primary and activated sludge are digested aerobically, an additional factor has to be considered. Primary sludge, although organic and particulate in nature, contain little biomass. Most of the material represents an external food source for the active biomass contained in the biological sludge, which therefore will reduce the amount of cellular material required for energy of maintenance. Hence, longer retention times are required to achieve equivalent stabilization when primary and activated sludge mixtures are digested rather than when activated sludge is digested alone. Aerobic digestion of trickling filter humus constitutes a condition intermediate to these two extremes but can be reasonably approximated by the activated sludge reactions (Randall et al 1974). Aerobic digestion is a viable alternative to anaerobic digestion for sludge stabilization.

1.4 BIO-KINETICS AND ITS IMPORTANCE

The design of any biological wastewater treatment system must depend on the proper relationships between the organic matter in the wastes and the microorganisms which can metabolise the organic matter, the generation time of the microorganisms, the temperature of the treatment system, pH, the nutrient elements in the waste, the wastewater retention period in the system and other environmental factors. Bio-kinetics are based on the actual environment and the biological metabolic activities in the system. Hence, the design of biological wastewater treatment based on biokinetics will have a better control over environment and biological community in the system. For a specific waste, a biological community and proper set of environmental conditions, the biokinetic coefficients are fixed. Hence design of biological treatment system based on the bio-kinetic parameters will be more rational than designs based on thumb rules.
1.4.1 Relevance of the Present Study

Several quantitative mathematical models have been developed over the period to describe the kinetics of tannery waste treatment processes. However, successful application of these models to design is contingent on the use of a number of kinetic parameters which in turn depend on the nature of the wastewater. The values of biokinetic parameters for tannery wastewaters are not available for the biological treatment systems under Indian conditions. Hence there is a need to evaluate these parameters for aerobic and anaerobic systems. To accomplish this objective, experiments were conducted using chrome tanning wastewaters and distillery wastewater.

1.4.2 Microbial Growth Kinetics

Models derived from growth kinetics are based on concepts from microbial continuous culture theory that was developed by Monod (1949). The model developed is based on the relationship between the growth rate of microorganisms and the substrate concentration. There are two approaches that have been used to model the activated sludge process. Lawrence & McCarty (1970) based their model on the continuous model of Monod which predicts that the microbial logarithmic growth rate is continuous function of substrate concentration. Eckenfelder (1966) has based his design procedure on the discontinuous model. The two approaches have been extensively applied in developing design procedures. Each of these models is discussed in detail below.

The equations developed by Lawrence and McCarty (1970) are based on the acceptance of two basic equations. The first equation is a rearrangement of the Monod equation that relates the rate of substrate utilization to the concentration of microorganism in the reactor and to the substrate surrounding the microorganism. The equation has the form
Where ‘k’ is the substrate utilization coefficient 
Ks is the half-velocity constant and 
Se is the effluent substrate concentration.

The second basic equation describes the relationship between net growth rate of microorganism and rate of substrate utilization.

\[
\frac{dX}{dt} = \frac{ds}{dt} - Y \frac{dX}{dt} - Kd X \\
\]

where 
Y = Yield coefficient
Kd = Endogeneous decay coefficient and 
X = Microorganism concentration

While developing the equations, Lawrence and McCarty emphasise an operational parameters called sludge age or biological solids retention time which is defined as

\[
\theta_c = \frac{\text{Total active microbial mass in treatment system}}{\text{Total quantity of active microbial mass withdrawn daily}}
\]

Lawrence and McCarty developed an expression for Se and VX using the definition of \( \theta_c \) and equations (1) and (2) as follows.

\[
Se = \frac{Ks (1 + Kd \theta_c)}{\theta_c (Y - Kd)^{-1}}
\]

\( \text{...}(3) \)
\[ VX = \frac{Y \theta_c (S_0 - S_e)}{1 + K_d \theta_c} \]  

where \( \theta_c \) is the mean cell residence time and \( V \) is the volume of the reactor.

