REPUBLIC OF TURKEY
YILDIZ TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

APPLICATION OF ELECTROCOAGULATION/ ELECTRODIALYSIS TREATMENT FOR THE RECOVERY AND REUSE TANNERY WASTEWATER

ABDALHADI DEGHLES

PhD. THESIS
DEPARTMENT OF ENVIRONMENTAL ENGINEERING
PROGRAM OF PHD OF ENVIRONMENTAL ENGINEERING

ADVISER
ASSIST. PROF. DR. UGUR KURT

İSTANBUL, 2016

REPUBLIC OF TURKEY

YILDIZ TECHNICAL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

APPLICATION OF ELECTROCOAGULATION/ ELECTRODIALYSIS TREATMENT FOR THE RECOVERY AND REUSE TANNERY WASTEWATER

A thesis submitted by Abdalhadi DEGHLES in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY** is approved by the committee on 04.02.2016 in Department of Environmental Engineering, PhD of Environmental Engineering Program.

Thesis Adviser

Assist. Prof. Dr. Ugur KURT

Yildiz Technical University

Approved By the Examining Committee

Assist. Prof. Dr. Ugur KURT

Yildiz Technical University ______________________

Prof. Dr. Ismail TOROZ, Member

Istanbul Technical University ______________________

Prof. Dr. Huseyin SELCUK, Member

Istanbul University ______________________

Prof. Dr. Mehmet CAKMAKCI, Member

Yildiz Technical University ______________________

Prof. Dr. Yasar AVSAR, Member

Yildiz Technical University ______________________

This study was supported by the Prime Ministry of Republic of Turkey, Presidency for Turks Abroad and Related communities (YTB) Grant No: 57270. And was supplied by YTU – Office of Scientific Research Projects Coordination (Yildiz Technical University) Grant No: 2015-05-02-DOP08 and 2012-05-02-KAP02.

ACKNOWLEDGEMENTS

This thesis is especially dedicated to soul my parents, I am extremely sorry. To my wife, Rana, for her support, understanding sacrifice over these years and also to my beautiful sons, Taim and Zain Edin, who were eagerly waiting for me every night to come back home , although I couldn’t spend as much time as I wished with them, I am true grateful.

I am grateful to the public of turkey and especially Turkish Ministry of Higher Education for awarding me a scholarship to earn a degree in the doctor of philosophy in environmental engineering, really thanks a lot. And also I would like to thank YTU-Office of Scientific Research Projects Coordination for their continuously support.

The author would like to express his sincere gratitude to A/Prof. U.KURT for his supervision, encouragement, invaluable guidance and inspiration provided during the course of this study and providing the necessary facilities for this study.

I wish to express appreciation to Prof. Dr. I. TOROZ, Prof. Dr. H. SELCUK, Prof. Dr. M. CAKMAKCI and Prof. Dr. Y. AVSAR for their helpful comments and assistance.

Most importantly, I would like to express my deepest thanks to my brothers, sisters and members of my family in Palestine who have provided continued support throughout this study and indeed for my entire life. Also I would like to thank my friends Dr. Wisam Elmasry and Hazem Jouda for their support and help.

I would also like to thank Dr. F.ILHAN and Dr. H. AKIF KABUK for their laboratory assistance. The assistance provided by the faculty of civil engineering throughout department of environmental engineering is also appreciated.

February, 2016

Abdalhadi DEGHLES

TABLE OF CONTENTS

Page

LIST OF SYMBOLS

A_{eff}	Effective membrane area (cm^2)
As	Anode surface area (cm^2)
A_s/V	Surface area to volume ratio
C	Coulomb
C_0	Initial concentration (mg/l)
C_i^{fc}	Concentrate Concentration (mol/m^3)
C_i^{fd}	Dilute Concentration (mol/m^3)
EEC	Electrical Energy Consumption (KWh/m^3)
F	Faraday’s constant (96500 C/mol)
i	Current density (mA/cm^2)
I	Current (A)
M	Molar mass
mS/cm	Conductivity
N	The number of electrons in oxidation/reduction reaction
Q	Flow rate (ml/min)
R	The gas constant (8.314 J/mole k)
R_{AEM}	Specific resistances of the AEM (Ωcm^2)
R_{CEM}	Specific resistances of the CEM (Ωcm^2)
T	Absolute Temperature (K)
V	Volume of the reactor (L)
W	Quantity of electrode material dissolved (g of M per cm^2)
z	Number of electron transfer

LIST OF ABBREVIATIONS

AEM	The anion-exchange membranes
ANOVA	Analysis of variance
BI	Biodegradability Index
BMED	Bipolar Membrane Electrodialysis
BOD	Biochemical oxygen demand
BP-S	bipolar electrode in serial connections
C.L	Confidence Limit
CEM	Cation-Exchange Membranes
COD	Chemical Oxygen Demand
DOF	Degree Of Freedom
EC	Electrocoagulation
ED	Electrodialysis
EF	Electrofenton
HRT	Hydraulic Retention Time
MP-P	Monopolar Electrodes in Parallel Connections
NH_3-N	Ammoniacal Nitrogen
OA	Orthogonal Array
OTIR	Organized Tannery Industrial Region
S/N	Signal-to-Noise Ratio
SEC	Specific Energy Consumption
SS	Suspended Solids
TOC	Total Organic Carbon
TWWT	Tannery WasteWater Treatment

LIST OF FIGURES

Page

LIST OF TABLES

ABSTRACT

APPLICATION OF ELECTROCOAGULATION/ELECTRODIALYSIS TREATMENT FOR THE RECOVERY AND REUSE TANNERY WASTEWATER

Abdalhadi DEGHLES

Department of Environmental Engineering
PhD. Thesis

Adviser: Assist. Prof. Dr. Ugur KURT

Tannery industry is known widely as one of the highest consumers of water as well as playing a key role in the economic sector of many countries. A few decades ago, water and energy sources were classified as the top two challenges for the twenty-first century. Wastewater treatment has been considered as an efficient tool for managing water and energy sources. Until relatively recently, little has been done of effective technique “zero effluent” to conserve them.

In this context, electrochemical treatment technology has achieved much attention due to its attractive advantages as: simple, fast, reliable, and cost-effective operation for the treatment of wastewater.

In this work, a batch electrocoagulation (EC) technique for tannery wastewater treatment was examined using iron and aluminum electrodes. It involves dissolution of metal from the anode with simultaneous formation of hydroxyl ions, and generation of hydrogen gas at the cathode The effects of operating parameters that include current density, initial pH, and electrolysis time on EC performance were accomplished by measuring of COD, Color, Cr, and NH_3-N as control parameters.

Firstly, EC performance on tannery wastewater was tried with discontinuous system by using Taguchi Statistical Method. COD removal efficiencies were reached 64.4% for Al and 63.3% for Fe electrodes.

After that, performance of the electrocoagulation (EC) process on the continuous system was also measured. The effects of the same operating parameters on the pollutants removal efficiency, sludge and hydrogen gas production were investigated in order to optimize process performance. In the case of aluminum electrodes, The results showed that for tannery wastewater with an influent pH adjusted at about 6, the use of a current density of 14 mA/cm^2, and an EC time of 125 min, gave access to pollutants (COD, Color, Cr, and NH_3-N) removal efficiency 73, 94, >99 and 51%, respectively. The energy yield of harvested hydrogen was 60 % of the energy demand as kCal of the electrocoagulation process. However, in the case of iron electrodes, with effluent pH adjusted at about 7, the use of a current density of 14 mA/cm^2, and an EC time of 125 min, gave access to pollutants (COD, Color, Cr, and NH_3-N) removal efficiency 67, 93, >99 and 46 %, respectively. And also, the energy yield of harvested hydrogen was 58 % of the energy demand as kCal of the electrocoagulation process. Thus, the energy costs for two cases were found to be 0.675 \$/m^3 wastewater. And also the amount of dried sludge was 0.35 kg/kg chemical oxygen demand removed. It could be seen that hydrogen gas production coupled with pollutants removal efficiency by EC continuous mode would be an effective approach for energy recovery and wastewater reutilization.

As the end of the studies, the optimized electrocoagulation process was then integrated with electrodialysis (ED) process for the treatment of tannery effluents. In case of treated tannery by EC with aluminum electrodes, ED process was effectiveness where the removal efficiency of COD, NH_3-N, Cr and color were 92,>99, >99, >99 % respectively corresponds to conductivity value of 1.5 mS/cm at 25 minute. While, in the case of treated tannery by EC with iron electrodes, ED process was also efficient for removal pollutants, the removal efficiency of COD, NH_3-N, Cr and color were 87, >99, >99, >99 % respectively corresponds to conductivity value of 1.5 mS/cm at 75 minute.

It is noticeable that the effluent treated with combined EC- ED techniques presents very similar values for the same parameter as the ones presented by Turkish dischargeable legislation as well as guidelines for using reclaimed wastewater in irrigation for the states of Turkey, Palestine and Jordan.

Key words: Tannery Wastewater, Electrocoagulation, Hydrogen gas production, Electrodialysis, sludge characterization.

ÖZET

DERİ ENDÜSTRİSİ ATIKSULARINDA MADDE VE ENERJİ GERİ KAZANIMI, SUYUN YENİDEN KULLANILMASINDA ELEKTROKOAGÜLASYON-ELEKTRODİYALİZ ARITMA YÖNTEMİ

Abdalhadi DEGHLES

Çevre Mühendisliği Anabilim Dalı
Doktora Tezi

Tez Danışmanı: Yrd. Doç. Dr. Uğur KURT

Deri Endüstrisi bir çok ülkenin ekonomisinde oynadığı önemli rol kadar, yüksek su kullanımı olan bir sektördür de. Son yıllarda, 21. Yüzyıl için olabilecek en büyük iki sorun su ve enerji kaynaklarındaki sıkıntılar olarak sıralanmaktadır. Atık su arıtımı su ve enerji kaynakları yönetiminde etkin bir araç olarak dikkate alınmaktadır. Bu kaynakların korunması için elzem olan “Sıfır Atık Teknolojis” son zamanlarda biraz biraz kullanılmaya başlanmıştır.

Bu bağlamda, Elektrokimyasal Arıtma Teknolojileri atık su arıtımında kolaylığı, hızlı olması, güvenilirliği ve ekonomik işletme maliyetleri gibi cazip avantajları nedeniyle oldukça başarılı olmaktadır. Hem değerlendirilebilir arıtılmış atık su eldesi, hem de enerji geri kazanımı açısından önem arz etmektedir.

Bu çalışmada, Tabakhane Atıksuyu arıtımı için elektrokoagülasyon (EC) tekniği demir(Fe) ve aluminyum(Al) elektrotlar kullanılarak çalışıldı. EC işlemi eş zamanlı olarak anottan koagülan metalin çözünmesi ve katotta hidroksil iyonları ve hidrojen gazı

oluşumu şeklinde gerçekleşir. EC performansı üzerinde işletme parametreleri olarak akım yoğunluğu, başlangıç pH'sı ve elektroliz süresinin etkileri, kontrol parametreleri KOİ, renk, Cr ve NH_3-N ölçümleri ile araştırıldı. İlk olarak Tabakhane Atıksuyu üzerinde EC performansı Taguchi istatistik yöntemi kullanımı ile denendi. Al elektrot için % 64.4 ve Fe elektrot için % 63.3 KOİ giderim verimine ulaşılabildiği görüldü.

Sonrasında, sürekli sistem üzerinde EC performansı ölçüldü. EC prosesi performansını optimize etmek için aynı işletme parametrelerinin kirlilik giderim verimine etkileri araştırıldı. Al elektrot ve pH:6.0, akım yoğunluğu 14 mA/cm^2 ve elektroliz süresi 125 dakika için KOİ, renk, Cr ve NH_3-N giderim verimi sonuçları sırasıyla; % 73, % 94, >% 99 ve % 51 olarak tespit edildi. Üretilen hidrojen gazının ihtiyaç duyulan enerjiyi karşılama oranı kCal olarak % 60 oldu. Fe elektrot ve pH:7.0, akım yoğunluğu 14 mA/cm^2 ve elektroliz süresi 125 dakika için ise, KOİ, renk, Cr ve NH_3-N giderim verimi sonuçları sırasıyla; % 67, % 93, >% 99 ve % 46 olarak belirlendi. Aynı zamanda, Üretilen hidrojen gazının ihtiyaç duyulan enerjiyi karşılama oranı kCal olarak % 58 oldu. Enerji maliyeti her iki durum için de 0.65$/$m^3$ atıksu olarak bulundu. Giderilen KOİ'ye karşılık oluşan çamur miktarı 0.35 kg kuru çamur/kg KOİg oldu. EC sürekli sistem arıtma çalışmaları ile hem kirlilik giderim verimliliğinin, hem de hidrojen gazı üretiminin atıksuyun yeniden kullanımı ve enerji geri kazanımı yaklaşımında etkili olduğu görüldü.

Son çalışmalar olarak; Tabakhane Atıksuyunun arıtımı için optimize edilmiş elektrokoagülasyon çalışmaları elketrodiyaliz(ED) prosesi ile entegre edildi. Al elektrotlu EC prosesi çıktıları ile gerçekleştirilen ED prosesinin kirlilik parametreleri gideriminde etkin olduğu görüldü. 1.5 mS/cm iletkenlik değerine ulaşılan 25. dakikada KOİ, renk, Cr ve NH_3-N giderim verimi sonuçları sırasıyla; %92, >%99, >%99 ve >%99 olarak belirlendi. Fe elektrotlu EC prosesi çıktıları ile 1.5 mS/cm iletkenlik değerine ulaşılan 75. dakika çalışmasında ise, KOİ, renk, Cr ve NH_3-N giderim verimi sonuçları sırasıyla; % 87, >% 99, >% 99 ve >% 99 olarak gerçekleşti.

EC-ED kombine sistemi ile arıtılmış atıksuların Türkiye'deki atıksu deşarj mevzuatı ile uyumlu olduğu, dahası Türkiye, Filistin ve Ürdün için sulama suyu şeklinde kullanılmasının da mümkün olabileceği dikkate değer bir durum olarak kaydedilmiştir.

Anahtar Kelimeler: Tabakhane Atıksuyu, Elektrokoagülasyon, Hidrojen gazı üretimi, Elektrodiyaliz, Çamur karakterizasyonu.

CHAPTER 1

INTRODUCTION

1.1 Literature Review

A few decades ago, water and energy sources were classified as the top two challenges for the twenty-first century [1]. Increasing pollution from point and non-point sources such as industry and agriculture, respectively, the ever-increasing population, urbanization and climatic changes, all of these are being leaded to decline water quality and quantity [2, 3]. Wastewater treatment has been considered as an efficient tool for managing water and energy sources. Until relatively recently, little has been done of effective technique "zero effluent" to conserve them.

Billions of liters of industrial wastewater are produced every day with large quantity of aqueous waste [4]. Leather and environment can be described as two sides of the same coin due to the fact that potential wastes from meat industry (i.e. skins and/or hides) are used in the leather industry via tanning process [5]. Overall, tannery industry is known widely as one of the highest consumers of water as well as playing a key role in the economic sector of many countries. The global leather industry produces about 18 billion square feet of leather yearly with an estimated value of about $40 billion [6].

Besides, leather industry is described as a hard process which involves in serious operations can be given as**:** beam house operation, tanyard operation, post-tanning operation and finishing operation [7]. At each operation several of chemical materials are used such as acids, alkalis, chromium salts, tannins, solvents, sulphides, dyes and auxiliaries. Ultimately, they produce large amounts of potentially toxic wastewaters containing both organic and inorganic compounds [8, 9].

Tanneries, ultimately, generate wastewater in the range of 30–35 L Kg^{-1} skin/hides process with variable pH, high concentration of suspended solid, BOD, chromium, COD, NH_3-N and sulfides as well as low biodegradability [7, 10, 11]. Discharging tannery wastewater into water body without treatment can affect in aquatic life unconstructively .Thus, there is an increasing environmental alarm with regard to tanneries in view of the fact that high consumption of the water, the complex characteristics, economic sector, and environmental regulations. It should be, absolutely, searched a cleaner technology, economically as well as environmentally sustainable tannery wastewater treatment technologies [12, 13].

There are many options that utilize for the treatment of tannery wastewater such as biological process [11, 14-16], and physical -chemical process [17-19]. In this context, conventional biological treatment does not always achieve satisfactory performance due to the toxicity of the tannery wastewater that will affect the development of the bacteria and it is characterized by low biodegradability. Also traditional physical–chemical processes are comparatively expensive, and may lead to secondary pollution because it needed additional chemicals [20-21]. The limits forced are set with the aim of protecting the environment. Absolutely, the treatment and reuse of wastewater has become necessity. For these reason, we require to expand innovative and inexpensive techniques for the treatment of tannery wastewater. In recent years, there has been increasing interest and effective process in the use of electrochemical methods for the treatment of industrial wastewaters.

Electrochemical technologies are distinct as a “green technology” due to the fact that the main reagent, the electron. Hence, they present promising approaches for the hindering of pollution problems in the process industry. Nowadays, electrochemical technologies have reached such a state that they are not only comparable with other technologies in terms of cost but also are more efficient and more compact. Ultimately, it is a great attention to use in treatment of water/ wastewater due to have attractive advantages such as environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation, and cost effectiveness [22, 23].

Electrochemical technologies have explored in recent year in environmental applications especially for treating water/wastewater. One of these processes is electrocoagulation (EC) which has achieved much attention due to its attractive advantages as: simple, reliable, and cost-effective operation for the treatment of wastewater. In fact, it involves dissolution of metal from the anode with simultaneous formation of hydroxyl ions, and generation of hydrogen gas at the cathode which can be recovered for use as energy source or a reactant for other industrial applications [24]. There are a vital advantages of EC as a low sludge production technology; secondly, the EC flocs are relatively large, contain less bound water, more stable, and amenable to filtration and therefore is not required to chemical aids (green process) [25]. The fitting choice of EC materials is very essential electrode materials, generally, are aluminum and iron. They are cheap, readily available, and have been proven effective [26]. Yet, EC has satisfactory been utilized decades to treat wastewater of olive mill [27, 28], metal plating [29], domestic [30], tannery [4, 31-33], rose processing [34], chromium removal (VI) [35], textile industry [36], etc. However, the continuous mode of the EC process has been less investigated, except in a few studies [37-42]. Based on literature reviews, so far no other studies have taken into account the aspect of hydrogen recovery from the electrocoagulation process. Hydrogen is a main by-product of the electrocoagulation process as it is generated at the cathodes by water electrolysis. With an effective gas-liquid-solid separation process, high quality hydrogen can be recovered from the electrocoagulation process and used as an energy source or as a reactant for industrial processes.

Thus, membrane technology has been applied in tannery wastewater treatment and recycling [43- 45]. The prominent advantage for membranes process is that concentration and separation are achieved without changing the physical state or the need to use chemical products [46].One of the most important of the membrane technology or electrochemical separation process is electrodialysis (ED), in which electrically charged membranes and an electrical potential difference are used to separate ionic species from an aqueous solution and other uncharged components. ED is considered an electrodriven membrane process involving ion exchange membranes are not only a part of applied in electrochemistry but also belong to the field of separation techniques [47]. *Compared to other* kinds of *membrane technologies*, it uses an electrical current, rather than pressure, to induce the ions to pass through the membrane; the use of pressure is a major cost factor for other membrane processes. And also, it can be used a low levels of electrical current, which helps to reduce the cost of ED In addition, ED has attractive characteristics such as a high selectivity, a high product recovery ratio and can destroy at least some of the components in the raw water (drinking or waste), and it can run continuously. And also, ED does not require treatment chemicals “green technology”, and cost effectiveness [46, 48, 49], all of these advantages may be pointed out to the utilize ED in the future as an effective techniques. However, unlike monopolar electrodialysis compared with bipolar membrane electrodialysis (BMED). This is because the last has an a vital advantage which anions and cations are separately removed from the sample and combined with H^+ and OH^- ions by means of a bipolar membrane so that separate acidic and alkaline solutions are attained [50] .

Anyway, electrodialysis has been applied in water /wastewater treatment and also for processing rinse water from electroplating industry [51, 52]. The use of ED is expected to continue to increase in the future.

Sometimes it becomes necessary to use two or more methods of treatment, i.e. hybrid processes, to ensure efficient treatment of wastewater [53]. Electrocoagulation has been shown to be a better option in the removal of organic compounds, heavy metals present in the wastewaters. And also increased the biodegradability index (BI) of the effluents [54- 56]. So, elctrocoagulation can be fabricated into water treatment with membrane technologies. EC has been combined with microfiltration (MF) for control of virus in surface water [57], with nanofiltration (NF) to treat textile wastewater [58], with electro-oxidation (EO) to treat industrial wastewater [59].

There are a various types of studies performed for treatment of tannery wastewater by various combined process [60-65]. As mentioned before, so far no other studies have taken into account to the investigation of integrated process (EC-ED) combining membrane technologies (ED) and electrocoagulation processes (EC) in the treatment of tannery effluents. EC is used for the degradation of organic matter. ED allows the ionic species separation, which produces water suitable for reuse in irrigation or goes to deep sea, and to reuse in leather process according to standard legislation.

1.2 Objective of the Thesis

As well known, tannery industries are among the most polluting industries in terms of the volume and the complexity of treatment of its effluents discharge. And also, it has an effective economic value for many countries, and strict environmental regulations for influent. The limits forced are set with the objective of protecting the environment. Absolutely, the treatment and reuse of wastewater has become necessity.

The aim of this thesis is the investigation of integrated process (EC-ED) combining membrane technologies; electrodialysis (ED) and electro-coagulation processes (EC) in the treatment of tannery effluents. EC is used for the degradation of organic matter. ED allows the ionic species separation, which produces water suitable for reuse in irrigation or goes to deep sea, and to reuse in leather process according to standard legislation. The experiments are performed at a laboratory scale in order to evaluate the performance of each process and to optimize the experimental conditions for the integrated process.

The prime objectives of the present thesis which they are the reduction of the pollution from tannery industry, and to thoroughly assess and design a new treatment plant, including experimental analysis when necessary, as following:

- To make sure environmental protection
- To characterize the tannery wastewater in terms of: pH, conductivity, chemical oxygen demand (COD), Chromium (Cr), Ammoniacal nitrogen (NH_3-N), color and suspended solids (SS).
- To determine the optimal conditions for organic and inorganic pollutant removal.
- To verify the sludge production.
- To evaluate the recovery of hydrogen gas production
- To determine the recovery of the pollutants
- To achieve enhanced treatment results, less energy consumption throughout the system and ultimately a cost effective system, with an improved end result.

To achieve the presented study objectives, the overall study was separated into the four primary parts as shown the following:

Part I Definition of related problem

Related problem is defined as:

- Literatures survey on the fundamental of the EC and ED processes.
- Review of TWWT by different methods especially EC technology.
- Expert arguments are taken.
- Selection of tannery industrial region in Istanbul.

- Collection of samples.
- Characterize of samples.
- And experiment set up.

Part II Designing and constructing a batch of electro-coagulator

This part will be involved in:

- The EC cell (discontinue system) is prepared and characterized.
- The removal and appropriate EC technology are assessed for TWWT.
- The effects of various operating parameters on the efficient removal of pollutants will be investigated. These parameters can be given as; current density, electrolysis time, pH solution.
- Taguchi method is carried out in order to design the experiments and to optimize the experimental results.
- The optimum conditions are discussed for removal of pollutants in batch EC by using the prepared electrodes; (Aluminum and Iron).
- The pollutant removal efficiency is determined on the efficient process and also economic view.
- Result interpretation and discussions.

