DESIGN A TERTIARY WATER TREATMENT PLANT IN A TANNERY

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CERTIFICATE

This is to certify that work **"Tertiary water treatment plant in a Tannery"** in this thesis completed by Ms. Zoha Ahmad, Ms. Zoha Arif, Ms. Areej Mahmood, and Ms. Zaineb Ijaz from the tenure of fall to spring semester 2022-23 under the supervision of Dr Asad Ullah Khan at the school of Chemical and Materials Engineering (Scme), National University of Sciences and Technology, H-12, Islamabad, Pakistan.

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DEDICATION

This FYP thesis is dedicated to individuals who believed in the potential of this group, especially, our beloved families, friends and teachers who played a significant role in bringing us this far.

ABSTRACT

Advance Oxidation processes (AOPs) are advanced water treatment techniques that utilize highly reactive oxidizing agents to remove or degrade organic and inorganic pollutants in water. Electro-Fenton is one of them. These processes involve the generation of hydroxyl radicals (·OH), which are powerful oxidants capable of breaking down a wide range of contaminants. Hydrogen peroxide (H2O2) is used as a standalone oxidant or in combination with other processes to produce ·OH radicals. The reaction between H2O2 and a catalyst (such as iron, titanium dioxide, or ultraviolet light) generates ·OH radicals that can degrade contaminants. Siddique Leather works have daily water capacity of 1500 m3/d. The industry installed a secondary treatment process for chrome recovery and biological treatment for sludge. The objective of our project is to reduce COD or BOD to desired amount (i.e., COD to 150 mg/L or BOD to 100mg/L) and to meet specification of fresh water extracted from bore holes.

The implemented technique gives 88% recovery of water and almost all the persistent organics are removed while following NEQ's standards.

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CHAPTER 1

INTRODUCTION

1.1 About the company

Siddique leather works is one of the most modern tanning industries in Pakistan. Their mission is to make the finest leather with available recourse and uphold the highest customer satisfaction while maintaining the financial and moral well-being of all stake holders via an Islamic value system. Industry follows many steps to ensure environmental sustainability. SLW has installed a water treatment plant, lime recycling plant and soak water recycling system to stop the discharge of chemicals and harmful substances in water. The company has also taken steps toward efficient utilization of energy. SLW has shifted to renewable energy resources as an environmentally friendly source of energy.

1.2 Why is treatment important?

Our industry has already been doing primary and secondary treatment for removal of activated sludge. The purpose of tertiary treatment is to provide a final polishing treatment stage prior to discharge or reuse of the wastewater. The tertiary treatment process is used to improve the quality of the effluent which has resulted from primary and secondary treatment processes. Electro Fenton process degrade many impurities using hydroxyl radical ions. This technique is efficient, economical and easy to use.

1.2.1 Tanning process:

By removing impurities and other components the tanning industry enables the conversion of biodegradable animal leather into nonbiodegradable leather. Since the wastewater produced in this process contains both biodegradable substances like lipids, proteins, and carbohydrates as well as polluting substances like solvents, additives, and toxic heavy metals typical of the process, this greatly influences the quality of the water.

1.2.2 Wastewater treatment:

Wastewater treatment is a process that cleans up and gets rid of impurities in wastewater so that it can be transformed into effluent and sent back into the water cycle. Industrial wastewater treatment refers to the procedures used to treat wastewater produced as an unwanted byproduct by industries. After treatment, the industrial wastewater (or effluent) may be released into the environment, a sanitary sewer, or surface water.

1.2.3 Types of treatment:

Primary treatment:

Material that will either float or easily settle out by gravity is removed during primary treatment. It involves the mechanical procedures of commination, grit removal, screening, and sedimentation. Primary wastewater treatment is a crucial part of the water treatment process. It removes large debris, suspended solids and floating solids from wastewater so the water can enter secondary treatment.

Secondary treatment:

Secondary treatment eliminates soluble organic materials that was not removed by the primary treatment. It also eliminates a greater proportion of the suspended particles. Biological methods are typically used to remove contaminants, in which bacteria eat organic impurities as food, transforming them into carbon dioxide, water, and energy for their own growth and reproduction. Secondary treatment removes 85-90 percent of BOD, TSS, and a minor amount of nitrogen, phosphorus, and heavy metals from wastewater.

Tertiary treatment:

The final stage of the multi-stage wastewater cleaning process is tertiary water treatment. Inorganic chemicals, bacteria, viruses, and parasites are all removed during the third stage of treatment. After these dangerous compounds have been removed, the treated water is safe to reuse, recycle, or release into the environment. Tertiary treatment eliminates matter from wastewater that could be harmful to the environment. The process removes materials such as heavy metals, toxic chemicals, and other pollutants.

1.2.4 Total dissolved solids (TDS):

Total dissolved solids (TDS) are the quantity of minerals, metals, organic material, and salts dissolved in a given volume of water, represented in milligrams per liter. It is directly related to water quality and purity, notably in water purification systems. Total dissolved solids can be suspended in a variety of ways, including Molecular Ionized Micro-granular (colloidal sol).

Total dissolved solids levels have an impact on everything that lives in, drinks, or uses water.

1.2.5 Total suspended solids (TSS):

Total suspended solids (TSS) are the dry weight of non-dissolved suspended particles in a sample of water that can be trapped by a filter and analyzed using a sintered glass crucible filtration device. TSS is a water quality metric that is used to assess the quality of any sort of water or water body, such as ocean water or wastewater following treatment in a wastewater treatment plant.

1.2.6 COD:

The **chemical oxygen demand**, or COD, of water is a measure of its ability to consume oxygen during the decomposition of organic substances in the water. In other words, it is the amount of oxygen required to oxidize the organic matter present in a given volume of water.

1.2.7 BOD:

The amount of oxygen consumed by bacteria and other microorganisms while decomposing organic materials under aerobic circumstances is referred to as **biological oxygen demand**. Small amounts of oxygen in the form of dissolved oxygen (DO) can be found in every lake or stream. Dissolved oxygen is an essential component of natural water bodies, sustaining aquatic life and the aesthetic qualities of streams and lakes.

Table 1 Impurities present in wastewater from Tannery.

WASTEWATER FLOW RATE		
m3/hr	62.5	
l/hr	62500	
Types of Impurity	**Concentration (mg/l)**	**Desired (mg/l)**
COD	250	150
BOD	200	80
PH	7-8.7	6.5-7.5
Sulphides	0.5	1
TSS	100	200
Total kjeldahl nitrogen (TKN)	0.45	NGVS
Chrome VI	0.24	1

The table above shows the specs of water effluent from secondary wastewater treatment followed by SLW. This data is provided by the industry and forms the basis for our project.

1.2.8 Our goals:

To reduce COD or BOD concentration to desired amount

To meet the specification of fresh water extracted from bore hole.

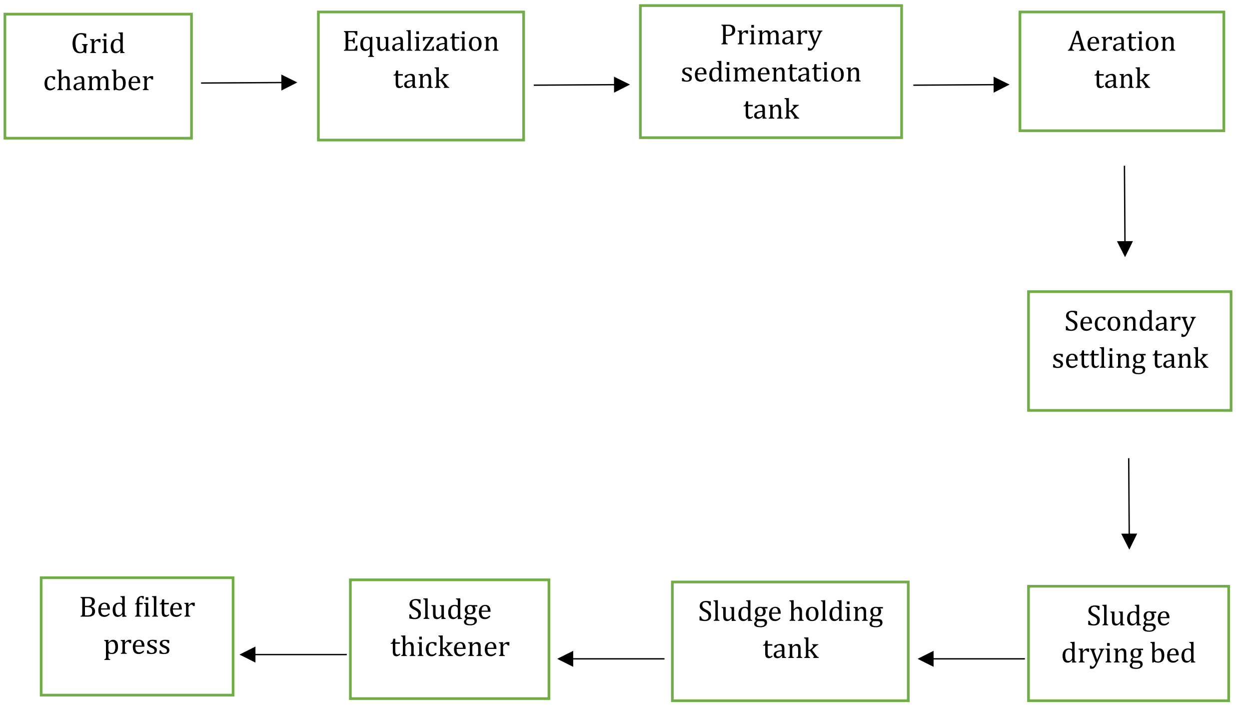


Figure 1 Secondary wastewater Treatment in SLW

The figure above shows the process previously used by our industry for secondary wastewater treatment that includes gravity settling and biological sludge treatment as the main part of our process. The effluent from this treatment will be our main concern for employing the tertiary treatment.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction:

The advanced oxidation process (AOP) and reverse osmosis (RO) technologies, on which the proposed tertiary treatment plant for the tannery is based, are the main subjects of this chapter's literature study. A review of the advanced oxidation process leads the chapter, which is then followed by an investigation of various Fenton process varieties. The decision to use the electron Fenton procedure for this project is then explained. The chapter concludes with a discussion of reverse osmosis and the rationale behind include it in the plan.

2.2 Tanning Processes:

The process of producing leather must include tanning. It entails treating untreated animal hides and skins with certain chemicals, referred to as tanning agents, to make the untreated hides into a material that is robust, flexible, and less prone to breakdown.

There are only two ways to tan:

2.2.1 Vegetable tanning: Tannins from plant sources, like tree bark extracts, are used in the process of "vegetable tanning." Although the procedure takes time, the high-quality leather it produces has distinctive qualities. Vegetable tanning often produces effluent that is rich in organic contaminants and color.

2.2.2 Chromium Tanning: This process uses chromium (III) salts, especially chromium (III) sulphate, which may quickly create soft, flexible leather. Because of this method's effectiveness and adaptability, it is increasingly commonly employed. However, chromium tanning generates highly toxic effluent including chromium salts, which, if not properly handled, may be hazardous to the environment and people's health.