### 1.4.3 Substrate Removal Kinetics

Under certain conditions, substrate removal in suspended growth system can be approximated as follows. The substrate removal is directly proportional to the rate at which new cells are produced.

\[
\frac{dS}{dt} = \mu_{\text{max}} \left( \frac{S_e}{K_s + S_e} \right) X
\]

or

\[
\frac{dS}{dt} = \frac{\mu_{\text{max}}}{Y} \left[ \frac{S_e}{K_s + S_e} \right] X
\]  

...(5)

Two boundary conditions may now be considered.

Case (i) when \( S_e > > K_s \), equation (5) simplified to

\[
\frac{dS}{dt} = \frac{\mu_{\text{max}}}{Y} X
\]  

...(6)

or

\[
\frac{dS}{dt} = k \ X
\]

Where \( k = \frac{\mu_{\text{max}}}{Y} \) = maximum substrate utilization rate per unit time per unit mass of microorganisms (time\(^{-1}\)). This signifies that the substrate concentration is so high that it does not affect the removal rate, which depends only on the concentration of microorganisms \( X \). Thus, the substrate removal is zero order with respect to substrate concentration, but first order with respect to organism concentration.
Case (ii) where \( \text{Se} \ll \text{Ks} \), equation (5) simplifies to

\[
\frac{ds}{dt} = \frac{\mu_{\text{max}}}{Y \text{Ks}} \text{Se} \text{X}
\]

or

\[
\frac{ds}{dt} = K' \text{Se} \text{X}
\]

Many wastewaters including domestic sewage often fall in this category as treatment requirements indicate that final effluent BOD concentration to be kept at a minimum. Thus when completely mixed reactors are used, their concentrations are the same as that required in the effluent. These concentrations may be lower than the Ks values and hence their removal kinetics may fall in this category. Under such conditions, \( K' \) values are readily determined from graphical plots of \( (\text{So} - \text{Se})/\text{Xt} \) against \( \text{Se} \) which tend to give straight line whose slope equals \( K' \).

The advantage in using this approximation is that only one parameter, \( K' \), is required for design purposes, whereas in the Monod's case, three constants, \( K_s, K_d \) and \( \mu_{\text{max}} \) are required to be known.

EcKenfelder (1976) has shown that actual substrate removal data give a better fit when the initial substrate concentration is also taken into account by plotting \( \text{So} \left[ (\text{So} - \text{Se})/\text{Xt} \right] \) against \( \text{Se} \). The slope of the line gives the value of the treatability rate \( K'' \) per unit time where

\[
K'' = K' \text{So}
\]

The use of the rate constant \( K'' \) implies that, at a constant organic loading, the effluent sludge BOD is directly proportional to the influent BOD in the plant.
1.4.4 Overall Substrate Removal Rates

The $K$ values are given as per unit time per unit solids and therefore, in their use the designer has to decide first what the microbial solid concentration $X$ in mg/l will be in the reactor as a result of recycling. Thus $K_s$, the overall substrate removal rate per unit time at the solid concentration prevailing in the reactor is

$$K_s = K X$$

and from equation (6)

$$\frac{ds}{dt} = K_s S_e$$

Which indicates that substrate removal is first order with respect to the substrate concentration in the reactor. Consequently, the substrate removal efficiency for completely mixed reactors can be estimated from the equation.

$$S_e = \frac{S_0}{1 + K_s t}$$

Experiments were conducted on the performance of activated sludge process in tannery waste treatment (Thabaraj 1962). It was found that an aerated solids concentration of 3000 - 4000 mg/L the BOD of the presettled and diluted vegetable tannery waste could be reduced from 988 mg/L to 34 mg/L with 24 hr aeration. Treatment of 30% settled tannery waste and 70% sanitary sewage by activated sludge process was studied (Chakrabarthy et al 1965) using an influent having a BOD ranging from 1000 - 14000 mg/L and about 90% BOD removal was obtained. Good
biological purification in an activated sludge system was attained by diluting tannery effluent with domestic sewage (Kubelka 1957).

