# INTEGRATION OF OZONATION AND ACTIVATED SLUDGE PROCESS FOR SLUDGE REDUCTION IN TANNERY EFFLUENT TREATMENT

*A thesis submitted to the school of graduate studies of Addis Ababa University in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering with Specialization in Leather Technology*


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**Abbreviations**

| | | |
|---|---|---|
| AS | : | Activated sludge |
| APHA | : | American Public Health Association |
| ASP | : | Activated sludge process |
| BOD | : | Biochemical oxygen demand |
| CETP | : | Common effluent treatment plant |
| EAS | : | Excess activated sludge |
| ETP | : | Effluent treatment plant |
| F/M | : | Food to microorganism ratio |
| HRT | : | Hydraulic retention time |
| MLSS | : | Mixed liquor suspended solids |
| MLVSS | : | Mixed liquor volatile suspended solids |
| PST | : | Primary settling tank |
| RAS | : | Return activated sludge |
| SS | : | Suspended solids |
| SRT | : | Sludge retention time |
| SST | : | Secondary settling tank |
| TDS | : | Total dissolved solids |
| TWW | : | Tannery wastewater |
| UASB | : | Up flow anaerobic sludge blanket |
| WAS | : | Waste activated sludge |
| UMS | : | Unsettlable micro solids |

## Abstract

In tannery wastewater treatment plants, sludge comprising of primary and secondary sludge is generated. If the concentration of Cr (III) exceeds 5000 mg/kg, then it is considered as hazardous wastes and this sludge has to be disposed in hazardous waste landfill site as per existing statutory requirements in India. Further, for disposal of wastes into hazardous landfill, the amount of organics concentration in the sludge shall not exceed 20% and if so, then these wastes are not permitted to be disposed in hazardous wastes landfill. Currently, lime and fly ash are added to the wastes to reduce the concentration of organics. Hence, there is urgent need for treatment methods to reduce of organic content in sludge before disposal into hazardous landfill. In this study, attempt was made to reduce the volatile solids generated from secondary biological sludge using advanced oxidation process (AOP) i.e., ozonation. Lab scale aerobic process using sequential batch reactor (SBR) for treatment of tannery wastewater and ozonation of excess sludge generated from SBR were carried out with 24 hrs cycling time. SBR was operated with primary treated tannery wastewater and excess sludge generated was ozonated and returned back to SBR reactor. The performance of sequential batch reactor (SBR) operated with tannery wastewater alone as control and another SBR operated with tannery effluent along with ozonated excess bio-sludge were studied and compared. It was observed that 15 minutes is the optimum ozonation time for oxidation of excess sludge from SBR treating primary treated tannery waste water as influent and the optimum ozone dose respective to optimum ozonation time is found to be 0.168g-$O_3$/g-MLSS.

It was observed that COD in the final effluent was reduced to total and soluble COD concentrations in the range of 548.2mg/l and 379.2mg/l for control SBR and 537.581mg/l and 376.049 mg/l for SBR with ozonated sludge respectively at total cycling time of 24 h. In terms of overall sludge reduction, 35.1% reduction of the excess sludge could be achieved by ozone treatment at 0.168 g-$O_3$/g-MLSS.

# 1. Introduction

Biological treatment is the most commonly used technology in wastewater treatment. Among biological treatment technology, activated sludge process (ASP) has been conventionally employed to treat a wide variety of wastewater, and over 90% of the municipal wastewater treatment plants use it or one of its modifications as the core part of the treatment process. Similarly, in treatment of tannery effluent also, ASP or its modifications has been employed in biological treatment process.

A considerable volume of sludge is generated during operation of activated sludge process, a part of which should be withdrawn (excess biomass) and disposed in order to maintain appropriate level of biomass concentration in the aeration basin. It must be noted that the excess sludge generated from the biological treatment process is a secondary sludge which results in generation of solid waste that must be disposed of in a safe and cost-effective way. Processing and disposal of excess sludge is one of the most serious problem encountered in wastewater treatment in terms of environment, finance and technology so that it accounts for considerable amount of the total expense of wastewater treatment plant [1, 2].

The conventional disposal methods such as landfilling, opening dumpings, etc may cause secondary pollution problems and are strictly regulated in many countries. Therefore, prior to safe disposal solids and bio solids are stabilized to reduce pathogens, eliminate offensive odor and inhibit and reduce or eliminate the potential for putrefaction. There are various methods of sludge disintegration including mechanical, thermo, chemical, biological and oxidative treatments. From these sludge disintegration/ reduction methods, this research work focuses on reduction of excess sludge by oxidative treatment method. In this study, optimum ozone dosage and optimum ozonation time specific to excess sludge emanating from tannery effluent treatment plant was estimated, and also the economic aspects of Integration of

Ozonation and Activated Sludge Process (ASP) for sludge reduction in Tannery Effluent Treatment has been carried out.

### 1.1. Statement of the Problem

Biological treatment is the most economical and environmental friendly technology for wastewater treatment. In biological treatment, activated sludge system or one of its modifications has been employed to treat a wide variety of wastewater including tannery effluent. During treatment of wastewater using ASP, considerable volume of sludge is generated, a part of which should be withdrawn and disposed to maintain biomass concentration. The excess sludge generated from the biological treatment process is a solid waste which needs to be disposed off in a safe and cost-effective way. Processing and disposal of excess sludge is one of the most serious problem encountered in wastewater treatment in terms of environment, finance and technology so that it accounts for 50–60% of the total expense of wastewater treatment plant [4]. Treatment of the excess requires much cost and energy, and has been a serious issue because of lack of landfill space and due to strict environmental regulations. The amount and characteristics (i.e. high organics content, toxic materials) of sludge make it difficult to find and apply sludge management strategy in reality. Hence, there is urgent need to develop a process for reduction of excess sludge and the same has been gathering attention in industrial wastewater treatment sector.

A conventional treatment to stabilize excess activated sludge is the anaerobic digestion process; however, due to the complicated, non-homogeneous nature of sludge, it requires long retention times to meet sludge reduction efficiencies as well as high construction cost. In order to maximize the reduction efficiency in digesters, solids contained in sludge need to be destructed and converted to readily degradable substance. A number of processes including thermal energy, ozonation, alkaline, high pressure, mechanical disintegration, acidification

and ultrasound have been investigated for decomposition and pre-treating of waste sludge. Among these processes, ozonation is of special interest because it has high oxidation potential, no oxidant residues are remaining and no increase in salt concentration occurs [1, 2].

## 1.2. Objectives

### 1.2.1. General objective

General objective of this work is to reduce excess sludge emanating from SBR while treating tannery wastewater, by application of ozonation to the excess sludge and treating the ozonated sludge back in the same SBR.

### 1.2.2. Specific objectives

- To determine overall sludge reduction with ozonation
- To determine the optimum ozone dosage and optimum ozonation time for disintegration of secondary sludge
- To investigate the economical feasibility for integration of ozonation and biological process for sludge reduction in Tannery Effluent Treatment.

## 1.3. Scope of the Study

This thesis work includes collection of waste effluent samples from primary clarifier effluent, estimation of overall percentage of sludge reduction, estimation of ozonation time for application of ozonation and respective optimum ozone dosage for disintegration of sludge and finally investigation of economical feasibility for Integration of Ozonation and Activated Sludge Process for sludge reduction in Tannery Effluent Treatment.

## 1.4. Significance of the Research

Excess sludge is an inevitable product of wastewater treatment process with activated sludge process. As already mentioned, treatment of the excess sludge requires much cost and energy, and has been a serious issue because of lack of landfill space and strict environmental regulations. Hence, reduction of excess sludge has been gathering attention in wastewater

treatment sector. At present, solid waste from wastewater treatment plants (dewatered sludge) is one of the main problems encountered in tanneries. Considerable volume of excess secondary sludge is generated from tannery common effluent treatment plants and also increases the volatile solids content in dewatered sludge (maximum limit accepted for disposal in hazardous landfill is 20%). Therefore, the main aim of this work is reduction of excess secondary sludge and hence total operation cost including disposal cost, transportation cost and other related costs by application of ozonation.

- Solids destruction and reduction which results in reduction of generation of excess secondary sludge.
- Reduction of volatile solids percentage which results in nearing the values to meet the compliance of regulations.
- Reduction of sludge volume by increasing the settlability of sludge.
- Reduction of sludge treatment and disposal cost.
- Reduction of total operation cost.
- Reduction of digester volume.

# 2. Literature Review

## 2.1. Introduction

Activated sludge process is the most widely used biological wastewater treatment process for the degradation of organic matter and removal of nutrients from domestic and industrial wastewater. The conventional activated sludge process consists of biological treatment in an aeration basin, secondary clarification, sludge recycling and sludge wastage. The activated sludge process mainly relies on bio-flocculation, aggregation of microorganisms and microbial products. Microorganisms in bioflocs oxidize organic matter into end products

($CO_2$, $NO_3$-$N^+$, $SO_4$, and $PO_4$) and synthesize new biomass. Dense and large flocs are separated from the liquid in a secondary clarifier by gravity settling. Settled bio-solids are recycled or wasted from the secondary settling tank. The purpose of recycling thickened mixed liquor is to maintain the desired concentration of biological suspended solids (MLSS) in the aeration basin and the purpose of sludge wasting is to control the solids retention time (SRT) for reliable treatment [3].

The reason why activated sludge is currently the most widely used process is that it is flexible, reliable, can produce a high degree of nitrification and can stabilize insoluble organic matter. However, one of its main disadvantages is the generation of excess sludge. Although the activated sludge process works efficiently, the growth of microorganism results in the production of excess biomass that requires disposal to control the solids retention time (SRT). To treat this excess sludge, a combination of digestion, chemical treatment, dewatering, and thickening is generally used. The treatment for excess sludge can account for up to 60% of a plant's total operating cost and also adds to the capital cost of the facility.

**Sludge reduction mechanism**

Physical/Chemical sludge reduction technologies

- Solublize sludge solids and lysis of cells, thereby increasing the rate of degradation
- Render the non-degradable organic fraction degradable, thereby increasing the extent of degradation

Bulking sludge causes major problems in wastewater treatment plants that deal with biological nutrient removal in activated sludge processes. Bulking sludge is caused by filamentous bacteria, which have a negative impact on the sludge settling properties. Wastewater treatment plants suffer from this type of problem with bulking sludge which

creates a stable layer at the surface that does not settle in the clarifier. In order to solve this problem, onsite generated ozone was used to decrease the amount of filamentous bacteria in the return activated sludge flow. Ozone is a strong oxidant suitable for non-specific bulking control. It stresses the filamentous bacteria causing inactivation through cell wall disintegration. The ozone treatment resulted in decreased abundance of filamentous bacteria. Ozone treatment of the recycled activated sludge improves the settling properties of bulking sludge, without interfering with other important microbiological processes like nitrification [4].

## 2.2. Reduction of sludge by ozone treatment and production of carbon source for denitrification

The feasibility of ozone treatment of municipal sludge for sludge reduction and carbon source production has been investigated. Significant accumulation of solubilised organics and unsettlable micro solids (UMS) was observed at relatively low ozone dosages while mineralization became dominant at higher dosages. Batch denitrification experiments showed that the solubilized organics and the UMS could be utilized as carbon sources for nitrogen removal. In terms of overall sludge reduction, 54% reduction of the total sludge mass could be achieved by ozone treatment at 0.2 g-$O_3$/g-MLSS [4].

Sludge disintegration has been commonly practiced as a pre-treatment for sludge digestion. There are various methods of sludge disintegration including mechanical, thermal, chemical, biological and oxidative treatments. Application of sludge disintegration, however, is not limited to sludge digestion. Recently, sludge disintegration has been proposed to produce internal carbon source for biological nutrient removal. On the other hand, disintegration of wastewater sludge by ozone has been reported to control sludge bulking during conventional activated sludge processes. More recently, ozone treatment of excess sludge followed by

recirculation of the treated sludge into the bioreactor was reported to effectively reduce excess sludge [4].

Biological treatment of wastewater results in the generation of a considerable amount of waste activated sludge that has to be treated. Sludge treatment and disposal represents a decisive factor for design, operation and costs of wastewater treatment, especially for large treatment plants. Since, the costs of sludge treatment are high, representing 50–60% of the total operating costs of the wastewater treatment [5], much attention has been focused on advanced sludge treatment processes to reduce the amount of sludge produced. Many techniques on sludge minimization have been developed recently. Ultrasonic treatment, ozone oxidation, mechanical disintegration, alkaline treatment, thermal treatment, and biological hydrolysis with enzymes were investigated for sludge disintegration purpose by several researchers in half-scale and lab scale plants. Ozone oxidation is one of the commonly used advanced oxidation techniques. Through the implementation of sludge ozonation, refractory organic structures are oxidized and converted into biodegradable low-molecular compounds. Basically, the disintegration process is accomplished by the application of ozone to break down cell walls. Thus, cell walls are fragmented; intracellular compounds are released into the liquid phase of sludge [6], and sludge ozonation causes an increase of total organic carbon in the sludge supernatant. The other effects of sludge ozonation have been reported to cause a decrease of both total suspended solids and volatile suspended solids in the ozonated sludge. Ozone oxidation of sludge has been considered as a pre-treatment unit operation prior to a biodegradation process (aerobic/anaerobic digestion). The ozonated sludge can be utilized as a substrate in the anaerobic biological processes. Full-scale and laboratory studies suggest that ozonation could even lead to a process with no excess sludge production at source [7, 8].

The efficiency of ozonation as a method of excess sludge reduction is highly dependent on process operating parameters. Especially, ozone dose and dosing method have played an important role on disintegration efficiency. Compared with different dosing methods of bubble system and micro bubble system in a lab scale, and reported that in the micro bubble system, more than two times of COD and TN, and eight times of TP were released into the supernatant compared with the bubble contactor at the same dose, and the sludge solubilization efficiency reached 25–40% for the micro bubble system and 15–30% for the bubble system at ozone doses of 0.06–0.16 g O3/g TSS [9].

Table 2.1 Characteristics of biological sludge

| **Parameters** | **Average values** |
|---|---|
| pH | 6.92 |
| EC (electrical conductivity) µS/cm | 7 |
| DS (dry solids), % | 1.42 |
| VS( volatile solids), % | 52.15 |
| SS (suspended solids), mg/l | 10100 |
| VSS (volatile suspended solids), mg/l | 7300 |
| SCOD (soluble chemical demand), mg/l | 240 |
| DOC (dissolved organic carbon), mg/l | 102.2 |
| TN (total nitrogen in sludge supernatant), mg/l | 8 |
| TP (total phosphorous in sludge supernatant), mg/l | 40.2 |
| CST (capillary suction time), s | 17.3 |

### 2.2.1. Use of ozone as pre-treatment for excess sludge reduction

Ozone is a strong chemical oxidant; it has already been applied in wastewater treatment for the removal of refractory COD from secondary effluent and also to help control sludge bulking and foaming [3].

Recently, the use of ozone has been attempted to reduce excess sludge production in the ASP by enhancing cryptic growth. Excess sludge is exposed to ozone in order to induce cell lysis and solubilisation; treated sludge is then returned to the aeration tank for oxidation of the soluble organics generated. It is believed that after ozone exposure, part of the excess sludge is mineralized to $CO_2$ and water, while another fraction is solubilised to biodegradable organics. Microbial growth in an ASP under such conditions results in a net lower microbial growth yield compared to a conventional ASP. More than 50% of the carbon obtained after ozonation of the returned activated sludge is biodegradable.

