ISLAMIC UNIVERSITY OF TECHNOLOGY

DHAKA, BANGLADESH

ORGANISATION OF ISLAMIC COOPERATION

Study of the Applicability of Chemical Precipitation and Electrocoagulation Method for Chromium Recovery in CETP at Savar Leather Industrial Park

B.Sc. Engineering (Mechanical) Thesis

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March 2021

Research Certification

The thesis title **“Study of the Applicability of Chemical Precipitation and Electrocoagulation Method for Chromium Recovery in CETP at Savar Leather Industrial Park”** submitted by **Sazedur Rahman (160011018), Tasdee Al Karim (160011080) and Munabbih Hasan Nadid Khan (160011081)** has been accepted as satisfactory in partial fulfillment of the requirement for the Degree of Bachelor of Science in Mechanical Engineering on March 2021.

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Candidate's Declaration

It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or professional qualification.

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Abstract

When we visited tanneries at Savar Tannery Industrial Estate in order to gain a deeper understanding of the leather tanning industry of Bangladesh, we realized that the lack of environmental compliance certification is holding the industry back from further development. That is why we decided to work on one of the leading concerns, the release of chromium to the environment. We conducted a thorough search for applicable methods, conducted feasibility studies on the selected topics by analyzing the input water conditions and finally calculated the expected method outcome in regard of collected data. We tried to collect up to date information relating to water conditions and cost analysis. We predicted Chemical Precipitation to be at least 99.5% efficient in removing chromium from the wastewater. The efficiency of CP depends on selected coagulant and pH of inlet water. The amount of chromium in outlet water comes within the allowable limit after one treatment. Electrocoagulation on the other hand gives vastly different efficiencies for different electrodes. Whichever electrode we choose; it takes a minimum of two treatments to bring the chromium content within the allowable limit. We found that aluminum and iron both can be used as electrodes in a EC unit at Savar CETP successfully. Our study gives the concerned authority a reference if they choose to add a chromium recovery unit to the existing CETP. It is of great importance that the industry takes necessary steps to ensure environmental compliance and our study might help achieve that. We could not conduct practical experiments due to the pandemic situation. So, we hope others will build on our research and carry out the experiments using the tannery waste water from Savar TIE. Our study

indicates that a chromium recovery unit in conjunction to the Savar CETP will be enough eliminate concerns regarding chromium pollution.

Acknowledgements

We express our deepest gratitude to our thesis supervisor Prof. Shamsuddin Ahmed, for his guidance from the beginning to the end of the project. We acknowledge his each and every advises, suggestions and comments which inspired us throughout our thesis.

We would like to thank Mr. Tahsin Sejat Saniat, for his valuable guidance and inspirations that encouraged us. We are deeply grateful to him for sharing his insights and pointing out the strategies which were necessary for us to complete the thesis.

We would also like to acknowledge the help provided by Md. Ismail Hossain from R.K Leather Complex, Mr. Shah Alam from Chowdhury and co. and also Mr. Sushanta Kumar Paul and Mr. Dilip Khajuri of Apex leather tanning industry in helping us collecting the data required for our project as well as providing us with the necessary informations about the CETP of Savar Leather Industrial Park.

We also place on record, our gratitude to one and all, who directly or indirectly, have lent their hand in this venture.

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Abbreviations

BDT- Bangladeshi Taka

BOD- Biochemical Oxygen Demand

CETP- Central Effluent Treatment Plant

COD- Chemical Oxygen Demand

CP- Chemical Precipitation

CRU- Chrome Recovery Unit

DPDC- Dhaka Power Distribution Company

EC- Electrocoagulation

ETP- Effluent Treatment Plant

GDP- Gross Domestic Product

LWG- Leather Working Group

pH- Potential of Hydrogen

STP- Sludge Treatment Plant

TDS- Total Dissolved Solid

TIE- Tannery Industrial Estate

WTP- Water Treatment Plant

1. CHAPTER 1

1.1. INTRODUCTION

Bangladesh is a developing country with a population of 163 million and area of 1,47,570 square kilometers [1], making it one of the most densely populated countries in the world. It has one of the fastest growing economies in the world with an average GDP growth of 7.2% over the past 5 years [2]. The industrial sector contributed 31.15% of total GDP in economic year 2018-2019 [3].

Leather is the basis of one of the oldest industries in Bangladesh and plays a significant role in the national economy with a good reputation worldwide. This is an agro-based by-product industry with locally available indigenous raw materials having a potential for export development and sustained growth over the coming years [4]. It has enough scope for both vertical and horizontal expansion in terms of economic return and social benefits (Sharif and Mainuddin, 2003). Currently China is the market leader in terms of leather exports contributing 25% of global production [5]. But they are shifting their focus away from leather. This is a great opportunity for Bangladesh. As Bangladesh is not dependent on any other country for the prime raw material (raw hide), this could potentially be our biggest foreign exchange earner.

Leather industries in Bangladesh are traditional and to some extent modernized. It is confronted with numerous problems and constraints, of which, some are continual, and others are modern and problematical. The problems and constraints of the industries relate to raw materials, technical, financial, environmental, marketing and export [6].

For the longest time the leather tanning industry in Bangladesh was based around Hazaribagh area in Dhaka. But due to the pollution concerns, a relocation project was conceived in the

1990s. The project finally started in 2014 when the government allocated land for 155 tanneries in Savar Tannery Industrial Estate (TIE). The relocation met completion in 2017.

The Central Effluent Treatment Plant in Savar TIE was the core of the relocation project. With a capacity of 30,000cm^3, it was built to avoid environmental pollution and ensure environmental compliance. But according to reports, the CETP is not fully functional till date. While some supporting components like Water Treatment Plant, Sludge Treatment Plant, Dewatering Tanks etc. have been installed, the absence of a chromium recovery unit is a major obstacle in achieving environmental compliance certification.

Chromium is an industry specific pollutant. Only 60-70% pollutants are used up in each treatment. So, there is a massive recovery and recycling opportunity. Untreated and mismanaged chromium sludge can make its way to human food which poses serious health threats and environmental hazards. An efficient chromium recovery plant will also help recycle more water. Moreover, the usage recycled chromium will yield financial benefits for the tannery. That is why we decided to focus on the chromium recovery technologies that may possibly be applicable in Savar Tannery Industrial Park.

1.2. RESEARCH PROBLEM STATEMENT

Here are the problems and constraints of the Bangladesh leather tanning industry listed under different categories.

Raw Materials

- Seasonality problems in raw hide supply
- Pre-mortem defects like diseases, insect bites, parasites, ticks, cuts, wounds etc.
- Dependent on import for chemicals

Finance and Marketing

- Lack of relevant education, managerial capacity and marketing knowledge
- High interest rate in banks and volatile bank policies
- Shortage of working capital in the industry

Technical

- Inadequate skilled workforce
- Lack of proper training

Environmental

- Incomplete effluent treatment
- Unplanned drainage
- Insufficient solid waste management
- No recycling of resources

The industry is currently facing two major challenges. These need to be addressed immediately in order to ensure the survival and growth of the industry.

The first challenge is to achieve environmental compliance by implementing a proper effluent treatment system. Given the existing condition of CETP and other supporting components, ensuring environmental compliance has currently become a top priority for the sustainability of the industry [7].

The creation of the Tannery Industrial Estate and relocation of tanneries from Hazaribag was centered around the Central Effluent Treatment Plant in Savar. The capacity capacity to treat 30,000 cm^3 of effluents a day, the CETP is built to avoid environmental pollution and to ensure environmental compliance of the industry in the new location. As mentioned above, the CETP is accompanied by other supporting components like the Chrome Recovery Unit (CRU), Water Treatment Plant (WTP), Sludge Treatment Plant (STP), and a dumping yard. Reportedly, the CETP is not running at its fullest efficiency as some of the facilities are yet to be installed [7].

We have decided to address the environmental compliance issue in our paper and present a partial solution to the problem. A chromium recovery unit will not only help our tanneries to meet environmental compliance, but also benefit the industry financially by recycling valuable resource.

1.3. GOALS AND OBJECTIVES OF STUDY

The goal of our research is to study about advanced methods of chromium recovery and evaluate their applicability in the CETP at Savar Tannery Industrial Park. We hope our research will enlighten the concerned authority when they take decision regarding the installation of Chromium Recovery Unit at the Central Effluent Treatment Plant.

The objectives of the study:

- Identifying advanced methods of chromium recovery
- Understanding the working principles of the different methods
- Based on collected data, calculate the outcome of application for selected methods
- Select the methods that bring the amount of chromium in the treated water within the allowable limit
- Conduct feasibility analysis on the methods that brought the amount of chromium within allowable limit
- Calculate the estimated installation cost
- Calculate the estimated operating cost
- Present a comparison between selected methods
- Present our thoughts on the application of such methods in the CETP at Savar Tannery Industrial Park

1.4. SCOPE AND LIMITATION OF STUDY

For our research purpose we conducted field visits first to Hazarinagh old tannery area and Savar Tannery Industrial Park. We decided and proceeded on our topic based on the remarks of industry insiders. We communicated with both large firms and smaller firms. Our research covered the points they were most concerned with. We tried to present a solution which will bring the amount of chromium in treated water below the allowable limit, which in turn will allow the concerned tanneries to get Leather Working Group (LWG) accreditation. This is a major concern for the industry. The tanneries will be able to sell to a much larger market at far better rates if they achieve LWG accreditation.

We collected relevant data from a few tanneries and other published literature, articles and covered the water condition of raw tannery waste water, effluent treatment process, treated wastewater and water condition of Dhaleshwari river in our study. We could collect almost all the required data from fairly recent sources. We used the information to calculate the outcome of our proposed methods. Some reasonable assumptions were made to make our calculations simpler.

We covered the cost aspect also. Installation and operating costs were estimated from collected data and feasibility tests were done. Comparison was done based on service life, efficiency, cost, ease of service, installation expense and labor cost.

We faced some limitations due to the pandemic situation. We had planned to conduct some experiments to determine the efficiency of the selected methods by using waste water collected directly from the tanneries. But due to the pandemic, we could not carry out our plan. Instead we did a qualitative analysis of published works and calculated the predicted outcome.

1.5. METHODOLOGY OF STUDY

For our research, we followed a certain methodology. We first went on field visits at Hazaribagh leather tannery area and Savar Tannery Industrial Estate. We visited different tanneries and learned about the leather tanning process. We talked to the tannery officials to in hopes of identifying their problems. They were very clear in voicing their concerns about the industry. From our observation and their statements, we decided on a specific problem to focus on.

We started gathering relevant information regarding our issue of choice and then we analyzed the problem in the light of collected information. The problem was validated by collected data. After validation we proceeded to choose solution methods. We went through different published articles, papers and talked to people from the industry to gather some options which would possibly solve our problem. After choosing a handful of methods, we proceeded to study relevant literature and conduct feasibility studies of the different methods.

We took the feasible options and calculated our output water conditions for a defined water condition. After comparing the results with our desired values, we finally conducted through evaluation of the feasible methods. Finally, we presented our chosen methods alongside chemical and economic evaluation.

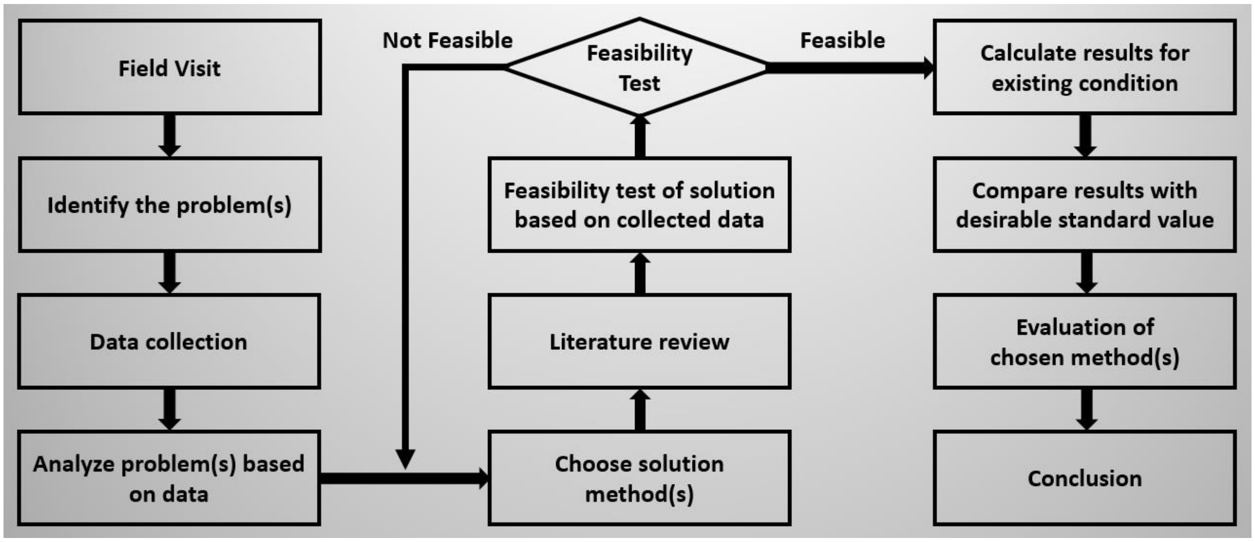

Figure 2.1 Methodology of study

1.6.CONTRIBUTION OF OUR STUDY

Our research proposes an economically viable solution for the leather tanning industry of Bangladesh. This industry is very promising and might be our top foreign exchange earner in the future. Because of environmental compliance issue, our leather has a limited market. The financially capable tanneries are trying to build Effluent Treatment Plants of their own which is very expensive. Moreover, the lower and mid-level tanneries cannot afford ETPs of their own. Our solution only adds a unit to the existing CETP and completely takes care of one of the environmental concerns.