Studies were conducted on anaerobic digestion of spent vegetable tan liquor with a view to reduce bulk of the BOD from total tannery waste by more economical method (Chakraborthy and Trivedi 1965), but the result indicated that although about 95% BOD removal could be obtained, a high detention period was necessary to achieve this purification. Experiments on the oxygen activated sludge system treating tannery effluent were conducted (Mamoru Kashiwaya 1980). The use of aeration to remove sulphide from limeyard wastes was studied (Bailey et al 1967). The results of the experiment conducted on the activated sludge system to reduce the organic nitrogen and sulphide components along with BOD, COD and suspended solids from lime sulphide unhairing effluents have been reported (Cooper et al 1976). The suitability of activated sludge process for treating combined sewage and tannery wastes from tanneries were studied (Rajamani and Madhavan Krishna 1983).

Studies on the treatment of chrome tannery effluent containing COD 7300 - 9600, BOD 2800 - 3600 mg/L was conducted (Rak et al 1975). The effluent was led through a sedimentation tank where the BOD was reduced to 1100 - 1300 mg/L. Then the wastewater was mixed with activated sludge and aerated to obtain the decrease in COD and BOD to 1000 - 1400 and 240 - 530 mg/L respectively.

Anaerobic stabilization of sludge from treatment of tannery wastewater was reported (Svancer and Jan 1982) and it was given that anaerobic predigestion of raw active sludge improved the aerobic tannery waste treatment and gave a steady flow of gas containing ~ 75% CH$_4$. Studies on the treatment of tannery beamhouse waste with a bench scale anaerobic reactor was conducted (Tunick et al 1981). It was said that
wastewater with 2000 - 15000 mg/L COD is treated in an anaerobic reactor for 4 months to give a COD removal of about 60%.

Pretreated tannery beamhouse wastewaters were treated with an anaerobic process to routinely remove 60% of applied total COD with hydraulic retention time of 1 day (Friedman 1982). Rotating biological contractor and activated carbon treatment of tannery wastewater was studied (Rest et al 1982) where RBC removed 96% BOD and 75% COD. Experiments were conducted on the combined anaerobic fermentation biochemical aeration for treatment of tanning wastewater (Zhu et al 1983) which removed COD, S² and suspended solids 94, 95 and 85% respectively. Anaerobic treatment of tannery wastewater was conducted (Bailey 1983) followed by aerobic polishing removed 60% of total COD with 60 hour hydraulic detention times.

The anaerobic treatment of tannery wastewater was studied (Yong and Huang 1987) and observed that COD removals of 60-70% were obtained with initial COD levels of 8450-8600 mg/L and the treatment followed a first order reaction kinetics. The experimental treatment of chemically treated tanning wastewaters by 2 - stage activated sludge process was carriedout (Dembinska 1990) which gave BOD removals of 95.5% for chrome tanning effluents and 90% for mixed vegetable - chrome tanning wastewaters. Tannery wastewater was treated using upflow anaerobic fixed film, fixed bed reactors with detention times of 0.5 to 10 days, flows of 1.70 - 34 L/day and influent COD of 1000 - 8000 mg/L at pH 6.2 - 7.9 (Sihorwala 1991).

The excess of activated sludge obtained after biological treatment of mixed sewage, 90% effluent from chrome and vegetable tanning with 10% domestic sewage was studied (Gorecki 1976) for its efficiency for agricultural and fertilizer value.
Experiments were conducted on a laboratory scale completely mixed continuous flow activated sludge system to treat settled chrome tannery wastewater (Guruswamy et al. 1992) and observed that the BOD and COD removal ranged from 84 to 96%. Studies were also carried out on activated sludge treatment of vegetable tannery waste (Elangovan et al. 1994). It was found that the BOD and COD removal ranged from 85 to 95% and evaluation of kinetic constants have been done. The activated sludge treatment of vegetable tanning waste admixed with 10, 25 and 50% settled sanitary sewage was carried out (Elangovan et al. 1995) and found that the BOD removal ranged from 87 to 96%. It was also observed that the treatability rate increased from 7.36 to 8.92/day for vegetable tanning waste as the percentage of sewage mix increased from 10 to 50%.