Raw Animal Hide

↓

Cleaning/Soaking

↓

Tanning Agent Application

↓

─> Vegetable Tanning

└─> Chromium Tanning

↓

Leather

Figure 2.1 Tanning process

2.3 Wastewater Treatm

Disposing of untreated tannery effluents into the environment can have detrimental effects on both the ecosystem and human health. Consequently, a successful treatment program is crucial. Some popular forms of therapy include the ones listed below:

2.3.1 Process of Activated Sludge: This technique relies on aerobic microorganisms to break down organic contaminants in wastewater. Although the activated sludge system is reliable and cost-effective, the production of waste biomass (sludge) calls for careful control.

Utilizing bacteria, algae, or fungus to break down organic contaminants and create less toxic compounds is known as a biological treatment. Biomedical interventions are sustainable and kind to the environment. However, the efficacy of these processes may be constrained by environmental variables including temperature, pH, and the kind of pollutant.

Tannery Wastewater

↓

Aeration Tank

↓

Clarifier

↓

Activated Sludge

Figure 2.2 Activated Sludge Process

2.4 Advance Oxidation Process:

Wide-ranging organic and inorganic contaminants can be effectively removed from wastewater using the advanced oxidation process (AOP). With the help of ozone (O_3), hydrogen peroxide (H_2O_2), and ultraviolet (UV) radiation, extremely reactive hydroxyl radicals (•OH) are produced throughout this process. These hydroxyl radicals have a high capacity for oxidation and can break down resistant organic contaminants into less dangerous substances. Through the use of extremely reactive hydroxyl, hydroperoxyl, superoxide, and sulphate radicals, AOPs have become one of the most promising methods for the partial or total mineralization of developing contaminants1. AOPs provide a potent method for cleaning wastewater and addressing the problems brought on by the presence of dangerous chemicals by harnessing the strength of these radicals.

2.4.1 Types of Fenton Process:

There are several AOP versions, each with its own oxidizing chemicals and procedures:

Photochemical AOPs: These produce hydroxyl radicals by using UV or visible light.

AOPs of the electrochemical variety: These generate hydroxyl radicals using an electrical current.

Sonochemical AOPs: Ultrasound is used in sonochemical AOPs to produce hydroxyl radicals.

Regarding price, efficiency, scalability, and the types of pollutants that may be treated, each kind has certain benefits and drawbacks.

A well-known advanced oxidation process (AOP) is the Fenton process, which involves reacting hydrogen peroxide with a ferrous catalyst to produce hydroxyl radicals. Homogeneous and heterogeneous Fenton processes are the two primary varieties. Both the hydrogen peroxide and the ferrous iron catalyst are present in the homogeneous Fenton reaction, often in an aqueous solution. The heterogeneous Fenton procedure, on the other hand, includes immobilizing the catalyst on a solid substrate, enabling improved separation and recyclability.

Additionally, there are other iterations of the Fenton process, each with their own advantages and disadvantages. Conventional Fenton, photo-Fenton, and electron Fenton are some of these varieties. Under typical circumstances, conventional Fenton makes use of the hydrogen peroxide and ferrous iron reaction. The process of photo-Fenton uses UV or visible light irradiation to boost the production of hydroxyl radicals. Using an electrochemical setup, Electron Fenton generates hydroxyl radicals by transferring electrons to the catalyst.

Regarding reactant doses, reaction speeds, and energy needs, each Fenton process variant has certain benefits and drawbacks. The precise pollutants being targeted, the required treatment efficiency, and financial factors all play a role in the decision of which Fenton process variation to adopt.

Fenton Process and its Subsequences:

AOP, known as the Fenton process, generates hydroxyl radicals using hydrogen peroxide and a ferrous catalyst. The Fenton process has several variations, including:

Homogeneous Fenton: In this method, the solution contains both a ferrous iron catalyst and hydrogen peroxide.

Heterogeneous Fenton: In this method, the catalyst is immobilized on a solid support, making it simple to separate and recycle.

Photo-Fenton: This method boosts the production of hydroxyl radicals by combining the Fenton reaction with UV or visible light irradiation.

Electron Fenton: In this method, electrons are transferred to the catalyst using an electrochemical cell to produce hydroxyl radicals.

2.4.2 Why Electron Fenton Process:

The electron Fenton process has been chosen as the preferred advanced oxidation process (AOP) for the tertiary treatment facility in this study. Using electricity, the electron Fenton process produces ferrous ions on-site, which are subsequently mixed with hydrogen peroxide to create hydroxyl radicals. This AOP option has several benefits that make it ideal for the treatment of tannery effluent.

The electron Fenton procedure has the benefit of using less chemicals. The requirement for introducing external ferrous iron is eliminated or much diminished by electrochemically producing ferrous ions. This lowers costs and lessens the need for chemical additions.

The decreased sludge production is another benefit. The electron Fenton method produces less sludge throughout the treatment phase than other AOPs. This might make dealing with and getting rid of garbage produced during wastewater treatment simpler.

The electron Fenton method also offers improved process control. The production of hydroxyl radicals can be precisely controlled when an electrochemical cell is used. As a result, the treatment procedure can be properly regulated, resulting in the effective breakdown of organic pollutants in the tannery wastewater.

The electron Fenton method emerges as a viable option for the tertiary treatment of tannery wastewater in light of these concerns. It provides benefits like fewer chemical consumption, less sludge production, and improved process control, all of which help to effectively and efficiently.

2.4.3 Benefits of the advanced oxidation electron Fenton process:

The electron Fenton method is a good option for the tertiary treatment of tannery effluent because it offers several particular characteristics. It permits the electrical production of ferrous ions locally, which combine with hydrogen peroxide to form hydroxyl radicals. This method saves money and makes waste disposal simpler since it uses fewer chemicals and creates less sludge. Additionally, it permits fine-grained control over the therapeutic procedure, which may increase therapeutic effectiveness.

2.4.4 Future Prospects:

With continued research into novel catalysts, optimization of process variables, and integration with other treatment technologies, AOPs have a bright future. Future developments that might make AOPs more efficient and sustainable include the utilization of solar energy for photocatalytic AOPs, the creation of nanomaterial-based catalysts, and improved process control techniques.

2.5 Reverse Osmosis:

A semipermeable membrane is used in the reverse osmosis (RO) method of water purification to successfully remove ions, molecules, and bigger particles from drinking water. Dissolved solids and pollutants are separated from water using a membrane-based procedure. By applying pressure to the water, the membrane allows the solvent molecules to pass through while retaining dissolved solutes and contaminants, producing cleaned water on the permeate side. Due to its capacity to produce high-quality filtered water by removing a variety of impurities, RO has achieved broad use in a variety of applications, including the treatment of industrial effluents and brackish water.

2.5.1 Why Reverse Osmosis:

Reverse osmosis (RO) is incorporated into the proposed tertiary treatment plant since it has many benefits. First and foremost, RO effectively removes dissolved organic and inorganic pollutants, including salts, heavy metals, and trace pollutants, resulting in the creation of high-quality treated water. Furthermore, because of its high rejection rate and stable and continuous barrier against pollutants, RO ensures a powerful purification procedure. Finally, RO systems are appropriate for installation in small spaces due to their compact and modular design, making them an efficient choice for the wastewater treatment plant at the tannery.

In conclusion, this chapter gave an overview of reverse osmosis technology as well as the electron Fenton process, an advanced oxidation process (AOP). The advantages of the electron Fenton process, such as its lower chemical consumption and improved process control, favor its selection as the AOP. Reverse osmosis is being integrated because it is efficient at eliminating dissolved impurities, has a high rejection rate, and can be installed in small places. These technologies serve as the cornerstone for building the tannery's proposed tertiary treatment plant.

2.6 Conclusion:

The chapter has covered the intricacies of tanning, its effects on the environment, and the requirement for an efficient wastewater treatment procedure that goes along with it in detail. Due to their numerous benefits, the electron Fenton process, an AOP, and RO have been highlighted as prospective contenders for the proposed tertiary treatment facility. These technologies have a bright future ahead of them since ongoing developments are anticipated to increase their efficiency and efficacy.

CHAPTER 3

PROCESS DESCRIPTION

The process opted for tertiary water treatment was electro Fenton process. It was 88% efficient in removing the persistent organics present within our effluent. Among AOPs, Fenton technology is very attractive due to its simplicity, low cost, high performance, and the lack of toxicity of Fenton’s reagents (ferrous ion and hydrogen peroxide).

3.1 Electro Fenton process:

The Electro-Fenton process is treatment technology for wastewater. Electro-Fenton utilizes hydroxyl radicals to oxidize hazardous contaminants and is especially useful to treat recalcitrant compounds that are not easily degraded in conventional water and wastewater treatment plants. The EAOPs process is a new technology that has clean, efficient and economical processing in removing pollutants in water.

3.1.1 Mechanism

During the Fenton process, ferrous ion (Fe2+) catalyzes hydrogen peroxide (H2O2) into OH•, which is a highly reactive and strong oxidizing agent that can react with most organic compounds containing C-H and C-C bonds at near diffusion-controlled rates. Compared with the conventional Fenton process, electro-Fenton process avoids the transport and storage of external H2O2 with in situ generated H2O2 on the cathode and therefore is an environmentally friendly technology as chemical usage has been reduced and sacrificial production of Fe2+ on the anode. OH• generation was also observed at the anode by the oxidation of water.

3.1.2 Why OH radical?

OH• is the second strongest oxidizing agent preceded by F2 (Table 1). OH• has a standard potential as high as 2.80 V (vs. SHE), indicating its extraordinary ability to obtain electrons from other materials and to oxidize other substances.

Hydroxyl radicals react rapidly with RH and start a radical oxidation chain mainly by abstracting a hydrogen atom from C-H, N-H, or O-H bonds.

Adding to an unsaturated bond such as C═C bonds or aromatic rings (ArH)

Examples:

1- C7F15COOH (perfluorooctanoate) is an organic compound. OH• attacked C7F15• that was generated from C7F15COO− and formed C7F15OH. The formation of C6F13COO− was resulted from C7F15OH after intramolecular rearrangement and the produced shorter PFOA chain followed the same reactions as those of C7F15COO− until complete mineralization.

2- Acid red 97 (AR97, C32H20N4S2O8Na2). OH• was observed to attack the azo bonds (−N═N−) initially, and then degraded the products (I–IV) to hydroxylated or poly hydroxylated derivatives via hydroxylation. These derivatives were further oxidized to quinoid structures (V–XI) and formed carboxylic acids via ring opening. Finally, carboxylic acids were converted to CO2 and H2O.