### 2.2.2. Effects of sludge ozonation

The effect of sludge ozonation is determined in terms of mineralization, solubilisation and changes in residual solid characteristics. The extent of mineralization by measuring the total COD (TCOD) and the extent of solubilization are obtained by measuring soluble by measuring soluble COD (SCOD). Both the solubilization and the mineralization increase with ozone dosage except for the decrease in SCOD at very high ozone dosages. The fraction of solubilization and unsettled micro-solids (UMS) significantly increase with the ozone dosage at relatively low ozone dosages while the fraction of mineralization is relatively small. However, the mineralization becomes dominant at higher ozone dosages. The data can be interpreted as sequential reactions involving solubilization by cell disintegration and hydrolysis, and subsequent oxidation of the solubilized organics into carbon dioxide. A

steady increase of soluble nitro- gen concentration is observed with ozone dosage, also indicating the sequential reaction of solubilization and mineralization. As the sludge reacted with more and more ozone, the organic fraction of particles decreases while the solubilized fraction increases. This could result in changes of the rate of mineralization, the second step reaction, exceeding that of solubilization. Another interesting aspect of sludge ozonation is the increase of UMS. In general, sludge ozonation tends to increase the settleability of sludge [10, 11].

As far as the reduction of sludge mass is concerned, the amount of mineralization appears to be the most important aspect. However, sludge reduction by mineralization requires an unrealistically high ozone dosage. If the organic-rich solubilized and/or the unsettled fraction of ozonated sludge can be used as a carbon source for biological nitrogen removal, a substantial reduction of sludge can be achieved even at a relatively low ozone dosage. For example, more than 50% reduction of solid mass is possible at 0.2 g-$O_3$/g-MLSS with an additional saving on the cost of the external carbon source in the biological nitrogen removal process.

Although the rate of denitrification is affected by the amount of carbon supply, the supernatant from the ozonated sludge could be utilized as a carbon source for denitrification. Once the sludge flocs are solubilized and/or broken into unsettlable pieces, they become biodegradable regardless of the ozone dosage.

Table 2.2 comparisons between ozonated sludge and other carbon sources commonly used for denitrification [3]

| Carbon source | Denitrification rate$gNO_3$-N/g VSS.d | Typical |
|---|---|---|
| Methanol | 0.12-0.90 | 0.43 |
| Wastewater | 0.03-0.11 | 0.07 |
| Endogenous | 0.017-0.048 | 0.035 |
| Solublized organics by ozonation | 0.011-0.081 | 0.05 |

In Table 2.2, the feasibility of the solubilized organics and the UMS after ozone treatment as a carbon source is compared with other carbon sources commonly used for denitrification. It should be noted that the supernatant from the ozonated sludge also contains some nitrogen. At ozone dosages below 0.5 g-$O_3$/-g-MLSS, however, the carbon/nitrogen ratios of the supernatants become larger than 20, indicating that recycling of the supernatants to the raw wastewater influent stream can increase the overall carbon/nitrogen ratio. Significant accumulation of solubilized organics and UMS observed at relatively low ozone dosages while mineralization is dominant at higher dosages.

### 2.2.2. Costs associated with excess sludge handling and disposal

Operation and maintenance costs of a secondary wastewater treatment plant, including the cost of sludge treatment and disposal can be divided into four major categories: personnel, energy, chemicals and maintenance. Personnel and energy costs account for about 85% of the total cost, 36% of the total plant operating cost is the energy consumption in aeration and

pumping systems (wastewater and sludge included). Sludge treatment alone, accounts for more than 32% of the total plant energy consumption. If sludge handling, transportation and final disposal are added then the total cost for sludge treatment and disposal may be up to 40-65% of the total operating cost [4].

The ideal solution to alleviate both cost and space availability problems would be the direct reduction of sludge within the activated sludge process, even if the amount of primary sludge due to its nature cannot be reduced substantially the reduction of ASP sludge (secondary sludge) is possible.

**Sludge costs**

Sludge handling and disposal make up 40-60% of WWT costs ($200 - $900/dry tons). Costs increasing due to:

- increasingly stringent regulations (emissions and toxins)
- increasing sludge handling input costs
- shrinking landfill capacity
- urbanization (increasing distances from landfill)
- public concerns over safety /odor
- replacing aging equipment / infrastructure etc

Options for sludge reduction

Long sludge age systems

- Lagoons and ponds - SRT of 30+ days
- MBR- operation of ASP at 10-20g/l

Lysis systems: Mechanical grinders - comminution, Chemical - Ozonation, Alkali, Ultrasound, Thermal methods.

**Ozonation for cell lysis**

Ozonation lysis approach is applied to secondary (excess) sludge where excess sludge is exposed to ozone and hence ozone attacks cell wall. Cells contain approximately 90-95% liquid cellular compounds (COD). This COD is released from lysed cells and oxidized in the basin. [12]

1. Ozone penetrates cell wall
2. $O_3$ contacts cell wall
3. Bacterial cell to be ozonated in contactor
4. Ozone oxidizes cellular compounds causing lysis
5. Cell with lysis ‘pockets’ after contact with ozone
6. Lysed cell- returned to basin, where COD is released
7. Solid waste effectively transformed to “food” for biomass in basin

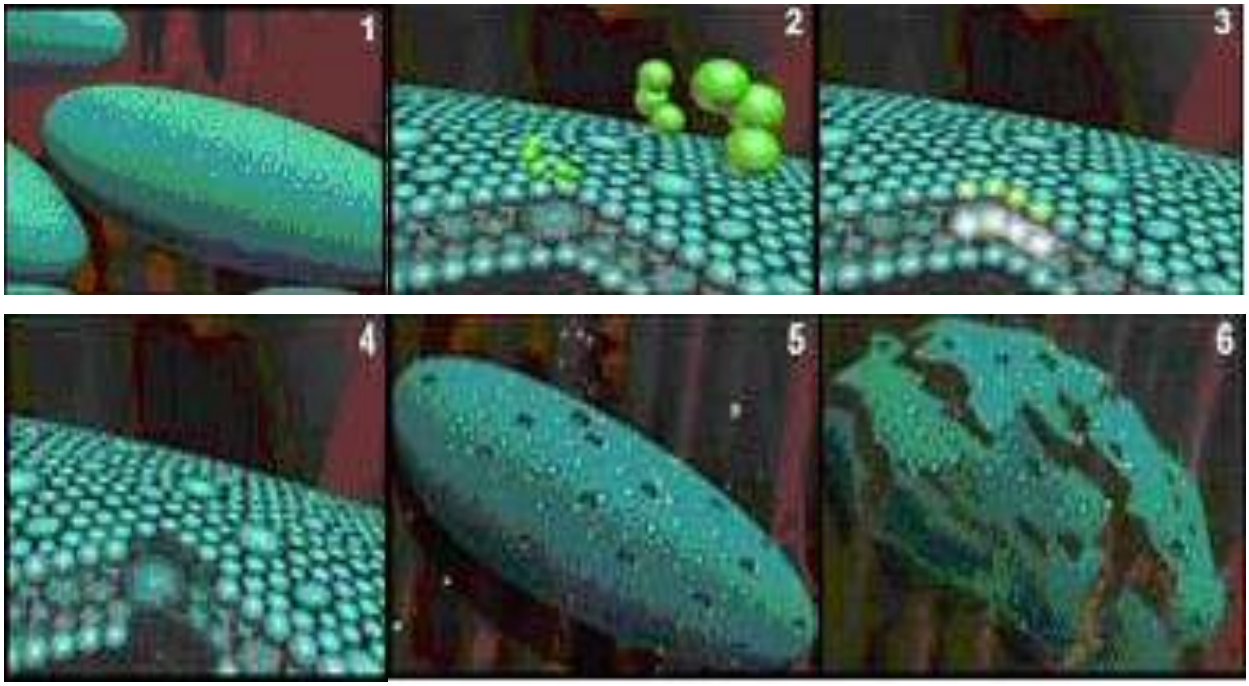


Figure 2.1 Principle of disintegration of secondary bio-sludge by Ozonation

Lysis with Ozone

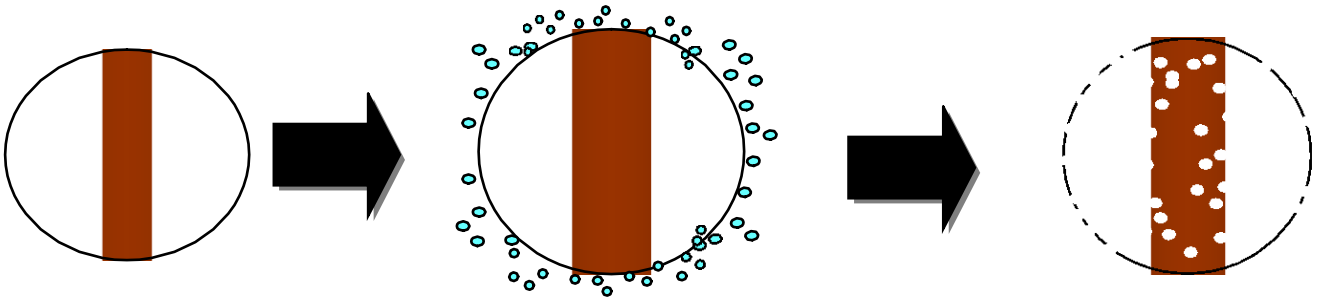

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Figure 2.2 Steps during lysis with ozone

1. Bacterial cell
2. Ozone attacks cell wall
3. Lysis ‘pockets’ formed and COD leaks out into treatment basin

The only goal of sludge ozonation is lysis and the treatability of lysis product;

- lysis product has high treatability
- bio kinetic rates similar to plant influent
- Lysis product composition has optimal nutrient distribution; COD: N:P = 100:10-15: 5-8.

Significant reduction of filamentous bacteria; filamentous organisms are effectively controlled by ozone, sludge ozonation reduces filamentous populations, large surface area: high vulnerability to ozone, significant reduction in Nocardia, Parvicella, Thiotrix sp, etc, and sludge reduction effects are sustained. [12]

Table 2.3 Sludge Ozonation summary [12]

| **Parameters** | **Pre-ozonation** | **Post-ozonation** |
|---|---|---|
| Sludge generated (dry) | 2 tons/day | 0.4 tons/day |
| % dry solids | 18% | 22% |
| SVI (ml/g) | 80-100 | 50-60 |
| $O_3$ usage | - | 0.07 kg $O_3$ / kg SS removed<br>(70 kg $O_3$ /dry of what?? ton) |
| Foaming | 20 cm above the liquid | Nil |
| Treatment capacity | 80% COD removal<br>60% TN removal | 80% COD removal<br>60% TN removal |

## 2.3. Leather Manufacturing Technology

### 2.3.1. Introduction

The history of leather production goes right back to prehistoric times, when primitive methods were developed for treating animal hides and skins so that they could be used for clothing to protect people from the elements [13].

It is to be assumed that the raw hides and skins were at first merely dried and preserved by smoking until with the advance of civilization, it was found that they could be made much more durable by treating them with vegetable matter containing tannin (crushed bark, wood or fruits). It was also discovered that by suspending the hides in water (controlled decomposition process) treating them with ash (liming), it was possible to remove the hairs if the "tanned" hide material was not to be used as fur but as leather.

In addition to various types of vegetable tannage (bark tannage), chamois tannage with fish oil, fat or oil is also known to have existed in ancient times and is still sometimes practiced today. White tannage with alum was presumably a later addition to the methods used by the early tanners [13-15].The practice of dyeing (originally painting) leather with colored materials of vegetable, animal or mineral origin likewise goes back thousands of years.
From these early beginnings a craft steeped in tradition developed over the centuries. Following the introduction of chrome tannage about the end of the $19^{th}$ century, this craft evolved into an industry of great economic significance which has now become established throughout the world [14].

### 2.3.1. Operations Involved in Leather Production

Leather processing essentially consists of series of physical and chemical operations where by the raw hide or skin of an irregularly shaped, low strength organic material that can putrefy is given an almost constant thickness and such characteristics as incorruptibly, good flexibility, high tensile strength, abrasion resistance and finish with good appearance finally come out as finished leather. Hides and skins have the ability to absorb tannic acid and other chemical substances that prevent them from decaying, make them resistant to wetting, and keep them supple and durable. The surface of hides and skins contains the hair and oil glands and is known as the grain side. The flesh side of the hide or skin is much thicker and softer [13, 14, and 17].The tannery operations can be broadly divided into four sections; beam house operations, tanning operations, post-tanning operations and drying and finishing operations.

#### *2.3.1.1. Beam house Operations*

Before tanning the main important operations for leather manufacturing are done in beam house. Beam house operations consist of Soaking, Liming, Deliming, Bating, Pickling, Depickling and Degreasing (if necessary) etc.

**Trimming**

First of all the selected tannable hides and skins are trimmed to remove the tail, shoulder, flanks, neck and trimmable portions correctly. Then these are weighted carefully and the entire chemicals percent will be based on these weights [16].

**Soaking**

Soaking is the first tannery operation. During curing, hides and skins lost large amount of its physiological content of water and unless regains this water during soaking operations, good

quality leather cannot be produced. The associated wastes during soaking are chlorides, bloods, dirt and hair [15, 16].

The process of soaking can be classified into three stages:

I. Pre-soaking (dirt soaking)-in dirt soaking, 300-400% of water is used to remove the unwanted materials
II. Main soaking- the purpose of main soaking is to re-hydrated the material. In this operation, water, non-anionic wetting agent (0.2% concentrated), soda ash (0.2% concentrated) and preservatives (0.5% concentration) are used.
III. Final soaking- only water is used for the washing purpose in this operation

**Liming**

Liming is a very important operation for leather manufacture. The qualities of the finished leather are largely controlled in liming process. Liming is the operation in which the soaked hides and skins are treated with 2-10 per cent milk of lime with or without the addition of sharpening agents like sulphides, cyanides, amines, etc. Unhaired hairs, spills of sulphide and lime sludge are the main waste. The liquor discharged from this operation has high sulphide content and fine hairs that are responsible for high SS, COD and BOD load.

The process of liming can be broadly classified into two parts [16]:

I. Liming- lime (8-10%) along with sodium sulphide (3%) is applied to the skin to remove hair
II. Re-liming – to open up fibrous structure, lime, soda ash, caustic soda, etc., are applied.

**Fleshing**

Fleshing can be carried out at several stages of the process. The different fleshing operations are the following: green fleshing (raw fresh and chilled hides/skins, green fleshing (soaked -

salted- hide/skins), lime fleshing, and pickle fleshing.The fleshing operation aims to remove excess connective tissue and fat from the flesh side of the hides and skins. If fresh hides are being used, green fleshing takes place before soaking. If salted hides are used, green fleshing is carried out after soaking. Lime fleshing is carried out after liming. Sheepskins can also be fleshed after pickling. Sheepskins are generally fleshed at two stages in the process, whereas hides are generally fleshed once.

There are no chemicals used for fleshing of hides and skins, other than that operators may use sawdust or an alternative to get a better grip of the slippery hides. The fleshing machines generally use water to wash away the fleshings [14, 17].

**Splitting**

Splitting can be carried out most commonly on the following substrates: limed pelts, pickled pelt sheepskins, tanned leathers, crust leathers. Depending on where the splitting is carried out, the use of chemicals and water in subsequent processes will be reduced, as only the required part of the hide is processed. Therefore, the earlier splitting is carried out, the fewer chemicals and the less water used to process the hides and skins. However, tanneries do not always split in the limed stage for technical reasons or the specifications of the final product. When sheepskins are split in the pickled state to produce chamois leathers, a solution of surfactants is used on the splitting blade to increase the grip on the greasy skins, and reduce fat build up on the blade [15].

**Deliming**

After liming the unhaired and fleshed hides and skins known as pelt are taken for the next operations called deliming. The alkali present in the pelt is of two types; free alkali & combined alkali. The free alkalis can easily be removed by repeated washing with water or by pressing the pelt under the high pressure, but for removal of combined alkali chemical

treatment is always necessary. The process is carried out by washing and by using water combined with neutralizing chemicals. Chemicals used are ammonium chloride or sulphate, 0.5– 2.0 percent acids (lactic, formic, boric and mixtures), acidic salts, sodium bisulphite, hydrogen peroxide [14].