Our research may help the relevant authority to take a decision regarding the upgradation of our existing CETP. We hope someone will follow up our study and conduct field experiments which we could not complete due to the pandemic situation.

1.7. ARRANGEMENT OF THE THESIS

Our thesis is divided in 5 chapters including the introduction and conclusion. The key information and findings are in chapter 3 and 4.

2. CHAPTER 2

2.1. INTRODUCTION

Our research was heavily dependent upon literature review as we were unable to perform any practical experiment. We sourced information from journal paper, literary article, news article and books. We used internet as our primary medium to source relevant papers and articles. For general information regarding the leather tanning industry and the impact of the industry on the economy of Bangladesh we used different news articles and information based websites.

To gather information regarding the water condition of wastewater, treated wastewater and Dhaleshwari river, we consulted a few local papers. The information regarding CETP was gathered from news articles and ‘Promoting Decent Work and Acceptable Working Conditions in the Tannery Sector in Bangladesh: Tannery Sector and its Relocation’ [7] was used extensively.

For presenting our solution we focused on an array of papers among which ‘Removal of chromium from tanning wastewater and its reuse’ [50] must be mentioned separately.

2.2. LITERATURE REVIEW CONTENTS

2.2.1. Study of Chemical Precipitation

Chrome tanning process releases chromium as pollutants to the environment. ***Fabiani et al.*** conducted a study where he provided the possibility of recovering chromium from wastewater [8]. Several types of methods have been followed to remove the toxic metal ions from the solution. Studies done by ***Ludvic, Belay, Adeel et al., Gebre et al., Bedemo et al.*** proved the success of chemical precipitation, ion exchange, reverse osmosis, adsorption, membrane process and a few others where Chemical precipitation was suggested as the best one [9][10][11][12][13].

Studies by ***Kocaoba and Akin, Barbooti et al., Mottalib et al., Terfie and Asfaw,*** shows us the complexities in applying chemical precipitation, as the process depends on factors like pH, precipitating agent, rate of precipitation, sludge volume and a few other parameters [14][15][16][17].

EEPA have concluded that chromium used in chrome tanning are harmful for environment and causes hazardous effects for plants, animals and microorganisms [18]. So treatment is essential. ***Alves et al.*** pointed out that through primary treatment systems like biological or physio chemical processes it is still not possible to keep the chromium content at the standard limit [19].

Minas et al. conducted study using different precipitating agents and concluded the best results for MgO [20] and ***Abbas et al.*** to further prove and state the facts clearly conducted experiments based on NaOH, [$Ca(OH)_2$], MgO and $Al_2(SO4)_3 \cdot 18H_2O$ for reduction of Chromium and and found better results where MgO and $Ca(OH)_2$ was used [21].

Study by ***Guidance*** stated about the solubility of the precipitates which influences the separation of chromium from the solution **[15]**. ***Esmaeili et al*** stated the factors which influenced the separation process in chemical precipitation in which pH, precipitating agents, mixing time was mentioned [22]. In this paper, we simplified our study and based on the data of some of the factors we apprehended the feasibility of Chemical precipitation in Savar CETP and calculations based on the efficiency level of the precipitating agents were performed, which validated the possibility of ensuring a chromium recovery method for recovering Chromium.

2.2.2. Study of Electrocoagulation

A lot of environmental problems are related with leather industry because of the inception of large amount of solid and liquid wastes as well as gaseous emissions and unpleasant odors [23] during the leather manufacturing process. Chromium is the most employed substance during the leather tanning since it presents the most appropriate ratio: product quality characteristics/cost [24]. Electrocoagulation is a process consisting of creating metallic hydroxide flocks within the wastewater by electrode dissolution of soluble anodes [25]. The electrocoagulation has successfully been employed for treatment of different wastewaters such as urban wastewaters [26], textile industries [27][28], laundry wastewater [29], restaurant wastewater [30], electroplating wastewater [31], chemical mechanical, polishing wastewater [32][33], olive mill wastewater , dairy and tannery wastewater [34][35], pulp and paper mill industry wastewater [36][37], baker's yeast wastewater [38] and slaughterhouse wastewater [39]. Also EC removes bacteria, viruses, and cysts [40]. Meanwhile, EC process has been widely used in the removal of arsenic [41], phosphate [42], sulfide, sulfate and sulfite [43], boron [44], nitrate [45] and chromium [46][47]. It is possible to recycle the tanning wastewater, passing them through a sieve, do a chromium solution analysis and replenish the amount of chromium salt and chemical inputs required for the process. Tests were conducted on an industrial scale for reuse of tanning wastewaters in a tannery in Brazil[48]. "The proposed direct reuse of chrome baths is even more important because chromium is a chemical of great environmental impact [48]". EC is one of the most used techniques to treat a wide variety of wastewaters. EC produces electrochemical coagulants that have the ability to remove a wide array of pollutants from wastewaters. The most preferable electrode materials in electrochemical coagulation are Al or Fe [49], creating a unique chemical/physical environment, which allows destabilization of the pollutant matter and its subsequent coagulation and flotation, thus avoiding addition of another coagulant agent [50]. Electrocoagulation does not require any chemical species as coagulating agents and is being used successfully in many industrial wastewater treatment [51].

3. CHAPTER 3

3.1. INTRODUCTION

The usage of heavy metals in industrial activities presents threat to our environment immensely due to the fact that the by-products and wastes are not treated, whereas these are later on dumped on land and water. In our research study, Chromium (Cr) have been used which is termed as a heavy metal due to its physical and chemical properties (*Metals with density exceeding 5g per cubic centimeter are heavy metals)* [52]. Chromium is soluble in water, toxic and causes carcinogenicity, mutagenicity, and teratogenicity in humans, animals, and plants [53]. Its hazardous characteristics are polluting our land and water as well as destroying our aquatic environment. Its harmful for human health [10][11][13][54]**.** Chrome tanning in leather industries doesn't fully utilize the chrome and wastage of chrome is around 30-40%. The removal and recovery of Chrome from chrome tanned leather industries thus becomes a principal task for ensuring economic and environmental stability [52]. In our case, wastage of chrome is obstructing our production of quality leather and impeding our production at a great rate. In order to remove and recover the chromium, processes like Adsorption, Electrocoagulation, Chemical precipitation, Membrane separation, Ion exchange, and Electro-dialysis have been adopted and implemented all across the world. This thesis work will solely focus on two of the removal and recovery process termed as Chemical precipitation and Electrocoagulation in order to diminish the wastage of chromium in Savar CETP.

3.2. RESEARCH FRAMEWORK

In order for us to collect the data for our study, we had to follow certain steps to ascertain how to analyze and evaluate the existing situation and propose our study results.

Initially to understand the situation of Leather tanning industry, we performed a field trip to Hazaribagh and Savar and had a discussion with Md. Ismail Hossain from R.K Leather Complex, Mr. Shah Alam from Chowdhury and co. and Mr. Sushanta Kumar Paul from Apex. They provided us with the necessary data about leather tanning using chromium and pointed us the major issue regarding this sector which was the LWG accreditation and Environmental pollution. Based on their data we analyzed the situation and specified the problem to be of wastage of chrome. After studying through various papers regarding the Dhaleshwari river beside Savar CETP and of various tanneries we compared the data of Apex tannery with that of Addis Ababa tannery and also with that of a Colombian tannery. Approximate resemblance of data was found with the data of Apex tannery. This proved the feasibility of applying Chemical Precipitation and Electrocoagulation to recover Chromium in Savar CETP. We studied the applicability of the processes and calculated using the experimental data, specified the parameters for our research and obtained results which concluded our thesis study.

3.3.CHEMICAL PRECIPITATION

Chemical Precipitation is an esteemed method for removing heavy metals and wastes due to its affordability and un-complication. The process involves usage of precipitants in a chemical solution where precipitates or solids are formed at the bottom of the solution due to chemical reaction. A supernatant liquid is formed by the conversion of the solution into a super saturated solution or due to the change of state of chemical substance from liquid to solid. Usual precipitation techniques utilize Sulphide and Hydroxide precipitant [22][52][55]. In our thesis study, we have taken the data regarding the coagulants calcium hydroxide [$Ca(OH)_2$], sodium hydroxide (NaOH), magnesium oxide (MgO) which are implemented in different tanneries [56]. This method was selected for implementation due to its level of efficiency, high degree of selectivity, economic advantage and simple infrastructure. This method allows an efficiency level of at least 99%. Through this process exclusively Chromium can be separated and rest of the supernatant can be further treated in the effluent treatment plant. The straightforward mechanism allows easy handling and extraction.

Table 3-1 Comparable parameters

Parameter	Unit	Raw waste-water (Inlet)	Treated water (Outlet)	Allowable limit	Status
COD	Mg/L	4870	505	-	X
BOD	Mg/L	1200	40	<100	Achieved
Chromium	Mg/L	64	2.5	<2	X

Source: Bureau of Research, Testing and Consultation (BRTC), BUET, March 2019

From table 3-1 we can specify that the water condition of Savar CETP is not in the allowable range and is hazardous for land and water. The given data shows the effluent condition to the inlet of the CETP. The effluents of the tanneries are not fully treated and are sometimes by passed, as such, the hazardous wastes are disposed in the river leading to aquatic deaths and endangering the nearby lands. So in order to make sure that Chromium is recovered in high quantity, modifications will be done to the effluent treatment plant.