3.1.3 Reactions:

OH + organics ------> products + CO_2 + H_2O

•OH + organics ------> O_2 + H_2O

3.1.4 Process conditions:

pH= 3 Acidic

Temperature= 45 C

Electrolyte= Sodium Sulphate

3.1.5 Process Flow Diagram:

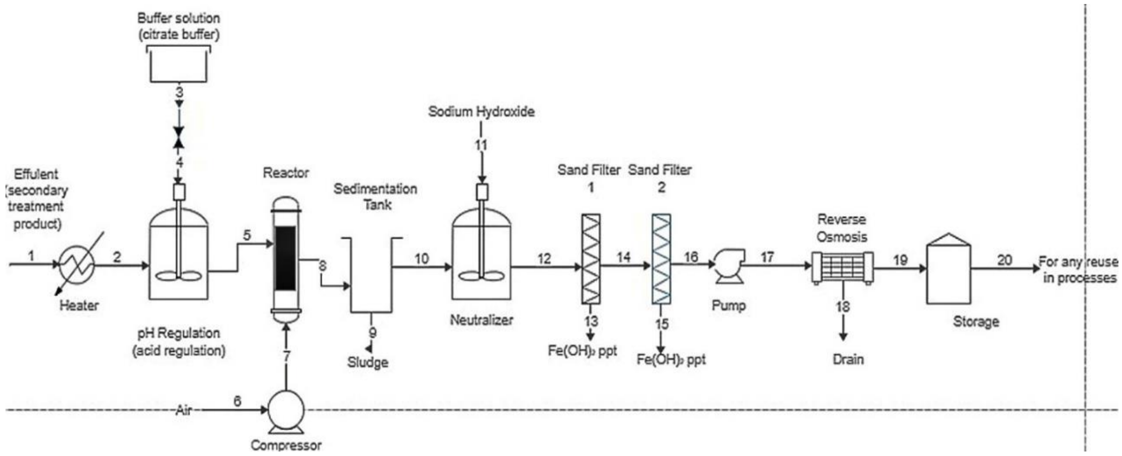


Figure 3.1 Process Flow Diagram for Tertiary Water Treatment

3.1.6 Heater:

The process starts with heating the 62500 L/hr of water in a heater. And then regulation of pH to meet electro Fenton process requirement.

3.1.7 pH Regulator:

A buffer solution is preferred to maintain a pH of 3. For this purpose, 125L of sodium citrate dihydrate and citric acid is introduced to 62500L of water per hour.

3.1.8 Reactor:

Reactor is the main part of our process. Electro Fenton reaction takes place in reactor. A compressor provides air which fulfills the demand of oxygen in the reactor. There are two electrodes: iron anode and Graphite sheet carbon cathode. The oxygen helps in the generation of H2O2 which further oxidizes to OH radical. The OH radical has the most reduction potential after Fluorine. So, it reacts with organics to decompose them into simpler Hydrocarbons CO2 and H2O.

3.1.9 Sedimentation tank:

It is used to remove the TSS present in our water, noted to be 100mg/l. The coagulating agent used is PACl (poly aluminum chloride) has been added. The amount of coagulant is 600mg/l. The coagulant comes out with TSS. The removal efficiency is 55%.

3.1.10 Neutralizer:

In neutralizer tank, pH changes from 3 to 7 (neutral), ferrous ions (Fe2+) can indeed undergo oxidation reactions in the presence of oxygen and certain pH conditions, resulting in the formation of iron hydroxide, commonly known as "iron sludge". This iron sludge is removed in sand filters present on the downstream of neutralizer.

3.1.11 Reverse Osmosis:

The presence of sodium citrate dihydrate for maintaining pH and use of sodium sulphate as electrolyte introduces TDS in water. Reverse osmosis is the best technique used for the removal of these dissolved solids.

CHAPTER 4

MATERIAL BALANCE

4.1 Introduction and Importance:

A mass balance, also known as a material balance, is a method of applying mass conservation to the analysis of physical systems. Mass flows that would have been unknown or difficult to assess without this technique can be identified by accounting for material entering and leaving a system. For example, mass balance theory is used to build chemical reactors, examine alternative chemical production processes, and predict pollution dispersion and other physical system activities. The mass balance for a system without a chemical reaction is

Input=Output + Accumulation

The phrase "mass balance" refers to an accounting technique that compares inputs (such as plastic trash) to outputs from a recycling or manufacturing process to calculate the recycled content. Mass balance is a chain of custody approach that tracks the net amount of sustainable materials as they move through a system or supply chain and guarantees that these materials are appropriately allocated to finished goods based on auditable bookkeeping. As the mass balance technique focuses on net material flow, material characteristics can be assigned to products in the form of "credits," even if this is not related to the actual sourcing composition of the product.

The mass balance chain of custody approach enables many sectors to gradually transition to more sustainable practices and material utilization.

The general rule for the mass balance in a system box is:

Input + Generation – Output – Consumption = Accumulation

4.1.1 HEATER:

$$In + Generation = Out + consumption + Accumulation$$

Since

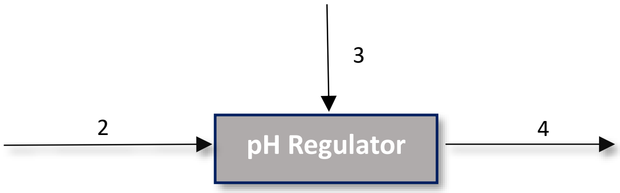
$$Generation = Consumption = Accumulation = 0$$

Thus,

$$In = out$$

$$Stream\ 1 = Stream\ 2 = 62500L/hr$$

4.1.2 pH REGULATOR:



$$\boldsymbol{In + Generation = Out + consumption + Accumulation}$$

Since

$$Generation = Consumption = Accumulation = 0$$

Thus,

$$\boldsymbol{In = out}$$

$$Stream\ 2 + Stream\ 3 = Stream\ 4$$

$$Stream\ 2 = 62500L/hr$$

$$Stream\ 3 = ?$$

CALCULATION of STREAM 4:

$$Stream\ 3 = Volume\ of\ buffer$$

$$pH = -log\lfloor H^{+} \rfloor$$
$$pH = 3$$
$$\lfloor H^{+} \rfloor = .0001$$
$$moles\ of\ buffer = \dot{V} * \lfloor H^{+} \rfloor$$

Where $V' = 62500$

$$Volume\ of\ buffer = \frac{moles\ of\ buffer}{molarity}$$

$$Volume\ of\ buffer = \frac{62500 * .0001}{0.05}$$

$$\boldsymbol{Volume\ of\ buffer = 125L/hr}$$

Thus, the overall mass balance becomes as follow;

$$62500 + 125 = 62625$$

$$\boldsymbol{Out = Stream\ 4 = 62625L/hr}$$

BUFFER PREPERATION

For 125L preparation using molarity of 0.05M

Mass of citric acid: 1088.12 g

Mass of Sodium citrate dihydrate: 172.416g (0.58 moles)

- Prepare 100 L of distilled water in a suitable container.
- Add 172.416 g of Sodium Citrate dihydrate to the solution.
- Add 1088.12 g of Citric Acid to the solution.
- Adjust solution to final desired pH using HCl or NaOH
- Add distilled water until the volume is 125 L.

Table 2 pH Regulator

COMPONENTS	PARAMETER	UNITS	IN	OUT
Water	Volumetric Flow Rate	L/hr.	62500	62500
Buffer Solution		L/hr	125	125
Total		L/hr	62625	62625

Table 3 pH Regulator Parameters

PARAMETERS	UNITS	IN	OUT
pH	mg/L	7	3
COD	mg/L	25	250
BOD	mg/L	0	200
TSS	mg/L	20	100
Na^+	mg/L	0	0.64
Citrate Ion	mg/L	10	19.2
Temperature	℃	45	45

SODIUM ION

$$1\ mole\ of\ Sodium\ citrate\ dihydrate\ gives\ 3\ moles\ of\ Sodium\ ion$$

$$.58\ mole\ of\ Sodium\ citrate\ dihydrate\ gives\ 1.74\ moles\ of\ Sodium\ ion$$

In PPM,

$$Na^{+} = moles * molarmass * \frac{1}{V'} = 1.74 * 23 * \frac{1}{62625} = 0.647 mg/L$$

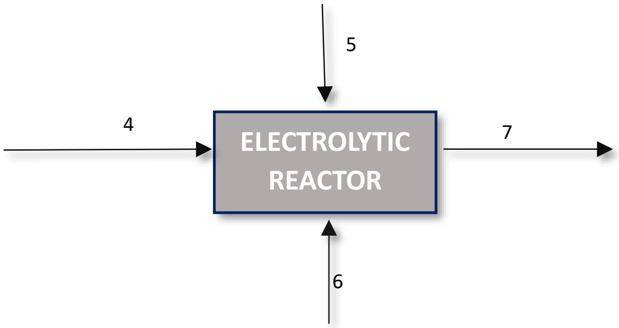
CITRATE ION

$$1\ mole\ of\ Citratic\ acid\ dihydrate\ gives\ 1\ moles\ of\ Citrate\ ion$$

In PPM,

$$Citrate\ ion = mass * \frac{1}{V'} = 1088.12 * \frac{1}{62625} = 19.2 mg/L$$

4.1.3 ELECTROLYTIC REACTOR:



$$\boldsymbol{In + Generation = Out + consumption + Accumulation}$$

Since

$$Generation = Consumption \neq 0$$

$$Accumulation = 0$$

Assumptions:

The following compounds constitutes to the COD ad BOD level. It is assumed that 1 mole of each constituent contribute to COD of level 200mg/l and that of BOD to 150mg/l

Components:

Table 4 Persistent Organic Components from Tannery Wastewater

NAME	**FORMULA**
2, 2, 4-Trimethyloxepane	$C_9H_{18}O$
2-2-hydroxypropyl) cyclohexanone	$C_9H_{16}O_2$
Dibutyl phthalate	$C_{16}H_{22}O_4$
Octacosane	$C_{28}H_{58}$
Tetratetracontane	$C_{44}H_{90}$
Bis(2-methoxyethyl) phthalate)	$C_{14}H_{18}O_6$
Eicosane	$C_{20}H_{42}$
Docosane	$C_{22}H_{46}$
1,2-Benzenedicarboxylicacid diisoctyl ester	$C_{24}H_{38}O_4$
2,6,10-Dodecatrien-1-ol-3,7,11-Trimethylacetate	$C_{17}H_{28}O_2$
Hexatriacontane	$C_{36}H_{74}$
2,6,10,15-Tettramethylheptadecane	$C_{21}H_{44}$
Tricosane	$C_{23}H_{48}$
9-Methylnonadecane	$C_{20}H_{42}$

From the reactions

$C_9H_{18}O+52OH \text{---->} 9CO_2+35H_20$

$C_9H_{16}O_2+48OH \text{---->} 9CO_2+32H_20$

$C_{16}H_{22}O_4+78OH \text{---->} 16CO_2+50H_20$

$C_{28}H_{58}+ 170OH \text{---->} 28CO_2+114H_20$

$C_{44}H_{90}+ 266OH \text{---->} 44CO_2+178H_20$

C14H18O6+ 62OH----> 14CO2+40H20

C6H12O3+ 30OH----> 6CO2+21H20

C20H42+ 122OH----> 20CO2+82H20

C22H46+ 134OH----> 22CO2+90H20

C24H38O4+ 126OH----> 24CO2+82H20

C17H28O2+ 92OH----> 17CO2+60H20

C36H74+ 218OH----> 36CO2+146H20

C21H44+ 128OH---->21 CO2+86H20

C22H46+134 OH----> 22CO2+90H20

C23H48+140 OH----> 23CO2+94H20

For **<u>100% Conversion</u>**:

$$\bullet OH\ Required = 2772\ moles$$

In real-time data, 10% of $\bullet OH$ are obtained from H2O itself

$$\bullet OH\ (from\ water) = \bullet OH * 0.1$$

$$\bullet OH(from\ water) = 277.2\ moles/hr$$

$$\boldsymbol{\bullet OH(required) = 2494.8\ moles/hr}$$

For **<u>88% Conversion</u>**

$$\bullet OH(real) = \bullet OH(req) * 0.88$$

$$\boldsymbol{\bullet OH = 2494.8 * 0.88 = 2195.6 = 2196\ moles/hr}$$

CONSUMPTION OF WATER:

Thus for required hydroxyl radical amount, water consumed will be given as follow

$$H_2O\ (Consumed) = 249.48\ moles/hr$$

IN VOLUME

$$H_2O\ (Consumed) = (moles/hr) * (molarmass) * \frac{1}{density}$$

$$H_2O\ (Consumed) = (249.48) * (18) * \frac{1}{1000}$$

$$\boldsymbol{H_2O\ (Consumed) = 4.49\ L/hr}$$

For 88% conversion, Production of water is given as

GENERATION OF WATER:

$$H_2O = 1588\ moles/hr$$

$$H_2O(88\%) = 1588 * 0.88$$

$$\boldsymbol{H_2O(88\%) = 1397 moles/\ hr}$$

IN VOLUME

$$H_2O\ (Generated) = (moles/hr) * (molarmass) * \frac{1}{density}$$

$$H_2O\ (Generated) = (13397) * (18) * \frac{1}{1000}$$

$$\boldsymbol{H_2O\ (Generated) = 25.146\ L/hr}$$

Thus,

Inlet Streams

$$Stream\ 4 = 62625 L/hr$$

$Stream\ 6 = 2400 L/hr$ (from reference)

ELECTROLYTE CALCULATIONS:

Type of electrolyte: Na_2SO_4

$$Amount\ of\ Na_2SO_4 = (Volume\ of\ water) * (Concentration)$$

$$Amount\ of\ Na_2SO_4 = 62625 * 0.02$$

$$Amount\ of\ Na_2SO_4 = 1252\ moles/hr$$

$$Volume\ of\ Na_2SO_4 = (moles/hr) * (molarmass) * \frac{1}{density}$$

Molar mass of Na_2SO_4 =142.04 g/mol

Density of Na_2SO_4 = 2.66g/cm^3

$$Volume\ of\ Na_2SO_4 = 66.74\ L/hr$$

$$\boldsymbol{Stream\ 5 = 66.74 L/hr}$$

$Outlet\ Streams$

$$Stream\ 7 = ?$$

CALCULATION of STREAM 7:

$$In + Generation = Out + consumption$$

$$62625 + 66.8 + 25.14 = Out + 4.49$$

$$\boldsymbol{Stream\ 7 = 62712.45}$$

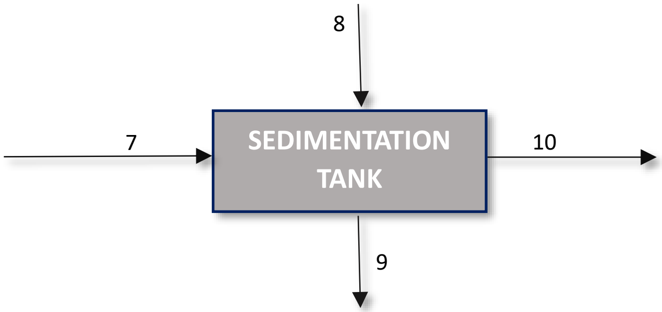
Table 5 Reactor Balance

COMPONENTS	PARAMERTER	UNITS	IN	OUT
Water	Volumetric Flow Rate	L/hr	62625	62625
Na_2SO_4		L/hr	66.8	66.8
Air		L/hr	2400	2400
Water consumption		L/hr	4.9	
Water Generation		L/hr	25.14	
Total	Volumetric flow rate	L/hr	62712.45	62712.45

Table 6 Reactor Parameters

Parameters	Units	In	Out
pH		3	3
COD	mg/L	250	30
BOD	mg/L	200	20
TSS	mg/L	100	100
Temperature	℃	45	45
Na^+	mg/L	0.6472	918.9
$SO_4{}^{-2}$	mg/L	0	1914.7
Citrate	mg/L	19.2	19.2
Fe+2	mg/L	0	1953.94

4.1.4 SEDIMENTATION TANK:



$$\boldsymbol{In + Generation = Out + consumption + Accumulation}$$

Since

$$Generation = Consumption = 0$$

$\boldsymbol{Accumulation \neq 0}$ Represented as Stream 9

Thus,

$$In = out$$

$$Stream\ 7 + Stream\ 8 = Stream\ 9 + Stream\ 10$$

$$Stream\ 7 = 62712.45 L/hr$$

$$Stream\ 8 = 600 mg/L$$

Stream 8 represents **coagulant** which is **POLYALUMINIUM CHLORIDE**

From the references, it is observed that for sedimentation of tannery wastewater, PACI is very effective and gives good results.

The amount used at the given pH i.e., 3 is **600mg/L.**

SPECIFICATIONS:

- All of coagulant is removed with TSS.
- Removal of TSS= 55%

$$TSS(7) = \frac{100mg}{L} * \frac{62712.04L}{hr} = 6271204\frac{mg}{hr} = 6271.245g/hr$$

$$TSS(9) = TSS(in) * 0.55 = 6271.245 * 0.55 = 3449.2g/hr$$

$$TSS(10) = TSS(in) * 0.45 = 6271.204 * 0.45 = 2822.06g/hr$$

CALCULATION OF STREAM 9:

$$Stream\ 9 = TSS(9) + H_2O(9)$$

Assumption: 10% moisture content

$$H_2O(9) = 0.1 * 62.7\ x10^6 = 62.7\ x10^5$$

$$Stream\ 9 = 62.7\ x10^5 + 3449.2 = 6.31\ x10^6 g/hr$$

$$Mass\ of\ sludge = \dot{V}\{C\imath n(Tss) + C\ coagulant - Cout(Tss)\} + mass(H2O)$$

$$\boldsymbol{Mass\ of\ sludge = 6.31X10^6\ g/hr}$$

CALCULATION OF STREAM 10:

$$Stream\ 10 = Stream\ 7 - Stream\ 7 * 0.1$$

$$\boldsymbol{Stream\ 10} = 62712.45 - 6271.245 = 56441.2 = \boldsymbol{56441.2l/hr}$$

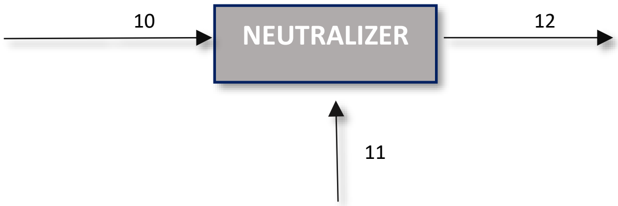
Table 7 Sedimentation Tank Balance

COMPONENTS	PARAMETER	UNITS	IN	OUT	Sludge (TSS)
Water	V'	L/hr	62712.45	56441.2	6271.2
TSS	ppm	mg/L	100	45	55
Coagulant	ppm	mg/L	600	0	600

Table 8 sedimentation Tank Parameters

PARAMETERS	UNITS	IN	OUT
pH	mg/L	3	3
COD	mg/L	30	30
BOD	mg/L	20	20
TSS	mg/L	100	45
Temperature	°C	45	45

4.1.5 NEUTRALIZER:



$$\boldsymbol{In + Generation = Out + consumption + Accumulation}$$

Since

$$Consumption = Accumulation = 0$$

Thus,

$$\boldsymbol{In = out}$$

$$Stream\ 10 = Stream\ 12$$

All of Stream 11 Will be present in water stream in dissolved form. At the given process conditions, the solubility of NaOH is enough to dissolve the amount calculated.

$$Stream\ 10 = 56441.2L/hr$$

$$Stream\ 12 = 56441.2$$

CALCULATION OF STREAM 11:

$1C_6H_8O_7 + 3NaOH \dashrightarrow 3H_2O + Na_3C_6H_5O_7$

Using Stoichiometric equations

$$1\ mole\ (citrate) = 3\ mole\ (NaOH)$$

For 5.66 moles of citric acid

$$5.66\ mole\ (citrate) = 3 * 5.66\ mole\ (NaOH)$$

$$5.66\ mole\ (citrate) = 16.99\ mole\ (NaOH)$$

GENERATION OF WATER:

For complete neutralization of citrate buffer, 3 moles of water will be produced given that 1 mole of citric acid is being neutralized.

$$H_2O\ (Generated) = (moles/hr) * (molarmass) * \frac{1}{density}$$

$$H_2O\ (Generated) = (16.99) * (18) * \frac{1}{1000} = \mathbf{0.305l/hr}$$

$Fe^{+2} + 2NaOH\ --\rightarrow Fe\,(OH)_2 + 2Na^{+1}$

For 5.66 moles of citric acid

$$1\ mole\ (Iron) = 2\ mole\ (NaOH)$$

Given 2196 moles of Iron are produced

Shift in pH from 3 to 7 can cause 80% of iron to precipitate out.

$$1756.8\, mole\ (citrate) = 2 * 1756.8\, mole\ (NaOH$$

$$1867\, mole\ (citrate) = 3513.6\, mole\ (NaOH)$$

$$Total\ NaOH\ required = \ 3513.6 + 16.99 = 3530.59\, moles$$

Molar mass of NaOH = 40g/mol

$$\boldsymbol{Amount\ of\ NaOH\ required = \ 3530.59 * 40 = 141.2 kg/hr}$$

Table 9 Neutralizer Balance

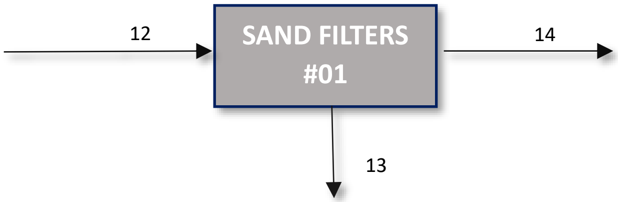
COMPONENTS	**PARAMETER**	**UNITS**	**IN**	**OUT**
Water	V’	L/hr	56441.2	56441.405
NaOH		Kg/hr	141.2	0

Table 10 Neutralizer Parameters

PARAMETERS	**UNITS**	**N**	**UT**
pH	mg/L	3	7
COD	mg/L	30	30
BOD	mg/L	20	20
TSS	mg/L	100	45
Fe(OH)2	mg/L	0	2796.9
Na^+	mg/L	918.9	2358.9
$SO_4{}^{-2}$	mg/L	1914.7	1914.7

Citrate	mg/L	19.2	38.16
Fe^{+2}	mg/L	1953.94	434.2
Temperature	°C	45	44.25

4.1.6 SAND FILTERS # 01:



$$In + Generation = Out + consumption + Accumulation$$

Since

$$Generation = Consumption = Accumulation = 0$$

Thus,

$$In = out$$

$$Stream\ 12 = Stream\ 13 + Stream\ 14$$

Stream 13= negligible as very minute amount of water will be lost in this process i.e. 0.1% loss thus, Stream 13 can be given as 0

$$Stream\ 13 = 0$$

$$Stream\ 12 = Stream\ 14 = 56441.405\ l/hr$$

REMOVAL SPECIFICATION:

TSS: 70% removal

Fe $(OH)_2$: 97%

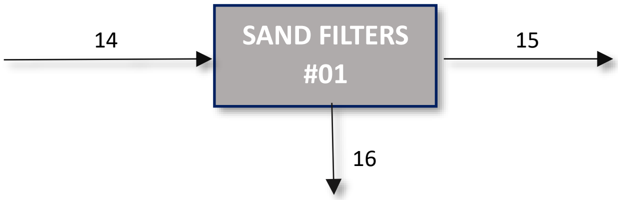
Table 11 Sand Filter #01 Balance

COMPONENTS	PARAMETER	UNITS	IN	OUT (14)	PPT. (13)
Water	V’	L/hr	56441.405	56441.405	Negligible
Fe (OH)2	ppm	mg//L	2796.9	56.9	2740
TSS	ppm	mg/L	45	13.5	31.5