Part III Designing and constructing a continuous of electro-coagulator

Based on the results that will be obtained from batch experiments (optimum conditions):

- The continuous EC system is designed and fabricated.
- The effects of current density , detention time, pH initial, inlet flow rate and others parameters will be examined.
- The removal efficiency of the pollutants will be pointed out based on: the water quality, hydrogen gas production, and the sludge characteristics.
- Result interpretation and discussions

Part IV Hybrid process

This part will be based on the results production from electrocoagulation continuous mode:

- The effluent wastewater that is treated by a closed system at optimum conditions even Fe and Al electrodes will be imposed to ED cell.
- The optimization of studies will be focused on:
  a) Sure environmental protection
  b) Standard environmental legislation
  c) Minimal energy consumption
  d) Capacity of recovery substances
- Result interpretation and discussions.
- Conclude and write of dissertation manuscript.

1.3 Hypothesis

Globally, the tannery industry is currently undergoing radical transformation due to pollution and discharge legislations. Tannery industry is known widely as one of the highest consumers of water as well as playing a key role in the economic sector of many countries. Tannery industries are among the most polluting industries in terms of the volume and the complexity of treatment of its effluents discharge. A few decades ago, water and energy sources were classified as the top two challenges for the twenty-first century. Wastewater treatment has been considered as an efficient tool for managing water and energy sources. Until relatively recently, little has been done of effective technique "zero effluent" to conserve them. Based on literature reviews, so far no other studies have taken into account the investigation of a hybrid technique for tannery wastewater as EC with ED process. This thesis examines the use of electrocoagulation treatment process followed by electrodialysis process of a tannery effluent sample.

CHAPTER 2

GENERAL INFORMATION

This chapter presents the state-of- art of the chemical reduction and treatment technologies applied to leather wastewater. An introduction of the common production technologies, water consumption and wastewater characteristics is first presented and consequently wastewater treatment options are compared. Thus, the electrochemical treatment technologies are assessed.

2.1 Wastewater

Water is formed as a combination of two parts, hydrogen and oxygen as H_2O. In general, water is not pure composition of hydrogen and oxygen. Pure water is, on the other hand, only synthetic in a laboratory. Currently, water scarcity has been spread among countries, societies, and communities due to increasing in both population and consumption of natural resources to assist endless requirements, in addition, to pollution from discharge of domestic and industry. Figure 2.1 offers the example of partially closed water cycle.

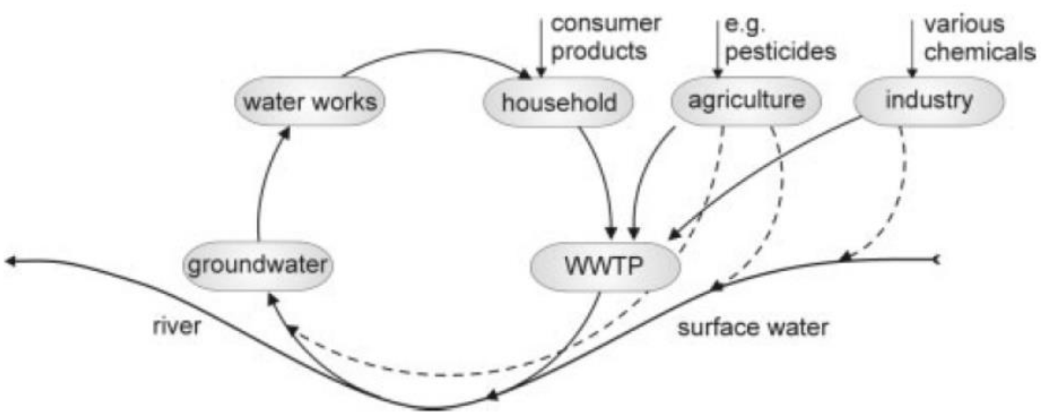

Figure 2.1 Schematic of water cycle

Of late, treatment of wastewater is indispensable tool to avoid deterioration of water quality/quantity and public health, due to reduce variety of different pollutants that generated from domestic and industry wastewater. Wastewater is water that has been contaminated by use. In terms of its composition, wastewater is not homogeneous but as diverse as its possible sources.

2.2 Tannery industry

2.2.1 Leather production and chemical use

Globally, the leather industry is currently undergoing radical transformation due to pollution and discharge legislations. Leather and environment can be described as two sides of the same coin due to the fact that potential wastes from meat industry (i.e. skins and/or hides) are used in the leather industry via tanning process. It involves in a serious operations to convert skins or/and hides to manufacture leather finished**.** These operations can be given as: beamhouse operation, tanyard operation, post-tanning operation and finishing operation [5, 66].

Chemicals being use in the production processes are depending on the raw material, and the end product depends on the tanning process which may lead to produce a wide range of waste with different type and amounts [10, 67]. Yet, at each stage, various chemicals are used and a variety of materials are expelled in Figure 2.2. With annual global processing capacity of 9×10^9 kg hides and skins, during tanning process at least about 300 Kg chemical are added to per ton of hides [5, 11] Thus, more than one hundred different chemicals used in leather production which generated about 350,000 ton/y of inorganic and heavy metal salts, acids, alkalis, soaps, tensioactives, oils, waxes, solvents, dyes, and many others compounds that are not completely fixed by skins and remain in the effluents especially present in commercial chrome tanning methods gives rise to only about 50-70% chromium uptake. Additionally, chromium(III) salts and sulfur compounds are the main pollutants released in tannery wastewaters and in the atmosphere [5,16,68, 69].

Moreover, in the retanning process, synthetic tannins (Syntan), oils and resins are added to form softer leather at unstable doses [68]. Syntans are characterized by complex chemical structures, because they are composed of an extended set of chemicals such as phenol-, naphthalene-, formaldehyde- and melamine-based syntans, and acrylic resins.

Thus, among the synthetic tannins, the ones based on sulfonated naphthalenes and their formaldehyde condensates (SNFC) play a primary role, for volumes and quantity used [70].

2.2.2 Wastewater generation and characterization

Tannery industry is known widely as one of the highest consumers of water. The volume of effluent tannery wastewater and its characteristics vary from tannery to tannery depending on the raw material, finishing product and the production process. However, an average of 30–35 m^3 of wastewater is produced per ton of raw hide, with variable pH, and high concentration of suspended solid, BOD, sulfides, chromium and with high COD value (27,600 $mgL^{-1)}$ in the beam house area **.**The tannery wastewaters may be characterized by several key parameters such as pH, conductivity, sulfide, chromium, BOD, TOC, COD and suspended solids. Thus, organic pollutants (proteic and lipidic components) are originated from skins (it is calculated that the raw skin has 30% loss of organic material during the working cycle) [5, 10, 11, 66, 71].

They reported that the beamhouse wastewater is characterized by an alkaline pH and the tanning effluent by a very acidic pH as well as high COD correspond to value of 27,600 mgL^{-1} [10]. Thus, a massive amount of common salt was used for preserving animal skin, about 15% (w/w) to 40% (w/w) and it is removed during the soaking [72]. It is estimated that, 64% of total COD and 56% of total suspended solids are produced from beamhouse processes [5].

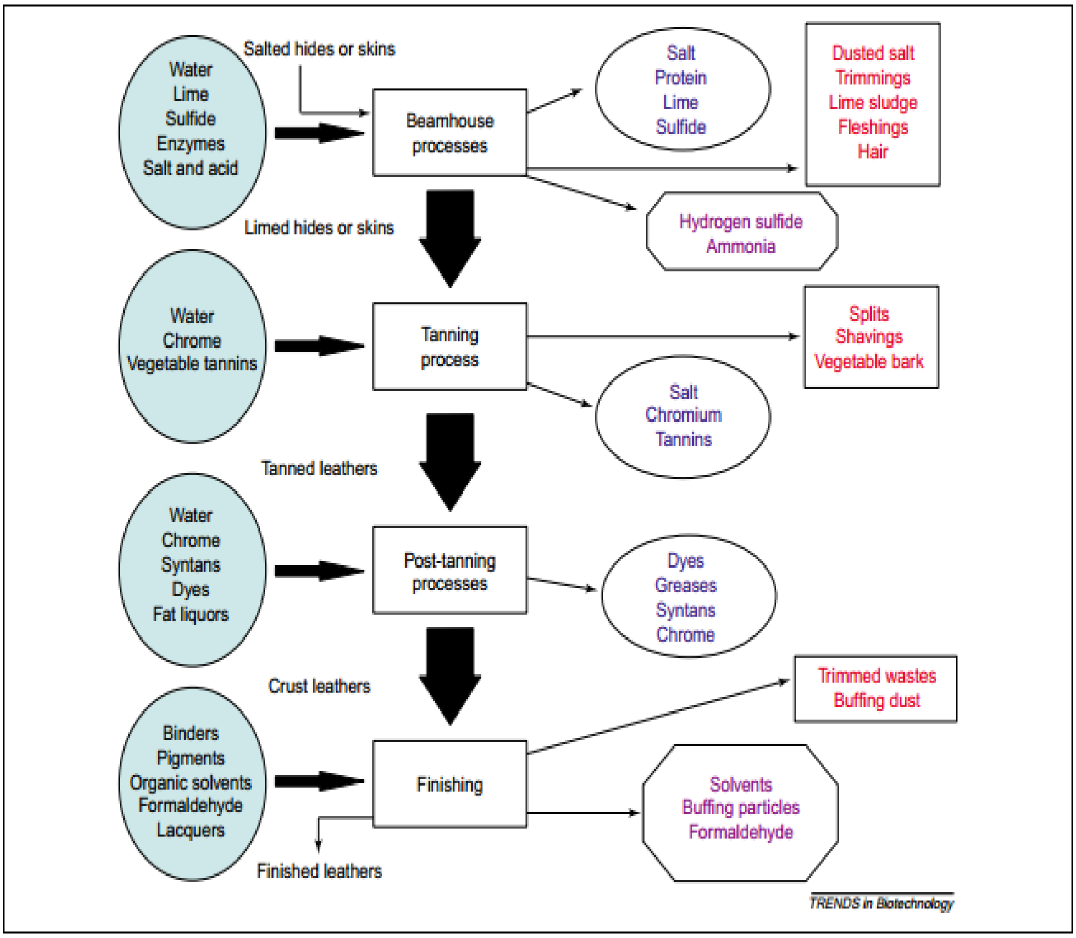

Figure 2.2 Inflow–outflow diagrams for leather processing

Temporarily preserved (salted) hides and skins are treated with a variety of chemicals in a water medium, through a series of unit processes and operations, to produce leathers. This leads to a variety of solid (red text), liquid (blue text) and air (purple text) pollutants at various stages of processing [5, 66].

Table 2.1 summarizes the average composition of tannery processes effluents.

Para-meter	**Soaking**		**Unhairing liming**		**Bating deliming**		**Pickli-ng**	**Chrom tannin-g**	**Re-tanning**		**Ref.**
	Min	Max	Min	Max	Min	Max	Min.	Max.	Min	Max	
pH	7.7	-	11.9	-	8.6	-	3.6	-	5	-	[10]
	6	10	12.5	13	6	11	4	3.2	4	10	[71]
T [^{0}C]	10	30	10	25	20	35	-	-	20	60	[71]
NH_3-N	850	-	380	-	3800	-	670	-	-	530	[10]

Table 2.1 (cont'd)

Cr	-	-	-	-	-	-	-	4100	-	3000	[71]
Sulfide	-	-	2670	-	134	-	-	-	-	-	[10]
	0	700	2000	3300	25	250	-	-	-	-	[72]
Cl	17000	50000	330	25000	2500	15000	8950	2000	5000	10000	[71]
	15000	30000	-	-	-	-	20000	30000	-	-	[72]
COD	31000	-	58000	-	5325	-	2900	-	4365	-	[10]
	5000	11800	20000	40000	2500	7000	800	400	15000	75000	[71]
	3000	6000	-	-	-	-	1000	3000	-	-	[72]
BOD_5	2000	5000	5000	20000	1000	4000	100	250	6000	15000	[71]
TSS	2300	6700	6700	25000	2500	10000	-	-	-	-	[71]
	25000	40000	-	-	-	-	30000	70000	-	-	[72]

During liming-unhearing operation, Lime and sodium sulfide or sulfyhydrateare typically are used. On the other hand, increasing of environmental pollution by emission volatile compounds generated from organic solvents which are most widely used chemicals in degreasing step [71]. The wet-end re-tanning, dyeing and fat liquoring processes have only a minor impact on the total salt load dominantly originated from the hides in the initial pre-soak and main soak. The tanning wastewater contains the highest concentration of total chromium (up to 4950 mgL^{-1}) [73]. Table 2.1 summarizes the average composition of tannery processes effluents.

However, table 2.2 reports the average composition of mixed effluents of leather tanneries. The average influent chromium (III) concentration varies in a wide range (30–570 mgL^{-1}) depending on the tanning process applied. Very high salinity is reflected by a concentration of TDS (37,000 mgL^{-1}). Generally tannery effluents are rich in nitrogen, especially organic nitrogen but very poor in phosphorous. Although COD is the most common parameter used in tannery wastewater characterization, TOC is more reliable than COD since the high concentration of chlorides and sulphides of these effluents can affect significantly the analysis of COD.

Table 2.2 Characteristics of tannery wastewater.

pH	**COD**	**NH3-N**	**S^{-2}**	**Cr**	**Ref.**
10.5	3114	33	33	83	[74]
8.4	4947	95	52	168	[75]
7.5 - 9	5,000-10,000	*	*	100	[76]
7.7	2426	335	286	29.3	[64]
6.6	6855	70.5	*	140	[18]
7.08	*	128	*	90-100	[15]
7.2	2810	130	89	62	[77]
8.3	3100	*	*	*	[78]
7.4	1470	180	440	*	[31]
7.9-9.2	2533	118	860	258	[79]
7-8.7	4100 -6700	*	*	11.5-14.3	[80]
6-8.2	12,000-23,000	*	30-130	*	[81]
7.7	2200	*	*	*	[82]
8	1803	70	*	*	[83]
7.79	2155	168	35.8	50.9	[84]
4.1	2500-3000	180	*	570	[85]

COD: Chemical Oxygen Demand; S^{-2}: Sulfide; Cr (III): Chromium; *: not detected, all parameters as mgL^{-1}.

2.2.3 Biodegradation characteristics

Biodegradability particulars are expressed in a term BOD_5/COD or BOD_5/TOC ratios. In tannery wastewater BOD_5 is considered as disputable parameter due to contain many inhibitors [75]. Regarding the BOD_5/COD ratios, it was very low in comparison with domestic wastewater due to low biodegradability in influent wastewater. Meanwhile, COD can give more trust worthy details about the composition of this kind of wastewater. So, COD fractionation is necessary for tannery wastewater to identify the biodegradability and inert COD components due to correlate with the inhibitor effect of the particulate portion of the tannery wastewater [78]. On the other hand, Total Organic Carbon (TOC) is very important parameter due to effect on the analysis of COD, especially in tannery wastewater treatment which has a high concentration of chloride and sulfide.

2.3 Treatment options

Nowadays, ecological factors became the focus of much superior attention. The ideology of cleaner technology can be shown as: (a) Prevention is better than reuse (b) Reuse is better than recycling and (c) Recycling is better than disposal. Based on literature reviews, there are many processes that have been carried out in tannery wastewater treatment, ranging from the simple to the advanced complicated methods. These methods include biological treatment (aerobic and anaerobic treatment), physico-chemical treatment, ion exchange, membrane filtration, and electrochemical systems [86].

2.3.1 Coagulation and flocculation

Wastewater usually contains several impurities, which consist of clay minerals and proteins with different sizes. Removing of the colloidal and suspended matter is very slow and impossible by sedimentation. As a result, they need to be agglomerated by coagulation and flocculation before can be settled out. Generally, Aluminum and ferric salts are widely used as coagulants in water and wastewater treatment. The mechanisms of coagulation process are involved as ionic layer compression adsorption and charge neutralization, inter particle bridging, and sweep coagulation [17, 19].

Coagulation and flocculation (CF) process have been investigated in tannery wastewater treatment, by utilizing inorganic coagulants such as aluminum sulphate ($AlSO_4$), ferric chloride ($FeCl_3$), ferrous sulphate ($FeSO_4$) to reduce organic load (COD) and suspended solids (SS) as well as to remove toxic substances, such as chromium before biological treatment [17-19]. Besides, pH is considered as a specific parameter in CF so it’s affected by many factors such as; type of coagulant, characteristics of wastewater, and also the dosage of coagulant. Ultimately, they studied the influence of pH and coagulant dosages on the coagulation process as a tool for treating tannery wastewater to optimize conditions for removal organic matter and suspended solids as well as chromium. They reported that a removal range of 30–37% of total COD, 74–99% of chromium and 38–

46% of SS using 800 $mgL^{-1}$of alum at 7.5 pH for pre-settled tannery wastewater containing 260 $mgL^{-1}$of SS, 16.8 $mgL^{-1}$of chromium, 3300 $mgL^{-1}$of COD at pH 9.2. And they noticed that $FeCl_3$ has proved better results than alum [17]. Thus, the removal efficiency of COD and total chromium were 40–70%, and >99% respectively from leather tanning wastewater using $FeSO_4$, $FeCl_3$and alum [67]. On the other hand, under several doses of alum (800–900–1000–1200 mgL^{-1}) (poly aluminum ferric chloride) PAFC were used for treating raw tannery wastewater (Italy). They evaluated the optimum conditions as pH 8.5 and 900 $mgL^{-1}$of PAFC which resulted in high removal of COD (>75%) and TSS (>95%) [18].

2.3.2 Biological treatment

2.3.2.1 Aerobic processes

As well known, biological processes are specified for treating industrial wastewater to reduce organic contents. Besides they have cost-effective over the chemical oxidation. They are carried out for treating tannery wastewater to reduce organic contents [14]. As mentioned above, several of chemical materials use in leather processing which are impacting on the biological treatment due to their low biodegradability. As a result, presence of 10 mg/l of trivalent chromium (Cr^{+6}) inhibited the growth of acclimatized activated sludge and caused a significant decrease in specific growth rate (μ_m) and heterotrophic (Y_H) values [87]. However, the concentration of chromium had less influence on dentrification bacteria than nitrification bacteria [88]. Sequencing batch reactor (SBR) was used to treat tannery wastewater; to measure the removal efficiency of COD. It has proven to be more capable of carrying out biological processes such as nitrification and denitrification in the presence of inhibiting substance [15]. SBR technology is formed as a reliable treatment for tannery wastewater due to the flexibility of its operation. (SBR) was investigated for treating tannery wastewater; they reported that the removal efficiency of COD was 79% [11]. Nevertheless, a full-scale activated sludge plant has been used for treating leather-tanning wastewater to evaluate the impact of temperature on organic carbon and nitrogen removal. It was noticed that the temperature changes had a minor influence on COD removal efficiency (4–5%) while the total nitrogen removal was highly affected by the temperature. Besides, the presence of sulphide, chromium, chloride and fluctuation in temperature has adverse effects on nitrification process [89].

2.3.2.2 Anaerobic processes

In the period from 1979 to 2008, authors used website www.scirus.com as a research tool, they found 63 articles dealing with the application of anaerobic processes in tannery wastewater treatment. Among them, 12 referred to vegetable tannery wastewaters or to synthetic wastewater simulating vegetable tannery wastewater, while the remaining referred to chromium tannery wastewater [81].

Anaerobic filters (AF) composed of both up-flow anaerobic filters (UAF) and down-flow anaerobic filters (DAF) and Up-flow Anaerobic Sludge Blanket (UASB) reactors are mainly used in anaerobic treatment for tannery wastewater [82,86].

However, the anaerobic digestion of tannery soak liquor was studied using a UASB. COD removal reached 78% at an OLR of 0.5 kg COD m^3d^{-1}, a HRT of 5 days and a TDS concentration of 71 gL^{-1} [82]. And also, some experiments are investigated to estimate the methane production potential and volatile suspended solids for tannery waste sludge by utilizing expanded granular sludge bed (EGSB) and to anaerobic baffled reactor (ABR). They resulted that the specific methane production potential at 55 C is estimated to be 0.617 m^3 kg $^{-1}$ of volatile suspended solids for tannery waste sludge, 0.377 m^3 kg $^{-1}$ for tannery waste trimmings and 0.649 m^3 kg^{-1} for tannery waste fleshing. Besides concerns such as chromium content, salinity and temperature fluctuations were also addressed. Chromium content and salinity showed no adverse effects; however a reactor temperature reduction of 4.4 ^{0}C led to a drop in biogas production of 25%, indicating a requirement to keep the temperature constant at 55 ^{0}C [90].

2.3.2.3 Wetlands and ponds

Constructed wetlands (CWs) may be motivating option for treating leather tannery wastewater. The influence of pH, temperature and dissolved oxygen on a pilot-scale advanced integrated wastewater pond system (AIWPSs) were investigated for treating tannery wastewater, they concluded that a combination of advanced facultative pond (AFP), secondary facultative pond (SFP) and maturation pond (MP) all arranged in series, go before with simple pretreatment can adequately treat raw combined tannery wastewater [91]. CWs are used to treat the effluent of conventional biological treatment system operating at a tannery site, they noticed that CWs were efficient in removing COD and BOD_5 with removal efficiencies varying between 51 and 80% for COD (inlet:

68-425 mg L^{-1}) and between 53 and 90% for BOD_5 (inlet: 16-220 mg L^{-1}) [92]. And also, chromium can be sustained in wetlands with non-specialized media [93]. Constructed wetlands may offer reliable option when biological process is used as primary treatment for tannery wastewater.

2.3.3 Membranes process

Recently, membranes technologies have been interested in reducing their costs, as well as application possibilities are still extended. The use of membrane technologies applied to the leather industry represents an economic advantage, especially in the recovery of chromium from residual waters of leather tanning. Microfiltration (MF), Ultra- filtration (UF), Nanofiltration (NF) and reverse osmosis (RO) applied in leather industry for the recovery of chromium from spent liquors [71, 94- 96]. Removal of the salts and effluent of biological treatment of tannery is in the brightness for using membranes technologies [97]. Moreover, Membrane Bio-Reactors (MBR) are more attractive than conventional activated sludge process (CASP) for tannery wastewater treatment due to has several advantages such as, eradication of settling basins, independence of process performance from filamentous bulking and hasn't mechanisms that affecting on settle-ability. However, the main shortcoming of membrane application is a significant fouling due to the clogging, adsorption and cake layer formation by the pollutants onto the membrane. One of such alleviation to overcome this problem is a hybrid process where membrane technology is combined with other treatment process [70, 98].

2.3.4 Advanced oxidation processes

Advanced oxidation process (AOP) has been applied to treat tannery wastewater by interesting in the removal efficiency of COD and TOC. Using strong oxidizing agents (O_3, H_2O_2), and/or catalysts (Fe, Mn, TiO_2), sometimes supported in UV light which has high-energy radiation. Hydroxyl radicals which are characterized as very powerful oxidants, quickly and unselectively, are generated and utilized for removing organic compounds [99,100]. Table 2.3 summarizes several of AOPs applied to tannery wastewater and chemicals.