Rational design and cost analysis for conventional and extended aeration activated sludge process for tannery waste was studied (Elangovan et al. 1996) and the cost curves were generated for settled chrome tanning waste, settled vegetable tanning waste, chrome tanning waste admixed with 10, 25 and 50% sewage and anaerobically treated chrome and vegetable tanning wastes. Analysis of cost benefit for tannery effluent treatment for biogas recovery was made (Szpyrkowicz 1996) and proved that the biogas production be utilized for converting waste into a resource and simultaneously abating the pollution problems in the environment. Studies on the ozonation of biologically pretreated tanning wastewater and the influence of the applied specific ozone consumption onto a subsequent biological treatment were conducted (Jochimsen et al. 1997) and the combining sum parameters such as COD, UV absorbance, mineralization and partial oxidation effects could be differentiated. Characterization and pretreatment of tannery wastewater was carried out (Parwana et al. 1997) and observed that pollutants like suspended solids, BOD, COD, chromium and sulphide was 33.3, 31.6, 20.6, 69.1 and 80% respectively.
1.5 GENERAL CHARACTERISTICS OF DISTILLERY EFFLUENTS

Bio-ethanol is mainly produced by the fermentation of distilled sugarcane molasses solution. After fermentation, alcohol is separated by distillation and the residual liquor is discharged as distillery spent wash or effluent. The effluents as such discharged from the plant is hot (about 60 to 70°C), highly coloured (dark brown), acidic and possess and objectionable odour. The BOD value is extremely high. Likewise the values of suspended solids, dissolved solids, chlorides, sulphates and nitrogen are also too high. The potassium content of the effluent is used for irrigation.

Though distillery effluents do not contain any toxic substances, it creates toxic conditions in the receiving stream by immediate depletion of dissolved oxygen resulting in massive fish kills, destruction of flora and fauna, production of foul odours, and discoloration of streams. Most of the distilleries stagnate their effluents on lands as ponds. This type of stagnation is not a good practice as there are chances for seepage and subsequent ground water pollution. Further, the obnoxious odour spreads to a few kilometers and it is a serious public health problem.

1.5.1 Treatment Processes

Treatment of distillery waste could be made economical if recovery of potash and vitamin B₁₂ are made. As the BOD of the distillery effluent is abnormally high, they are subjected to anaerobic digestion or anaerobic lagooning followed by aerobic biological processes. Anaerobic digestion is reported to reduce the BOD of raw wastes by about 90%. Methane is recovered as a by product during digestion.

When land is available, anaerobic lagooning is the cheapest and effective method. The major disadvantage is the production of foul odours
due to the evolution of volatile gases. The production of odours can be limited by establishing proper anaerobic activity in the lagoon. Effluents from anaerobic treatment still contain high BOD and cannot be discharged as such into water courses and hence further oxidized either by trickling filter or by activated sludge or in aerated lagoon or in oxidation ditches.

In the case of aerated lagoons, the detention period is longer, and about 90% BOD removal is achieved. Even then, the effluent from the aerated lagoons requires further treatment in a polishing lagoon with a detention period of about one day.

Studies on the pilot plant for treatment of cane-sugar waste was carried out (Bhaskaran and Chakrabarty 1966) using anaerobic digestion followed by stabilization in an aerobic oxidation pond with overall removal efficiency of 90%. Anaerobic digestion of cane sugar wastes was conducted (Sinha and Thakur 1967) and observed that removal of BOD varied from 88.8 to 95.8% and also the BOD of the effluent increased with the BOD of the influent when the digester load was increased. Experiment was conducted on a low cost waste treatment method for the disposal of distillery spent wash (Subba Rao 1972). It was reported that the effluent with BOD 2500-3000 mg/L was reduced up to 600 mg/L at an optimum BOD loading of 0.070 kg BOD/m$^3$/d.