Table 12 Sand Filter #01 Parameters

PARAMETERS	UNITS	IN	OUT
pH	mg/L	7	3
COD	mg/L	30	30
BOD	mg/L	20	20
TSS	mg/L	45	31.5
Fe (OH)2	mg/L	2796.9	55.9
Temperature	°C	44.25	44.25

4.1.7SAND FILTERS # 02



$$In + Generation = Out + consumption + Accumulation$$

Since

$$Generation = Consumption = Accumulation = 0$$

Thus,

$$\boldsymbol{In = out}$$

$$Stream\ 14 = Stream\ 15 + Stream\ 16$$

Stream 16= negligible as very minute amount of water will be lost in this process i.e. 0.1% loss thus, Stream 16 can be given as 0

$$Stream\ 16 = 0$$

$$Stream\ 14 = Stream\ 15 = 56441.405\ l/hr$$

REMOVAL SPECIFICATION:

TSS: 70% removal

Fe (OH) $_2$: 97%

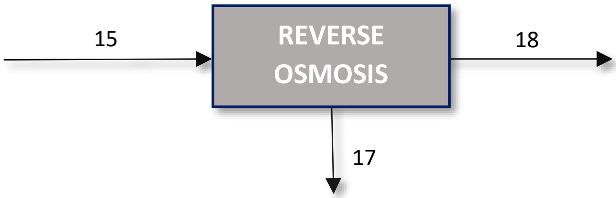
Table 13 Sand Filter #02 Balance

COMPONENTS	PARAMETER	UNITS	IN	OUT(15)	PPT.(16)
Water	V'	L/hr	56441.405	56441.405	Negligible
Fe(OH)2	ppm	mg//L	56.9	1.12	55.7
TSS	ppm	mg/L	13.5	2.025	11.475

Table 14 Sand Filter #02 Parameters

PARAMETERS	**UNITS**	**IN**	**OUT**
pH	mg/L	7	3
COD	mg/L	30	30
BOD	mg/L	20	20
TSS	mg/L	13.5	2.025
Fe(OH)2	mg/L	55.9	1.11
Temperature	°C	44.2	44.2

4.1.8 REVERSE OSMOSIS:



65% Recovery

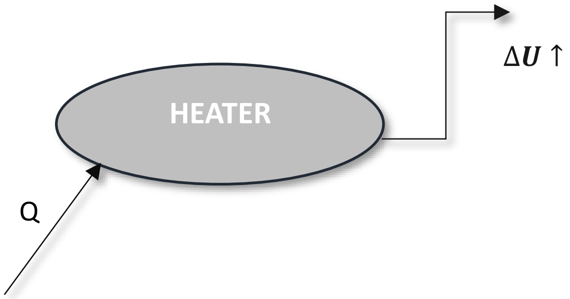
Table 15 Reverse Osmosis balance

COMPONENTS	PARAMERTER	UNITS	IN	OUT	
				PERMEATE (18)	**CONCENTRATE (17)**
water	V’	L/hr	56441.405	36686.91	19754.5
TDS	ppm	mg/L	4751.7	712.755	4038.9

CHAPTER 5

ENERGY BALANCE

HEATER



Overall relation for energy balance is given as

$$\Delta H = Q + W$$

In heater, no work done is being produced

Thus, $\boldsymbol{workdone = 0}$

The equation is reduced to

$$\Delta H = Q$$

$$Q = mcp\Delta T$$

$$\Delta H = Q = mcp\Delta T$$

Where

m=mass of water= 62500kg/hr

cp= specific heat of water= 4.18KJ/K-Kg

ΔT= difference in temperatures of inlet and outlet streams= $(45\text{-}25)^0$C

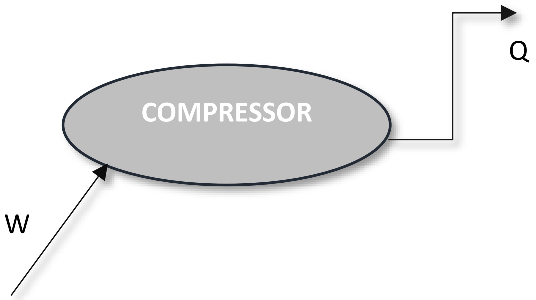
$$\boldsymbol{\Delta H = (62500) * (4.18) * (20)}$$

$$\Delta H = 5.37\ x10^3 KJ/hr$$

$$\boldsymbol{\Delta H = 1.49\ x10^3 J/s}$$

$$\boldsymbol{DUTY} = \boldsymbol{\Delta H} = 1.49\ x10^3\ watts = \boldsymbol{1.49\ KW}$$

COMPRESSOR



Overall relation for energy balance is given as

$$\boldsymbol{\Delta H = Q + W}$$

In compressor, work done is done on air to compress it

Thus, above relation is modified as follow:

$\boldsymbol{Win + \dot{m}H_1 = Qout + \dot{m}H_2}$

We know,

$$\boldsymbol{Q = mcp\Delta T}$$

Therefore, above equation is modified as follow

$\boldsymbol{Win + \dot{m}H_1 = mcp\Delta T + \dot{m}H_2}$

Where

m=mass of air= 0.802 x10^{-3}Kg/sec (converting 2400L/hr in SI units)

cp= specific heat of air

ΔT= difference in temperatures of inlet and outlet streams=

T_1 (inlet temperature) =25^0C

T_2 (outlet temperature) =?

P_1 (inlet pressure) = 1 Bar= 101.3Kpa

P_2 (outlet pressure) = 8 Bar= 800Kpa

Using relation to find the outlet temperature of the air stream if compressed from1 to 8 bar.

$$\boldsymbol{T_2 = T_1(\frac{P_2}{P_1})^{\frac{\gamma-1}{\gamma}}}$$

Where $\gamma = \frac{cp}{cv}$

For air,ra $\gamma = 1.410$

Thus,

$$T_2 = (\frac{800}{101.3})^{\frac{1.410-1}{1.410}}$$

$$\boldsymbol{T_2 = 543.48\ K}$$

Using property tables for air, we find the enthalapies at both inlet and outlet temperature.

H_1 (inlet enthalp) = 298.35KJ/kg

H_2 (outlet enthalp) = 689.22KJ/Kg

cp_1 (at 298K) =1.005KJ/Kg-K

cp_2 (at 677.3K) = 1.069KJ/Kg-K

Now as we have all the parameters, we substitute their values in the equation

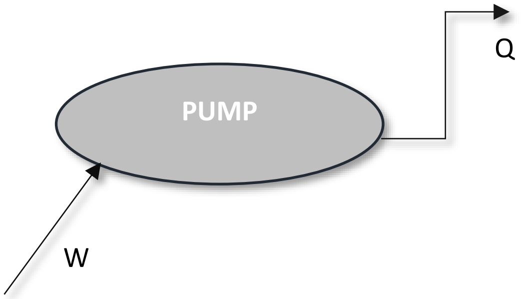
$\boldsymbol{Win + \dot{m}H_1 = mcp_2\Delta T + \dot{m}H_2}$

$Win + 0.802\ x10^{-3}(689.22)=(0.802\ x10^{-3)}(1.069)(379.3) +$
$0.802\ x10^{-3}(298.35)$

$$Win = 0.325 + 0.55 - 0.239$$

$$Win = 0.638KJ$$

PUMP



Overall relation for energy balance is given as

$$\boldsymbol{\Delta H = Q + W}$$

In compressor, work done is done on air to compress it

Thus, above relation is modified as follow:

$$\eta\boldsymbol{P} = \boldsymbol{Volumetric\ flowrate} * (\boldsymbol{P}_2 - \boldsymbol{P}_1)$$

Where

V'=volumetric flow rate of water= 56441.405L/hr

Converting it into the SI unit, we get

V'=0.0156m^3/s

cp= specific heat of water= 4.18KJ/K-Kg

ΔP= difference in pressure of inlet and outlet streams= (830-101.3)kpa

η=efficiency of pump=75% (assumed to be isentropic)

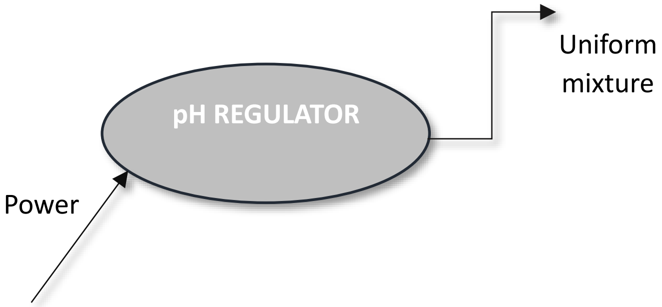
Substituting values in the given relation,