2.3.4.1 Fenton processes

Fenton process is utilized for destroying organic pollutant; based on the generation of very reactive free radicals, especially hydroxyl radicals ($^{\bullet}OH$), which have a stronger oxidation potential. It is attained by reaction hydrogen peroxide (H_2O_2) with ferric (Fe^{3+}) and ferrous (Fe^{2+}) iron in acidic aqueous solution, a complex redox reaction will occur as the following: [83]

$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + OH^{\bullet} + OH^{-} \quad (2.1)$$

$$Fe^{3+} + H_2O_2 \longrightarrow FeOOH^{2+} + H^{+} \quad (2.2)$$

$$FeOOH^{2+} \longrightarrow HO_2^{\bullet} + Fe^{2+} \quad (2.3)$$

$$Fe^{3+} + HO_2^{\bullet} \longrightarrow Fe^{2+} + O_2 + H^{+} \quad (2.4)$$

Thus, the reaction characteristics like (pH, temperature and the quantity of organic and inorganic constituents) are considered significant factors in FO process. For instance, at low pH (3), high temperature (43–45 °C) and high aromatic compound; the FO process was attractive for treating tannery wastewater. Several studies have been successfully employed to treat tannery wastewater by FO process [83, 99, 101-102].

Table 2.3 Chemical oxidations and AOPS applications to tannery wastewater.

Wastewater characteristics	**COD_i (mg/l)**	**AOPS**	**Results**	**Ref.**
Coagulated/ Flocculated tannery wastewater	2365	Ozone	17% of COD removal 12% of TOC removal 24% of BOD removal pH 11	[99]
Settled tannery wastewater (STW) Biologically treated tannery wastewater (BTW)	1785 835	Ozone	STW 6% of COD removal t 5 min ozone flow-rate of 42.8 mg /min. BTW 30% of COD removal t 5 min ozone flow-rate of 42.8 mg /min	[14]
Pre-alkalized tannery wastewater	2177	Ozone	COD removal from 30% to 70% after 120 min when ozone flow rate increased from 1 to 8 g/h.	[106]

Table 2.3 (cont'd)

Synthetic tannery wastewater	2080	Electrochemical treatment	Both electrodes rapidly oxidized the tannic acid in the first 2 h. PbO_2 gave faster COD removal than $Ti/TiRuO_2$. the $Ti/TiRuO_2$ required the same energy consumption for complete COD removal, it was more stable and not release toxic ions.	[9]
Raw tannery wastewater	2810	Electrochemical treatment	70% of COD removal 840 mg/L H_2O_2 Electrical power of 15.0 W, t 10 min pH 3. In neutral pH with 1670 mg/L oxidant dose and 15.0 W, 58% COD removal was obtained in 10 min	[77]
Equalized tannery wastewater	TOC 1005	Electrochemical treatment	82.6% phenol removals at 20 mA/cm ^{2}, 78.5%, at 50 mA/cm ^{2}, and 83.9% at 100 mA/cm ^{2}, after 5 h of electrolysis. After 5 h of electrolysis, TOC removals are 14.3, 31.3, and 40.5% at 20, 50, and 100 mA/cm^2	[100]
Tannery liming drum wastewater	25,300	Electrochemical treatment	Aluminium electrodes: 62% COD removal pH 3–5 Mild steel electrodes: 82%, COD removal Current density 35 mA cm − 2, t 10 min electrolysis time pH 3	[107]
Equalized Tannery wastewater	17,618 and 12,225	Electrochemical treatment	51–56% COD removal 30–70% TSS removal >98% Cr removal >96% Turbidity removal	[4]

Table 2.3 (cont'd)

Synthetic tannery wastewater (STW) Pickling wastewater (PW)	1188	Electrochemical treatment	After 15 min strong reductions on Cr and Fe concentrations were attained, reaching 0.24 and 3.16 mg /l respectively, which are below the limits recommended by the Brazilian environmental norm for discharge of wastewater into freshwater bodies?	[103]
Raw tannery wastewater	1803	Fenton	70% COD removal t 20 min 90% COD removal t 240 min.	[83]
Coagulated/ Flocculated tannery wastewater.	2365	Photocatalysis (UV/TiO2)	6% COD removal—pH 3 11% TOC removal—pH 3 15% BOD removal—pH 7	[99]
Equalized Tannery wastewater	11,878	Photo-Fenton (UV/Fe2+/H2O2)	0.4 g L− 1 Fe^{2+} and 15 g L− 1 H_2O_2 540 min of irradiation time 90% COD removal 50% TSS removal	[105]
Synthetic solution of tanning agents: synthetic tannins (ST) and oils (OL)	ST: 300 OL: 300	Fenton	ST: $H_2O_2/FeSO_4$ 600/500 (w/w) pH 3 – T 40 °C 80–90% of COD removal OL: $H_2O_2/FeSO_4$ 600/750 (w/w) pH 3,T: 43 °C 95% of COD removal t: 30 min	[101]
Synthetic solution of synthetic tannins (ST)	300	Photo-Fenton (UV/Fe^{2+}/H2O2)	$H_2O_2/FeSO_4$ 300/750 (w/w) After 15 min of oxidation by PF-A and PF-C the COD removal efficiency of initial 300 mg/l equivalent of ST was 78% and 76% respectively	[104]
Equalized Tannery wastewater	11,878	Photo-Fenton (UV/Fe2+/H2O2)	0.4 g L− 1 Fe^{2+} and 15 g L− 1 H_2O_2 540 min of irradiation time 90% COD removal 50% TSS removal	[105]

2.3.4.2 Photo oxidation processes

Hydroxyl radicals are generated by uses a strong oxidizing agents such as (O_3, H_2O_2) and/or catalysts (Fe, Mn, TiO_2). Sometimes, it is supported in activity by high-energy radiation, e.g., UV light. Hydrogen peroxide is irradiated with UV photolysis t to produce hydroxyl radical

$$H_2O_2 + h\nu \longrightarrow 2 \bullet OH \tag{2.5}$$

This process is known photo oxidation which may occur via one of three general pathways: hydrogen abstraction, electron transfer and radical addition. Several studies have been carried out to treat tannery wastewater by photo oxidation process. However, ultraviolet photolysis (UV) didn't change the parameters COD, TOC and toxicity to D. magna in untreated tannery wastewater [99]. Thus, it is not sufficient for destroying the organic structure of leather tanning wastewater [104], and also, photo oxidation has been investigated on coagulated tannery wastewater, they concluded that although COD and UV_{254} decreased gradually during the oxidation time, the color intensity of treated wastewater increased [108].

Photo-Fenton process is produced more hydroxyl radicals in comparison to the conventional Fenton (Fe^{2+} with hydrogen peroxide) or to the photolysis. It achieves when hydrogen peroxide and UV radiation are combined with Fe^{2+} or Fe^{3+} oxalate ion [109]. However, UV light was very effective on degradation rate due to production of $HO^{\bullet}$ and Fe^{2+}. Besides, •OH are also produced via direct H_2O_2/ UV-C photolysis (slow reaction) and the reaction of H_2O_2 with Fe^{2+} produced by photo reduction of Fe^{3+} [102] .

2.3.4.3 Ozone based processes

To achieve maximum extent of degradation in an energy efficient way, the important operating parameters for the ozonation process can be given as: pH of the system (hydroxyl radicals are generated from ozone decay at higher pH, whereas the molecular ozone remains as the main oxidant at low pH values), Ozone partial pressure, Contact time and interfacial area, Presence of radical Scavengers, Operating temperature, Presence of catalyst, Combination with other oxidation processes [109]. However, Ozonation has been examined the removal efficiency of COD and color in effluent tannery wastewater, it has been observed that a maximum of COD removal efficiency of 92% has been achieved under optimum operating conditions. Further the biodegradability index of the tannery effluent has increased from an initial value of 0.18

to 0.49. So it may be used as prior to biological treatment to enhance high color removal efficiencies and convert refractory organics to biodegradable organic compound. But with pre-ozonation, it should be point out that ozone can also oxidize the biodegradable fraction of influent COD. Seeing as ozonation competes with biological treatment under these conditions this is an undesirable result [14].

2.3.4.4 Photo-catalysis

The important operating parameters, which affect the overall destruction efficiency of the photo-catalytic oxidation process, can be given as: amount and type of the catalyst, reactor design, and wave length of the irradiation, initial concentration of the reactant, temperature, radiant flux, pH, and aeration, effect of ionic species. It can be used effectively sunlight or near UV light for irradiation, which should result in economic saving especially for large-scale operations. One of the main drawbacks of photo-catalysis process, Compared to conventional chemical reaction rates, reaction rate of photo-catalytic processes is usually slow and there is a need to provide large amounts of active catalyst in the reactor [109].

A small number of studies have been applied in tannery wastewater treatment by photo-catalysis oxidation they observed that despite of high removal COD, there are increasing of toxicity to D. magna and also to Artemia salina after UV/TiO_2 treatment [99,108].

2.3.5 Electrochemical treatment

Using electricity offers promising approaches for the prevention of pollution problems in the process industry. Due to it is characterized as environmental compatibility “green technology” due to have a clean reagent “the electron”. In addition, electrochemical technologies have attractive benefits can be given as: versatility, energy efficiency, safety, selectivity, amenability to automation, rapid reaction and cost effectiveness. And also, compared with other technologies they are considered more efficient, cost effective and more compact [3, 22,103]. The kinetics of the electrochemical process have been found up to 100-fold faster than biological oxidation process [8]. However, electrochemical processes have been applied successfully for treating tannery wastewater. These include electro-fenton, electro-flotation, electro-oxidation and electro-coagulation. We will to address these processes in chapter three.

2.3.5.1 Electro-Fenton (EF)

Electrofenton (EF) is considered an electrochemical process which is characterized as an eco-friendly methods as well as environment friendly. Since is not using any harmful reagents and also does not create secondary pollutants. However, it has two different configuration, the first one that the EF reagent is added to reactor from outside and inert electrodes are used as anode material while the second configuration, only hydrogen peroxide is added from outside and Fe^{2+} is supplied from iron sacrificial anode. Compared to the conventional Fenton process, the electro-Fenton process has the advantage of allowing better control of the process and avoiding the storing and transport of the H_2O_2. So, continuously H_2O_2 is supplied to the contaminated solution by a two electron oxygen reduction in an acidic medium according to Eq. (2.6). The typical mechanism of E-Fenton process is illustrated in Figure 2.3.

$$O_2 + 2H^+ + 2e^- \rightarrow = H_2O_2 \tag{2.6}$$

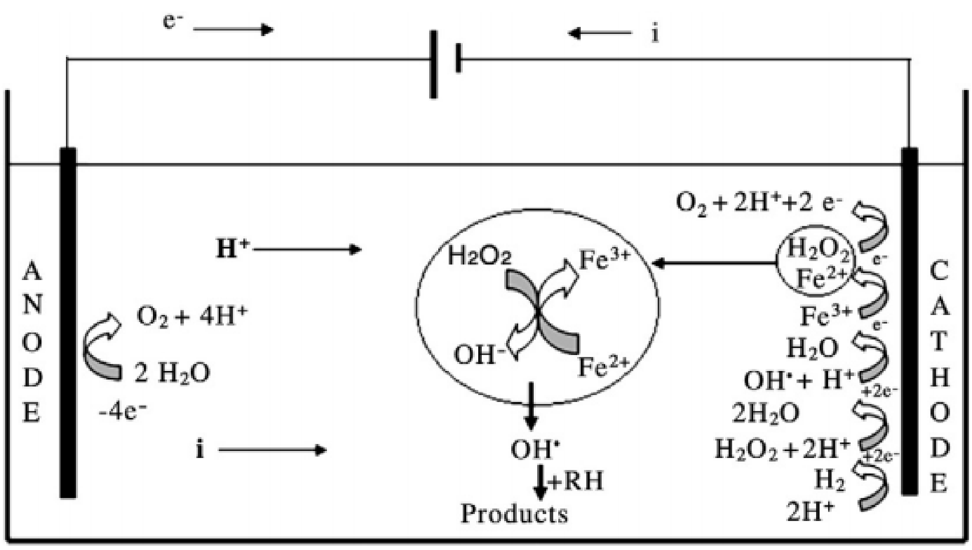

Figure 2.3 Reaction mechanism of E-Fenton process [110]

An effluent wastewater from organized tannery industrial regions with local sewerage discharge limit (COD 800 mgL^{-1}) was treated by EF. They noticed that 99.5% of sulfide was attained in 12 minutes, and also COD reduction altered from 41% to 99% based on different variables such as wastewater type, electrical energy consumption, reaction time, etc. [77].

2.3.5.2 Electro oxidation (EO)

Study on electrooxidation (EO) for wastewater treatment goes back to the 19th century, when electrochemical decomposition of cyanide was investigated [23]. Electrooxidation (EO) can be recognized by both the direct and indirect processes and depends on the treatment conditions and on the nature of the electrode materials. However, a large amount of salt, chiefly chlorides, makes the tannery wastewater particularly agreeable for electrochemical purification, offering the possibility to couple both direct and indirect electro-oxidation [8, 12, 23,103]. Different of anodic materials (graphite, Ti/Pt, Ti/Pt-Ir, Ti/RuO, Ti/PbO and other anode materials) were investigated to assess its effectiveness on the treatment efficiency [8, 9, 12]. The efficiency of wastewater treatment was found to be a function of the electrocatalytic properties of the anode material, Ti/Pt-Ir giving the best performance.

It has established that electrochemical oxidation was uneconomic process due to the very high energy requirements, while the process was found to be competitive in costs of operation and treatment performance when applied as a final polishing step or as an alternative unit for nitrification and dentrification. Besides, the kinetics of the electrochemical process have been found up to 100-fold faster than biological oxidation process [8].

2.3.5.3 Elctrocoagulation (EC)

2.3.5.3.1 Historical perspective of EC

Electro-coagulation (EC) is not a new technology. During the late 19th century, EC has been practiced for wastewater treatment in London, in the following decades; also appointed in the United States and Europe to treat municipal and industrial wastewater. At those times, EC was not popularity and limited success due to seeming higher operating costs, the ready availability of mass-produced alternatives for chemical coagulant dosing, and these studies are done as empirical without insight on the fundamental chemical and physical mechanisms. By 1930s however, all such of plants had been neglected due to these problems. Currently, electrocoagulation process is undergoing rebirth, and also it has formed a nook in the wastewater industry, proving to be reliable and effective technologies and it has been fitting applied to treat several of industrial wastewater [53,111,112].

2.3.5.3.2 Theory of EC

Electro-coagulation (EC) is considered an indispensable technique for treating industrial wastewater due to eco-friendly and cost-effective process. The driving force for this technique is a direct current source between metal electrodes engrossed in wastewater. Generally, EC utilized aluminum or iron electrodes which are dissolved in electrolysis, creating an array of coagulant species and metal hydroxides, to destabilize and aggregate the suspended particles or precipitates and adsorb dissolved contaminants (e.g. dissolved organic matter). Though, in EC process the coagulating ions are produced 'in situ' and it involves six main processes: (i) electrophoresis and aggregation due to charge neutralization; (ii) precipitation due to collective cation or hydroxyl ion with pollutant; (iii) bridge coagulation resulting by interaction between metallic cation with OH^- to form a hydroxide, which has high adsorption properties therefore bonding to the pollutant; (iv) sweep coagulation when the hydroxides form larger lattice-like structures and sweeps through the water; (v) oxidation of pollutants to less toxic species; (vi) electro-flotation or sedimentation and adhesion to bubbles lead to remove the pollutants. Briefly, Figure 2.4 shows the interactions occurring within an electro-coagulation reactor [23, 25].

2.3.5.3.3 Reaction types involved in the EC process

Electrolysis is a process in which oxidation and reduction reactions take place when electric current is applied to an electrolytic solution. Coagulation and hydrodynamics are forming the origin of electrocoagulation. Electrocoagulation is based on dissolution of the electrode material used as an anode. This so-called "sacrificial anode" produces metal ions which act as coagulant agents in the aqueous solution in situ [112]. At its simplest, an electrocoagulation system consists of an anode and a cathode made of metal plates, both submerged in the aqueous solution being treated. The electrodes are usually made of aluminum, iron, or stainless steel (SS), because these metals are cheap, readily available, proven effective, and non-toxic.

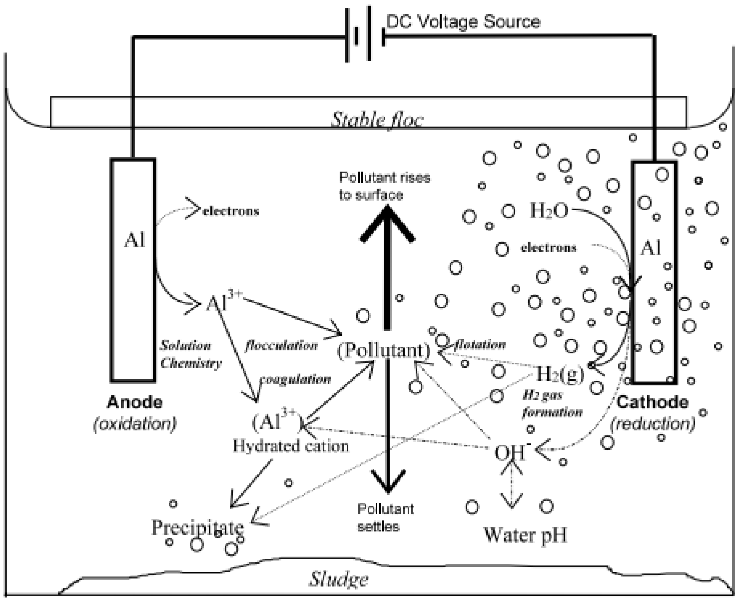

Figure 2.4 Interactions occurring within an electro-coagulation reactor [111]

An electrical current is passed through a metal electrode; the anode material undergoes oxidation, while the cathode will be subjected to reduction or reductive deposition of elemental metals.

Aluminum electrode:

In the case of aluminum, main reactions can be given as;

Anode $$Al(s) \rightarrow Al^{3+} + 3e^{-} \quad (2.7)$$

Cathode $$3H_2 0 + 3e^{-} \rightarrow 3/2\, H_2(g) + 3OH^{-} \quad (2.8)$$

Al^{3+} and OH^{-} ions generated by electrode reactions (2.7) and (2.8) react to form various monomeric species, which finally transform into Al $(OH)_{3}$(s) according to complex precipitation kinetics.

Overall: $$Al^{3+} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H^{+} \quad (2.9)$$

newly formed amorphous $Al(OH)_{3(s)}$ “sweep flocs” have large surface areas, which are useful for a rapid adsorption of soluble organic compounds and trapping of colloidal particles. Finally, these flocs are removed easily from aqueous medium by sedimentation or H_2 flotation.

However, depending on the pH of the aqueous medium other ionic species, such as Al $(OH)_2^{+}$, Al_2 $(OH)_2^{4+}$ and Al $(OH)_4^{-}$ may also be present in the system. Examination of the pE–pH equilibrium diagram reveals that under appropriate conditions various forms of charged multimeric hydroxo Al^{3+} species may be formed as it can be seen in reaction 2.10:

$$nAl(OH)_3 \rightarrow Al_n(OH)_{3n} \quad (2.10)$$

For example, the structures of dimeric and polymeric Al3+ hydroxo complexes are shown in Figure 2.5:

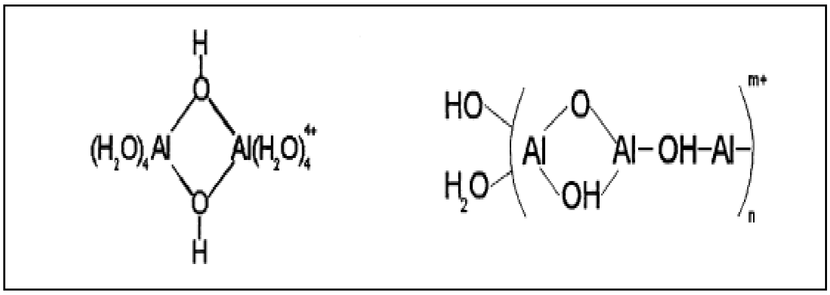

Figure 2.5 Polymeric aluminum species in EC process

Iron electrodes

Iron upon oxidation in an electrolytic system produces iron hydroxide, Fe (OH) $_n$, where n = 2 or 3. Two mechanisms have been proposed for the production of Fe (OH) $_n$. [53, 113].

Mechanism 1

Anode: $$Fe_{(s)} \rightarrow Fe^{+2}{}_{(aq)} + 2e^- \quad (2.11)$$

Solution: $$Fe^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Fe(OH)^2{}_{(s)} \quad (2.12)$$

Cathode: $$2H_2O_{(l)} + 2e^- \rightarrow 2OH^-{}_{(aq)} + H_{2(g)} \quad (2.13)$$

Overall: $$Fe_{(s)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + H_{2(g)} \quad (2.14)$$

Mechanism 2

Anode: $$4Fe_{(s)} \rightarrow 4Fe^{+2}{}_{(aq)} + 8e^- \quad (2.15)$$

Solution: $$4Fe^{+2}{}_{(aq)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H^+{}_{(aq)} \quad (2.16)$$

Solution: $$8H^+{}_{(aq)} + 8e^- \rightarrow 4H_{2(g)} \quad (2.17)$$

Overall: $$4Fe_{(s)} + 10H_2O + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)} \quad (2.18)$$

The Fe (OH) $_n$(s) formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complication or by electrostatic attraction, followed by coagulation.

2.3.5.3.4 Benefits and drawbacks of EC technique

EC has vital characteristics to be good-looking technique compared to others. Currently, it is considered as the well-liked technique in wastewater treatment as well as other related water management issues. Although EC has many advantages for treating wastewater and also has some disadvantages, which can be given as benefits and drawbacks:

1. EC is an efficient technique due to high adsorption of hydroxide on mineral surface “in situ”.
2. EC needs simple equipment and can be fabricated practically for any size.
3. It is easy to operate, cost-effective and as well as relatively low costs of operating.
4. Virtually, there is no need to any chemical addition, and no possibility of secondary pollution “green technology”.
5. It requires low current which can be carried out by fuel cell, solar energy and wind. And it can be applied in rural areas where electricity is not available.
6. EC generates agreeable, clear, colorless and odorless water.
7. It produces low sludge as metallic oxides/hydroxides which are easy to be readily settable and easy to de-water.
8. It removes the smallest colloidal particles efficiently by flotation due to generate gas bubbles during electrolysis.
9. EC is generated large flocs, contains less bound water, is acid-resistant and more stable, and therefore, can be separated faster by filtration.

However, EC also has some disadvantages. These disadvantages can be described as:

1. The “sacrificial anodes” need to be replaced periodically. Which are dissolved in water stream as a result of oxidation?
2. It requires high conductivity of wastewater suspensions.
3. Gelatinous hydroxide may tend to solubilize in some cases.
4. It may be suffered the loss of efficiency because of impermeable oxide formation on the cathode.

5. The cost of operating EC may be high many places due to high costs of electricity [32, 53].

2.3.5.3.5 Reactor design and operation issues

To date, EC is characterized as a fuzzy process due to lack of literature and published data on the electro-coagulation reactor design and operation. Follow-on, there is no single empirical or systematic approach has appeared in the design of EC reactors. Ultimately, there is a little guidance for a priori reactor design or performance prediction [25, 112]. Hence, we highlight key features of the system through two sections: physical and chemical design.