As a result of the reaction of this chemicals with the lime and sulphide chemicals of the pelt the most dangerous gas will evolve. This gas is hydrogen sulphide and ammonia gas. To protect employees from the exposure of this gas usually sodium bisulphate is added together with the deliming agent. However during drain of the drum either this gas may generate and make employees feel discomforts. The use of gaseous $CO_2$ instead of ammonium salts has been increasing [13, 16].

**Bating**

Limed and partially delimed pelts sometimes require additional treatment known as bating. Bating is done to remove rest lime, swelling and plumping. The chemical used is often a 0.5 per cent bating material, which consists of 50 per cent wood flour (or another carrier), 30 per cent deliming agent (ammonium chloride) and 1-5 per cent pancreatic enzyme.

**Degreasing**

Degreasing is the process of removing fats from the skin. This is especially important in sheepskin tanneries as the fat content of their raw material is large. The process uses solvent degreasing. Solvents, which are increasingly substituted or combined with surfactants and/or enzymes, include perchloroethylene, monochlorobenzene and kerosene [15].

**Pickling**

In leather processing pickling is very important and essential operation prior to mineral tannage. The treatment of delimed or bated pelts with a solution of acid and salts is known as pickling which takes the pelts acidic condition to absorb chrome and being down the pH for chrome fixation. The chromium salts used for chromium tanning are not soluble under

alkaline conditions and will precipitate if added to high pH hides (Leather Facts 1977). The most common acids being used are sulphuric acid and formic acid. Other acids that can be used include hydrochloric acid, boric acid and other weak organic acids, e.g. acetic acid, lactic acid. The salt is used first to prevent the acid swelling of hides. Then finally acid is added so that its final pH is <1.0 [17].

Typically, acids would be added as 0.5 % – 3 % of the weight of the raw materials. Common salt is usually used in concentrations between 6 % (bovine hides) and 14 % (mainly pickled pelt skins). Alternative salts include sodium sulphate and potassium chloride.

If pickled pelt sheepskins are going to be vegetable tanned, they will firstly be de-pickled using either sodium acetate or sodium bicarbonate.

#### *2.3.1.2. Tanning Operation*

In leather manufacture the most outstanding process is tanning. The process of converting the putrescible hides and skins into non-putrescible leather is called tanning. The materials which are used for tanning are called tannins. There are various processes of tanning such as- chrome tanning, semi-chrome tanning, vegetable tanning, oil tanning, Zr tanning, alum tanning, white tanning etc [16].

For the tanning process a large variety of chemicals is necessary and only a part of these chemicals are taken up in the hides and skins. As a result, effluents are generated from tanning operations that have a low pH and carry the part of the chemicals that was not integrated. The substances released depend on the type of tanning applied [13].Tanning auxiliaries are intended to produce a desired modification of the tanning effect without developing a tanning action. Complex active and buffering substances are used for mineral tanning. Surfactant auxiliaries are added to disperse the tanning agents and accelerate the complete penetration of tannin as well as to influence the emulsion and electrolyte stability of

other auxiliaries (for mineral and vegetable tanning) [23, 25].

### i. Chrome tanning

Chrome tanned leather accounts for approximately 90 % of all the leather produced in the world. The most commonly used tanning agent is a basic chromium sulphate. Tanning is completed with a basification to bind the chromium in the leather. Chemicals used in tanning are: chrome tanning salts with in average of 14 per cent Cr (used in amounts of 8-12 per cent for common processes and 5-6 per cent for low chrome processes), 1.0 per cent sodium bicarbonate (basifying agent to adjust pH), 0.5 per cent masking agent (sodium formate), and up to 0.9 per cent fungicide.

The pelt after tanning process will have non-biodegradable nature and then called leather wet blue. Since the chrome uptake rate of the tanned leather is 70% of the input, the rest 30% will be discharged through the effluent. The discharged chrome liquor contains the poisonous pollutant chromium [13].

Objects of Tanning:

- To convert the putrescible hides and skins into non-putrescible leather.
- To raise the shrinkage temperature and to increase the resistance to hot water.
- To reduce the ability to swell when wet back.
- To increase the strength properties of leather.
- To stabilize the leather against enzymatic degrading.

### ii. Vegetable tanning

The plant extracts applied for vegetable tanning are either polyphenolic compounds (condensed vegetable tannins) or esters of glucose and Gallic acid (hydrolysable vegetable tannins), which are leached (with water) from wood, barks, leaves, roots etc.The most commonly used vegetable tannins extracts are: Natural Quebracho, Soluble Quebracho,

Mimosa, Natural Chestnut, Sweetened Chestnut, Myrobolans, Valonia etc.

**Samming and Shaving**

Samming and shaving can also include in tanning operation where summing brings leather to a uniform semi-dewatered state. The leather is passed through a samming machine that squeezes surplus water out of the leather. On the other hand, shaving is a mechanical process that controls the leather thickness. Chrome containing liquor and wet blue leather shavings and pieces are the major wastes of the summing and shaving operation, respectively [17].

### *2.3.1.3. Post tanning Operation*

**A. Neutralization**

The process of deacidification or the excess of free or easily liberated strong acid in leather, prior to, retanning, dyeing and fat liquoring, is popularly called neutralization.

Objects of neutralization include: remove the neutral salts and uncombined chromium salts from the leather, neutralization of free acid in the leather formed by the hydrolysis of the chrome complex, control the affinity of the leather for anionic materials, particularly dyestuff and anionic oil emulsions by regulating its electrostatic charge [15].

**B. Re-Tanning**

Mineral tanned leathers; particularly chrome or aluminium tanned leathers are always retanned with retanning chemicals with a view to modifying the properties of the finished leather to suit modern demand. A wide variety of chemicals can be used for the retannage of leather. They can generally be divided into the following categories: vegetable tanning extracts, syntans, aldehydes, mineral tanning agents and resins [14].

**C. Dyeing**

To colour the leather as required by the customer, this should be an even colour and should

cover any grain defects. The colour should be light fast and wash fast if the finish is not covering. Typical dyestuffs are water based acid dyes. Basic and reactive dyes are less commonly used.

**D. Fat liquoring**

It is very important operation for leather manufacturing and it depends on the type of leather to be manufactured. Leathers must be lubricated to achieve product specific characteristics and to re-establish the fat content lost in the previous procedures. The oils used may be of animal or vegetable origin, or might be synthetics based on mineral oils [16].

The objects of fat liquoring are:

- To improve the softness of the leather.
- To improve the sliding properties of the leather.
- To improve the toughness, water-repellent properties of the leather.

### *2.3.1.4. Drying and Finishing Operation*

**Drying**

The primary purpose of drying is to remove moisture. However, at this stage, drying is more than just moisture removal. Drying is one of the most important steps in maintaining leather quality. It affects the feel, softness, area, and even colour of the tanned hide/skin [14].Drying techniques include samming, setting, centrifuging, hang drying, vacuum drying, toggle drying and paste drying. Generally samming and setting are used to reduce the moisture content mechanically before another drying technique is used to dry the leather further. After drying, the leather may be referred to as crust. Crust is a tradable intermediate product.

**Finishing**

After the leathers are fat liquored and dyed following the tanning process, they are processed with a series of coatings on the surface in order to improve their resistance and produce

appealing and uniform surface effects.The overall objective of finishing is to enhance the appearance of the leather and to provide the performance characteristics expected of the finished leather with respect to [14, 17]: Colour, Gloss, Handle, Flex, adhesion, rub fastness, as well as other properties including extensibility, break, light and perspiration fastness, water vapour permeability and water resistance as required for the end use [17, 16].

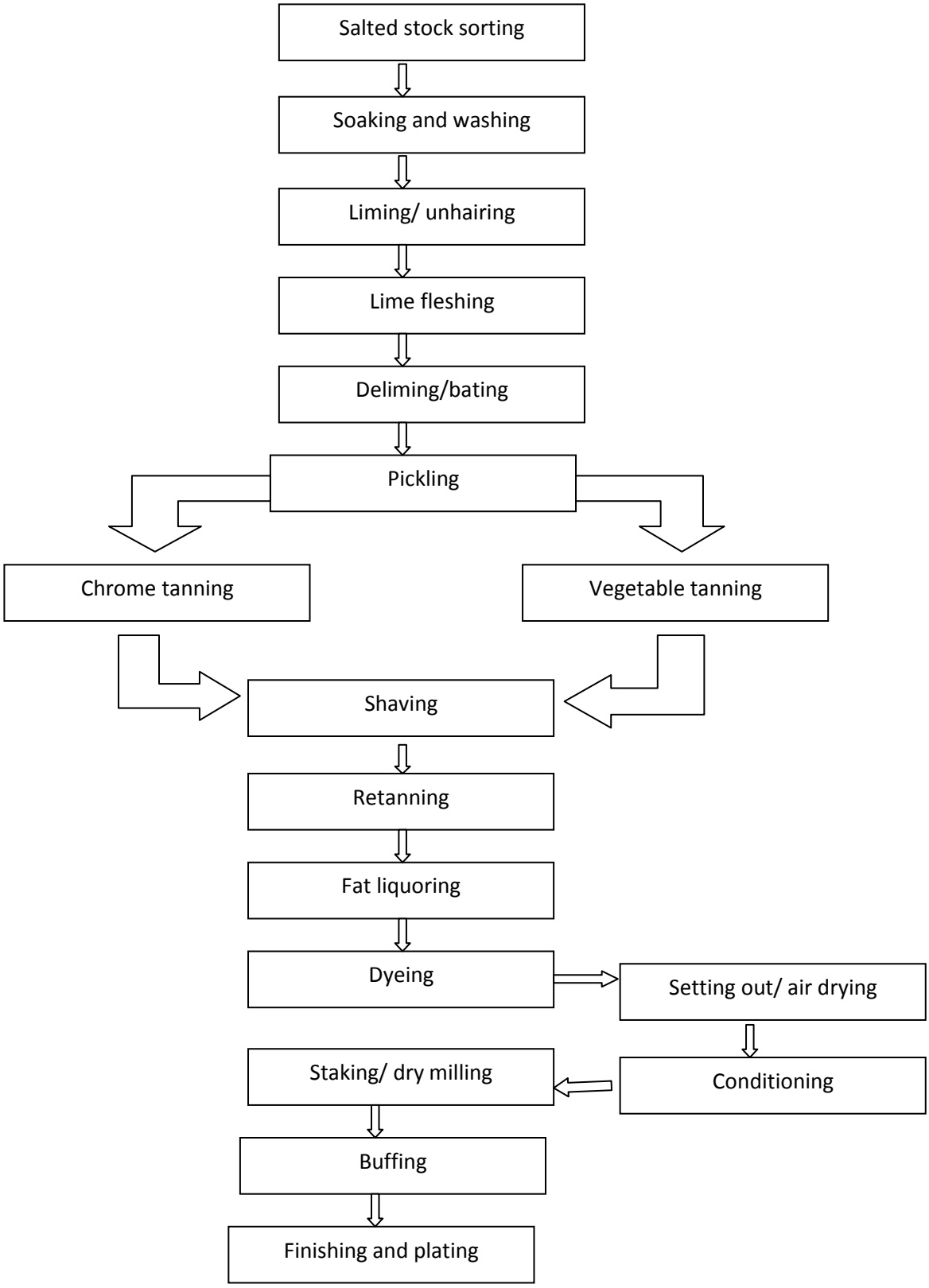



Figure 2.3 General flow diagrams of leather processing

### 2.3.2. Pollution Load of Leather Processing Operations

Tannery is universally recognized as a ‘dirty’ industry, and because of this reputation very often is unpopular with the general public and even considered erroneously more dangerous than other industrial activities not having such direct and evident unpleasant impact. It must be clearly said that tannery is an unpleasant industry but not harmful and dangerous. This is well demonstrated by the fact that specific illnesses associated to the leather manufacture do not exit [18].

The leather tanning process involves an important consumption of water and generates a complex pollution consisting of a mixture of organic and inorganic substances make quite difficult and costly to treat if compare with that of other industries. Approximately 30-40 litres of water is used for processing one Kilogram of raw hide/skin into finished leather with peak up to 60 litres per kilogram of hide/skin of processed raw material green or wet-salted weight [18, 19].

Composite untreated wastewater of hide or skin is turbid, colored, and foul smelling. It consists of acidic and alkaline liquors, chromium; sulphide; nitrogen; biochemical oxygen demand (BOD); chemical oxygen demand (COD); chloride; and high levels of fat. Suspended solids are usually half of chloride levels. Wastewater may also contain residues of pesticides used to preserve hides during transport, as well as significant levels of pathogens [20]. Significant volumes of solid wastes are produced, including trimmings, degraded hide, and hair from the beam house processes. The solid wastes can represent up to 70% of the wet weight of the original hides. In addition, large quantities of sludge are generated. Decaying organic material produces strong odour. Hydrogen sulphide is released during dehairing, and

ammonia is released in deliming. Air quality may be further degraded by release of solvent vapours from spray application, degreasing, and finishing (for example, dye application) [21].

In general, the quantity of water usage and nature of wastewater discharge varies from process to water usage and wastewater discharge per ton of hide /skin for different process are shown in the Table 2.4.

## 2.4. Characteristics of Tannery Wastewater

The wastewater generation per unit quantity of raw material processed by the tanneries as well as the characteristics of the wastewater are dependent primarily on the type of tanning practised. But even for a particular type of tanning, the wastewater quantity and quality vary with

- The type of raw material used, whether skins or hides
- The sources of the raw material which may be local or foreign
- Variations in processing depending on market demand
- Prevailing tanning practices in the region, the industry being tradition-bound and highly conservative
- Quality of the water supply particularly in regard to its total dissolved solids (TDS) content.

The wastewater from tanneries is discharged as batches from different sections at different times. The characteristics of the sectional wastewater are highly variable. Some streams are highly acidic (low pH) and some are highly caustic (high pH).

Table 2.4 Characteristics of Composite Wastewater from tanneries (align in one page please)

| **Sl №** | **Parameters** | **Raw to EI** | **Raw to finish** | **Raw to wet blue** | **Wet blue to finish** | **EI to finish** |
|---|---|---|---|---|---|---|
| 1 | pH | 8.0-9.6 | 7.4-8.5 | 8.3-9.2 | 3.7 - 4.7 | 3.5-5.6 |
| 2 a | Alkalinity as $CaCO_3$ | 2000-5000 | 900-2000 | 1800-2800 | -- | -- |
| 2 b | Acidity as $CaCO_3$ | -- | -- | -- | 600-1700 | 500-1100 |
| 3 | $BOD_5$ -20$^oC$ | 3000-6000 | 1000-2500 | 1300-3000 | 500 - 1000 | 600-2000 |
| 4 | COD | 7000-15000 | 2400-6000 | 3000-7000 | 1000-3000 | 2500-7500 |
| 5 | Chloride as $Cl^-$ | 7000-12500 | 5000-9500 | 6000-13500 | 400-1500 | 150-700 |
| 6 | Oil & Grease | 60-150 | 40-80 | 15-45 | 20-50 | 30-70 |
| 7 | Dissolved Solids | 14000-20000 | 12000-18000 | 15000-20000 | 3000-7000 | 3500-7000 |
| 8 | Suspended Solids | 2000-4000 | 2000-4500 | 2600-5400 | 300 - 800 | 800-1500 |
| 9 | Sulfide as $S^-$ | 10-70 | 20-180 | 50-270 | - | - |
| 10 | Total Chromium as Cr | - | 80- 400 | 150-340 | 125-250 | 80-120 |
| 11 | Wastewater volume/tonne raw material | 15-25 $m^3$ | 30 -50 $m^3$ | 20-30 $m^3$ | 15-25 $m^3$ (on wet blue weight) | 35-50 $m^3$ (on EI weight) |

Note: 1. all values other than pH and wastewater volume are in mg/L)

2. One tonne of raw hides will produce 400 kg Wetblue/250 kg EI leather.

It may be seen from Table 2.4 that the major pollutants in tannery wastewater are:

- TDS consisting mainly of $Cl^{--}$ and $SO_4^{=}$
- Organic content as indicated by BOD, COD and Oil & Grease values
- Suspended solids
- Sulphides
- Chromium is present in tannery wastewater as $Cr^{3+}$, which has much lower toxicity than $Cr^{6+}$.