$$0.75P = 0.0156\ * (830 - 101.3)$$

$$\boldsymbol{P = 15.22\ x10^3\ watts}$$

$$\boldsymbol{DUTY = P = 15.22\ KW}$$

pH REGULATOR



Using relation

$$\boldsymbol{Bluk\ velocity = scale\ of\ agitation\ * 6ft/min}$$

SCALE OF AGITATON

Table 16 Scale of Agitation

1	Quite mild
3	Normal
6	Vigorous
10	Violent

Scale of agitation required= **normal =3**

$$Vc = 3 * 6ft/min = 0.1m/s$$

$$Pumping\ rate = Vc * area$$

Where area= $\frac{\pi D^2}{4}$ and diameter is 3.5m

$$Pumping\ rate = 0.1 * \frac{\pi(3.5^2)}{4}$$

$$Pumping\ rate\ (Q) = 0.96m^3/s$$

Now using

$$Nq = \frac{Q}{ND^3}$$

For **Turbine type of agitation having 4 blades**

$$\boldsymbol{Nq = 0.79\ ; Np = 1.27}$$

Np is power number

Nq is flow number

$$N = \frac{Q}{NqD^3} = \frac{0.96 * 60}{(0.79) * 3.5^3} = 1.7\ rpm$$

$$\boldsymbol{Power = Np * p * N^3 * D^5}$$

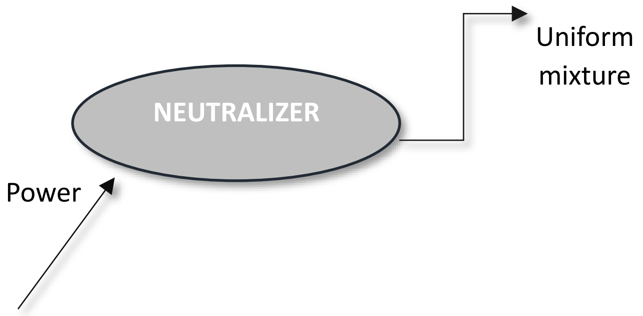
$$Power = (1.27)(1000)(1.7)^3(3.5)^5$$

$$\boldsymbol{Power = 0.015\ x10^3\ watts}$$

Conversion factor of

$$Power = Np * p * N^3 * D^5 * \frac{1}{60 * 60 * 60 * 1000} = KW$$

NEUTRALIZER



Using relation

$$\boldsymbol{Bluk\ velocity = scale\ of\ agitation\ * 6ft/min}$$

SCALE OF AGITATION

Table 17 Scale of Agitation

1	Quite mild
3	Normal
6	Vigorous
10	Violent

Scale of agitation required= **normal =3**

$$Vc = 3 * 6ft/min = 0.1m/s$$

$$Pumping\ rate = Vc * area$$

Where area= $\frac{\pi D^2}{4}$ and diameter is 3.4m

$$Pumping\ rate = 0.1 * \frac{\pi(3.4^2)}{4}$$

$$Pumping\ rate\ (Q) = 0.9m^3/s$$

Now using

$$Nq = \frac{Q}{ND^3}$$

For **Turbine type of agitation having 4 blades**

$$\boldsymbol{Nq = 0.79\ ; Np = 1.27}$$

Np is power number

Nq is flow number

$$N = \frac{Q}{NqD^3} = \frac{0.96 * 60}{(0.79) * 3.4^3} = 1.08\ rpm$$

$$\boldsymbol{Power = Np * p * N^3 * D^5}$$

$$Power = (1.27)(1000)(1.08)^3(3.4)^5$$

$$\boldsymbol{Power = 0.003\ x10^3\ watts}$$

Conversion factor of

$$Power = Np * p * N^3 * D^5 * \frac{1}{60 * 60 * 60 * 1000} = KW$$

Table 18 Neutralizer Energy Balance

ENTHALPIES

$1C_6H_8O_7$ + 3NaOH ---→ $3H_2O$+ $Na_3C_6H_5O_7$	
ΔH (reactants)	*-15981.508 KJ*
ΔH (products)	*7580.16 KJ*
ΔH (reaction) **For 5.7 moles of citric acid**	**23561.668 KJ**
$Fe^{+2} + 2NaOH \ --\rightarrow Fe(OH)_2 + 2Na^{+1}$	
ΔH (reactants)	*-1650864.96 KJ*
ΔH (products)	*-1850693.392 KJ*
ΔH (reaction) **For1756.8 moles of Fe^{+2}**	**-199818.43 KJ**
NET Enthalpy	-176256.76 KJ

Overall relation for energy balance is given as

$$\boldsymbol{\Delta H = Q + W}$$

In mixer, no work done is being produced

Thus, $\boldsymbol{workdone} = \mathbf{0}$

The equation is reduced to

$$\Delta \boldsymbol{H} = \boldsymbol{Q}$$

$$\boldsymbol{Q} = \boldsymbol{mcp}\Delta \boldsymbol{T}$$

$$\Delta \boldsymbol{H} = \boldsymbol{Q} = \boldsymbol{mcp}\Delta \boldsymbol{T}$$

Where

m=mass of water= 56441.45 kg/hr

cp= specific heat of water= 4.18 KJ/K-Kg

ΔT= difference in temperatures of inlet and outlet streams=?

$$-176256.76 \text{ KJ} = (56441.45) * (4.18) * \Delta T$$

$$\Delta \boldsymbol{T} = -\mathbf{0.74}$$

$$\Delta T = (T_2 - T_1) = (T_2 - 318) = -0.75$$

$$\boldsymbol{T}_2 = \mathbf{318 - 0.75 = 317.25}\boldsymbol{K}$$

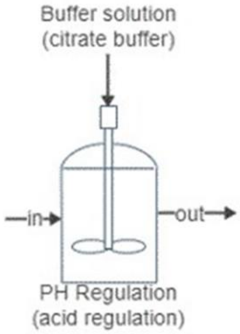
CHAPTER 6

EQUIPMENT DESIGN

PH REGULATOR:

Flow rate: 62.62 m^3 /hr

Retention time: 1 hr



Formula

$$\boldsymbol{Time = \frac{Volume}{flow\ rate}}$$

Volume= (time x flow rate) +overflow allowance

Volume= (1hr x 62.62) +10%

= 62.62+6.262

Volume = 68.88 m^3

DIMENSIONS CALCULATIONS

Volume (cylindrical) = $\pi\frac{D^2H}{4}$

H=2D V=$\pi/4\ D^2$ H

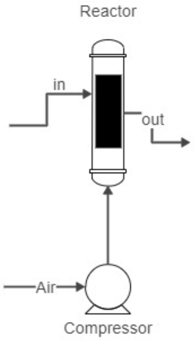
D=3.5m H=7.04m

Tank: Cylindrical

ELECTROLYTIC REACTOR

CALCULATIONS OF CURRENT:

Formula



$$n = \frac{FVd(h2O2)}{I.dt} x\,100$$

$$I = 96485x\,\frac{\frac{1}{3600}}{2\text{x}3600}\,x0.6\text{x}100$$

Moles of H_2O_2= 0.6moles/s

$$\boldsymbol{I = 817\ A\ for\ 1\ hour}$$

CALCULATIONS OF POWER:

$$power = IV = 0.528\ KW\ (\text{for } 220V)$$

CALCULATIONS OF SURFACE AREA:

Formula

$$Surface\ Area = \frac{Required\ Current}{Current\ Density}$$

$$current\ density = 50\ A/m^2$$

$$required\ current = 817\ A\ for\ 1\ Hour$$

$$\boldsymbol{Surface\ Area\ of\ electrode = 16.34\ m^2}$$

CALCULATIONS OF DISTANCE B/W ELECTRODE:

Formula

$$\text{Distance} = \frac{K\ x\ Area}{G}$$

(C) Conductance = 3.5 x 10^6mho

(K) Specific Conductance = 1.8 x 10^6mho/m

Distance = $8.\,4m^2$

Table 19 Electrode Specifications

PARAMETERS	DESIGN SPECIFICATION
Area of electrode	$16.34m^2$
Electrode	Anode: Iron Cathode: Graphite
Distance b/w electrode	$8.4m^2$

CALCULATIONS OF VOLUME:

Flow rate: 62.6 m^3 /hr

Retention time: 1 hr

Formula

$$\boldsymbol{Time = \frac{Volume}{flow\ rate}}$$

Volume= (time x flow rate) +overflow allowance

Volume= (1hr x 62.6) +10%

= 62.6+6.26

Volume = 68.86 m^3

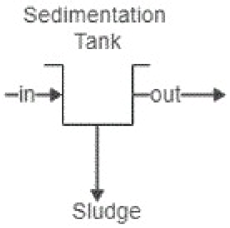
DIMENSIONS CALCULATIONS

Type of Tank: Cylindrical

Volume (cylindrical) = $\pi\frac{D^2H}{4}$

H=2D V= $\pi/4\ D^2$ H

D=3.526m H=7.0529m



SEDIMENTATION TANK

CALCULATIONS OF SETTLING VELOCITY

Parameters

$D_p = 22\ x\ 10^{-6}$ m

$\rho_p = 1670\ kg/m^3$

g = 9.8 m/s

$\rho_F = 1000\ kg/m^3$

C_o = 100mg/l

K = $D_p(\frac{g\rho_F(\rho_p-\rho_F)}{\mu^2})^{\frac{1}{3}}$

K = $22x10^{-6}(\frac{9.8(1000)(1670-1000)}{(1x10^{-3})^2})^{\frac{1}{3}}$ =0.4

For k<3.3, $\mu_t = \frac{gD_p{}^2(\rho_p-pf)}{18\mu}$ = $1.78x10^{-4}$m/s

CALCULATIONS OF OVER FLOW RATE

$$\boldsymbol{\psi = C_o\ x\ \mu_t = 1.78x10^{-5}kg/m^2s}$$

CALCULATIONS OF SURFACE AREA

Formula

$$\boldsymbol{Surface\ area} = \frac{volumetric\ flow\ ratex\ C_{\mathrm{o}}}{over\ flow\ rate}$$

Type of Tank: Cylindrical

$$area = 2\pi rh + 2\pi r^2$$

Cylindrical relation of height to diameter ratio: 1:2 i.e. $\boldsymbol{H = 2D = 4r}$

$$area = 8\pi r^2 + 2\pi r^2 = 10\pi r^2$$

Volumetric Flow Rate = 0.017 m^3/sec

$$\boldsymbol{Surface\ area} = \frac{volumetric\ flow\ rate\ x\ C_{\mathrm{o}}}{over\ flow\ rate} = \boldsymbol{95.1m^2}$$

CALCULATIONS OF DIMENSIONS:

$$r = \sqrt{\frac{area}{10\pi}} = \sqrt{\frac{95.1}{10\pi}} = 1.7m$$

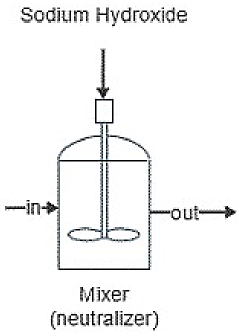
$$D = 2r = 2(1.7) = 3.4m$$

$$h = 2D = 2(3.4) = 6.8m$$

$$\boldsymbol{Volume\ of\ tank} = \pi r^2 h = \boldsymbol{62.6m^3}$$

$$\boldsymbol{Retention\ Time} = \frac{volume\ of\ tank}{Volumetric\ flow\ rate} = \frac{62.6}{0.017} = 3682s = \boldsymbol{1.02hr}$$

NEUTRALIZER:



Flow rate: 56.441 m^3 /hr

Retention time: 1 hr

FORMULA

$$\boldsymbol{Time = \frac{Volume}{flow\,rate}}$$

Volume= (time x flowrate) +overflow allowance

Volume= (1hr x 56.441) +10%

= 62.08 m^3

Volume = 62.08 $\boldsymbol{m^3}$

DIMENSIONS CALCULATIONS

Type of Tank: Cylindrical

Volume (cylindrical) = $\pi D^2 H/4$

H=2D V=π/4 D^2 H

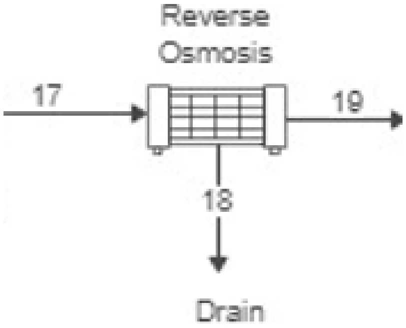
D=3.4m H=6.8m

REVERSE OSMOSIS:

Table 20 Reverse Osmosis Membrane Design Specifications

PARAMETERS	DESIGN SPECIFICATIONS
Membrane material	Composite Polyamide
Membrane module	Low Fouling Spiral Wound
Membrane active area	1958.7 ft^2 (181.97 m^2)
Diameter	4 inch
Length	40 inch
% Separation Factor	97.75 %
Permeate recovery	65 %
Permeate flow	36 m3/h
Flux decline	15 %
Osmotic pressure	4.8 bar
Pump pressure	8.3 bar

CALCULATIONS FOR ACTIVE AREA



$$\text{Active Area} = \frac{\text{Design Permeate Flow}}{\text{Design Flux} \times N_E}$$

Number of elements = N_E=8

Design permeate flow=36687.04 m^3/hr

Design flux =25.2 L/m^2hr

$$\text{Active Area} = \frac{36687.04}{25.2\times 8} = \mathbf{181.97}\boldsymbol{m^2}$$

CALCULATIONS FOR % SEPARATION FACTOR:

% Separation Factor=$\frac{C_f - C_p}{C_f} \times 100$

C_f = Concentration of TDS in feed stream=4267 mol/l

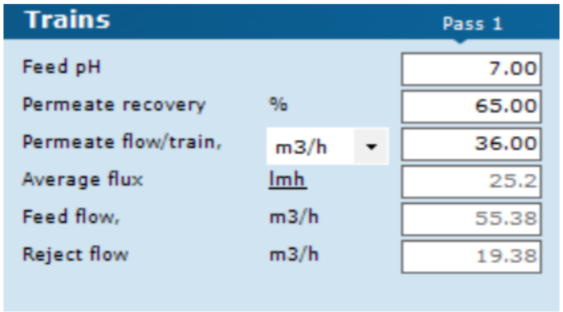
C_p= Concentration of TDS in permeate stream=95.89 mol/l

% Separation Factor=$\frac{4267 - 95.89}{4267} \times 100$

% Separation Factor=**97.75%**

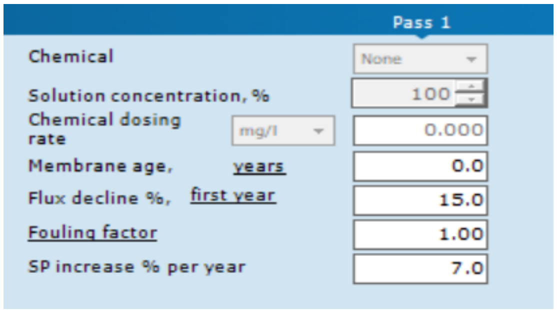
Software:

Ims Design



		Pass 1
Feed pH		7.00
Permeate recovery	%	65.00
Permeate flow/train,	m3/h	36.00
Average flux	lmh	25.2
Feed flow,	m3/h	55.38
Reject flow	m3/h	19.38

Figure 6 7 IMS Design Specifications for Reverse osmosis



		Pass 1
Chemical		None
Solution concentration, %		100
Chemical dosing rate	mg/l	0.000
Membrane age,	years	0.0
Flux decline %,	first year	15.0
Fouling factor		1.00
SP increase % per year		7.0

Figure 6 6 IMS Design Membrane Specifications

CHAPTER 7

ECONOMIC ANALYSIS

PH REGULATOR

FORMULA

$$Ce = CS^n$$

Table 21 Tank Type

TYPE	**MATERIAL**
Horizontal Tank	Carbon Steel

Table 22 pH Regulator Specs

TYPE FACTOR	1
COST	\$2900
INDEX	0.6
CAPACITY	68.88m^3

$$Ce = \$36724.0$$

Table 23 Tank Type

TYPE	MATERIAL
Agitation (Turbine Agitator)	Carbon Steel

Table 24 pH Regulator Specs

TYPE FACTOR	0.5
COST	$3000
POWER	0.15KW

$$Ce = (3000)(0.015)^{0.5}$$

$$\boldsymbol{Ce} = \$\mathbf{367}$$

$$\boldsymbol{Total\ cost} = \$37091.4 = \$\mathbf{0.037M}$$

NEUTRALIZER

FORMULA

$$\boldsymbol{Ce = CS^n}$$

Table 25 Tank Type

TYPE	MATERIAL
Horizontal Tank	Carbon Steel

Table 26 Neutralizer Specs

TYPE FACTOR	1
COST	$2900
INDEX	0.6
CAPACITY	$62.08m^3$

$$\boldsymbol{Ce = \$34528}$$

Table 27 ***Tank Type***

TYPE	**MATERIAL**
Agitation (Turbine Agitator)	Carbon Steel

Table 28 Neutralizer Specs

TYPE FACTOR	0.5
COST	$3000
POWER	0.003KW

$$\boldsymbol{Ce = \$164}$$

$$\boldsymbol{Total\ cost = \$34692.3 = \$0.034M}$$

ELECTROLYTIC REACTOR

$$Ce = CS^n$$

Table 29 ***Electrolytic Reactor Type***

TYPE	**MATERIAL**
Agitator Reactor	Carbon Steel

Table 30 Electrolytic Reactor Specs

TYPE FACTOR	1
COST	\$31000
INDEX	0.45
CAPACITY	$68.86m^3$

$$\boldsymbol{Cost} = (31000) * 68.8^{.45} = \$\boldsymbol{0.239M}$$

$$\boldsymbol{Cost} = \$239400 = \$\boldsymbol{0.239M}$$

SEDIMENTATION TANK

$$Ce = CS^n$$

Table 31 Sedimentation Tank Type

TYPE	**MATERIAL**
Horizontal Tank	Carbon Steel

Table 32 Sedimentation Tank Specs

TYPE FACTOR	1
COST	\$2900
INDEX	0.6
CAPACITY	$62.6m^3$

$$Ce = \$34701.0$$

$$\boldsymbol{Cost} = \mathbf{0.034M}$$

STORAGE TANK

FORMULA

$$\boldsymbol{Ce = CS^n}$$

Table 33 ***Storage Tank Type***

TYPE	**MATERIAL**
Cone roof	Carbon Steel

Table 34 Storage Tank Specs

TYPE FACTOR	02
COST	\$2900
INDEX	0.55
CAPACITY	$40.3m^3$

$$Ce = \$44294.07$$

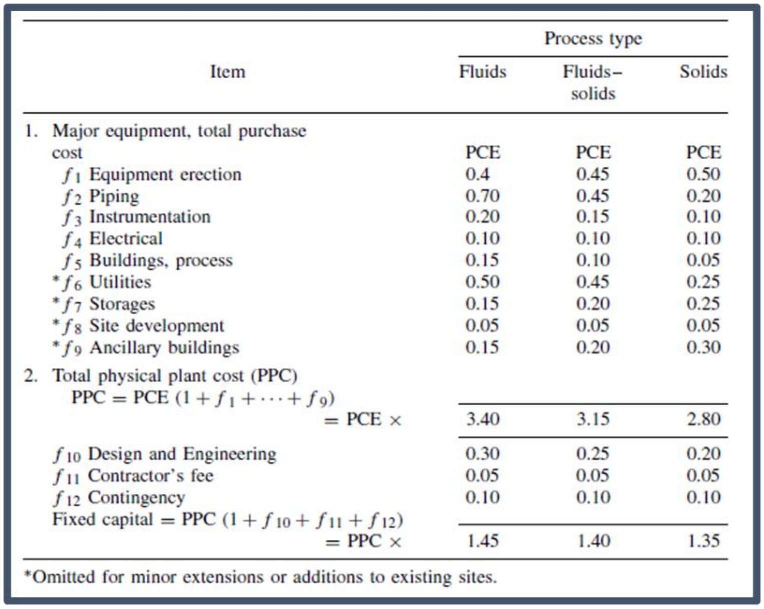
$$\boldsymbol{Cost} = \$\mathbf{0.044}$$

OVERALL COST OF ALL EQUIPMENTS:

Table 35 Purchase Cost Of all Equipment

EQUIPMENT	COST IN USD($ M)
Heater	**$ 0.011**
Compressor	**$ 0.017**
Pump	**$ 0.067**
pH Regulator	**$ 0.061**
Sedimentation Tank	**$ 0.034**
Reactor	**$ 0.239**
Neutralizer	**$ 0.058**
Reverse Osmosis	**$ 0.022**
Storage Tank	**$ 0.044**
Sand Filter	**$ .016**
PCE = PURCHASE COST OF EQUIPMENT = $ 0.55 MILLION	

PHYSICAL PLANT COST



Item	Process type Fluids	 Fluids–solids	 Solids
1. Major equipment, total purchase cost	PCE	PCE	PCE
f_1 Equipment erection	0.4	0.45	0.50
f_2 Piping	0.70	0.45	0.20
f_3 Instrumentation	0.20	0.15	0.10
f_4 Electrical	0.10	0.10	0.10
f_5 Buildings, process	0.15	0.10	0.05
*f_6 Utilities	0.50	0.45	0.25
*f_7 Storages	0.15	0.20	0.25
*f_8 Site development	0.05	0.05	0.05
*f_9 Ancillary buildings	0.15	0.20	0.30
2. Total physical plant cost (PPC) PPC = PCE $(1 + f_1 + \cdots + f_9)$ = PCE ×	3.40	3.15	2.80
f_{10} Design and Engineering	0.30	0.25	0.20
f_{11} Contractor's fee	0.05	0.05	0.05
f_{12} Contingency	0.10	0.10	0.10
Fixed capital = PPC $(1 + f_{10} + f_{11} + f_{12})$ = PPC ×	1.45	1.40	1.35

*Omitted for minor extensions or additions to existing sites.

Figure 4 Coulson's and Richardson's Chemical Engineering Vol 6 Economic Analysis

Total PPC =PCE x 3.15

$$Total\ PPC = 0.55\ x\ 10^6 * 3.15$$

$$\boldsymbol{Total\ PPC} = \$\mathbf{1.32\ x\ 10^6}$$

FIXED CAPITAL

$$Fixed\ Capital = PPC\ (1 + 0.3 + 0.1)$$

$$Fixed\ Capital = 1.32\ \ x10^6\ (1 + 0.3 + 0.1)$$

$$\boldsymbol{Fixed\ Capital} = \$\mathbf{1.85\ x10^6}$$

WORKING CAPITAL

$$Working\ Capital = \ Fixed\ capital\ x\ 0.05$$

$$Working\ Capital = \ 1.85\ x10^6\ x\ 0.05$$

$$\boldsymbol{Working\ Capital = 0.09\ x10^6}$$

Total PPC	**$1.32M**
Fixed Capital	**$1.85M**
Working Capital	**$0.09M**

VARIABLE COST

Table 36 Variable Cost

RAW MATERIALS	**COST**	**COST FOR CONSUMPTION$*$ 10^3 /YEAR**
NaOH	$0.62/Kg	$729
PACI	$0.42/Kg	$2.098
Citric acid	$4.49/Kg	$40.307
Sodium Citrate dihydrate	$1.15/Kg	$1.640
Iron Electrode	$0.2/Kg	199.8
Na_2SO_4	$0.105/Kg	$157.3
Compressed Air	$\$0.006/m^3$	$\$0.9*10^{-3}$
Utilities (Power)	$0.15/MJ	$0.187

TOTAL VARIABLE COST = $1.3MILLION

FIXED COST

ANNUAL OPERATING COST

$$Variable\ Cost\ =\ \$1.35\ million$$

$$Fixed\ Cost\ =\ \$0.54\ million$$

$$Total\ Annual\ Operating\ Cost\ =\ Variable\ cost\ +\ Fixed\ cost$$

$$\boldsymbol{TOTAL\ COST = \$\ 1.89\ MILLION}$$

COST IN 2023

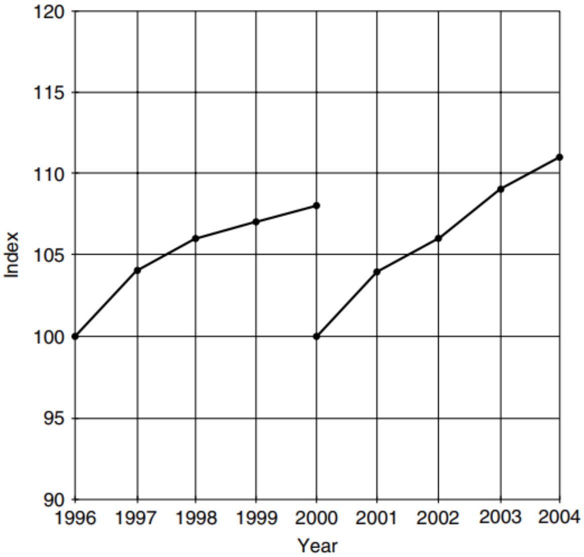


Figure 5 Cost Index from Year 1996- Year 2004

$$Index\ in\ 2004 = 111$$

$$Index\ in\ 2023 = 178$$

$$Cost\ in\ 2023 = \frac{(cost\ in\ 2004)x(index\ in\ 2023)}{(index\ in\ 2004)}$$

$$Cost\ in\ 2023 = \frac{(\$1.89\ x10^6)x(178)}{(111)}$$

$$\boldsymbol{Cost\ in\ 2023 = \$30.5M}$$

BENEFIT TO COST ANALYSIS

ASSUMPTIONS:

Cost of human life = $100000

Cost of aquatic life = $50000

No of humans affected = 50

BENEFIT = 100000(human life) + 50000(aquatic Life)

$$\boxed{\boldsymbol{\frac{B}{C} RATIO\ =\ 2.67}}$$

CHAPTER 8

HAZOP ANALYSIS

A Hazard and Operability study of the proposed is fundamental to its technical feasibility from a safety point of view. Conventionally, such analyses usually involve using specific guidewords to assess the cause, effects, and preventative measures for the process. Examples of said guidewords may be “high temperature”, “low pressure” or something else of the sorts.