- Physical design issues

The design of EC process is indispensible step to achieve optimum operation and efficiency. It should take account the following physical factors:

1. Continuous versus batch operation

The electro-coagulation reactor design is categorized as continuous or batch systems. The first category has applied as continuous feed wastewater and operating under (pseudo) steady-state conditions. Batch operation on the other hand generally is operated with a fixed wastewater volume per treatment cycle but suffers from changing conditions within the reactor with time [3, 23,112]. The continuous mode of operation is applied satisfactory in industrial process for large effluent volumes. But the batch reactors are fitting to laboratory and pilot plant scale applications. The typical batch mode of operation and schematic diagram for continuous mode of operation are shown in Figure 2.6.

2. Reactor geometry

Reactor geometry affects on this operational parameters, including bubble path and size, flotation effectiveness, floc formation, fluid flow regime and mixing/settling characteristics. [25].

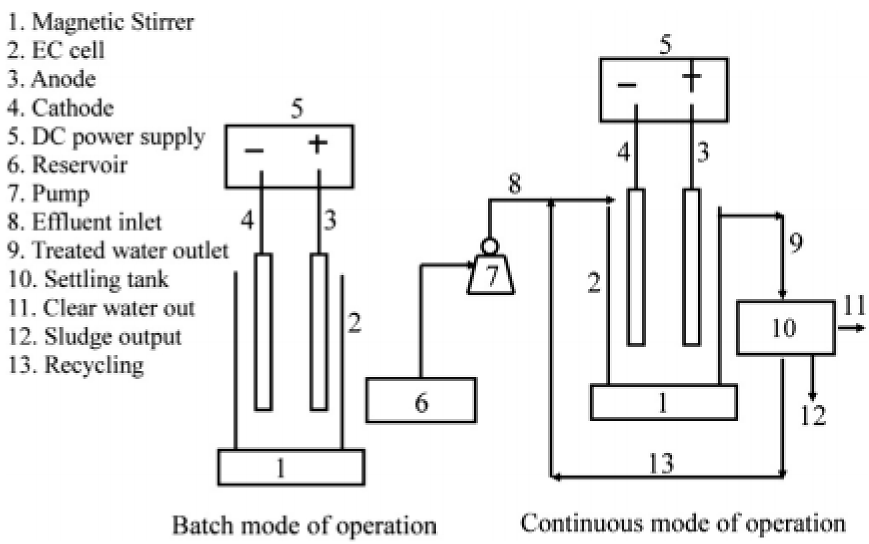

Figure 2.6 Schematic diagram of batch and continuous mode of operation, adapted by [36]

3. scale-up

There are two types of scale-up the first laboratory scale-up and the second full scale equipments. The surface area to volume ratio (A_s/V) was played as being significant scale-up parameter. The electrode area influences current density, position and rate of cation dosing, as well as bubble production and bubble path length [112]. Authors have been concluded that where the area to volume ratio (A_s/V) increases the optimal current density decreases and the treatment time also decrease. But, there is no signal that it has been utilized as a design guide [114]. However, table 2.4 refers to several values of electrode area to reactor volume ratio (As/V) and current density.

Table 2.4 Electrode surface area to reactor volume ratio (As/V) and current density (A/m²)

Reference	**As/V ($m^2\backslash m^3$)**	**Current density ($A\backslash m^2$)**
[112]	10. 5	3. 4 - 27
[114]	16.8	25-250
[26]	18.6	30-80
[39]	6. 4 - 34. 6	1.12 - 289

4. Current density

Current density has a major role during the electro-coagulation process. It can be defined as the current is imposed to electrode divided by active area of the electrodes. Current density is one of influencing factors of EC process by depending on some parameters; coagulant dosage rate, bubble production rate, size and growth of the flocs. The changeable of the current density easily controls these parameters. Authors reported that the array of current densities from 10 to 2000 A m^{-2} have been reported from 16 literature sources. Most of them reported current densities ranging from 10-150 A m^{-2} [25]. So it could be pointed out that the pollutants removal efficiency is based on the optimum current density. In the other words, an increase in current density above the optimum current density does not result in an increase in the pollutant removal efficiency as sufficient number of metal hydroxide flocs is available for the sedimentation of the pollutant. Besides, there is an increase in the current density with an increase in the conductivity. Sometimes the conductivity of the low-conductivity wastewater is adjusted by adding sufficient amount of salts such as sodium chloride or sodium sulphate to reduce energy consumption [36, 115, 116].

Basically, in the electro-coagulation experiment, commonly electrode assembly is connected to an external direct current source [53]. The amount of metal dissolved or deposited is directly proportional to the amount of electricity passed through the electrolytic solution. A simple relationship between current density (mA /cm^2) and the amount of substances (M) dissolved (g of M/cm^2) can be derived from Faraday's law (2.19):

$$W = J \times t \times \left(\frac{M}{N}\right) \times F \qquad (2.19)$$

where W is the quantity of electrode material dissolved (g of M per cm^2); J is the applied current density (mA/cm^2); t the electrolysis time in s; M the relative molar mass of the electrode material under study; n the number of electrons in oxidation/reduction reaction; and F is Faraday's constant (96,500 C/mol).

The concentration of electrode material dissolved in the solution can be easily calculated from the following equation (2.20):

$$Q_c = As\, W/V \qquad (2.20)$$

Where, Q_C is the concentration of electrode material dissolved in the solution (mg/l); As is the anode surface area (cm^2); W is the electrode material dissolved in the solution (mg/cm^2); and V is the volume of the treated water (L).

It is anticipated that there should be an agreement between the calculated amount of substances dissolved as a result of passing a definite quantity of electricity and the experimental amount determined [21].

- Chemical design issues

The performance and reliability of EC process will be affected by control, operation and chemical interaction. In the chemical design, the electrode material, electrode passivation and operational region should be considered.

1. Electrode material

Electrode material is playing a significant operator on the performance of EC process. The anode material evaluates the cation introduced into solution. Several researchers have studied the choice of electrode material with variety theories as to the preference of a particular material [25]. Generally, the materials engaged in electro-coagulation are aluminum or iron due to high coagulation efficiency and relatively cheaper, respectively [23]. It has been seen by [117] that the aluminum surface has a higher efficiency than steel in electro-coagulation, due to in situ creation of dispersed aluminum-hydroxide complexes as through hydrolysis of the aluminates ions, while in the case of steel electrode don't occur.

2. Passivation

Electrode passivation is considered as one of the most challenges of the efficiency of EC process. The accumulation of an inhibiting layer (usually an oxide) on the electrode's surface is undesirable for anode dissolution and electrocoagulation operation. This leads to increase the cell potential due to resistance. However, it does not affect either the coagulant or bubble production rates. It is absolutely needed to clean the electrodes mechanically and periodically to limit or to prevent the passivation materials. This maintains the reliability of the electrodes and ensures anodic dissolution at a constant rate. Also these impermeable layers prevent the effective current transport between the anode and cathode [3].

Electrode passivation, exclusively of aluminum electrodes, has been widely observed and recognized as detrimental to reactor performance. Generally, the formation of an inhibiting layer, an oxide on the electrode surface, will prevent metal dissolution and electron transfer, thereby limiting coagulant addition to the solution. Continuously, the thickness of this layer increase, reducing the efficiency of the electrocoagulation process [21]. There are several methods for preventing and/or controlling electrode passivation, as can be given as:

- ✓ Changing polarity of the electrode.
- ✓ Hydromechanical cleaning.
- ✓ Introducing inhibiting agents.
- ✓ Mechanical cleaning of the electrodes [25].

2.3.5.3.6 Electrodes Assignment

Generally, simple EC cell has consisted from two electrodes. For effective of electro-coagulation process it may be essential to interchange the polarity of the electrodes irregularly. Due to potential rate of metal dissolution, using two electrodes is not suitable for wastewater treatment. "Sacrificial electrodes" which is defined as conductive plates utilized in EC fabrication [21]. To achieve a high performance of EC process it needs to use of electrodes with high surface area and also use electro-coagulation cell with different mode of electrode connections [3]. Generally, there are three connection modes which are exposed in Figure 2.7.

The first mode, monopolar electrodes in parallel connections (MP-P): means that the anode and cathode are connected as parallel which is characterized as low potential difference and also the current is divided between all the electrodes to the resistance of individual cells. The second, monopolar electrodes in serial connections (MP-S): in this mode each pair of sacrificial electrodes is internally connected with each other. The inclusion of the cell voltages causes a higher potential difference for a given current. The last mode, bipolar electrode in serial connections (BP-S): in this connection mode, the outer electrodes are connected to the power supply and there is the no electrical connection between the inner electrodes [36].

Authors studied the treatment of textile wastewater and compared the performances of various electrode connection modes as a function of wastewater pH, current density and operating time [118]. They noticed that MP-P mode is the most cost effective for both aluminum and iron electrodes.

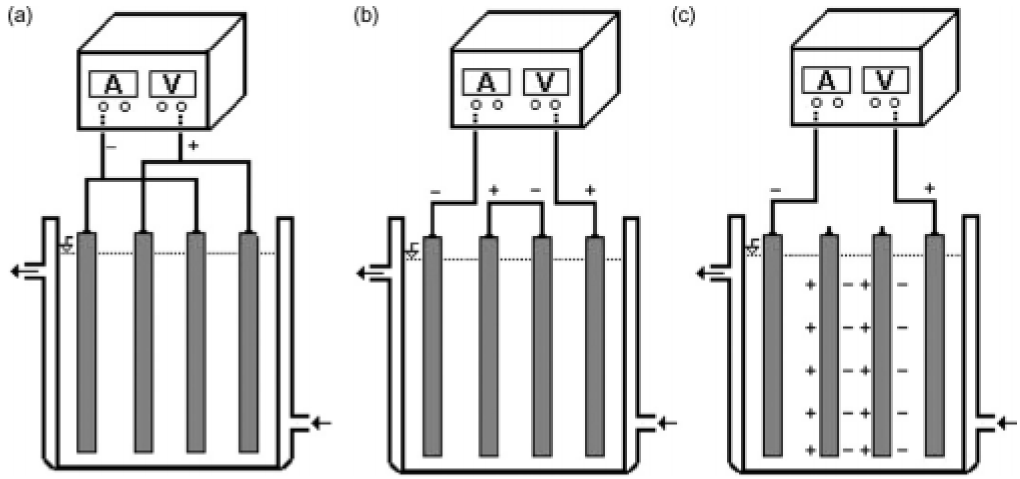

Figure 2.7 (a) MP-P system, (b) MP-S system, and (c) BP-S system, adapted by [36]

2.3.5.3.7 Application of EC

Electrocoagulation (EC) is a simple and efficient method. It has satisfactory been utilized for decades to treat many types of wastewater. Most of the articles published on EC focus on the removal of some specific pollutant or pollutants from synthetic or real solutions. The majority of these application studies can be given as the following categories:

- Removal of organic material from wastewaters or synthetic solutions

Many studies have been reported in the literature using electrocoagulation for the treatment of different types of wastewater and are shown in supplemental Table 2.5. High removal is typically achieved with optimum parameters. Aluminum, iron and combination electrodes can be used. Nearly, iron and aluminum electrodes give the same organic matter removal, whereas higher color removal is achieved with aluminum electrodes.

- Removal of metal ions (heavy metals) and other compounds

Generally, several of many industries have contained a massive concentration of heavy metals; such as tannery, electroplating, textile industries, etc. Industrial wastewater has become one of the severe environmental concerns. Due to have toxic metals such as Cd, Cr, Cu, Ni, Zn, Pb and other compounds which are toxic to living organisms and harmful to the environment when they are directly discharged into the water bodies. They can be easily absorbed by fishes and vegetables due to their high solubility in the aquatic environments and may accumulate in the human body by means of the food chain. It is indispensable to treat wastewater containing toxic metals to remove their adverse effects on human and ecology. Recently, there are many of techniques that are used for heavy metal removal from wastewater; such as ion-exchange, adsorption, chemical precipitation, membrane filtration, flocculation, coagulation, flotation and electrochemical methods [119]. Table 2.6 presents various studies that applied for removal of heavy metals and toxic compounds using electrocoagulation process. It can be seen from table 2.6 that the removal efficiency of heavy metal was reached to complete removal or high at optimum conditions.

- Combination of EC with other methods

Based on literature reviews, EC process seems to be an efficient method in the pretreatment of the industrial wastewater when optimal conditions are satisfied. So to make sure environmental protection, sometimes, we need (hybrid process) two or more techniques. Electrocoagulation in combination with other treatment methods is a safe and effective way for the removal of pollutants. Table 2.7 shows a various studies of combination of electrocoagulation with other treatment techniques.

- Comparison of EC with other technologies

Table 2.8 shows various Studies that have been conducted to compare electrocoagulation process with other conventional methods. It can be seen from that electrocoagulation results seem a good output compared with other methods for the same concentration of pollutants.

Table 2.5 Electrocoagulation used for treatment of different types of wastewater

Type of wastewater	**Anode-cathode material**	**Optimum operating conditions**	**Pollutants concentration [mg/l]**	**Optimum removal efficiency (%)**	**Ref.**
Tannery wastewater containing organic and inorganic pollutants	Fe	pH: 7-9 CD: 22.4 A/m^2 t : 20 min	COD: 4100-6700 BOD: 630-975 Cr: 11.5-14.3 TSS:600-955 Color: 3800-6330 TKN: 144-170	COD: 95 BOD: 96 Cr: 100 TSS: 96 Color:98 TKN:62	[80]
Tannery wastewater	Ms –Ms Al - Al	pH: 9.5, 8.5 C: 1A t : 60 min	COD : 2413.1 NH3-N: 223.4 TOC: 1000.4 Sulfide: 112.3	COD: 68 NH3-N: 43.1 TOC: 55.1 Sulfide: 96.7	[32]
tanner y liming drum wastewater	Fe	pH: 3 CD: 35 mA/cm^2 t: 10 min	COD: 25,300 Sulfide: 3000	COD: 82 Sulfide: 90	[107]
tannery wastewater	Al	pH: 7.3 CD: 75 A/m^2 t: 45 min	COD: 7680 BOD_5: 1326 Cr: 18.40 $N\text{-}NO_3$: 299 Turbidity: 248	COD : >90 BOD_5: >90 Cr: 100 $N\text{-}NO_3$: 100 Turbidity: 100	[6]
tannery wastewater	Fe	pH: 7.0 CD: 68 mA/cm^2 t: 45 min	COD: 17,618 Turbidity: 1,016 Cr: 44	COD: 55.7 Turbidity: 99.2 Cr: 98.7	[3]
tannery wastewater	Fe	pH: 7.4 CD: 33.3 mA/cm^2 t: 5/30 min	COD: 3700 Sulfide: 440 Cr: 22 SS: 2690	COD : 46/56 Sulfide : 25/97 Cr: nd/97 SS: nd/70	[31]

Table 2.5 (cont'd)

Raw tannery wastewater	Fe	pH: 7.0 CD: 50 mA/cm^2 t: 25 min	COD: 2200-3000 Cr: 570 Color: 824	COD: 63.3 Cr : 99.7 Color :82	[85]
	Al	pH: 6.0 CD: 50 mA/cm^2 t: 25 min		COD:64.4 Cr : 99 Color: 88	
Tannery wastewater	Fe -Al	pH: 6.8 CD: 20 mA/cm^2	COD: 3200	COD: 52	[120]
olive mill wastewaters	Al-Al Fe -Fe	pH: 4.3 C: 1A t: 45min	COD: 5690	COD: 58.7 for Al COD: 53.4 for Fe	[121]
Domestic wastewater	Fe -Fe	pH: 7.4 C: 0.12 A t: 5-15 min	COD: 380	COD: 60	[30]
Textile wastewater	Al-Al	pH: 7.0 CD: $80A/m^2$ t: 70 min	COD: 1260 Turbidity: 1310	COD: 70 Turbidity: 90	[122]
Textile dye wastewater	Al -Al	pH: 6.0 CD:31.25m A/cm^2 t: 14 min	COD: 2500 Dye: 80-100	COD: > 80 Color : > 95	[42]
Orange II dye (Azo) solution	Al -Al	pH: 6.5 CD:160 A/m^2 HRT: 8.6 min	Dye: 10	Color: 95	[123]
dye-containing wastewater (Blue 140 and Direct Red 23)	Fe -Fe	CD: 30/40 A/m^2 t: 5/5 min	Dye : 100/100	COD: 93 Color :99 TS: 89	[124]

Table 2.5 (cont'd)

Textile wastewater	Fe –Fe Al –Al	pH: 11 CD:200 A/m^2 t: 10 min	*	COD: 76 for Fe COD: 65 for Al	[116]
Rose oil processing wastewater	Fe -Fe	pH: 6.4 CD:80 A/m^2 t: 20 min	COD: 9500 BOD_5:4950 Turbidity : 750 TS:7690	COD: 80 BOD_5: n,d Turbidity: 81 TS: n.d	[34]
Restaurant wastewater	Al –Al	pH: 6.0-9.5 CD: 30-80 A/m^2 t: 90 min	COD : 3000	COD: 84.1	[40]

Table 2.6 Removal of metals and other compounds by electrocoagulation

Metal or compound	**Concentration (mg/L)**	**Anode-cathode**	**Removal efficiency (%)**	**Reference**
Cr(III), Cr(VI)	887.29, 1495.27	Fe-Fe	>99	[125]
NO3, As(V)	300, 1	MS-MS	84,75	[126]
Humic acid	20	Al-Al	97.8	[127]
As	0.15	Al-Fe	99	[128]
Fe	10	Al-Al	99	[129]
Cu(II), Zn(II), Cr(VI)	50	Al-Al	99,99,83	[29]
F^-	5	Al-Al	96	[130]
PO4-P	25	Al-Al	100	[131]
TOC	2260	Al-Fe	79	[132]
NO_2-N, NH_3-N	5	Fe-Fe	100, 15	[133]
SO_4^{2-}	100	Al-Al, Fe-Fe	72,68	[33]

Table 2.7 Combination of electrocoagulation with other methods

Wastewater source	**Hybrid process**	**Removal efficiency %**	**Reference**
Tannery	EC + Photo-Fenton	COD : 99, TSS: 70, Cr :>99	[105]
Tannery	EC + Electroflotation + Fluidized bed anaerobic reactor	COD : 90	[134]
Olive oil mill	EC + Ultrafiltration	COD : 96	[135]
Textile	EC + Electroflotation	COD :80, Turbidity: 76, SS :85, BOD: 89, Color :93	[115]
Textile	EC + Nanofiltration	Color (>99)	[158]
Synthetic solution	EC+ Electrooxidation	COD : 93	[136]
Paper mill	EC_{Al} + Adsorption EC_{Fe}+ Adsorption	COD : 98 COD : 93	[137]
Laundry	EC + Electroflotation	COD : 62	[138]
Industrial	EC + Electroflotation	F^- : 86	[139]
Distillery	EC + Ozonation	COD : 83	[140]

Table 2.8 Comparison of EC with other technologies

Type of wastewater	**Parameter removal**	**Result (%)**	**Ref.**
Electroplating wastewater	Cr(III), Cr(VI)	EC: >99 for both Cr(III) and Cr(VI) Coagulation (Ferric chloride): Cr(III): 52.6 , Cr(VI) : 25.8	[125]
Tannery wastewater	COD, Cr	EC: COD: 25, Cr: 24.6 EC + Adsorption: COD: 92, Cr: 75 Adsorption: COD: 50, Cr: 77	[141]
Textile wastewater	COD	EC: 23 EC - Alum: 65 EC - Polyaluminum chloride: 80	[142]

Table 2.8 (cont'd)

Synthetic dye solution	Reactive blue 19	EC: 44 EC + Ozonation: 96 Ozonation: 10	[143]
Metal plating	Cr	EC: 99.9 in 20 min Coagulation (Aluminum sulfate and ferric chloride): >99	[144]
Textile	Color	EC: 100 Coagulation (Alum): <5	[145]

2.3.5.3.8 Economic evaluation

The operating cost is considered a vital parameter that affects s the implementation of any method of wastewater treatment. Generally, the costs of electrocoagulation process are determined as the cost of energy consumption and the cost of electrode consumption. Sometimes the cost of addition chemical materials is taken into consideration such as: for increasing the solution conductivity or varying the pH of the solution. Anyway, the operating cost of electrocoagulation can be measured by following equations.

- Electrode consumption (a E_C) (Kg/m^3)

Electrode consumption is evaluated according to Faraday's law as the following equation (Eq. (2.21)):

$$Electode_{Consumption} = \frac{(I \times t \times M_w)}{(z \times F \times \upsilon)} \quad (2.21)$$

where F is the Faraday's constant (96,485 C/mol), Mw is the molar mass of electrode type as in iron (56 g/mol), aluminum (27 g/mol), and z is the number of electron transfer (z Fe: 2) and (zAl:3).

- Energy consumptions (b E_C) (KWh/m^3)

Energy consumption is calculated via the following equations (Eq. (2.22)):

$$Energy_{Consumption} = \frac{V \times I \times t}{\upsilon} \quad (2.22)$$

Where Energy consumption is the energy consumption (kWh/m^3), V is the voltage (Volts), I is the current (Amperes), t is the EC time (hour), and v is the volume of the treated wastewater (m^3).

- ➢ Chemical consumption (c C_C) (Kg of chemical /m^3) = Chemicals used/m^3 of effluent
- ➢ Operating cost (cost/m^3) = a E_C + b E_C + c C_C (2.23)

In this context, authors studied the removal of organic and inorganic pollutants from a wastewater of leather finishing industrial process using electrocoagulation. They documented that the operational cost for the electrocoagulation was found to be US $ 1.7 per m^3 of the treated tannery effluent as compared to the cost of US $ 3.5 per m^3 of the treated effluent for conventional methods.

2.3.5.4 Electrodialysis (ED)

2.3.5.4.1 Theory

ED is an electrochemical separation process in which ions are transferred through ion exchange membrane under the influence of an electrical potential difference used as a driving force. ED uses a driving force to transfer ion species from one solution through cathode (positively charged ion) and anode (negatively charged ion) to another (a concentrate water stream), creating a more diluted stream [146]. Figure 2.8 illustrates an electrodialysis process. The ion exchange membranes are the most used in ED processes. The membranes are really of two fundamental types: cation-exchange membranes (CEM) and anion-exchange membranes (AEM).

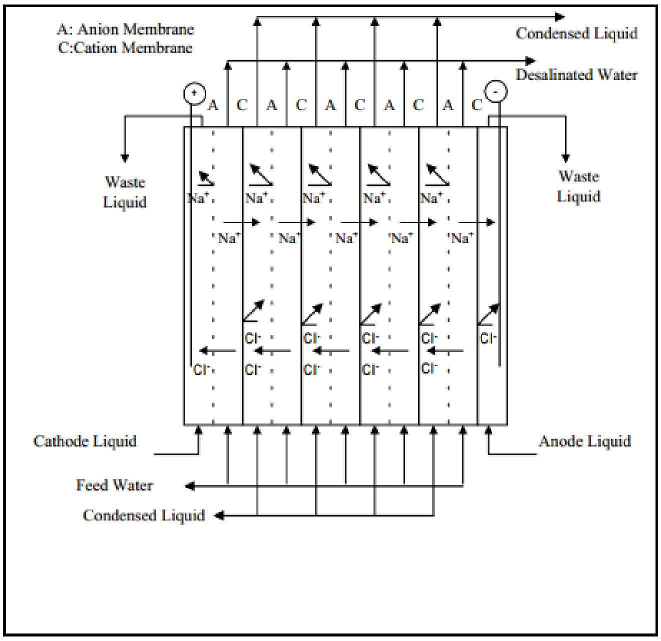

Figure 2.8 Principle of electrodialysis

2.3.5.4.2 Mass transport and balance in an ED system

ED cell pair is composing from two compartment bounded by a CEM and AEM as shown in Figure 2.9. Mass transport is determined by amass balance, which hypothesis that all components that removed from feed will be transferred to the concentrate. A concentration gradient expands in x- direction while the solution flows through the compartments in the direction of the x- coordinate. So, the flow in the x-direction is determined by convection due to hydrostatic pressure gradient. On the other hand, the flux in the z-direction is determined by migration and diffusion due to electrical potential gradient and difference concentration between the dilute and concentrates [147].