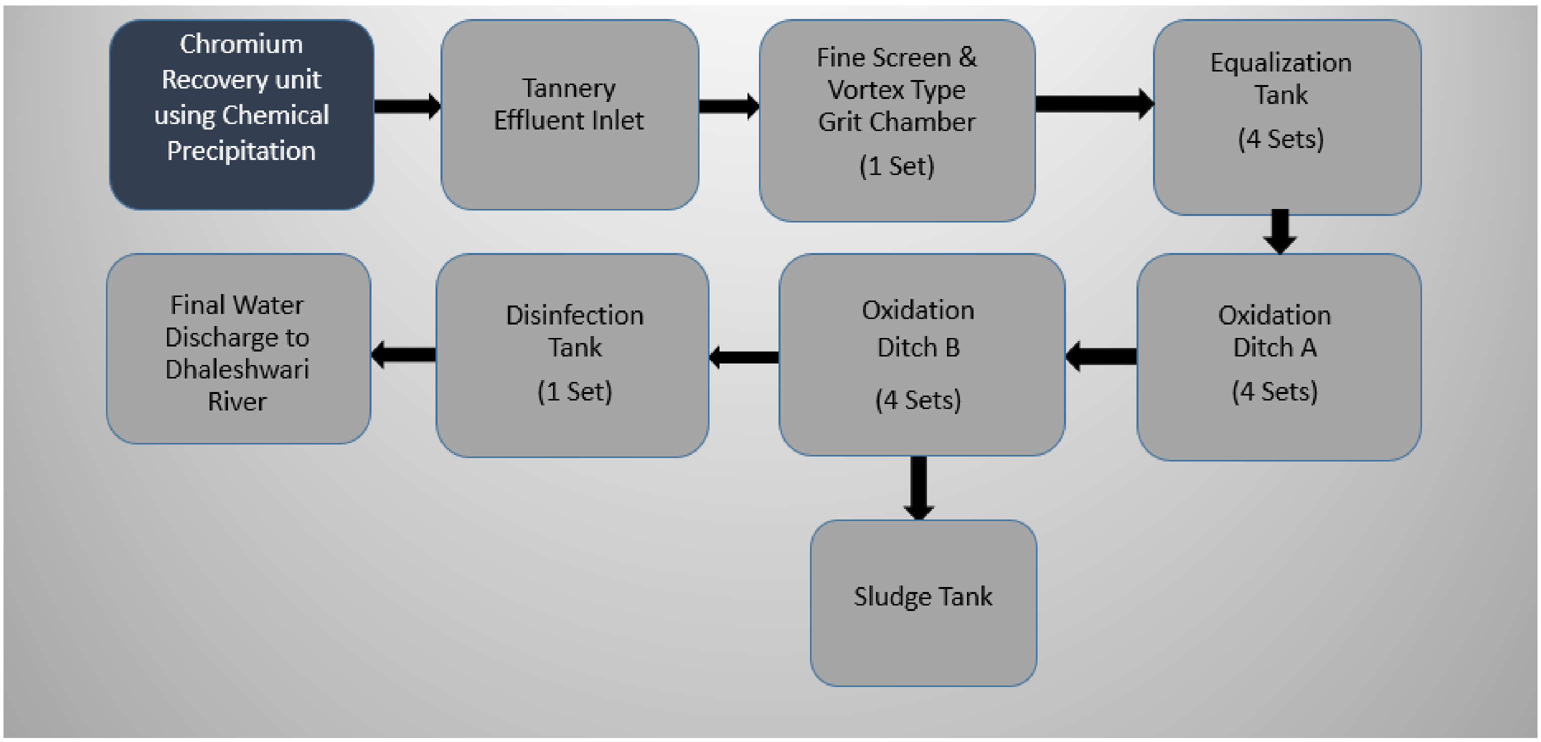

Figure 3.1 Modified Effluent Treatment Plant

3.3.1. Chromium Recovery Unit

Heavy metal Chromium can endanger the surroundings if not recovered through proper means. From *table 3.1* it was observed that the chromium is not in the required range. To control the chromium wastage a new unit known as Chromium recovery unit can be utilized.

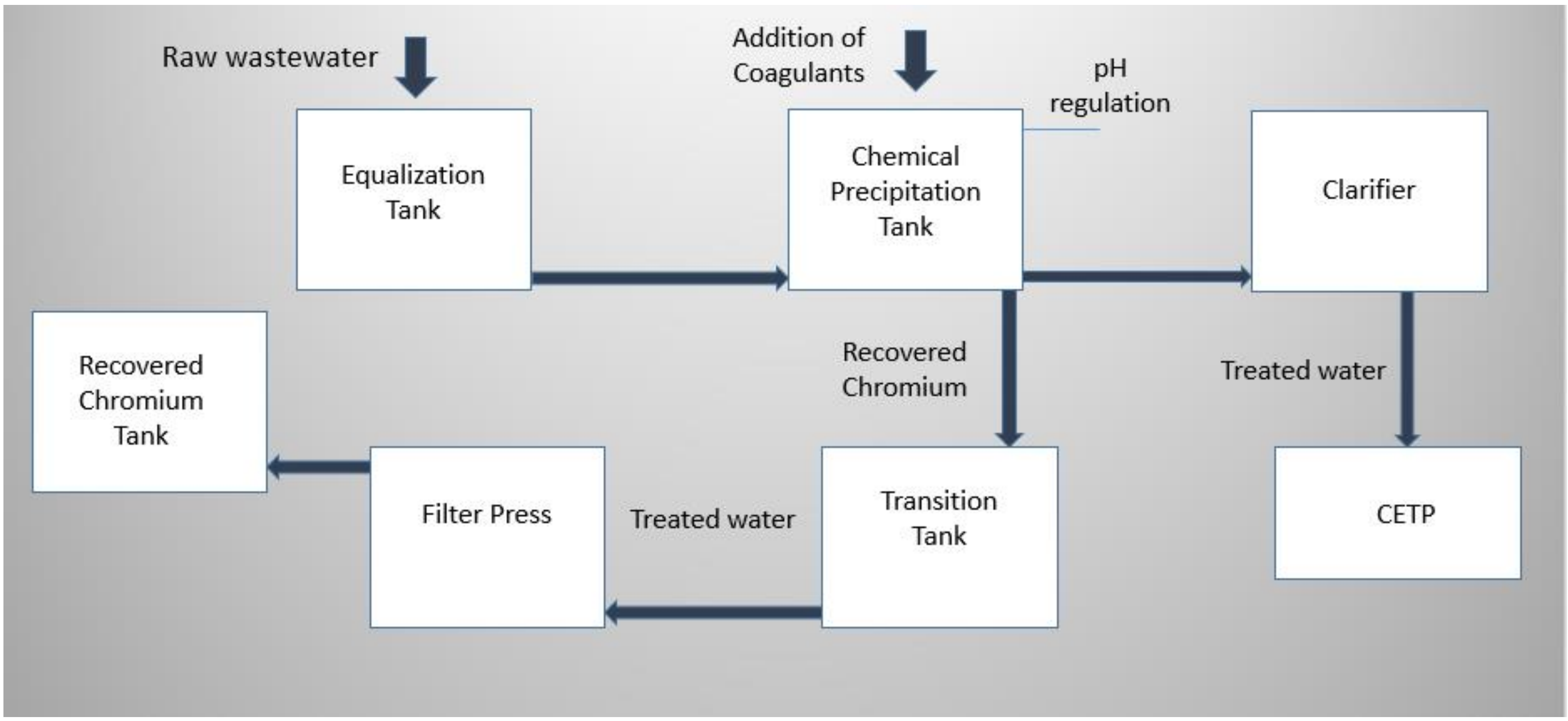

Figure 3.2 Chromium recovery Unit

3.3.1.1. *Equalization tank*

Untreated waste water enters into the Chromium recovery unit through the Equalization tank. This tank acts as a medium to resist the unsteady flow rates and pass it on as a uniform flow to the next sub unit. It is rectangular in shape and consists of inlet and outlet pipes with pump and air diffusers at the bottom of the tank in order to break down the pollutants with the help of microbes present in the water.

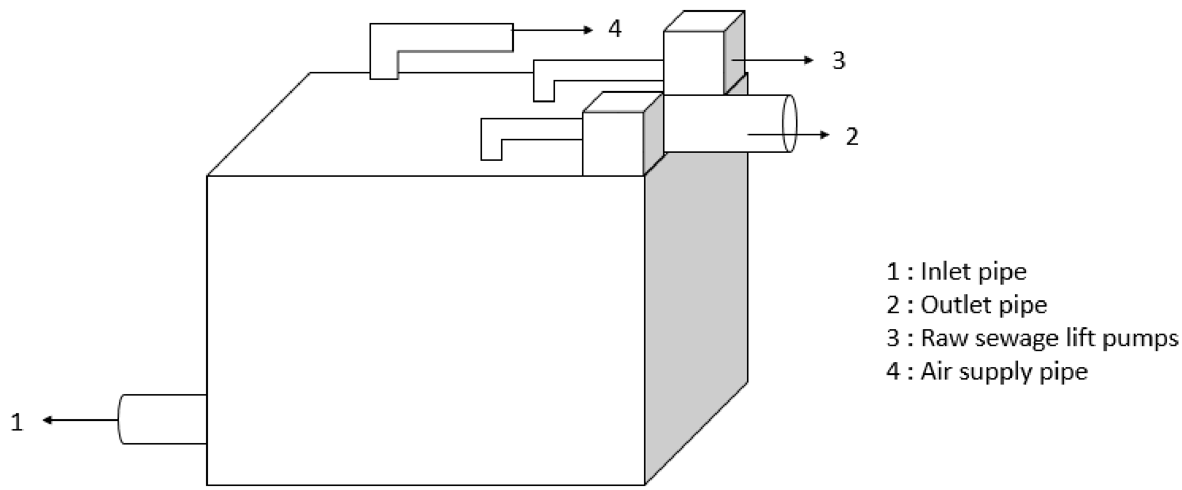

Figure 3.3 Equalization tank

3.3.1.2. Chemical precipitation tank

Coagulants [NaOH/MgO/$Ca(OH)_2$] will be added in this stage. Precipitation will occur and Chromium will deposit at the bottom of the tank which will be taken out through an outlet at the bottom and the rest of the effluents will be pumped out through a lift pump to the clarifier. A pH regulator will be present which will regulate the pH level of the chemical solution.

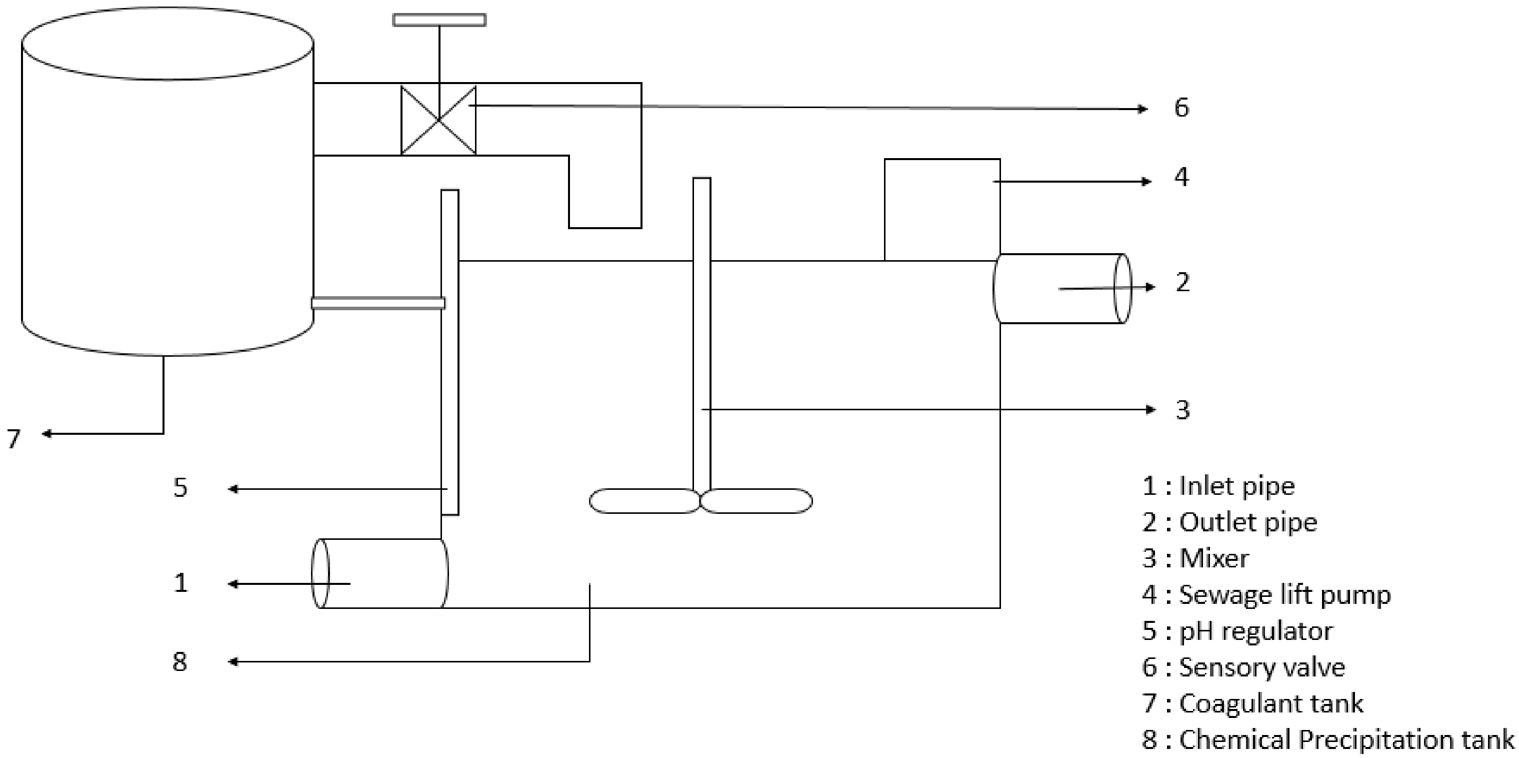

Figure 3.4 Chemical Precipitation tank

3.3.1.3. Transition tank

The recovered chromium will initially be stored in this tank. When a certain level of Chromium will be stored in the tank, then the chromium will be pumped through to the filter press. A certain feed pressure needs to be developed in order for the chromium mixed with water to pass through. Water in required amount will be added in it and will be forwarded to filter press.