## 2.5. Tannery Wastewater Treatment

A comparison of the values given for raw tannery wastewater in table 2.4 with the limits given for effluent discharge indicate the need for substantial treatment of tannery wastewater whatever be the method of their final disposal.

### 2.5.1. Treatment Technologies for Tannery Wastewater

Presently, tannery wastewater is being disposed off on land or into water-courses/surface drains or municipal sewers. The main objectives of tannery wastewater treatment are to reduce TDS, $Cr^{3+}$, BOD, COD and SS of the raw wastewater to levels acceptable for such methods of disposal. The treatment methods generally adopted include the following steps.

- Segregation of specific sectional wastes and their separate treatment and disposal
- Pre-treatment at the tannery
- Primary treatment including equalisation

- Secondary biological treatment
- Sludge dewatering and disposal

### 2.5.2. Segregation of Specific Sectional Wastewater and their Separate Treatment and Disposal

#### *2.5.2.1. Soak wastes and pickle wastes*

One of the major pollutants in tannery wastewater is high TDS. The problem is most pronounced in the case of Raw to EI, Raw to wet blue and raw to finish tanning with the TDS in their composite effluents often exceeding 20,000 mg/L. The high TDS arises partly from the salt used for preservation of the raw hides and skins before they reach the tanneries. Part of the high TDS also arises from the tanning process.

To reduce the TDS in the wastewater, the salted hides and skins received at the tanneries are dusted as a first step to remove the salt crystals adhering to the hides, which would otherwise get into the wastewater. As a further step, when the raw skins/hides are soaked. (Which is effected in two or more serial steps) the first soak (Soak I), which will be the most saline, is segregated and evaporated in solar evaporation basins. The evaporated salt is scraped off periodically and disposed off along with the pre-dustings. Pickle wastes also contribute greatly to TDS and at times they also are segregated and treated in the solar evaporation basins along with the soak I wastes. Pre-dusting of the skins and hides and segregation and separate treatment of the Soak I wastes and pickle wastes will reduce the TDS in the final composite effluent greatly though not to the level stipulated [2100 mg/L] in IS: 2490 for discharge on land or into inland waters or into sewers.

#### *2.5.2.2. Segregation of spent chrome liquor and chrome recovery*

Chromium ($Cr^{3+}$) is a major pollutant in the wastewater from all tanning processes other than Raw to EI tanning. The chromium is discharged in the spent chrome liquor from chroming and rechroming in Raw to finish tanning, chroming in Raw to wet blue tanning, rechroming in Wetblue to finish tanning and from semi-chroming in EI to finish tanning.

The chromium concentrations in the composite wastewater from various tanning processes range from 80 to 400 mg/L whereas the discharge limits for $Cr^{3+}$ is as low as 2 mg/L. Neutralisation of the composite wastewater to a pH of about 8.0 followed by settling and secondary biological treatment can meet the limit fixed for $Cr^{3+}$. However such treatment greatly increases the quantity of sludge to be disposed off and because of the presence of $Cr^{3+}$ the entire sludge from the ETP will get categorised as hazardous requiring its cautious disposal. The chromium problem in tannery wastewater can be largely met by segregating the spent chrome liquors. Recovered chromium from them can be reused in the tanning process itself. The method has been proved to be cost-effective in Raw to wet blue tanning and Raw to finish tanning and is being adopted increasingly.

Chrome recovery is generally carried out at the individual tanneries even when CETPs are proposed. However, when the tanneries are small, the spent Cr liquor from different tanneries is transported in tankers to a common facility and the recovered Cr is transported back to the concerned tanneries.

### 2.5.3. Pre-treatment at Individual Tanneries

When Common Effluent Treatment Plants (CETPs) are provided to serve groups of tanneries, it is common to provide some degree of pre-treatment at the individual tanneries before their wastewater are drained to the common collection systems leading to the CETPs. The pre-

treatment steps are intended to avoid blockage of the collection system and also prevent corrosion in the collection system by acidic wastes. Pre-treatment consists of pre-screening, neutralisation and pre-settling. Pre-screening is provided inside the tannery in the various sectional drains. Neutralisation and pre-settling are carried out after all the sectional wastes are collected together. Some degree of equalisation is also achieved at this stage incidentally. The pre-treatment steps barring pre-screening are omitted when the individual tanneries have independent wastewater treatment plants located in tannery premises themselves.

#### *2.5.3.1. Primary Treatment*

Primary treatment is provided at the ETP sites with the objective of equalising, neutralising and clarifying the wastewater, before they are taken for secondary biological treatment. Irrespective of any pre-treatment that may have been provided the following primary treatment steps are provided at the ETP sites.

- Screening
- Grit removal
- Flow measurement
- Equalisation
- Chemical treatment
- Primary settling

The flow scheme for primary treatment will depend on whether the wastewater reaches the treatment plant by pumping or by gravity.

### 2.5.4. Secondary Biological Treatment

Secondary biological treatment aims at reducing the SS and BOD/COD of the tannery wastewater most importantly along with their parameters to acceptable levels. Secondary treatment has generally been by the activated sludge (AS) process. However, as the wastewater will carry high BOD even after primary treatment, the AS plants will consume much power. In an attempt to reduce power requirements, anaerobic treatment has been provided at times before the Activated Sludge step. So far only up flow anaerobic filters and anaerobic lagoons have been tried for anaerobic treatment and the success has been poor in both cases. Recent studies indicate that the Upflow Anaerobic Sludge Blanket (UASB) process may be more effective than anaerobic lagoon in treating tannery wastewater. However, the latter method is yet to be adopted on plant-scale.

### 2.5.5. Sludge Dewatering and Disposal

The sludge from primary and secondary treatment is generally dried on sand drying beds (SDB) and then dumped on land. However, in the case of some large CETPs constructed recently mechanical dewatering has been adopted in preference to SDB to reduce land requirements.

### 2.5.6. Sludge Dewatering and Disposal

The physical, chemical and biochemical treatment of tannery wastewater produces considerable amounts of sludge. The wastewater from a raw to finish tannery may produce as much as 0.5 tonne of dry solids per million litres of wastewater treated. The sludge will contain moisture of about 95% and the wet sludge production will be 10 tonnes per million litres. For easy handling of sludge dewatering is necessary. This reduces volume and weight

of sludge to be transported and disposed. Sludge dewatering systems range from simple sludge drying beds to complex mechanical units such as centrifuges, vacuum filters and filter presses. Sludge from tannery wastewater treatment has commonly been dewatered using sludge drying beds. In recent years, in some large common effluent treatment plants, sludge centrifuges and vacuum filters have been adopted because of the non-availability of the large area required for drying beds.

## 2.6. Activated Sludge Process

### 2.6.1. General features

The basic components of the activated sludge process are shown in the figure. In this process, the primary treated wastewater is brought into contact with pre-formed microbial flocs (activated sludge) in an aeration tank and aerated when the microbes oxidise a major part of the organic matter in the wastewater reducing its BOD. The microbes also use a small part of the organic matter for the formation of new microbial cells thus adding to the activated sludge mass initially added.

The aerated wastewater with the recycled and newly formed sludge is termed mixed liquor. The mixed liquor is led from the aeration basin to a secondary settling tank (SST) where the sludge settles down and the clear supernatant flows out as the final effluent. The settled sludge is withdrawn from the SST continuously and recycled to the head of the aeration tank as return activated sludge (RAS) to serve as the pre-formed microbial flocs mentioned earlier. The recycling of sludge from the SST to the aeration tank is an essential feature of the activated sludge process without which the process would be only plain aeration and would have poor efficiency.

If the sludge from the SST were to be returned to the aeration tank fully, the sludge would gradually increase in the system beyond its holding capacity and will start flowing out with the final effluent affecting its quality. To avoid this, part of the sludge from the system, equal to the sludge mass newly formed is wasted daily. The sludge wasted is termed as waste activated sludge (WAS) or excess activated sludge (EAS).

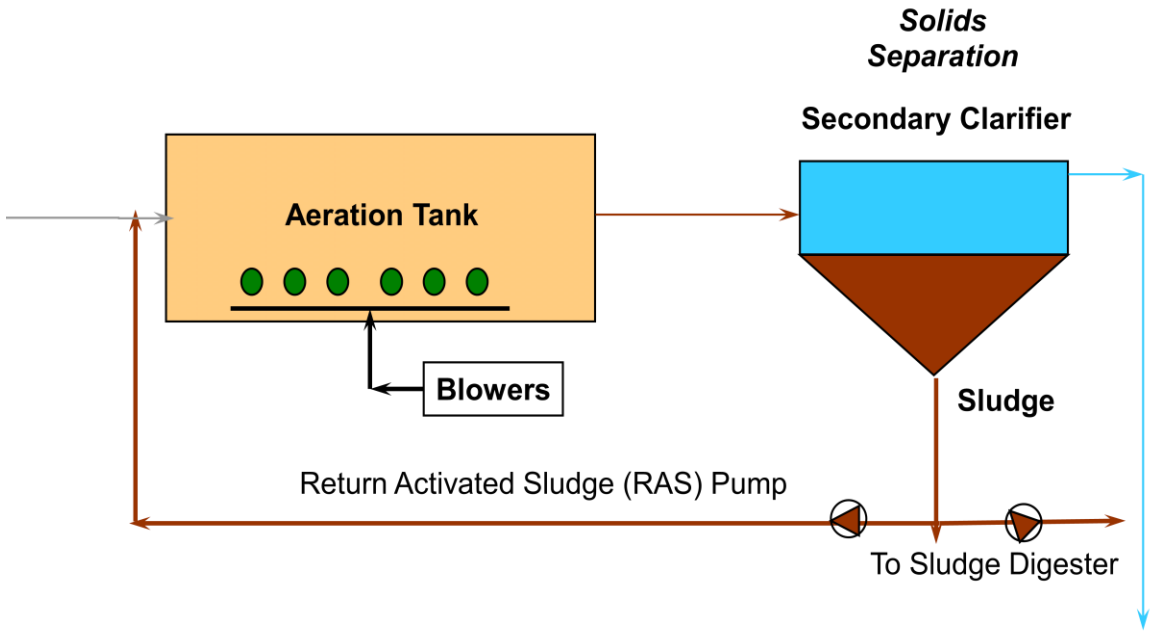



Figure 2.4 Conventional Activated Sludge Process

Table 2.5 Quantity of excess sludge generated in different ASP [22]

| **Treatment type** | **Dry solids kg/1000m$^3$ of waste water treated** | |
|---|---|---|
| | **Range** | **Typical** |
| Activated sludge | 70-100 | 80 |
| Extended aeration | 80-120 | 100 |
| Aerated lagoon | 80-120 | 120 |

Table 2.6 Physical characteristics of primary and secondary sludge [22]

| **Sludge type** | **Water content %** | **Specific gravity** | **Dry solids %** | |
|---|---|---|---|---|
| | | | **Range** | **typical** |
| Primary | 95-97 | 1.02 | 3-5 | 4 |
| Secondary | 98.8-99.2 | 1.005 | 0.8-1.2 | 1 |

Excess sludge production and organics removal in the activated sludge process, the kinetics of microbial growth determines substrate utilization and biomass production in the ASP [22]. A detailed description of microbial kinetics is out of the scope of the present study and only the most important terms related to biomass production will be further developed. During biological treatment the removal of organic compounds and cell growth take place at the same time, the ratio of biomass produced relative to the amount of substrate consumed is defined as the biomass growth yield (Y). For the treatment of municipal wastewater containing a large number of organic compounds, Y is based on a measurable parameter reflecting the overall organic compound consumption, such as BOD, total organic carbon (TOC) or chemical oxygen demand (COD).When $O_2$ and $N_2$ are used as electron acceptors during organic compounds oxidation, the microorganisms produce energy in the form of adenosine tri phosphate (ATP), which in turn is used to build new cellular constituents and increase cell mass to a certain level, above which, the cell will divide.

Due to environmental constraints and other factors the cellular biomass present in the system may decay. This process called lysis leads to the release of organic matter into the bulk liquid, which can be reutilized by the bacteria to generate more cells (cryptic growth). Part of the energy produced from the biological oxidation of organics is not used for growth but to

maintain the cell's integrity, cell repair and activity, this fraction is called maintenance metabolism and it groups and accounts for all non-growth activities (i.e. osmosis equilibration, transport of nutrients, repair, and motility amongst others). The goal for sludge reduction in the ASP then is to somehow decrease the overall biomass yield.

If the strength of the wastewater entering the aeration tank is determined by its COD (dissolved and particulate fractions) then, during biological treatment a portion of influent COD is oxidized to $CO_2$ and water and the remaining portion is converted into biomass. COD oxidation requires oxygen and biomass growth produces excess sludge; thus oxygen supply and sludge production are two very important issues related to the operation of an ASP. Oxygen supply accounts for 30-40% of the total operational cost of an ASP treatment plant [22], while sludge treatment and disposal accounts for 25-60% [23]. If it is assumed that glucose is the major organic carbonaceous source in the wastewater and biomass composition is described by the formula $C_5H_7O_2N$, then neglecting nutrients other than $N_2$:

**Microorganisms**

$$3C_6H_{12}O_6 + 8O_2 + 2NH_3 \longrightarrow 2C_5H_70_2N + 8CO_2 + 14H_2O$$

In practice COD and VSS are used to represent the organic matter and the new biomass.
The theoretical Y expressed in terms of COD is 0.39 g cells/g COD used. However, due to cell maintenance functions the actual Y would be lower than the theoretical Y determined. The biomass COD equivalent is 1.42 g $O_2$/g cells.

The total oxygen needed for substrate oxidation and endogenous respiration can be determined from the difference between the COD removed and the COD equivalent to

biomass produced. This implies that the oxygen requirement for a conventional ASP is inversely related to the sludge production; lower sludge production has higher oxygen requirements. Oxygen required for each unit of COD removed can be determined as:

$$oxygen\ consumed = COD\ removed - cells\ produced\ as\ COD\ equivalent$$

If 0.44g of oxygen is required for each gram of COD removed, the remaining portion (1 - 0.44 = 0.56 g) of the removed COD is assumed to be converted into biomass. For each gram of COD removed, 0.39 g (0.56/1.42) of biomass is produced, which represents the true biomass growth Y. When biomass undergoes death, decay and cell maintenance, a portion of their cell mass is converted into soluble secondary substrates that are further oxidized, reducing the amount of cells produced.

Table 2.7 Main treatment technologies used in excess sludge reduction at the source [22]

| **Treatment technology** | **Agent used** |
|---|---|
| Chemical | Ozone, alkaline hydrolysis, chlorine |
| Thermal | Thermal hydrolysis at temperatures greater than $150^0$C |
| Mechanical | Stirred ball mills, ultrasound, high pressure homogenizers |

The use of such technologies, besides helping to achieve significant excess sludge reduction might also help reduce operational costs in subsequent sludge treatment processes, such as anaerobic digestion, conditioning, dewatering and final disposal, even if the inclusion of any of them in a WWTP represents an initial investment and energy consumption.