These guidewords vary with the equipment under study within a system. Each component within a system must be considered for a thorough risk assessment. The guidewords are essentially deviations that may potentially be encountered within the equipment and help to imagine several possible scenarios. HAZOP involves,

1. Brainstorming what could possibly go wrong in the system. Listing down guidewords.
2. A qualitative risk assessment.
3. A “bottom-up” approach. Risk assessment relies on the observer’s predictive abilities and experience.

KEY WORDS:

1. Nodes: Pipe sections or vessels containing where process chemicals may be present.
2. Super nodes: Several nodes considered together as one node for quicker studies.
3. Hazard: Potential source of harm.
4. Harm: Actual injury or damage to equipment, personnel, or environment.
5. Risk: Probability of harm occurring and its associated level of damage.

METHODOLOGY:

1. Identify all major nodes and super nodes.

2. Identify why the node was chosen for the HAZOP study.

3. Choose a key process parameter for said node.

4. Apply all relevant guidewords for chosen parameter. These would result in unwanted deviations within the process. List down the deviations.

5. Determine the potential causes of the deviations identified and add them to the table.

6. For the deviations brainstormed, identify the outcomes they would lead to List these down as the consequences.

7. Once a node has been thoroughly studied, repeat steps 3 through 6 for the next node. Repeat this step till all chosen nodes have been accounted for.

pH Regulator:

Table 37 ***Hazop Analysis for pH Regulator***

PARAMETER	**GUIDE WORD**	**DEVIATION**	**POSSIBLE CAUSE**	**CONSEQUENCE**	**ACTION**
TEMPERA- -TURE	High/Low	High temperature Low temperature	Equipment malfunction Insufficient or excessive heat Supply control system failure due excessive mixing of buffer solution	**High temperature** pH sensor malfunction Chemical degradation System failure. **Low temperature** Lead to sluggish response Incorrect pH measurements.	Implement temperature monitoring and control systems. Install safety measures like temperature alarms. or shut-off valves.
PRESSURE	High/Low	High pressure, Low pressure	Equipment malfunction, clogged or leaking valves, insufficient or excessive pressure supply.	**High pressure** Damage the pH regulator, valves, or pipes. **Low pressure** Result in insufficient flow or inaccurate pH control.	Install pressure monitoring devices, safety relief valves, pressure regulators. Implement regular maintenance Inspection procedures.
Flow	No flow/ Excessive flow	No flow, Excessive flow	Pump or valve failure Blockages Leaks	**No flow** Can disrupt pH control leading to incorrect measurements. **Excessive flow** May overwhelm the system resulting in inaccurate pH control. or equipment damage	Install flow sensors, implement flow. alarms, ensure regular maintenance of pumps and valves, and establish preventive maintenance. protocols.

LEVEL	High/Low	High level, Low level	Sensor malfunction Blockages Leaks	High level Can cause overflow. Leaks Damage to the pH regulator. Low level May result in insufficient liquid supply or air entrainment.	Implement level monitoring systems, install level alarms, ensure regular calibration of sensors, and establish preventive maintenance procedures for valves and pipes.

Electrolytic Reactor

Table 38 ***Hazop Analysis for Electrolytic Reactor***

PARAMETER	**GUIDE WORD**	**DEVIATION**	**POSSIBLE CAUSE**	**CONSEQUENCE**	**ACTION**
TEMPERA--TURE	High /Low	High/Low temperature	**High temperature** Failure of temperature control system equipment malfunction Excessive redox reaction. **Low temperature** Insufficient heating failure of heating system	**High temperature** Risk of overheating decreased reactor efficiency Chances of electrical hazard **Low temperature** Reduced reaction rate decreased efficiency incomplete oxidation extended treatment time	Install temperature sensors and alarms to monitor and control temperature. Implement automatic shutdown mechanisms in case of deviation. Regularly maintain temperature. Ensure proper heat transfer and insulation in the reactor
PRESSURE	High /Low	High/ low pressure	**High pressure**	**High pressure** Equipment failure	Install pressure sensors and safety

			Failure of pressure control system Blockages valve malfunction. **Low pressure** Insufficient flow rate loss of pressure due to leaks equipment failure.	Leakage potential damage to the reactor vessel or associated piping. **Low pressure** Reduced reaction rate inadequate mixing poor performance of the oxidation process.	relief valves to monitor and control pressure. Implement pressure alarms and automatic shutdown mechanisms in case of deviations. Regularly inspect and maintain pressure Ensure proper maintenance of valves and piping systems.
FLOW	No Flow/ Excessive Flow	Insufficient or excessive flow	**No flow** Pump failure Blockages in the inlet piping Insufficient flow control. **Excessive flow:** Pump malfunction Valve failure Uncontrolled inlet flow	**No flow** Stagnation ineffective treatment reduced reactor performance. **Excessive flow** Poor mixing Inadequate contact time Decreased efficiency Potential overflow Leakage.	**Monitor and Control flow:** Install flow meters and alarms. **Flow deviations** Implement interlocks and automatic shutdown mechanisms. **Maintenance** Inspect and maintain flow control devices regularly. Ensure proper sizing and capacity of the flow control system
LEVEL	High/Low	High or Low liquid level	**High level:**	**High level** Potential overflow	**Monitor And Control Level.**

			Failure of level control system excessive flow rate malfunctioning discharge valves. **Low level:** Insufficient flow rate Leakage Improper level control	Reduced reactor efficiency. **Low level** Inadequate liquid volume compromised treatment performance.	Install level sensors and alarms. **Level deviations** Implement automatic shutdown mechanisms. **Maintenance** calibrate level control equipment regularly. Ensure proper sizing and capacity of the cell

Sedimentation Tank:

Table 39 ***Hazop Analysis for Sedimentation Tank***

PARAMETER	GUIDE WORD	DEVIATION	POSSIBLE CAUSE	CONSEQUENCE	ACTION
TEMPERATURE	High /Low	High temperature	Malfunctioning temperature control equipment High ambient temperature Excessive addition of coagulant	Accelerated sludge decomposition. Potential release of harmful gases Reduced settling efficiency time	Ensure proper cooling and temperature control mechanisms. Regularly monitor and maintain temperature within the specified range. Implement alarms or automatic shutdown systems for high temperatures

PRESSURE	High /Low	High pressure	Blockages or restrictions in outlet pipes Malfunctioning pressure relief valves Excessive sludge accumulation	Potential structural damage Increased risk of leakage or rupture Impaired settling performance	Regularly inspect and maintain outlet pipes to prevent blockages. Ensure proper functioning of pressure relief valves. Implement regular sludge removal procedures to prevent excessive accumulation
FLOW	Low /High	Low flow in the sedimentation tank	Pump failure or reduced pump capacity Clogged or obstructed inlet or outlet pipes Insufficient or malfunctioning flow control valves	Inadequate sludge settling Increased sedimentation time Poor separation of solids and liquid	Implement regular pump maintenance and monitoring. Periodically inspect and clean inlet and outlet pipes Install backup pumps or redundancy systems to mitigate pump failure risks
LEVEL	High /Low	High sludge level in the sedimentation tank	Malfunctioning level sensors or instruments Inadequate sludge withdrawal mechanisms Excessive sludge production or inflow	Reduced sedimentation efficiency Potential overflow or spillage Impaired wastewater quality	Ensure proper functioning and calibration of level sensors. Implement regular sludge withdrawal procedures. Monitor sludge production rates and adjust accordingly

Reverse Osmosis:

Table 40 Hazop Analysis for Reverse Osmosis

PARAMETER	GUIDE WORD	DEVIATION	POSSIBLE CAUSE	CONSEQUENCE	ACTION
TEMPERA- -TURE	High /Low	High temperature or low temperature in the RO system.	Equipment malfunction Inadequate heat transfer Improper insulation, Failure in temperature control systems.	High temperature can lead to reduced membrane performance or membrane damage, while low temperature can cause reduced efficiency or freezing.	Implement temperature monitoring and control systems, provide insulation, install safety measures to prevent extreme temperatures, and conduct regular maintenance.
PRESSURE	High /Low	High pressure or low pressure in the RO system	Pump failure Valve malfunction Blockages Leaks Inadequate pressure regulation.	**High pressure** result in membrane fouling or damage. **Low pressure** lead to reduced permeate production system inefficiency.	Install pressure monitoring and control systems. ensure proper pump and valve maintenance. Implement pressure safety measures establish regular system checks and maintenance procedures.
FLOW	No flow Low flow	No flow High flow Reverse flow	Pump failure Valve malfunction Blockages	**No flow** Can lead to system shutdown Reduce system efficiency	Install flow monitoring devices, implement flow control measures,

	High flow		Leaks Improper system design or sizing.	Reduce product quality. **High flow** Can cause operational issues Membrane damage. **Reverse flow** Membrane damage	conduct regular system checks, ensure pump and valve reliability, and establish maintenance procedures to prevent and address flow deviations.
LEVEL	High /Low	High level Low level in the RO system	Sensor malfunction Improper control Inadequate level control mechanisms Leaks	**High level** Lead to overflow Equipment damage Reduced system performance **Low level** Can result in pump cavitation. Membrane exposure Reduced system efficiency.	Implement level monitoring and control systems, ensure sensor reliability, install level alarms and safety measures, and conduct regular system inspections and maintenance.

CONCLUSION

This thesis research was concerned with the design of a tertiary treatment plant for a tannery that included reverse osmosis and Advanced Oxidation Processes (AOP). The major objectives were to generate an effluent that complied with the requirements for borehole water and lower the levels of Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) in the secondary treated tannery wastewater. The results obtained proved that these goals had been successfully attained. Both the COD and BOD levels were significantly lowered, from 250 mg/L to 30 mg/L and 200 mg/L to 20 mg/L, respectively. These values meet the specified BOD (80 mg/L) and COD (150 mg/L) standards. Additionally, the TDS separation factor was a remarkable 97.7%. COD Level: 30mg/l. The relevance of monitoring variables as well as the design, operation, energy balance, and cost analysis of the equipment were all topics covered in the thesis. The importance of AOPs in addressing persistent organic pollutants using cutting-edge treatment techniques like photocatalysis and ozonation was also emphasized. Overall, this thorough thesis offers insightful information on wastewater treatment, making it a useful tool for experts and scholars in the subject.

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