3.3.1.4. Filter Press

This machine is designed to work under a definite feed pressure. Membrane plates are used to distinguish and sort out solids particulates from the solution.

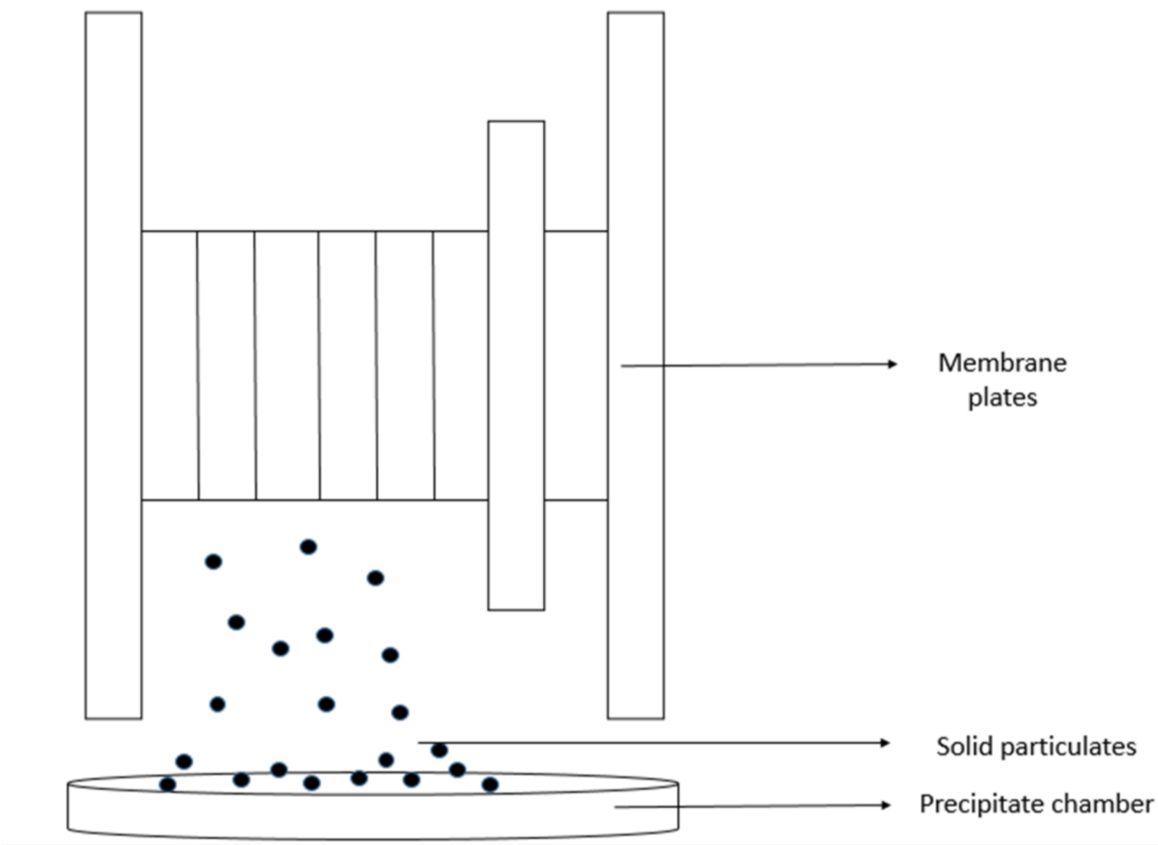

Figure 3.5 Filter Press

3.3.1.5. Recovered Chromium Tank

The recovered Chromium will be stored here and will be reused for Chrome tanning from this tank. The tank will be airtight and a motor will be connected to it so that, the recovered chromium can be supplied timely.

3.4. ELECTROCOAGULATION

Electrocoagulation is basically the electrolysis of wastewater to separate the waste materials from water and use it for further process or treatment. In this process, coagulants are formed by the application of electrolytic oxidation. From the anodes and cathodes, ions are liberated in the solution. The liberated ions react to form various monomeric and polymeric hydrolyzed species. The concentration of the hydrolysed metal species depends on the metal concentration and the solution pH. These hydrolysed metal species are responsible for the coagulation of pollutants from solution[57]. Chromium sludge is obtained in this way. Then using filtration process the water and chromium sludge are separated. There is no requirement of chemical species as coagulating agents in electrocoagulation and it is being used successfully in quite a lot of industrial wastewater treatment[51]. In electrocoagulation process, the electrodes that were found to be effective are aluminium, Copper and Iron. From experiments, the best result was found out from aluminium. The efficiency of chromium removal using aluminium electrode was 97.76% at 3.0 V and electricity was passed for 110min. in case of iron, the efficiency was 90.27% at 2.5V and passing electricity for 100min. For copper it was 69.91% at 2.0V and 100 min passing of electricity. Thus we can say that the increase in potential does not influence in removal of chromium.

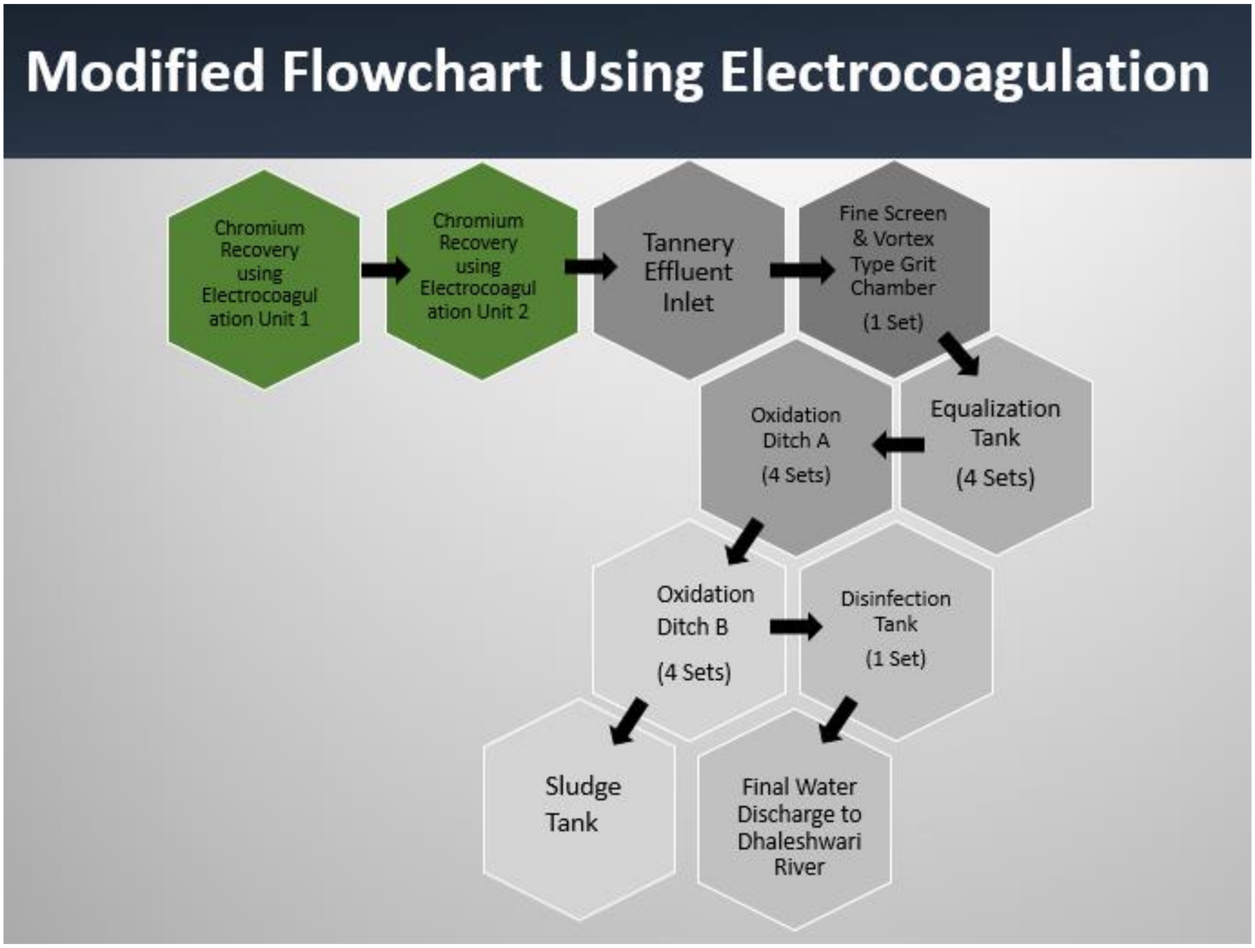

Figure 3.6 Modified flowchart using EC

The tannery water before entering the CETP will go through two EC units. Here chromium will be recovered and will be used for reusing. Then the water will be passed to the inlet of CETP. Here the water will be treated further. Basically in the EC unit chromium will be retained from the tannery water. The recovered chromium will be reused. As a result, both, it will not pollute the Dhaleshwari river. Also the chromium costing can be saved by reusing.

3.4.1. Chromium Recovery Unit

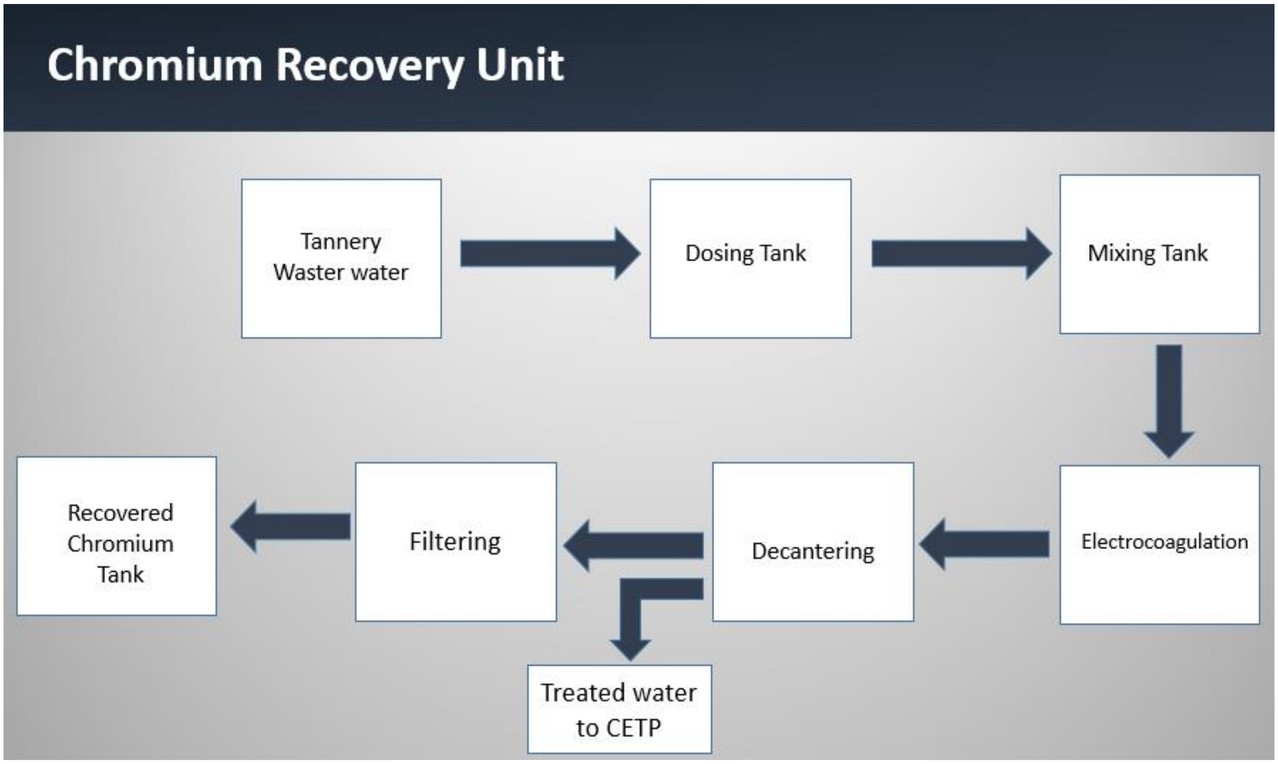

Figure 3.7 Chromium recovery unit using EC

3.4.1.1. *Tannery Waster Water Inlet*

All the waste of the tannery enters the electrocoagulation unit from this point. It is the center point of waste water entrance for every tannery.