### 2.6.2. Sequencing batch reactor

In the present study it was decided to use the sequencing batch reactor (SBR) to study excess sludge reduction. SBR for wastewater treatment is an ASP that operates in a sequence of fills, react, settle and draw cycles [24]. The unit operations involved in a SBR are equivalent to those in a conventional ASP (aeration, sedimentation), the main difference being that in the conventional ASP those processes take place in different tanks, while in a SBR they occur sequentially in the same reactor. Hence, SBR operates in time rather than space.Research on SBRs started as early as 1970. The basic scientific assumption that governed the development of SBR technology was that periodic exposure of the microorganisms to defined process conditions is effectively achieved in a batch-feeding system in which exposure time and frequency of exposure can be set independently of any inflow conditions [25]. SBR technology offers a great versatility in mode of operation, since aerobic and anaerobic phases can be implemented depending on the final effluent parameters desired; effluent concentrations as low as 10 mg TSS/L, 5 mg BOD/L and 5 mg total nitrogen/L have been achieved using SBR technology for municipal wastewater treatment [25]. Nowadays SBR technology is gaining a lot of acceptance all over the world due to the combination of the facts mentioned before and relatively less expensive operational costs, compared to continuous 51processes. Some of the most important advantages of the SBR technology are: simple automation, easiness to modify operational conditions, ability to select robust microbial communities, the capacity to retain treated effluent before release and the ability to adjust aeration, and the selection of the number of tanks in operation to meet loading conditions [25]. However, as with any other technology, inappropriate design and operation will cause the system to fail.

### *2.6.2.1. SBR process description*

The SBR process is characterized by a series of phases per cycle, the common phases are: fill, react settle, draw and idle; phases such as fill and react can be modified to attain certain process goals (i.e. they can be anoxic, aerated, mixed, non-mixed).

Table 2.8 main characteristics of time phases in one SBR cycle [25]

| **Time period** | **Main characteristics** |
|---|---|
| Fill | Effluent can be raw or primary settled wastewater, it also can be slow or dump fill, depending on the process goals. Some organics degradation takes place in this period of time. |
| React | Biological reactions which started during fill take place in this portion of the cycle. It can also be modified depending on process goals; usually sludge wasting takes place in this stage. Time dedicated to react can be as high as 50% or more of the total cycle time. |
| Settle | Solids separation take place in this stage and under quiescent conditions Effluent withdrawn takes place in this period of time , the mechanism |
| Decant | and time allocated for decant has to be design so that no solids exit with the effluent |
| Idle | This is the period between draw and fill, this stage can also be used for sludge wasting |

Sludge wasting can take place during react or after the clarified effluent has been discharged. This completes a cycle and the SBR is then available to start another one.

SBR technology application for the treatment of municipal wastewater has been increasing in the last decades, particularly in Europe and Asia. An extensive literature review on the use of SBR technology for different effluents, but the major application of SBR is still for the treatment of municipal wastewater, especially in small communities or in places with space limitations [22].

# 3. Materials and Methods

## 3.1. Materials

### 3.1.1 Wastewater

Waste water sample were taken from CETP Pallavaram tanners industrial effluent treatment Chennai India, at a point from primary clarifier effluent.

## 3.2. Chemicals and Equipments

### 3.2.1. Chemicals

Sulphuric acid, Silver sulphate, Potassium Dichromate, Mercuric sulphate, Distilled water, Potassium iodide, Potassium hydrogen phthalate, Oxygen cylinder, Nitrogen cylinder, Ferrous ammonium sulphate, Ferroine indicator, Starch indicator solution.

### 3.2.2. Equipments

SBR Reactor (4 L capacity), diffuser, aeration system with tubing, ozonation generator apparatus and bubble column reactor, Oven $105^0$ C, Muffle furnace $550^0$ C, Spectrophotometer (HACH, UV2500), Pipettizer, COD Digester and TKN digestion apparatus.


TKN apparatus


Spectrophotometer

Titration Stand Ozonation Apparatus

Figure 3.1 Major equipments and apparatuses used in the study

## 3.3. Description of major equipments

Ozonation generator is used to produce ozone and ozonation of the sample for a given period of time at specific ozone dose was carried in bubble column reactor. Oxygen gas (cylinder) is used as the source for the Ozonater to generate ozone. The Potassium Iodide solution traps are used for absorbing the residual / unused ozone from the Ozonation bubble column reactor. Spectrophotometer is used to measure the Chemical Oxygen Demand of the sample. TKN apparatus is used to determine the total Kjeldalh Nitrogen of a given sample.

**Software**

Design Expert 7.0, used for analysis of data.

## 3.4. Methods

### Oxidation of Sludge with Ozone

All analyses were done according to procedures given in Standard Methods (APHA, 1999). All analyses were triplicated and the values represent the mean of the measurements.Ozone was produced by the ozone generator with a maximum ozone production capacity of 5 g/h. The ozone produced from pure oxygen was bubbled through the reactor using a diffuser with the diameter of 15 mm and with the height of 25 mm. The reactor was made of pyrex-glass with a total reactor volume of 2 L; sample volume was 200 ml. Different ozonation periods ranged between 5 minutes and 45 minutes were used for evaluation of disintegration performance of sludge.

The sample used in this study is the effluent from the primary clarifier was collected from Common Effluent Treatment Plant treating tannery effluents at Pallavaram, Chennai, India. First, the ozone transfer efficiency of the Ozonater was determined. After the samples were Ozonated for different time duration, then the KI solution in the outlet traps was titrated against thiosulphate solution using starch indicator solution. To determine the optimum ozonation time; five primary treated wastewater samples were ozonated for 5, 10, 15, 30 and 45 minutes in bubble column reactor. Then total and soluble chemical oxygen demand was determined for each sample. The same experiment was repeated for three times and from the result readings of each experiment, the ozonation time which gives higher total COD and soluble COD, taken as optimum ozonation time.

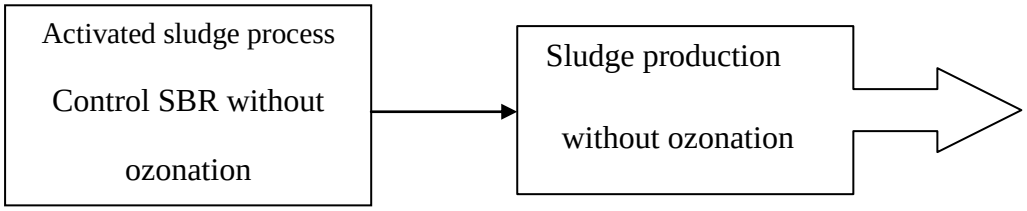

Figure 3.2 Ozonated samples at different time duration

**Sequential Batch Reactor**

To observe the effect of ozonation on excess sludge reduction, two sequential batch reactors were set up, one as control and another as experiment reactor. First both the reactors set to a level of 3500 mg/l of MLSS. Daily 1.5 litres of waste water effluent which was collected from the effluent of primary clarifier was fed to both the control and experiment reactors. Two hundred millilitre of well mixed liquor from the experiment reactor was taken for ozonation and it was fed back to the reactor after being ozonated for fifteen minutes determined optimum ozonation time. Daily 1.5 litres of clear effluent after settling was

discarded from both reactors. Daily the mixed liquor suspended solid (MLSS), total COD, soluble COD were determined for both the control and experiment reactors.

I.




II.

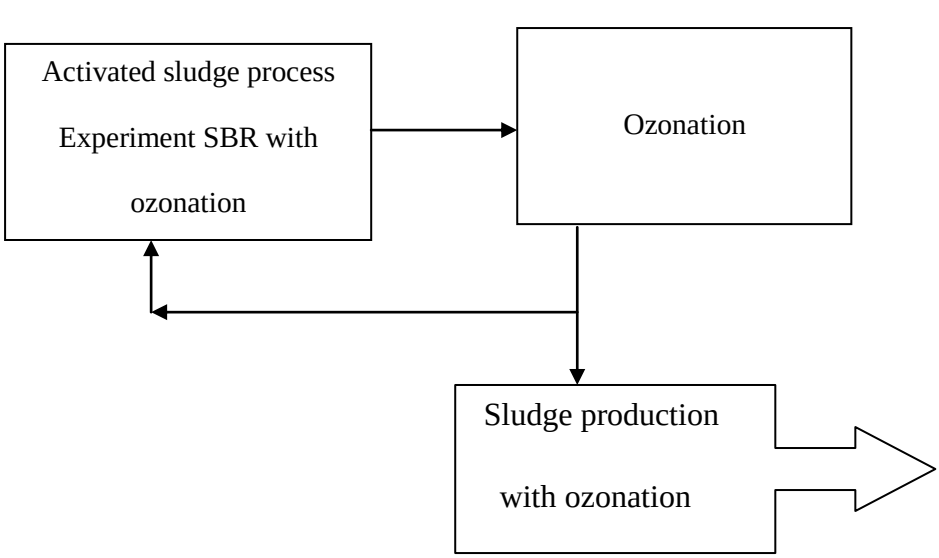



Figure 3.3 Process flow diagram showing the methodology followed for the study

## 3.5 Analytical Methods

The parameters that will be measured during the process were mentioned below with their standard procedures (APHA 1999).

### 3.5.1 Mixed Liquor Suspended Solids (MLSS)

The combination of raw sewage and biological mass is commonly known as Mixed Liquor. In all activated sludge plants, once the sewage (or industrial wastewater) has received sufficient treatment, excess mixed liquor is discharged into settling tanks and the treated supernatant is run off to undergo further treatment before discharge. Part of the settled material, the sludge (RAS), is returned to the head of the aeration system to re-seed the new sewage entering the tank. Mixed Liquor is a mixture of raw or settled wastewater and activated sludge within an aeration tank in the activated sludge process Mixed Liquor Suspended Solids (MLSS) is the concentration of suspended solids in the mixed liquor, usually expressed in milligrams per litre (mg/l).

A well-mixed sample was filtered through a weighed standard glass-fibre filter and the residue retained on the filter was dried to a constant weight at 103 to 105°C. The increase in weight of the filter represents the total suspended solids. If the suspended material clogs the filter and prolongs filtration, it may be necessary to increase the diameter of the filter or decrease the sample volume. To obtain an estimate of total suspended solids, difference between total dissolved solids and total solids is calculated.

$$mg\ total\ suspended\ solids\ per\ litre = [(A - B) * 100]/(sample\ volume, ml)$$

Where

A = weight of filter + dried residue (mg)

B = weight of filter (mg)

### 3.5.2 Chemical Oxygen Demand (COD) (Closed Reflux Colorimetric Method)

For measuring COD, closed reflux, colorimetric method was followed.

**Reagents preparation**

a. Digestion solution: To about 500 ml distilled water, 10.216 g potassium dichromate ($K_2Cr_2O_7$) which was previously dried at 103˚C for 2 hrs, 167 ml conc. $H_2SO_4$ and 33.3 g $HgSO_4$ was added. It was dissolved, cooled to room temperature and diluted to 1000 ml.

b. Sulphuric acid reagent: $Ag_2SO_4$ (crystals or powder) was added to conc. $H_2SO_4$ at the rate of 5.5 g $Ag_2SO_4$ /kg $H_2SO_4$. It was allowed to stand for 1 or 2 days.

**Preparation of calibration curve**

100 mg of Potassium hydrogen phthalate which was previously dried at 105˚C for 1 hr was weighed and made up to 250 ml with distilled water. The COD tubes were filled as indicated in the table 2.3 and left for digestion for 2 hours in COD digester. Absorbance of sample was measured in UV spectrophotometer at 600 nm.

Table 3.1 Composition of COD calibration samples

| KHP(ml) | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 | 1.2 | 1.4 | 1.6 | 1.8 | 2.0 |
|---|---|---|---|---|---|---|---|---|---|---|
| Distilled water (ml) | 2.3 | 2.1 | 1.9 | 1.7 | 1.5 | 1.3 | 1.1 | 0.9 | 0.7 | 0.5 |
| $H_2SO_4$ (ml) | 3.5 | 3.5 | 3.5 | 3.5 | 3.5 | 3.5 | 3.5 | 3.5 | 3.5 | 3.5 |
| $K_2Cr_2O_7$(ml) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |

**Estimation of total COD**

1 ml of the sample and 1.5 ml of water, 1.5 ml of potassium dichromate solution and 3.5 ml of sulphuric acid solution was added. The sample was left for digestion in the COD digester at 150˚C for 2 hours. Absorbance of sample was measured in UV spectrophotometer at 600 nm.

**Estimation of soluble COD**

About 5 ml of the sample was filtered through a 0.45 micron filter paper. 1 ml of the filtered solution was taken along with 1.5 ml of water, 1.5 ml of potassium dichromate solution and 3.5 ml of sulphuric acid solution and left for digestion in the COD digester at 150˚C for 2 hours. Absorbance of sample was measured in UV spectrophotometer at 600 nm.

**Calculation**

For calculating COD, the following formula was used:

$$\text{COD (mg/L)} = \frac{[(\text{Absorbance of sample}) - (\text{Absorbance of blank})] * 0.49509^* \text{ x} * 1000}{\text{Sample volume}}$$

Where

x = 1/ Slope

(Slope is obtained from the absorbance versus concentration graph for samples).

### 3.5.3 Ammonia Nitrogen (Titrimetric Method)

**Procedure**

***a. Preparation of equipment:*** Add 500 ml water and 20 ml borate buffer adjust pH to 9.5 with 6*N* NaOH solution, and add to a distillation flask. Add a few glass beads or boiling chips and use this mixture to steam out the distillation apparatus until distillate shows no traces of ammonia.

***b. Sample preparation:*** Use 500 ml dechlorinated sample or a known portion diluted to 500 ml with water. When NH3-N concentration is less than 100 μg/L, then use a sample volume of 1000 ml. Remove residual chlorine by adding, at the time of collection, dechlorinating agent equivalent to the chlorine residual. If necessary, neutralize to approximately pH 7 with dilute acid or base, using a pH meter. Add 25 ml borate buffer solution and adjust to pH 9.5 with 6*N* NaOH using a pH meter.

***c. Distillation:*** To minimize contamination, leave distillation apparatus assembled after steaming out and until just before starting sample distillation. Disconnect steaming-out flask and immediately transfer sample flask to distillation apparatus. Distil at a rate of 6 to 10 ml/min with the tip of the delivery tube below the surface of acid receiving solution. Collect distillate in a 500-mL Erlenmeyer flask containing 50 ml indicating boric acid solution for titrimetric method. Distil ammonia into 50 ml 0.04*N* $H_2SO_4$ for the ammonia-selective electrode method and for the phenate method. Collect at least 200 ml distillate. Lower distillation receiver so that the end of the delivery tube is free of contact with the liquid and continue distillation during the last minute or two to cleanse condenser and delivery tube. Dilute to 500 ml with water. When the phenate method is used for determining $NH_3$-N, neutralize distillate with 1*N* NaOH solution.

***d. Ammonia determination:*** Determine ammonia by the titrimetric method

***e. Sludge or sediment samples:*** Rapidly weigh to within ±1% an amount of wet sample, equivalent to approximately 1 g dry weight, in a weighing bottle or crucible. Wash sample into a 500-mL kjeldahl flask with water and dilute to 250 mL. Add a piece of paraffin wax to distillation flask and collect only 100 mL distillate.

***f.*** Titrate ammonia in distillate with standard 0.02*N* $H_2SO_4$ titrant until indicator turns a pale lavender.

***g. Blank:*** Carry a blank through all steps of the procedure and apply the necessary correction to the results.

**CALCULATION**

a. Sludge/Sediment Samples

$$\text{mg } NH_3\text{-N/kg} = \frac{(A - B) \times 280}{\text{g dry wt sample}}$$

Where:

$A$ = volume of $H_2SO_4$ titrated for sample, mL, and

$B$ = volume of $H_2SO_4$ titrated for blank, ml.

Determination of Mixed liquor Suspended Solid: Mixed liquor suspended solid (MLSS) for mixed liquor from both the experiment and control reactor was determined daily. MLSS was determined using standard methods for the examination of water and wastewater, SMWW2540 B.

Determination of Ozone dose: Ozone dose for the Ozonation apparatus was determined using standard methods for the examination of water and wastewater, SMWW2350E semi batch method.

Determination of Chemical Oxygen Demand: Chemical oxygen demand (COD) for effluents from both control and experiment sequential batch reactors was determined using standard methods for the examination of water and waste water, SMWW5220D closed reflux, colorimetric method.