High rate digestion of distillery effluent at 37°C on a laboratory scale was studied (Sen and Bhaskaran 1961) and reported a BOD removal efficiency of 80-85% at a maximum BOD possible loading of 3.0 kg/m$^3$/d. The use of diluted distillery spent wash in anaerobic digestion was studied (De et al 1969) and concluded that 1:3 dilution was optimum to obtain 89% BOD removal efficiency at a detention time of 5 days using a loading of 1.90 kg BOD/m$^3$/day. Studies have been carried out on the importance of mean cell residence time (Sherrard 1972) and it has been shown that the magnitude
of the difference between influent and effluent substrate concentration is nearly constant over the range of actual operating conditions.

Studies on the characteristics of distillery wastewater have been studied (Basu 1975) and it has been shown that the beet sugar molasses distillery waste was highly charged with organic matter. Experiment was conducted on autothermal aerobic digestion (Matsch et al 1977) and found that increase in temperature increases the rate of digestion and thus a decrease in the retention time required to achieve a stable sludge. Utilization, treatment and disposal of distillery wastewater was studied (Sheehan and Greenfield 1980) and it was observed that anaerobic treatment has been shown to be satisfactory in many cases at loadings of around 4 kg BOD m⁻³ day⁻¹.

Experiments were carried out on the anaerobic stabilization of distillery waste from cane sugar industry (Parthasarathy et al 1967) which have shown that an optimum BOD loading of 0.688 lb/cft/day for 12 days detention time to give BOD reduction of about 90%. A laboratory unit of biological disc had been set up to investigate its performance during digestion of wastes (Khan and Siddiqui 1972). The compact unit provides for anaerobic decomposition of non-settleable and dissolved fraction by a microbial slime growing on the rotating discs. The treatment of an undiluted beet molasses alcohol/yeast plant waste was reported (Londong 1969). Raw waste of 2375 - 8979 mg/L BOD was subjected to batch activated sludge treatment at loading of 0.97 - 6.21 kg BOD/m³/d and respective removals of BOD was about 82%.

Activated sludge treatment of a relatively high strength waste was also reported but with less success (Burnett 1973) and it was observed that with a 25% mixture of rum distillery waste in domestic sewage, only 1.3% reduction in COD was achieved in 37 days. Studies on cane sugar wastes and their disposal have been conducted (Chakrabarty 1964) and it has been
found that stabilization of the waste in anaerobic and aerobic ponds were most effective and economical. Treatment of sugar wastewater on high rate trickling filter was carried out (Shukla et al 1962) and from the experiment it was reported that reduction of 70% in the pollution of the waste was obtained, which increased to 92 - 95% after stabilization in a tank for 72 hour.

Activated sludge plant for treating wastewaters from a sugar factory was described (Chekurda 1962) and it was given that a total BOD reduction after treatment of the effluent was reported to be 68%. Studies on the effect of residues from distilleries on the wastewater treatment process have been conducted (Grau 1982) and it was reported that the treatment with a pre-clarification reduced BOD load by 50% using domestic sewage. Experiment on high-rate digestion of liquid wastes from molasses distillery was carried out (Sen 1961) and the treatment by anaerobic digestion in mesophilic temperature achieved BOD reduction about 96% in 40 days.

A study was conducted on treating wastewater of primary wine making plants (Gumbatova 1986) and it was found that the treatment efficiency could be increased by subjecting the effluent to coagulation before 2 - stage biological treatment in an aeration tank mixer at loads of 0.9 - 1 and 0.35 - 0.4 g BOD/g sludge. Studies on the treatment of wastewater, from sugar mills and distilleries were carried out (Iza 1987) and observed that the total COD removal efficiency was 94%. Study on a modified rotating biological contactor was conducted (Radwan and Ramanujam 1985) for the treatability of sugar cane wastewater and observed a COD removal of about 90%. Treatment of distillery waste by upflow anaerobic filter has been studied (Gadre et al 1986) and found that the COD removal was 77%.