3.4.1.2. *Dosing Tank*

Dosing tank is a sewage collection and control tank. Here sewage is passed to the next level at a controlled rate. It ensures the discharge rate required by the treatment process. The tannery waste will be passed to the treatment unit at a required rate by the dosing tank. There are different capacity of dosing tank.

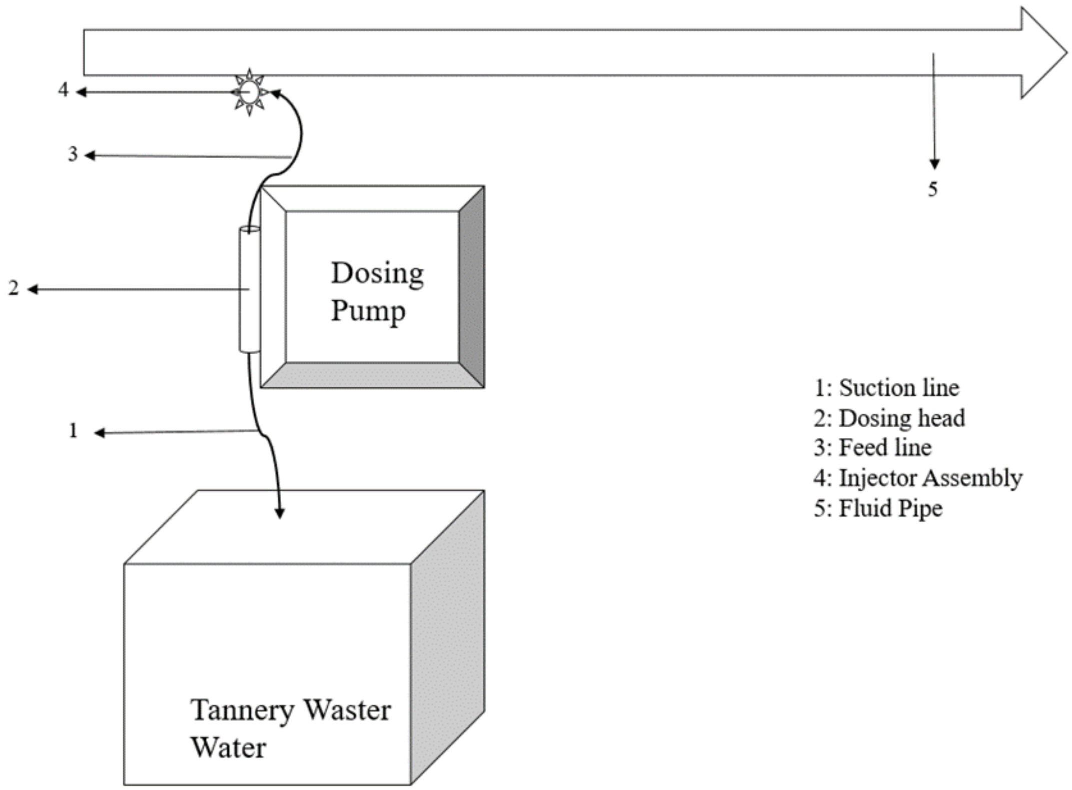

Figure 3.8 Dosing tank

3.4.1.3. Mixing Tank

In the mixing tank several components are mixed together to process the electrocoagulation. Here various hydrolyzed species are mixed to help in the formation coagulants. In the mixing tank, a smooth mixture of a plethora of materials is produced.

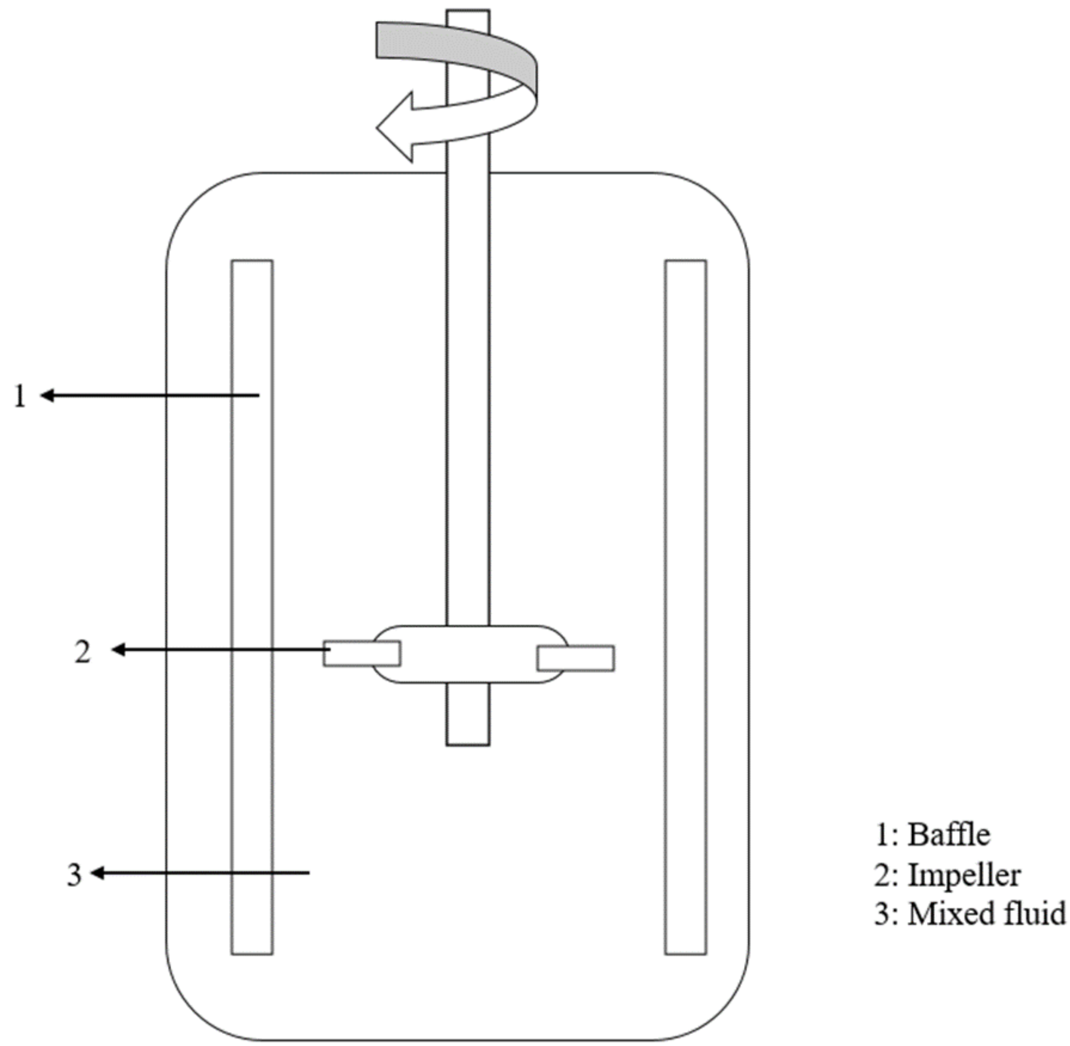

Figure 3.9 Mixing tank

3.4.1.4. Electrocoagulation Unit

In this part the destabilization of chromium takes place. The chromium waste of the tannery is separated in this chamber using the electrolysis process. Electrodes are used. Basically aluminium, copper and iron electrodes are used. The amount of voltage and passage of electricity is regulated for better results. In EC the anodes are called sacrificial anodes as they play the main part in eradication.

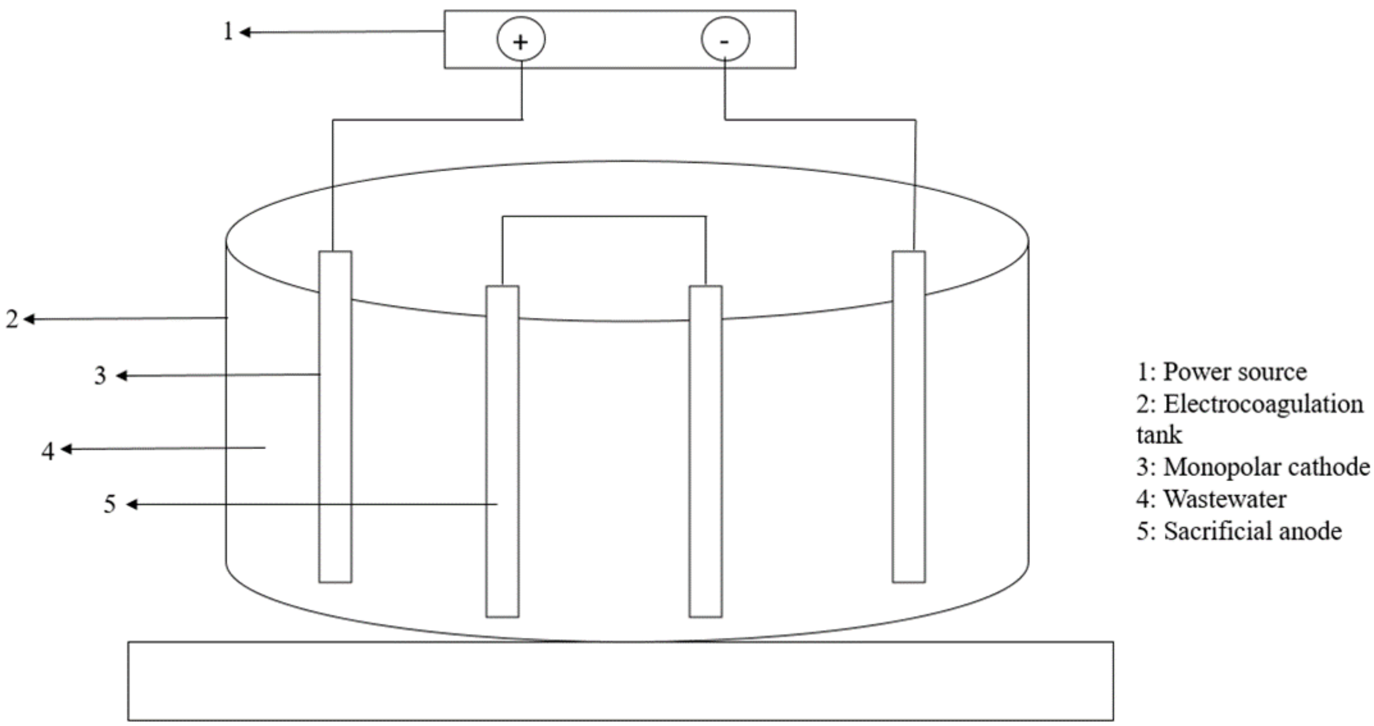

Figure 3.10 EC tank

3.4.1.5. *Decanting tank*

The solid particles are separated in this tank. This process is called decantation. This process involves the separation of liquid from solid and other immiscible (non-mixing) liquids, by removing the liquid layer at the top from the layer of solid or liquid below.

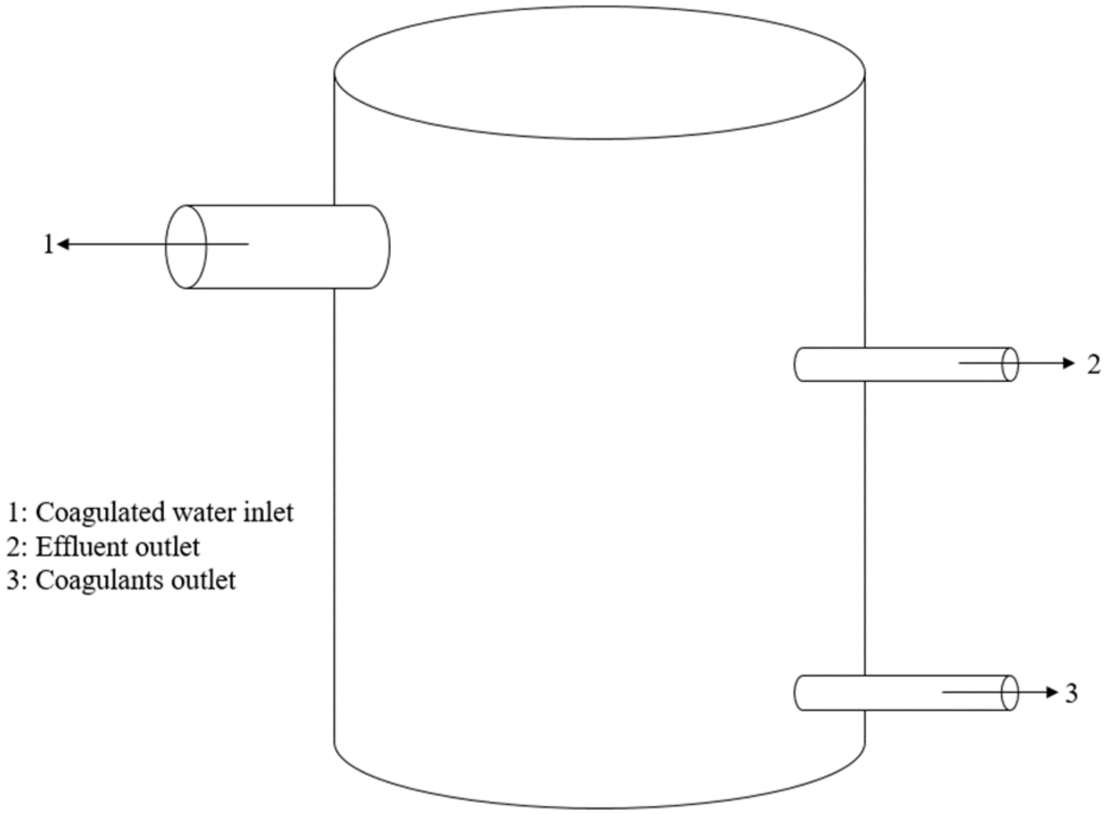

Figure 3.11 Decanting tank

3.4.1.6. Filtration tank

In this tank the coagulants after decantation process is filtered. As such the chromium is retained again and can be further used for tanning.