Determination of total Kjeldalh nitrogen: Total Kjeldalh nitrogen (TKN) for the effluents from both the control and experiment reactor was determined using standard methods for the examination of water and wastewater SMWW4500_$N_{org}$ macro-Kjeldalh method.

# 4. Result and Discussion

## 4.1. Optimum ozone dosage and optimum ozonation time

The effect of ozonation time on bio-sludge has been carried out for different time intervals upto 45 min and the total and soluble COD of sludge has been determined. The table 4.1 and the figures 4.1 and 4.2 show the profile of total and soluble COD for wastewater sample with MLSS (bio-sludge) after ozonation at different time period. Total and soluble COD was used as food to microorganisms in the reactor. From the Fig 4.2, it is observed that the total COD reduces with time from 3909 mg/L to 1433 mg/L with ozonation period of 45 min. However, it showed different profile of reduction of soluble COD with respect to time. With increase in ozonation periods upto 15 min, the soluble COD increased from 243 mg/L at initial

concentration to 469 mg/L at 15 min indicating release of lysis products into the solution. With further increase in ozonation period from 15 to 45 min resulted in reduction of soluble COD from 465 mg/L to 365 mg/L indicating that the soluble COD getting oxidised at higher ozonation period. Based on this investigation, it is observed that the ozonation period of 15 min is found to be optimum ozonation period. Hence, all the further experiments were carried at optimum ozonation period of 15 min. The optimum ozone dose respective to optimum ozonation time is estimated to be 0.168g-$O_3$/g-MLSS.

Table 4.1 Total and soluble COD of Ozonated samples

| **Ozonation time, min** | **Total COD, mg/l** | **Soluble COD, mg/l** |
|---|---|---|
| 0 | 3909 | 243 |
| 5 | 2997 | 330 |
| 10 | 2779 | 365 |
| 15 | 2432 | 469 |
| 30 | 1563 | 339 |
| 45 | 1433 | 365 |

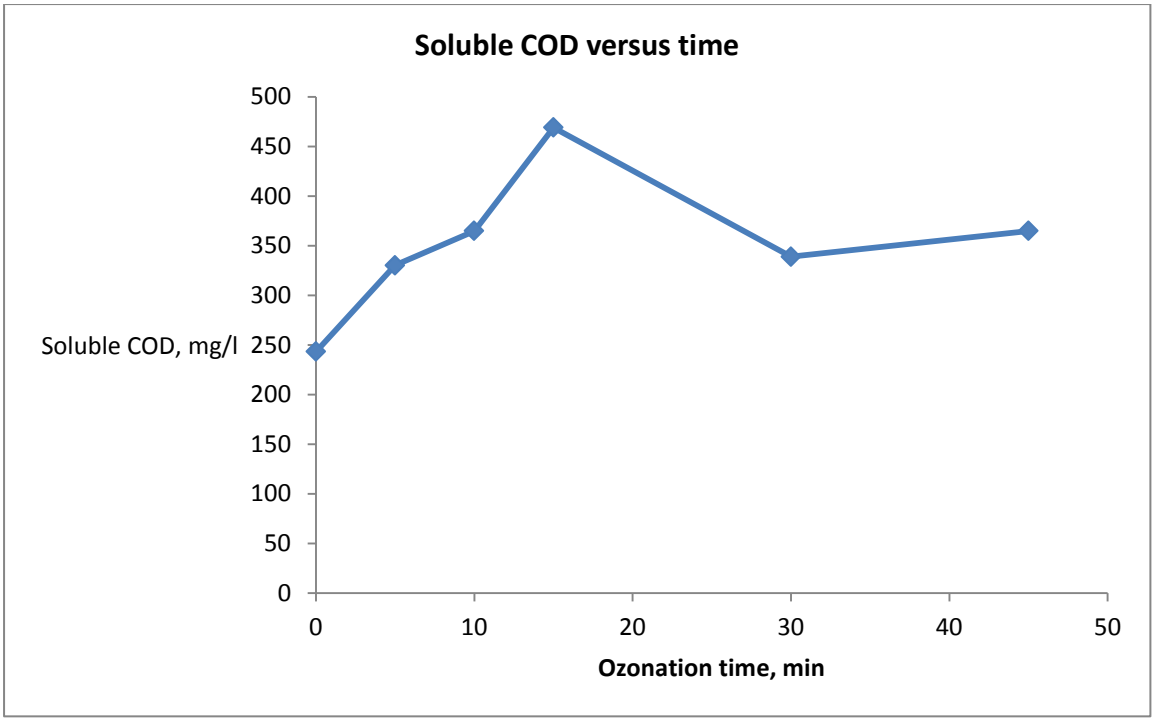



Figure 4.1 Soluble COD vs. Ozonation period

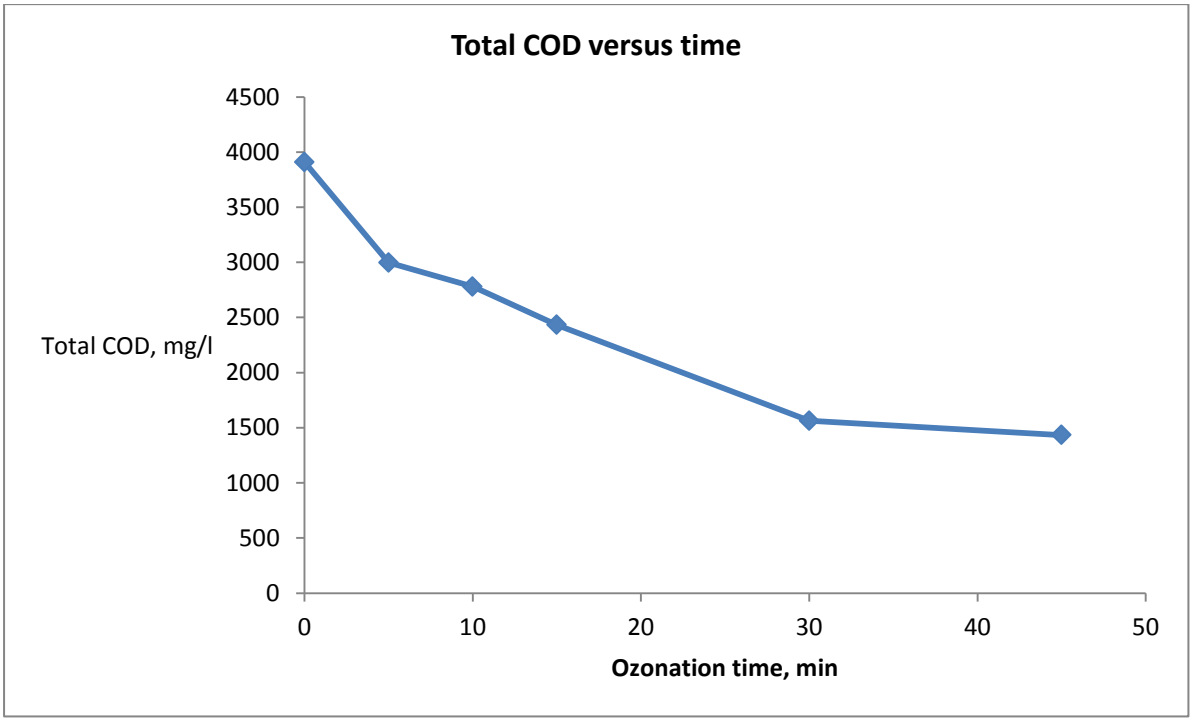



Figure 4.2 Total COD vs. Ozonation period

**Effect of Ozonation on chemical oxygen demand**

The lysis of the sludge induced by ozone is reflected in the evident reduction of the solids content in the activated sludge, and the increase in the soluble fraction of the sludge with ozone dose. In effect, the reduction of the amount of solids in the mixed liquor was up to 35.1% at 0.168 g $O_3$/g MLSS dosage. The efficiency of the sludge reduction is achieved at certain optimal ozone beyond which the ozone not only disintegrates the biomass cells but also mineralizes the soluble organics. It can be observed that the total COD of the ozonated sludge decreases with ozone dose resulting in a higher soluble COD fraction. The total COD decreased from 3,908 mg/L to 2,432 mg/L at 0.168 g O3/g MLSS, while the soluble COD content increased from 260 mg/L to 521 mg/L at the same dose. If a COD balance is applied to the ozonated sludge samples, the total COD decrease with ozone dose increase indicates that part of it was mineralized into $CO_2$.

It can be observed in the Figure 4.1 and 4.2 that as the ozone dose increases, the soluble COD concentration rises and the total COD concentration drops. It seems that the initial soluble COD concentration in the untreated sludge was considerable so that the ozone first mineralized this soluble fraction, and subsequently, it acted over the particulate fraction or biomass. At this stage, when the ozonation period ranged from 5 to 15 minutes the soluble COD had a significant increase. However, after fifteen minutes the soluble COD concentration increase was not significant any-more. The results suggest that at the ozonation periods higher than 15 minutes, the ozone not only solubilises the sludge, but it starts to mineralize the existing soluble organics in the medium, decreasing its efficiency for sludge disintegration.

## 4.2. Overall sludge reduction

Ozone is a very reactive oxidizing agent; it reacts with sludge compounds in two different ways, the direct and the indirect reaction. Both reactions occur simultaneously; the direct reaction rate is lower and depends on the structure of the reactants. In this study, ozone was used as an oxidant to induce the death and lysis of biomass, and to improve the biodegradability of the dead biomass, and then the ozonated sludge was recycled into MBR as substrate for further metabolism. Through batch study, it was found that ozone could disrupt the cell walls and cause the release of cytoplasmic materials from the cells, and then the amounts of soluble organics in the solution increased with ozonation time. With the rise of soluble organics, the amount of soluble organics to be mineralized increased as well, which would reduce the soluble organics content. For the counter action between these two aspects, a pseudo-balance could be achieved, and soluble organics would vary in a limited range. Sludge ozonation also increased the contents of soluble nitrogen and phosphorus in the solution. On the basis of batch study, a suitable ozone dosage of 0.168 g O3/g MLSS was found to be optimal for solubilising the biosludge and making it available for biological treatment in SBR.

In terms of overall sludge reduction, 54% reduction of the total sludge mass could be achieved by ozone treatment at 0.2 g-$O_3$/g-MLSS for municipal sludge. Compared to municipal sludge reduction the overall excess sludge reduction is 35.1% at 0.168 g-$O_3$/g-MLSS for the excess sludge from SBR treating primary treated tannery waste water as influent.

The overall sludge reduction by the application of ozone for excess sludge from sequential batch reactors of control and ozonated sludge is shown in the Table 4.2; excess sludge generated from the experiment reactor is less than that of control reactor both treating tannery wastewater and operated at same process conditions.

Table 4.2 Mixed Liquor Suspended Solid, MLSS and Excess MLSS for both control and experiment reactors

| Day | **MLSS, mg/l** | |
|---|---|---|
| | **control** | **Reactor** |
| 1 | 3500 | 3500 |
| 2 | 3750 | 3745 |
| 3 | 3900 | 3850 |
| 4 | 4020 | 3958 |
| 5 | 4139 | 4083 |
| 6 | 4300 | 4193 |
| 7 | 4480 | 4326 |
| 8 | 4720 | 4476 |
| 9 | 4935 | 4613 |
| 10 | 5114 | 4719 |
| 11 | 5296 | 4833 |
| 12 | 5483 | 4948 |
| 13 | 5723 | 5105 |
| 14 | 5981 | 5222 |
| 15 | 6220 | 5346 |

| Day | MLSS, mg/l | |
|---|---|---|
| | **control** | **Reactor** |
| 16 | 6451 | 5460 |
| 17 | 6660 | 5617 |
| 18 | 6922 | 5722 |
| | Percentage reduction of MLSS, 35.1% | |

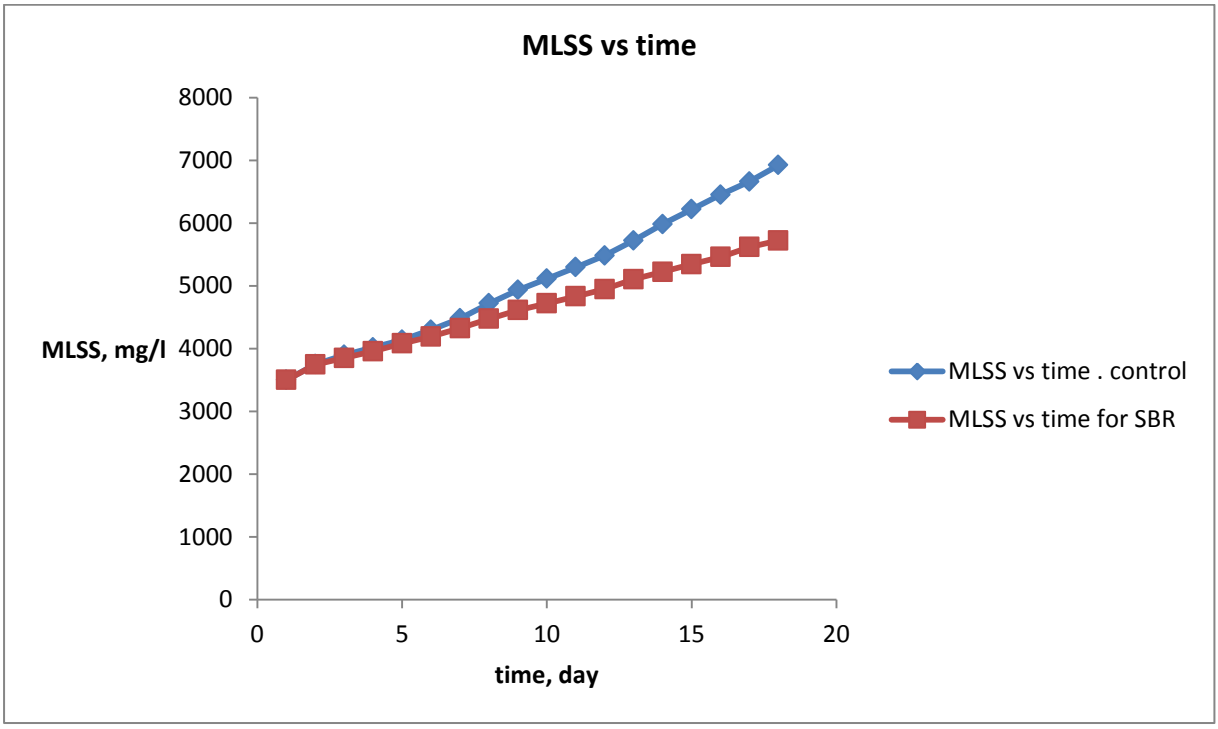



Figure 4.3 MLSS concentrations versus time for control and experiment reactors

Table 4.2 and figure 4.3 shows that the mixed liquor suspended solid for the control SBR exceeds that of experiment SBR.