Anaerobic treatment of distillery spent wash by advanced immobilized cell reactors was studied (Tapan Routh et al 1986) and it was found that the method is more efficient at much lower retention periods
followed by two phase anaerobic treatment with UASB showed COD removal of 60-67%. Studies with two anaerobic filters operated in series for primary treatment of distillery wastewaters have been carried out (Badrinath and Kaul 1984) at organic loads varying from 2 to 90 kg COD/m³/day corresponding to detention times of 0.26 to 11.8 day. The treatment of molasses fermentation wastewater in anaerobic filters at loadings rates varying from 2 to 12 kg COD/m³/day corresponding to detention times of 2.5 to 5.0 day has been studied (Corromdo et al. 1983) and about 57 - 79% COD reduction was achieved.

Studies on two stage upflow anaerobic filter for the treatment of partially treated distillery wastewater have been conducted (Subramanyam and Sastry 1989) and reported that by anaerobic lagooning, it showed COD removals varying from 93.0 to 71.5% at COD loadings varying from 8.33 to 50.0 kg COD/m³/day. Report is available on sugar refinery wastewater treatment in acidification lagoon, a UASB reactor, an aeration basin and a decantation basin (Garcia et al. 1987) and they have found that about 95% BOD removal could be achieved. The treatment of sucrose wastewater at high organic loading rates in anaerobic down flow stationary fixed film reactors (Van den Berg et al 1985) has produced higher treatment efficiency than upflow anaerobic blanket filter.

Experiment was conducted on anaerobic digestion of sugar mill wastewater in an UASB reactor operating at an organic loading rate of 13 kg COD/m³/d (Manjunath et al. 1988) resulting in 90% COD reduction. Studies on the treatment of sugar mill wastewater using anaerobic filter was carried out (Lolla et al. 1990) and reported that at a COD loading rate of 1.8 kg COD/m³/d, the treated effluent contained only 70 mg/L BOD. The treatment of distillery effluent by anaerobic and aerobic fermentation was studied (Ramendra and Maneesh Awasthi 1992) and reported a BOD removal of about 85% and 50 - 60% of biomethane recovery.
Applicability of upflow anaerobic sludge blanket reactor for treatment of distillery spent wash has been studied (Jayantha and Ramanujam 1995) and found that higher purification effects have been achieved at shorter residence time and the biogas recovery was 65-68%. Studies on the treatability of predigested distillery wastewater diluted with domestic sewage have been carried out (Vijayakumar et al 1995) and found that the BOD removal efficiency increased with increase in dilution and so treatability is improved by increasing the percentage of sewage.

Studies on the treatment of predigested distillery wastewater and evaluation of bio-kinetic coefficients in an activated sludge process have been conducted (Vaidyanathan et al 1995) and reported a maximum BOD removal efficiency of 85-90%. Anaerobic rotating biological drum contractor for the treatment of sugar mill effluents was reported (Hung et al 1983) and found that more than 80% COD stabilization was achieved. A two phase anaerobic digestion of sugar mill effluent was successfully carried out (Lettinga et al 1984) with 95% conversion efficiency of fatty acids into methane. Studies on the treatment of sugar effluents by UASB reactor was conducted (Pathe et al 1995) and reported that more than 90% COD removals were observed at the lower loadings upto 13 kg COD/m$^3$/day.

A study on the two stage anaerobic digester to treat distillery waste has been made (Gokuldas et al 1995) and it was observed that the overall BOD removal efficiency was 92.85% and COD removal was 81.73%. The feasibility of thermophilic anaerobic treatment of an alcohol distillery wastewater was studied (Harada 1996) using UASB reactor and the COD removals were relatively low about 39-67% while BOD removals were more than 80%. Studies on the anaerobic - aerobic treatment plants in fermentation industry producing bakers yeast from sugar beet molasses were conducted (Ciftci et al 1996) and observed that an average COD removal was 75% in the mesophilic anaerobic stage with a daily biogas production rates as high as 20,000 m$^3$/day. The effect of trace metals on the
anaerobic degradation of volatile fatty acids in molasses stillage was studied (Espinosa 1995) and observed that addition of trace metals to the influent significantly reduced the level of fatty acids and increased the COD removal efficiency from 44-58%. Experiment was conducted on the pollution profile of alcohol distilleries treating beet sugar molasses (Eremektar 1995) and observed that using an open steam and recycle of spent wash, COD load was practically unchanged with recycle while TDS increased significantly.