3.4.1.7. Recovered Chromium Tank

The recovered Chromium will be stored here and will be reused for Chrome tanning from this tank. And the treated water will pass to the inlet of CETP where it will be treated again before reusing or falling into the water

4. CHAPTER 4

4.1. INTRODUCTION

The collection of data for this thesis study was done physically by going on a field study. A visit to the Savar leather tanneries gave us an overview about the situation the leather industry is currently in. Personnel in charge helped us in having a full visit to the tanneries as well as provided us with the data relevant to the effluent water condition. Due to COVID-19 situation a full experimental setup and real time data collection was not possible. To mitigate this problem, data regarding the Dhaleshwari river condition was collected from the paper written by ***Sadia Marjia Ferdous, Rodoshi Ahmed, Muhtashim Rafiq Chowdhury, Ishraq Faruk and Dr. Rowshan Mamtaz*** as well as from the paper written by ***Md. Mahmudul Hasan & Md. Shakil Ahmed & Raofur Adnan***. To complete our study a thorough research was done by assessing the conditions and while doing our literature review we simplified the study to two main approaches which seemed feasible to apply in our Savar CETP. Analysis was done and verification about the relevance of application of the methods was completed by a comparative analysis of data collected from the Apex tannery and the data collected from the paper written by ***Fenta Minas, Bhagwan Singh Chandravanshi, and Seyoum Leta*** about Addis Ababa tannery and from the data collected from a Columbian tannery which was taken from the paper written by ***Bianca Mella∗, Ana Cláudia Glanert, Mariliz Gutterres***. Simplified calculation and graph generation was done which helped us conclude the general study regarding the data evaluation.

4.2. DATA COLLECTED

Data collection regarding the current effluent condition at the inlet of the CETP was collected from a report which presented that the effluent treatment is not up to the mark and does not meet the allowable limit. The data has been presented before in *table 3-1*. To make sure we understand the condition of the Effluent Treatment Plant, it was necessary to collect the data of Dhaleshwari river. We also collected the data which showed us the water quality at the outlet of the CETP. The Tannery outlet data was collected from the Apex tannery and the data of Addis Ababa and the Columbian tannery was collected directly from the paper. The data were taken from these papers as Addis Ababa tannery used Chemical Precipitation and Columbian tannery used electrocoagulation for recovering Chromium, which was relevant to our study and compared the data based on some of the parameters. A full quantitative study was not possible due to COVID-19 situation.

Table 4-1 Water quality of Addis Ababa tannery [20]

Parameters	Mean±SE	Minimum	Maximum
pH	7.33±0.36	6.90	8.05
Conductivity	18.5±0.60	17.5	19.6
BOD_5	2796±235	2340	3122
COD	7553±1295	5000	9213
NH_4^+–N	236±62	135	350
NO_3^- –N	343±8.8	330	360
TN	634±46	560	719
TP	16.0±2.6	12	21
S^{2-}	139±8	129	155
SO_4^{2-}	3345±473	2500	4136
Total Cr (composite)	139±3	134	143
Total Cr (chrome waste)	5010±7	5001	5023
TS	11342±465	10473	12066
TSS	3463±675	2596	4793
TSD	7879±827	6693	9470

*Conductivity in ms, pH is unit less and all other parameters in mg/L.

Table 4-2 Water quality of Savar tannery

Parameter (mg/L)	Savar Tannery (Apex)
COD	12100
BOD	2835
Chromium	5607
pH	3.4

Table 4-3 Water quality of Columbian tannery [58]

Parameter	Units	Average value	Colombian regulation standards (Act 1594)
Conductivity	mS/cm	12	
Chromium content	mg/L	5,200	1
COD	mg/L	23,350	2,000
BOD_5	mg/L	1,475	1,000
BOD_5/COD		0.06	
TOC	mg/L	7,500	
Colour		Intense green	
Salinity	%	7.2	
Viscosity	cP	1.0	
Density	g/cm^3	0.9	

Table 4-4 Characteristics of Dhaleshwari River Water Quality [59]

Parameters	Avg. Concentration at different Sampling Location (October 2017 – July 2018)			Max-Min Range	Avg. Conc.	Finding from previous studies (DoE, 2014)
	Upstream	Mixing	Downstream			
pH	7.48	7.46	7.35	6.30-8.20	7.43	7.78
DO (mg/L)	2.72	2.51	2.93	0.06 – 6.11	2.72	6.1
EC (μS/cm)	870	1430	760	170-2770	1020	658.1
TDS (mg/L)	372.7	793.8	353.4	108 - 1717	506.6	310.0
COD (mg/L)	27.1	93.4	24.9	9 - 310	48.5	-
BOD_5 (mg/L)	6.87	23.58	6.50	0.8 – 104	12.3	13.2
Cl^- (mg/L)	54.2	204.2	48.6	8 - 580	102.3	20
Cr (ppm)	0.03	0.65	0.06	0.006 – 2.4	0.25	-

Table 4-5 Seasonal Variation of Dhaleshwari River Water Quality [59]

Parameters	Avg. Concentration at different sampling locations at Dry (Dec-Feb) and Wet (May-July) period						Standards for Inland Surface water (ECR, 97)	EU Regulations for Surface Water Quality (EPA, 2001)
	Upstream		Mixing Point		Downstream			
	Dry	Wet	Dry	Wet	Dry	Wet		
pH	7.78	7.27	7.66	7.13	7.69	7.20	6.5-8.5	5.5-9.0
DO (mg/l)	1.06	3.05	0.70	2.49	0.68	3.03	5 or more	-
EC (μS/cm)	830	280	990	1490	890	290	---	1000
TDS (mg/l)	529.7	190.7	634.0	913.7	564.3	185.7	---	-
COD (mg/l)	29.0	20.7	45.7	136.7	31.3	20.7	---	40
BOD_5 (mg/l)	4.5	3.6	6.9	36.3	4.6	4.4	3 or less	3 or less
Cl^-(mg/l)	77.1	20.0	111.8	278.6	94.3	20.4	---	250
Cr (mg/l)	0.08	0.03	0.18	1.20	0.17	0.03	---	0.05

Table 4-6 Effluent quality characteristics from CETP [60]

Sl No.	WQ parameter	Unit	Standard for DW*	Standard for Inland SW**	Monsoon				Post-monsoon				Winter			
					Min	Max	Avg	Stdv	Min	Max	Avg	Stdv	Min	Max	Avg	Stdv
	Physical parameters															
1	Color	Pt-Co	15		4810	5320	5016.7	219.1	1170	3438	2304.0	1134.0	516	1735	1258.7	532.1
2	Turbidity	JTU	10		683.5	821.41	765.7	59.4	1420.6	1725	1572.8	152.2	495.11	1921	1435.6	665.1
3	Total dissolved solids (TDS)	mg/L	1000	2100	2.65	68.8	45.5	30.3	7.53	13.78	10.7	3.1	3.95	21.71	14.0	7.4
4	Suspended solids (SS)	mg/L	10	150	394	485	450.0	40.0	1071	2380	1725.5	654.5	314	1552	1135.7	581.0
	Chemical parameters															
5	pH		6.5-8.5	6–9	7.18	7.39	7.3	0.1	6.36	7.41	6.9	0.5	8.28	9.05	8.6	0.3
6	Alkalinity (as $CaCO_3$)	mg/L	---		485	524	502.7	16.1	658	940	799.0	141.0	1050	1251	1137.0	84.2
7	Electrical conductivity (EC)	μS/cm	1000	1200	5.07	12.04	9.4	3.1	12.93	20.6	16.8	3.8	4.02	9.65	7.0	2.3
8	Total hardness as $CaCO_3$ (TH)	mg/L	200–500		1026	1132	1096.0	49.5	1181	1190	1185.5	4.5	1285	1502	1367.3	96.0
9	Chloride (Cl^-)	mg/L	150–600	600	31	32	31.7	0.5	48	60	54.0	6.0	0	81	51.0	36.2
10	Sulfate (SO_4^{2-})	mg/L	400		360	530	448.3	69.6	390	690	540.0	150.0	455	919	734.7	201.1
11	Free chlorine	mg/L	0.2		0.32	0.41	0.36	0.04	0	0.41	0.21	0.21	0.41	0.51	0.45	0.04
	Oxygen regime															
12	Dissolved oxygen (DO)	mg/L	6	4.5–8	0.06	0.09	0.08	0.01	0.07	0.6	0.34	0.27	0.12	0.32	0.19	0.09
13	Chemical oxygen demand (COD)	mg/L	4	200	1161	2484	2029.0	614.0	2232	3134	2683.0	451.0	367	2205	1308.7	751.0
14	Biochemical oxygen demand (BOD)	mg/L	2	50	585	1290	1035.0	319.1	372	832	602.0	230.0	21	921	326.0	420.8
	Nutrients															
15	Total nitrogen (TN)	mg/L	0		113	240	195.7	58.5	184	187	185.5	1.5	21	665	262.0	286.8
16	Ammonia nitrogen (NH_3-N)	mg/L	0.5	50	5.6	45	30.9	17.9	38	105	71.5	33.5	13.2	482	191.0	207.5
17	Nitrite nitrogen (NO_2-N)	mg/L	< 1.0		0.028	0.081	0.1	0.0	0.048	0.31	0.2	0.1	0.05	0.5	0.3	0.2
18	Nitrate nitrogen (NO_3-N)	mg/L	10	10	0	9.6	3.2	4.5	1.8	1.9	1.9	0.0	0.3	3.1	1.4	1.2
19	Total phosphorus (TP)	mg/L	6		0	2.1	1.3	0.9	1.3	1.9	1.6	0.3	0.7	7.9	3.6	3.1
	Heavy metal															
20	Lead (Pb)	mg/L	0.05	0.1	0.09	0.12	0.10	0.01	0.07	0.10	0.09	0.02	0.15	0.27	0.21	0.05
21	Iron (Fe)	mg/L	1	2.0	5.92	6.27	6.15	0.16	5.28	12.65	8.97	3.69	2.66	10.23	6.18	3.11
22	Copper (Cu)	mg/L	1	0.5	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.00
23	Zinc (Zn)	mg/L	5	5.0	0.08	0.10	0.09	0.01	0.10	0.18	0.14	0.04	0.01	0.18	0.11	0.07
24	Cadmium (Cd)	mg/L	0.005	0.05	0.002	0.002	0.002	0.00	0.002	0.002	0.002	0.00	0.002	0.002	0.002	0.00
25	Chromium (Cr)	mg/L	0.05	0.5	7.52	9.64	8.6	0.9	7.52	10.81	9.2	1.6	9.2	12	10.8	1.2

4.3. DATA SCREENING

Data collected are used to specify and analyze the condition of the river as well as that of the effluent. Based on some fixed parameters, we conducted our study. The parameters selected were based on the data collected from the Apex tannery (*Table 4*-2) which are COD, BOD, Chromium content and pH. The data of the required parameters were separated and screening of data was done for the purpose of calculation.