The flow rate within the dilute and concentrate as well as current utilization has taken into account for material balance of mass transport within ED stack, as the following eq. (2.24):

$$(C_i^{fd} - C_i^d)Q^d = (C_i^c - C_i^{fc})Q^c = \frac{\zeta I}{\sum_c z_c \, v_C \, F} \tag{2.24}$$

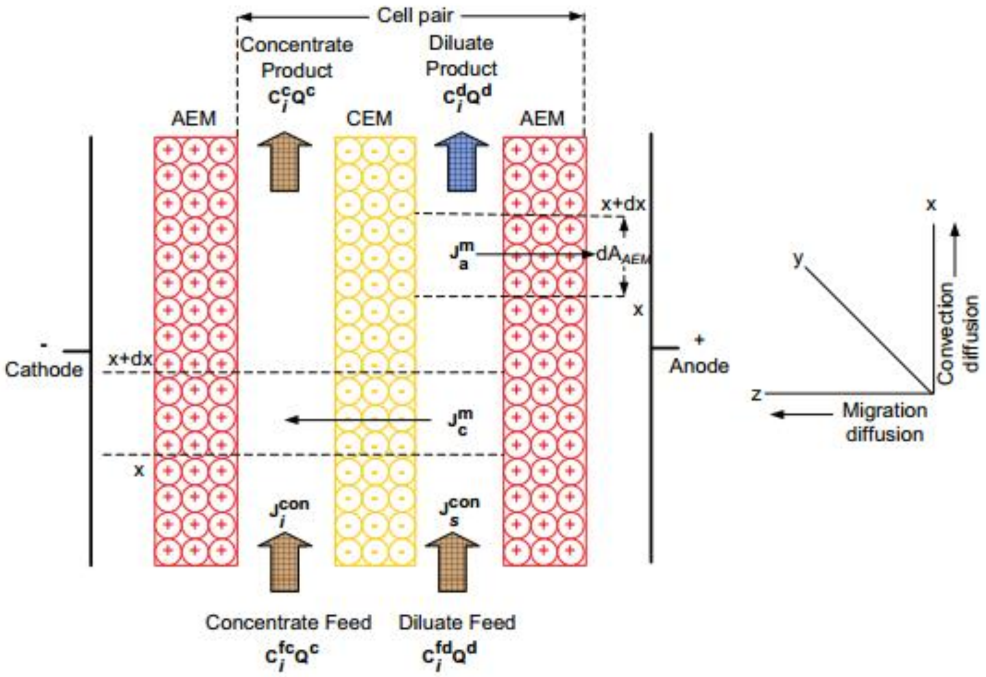

Figure 2.9 schematic illustrating mass transports in an ED cell pair (adapting from [147]).

Where C_i^{fd} and C_i^{fc} are the dilute and concentrate feed concentration mole/m^3 of a component subscript $_I$, C_i^d and C_i^c are the dilute and concentrate product concentration mole/m^3 , Qd and Qc are the flow rates of dilute and concentrate in parallel to the membrane surface m^3/s , I is the total current passing through a cell pair (A) , ζ is the current utilization (-) , z is the cation (subscript c) valance (C/mole) , v is the stiochiometric coefficient (-) , F is the Faraday constant (96,485 C/mole).

Over all, current efficiency (CE) is a vital parameter that determined the optimum range of applicability of ED. CE (usually $\zeta < 1$) is a measure of how effective ions are transported across the ion exchange membranes for a given applied current. This is dependent on current leakages across the stack transport of H^+ and OH^-, in addition to salt ions, the transport of water, and membrane selectively according to equation (2.25):

$$\zeta = n.\,electrical\ efficiency = n.\,л_s.\,л_w.\,л_m \qquad (2.25)$$

where, n is the number of cell pair, within the ED stack, $л_s$ is the membrane selectively, $л_w$ is the water transport efficiency, $л_m$ is the membrane manifold efficiency [146,147].

The ionic material balance can be utilized to evaluate the required membrane surface area. The membrane area is proportional to the amount ions removed from feed solution and calculated by eq. (2.26):

$$A_{eff} = \frac{Q^d\left(C_i^{fd} - C_i^d\right)zFn}{i\eta} \qquad (2.26)$$

A_{eff} is the effective membrane area (m^2), i is the current density (A/m^2) which should be approximately 80% of the limiting current density (LCD) [147].

2.3.5.4.3 Transport of ions in solution and through ion exchange membrane

Based on the extended Nernst–Planck equation and Donnan equilibrium, mass transport within ions solutions and transport of ions through ions exchange membrane are determined by three contributions, an electrical migration, a diffusion and a convective term, respectively as demonstrated in figure 3.8. Over all, the ionic flux in solution (J_i,, mole/ m^{2}s) and in a membrane (J_i^m, mole/ m^{2}s), is symbolized by the Nernst–Planck equations (2.27) & (2.28): [146]

Solution: $$J_i = -D_i\left(\frac{dC_i}{dx} + \frac{z_i\,FC_i}{RT}\,\frac{dQ}{dx}\right) \qquad (2.27)$$

Membrane: $$J_i^m = -D_i^m\left(\frac{dC_i^m}{dx} + \frac{z_i\,FC_i^m}{RT}\,\frac{dQ}{dx}\right) \qquad (2.28)$$

Where Di is the diffusion coefficient (m2/s), Ci the concentration, φ is the electric potential/ voltage applied, R is the gas constant (8.314 J/mole k), T is the absolute temperature (K), and superscript m refers to the membrane phase.

The Donnan equilibrium describes the idea that at equilibrium, the electrochemical potential of a component is equal in both solution and membrane phase (electroneutrality). In view of Na^+ and Cl^- ions in solution, electroneutrality is expressed as:

Solution: $$[Na^+] = [Cl^-] \quad (2.29)$$

Membrane: $$[Na^+]^m = [Cl^-]^m + [R^-]^m \quad (2.30)$$

Where, R^- is the fixed charge of the ion exchange membrane.

The amount of NaCl transferred through the ion exchange membrane can be given as:

$$C_{NaCl} = [Cl^-]^m = [Na^+]^m - [R^-]^m \quad (2.31)$$

Quantitative expressions of the Donnan equilibrium potential (electrochemical potential in each phase) can be given as:

Solution: $$\mu_i = \mu_i^0 + RT \ln m_i + RT \ln Y_{i+} Z_i FQ \quad (2.32)$$

Membrane: $$\mu_i^m = \mu_i^{mo} + RT \ln m_i^m + RT \ln y_i^m + Z_i F\varphi^m \quad (2.33)$$

Where, μ_i is the electrochemical potential (J/mole), μ_i^0 is the electrochemical potential under standard temperature and pressure conditions (J/mole), mi the mobility coefficient (mole m/Js) and y is the activity coefficient (-).

At equilibrium, the electrochemical potential between the solution and membrane phase are equal ($\mu_i = \mu_i^m$). The Donnan potential is determined by combining the last equations (3.27) & (3.28) to give the following eq. (2.34):

$$\varphi_{don} = \varphi^m - \varphi = \frac{RT}{z_i F}\ln\left(\frac{\gamma_i^m m_i^m}{\gamma_i m_i}\right) \quad (2.34)$$

An ideal permselective cation-exchange membrane would transmit positively charge ions only. The permselectivity approaches zero when the transference number within the membrane is identical to that in the electrolyte solution. Due to the Donnan exclusion the permselectivity of the membrane depends on the concentration of the electrolytes in the solution and on the ion exchange capacity of the membrane. However, Donnan exclusion occurs when ions with the charge as the fixed ions in the membrane are excluded and are not transported through the ion exchange membrane

[148]. The principles Donnan exclusion in ion exchange membranes is showed in Figure 2.10.

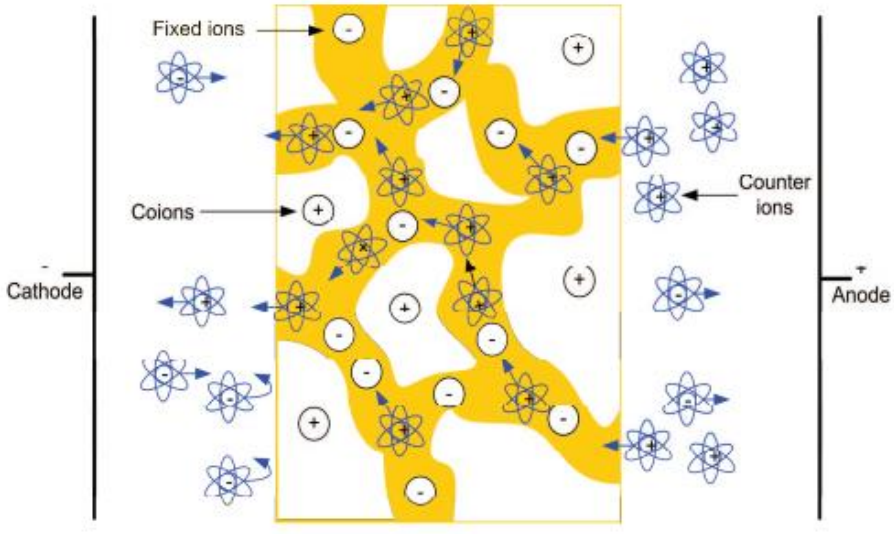

Figure 2.10 The principles Donnan exclusion in ion exchange membrane [147]

2.3.5.4.4 Concentration polarization and current density

Concentration polarization obstructs the optimization of membrane processes strictly. Due to the imbalance of hydrodynamic boundary layer resistance and membrane resistance—the membrane resistance becomes of the order of magnitude or even smaller than the hydrodynamic boundary layer resistance—concentration gradients evolve in the feed at the membrane surface. In its most prominent form, concentration polarization is observed by the fact that the transmembrane flux does not increase with increasing driving force and reaches a limiting flux. In electrodialysis with monopolar membranes, this limiting flux is called the limiting current density with the voltage drop across the membrane as a measure for the driving force [149]. Concentration polarization in ED is caused by differences between ion transport number in the electrolyte solution and the ion-exchange membrane. , ED is a good technology to investigate reduction of concentration polarization.

The current density i follow Faraday's law and is given by (2.35):

$$i = \frac{zDF(c_{b-}\ c_m)}{\delta(t^m - t^{b1})} \tag{2.35}$$

where t^m and t^{bl} are the transport numbers of the ion in the membrane and in the boundary layer, respectively, z is the valence of the ion, D is the salt diffusion coefficient, F is the Faraday constant, I is the electrical current density, c_b and cm are the concentrations in the bulk and at the membrane surface, and δ is the thickness of the boundary layer.

According to Figure (2.11 a) it can be seen If the electrical potential difference is increased, the current density will increase, leading to an increased in ions flux and consequently to a decreased ion concentration at the surface of the membrane. When the ion concentration at the membrane surface c_m approaches zero, a limiting current density (LCD) is reached so it is described by eq. (2.36):

$$i_{lim} = \frac{zDFc_b}{\delta(t^m - t^{bII})} \tag{2.36}$$

Additional increase in the driving force (electrical potential) at this point will not result in an increased in ion flux (Figure 2.11 b). In order to minimize the effect of polarization, the thickness of the boundary layer must be reduced and hence the hydrodynamics and cell design must be improved [47].

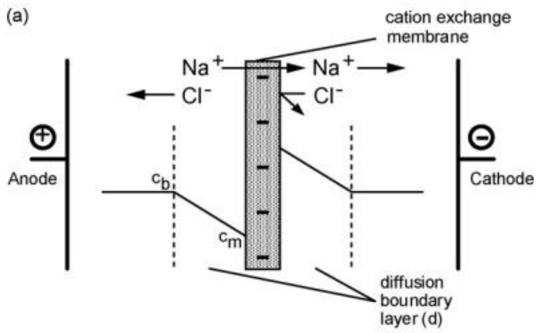

Figure 2.11 (a) Schematic illustration of the concentration polarization in electro-dialysis process [46]

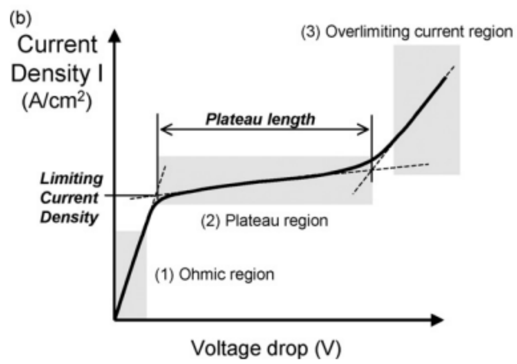

Figure 2.11 (b) typical current density–voltage drop curve for an ion-exchange membrane [149].

Generally, every ED unit installed in the world is designed following a simple rule: the maximum current flowing through a stack must be 80% of the limiting current density at the lowest concentration in the dilute, resulting in high membrane areas for the removal of salt in very dilute solution [47].

2.3.5.4.5 Energy requirements in ED

Energy consumption in an ED stack related to the salt concentration and the voltage drop in a stack. The energy requirements for ED can be explained by eq. (2.37):

$$\mathrm{E_{stack}} = \mathrm{I^2\ R_{stack} t} \qquad (2.37)$$

Where, E_{stack} is the energy requirements (Wh/L), R_{stack} is the electrical resistances of the ED stack (Ω) and t is the time (h).

Power consumption (Wh) during ED is expressed by eq. (2.38)

$$P = U.I \qquad (2.38)$$

Specific energy consumption (SEC,Wh/L) during ED is expressed by eq.(2.39)

$$\mathrm{SEC} = \frac{\Sigma \mathrm{P}}{\mathrm{VD}} \qquad (2.39)$$

Where, V_D is the volume of the dilute (L).

The electric resistance of a cell pair (R_{cell}), is the sum of the resistance of the membrane and the dilute and concentrate streams eq. (2.40):

$$R_{cell} = R_{AEMA} + R_D + R_{CEM} + R_C \qquad (2.40)$$

Where, R_{AEM}, R_D, R_{CEM} and R_C are the resistance of the AEM, dilute stream, CEM and concentrate stream respectively, as specified follow(2.41) &(2.42):

$$R_{AEM} = \frac{r_{AEM}}{A_{eff}} \qquad (2.41)$$

$$R_{CEM} = \frac{r_{CEM}}{A_{eff}} \qquad (2.42)$$

Where, r_{AEM} and r_{CEM} are the specific resistances of the AEM and CEM respectively (Ωcm^2).

The resistance of the dilute (R_D) and concentrate (R_C) are inversely proportional to the conductivity and therefore, to the salt concentration of the solution. Where (2.43) & (2.44):

$$R_D = \frac{h}{(kA_{eff})} \qquad (2.43)$$

$$R_C = \frac{h}{(kA_{eff})} \qquad (2.44)$$

Where k is the specific conductivity (S/m)

The eclectic resistance of the ED stack (R_{stack}) is calculated by eq. (2.45):

$$R_{stack} = nR_{cell} \tag{2.45}$$

However, Figure 2.12 shows the total desalination costs

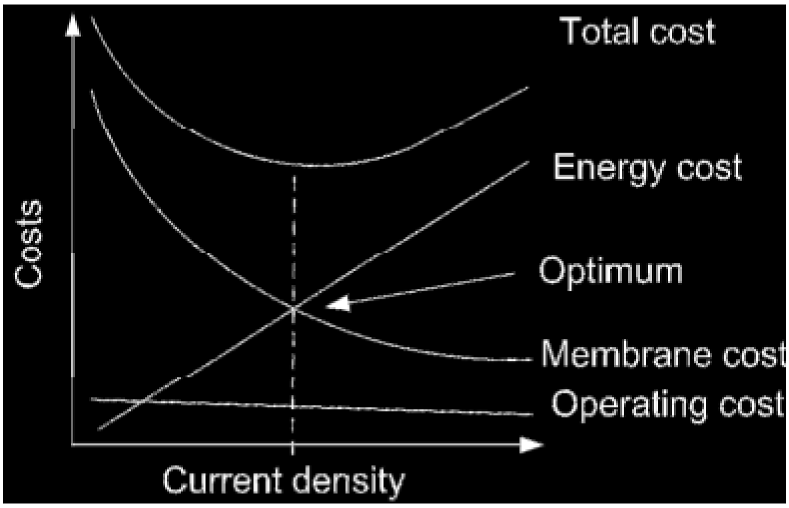

Figure 2.12 schematic of ED costs [146].

2.3.5.4.6 Inhibitors of membrane performance

The performance of ED process can be inhibited by membrane obstructions. Typically, the categories of membrane obstructions are fouling, scaling and poisoning. On the other words, inorganic and trace organic can lead to scaling and poisoning respectively. But numerous efforts can be undertaken to diminish the problems of membrane fouling, scaling and poisoning by such as pretreatment, there is still required for additional research on the mechanisms involved so that the performance of ED can be optimized.

- ❖ Membrane fouling

In ionic exchange membrane, fouling is defined as the accumulation of particulate, trace organic compounds and organic materials (OM) that adhere to the membrane surface and /or within the membrane through hydraulic or electric forces or other physical [150]. The AEM is generally, more sensitive to organic fouling than CEM due to electrostatic attraction between negative charged organics and the positively charged of AEM [151]. Thus oxidative agents can also be attacked the ion exchange membranes. This can result in membrane corrosion and decrease in the performance ED process. Membrane fouling is characterized as a decrease of membrane selectively, an increase in voltage drop and decreases the electrical conductance of the membrane.

Membrane fouling in ED system is influenced by several of electrochemical and physical properties of both membrane (e.g. resistance and zeta potential), and the foulants (e.g. charge, molecular size), together with the operation parameters of ED process (e.g. current density, pH solution and frequency). Thus the fouling characteristics of ion exchange membrane depend on their electric resistances, hydrophopocities, zeta potential and exchange capacity. However, the membrane cleaning can be divided into hydraulic, mechanical and chemical cleaning. Hydraulic cleaning includes alternate pressurizing and depressurizing and by changing flow direction. However hydraulic and chemical cleaning methods need additional chemical or tools leading to increase of the installed cost of the ED system as well as the operating/maintenance costs [150].

- ❖ Membrane scaling

Scaling is a hard process that involving crystallization and hydrodynamic transport mechanisms, the precipitation of soluble inorganic salts concentrates on the CEM while the lesser extent in the AEM occurs. The treatment of seawater by ED process results a membrane scaling due to has a limit solubility of salt species. Thus, pH solution, inorganic concentration as well as flow rate and the incidence of concentration polarization have suggestion for the scale formation process [152]. There are several methods to prevent scaling membrane include adjustment to the feed solution pH, physical mechanical, chemical of the membrane.

- ❖ Membrane poisoning

In the case of the trace organic compounds are small enough to penetrate the membranes other than whose mobility is so low that they still inside the membranes casing a poisoning. This poisoning might be also due to sorption of the organics on the membrane and the mass penetration by multivalent ions that direct to neutralize the fixed charge within membranes [153].

The pretreatment process has been reported to prevent membrane poisoning, such as microfiltration (MF), ultrafiltration (UF), activated carbon and membranes cleaning with concentration acids or bases (e.g. HCl, NaOH).

2.3.5.4.7 Application of ED

Electrodialysis process (ED) has been widely applied for the production of drinking and process water from brackish water and seawater, treatment of industrial effluents, recovery of useful materials from effluents and salt production [146]. The inorganic and trace organic compounds may be exposure from drinking water, thus their production in water treatment and the significance of this to water reuse. Absolutely, the removals of these compounds are essential. Regard to the removal of the inorganic ED has been satisfactory applied. Table 2.9 summarizes the removal investigated in several articles. It can be concluded that the removal efficiency depends on the feed concentration as well as pH.

Table 2.9 Removal of inorganic contaminants from water by electrodialysis (%)

Inorganic	**Concentration [mg/l]**	**pH**	**Removal efficiency (%)**	**Reference**
Boron	77	9-10	97	[154]
	64	8.3	25	[155]
Fluoride	10	7.9	97	[156]
	3	6.5	79	[157]
Nitrate	90	8.1	73-83	[158]
	210	7.7	90	[159]

One of the most important applications of electrodialysis in wastewater treatment systems is processing rinse water from the electroplating industry. Besides, ED has also proven a promising method in heavy metal wastewater treatment [119]. They investigated the removal of hexavalent chromium ions by using anew working system (ED pilot plant) which comprises from a set of ion exchange membrane. They resulted satisfactory that the maximum contamination level of chromium was 0.1 mg/L.

The effectiveness of ED for the separation of Cu and Fe and water recovery from solutions in copper electrowinning operations was studied. They established that ED proved very effective in the removal of Cu and Fe from the working solution. Thus ED has been utilized as modified cation exchange membranes to study the separation of Cr (III) from sodium ion [160].

ED has been utilized to investigate the effect of operating parameters on Pb^{2+} separation from wastewater. They established that the increasing voltage and temperature enhanced cell performance; however, the separation percentage decreased with an increasing flow rate. And also at concentrations of more than 500 mg/L, dependence of separation percentage on concentration diminishes [157].

2.4 Summary

The application of electrochemical process to water/wastewater treatment could be effective. Elctrocoagulation technique is indispensable for industrial wastewater treatment compared to other techniques, due to have various benefits including environmental capability, versatility, energy efficiency, safety, selectivity and cost effectiveness. Thus EC technique is described as simple equipment, easy operation, less operating time and decreased amount of sludge. However, it can be reported that further studies need to be investigated the effect of shape and geometry of the electrodes on the removal efficiency of the pollutants. Besides, EC is established as an efficient technique of a pretreatment option of other techniques. Moreover, membranes technologies (ED) offer a vital solution in environmental fields such as pollution reduction and water reuse, recycling valuable components from the waste streams. However the removal mechanisms in ED process should be addressed completely in order to design and implement large-scale ED processes. Based in our reviews the transport and removal of pollutants are dependent on the physiochemical characteristics of the membranes, the concentration of the feed and solution chemistry as well as interaction between solution and membranes.

CHAPTER 3

MATERIALS AND METHODS

Based on literature reviews, so far no other studies have taken into account the effective factors on EC treatment of tannery wastewater using the Taguchi method. And also so far no other studies have taken into account the aspect of hydrogen recovery from the electrocoagulation process. Moreover Until relatively recently, little has been done of effective technique "zero effluent" to conserve water and energy. The idea of ‘‘zero effluent’’ may be linked to a hybrid process i.e EC- ED process. This chapter has been outlined the wastewater sources and characteristics and the experimental set up and procedure as well as the analytical procedure.

3.1 Wastewater sources and characteristics

The samples analyzed in this work were collected from different outflow wastewaters of the Organized Tannery Industrial Region (OTIR) which is located in the Tuzla quarter of Istanbul, Turkey. With regard to OTIR, the treatment plant receives wastewater from 100 small tannery plants based on chrome and vegetables tanning. Generally, it has four treatment steps that can be given as: equalization, settling, aerobic activated sludge, and physiochemical treatment by chemical coagulation. The samples were put into PE containers, transported to laboratory in one hour, mixed very well, and conserved at 4˚C during the experiments. The composition of the wastewater sample is presented in Table 3.1. The sample was collected in December 2014.