Table 4.3 Total COD and soluble COD for the effluent for both control and experiment

| Days of operation | Total COD for effluent | | Soluble COD for the effluent | |
|---|---|---|---|---|
| | Experimental SBR | Control SBR | Experimental SBR | Control SBR |
| 1 | 524 | 546 | 366 | 363 |
| 2 | 524 | 546 | 366 | 363 |
| 3 | 524 | 546 | 366 | 363 |
| 4 | 554 | 546 | 376 | 379 |
| 5 | 554 | 528 | 376 | 379 |
| 6 | 533 | 528 | 371 | 379 |
| 7 | 533 | 528 | 371 | 369 |
| 8 | 515 | 520 | 365 | 369 |
| 9 | 515 | 520 | 365 | 392 |
| 10 | 563 | 567 | 390 | 385 |
| 11 | 537 | 585 | 376 | 388 |
| 12 | 546 | 567 | 383 | 371 |
| 13 | 533 | 528 | 363 | 387 |
| 14 | 546 | 554 | 385 | 422 |
| 15 | 576 | 585 | 408 | 408 |
| 16 | 537 | 589 | 396 | 396 |
| 17 | 554 | 576 | 386 | 350 |
| 18 | 511 | 511 | 361 | 363 |

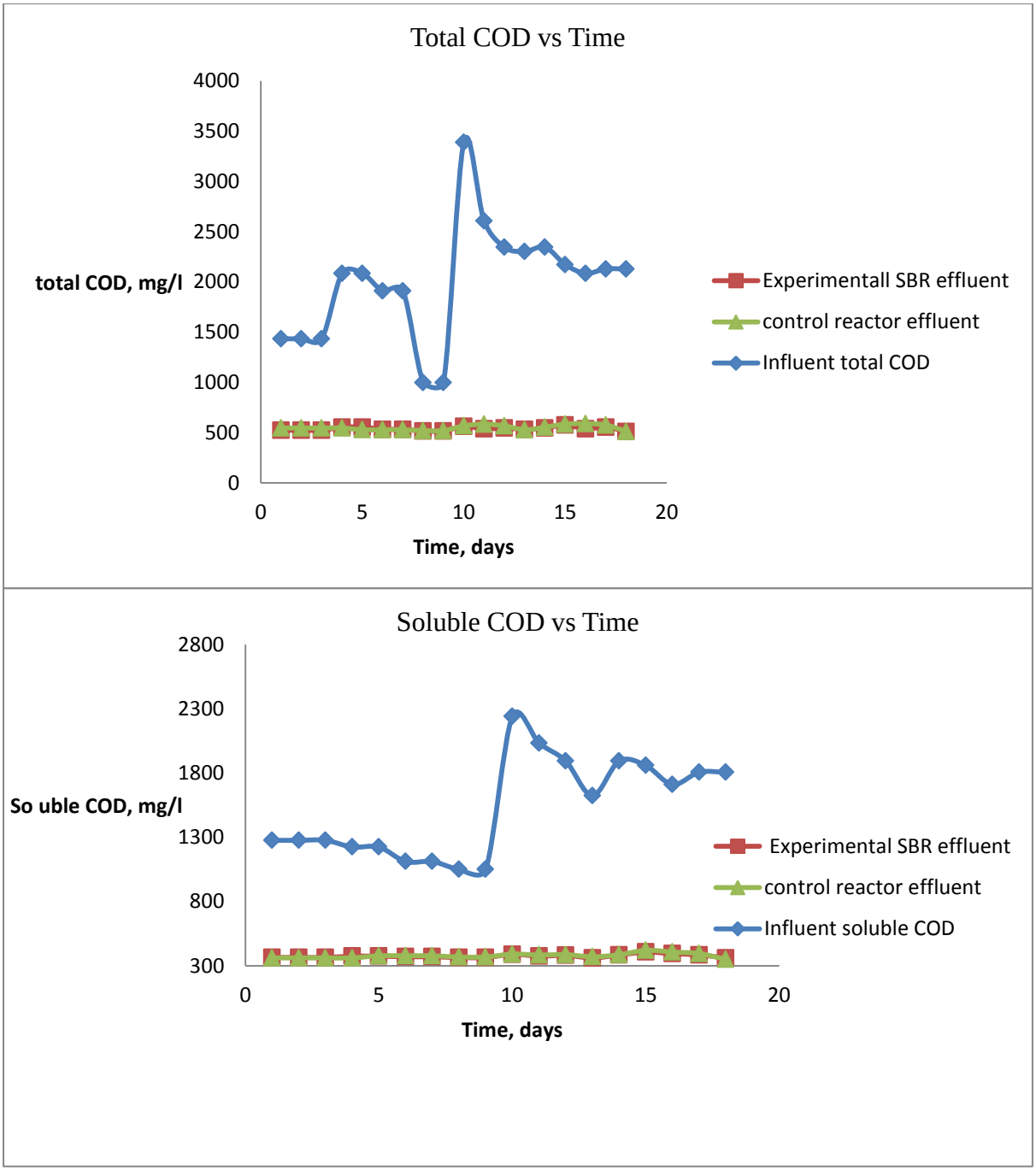



Figure 4.4 Total COD and Soluble COD versus time

From table 4.3 and figure 4.4, it is shown that total COD and soluble COD of the effluents from control and experiment SBRs are close to each other and to the discharge limit. It can be seen also that the addition of ozonated sludge does not affect the performance of biological treatment process.

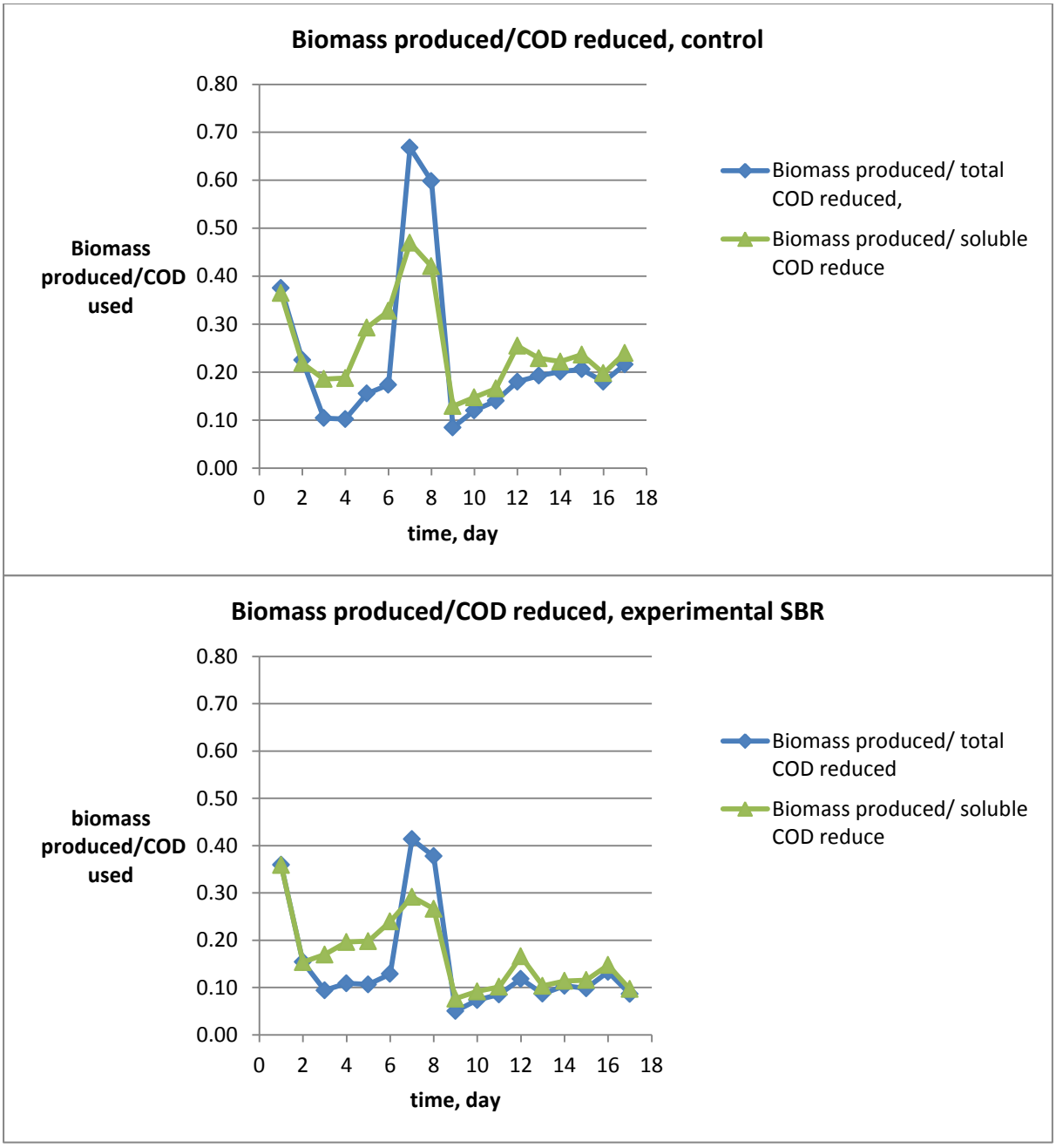
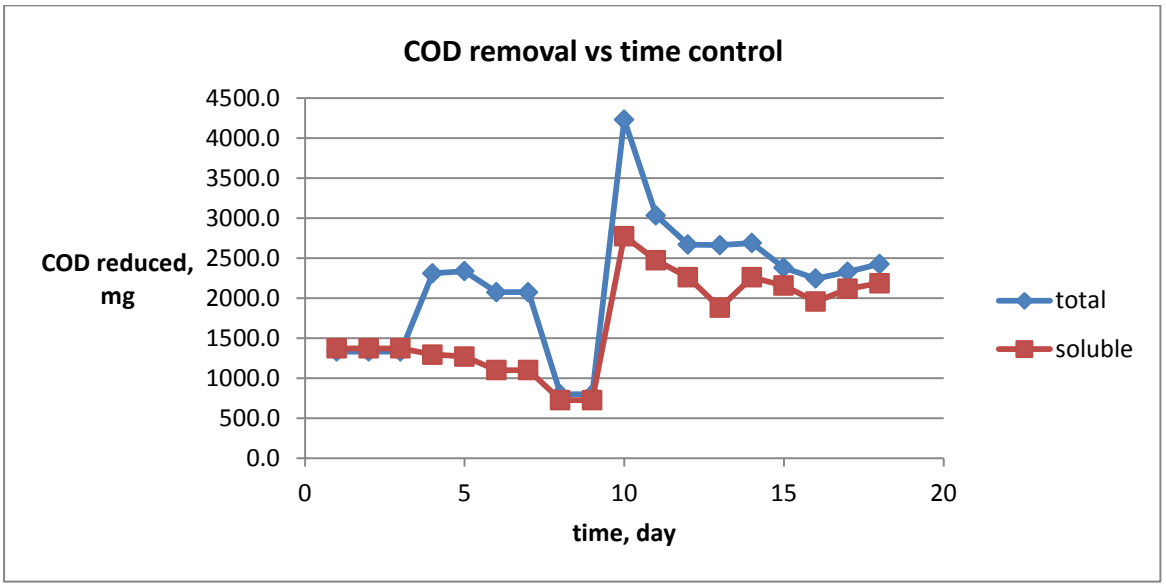



Figure 4.5 Biomass produced/COD reduced

From figure 4.5 it can be seen that biomass produced per COD reduced is less than the theoretical value (0.39).



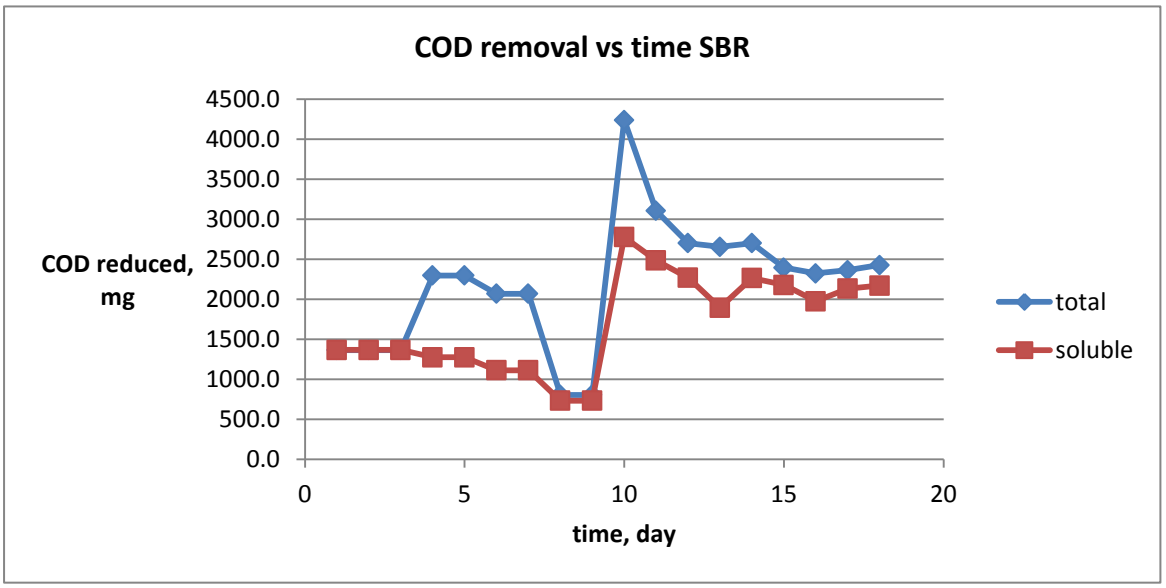




Figure 4.6 COD removed versus time for control and experimental SBRs

Table 4.4 TKN measurements for the effluent from the experiment SBR reactor

| **Initial Concentration = 200 mg/L Ammonia Nitrogen and HRT = 24 Hrs** | | |
|---|---|---|
| Day | Initial TKN (mg/L) | Final Effluent TKN (mg/L) |
| 1 | 212.8 | 123.2 |
| 4 | 207.2 | 100.8 |
| 8 | 207.2 | 84 |
| 12 | 201.6 | 78.4 |
| 15 | 201.6 | 72.8 |
| 18 | 201.6 | 72.8 |

From table 4.4, the TKN values for the effluent from the experiment SBR is very near or less than the discharge limit (100 mg/L).

## 4.3. Economical aspect of integrating ozonation to ASP for sludge reduction in Tannery Effluent Treatment

Pallavaram Tanners Industrial Effluent Treatment, PTIET Co. Ltd started in 1995 contains 113 tanneries working as wet blue starting raw material. Total area encompasses 1.2 hectares. Tanneries are located all around the CETP. Individual tanneries have their own pre-treatment. There are eight collection wells from where waste pumped into CETP. Previously BOD discharge standard was 30 mg/l but now working for zero liquid discharge. Design flow rate of 3000 $m^3$/day.

Energy consumption cost of about US$ 1.8 is needed to produce 1 kg of ozone gas. Based on the experimental data, the operating cost of sludge ozonation could be calculated. Taking the ozonated sludge flow rate = 0.01 Q (where Q stands for influent flow rate) and ozone dosage was 0.168g $O_3$/ g MLSS.

U$ 1.8 is needed to produce 1 kg of ozone gas

- SBR was maintained at about 3500 mg/l
- dosage was 0.168g $O_3$/ g MLSS

Thus, the sludge ozonation operating cost is equal to:

$$= (\text{US\$ } 1.8 * 10 \text{ kg MLSS/m3} * 0.168\text{kg O3/kg MLSS})$$

= US$3.024/m3 waste water.

Capacity: 3000 $m^3$/day

Ozonated sludge flow rate = 0.01Q = 0.01*3000m3/day = 30m3/day

Assuming 300days/yr becomes 9000m3/yr

The sludge ozonation operating cost is equal to;

US$3.024/m3 * 9000m3/yr = US$27216/ yr

Secondary sludge produced from conventional ASP will be:

[3000$m^3$/day] *[1.5kg/$m^3$]*[0.7]*[0.3] = 945 kg/day

= 283500kg/yr

Secondary sludge produced from ASP with ozonation will be:

Percentage reduction: 35.1%

[3000$m^3$/day] *[1.5kg/$m^3$]*[0.7]*[0.3]*[0.649] = 613.305 kg/day

= 183991.5kg/yr

Secondary sludge reduced due to ozonation

=283500kg/yr - 183991.5kg/yr

= 99508.5kg/yr or 99.508ton/yr

For treatment of hazardous sludge from wastewater treatment plant in hazardous waste landfill site is US$100 per ton.

Therefore, saving due to sludge reduction for treatment of hazardous waste in landfill site will be:

= [99.508.4ton/yr] * [$100/ton] = US$9950.8/yr

Whereas in a conventional wastewater treatment plant, the handling, treatment and ultimate disposal of wasted bio solids account for from 50% to 60% of the operating costs of the plant, which means that sludge ozonation process could reduce the operating cost of combined wastewater and excess sludge treatment.