Table 4-7 Effluent quality characteristics

Parameter (mg/L)	Addis Ababa Tannery
COD	7553 +-1295
BOD	2796 +- 235
Chromium	5010 +- 7
pH	7.33 +- 0.36

Table 4-8 Effluent quality characteristics

Parameter (mg/L)	Colombia Tannery
COD	23,350
BOD	1,475
Chromium	5,200

Due to bypassing of effluents and in efficient treatment and wastage of chromium, the CETP at Savar is not working at its full limit and as such the parameters are not fully meeting the standard allowable limit. This is obstructing our LWG as well as quality production of leather. According to our study and addition of our Chrome recovery unit we will perform a simplified study to ensure that the parameters are in the allowable range. We will solely focus our study only on the Chromium recovery unit. Due to COVID-19 situation a detailed experimental and quantitative analysis was not possible.

4.4. DATA ANALYSIS

4.4.1. Data Analysis using Chemical Precipitation

According to our study, ***Chromium recovery Unit (CRU)*** will operate before the treatment of the effluents. As huge amount of Chromium consisting chemicals exits from the tannery and as ***Chemical Precipitation (CP)*** has high degree of selectivity so most of the chromium can be recovered. We take three basic coagulants *Sodium Hydroxide [NaOH]*, *Calcium Hydroxide [$Ca(OH)_2$]* and *Magnesium Oxide or Magnesia [MgO]*. We take real time data of Chromium content of Apex tannery effluent (***5607 mg/L***) and using Unitary method we calculate the amount of Chromium recovered and the amount of Chromium at the outlet of the CRU.

Table 4-9 Simplified calculation of Chromium recovery using CP

Coagulants	Max Efficiency	Chromium Recovered from Chrome recovery unit (mg/L)	Amount of Chromium at the outlet of Chrome recovery unit (mg/L)
NaOH	99.97%	5605.3179	1.6821
$Ca(OH)_2$	99.97%	5605.3179	1.6821
MgO	99.98%	5605.8786	1.1214

At the outlet of the CRU we are able to get ideally an estimated value around 1.5 mg/L. From *Table 3-1* we get 64 mg/L at the inlet of CETP which in our case is around 1.5 mg/L. In practical conditions the estimated efficiency might not be so high. Even if that is the condition, the chromium content at the inlet of the CETP is less than 2 mg/L.

Now for 64 mg/l we get an estimated 2.5 mg/L at the outlet of CETP.

Table 4-10 Calculation of Chromium content

Condition	Chromium content at the inlet of CETP (mg/L)			Chromium content at the Outlet of CETP (mg/L)		
Without Chromium Recovery Unit	64			2.5		
With Chromium Recovery Unit	**NaOH**	**$Ca(OH)_2$**	**MgO**	**NaOH**	**$Ca(OH)_2$**	**MgO**
	1.6821	1.6821	1.1214	0.0657	0.0657	0.0439

4.4.2. Data Analysis using Electrocoagulation

From study, we suggested two EC unites will work before the tannery water entering the inlet of CETP. The EC unit will work for cleansing or retaining the chromium from the tannery water. The amount of chromium entering the first EC unit was 5607 mg/L. By using 3 types of electrodes, Aluminium, Copper and Iron we analyzed the tannery water contents at the inlet and outlet of EC. By analyzing the efficiency of the metals in EC, it was found out that at the outlet of EC Unit 2 the amount of chromium were 2.81 mg/L, 507.66 mg/L and 53.08 mg/L using aluminium, copper and iron electrodes respectively. Then the remaining water was passed to the inlet of CETP where further treatment of water was taken place.

Table 4-11 Simplified calculation of Chromium recovery using EC

Sample Metal	Max Efficiency	Chromium Recovered from Chrome recovery unit 1(mg/L)	Amount of Chromium at the outlet of Chrome recovery unit 1 (mg/L)	Chromium Recovered from Chrome recovery unit 2 (mg/L)	Amount of Chromium at the outlet of Chrome recovery unit 2 (mg/L)
Aluminium	97.76%	5481.40	125.6	122.79	2.81
Copper	69.91%	3919.85	1687.15	1179.49	507.66
Iron	90.27%	5061.44	545.56	492.48	53.08

4.5. DATA PRESENTATION

4.5.1. Data Presentation using Chemical Precipitation

The simplified calculation shows us that using any of the three basic coagulants at the CRU before treating of the effluents, considerable amount of Chromium can be recovered. The calculation provides satisfactory results as the standard limit is met.

Table 4-12 Presentation of results using CP

Condition	Chromium content at the inlet of CETP (mg/L)			Chromium content at the Outlet of CETP (mg/L)			Standard allowable limit (mg/L)
Without Chromium Recovery Unit	64			2.5			2
With Chromium Recovery Unit	**NaOH**	**$Ca(OH)_2$**	**MgO**	**NaOH**	**$Ca(OH)_2$**	**MgO**	2
	1.6821	1.6821	1.1214	0.0657	0.0657	0.0439	

Due to addition of coagulants the pH of the solution increases resulting in the insolubility or super-saturation of the solution. As such the Chromium removal efficiency increases greatly. With the increase of pH, the efficiency level of the coagulants increases gradually.

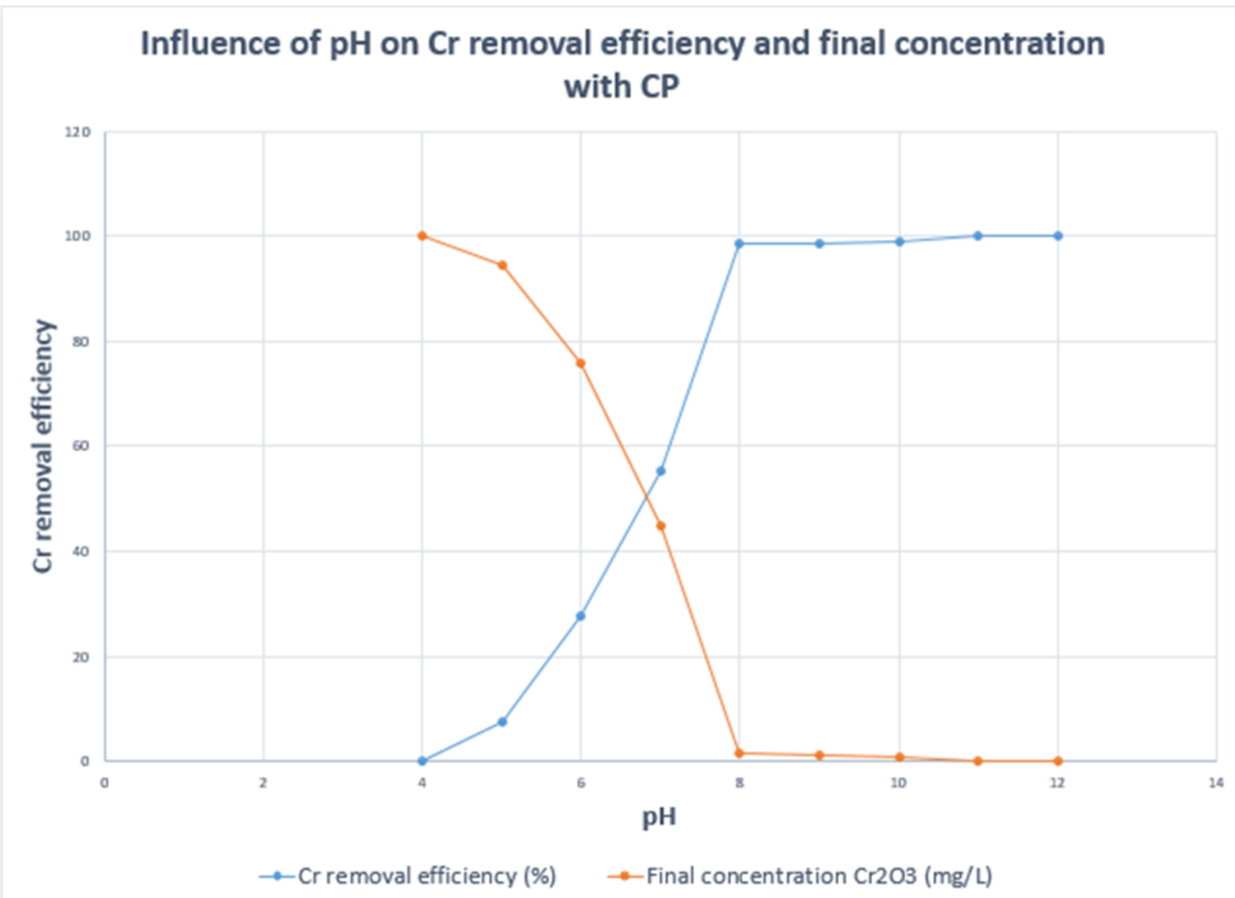

Figure 4.1 Chromium Removal Efficiency Vs pH graph [58]

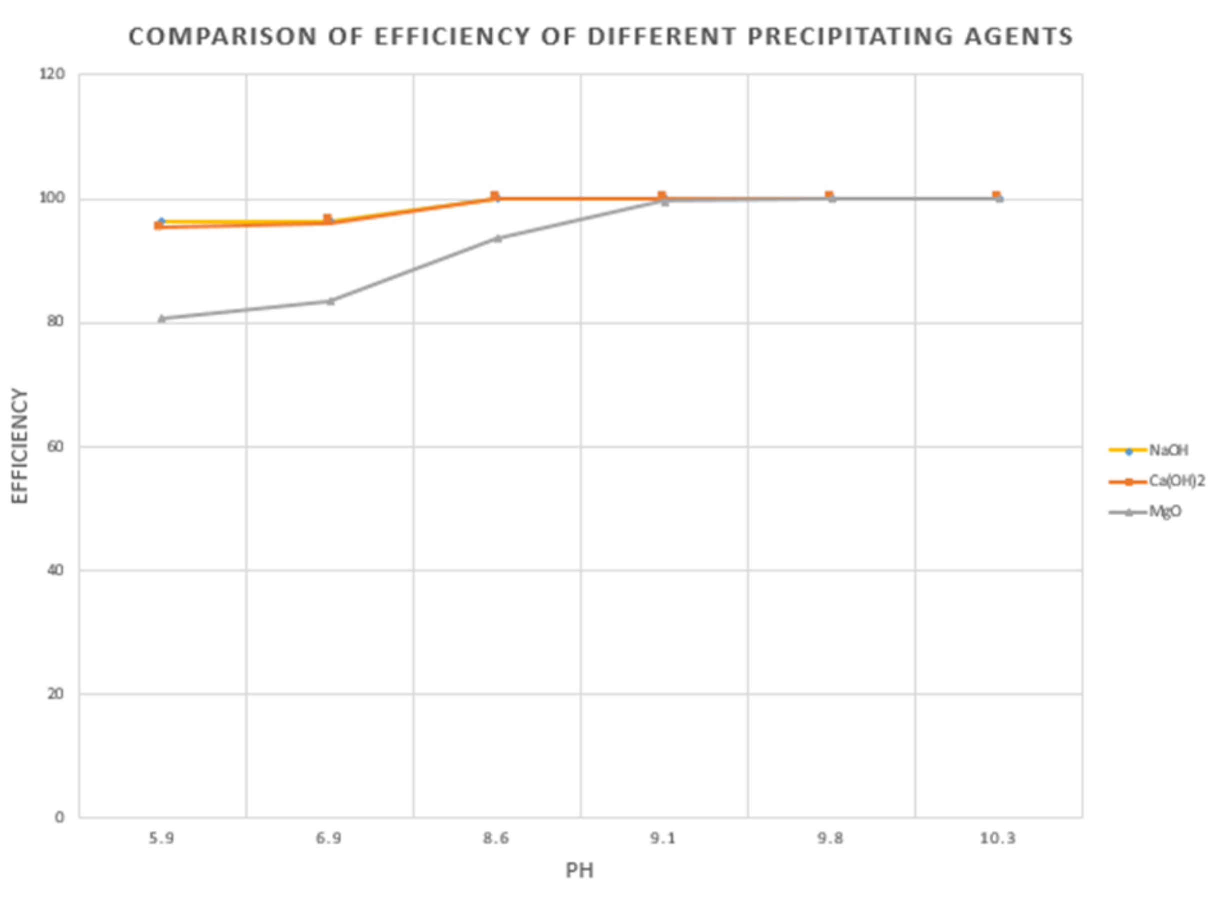

Figure 4.2 Efficiency Vs pH graph [58]

Accumulation of sludge at the CRU is also a parameter to determine which coagulants can be used in the CP method according to the plants requirement. NaOH gives the most amount of sludge and MgO provides with the lowest amount of sludge accumulation.