Table 3.1 Characteristics of raw tannery wastewater used in this study

Parameter	**Value**
PH	4.10 – 7.00
Conductivity	11.71 - 12.80
COD	1780 - 2800
Soluble COD	1440 - 1760
Suspended solids	430 - 910
Chloride	1690- 2000
Total chromium	425 - 570
Color	670 - 824
NH_3-N	145 - 180

Note: Color ADMI (10) Pt-Co, Conductivity: mS/cm., all other parameters as mgL^{-1}.

3.2 Experimental set up and procedure

3.2.1 Batch mode reactor

A schematic diagram of the experimental setup is shown in Figure 3.1. Hence, the experimental setup of the electrochemical reactor operated in a lab-scale batch mode of operation. It consists of a Plexiglas reactor with volume work 0.6 L, a pair of electrodes (Al or Fe), and DC regulated power supply. The anode and cathode, that have the dimensions of 9.0–5.0 cm, are placed vertically and parallel to each other with an inter-electrode distance of 5 cm. The available effective electrode area is 37 cm^2 for anodic reactions. The electrode plates are cleaned manually by washing them in distilled water prior to every run. The volume of effluent taken is 250 ml in the electrochemical reactor and the electrodes are connected to DC power supply (GPS-3030DD, 0–30.0 V, and 0.0–3.0 A). Thus, at the beginning of the experiment, the EC cell is thoroughly washed and rinsed with deionized water followed by rinsing with the sample solution. The cell voltage is periodically noted. The samples are taken at regular interval of time from the reactor and filtered using Whatman 42 filter paper.

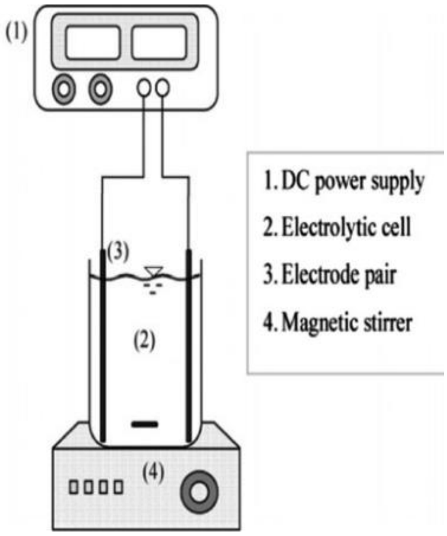

Figure 3.1 Schematic diagram of the experimental setup

Taguchi method was used to create a set of designed experiments by MINITAB software (version 16). The Taguchi method applies OA to reduce the number of experiments. OA refers to experimental matrix designed by L_i, where i is the number of trials of experimental matrix or total degree of freedom and includes a set of experiments where the settings of process parameters are changed. OA allows evaluating the effects of several process parameters to be determined efficiently. The selection of a suitable OA depends on the number of control factors and their levels [35]. In this study, Taguchi method was applied to determine the optimum condition of EC process. Similarly, the current density, initial pH, and electrolysis time were selected as control factors (parameters) during Taguchi orthogonal arrays experimental design. Each factor that consisted of five levels and L_{25} orthogonal array was taken to establish the optimal conditions for iron and aluminum electrodes with minimum number of experiments. The factors and their levels are presented in Table 3.2. However, the following steps should be determined to optimize performance characteristics that can be given as:

1. Recognition of the recital characteristics and choosing the process parameters to be assessed.
2. Determination of number of parameter levels.
3. Selection of the suitable orthogonal array.
4. Conduction of the experiments depends on the arrangement of the orthogonal array.

5. Calculation of the performance characteristics.
6. Analysis of the experimental results using the performance characteristics and ANOVA.
7. Selection of the optimal levels of process parameters.
8. Validation of the optimal process parameters through the confirmation experiment [161].

Table 3.2 Factors and their values corresponding to their levels to be studied in EC experiments (aluminum and iron electrodes)

Factors	**Levels**									
	1		2		3		4		5	
	I	II	I	II	I	II	I	II	I	II
A : Current density	10	10	20	20	30	30	40	40	50	50
B : pH	4	3	5	4	6	5	7	6	8	7
C: Time	5	5	10	10	15	15	20	20	25	25

Note: I: iron electrode, II: aluminum electrode; Current density (mA/cm^2); Time (minute)

In order to optimize the COD, total chrome, and color removal efficiencies process, experimental variables, their levels, and results were investigated as illustrated in Table 3.3. Taguchi method suggests the use of signal-to-noise (S/N) ratio to measure the quality characteristic deviating from the desired value. The optimum conditions should be determined using the S/N ratio of the results achieved from experiments designed by OA technique. There are three cases of S/N ratios: the larger-the-better, the smaller-the-better, and the nominal-the-better. In this study, the higher removal efficiency of pollutants is required for optimization EC process. Thus, the larger-the-better was selected based on COD, total chrome, and color removal efficiencies in two cases (iron and aluminum electrodes). The performance characteristics were evaluated using the following equation Eq. (3.1) [162]:

$$SNL = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y^2}\right) \qquad (3.1)$$

where SNL is the S/N ratio or the performance characteristics as “the larger-the-better”, y_i is the comparison variable in experiment i for a certain combination of control factor levels, and n is the number of experiments performed for that combination. In such cases, optimum operation conditions may have not been attained during the entire experimental section. So, an additive model may be needed in order to predict the performance value corresponding to the optimum operation conditions, where the following additive model may be applied, as Eq. (3.2):

$$Y_i = \mu + X_i + e_i \tag{3.2}$$

where μ is the overall mean of the performance value, X_i is the fixed effect of the quantity level combination used in i_{th} experiment, and e_i is the random error in the i_{th} experiment. Since Eq. (3.2) is a point estimation, which is calculated using experimental data in order to determine whether results of the confirmation experiments are sufficient or not, the confidence interval must be evaluated. At the selected error level, the confidence interval is calculated using the following equation (Eq. (3.3)) [163]:

$$Y_i \pm CI \left(CI = \sqrt{F_\alpha \left(1, f_e\right) \times v_e \times \left[\frac{1}{n_{eff}} + \frac{1}{S} \right]} \right) \tag{3.3}$$

where F α (1, f_e) is the F-ratio at a confidence level of (1 − α) against DOF 1, f_e is the error degree of freedom (DOF), n_{eff} is (N/ (1 + (total DOF associated in the estimate of mean))), N is the total number of results, S is the sample size for confirmation test, v_e is the error variance, and CI is the confidence interval. When the experimental results are presented in percentages (%) “As in our work”, before estimating Eqs. (3.2) and (3.3), Ω transformation for percentage values should be applied first using the following equation (Eq. (3.4)) [162]. The values of interest are then determined later by carrying out reverse transformation using the same equation.

$$\Omega(db) = -10\log\left(\frac{1}{p} - 1\right) \tag{3.4}$$

Where Ω (db) is the decibel value of the percentage value subjected to omega transformation and P is the percentage of the product obtained experimentally.

Table 3.3 Experimental variables, their levels and results of conducted experiments corresponding to L_{25} experimental plan

Trail no.	**Variables and their levels**			**COD $_{Re}$**		**Cr $_{Re}$**		**Color $_{Re}$**	
	A	**B**	**C**	**I**	**II**	**I**	**II**	**I**	**II**
1	1	1	1	21.0	17.0	47.9	20.0	5	10
2	1	2	2	29.0	32.3	63.2	30.0	25	30
3	1	3	3	33.9	38.0	80.0	60.0	53	39
4	1	4	4	38.5	40.7	94.0	78.0	77	60
5	1	5	5	40.5	47.5	96.7	88.0	85	70
6	2	1	2	36.0	30.1	83.6	33.0	35	33
7	2	2	3	40.0	41.6	95.2	55.0	77	43
8	2	3	4	44.6	45.8	99.5	88.0	85	72
9	2	4	5	48.6	49.8	100	94.1	82	71
10	2	5	1	36.0	36.0	93.8	64.0	64	45
11	3	1	3	45.9	33.6	95.6	50.0	90	53
12	3	2	4	48.0	50.0	97.8	92.5	83	75
13	3	3	5	50.2	54.9	98.7	100	79	79
14	3	4	1	40.6	38.2	95.0	72.0	80	57
15	3	5	2	43.0	55.0	100	94.6	77	76
16	4	1	4	49.7	40.7	98.7	77.0	87	70
17	4	2	5	55.0	54.9	100	100	86	80
18	4	3	1	40.0	37.8	89.5	64.0	67	50
19	4	4	2	47.5	55.8	96.3	96.9	85	73
20	4	5	3	48.5	57.4	99.1	100	76	78
21	5	1	5	55.3	46.5	98.2	98.9	89	84s
22	5	2	1	42.6	43.0	90.0	60.0	70	50
23	5	3	2	55.7	50.9	97.7	98.2	89	78
24	5	4	3	60.7	62.0	100	100	86	84
25	5	5	4	59.6	64.1	100	100	84	88

3.2.2 Continuous mode reactor

The experimental setup is schematically shown in Fig.3.2. The continuous-mode system used in electro-coagulation treatment consisted of: (1) a wastewater storage tank; (2) a peristaltic pump with an operating flow rate between 0.07 and 1140 ml\ min (Longer Pump, BT300-2J, China); (3) an electrochemical reactor with a set of five pairs of iron or aluminum electrodes; (4) gas separation tank; (5) sedimentation tank. The electrochemical reactor was constructed with Plexiglas having a dimension of 5.0×10.0×20 cm. It contained a set of 5 pairs of electrodes made of iron or aluminum, which reduced the working volume to 2.5 L. The electrodes were connected vertically with a gap distance of 7 mm. The configuration resulted in a total electrode working area of 45 cm^2.The electrodes were connected in monopolar parallel mode to a DC power supply and the electrochemical reactor was operated in continuous mode. The continuous electrochemical reactor was designed to work by an up-flow process. The tannery wastewater was fed in at the bottom of the reactor, flowed upward through the layers of the electrodes and drained out at the outlet located at the top of the reactor. The pump flow rate was adjusted to control the fluid residence time according to Eq. (3.5):

$$HRT = {}^{V}/_{F}\,, \tag{3.5}$$

where, HRT is the hydraulic retention time (min), V is the working volume of the reactor (L) and F is the flow rate (L min^{-1}). In this study, the working volume (V) was 2.5 L. The HRT was controlled to be equal to the required electrocoagulation time. For example, if the required electrocoagulation time was 5 min, the pump flow rate was adjusted to be 500 ml min-^{1}. If the required electrocoagulation time was 10 min, the pump flow rate was adjusted to be 250 ml min $^{-1}$.

However, electrodes (Al or Fe) were immersed in the reactor containing tannery wastewater and connected to DC power supply by wires; the reactor was closed tightly by silicon to prevent any gas leakage. The tannery wastewater (TWW) was taken from different outflow wastewater of the Organized Tannery Industrial Region (OTIR) located in the Tuzla quarter of Istanbul, Turkey.

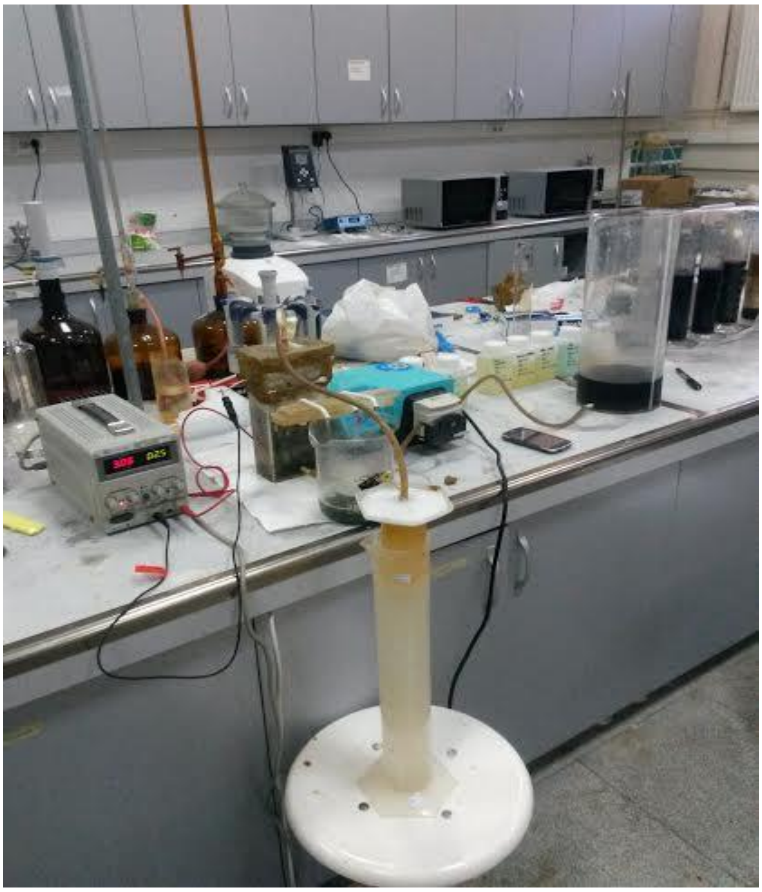

Figure 3.2 Schematic diagram of the experimental setup.

The raw TWW contained nearly 2500 -3000 mg\L of COD. Conductivity of the raw TWW was 11.71 mS cm^{-1} with an original pH of 4.10. The applied DC voltages (V) and the amperes (A) were monitored during the course of experiments. And also, the electrical energy supplied to the system was calculated using the following Eq. (3.6):

$$E_e = VIt, \qquad (3.6)$$

Where, E_e is the electrical energy supplied to the system by the DC power supply (J); V is the applied DC voltage; I is the current (A), and t (sec) is the duration of the applied DC voltage.

Pollutant removal efficiency was determined from the formula in Eq. (3.7):

$$\text{Pollutants removal efficiency } = (C_0 - C_f/C_0) * 100 \qquad (3.7)$$

Produced hydrogen gas was collected in the head space of the reactor and also calculated by water displacement method. In this study, two values of pH for aluminum even iron electrodes were selected in order to determine the effectiveness of the electrocoagulation according to pollutants removal efficiency as well as hydrogen gas production. Additionally, the effects of the operating parameters were then studied and the optimal conditions of electrocoagulation continuous system for tannery wastewater treatment were determined. The operating parameters and conditions are summarized in table 3.4.

Table 3.4 Conditions of operating parameters

Operating parameter	**Value**
Current density, mA/cm^2	7 and 14
Electrode number, pair	5 for Al or Fe
Electrode gap, cm	0.7
Wastewater volume	2.5 L
Inlet flow rate, ml/min	17, 20, 25, 33, 50 and100
Electrocoagulation time (min)	25, 50, 75, 100, 125, and 150
Initial pH	4.1, 6 for Al and 4.1, 7 for Fe electrodes

3.2.3 Electrodialysis process

The general experimental flow sheet used in this work is presented in Figure 3.3. The effluent used was collected from different outflow wastewaters of the Organized Tannery Industrial Region (OTIR) which is located in the Tuzla quarter of Istanbul, Turkey. Next, optimum operating conditions were determined at the end of the experimental studies. The optimum operating parameters and conditions are determined as summarized in table 3.5.

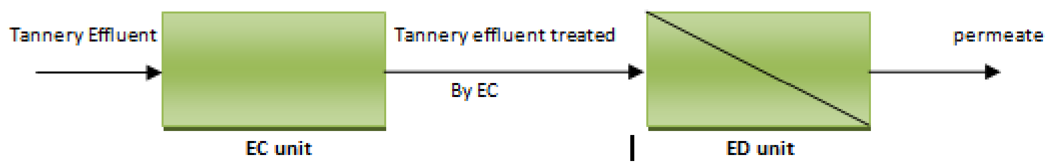

Figure 3.3 Schematic diagram of the experimental setup of the hybrid EC/ED process

Table 3.5 Optimum operating parameters and conditions

Operating parameter	**Value**
Current density, mA/cm^2	14
Electrode number, pair	5 for Al or Fe
Electrode gap, cm	0.7
Wastewater volume	2.5 L
Inlet flow rate, ml/min	20
Electrocoagulation time (min)	125
Initial pH	6 for Al and 7 for Fe electrodes

At these optimum parameters conditions, the ED technique was associated with EC technique. In this work; bipolar membrane electrodialysis (BMED) process was applied. A PCCell ED 64-4 unit and BMED 1-3 bench ED pump unit obtained from PCCell GmbH were utilized. Electrodialysis experiments were performed in a pilot scale ED system, using platinized titanium (Titane/Pt–Ir coated) electrode as anode and cathode with effective membrane area of 64 mm^2 per membrane, the distance between two membranes was 0.5 mm. The number of membrane pairs in the cell was one. During the whole experiment, conductivity, pH of solution and ampere drop across the membranes was recorded. Hydrogen chloride at a concentration of 0.01 M was used as electrode rinsing solution in all experiments. The effluent was fed into the concentrate and dilutes chambers in the ED cell. A constant potential of 24 V was applied. At the start of each test one sample was taken for analysis.

In this work; bipolar membrane electrodialysis (BMED) process was applied. A PCCell ED 64-4 unit and BMED 1-3 bench ED pump unit obtained from PCCell GmbH were utilized. The characteristics of ion exchange membranes used in ED process were shown in Table 3.6. And also, Experimental setup of ED process was shown with three different ways in Fig. 3.4 a–c for better understanding of the basic mechanism of ED process.

Table 3.6 Ion-exchange membranes characteristics

Membrane type	**Anion exchange membrane**	**Cation exchange membrane**
Thickness (μm)	180–220	160-200
Perm selectivity (0.1 m KCl/0.5 m KCl)	>0.95	>0.95
Functional groups	NH4Cl	SO3 Na
Surface potential (Ω cm^2)	1.0–1.5	0.75–3.0
Temperature stability, max (^{0}C)	60	60
Water content (wt %)	14	9
Chemical stability (pH)	0-9	0-11
Ion Exchange capacity (meq. g−1)	ca. 1.5	ca. 1

The tannery was pretreated previous to ED to prevent clogging on membrane surface by particulate matter. An electrocoagulation process was used to remove particulate matter. So the efficiency in degrading organic matter by the EC process was proved by the removal of color and odor and by significant reduction in COD as well as chromium. This pretreatment makes it possible to treat the effluent so that it then does not clog the membranes during ED.

3.3 Analytical procedure

The wastewater analyses were carried out in accordance with the Standard Methods for Examination of Water and Wastewater [164]. "pH, conductivity, COD, total chrome, NH_3-N and color were determined with (A Jenway 3040 brand, HACH HQ40d, closed reflux titrimetric method 5220C, A-Analyst 400, atomic absorption spectrometer, and HACH LANGE GmbH DR 5000 (spectrophotometer), respectively)". Merck analytical quality chemicals were used in the preparation of reagents.

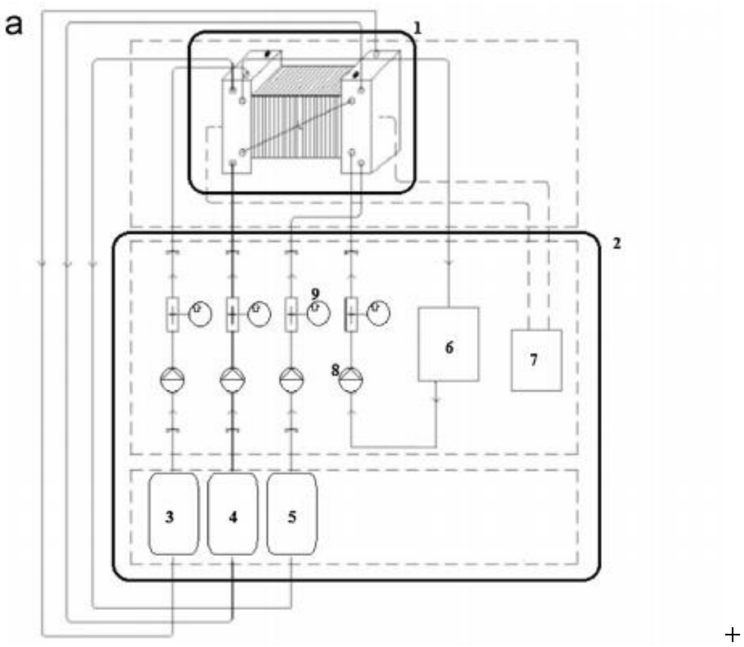

Figure 3.4 (a) Experimental setup (1: ED unit (ED 64-4); 2: ED pumping unit (BMED 1-3); 3: catholyte tank; 4: wastewater tank; 5: anolyte tank; 6: electrolyte tank; 7: DC power supply; 8: pump; 9: flow meter).

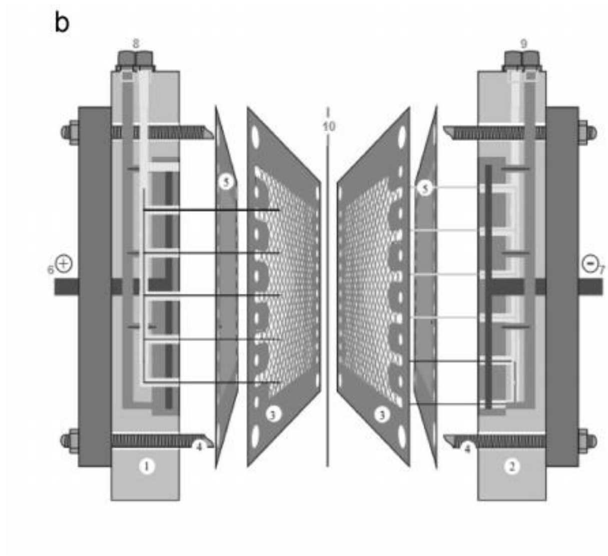

Figure 3.4 (b) Experimental setup (ED 64-4) (1, 2: electrodes and plates; 3: spacer; 4: screw set; 5: ion exchanger membranes; 6: anode; 7: cathode; 8,9: solution inlet/outlet; 10: bipolar membrane).

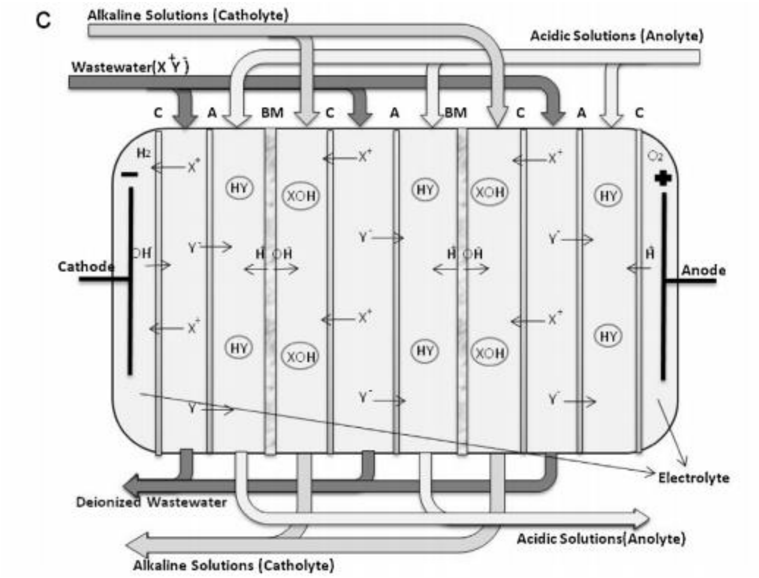

Figure 3.4 (c) Basic mechanism of bipolar membrane electrodialysis process (C: cation exchange membrane; A: anion exchange membrane; BM: bipolar membrane; X+, Y−; ionic pollutants), adapted by [59].