The effects of redox potential in a thermophilic laboratory scale two stage anaerobic digester to treat distillery wastewater have been studied (Phae et al 1996) and observed that about 90% COD removal was achieved with a gas production of 0.4 L/g COD. Studies on the kinetics of the anaerobic digestion of sugar mill mud waste were carried out (Sanchez 1996) and observed that the specific rate constant values obtained decreased from 1.76 to 0.05 L/d when the load of SMMW applied was increased from 40 to 140 ml. Treatment of distillery effluent using artemia has been studied (Abdul Rahaman et al 1992) and found that it reduced 69% of the total solids and 33.34% of BOD in the saline medium of 60 ppt. The treatment and disposal of industrial wastewaters were described (Glancy and Vincent 1997) including anaerobic treatment, effluent characterization, sampling and analysis of effluents and costs as well as treatment selection criteria. The performance of a 29 UASB reactor was studied using a high strength synthetic waste (Rao et al 1997) where the maximum organic loading rate achieved was 47 kg COD/m³/day at the lowest hydraulic retention period of 4.9 hour. Apparent and intrinsic kinetic parameters of substrate decomposition were estimated (Zaiat et al 1997) from the profiles of COD and VFA concentrations along the length of the horizontal flow anaerobic immobilized sludge reactor.

A comprehensive review of the methods for handling tannery and distillery wastewater showed that the wastewaters from such plants are generally high in both dissolved organic and inorganic materials, posing
particular treatment difficulties. Although a number of treatment procedures are being used or have been proposed, there is no widespread agreement on the most suitable methods. These discrepancies reflect in part the wide variations in the characteristics of tannery and distillery effluents and intern these are the result of different raw materials, agricultural practices and wastewaters operating techniques. In many studies to date detailed analyses of the effluents are not provided and this imposes limits on the relevance of the results to a particular situation. When the opportunity cost of land is low, direct irrigation often proves most cost effective. Also conventional design of the biological treatment systems treating tannery and distillery effluents gives little consideration to the biochemical reactions occurring in the treatment process.

1.6 SCOPE OF THE PRESENT WORK

Although adequate modern technology for tertiary treatment of tannery and distillery effluents is available, high cost involved make it less attractive resulting in poor quality discharges into waterways. As for chrome tannery effluent, chemical precipitation results in poor reductions of BOD and COD. For complete and successful treatment of the waste, an attempt is made in the present study to arrive at a low cost method for the removal of BOD and COD by anaerobic as well as aerobic oxidations using cowdung as the seed material. Also, information on the design of treatment plants based on biokinetic parameters for chrome tannery and distillery effluents is very limited and the prime objective of the present study is to determine the biokinetic parameters which enable us to describe the metabolic performance of the microorganisms when fed with the substrate and other components in the tannery and distillery effluent treatment processes.
The other objectives set forth for the present investigation are

(i) to find out the optimum pH at which the maximum chromium removal by a most economical and suitable alkali.

(ii) to achieve maximum removal efficiency of BOD and COD at optimum applied BOD load to reduce the pollutional hazards.

(iii) to apply modified Monod's equation to bring out the relation between the mean cell residence, food to microorganism ratio and BOD removal efficiency.

(iv) to evaluate biokinetic coefficients and to study the significance of parameters on the digestion processes.

(v) to study the effect of CaCO₃ in anaerobic digestion for enhancing biogas production.

(vi) to develop a mathematical model based on biokinetic parameters obtained in the present study and reported data for the prediction of BOD removal efficiency.

(vii) to confirm the order of bio-chemical reactions.