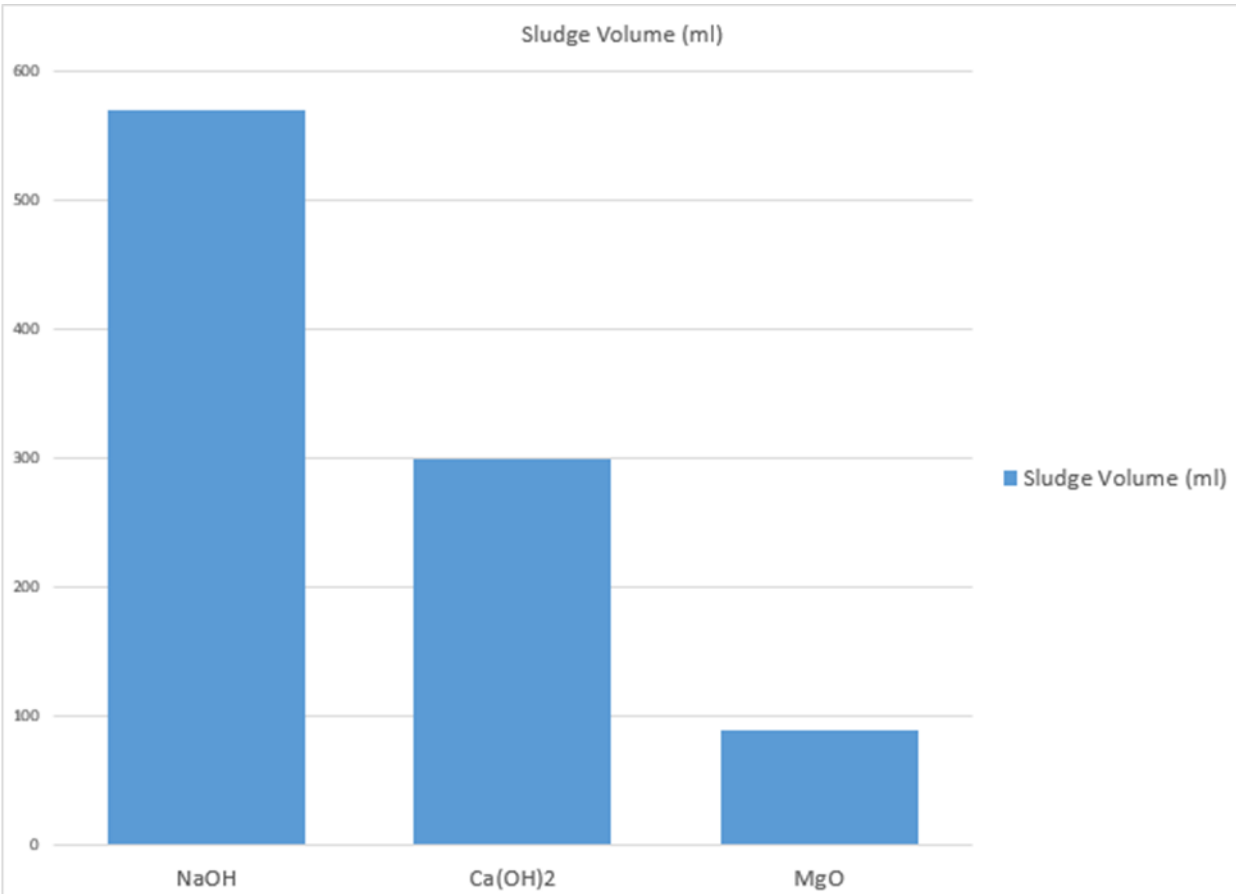

Figure 4.3 Bar graph of Sludge accumulation

4.5.2. Data Presentation using Electrocoagulation

After the chromium recovery in the 2 EC units. The tannery water is then passed to the CETP inlet for further treatment. At the inlet of CETP the amount of chromium is 2.81 mg/L, 507.66 mg/L and 53.08 mg/L using aluminium, copper and iron electrodes respectively. After effluent treatment, the chromium content in the water was 0.11 mg/L, 19.8 mg/L and 2 mg/L using aluminium, copper and iron electrodes respectively. Thus we can see that, we can meet allowable chromium limit by using aluminium and iron electrodes in the EC unit.

Table 4-13 Presentation of results using EC

Condition	Chromium content at the inlet of CETP (mg/L)			Chromium content at the Outlet of CETP (mg/L)			Standard allowable limit (mg/L)
Without Chromium Recovery Unit	64			2.5			2
With Chromium Recovery Unit	Aluminuim	Copper	Iron	Aluminium	Copper	Iron	2
	2.81	507.66	53.08	0.11	19.8	2	

The type of electrode and amount of electricity passed plays a great role in the EC method. The amount of electricity should be passed accordingly to get the desired efficiency for the electrolysis process.

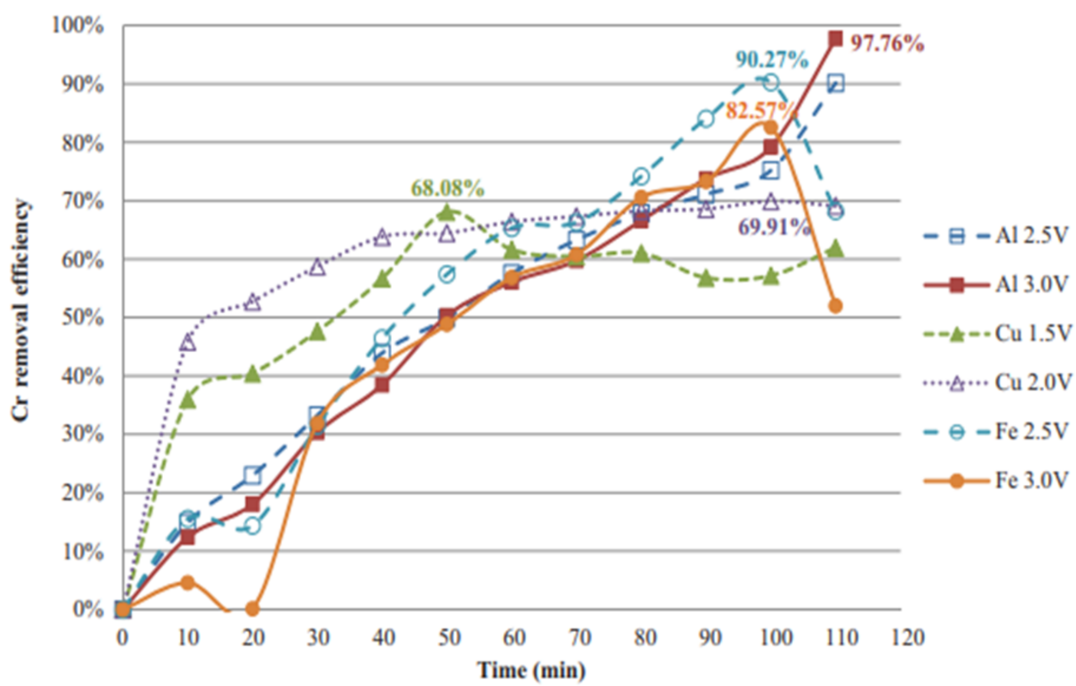

Figure 4.4 Chromium removal efficiency using different electrodes [58]

Table 4-14 Efficiency of metal electrodes

Metals	Electric Voltage	Time	Efficiency
Aluminium	3V	110min	97.76%
Copper	2V	100min	69.91%
Iron	2.5V	100min	90.27%

From here we can see that the maximum efficiency that can be obtained is 97.76% for aluminium. And for copper and iron it is 69.91% and 90.27% respectively. These efficiencies are obtained when the desired amount of electricity is passed for a fixed time. We saw that, using copper electrode we could not meet our desired allowable limit. So we will be neglecting copper electrode and focus on aluminium and iron electrode.

Cost analysis of metal electrodes:

Upon market analysis in the local market of Bangladesh, we found that the costing of metals was quite cheap and readily available. The costing per kg of metals are shown in the table below. Also from the website of Dhaka Power Distribution Company (DPDC) Limited we found out the electric cost per unit to be 9.80 taka (Flat rate). The tanneries go under the commercial rate.

Table 4-15 Cost of metal electrodes

Metal	Cost (Tk/kg)
Aluminum	**330**
Copper	**712**
Iron	**210**

Thus we can suggest that the EC method would be a feasible solution for the leather industries of Bangladesh.

4.6. DISCUSSION

From the required calculations and tables and graph we are able to specify that Chemical Precipitation gives us a higher efficiency in Chromium recovery. The standard limit to gain the LWG standards and to prevent the environmental hazard can be achieved by using Chemical precipitation in Chromium Recovery Unit (CRU). Through Electrocoagulation we have observed that, it is efficient enough if Aluminium or Iron is used. Copper is not efficient enough as it doesn't meet the required standards. But Electrocoagulation is cheaper than CP even though it requires two treatments opposed to one. Through research we have come to the conclusion that, both methods are applicable in Savar CETP and any one of them can be chosen based on the specific needs of the industry.

5. CONCLUSION AND RECOMMENDATION

5.1. SUMMARY OF THE WORK

In our research we decided to work for the betterment of the leather tanning industry which is one of the most promising industries of Bangladesh. We did field visits, read published articles and talked to industry insiders in order to identify problems in the leather sector. We listed out the most challenging problems and selected to tackle the environmental compliance issue.

After collecting recent data, we found that the treated waste water has excess amount of COD, TDS, Ammonia and Chromium. As chromium is an industry specific pollutant, we decided to focus on chromium.

We evaluated the different advanced methods of chromium recovery from industry waste water and then evaluated the different methods based on applicability. We decided to advance our research with chemical precipitation and electrocoagulation method of chromium recovery.

We studied about chemical precipitation and collected all relevant data. After finding practical examples of chemical precipitation being used in tanneries, we compared the water condition of tannery inlet to predict the applicability in Savar CETP. The predicted water outlet condition satisfied our expectations. We calculated the expected outlet water condition of CETP outlet. We also conducted the economic evaluation of chemical precipitation in Savar CETP.

We proceeded to follow similar research method for electrocoagulation. But in this case, we found that the outlet water condition did not meet our desired results. As electrocoagulation is a much cheaper method, we decided to add two chromium recovery in series in place of one and found that in this configuration, electrocoagulation met our expectation for chromium removal and recovery.

We proceeded to carry out a comparative analysis of the two methods and state their pros and cons. There is no clear winner between these two methods. According to the expectation of the relevant authority and considering other related issues, either one of the methods can yield good results for the industry.

5.2. CONCLUSION

When researching Chemical Precipitation (CP), our major findings were as follows:

- CP can realistically remove 99.5% chromium from tannery waste water considering waste water conditions of Savar Tannery Industrial State
- Efficiency is influenced by pH
- Desired values are achieved after single treatment of tannery waste water
- Offers high degree of selectivity
- The mechanism is quite simple
- The operating cost is quite affordable
- Sludge accumulation is dependent on coagulant of choice

When researching Electrocoagulation (EC), our major findings were as follows:

- Efficiency heavily depends on the material of the electrode
- Aluminum and Iron electrodes bring chromium content under allowable limit
- Two consecutive treatments are needed to achieve desired chromium content

- Requires more space than CP plant
- Installation and service complexity is higher than CP
- Operating cost is lower than CP

Benefits of our findings:

- Our findings indicate that CP and EC methods can be used practically on chromium recovery units in Savar CETP
- Gives an idea about the cost of chromium recovery treatment
- Gives a comparative analysis of CP and EC in the context of Bangladesh
- Can provide a guideline regarding choice of method for Chromium Recovery Unit to the relevant authority in charge of Savar CETP

5.3. RECCOMENDATION

Chromium Recovery Unit (CRU) is currently a good option in terms of cost and applicability. Through our study we were able to point out that, the current CETP at Savar is not working to its full capability and as such wastage of chromium is leading to environmental hazards. Besides, LWG accreditation is a necessity in order for us to capture the Leather industry market properly as we have the resources. We would suggest a more quantitative study regarding our work to make sure it is profitable and feasible in every aspect. Installation of a new Effluent Treatment Plant (ETP) is not an option and will only result in loss of money and time. As a developed CETP is already present, to make the most out of it, it would be beneficial if a Chromium Recovery Unit is installed. Not only it will be cost efficient but it will also save the environment from hazardous situations. Through our qualitative study it was discovered that, the two recovery methods- Chemical Precipitation and Electrocoagulation are quite efficient. A cost analysis of the Chromium Recovery Unit is suggested to ensure the practical feasibility so that it can be installed in a very short period of time.

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