CHAPTER 4

RESULTS AND DISCUSSION

In this work, the electrochemical techniques for tannery wastewater treatment have been conducted. The elctrocoagulation process was applied as a batch mode and continuous mode reactors using iron and aluminum electrodes. The effects of operating parameters that include current density, initial pH, and electrolysis time on EC performance were accomplished as a batch mode reactor. Taguchi method was carried out in order to design the experiments and to optimize the experimental results. L_{25} orthogonal array (OA, three factors in five levels), signal-to-noise (S/N) ratio (the larger-the-better), and analysis of variance were applied to find the optimum levels and relative magnitude of the effects of parameters.

And also the performance of a continuous electrocoagulation (EC) process was investigated. The effects of the operating parameters, such as current density, pH of solution and inlet flow rate, on pollutants removal efficiency, sludge production and recovery of hydrogen gas were investigated in order to optimize process performance. At optimum operating conditions that were determined in continuous mode reactor, the treated tannery effluents were imposed to electrodialysis process to achieve enhanced treatment results. The results and discussion for these processes can be emphasized as below:

4.1 Batch mode EC reactor

4.1.1 Determination of optimum parametric levels

The collected data were analyzed using Minitab “16 version” statistical software for the estimation of the effect of each parameter on the optimization criteria. Experimental results, with regard to the model, were liberated from Taguchi method and demonstrated in Table 3.3.

On the other hand, all levels of variables are situated in Table 3.2. During this work, COD, total chrome, and color results are expressed as percentage of removal (%) through the following equation Eq. (4.1):

$$\%\,\text{removal} = \left[\frac{(C_i - C_f)}{C_i}\right] * 100 \tag{4.1}$$

where, C_i is the initial concentration and C_f is the final concentration of the pollutant (mg/L and ptc).

The obtained results are shown in Figures. 4.1a, 4.1b, 4.1c, and 4.2a, 4.2b, 4.2c for iron and aluminum electrodes, respectively. The numerical value of the maximum point in each graph clarifies the best value of that particular parameter, situated in Table 3.3 for each parameter, and indicates the optimum conditions within the range of experimental conditions.

4.1.2 Effect of current density on EC process

Current density is considered as a vital parameter for pollutants removal efficiency in EC process due to its power. Current density is in charge of the metal hydroxide concentrations, reaction rate of the process, coagulant dosage, bubble production, moreover, the effects on growth of flocs. During this work, current density was examined at the range of 10–50 mA/cm^2 in order to assess effects on tannery wastewater treatment efficiency of EC process. Either iron or aluminum electrode can be noticed from Figures. 4.1a and 4.2a that when current density increased, the COD removal efficiency was increased but not as likely, and also, the removal efficiency of total chrome and color was increased, so the best level for total chrome and color removal efficiency was obtained at the fifth level (50 mA/cm^2) for aluminum electrode as shown in Figures. 4.2b and 4.3c, and for color removal efficiency. in the case of iron electrode as demonstrated in Fig. 4.1c. It can be pointed out that the optimum removal efficiency of total chrome in iron electrode was attained at the third level (30 mA/cm^2) as shown in Figure 4.1b.

4.1.3 Effect of initial pH on EC process

It was reported in prior studies that pH is a central factor that affects the performance of EC process [18]. In the case of iron electrode, Figures 4.1a, 4.1b, and 4.1c illustrates the effects of all performance criteria on COD, total chrome, and color removal efficiencies. As it can be seen in Table 3.2, original pH value of the wastewater is 4.1. The pH experiments were performed within the examined range demonstrated that optimal pH value was 7 (fourth level) for the best COD removal efficiency as founded in Figure 4.1a. It can be noticed from Figure 4.1c, COD removal is similar to the best color removal at pH 7 (fourth parametric level). Whereas the best removal efficiency of total chrome is pH 8 (fifth level) as shown in Figure 4.1b. And also, Figures. 4.2a, 4.2b, and 4.2c explain the optimum pH values for COD, total chrome, and color removal efficiencies for the case of aluminum electrode. It can be seen that the optimum pH was 7 (fifth parametric level).

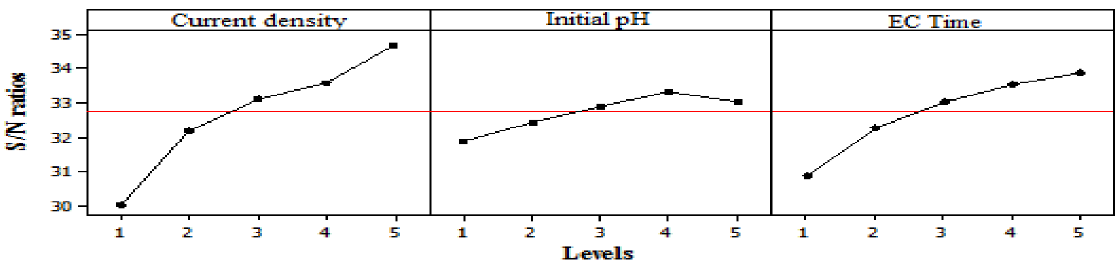

Figure 4.1 (a) The effect of each parameter on COD removal efficiency for iron electrode. On the left side, it shows the current density with different currents (10–50 mA/cm^2). In the middle, it presents different initial pH values from 4 to 8. On the right side, it explains EC time with different intervals from 5 to 25 min.

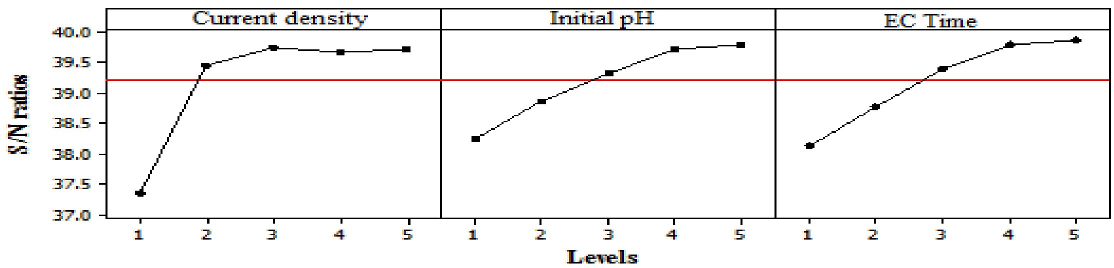

Figure 4.1 (b) The effect of each parameter on Cr removal efficiency for iron electrode. On the left side, it shows the current density with different currents (10–50 mA/cm^2). In the middle, it presents different initial pH values from 4 to 8. On the right side, it explains EC time with different intervals from 5 to 25 min.

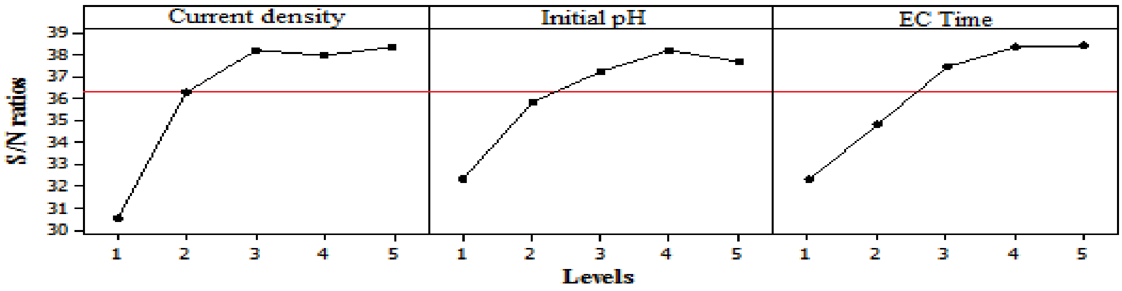

Figure 4.1 (c) The effect of each parameter on color removal efficiency for iron electrode. On the left side, it shows the current density with different currents (10–50 mA/cm^2). In the middle, it presents different initial pH values from 4 to 8. On the right side, it explains EC time with different intervals from 5 to 25 min.

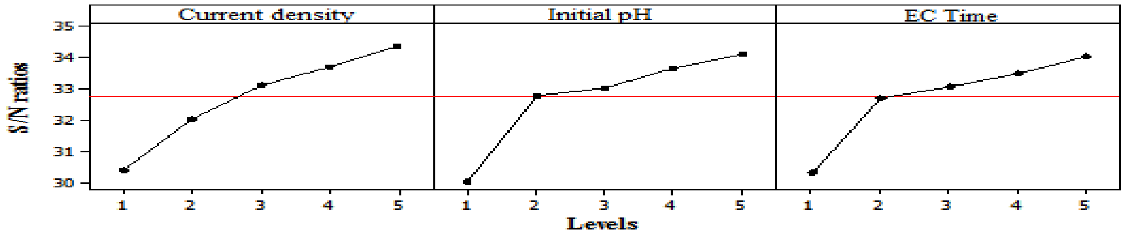

Figure 4.2 (a) The effect of each parameter on COD removal efficiency for aluminum electrode. On the left side, it shows the current density with different currents (10–50 mA/cm^2). In the middle, it presents different initial pH values from 3 to 7. On the right side, it explains EC time with different intervals from 5 to 25 min.

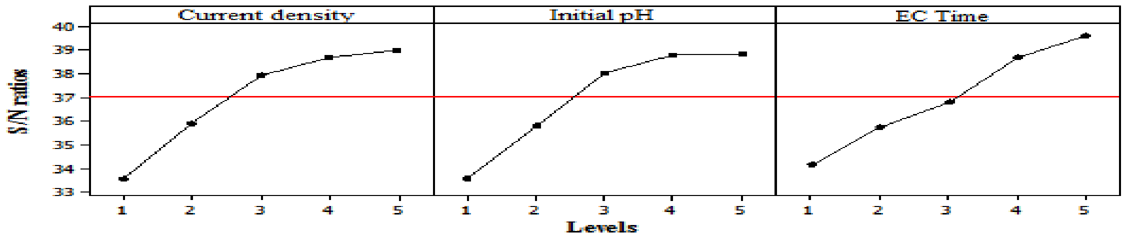

Figure 4.2 (b) The effect of each parameter on chrome removal efficiency for aluminum electrode. On the left side, it shows the current density with different currents (10–50 mA/cm^2). In the middle, it presents different initial pH values from 3 to 7. On the right side, it explains EC time with different intervals from 5 to 25 min.

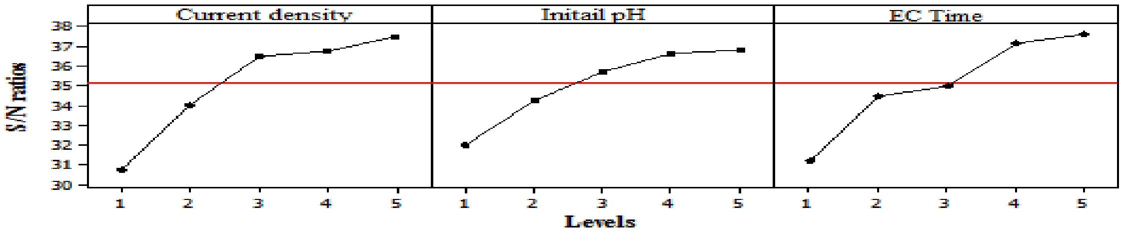

Figure 4.2 (c) The effect of each parameter on color removal efficiency for aluminum electrode. On the left side, it shows the current density with different currents (10–50 mA/cm2). In the middle, it presents different initial pH values from 3 to 7. On the right side, it explains EC time with different intervals from 5 to 25 min.

4.1.4 Effect of electrolysis time on EC process

There is a strong relationship between electrolysis time and formation of metal hydroxide which is responsible for removal of pollutants, and some parameters are time dependent. In this study, electrolysis time was given at the range of 5–25 min. In the two cases of iron and aluminum electrodes, Figures 4.1a, 4.1b, 4.1c, and Figures. 4.2a, 4.2b, 4.2c show the effect of electrolysis time on removal efficiency of pollutants. It can be concluded that the removal efficiency of COD, total chrome, and color increased with an increasing operation time. And the highest removal efficiency for all responses parameters was at the fifth level (25 min).

4.1.5 Statistic al analysis

Analysis of variance (ANOVA) was performed to examine the effective parameters and their confidence levels on the COD, total chrome, and color removal efficiencies. The function of the ANOVA is to explore which process parameters significantly affect the process responses. Table 4. 1 (panel a, b and c) illustrates the results of the ANOVA test for COD, total chrome, and color in iron and aluminum electrodes, respectively. According to S/N ratio analysis, it can be noticed from Table 4 (panel a, b and c) that the factors can be classified according to their significance as follows: in the case of iron electrode, current density > electrolysis time > initial pH for the COD, total chrome, and color removal efficiencies. Whereas the result of aluminum electrode was: initial pH > current density > time of COD, and total chrome removal efficiencies, while as, current density > time > pH for color removal efficiency.

In Taguchi's method, the confirmation test is important to verify the experimental results. The confirmation experiment is performed. In this study, after determining the optimum conditions and predicting the response under these conditions, a new experiment was designed and carried out with the optimum levels of EC parameters. Table 4.2 (a and b) shows the optimum working conditions. Thus, the equation omega transformation (Eq. (3.4)) was applied to evaluate the predicted value in order to clarify as percentage value of the result offered in Table 4.2. In addition, the percentage contribution of each factor effecting COD, total chrome, and color removal was calculated as illustrated in Table 4.1 using the following equation (Eq. (4.2)) [163]:

$$C\% = 100 \times \frac{Sum\ of\ squares}{Total\ sum\ of\ squares} \tag{4.2}$$

It can be noticed that the current density had the highest contributions to the variability of the experimental results for iron electrode. Contribution percentage on COD, total chrome, and color were attained as 61.6, 42.4, and 32.5, respectively. In the case of aluminum electrode, the initial pH was the highest contribution percentage for COD and total chrome as 35.3 and 31.4, moreover, for color was the lowest as 19.6.

Table 4.1 Results of the ANOVA test and contribution percentage

a: for COD removal performance

Variables	**DOF**		**SS**		**MS**		**F**		**P**		**C $_{\%}$ [b]**	
	I	**II**	**I**	**II**	**I**	**II**	**I**	**II**	**I**	**II**	**I**	**II**
A:CD	4	4	62.01	49.32	15.50	12.33	54.70	52.73	0.00	0.00	61.6	33.8
B: pH	4	4	6.28	51.45	1.57	12.86	5.54	55.01	0.01	0.00	6.3	35.3
C: Time	4	4	29.01	42.20	7.25	10.55	25.59	45.12	0.00	0.00	29	29
Error	12	12	3.40	2.81	0.283	0.233					3.1	1.9
Total	24	24	100.71	145.80								

b: for Total Chrome removal performance

Variables	**DOF**		**SS**		**MS**		**F**		**P**		**C $_{\%}$ [b]**	
	I	**II**	**I**	**II**	**I**	**II**	**I**	**II**	**I**	**II**	**I**	**II**
A:CD	4	4	21.51	105.31	5.38	26.33	6.39	11.66	0.01	0.00	42.4	31.5
B: pH	4	4	8.15	105.26	2.04	26.32	2.42	11.65	0.11	0.00	16.0	31.4
C: Time	4	4	10.98	97.16	2.75	24.29	3.26	10.76	0.05	0.01	21.6	29.0
Error	12	12	10.09	27.10	0.84	2.26					20.0	8.1
Total	24	24	50.75	334.83								

c: for Color removal performance

Variables	**DOF**		**SS**		**MS**		**F**		**P**		**C $_{\%}$ ^{b}**	
	I	**II**	**I**	**II**	**I**	**II**	**I**	**II**	**I**	**II**	**I**	**II**
A:CD	4	4	221.7	153.94	55.42	38.49	3.25	11.57	0.05	0.00	32.5	38.0
B: pH	4	4	113.3	79.62	28.32	19.91	1.66	5.98	0.22	0.01	16.6	19.6
C: Time	4	4	143.7	132.05	35.92	33.01	2.11	9.92	0.14	0.00	21.0	32.6
Error	12	12	204.5	39.93	17.04	3.33					29.9	9.8
Total	24	24	683.1	405.54								

Note: b. Contribution is defined as 100 *x* (Sum of squares / Total sum of squares), SS: sum of squares; DOF: degree of freedom; C%: contribution percentage, CD: current density (mA/cm^2). Time (minute)

4.1.6 Operating costs

The operating cost is considered a vital parameter that affects the implementation of any method of wastewater treatment. In this paper, the operating costs have been calculated for EC process under optimum conditions. Generally, the operating cost includes material (mainly electrodes) cost, electrical energy cost, as well as labor, maintenance, and other costs. However, in this study, the operating costs were calculated as energy consumption and elect rode material where as consumption quantities per m^3 of wastewater treated. Unit prices, given as Turkish market, 2015, are as follows: electrical energy price 0.1 $/kWh, electrode material price 0.2 $/kg, for iron and for aluminum 1.5 $/kg.

The electrode and energy consumptions in the EC process were calculated via the following equations (Eqs. (4.3) and (4.4)):

$$Energy_{consumption} = \frac{\mathrm{I} \times \mathrm{V} \times \mathrm{t}}{\mathrm{v}} \tag{4.3}$$

Where Energy consumption is the energy consumption (kWh/m^3), V is the voltage (Volts), I is the current (Amperes), t is the EC time (hour), and v is the volume of the treated wastewater (m^3).

Table 4.2 Optimum experimental conditions predicted and observed removal efficiency values (iron and aluminum electrode)

Perform. Criteria	**CD**		**pH_i**		**ET**		**Observed %**	**Predicted %**	**C.L %**
For iron electrode	level	value	level	value	level	value			
COD	5	50	4	7	5	25	63.3	58.3	50.2-66
chrome	3	30	5	8	5	25	99.7	99.9	99.9-100
Color	5	50	4	7	5	25	82.0	92.0	48-99.3
For aluminum electrode									
COD	5	50	5	7	5	25	64.4	60.0	52.7-66.9
chrome	5	50	5	7	5	25	99.0	99.7	92.2-99.9
Color	5	50	5	7	5	25	88.0	92.0	79.0-97.3

Note: CD; current density; ET: electrolysis time; C.L: confidence limit

Besides, electrode consumption was evaluated according to Faraday's law as the following equation Eq. (4.4):

$$Electrode_{consumption} = \frac{(I \times t \times M_W)}{(z \times F \times v)} \tag{4.4}$$

Where F is the Faraday's constant (96,485 C/mol), Mw is the molar mass of electrode type as in iron (56 g/mol), aluminum (27 g/mol), and z is the number of electron transfer (z Fe: 2) and (zAl:3). In this work, in the case of iron electrodes, operating costs for both of COD and color removals were calculated as 0.88 $\$/m^3$, besides, for chrome removal was 0.70 $\$/m^3$. However, in the case of aluminum electrode, operating costs for COD, chrome, and color removals were evaluated as 0.94 $\$/m^3$. Ultimately, EC process is an effective costs method for treating tannery wastewater compared with other methods.

4.2 Continuous mode EC reactor

The efficiency of EC process depends on several parameters such as: current density (j), electrolysis time (t), initial pH (pH_i), type of electrode material (Fe or Al) and distance separating the anode to the cathode (d). In order to enhance the process performance, the effects of current density, electrolysis time, type of electrodes and initial pH have been tested. In the present work, only the untreated tannery effluent was used.

4.2.1 Effect of current density, inlet flow rate and energy consumption on the pollutants removal efficiency for aluminum electrodes

In all electrochemical technologies, current density is considered a vital parameter for controlling the reaction rate within the electrochemical reactor [53]. It is well known that current density determines the production rate of coagulant, adjust also bubble production, and consequently affects the growth of flocs [37]. According to the conditions of operating parameter that listed in table 3.4 we investigated the effect of current density *j*, inlet flow rate and energy consumption on the efficiency of pollutants removal.

Figure 4.3.a and b show that the time required achieving steady-state conditions, i.e. the values on the plateau region, decreased when *j* increased from 7 to14 mA/cm^2 and then became nearly constant at about 125 min. An increase in current density from 7 to 14 mA/cm^2 yielded an increase in the efficiency of pollutants removal, i.e. COD, NH_3-N, total chrome, and color removal efficiencies were increased from 44- 61, 17-31, 98->99, and 81-90, %, respectively. This could be anticipated: when the current density increases, the amount of Al^{3+} cations released by the anode and therefore of $Al(OH)_3$ particles also increases.

As shown in figure 4.3.a and b, in addition, energy consumption was directly proportional to applied current density. The energy consumption increased from 4.5 to 6.75 KWh/m^3 with the increase in the applied current density. When the energy consumption was measured, the power requirement of electrocoagulation for pollutants removal was taken into account, while pumping energy was not considered.

Thus, figure 4.4.a and b has achieved, satisfactory, a steady state conditions. So, the values on the plateau region, decreased when *j* increased current density from 7 to14 mA/cm^2 and then became nearly constant at about 125 min. An increase in current density from 7 to 14 mA/cm^2 yielded an increase in the efficiency of pollutants removal, i.e. COD, NH_3-N, total chrome, and color removal efficiencies were increased from 53-73, 23-60, >99, and 85-95 %, respectively. However, the pollutants removal efficiency at pH 6 is found superior than pH 4.1 for aluminum electrodes.

As described in figure 4.4.a and b, in addition, it can be seen that the energy consumption was directly proportional to applied current density. The energy consumption increased from 4.5 to 6.75 KWh/m^3 with the increase in the applied current density. When the energy consumption was measured, the power requirement of electrocoagulation for pollutants removal was taken into account, while pumping energy was not considered. Conclusively, as the current density was increased, the pollutants removal efficiencies and the energy consumption increased.

Regard to the inlet flow rate, as seen in figure 4.3.a and b, figure 4.4.a and b, it was increased to 17, 20, 25, 33, 50 and 100 ml/min, the retention time directly decreased to 150, 125, 100, 75, 50, and 25 min. the pollutants removal efficiencies were decreased as the flow rate was increased. This showed that mixing by the rapid turbulent inlet to the reactor initially affected the pollutants removal efficiency. However, after the flow rate was increased somewhat, from 20 to 25 ml/min in this study, the influence of retention time decreasing was stronger than that of the mixing effect. The optimal flow rate could be considered to be 20 ml/min which is corresponding to 125 min. The result indicated that energy consumption was independent of the inlet flow rate, which is similar with its behavior according to pollutants removal. Despite the increasing of the inlet flow rate, the power consumption remained at 4.5-6.75 KWh/m^3 for figure 4.3 a and b and figure 4.4 a and b. The pumping energy was not taken into account on integrating the energy consumption.

Anyway, for the experimental conditions of figure 4.3 b and figure 4.4 b, optimum current density and inlet out flow seemed therefore to be 14 mA/cm^2, and 20 ml/min, as it can be considered that Y_{COD} = 61, 73% respectively, corresponds to the minimum acceptable value for EC process. However, fig.4.4 b has achieved the best condition according to our results, optimum current density, pH and inlet out flow or electrocoagulation time seemed therefore to be 14 mA/cm^2, 6.0 and 20 ml/min or 125 min, respectively, as it can be considered that Y_{COD} = 73 % , corresponds to the minimum acceptable value for EC process. At these conditions, thus, the removal efficiency of NH_3-N, Cr, and Color was 51, >99 and 95 % respectively, and the energy consumption was 6.75 KWh/m^3 in the case of aluminum electrodes.