## 4.4. Data analysis

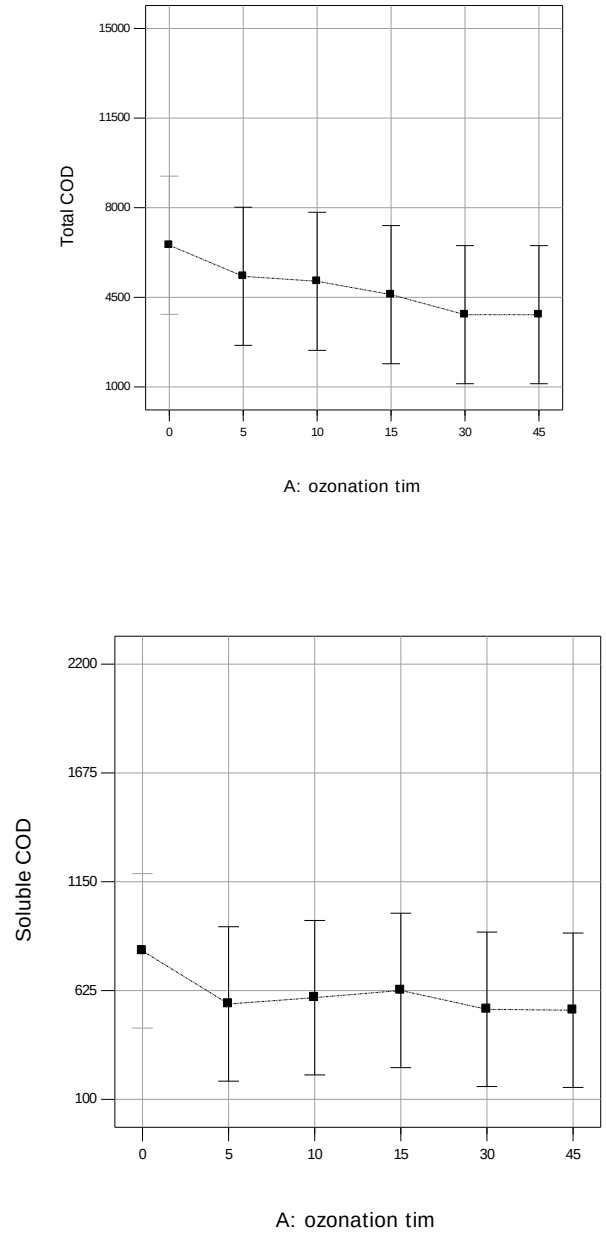



Figure 4.7 Graph of chemical oxygen demand at different Ozonation periods

The soluble COD at Ozonation period of fifteen minutes is higher which is needed and therefore taken as optimum Ozonation period for Ozonation of effluent sample from the experiment SBR reactor.

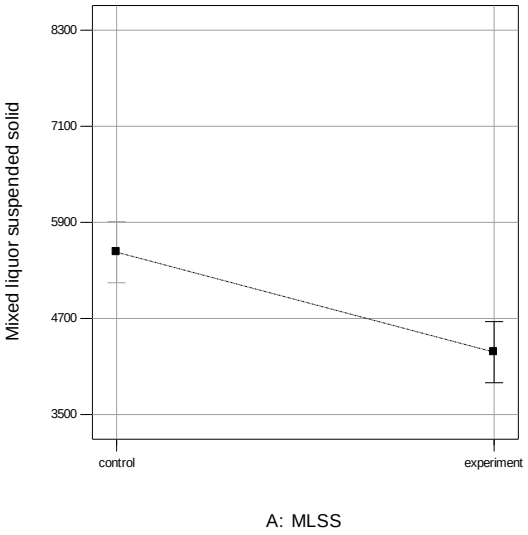



Figure 4.8 MLSS for both control and experiment

Table 4.5 Analysis of variance table for MLSS in control and experiment reactors

| | **Sum of squares** | **df** | **Mean square** | **F- value** | **p-value prob > F** |
|---|---|---|---|---|---|
| Model | 1.403E+007 | 1 | 1.403E+007 | 11.06 | 0.0021 |
| MLSS | 1.403E+007 | 1 | 1.403E+007 | 11.06 | 0.0021 |
| Pure Error | 4.312E+007 | 34 | 1.268E+006 | | |
| **Treatment means** | | | | | |
| Control | 5527.33 | | | | |
| experiment | 4278.83 | | | | |

From table 4.5 it is shown that the MLSS of the experiment SBR reactor is lower than the control. The P- value indicates that the difference between the mean MLSS of the experiment and the control SBR reactors is significant.

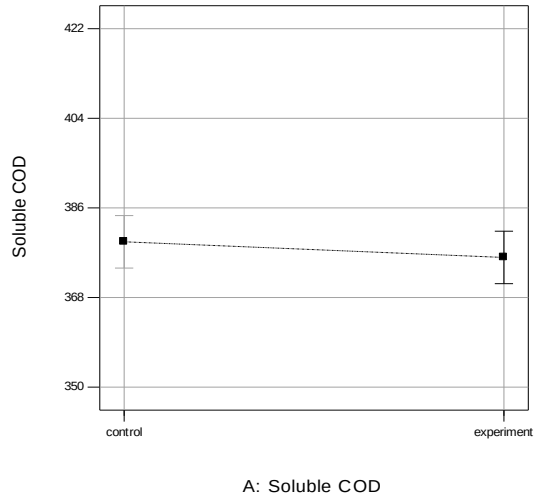



Figure 4.9 Soluble COD for the effluent from control and experiment reactors

Table 4.6 Analysis of variance table for soluble COD

| | **Sum of squares** | **df** | **Mean square** | **F- value** | **p-value prob > F** |
|---|---|---|---|---|---|
| Model | 88.54 | 1 | 88.54 | 0.37 | 0.5497 |
| Soluble COD | 88.54 | 1 | 88.54 | 0.37 | 0.5497 |
| Pure Error | 8243.54 | 34 | 242.46 | | |
| **Treatment means** | | | | | |
| Control | 379.19 | | | | |
| experiment | 376.05 | | | | |

From table 4.6 it is shown that the mean soluble COD for the experiment and control SBR reactors is almost the same. And the P-value indicates that the difference between the means of control and experiment soluble COD is insignificant.

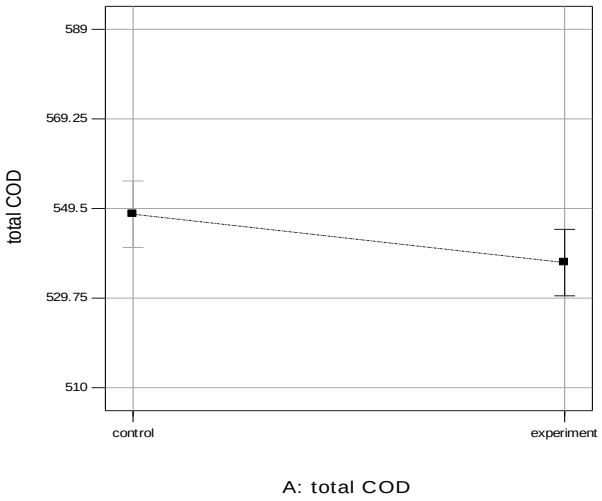



Figure 4.10 Total COD for control and experiment reactors

Table 4.7 Analysis of variance table for total COD

| | **Sum of squares** | **Df** | **Mean square** | **F- value** | **p-value prob > F** |
|---|---|---|---|---|---|
| Model | 1021.75 | 1 | 1021.75 | 2.18 | 0.1490 |
| Total COD | 1021.75 | 1 | 1021.75 | 2.18 | 0.1490 |
| Pure Error | 15930.59 | 34 | 468.55 | | |
| **Treatment means** | | | | | |
| Control | 548.24 | | | | |
| Experiment | 537.58 | | | | |

From table 4.7 it is shown that the mean total COD of the experiment and control SBR reactors is almost the same. And the P- value indicates that the difference between two mean total CODs of the reactors is insignificant.

# 5. Conclusion and Recommendations

## 5.1. Conclusion

Significant sludge reduction has been demonstrated by incorporating an Ozonation of excess sludge as compared to conventional activated sludge control system with a 24 hr retention time. With this sludge reduction, there has been no observation of deterioration in performance. One of the most important problems common effluent treatment plants have been facing is the production of excess sludge, to be treated and disposed. The sludge treatment and disposal can contribute to a large fraction of the total costs of wastewater treatment plant.

The reduction of excess sludge by means of ozonation appears to be feasible. The sludge solubilisation increases up to an optimum ozone dose after which its efficiency starts to deteriorate. The optimal ozone dose for sludge solubilisation was found to be about 0.168 g $O_3$/g MLSS. Further, it appears that at dosages higher than 0.168 g $O_3$/g MLSS, the ozone not only solubilises the sludge, but also starts to mineralize the existing soluble organics in the bulk MLSS, decreasing its efficiency for sludge disintegration.

It was observed that 15 minutes is the optimum Ozonation time for oxidation of excess sludge from SBR treating primary treated tannery waste water as influent. And the optimum

ozone dose respective to optimum Ozonation time was 0.168g-$O_3$/g-MLSS. It was observed that COD reduction was in the range of 548.236mg/l total COD and 379.185 soluble COD for control SBR and 537.581 total COD and 376.049 soluble COD for SBR with ozonated sludge at total cycling time of 24 h. In terms of overall sludge reduction, 35.1% reduction of the excess sludge could be achieved by ozone treatment at 0.168 g-$O_3$/g-MLSS.

This thesis work will be valuable if the common effluent treatment plants for leather industries are aware of the economic and environmental impacts due to the discharge of excess sludge by the use of conventional activated sludge process. The concentrations of organics in biosludge from biological wastewater treatment could be reduced by 35.1% resulting in overall reduction in organics from overall sludge (primary + secondary) from wastewater leading to reduction in sludge disposal cost. The significance of ozonation of excess sludge and feeding the filtrate back to the biological reactor is stated in this thesis work would lead to reduction in operational costs and meet the discharge limits.

## 5.2. Recommendations

Based on the presented results and on observations made during this research, the following topics of study are recommended to better understand the mechanisms of excess sludge reduction during Ozonation of excess sludge.

1. Characterization of the excess sludge before and after Ozonation helps to know exactly what physical and chemical changes are occurring due to Ozonation.
2. Optimization of ozone dose requirement for Ozonation of excess sludge emanating from common effluent treatment plants treating tannery effluent, by varying the ozone dose and reactor configurations.

3. The feasibility of Ozonation of excess sludge in combination with other processes like UV, thermal etc. for tannery waste water treatment plants.

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## Annexes

Annex 1: provisional standards for discharge of effluent by Ethiopian tanning and finishing industries.

| Parameter | Limit Value |
|---|---|
| Temperature | $40^{o}C$ |
| pH | 6 – 9 |
| $BOD_5$ at $20^{0}C$ | 90% removal or 200 mg/l, whichever is less |
| COD | 500 mg/l |
| Suspended solids | 50 mg/l |
| Total ammonia (as N) | 30 mg/l |
| Total nitrogen (as N) | 80% removal or 60 mg/l, whichever is less |
| Total phosphorus (as P) | 80% removal or 10 mg/l, whichever is less |
| Oils, fats, and grease | 15 mg/l |
| Mineral oils at oil trap or interceptors | 20 mg/l |
| Chromium (as total Cr) | 2 mg/l |
| Chromium (as Cr VI) | 0.1 mg/l |
| Chlorides (as Cl) | 1000 mg/l |
| Sulphides (as S) | 1 mg/l |

Annex 2: Indian Standards for Discharge of Industrial IS: 2490-1982

| S. № | Parameters | Into Inland Surface Water | Into Marine Coastal Waters | Into Public sewers |
|---|---|---|---|---|
| 1 | Colour/ Odour | - | - | - |
| 2 | Suspended Solids, mg/L | 100 | 100 | 600 |
| 3 | Particle Size Suspended Solids | Shall pass 850 micron IS sieve | Floatable Solids Max 3mm Settable Solids Max 850 microns | - |
| 4 | Dissolved Solids (In organic) mg/L Max | 2100 | - | 2100 |
| 5 | pH | 5.5-9 | 5.5-9 | 5.5-9 |
| 6 | Temperature $^{o}C$ | Shall not exceed 40 in any section of the stream within 15metres | 45 at the point of discharge | 45 at the point of discharge |
| 7 | Oil & Grease, mg/L, Max | 10 | 20 | 20 |

| № | Parameters | Into Inland Surface Water | Into Marine Coastal Waters | Into Public sewers |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| 8 | Total Residual Chlorine, mg/L, Max | 1 | 1 | - |
| 9 | Ammonical Nitrogen (as N), mg/L, Max | 50 | 50 | 50 |
| 10 | Total Kjeldahl Nitrogen (as N), mg/L, Max | 100 | 100 | - |
| 11 | Free Ammonia (as NH3), mg/L, Max | 5 | 5 | - |
| 12 | Biochemical Oxygen Demand (5 Days at $20^{o}C$), Max | 30 | 100 | 350 |
| 13 | Chemical Oxygen Demand, mg/L, Max | 250 | 250 | - |
| 14 | Arsenic (as As), mg/L, Max | 0.2 | 0.2 | 0.2 |
| 15 | Mercury (as Hg), mg/L, Max | 0.01 | 0.01 | 0.01 |
| 16 | Lead (as Pb), mg/L, Max | 0.1 | 1.0 | 1.0 |
| 17 | Cadmium (as Cd), mg/L, Max | 2 | 2 | 1 |
| 18 | Hexavalent | 0.1 | 1 | 2 |

| | | | | |
|---|---|---|---|---|
| | Chromium (as Cr6+), mg/L, Max | | | |
| 19 | Total Chromium (as Cr), mg/L, Max | 2 | 2 | 2 |
| 20 | Copper (as Cu), mg/L, Max | 3 | 3 | 3 |
| 21 | Zinc (as Zn), mg/L, | 5 | 15 | 15 |

| № | Parameters | Into Inland Surface Water | Into Marine Coastal Waters | Into Public sewers |
|---|---|---|---|---|
| 22 | Selenium (as Se), mg/L, Max | 0.05 | 0.05 | 0.05 |
| 23 | Nickel (as Ni), mg/L, Max | 3 | 5 | 3 |
| 24 | Boron (as B), mg/L, Max | 2 | - | 2 |
| 25 | Percent Sodium, Max | - | 60 | - |
| 26 | Residual Sodium | - | - | - |

| | | | | |
|---|---|---|---|---|
| | Carbonate, mg/L, Max | | | |
| 27 | Cyanide (as CN), mg/L, Max | 0.2 | 0.2 | 0.2 |
| 28 | Chloride (as Cl), mg/L, Max | 1000 | - | - |
| 29 | Fluoride (as F), mg/L, Max | 2 | 15 | 15 |
| 30 | Dissolved Phosphate (as P), mg/L, Max | 5 | - | - |
| 31 | Sulphate (as $SO_4$), mg/L, Max | 1000 | - | 1000 |
| 32 | Sulphide (as S), mg/L, Max | 2 | 5 | - |
| 33 | Pesticides | absent | absent | absent |
| 34 | Phenolic Compounds (as $C_6H_5OH$) mg/L, Max | 1 | 5 | 6 |
| 35 | Radioactive materials<br>a) Alpha emitters<br>b) uc/ml, Max | 10-7 | 10-7 | 10-7 |

Annex 3: photos of equipments used in the study


Figure 1: Sampling conical flasks and plastic bottles


Figure2: Digital weighing Balance


Figure3: SBR reactors for the control and Ozonation

Declaration

I, the undersigned, declare that this thesis is my original work and has not been presented for a degree in any university, and that all the source of materials used for the thesis has been appropriately acknowledged.

Declared by:

Name: _____

Signature: _____

Date: _____

Advisor: _____