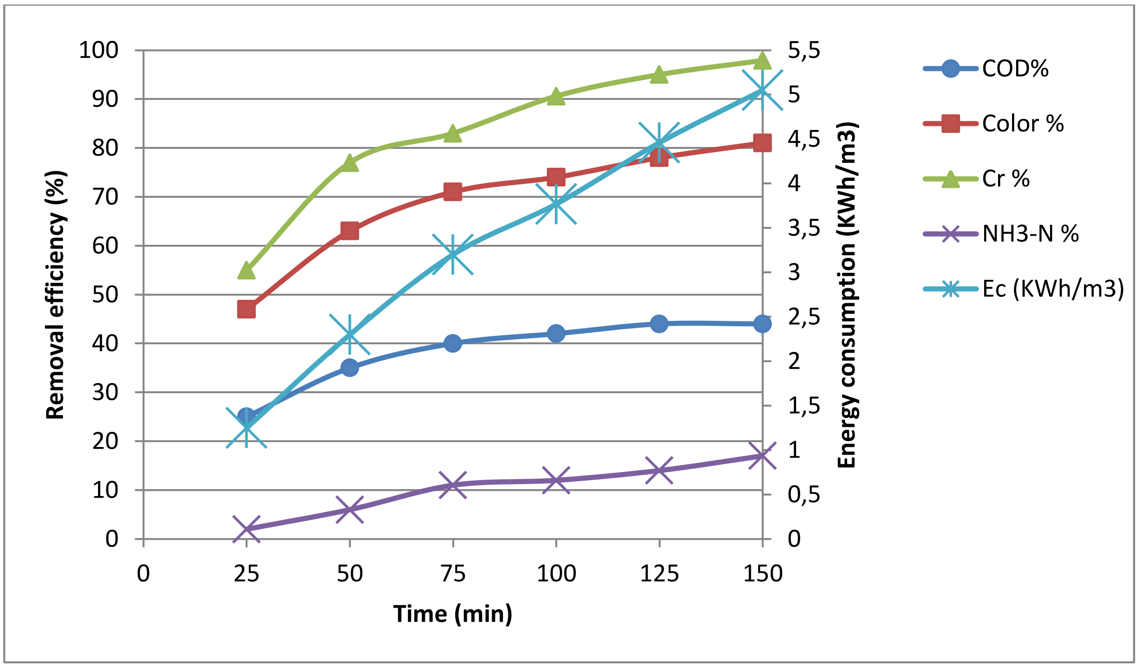

Figure 4.3 (a) Effect of current density on pollutants removal efficiency with time or inlet flowrate and energy consumption of electrocoagulation using aluminum electrodes (original pH 4.1, five pairs of Al electrodes, current density 7 mA/cm^2).

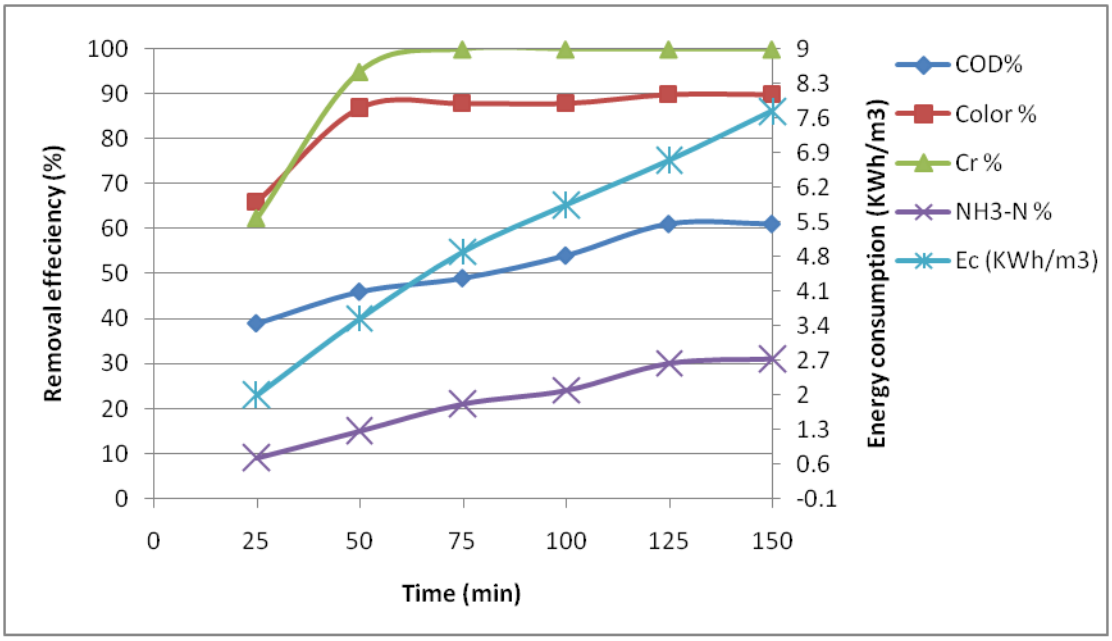

Figure 4.3 (b) Effect of current density on pollutants removal efficiency with time or inlet flowrate and energy consumption of electrocoagulation using aluminum electrodes (original pH 4.1, five pairs of Al electrodes, current density 14 mA/cm^2).

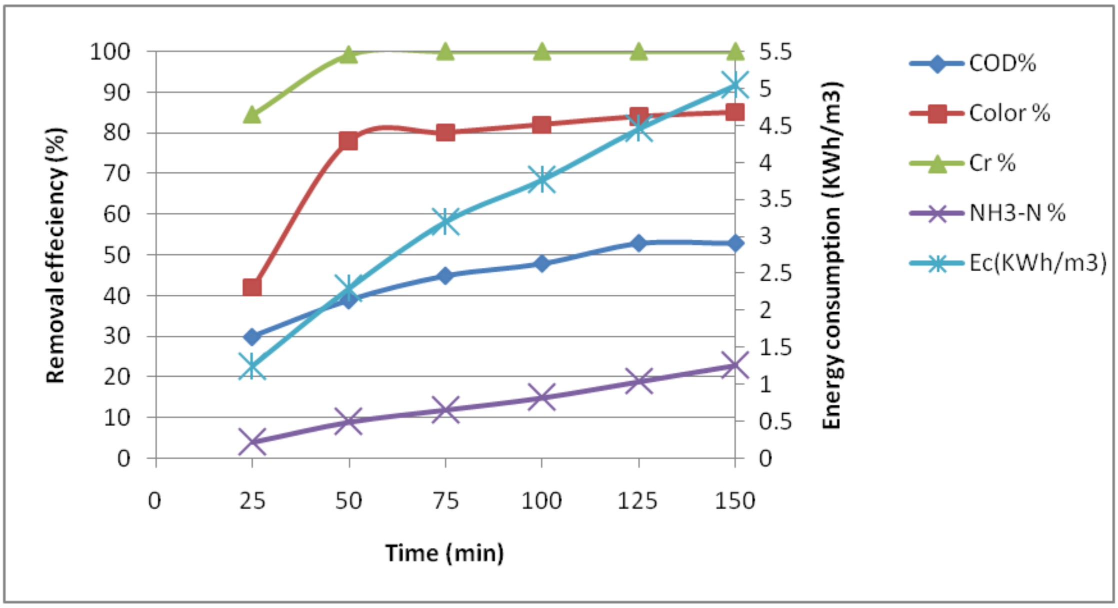

Figure 4.4 (a) Effect of current density on pollutants removal efficiency with time or inlet fowrate and energy consumption of electrocoagulation using aluminum electrodes (pH 6, five pairs of Al electrodes, current density 7 mA/cm^2).

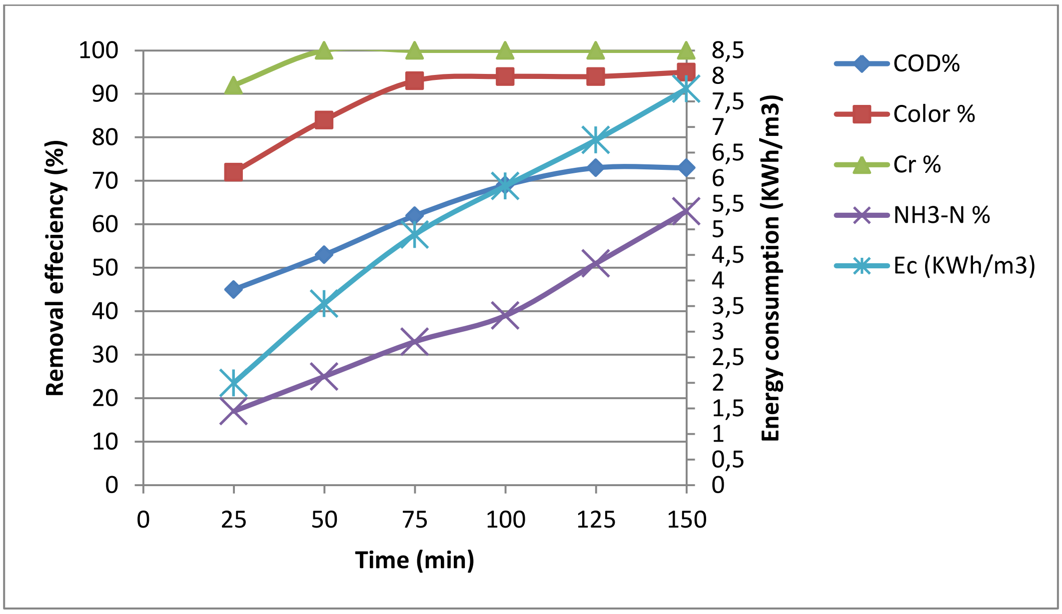

Figure 4.4 (b) Effect of current density on pollutants removal efficiency with time or inlet flow rate and energy consumption of electrocoagulation using aluminum electrodes (pH 6, five pairs of Al electrodes, current density 14 mA/cm^2).

4.2.2 Effect of current density, inlet flow rate and energy consumption on the pollutants removal efficiency for iron electrodes

It is well known that current density *(j)* is the major operating variable directly affecting on the performance of electrocoagulation process and operating costs. It is clearly evident that as the value of *j* increases from 7 - 14 mA/cm^2 a substantial increment in the pollutants removal was observed (figure 4.5a and b). Highest removal efficiency was achieved at14 mA/cm^2, as it can be seen in fig.4.b. This may be due to as the value of *j* increases, the amount of Fe^{+3} cations liberated by anode increases ,formation of monomeric ions and hydroxyl complexes increases and thus may be attributed to the adsorption of the hydrogen bubbles produced by electrodes.

Anyway, figure 4.5.a and b show the removal efficiency of the pollutants and the energy consumption as a function of current density and electrocoagulation time or the inlet flow rate. The pollutants removal efficiency was comparable for every combination of current density and electrocoagulation time. Therefore, when considering both pollutants removal efficiency and energy demand, figure 4.5.b seemed to be the most suitable for treating tannery wastewater. The pollutants removal efficiencies of COD, NH_3-N Cr, and Color were 53, 27, >99 and 76 % respectively, and the energy demand was 8.0 kWh/ m^3. As shown in figure 4.b, When the electrocoagulation time was increased from 25 min to 150 min at current density of 14 mA/cm^2, the removal efficiency of COD, NH_3.-N, Cr and Color was significantly increased from 36- 53, 12-27, 98.7->99 and 73-76 % respectively, The energy demand also increased from 2.10 to 8.0 kWh/ m^3.

Figure 4.6.a and b depict the removal efficiency of pollutants in term; COD, NH_3-N, Cr and color, the energy consumption as a function of current density and electrocoagulation time or inlet flow rate. The pollutants removal efficiency was comparable for every combination of current density and electrocoagulation time. Therefore, when considering both COD removal efficiency and energy demand, figure 4.6.b seemed to be the most suitable for treating tannery wastewater. The COD removal efficiency was 67 % and the energy demand was 6.75 kWh/ m^3 at 125 min. while, in figure 4.6.a the removal efficiency of COD was 45% and the energy consumption was 5.05 KWh/m^3 at 150 min.

Regard to the inlet flow rate, as shown in (figure 4.5.a and b, figure 4.6.a.b), it was increased to 17, 20, 25, 33, 50 and 100 ml/min, the retention time directly decreased to 150, 125, 100, 75, 50, and 25 min. the pollutants removal efficiencies were decreased as the flow rate was increased.

Based in our experimental conditions, it can be seen that the optimum condition was achieved in figure 4.6.b, optimum current density and inlet out flow or electrocoagulation time seemed therefore to be 14 mA/cm^2, and 20 ml/min or 125 min, respectively, as it can be considered that Y_{COD} = 67 %, corresponds to the minimum acceptable value for EC process. Thus, the removal efficiency of NH_3-N, Cr and color was 46, >99 and 93 % respectively, and also the energy consumption was 6.75 KWh/m^3.

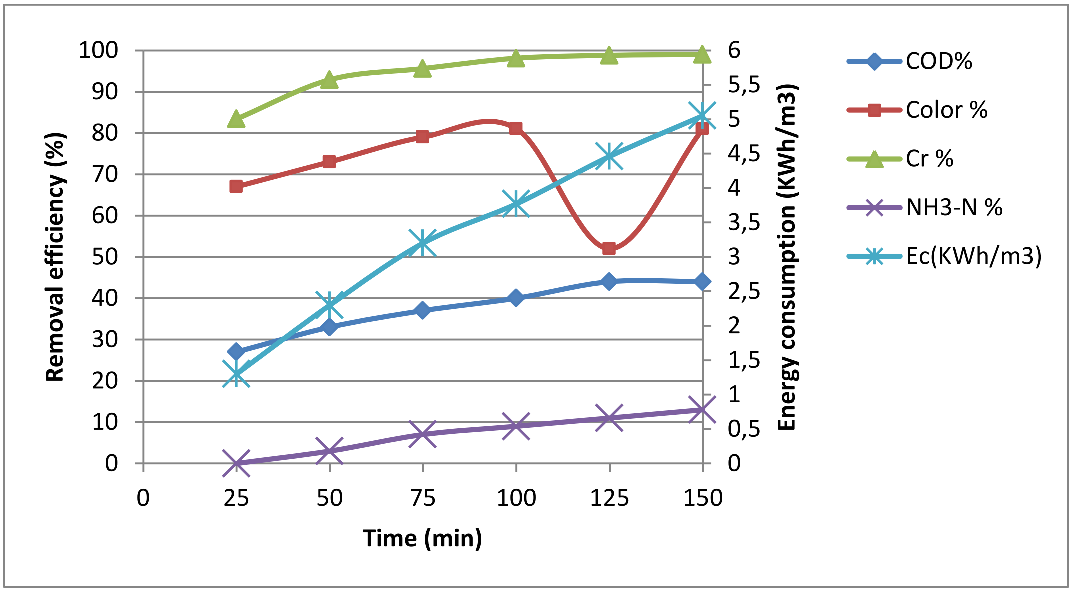

Figure 4.5 (a) Effect of current density on pollutants removal efficiency with time and energy consumption of electrocoagulation using iron electrodes (original pH 4.1, five pairs of electrodes, current density 7 mA/cm^2.

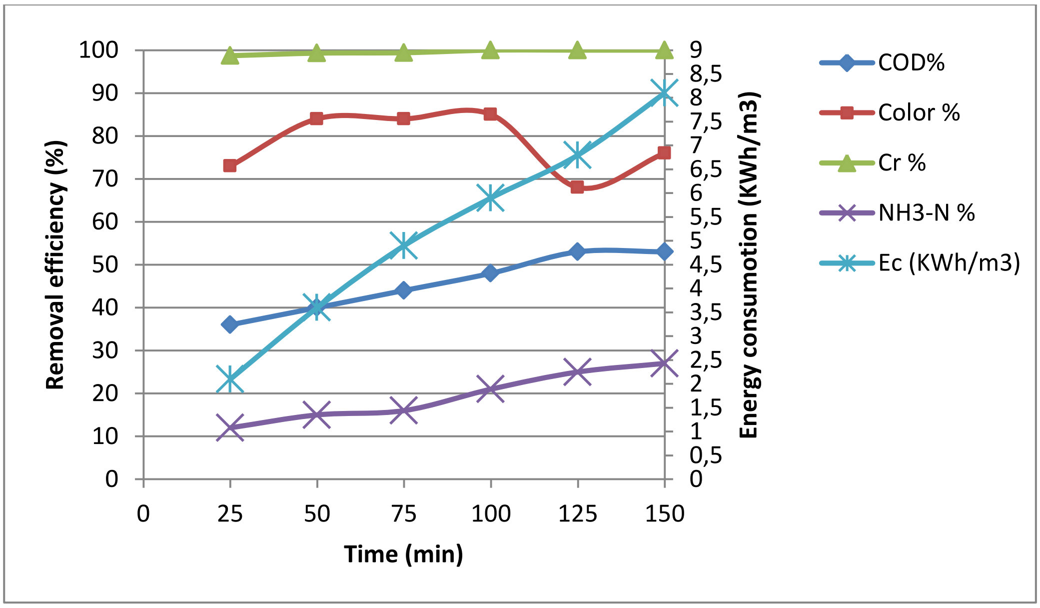

Figure 4.5 (b) Effect of current density on pollutants removal efficiency with time and energy consumption of electrocoagulation using iron electrodes (original pH 4.1, five pairs of electrodes, current density 14 mA/cm^2.

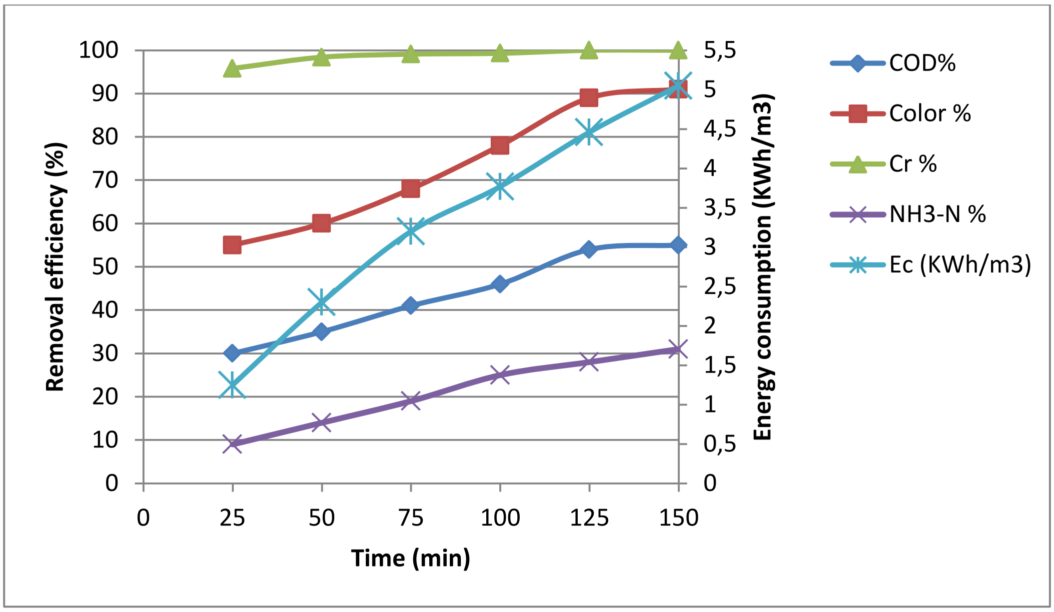

Figure 4.6 (a) Effect of current density on pollutants removal efficiency with time and energy consumption of electrocoagulation using iron electrodes (original pH 7, five pairs of electrodes, current density 7 mA/cm^2.

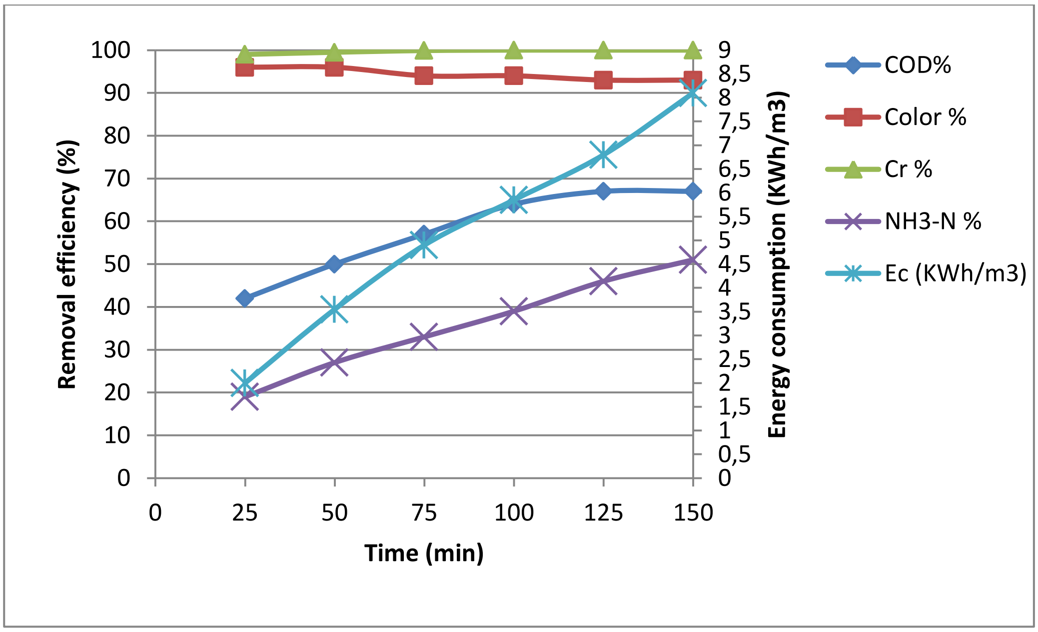

Figure 4.6 (b) Effect of current density on pollutants removal efficiency with time and energy consumption of electrocoagulation using iron electrodes (original pH 7, five pairs of electrodes, current density 14 mA/cm^2).

4.2.3 Changes of pH values

It has already been established that pH is a vital operating factor influencing the performance of electrocoagulation process [3]. Typically, pH of the medium is changing during the process, as observed also by other investigators [26]. This change depends on the type of electrode and the initial pH. The pH is continuously observed during the study.

The results are presented in Figure 4.7.a and b. In the case of A1 electrodes, it can be seen from Figure. 4.7. a, when current density and initial pH were 7 mA/cm^2 and 4.1 respectively, pH changed from 4.1 to 6.2. And also, when current density and initial pH were 14 mA/cm2 and 4.1 respectively, pH changed from 4.1 to 7.4. However, when current density and initial pH were 7 mA/cm^2 and 6 respectively, pH changed from 6 to 7.5. And also, when current density and initial pH were 14 mA/cm^2 and 6 respectively, pH changed from 6 to 9.48. It could be explained by the excess of hydroxyl ions produced at the cathode and by the liberation of OH^- due to the occurrence of a partial exchange of Cl^- with OH^- in $Al(OH)_3$ [32].

In the case of Fe electrodes, it can be noticed from Figure 4.7.b, when current density and initial pH were 7 mA/cm^2 and 4.1 respectively, pH changed from 4.1 to 6.35. And also, when current density and initial pH were 14 mA/cm2 and 4.1 respectively, pH changed from 4.1 to 6.5. However, when current density and initial pH were 7 mA/cm^2 and 7 respectively, pH changed from 7 to 8.1. And also, when current density and initial pH were 14 mA/cm^2 and 7 respectively, pH changed from 7 to 9.1. The pH of water is anticipated to be high after EC; this is may be due to ammonia stripping process.

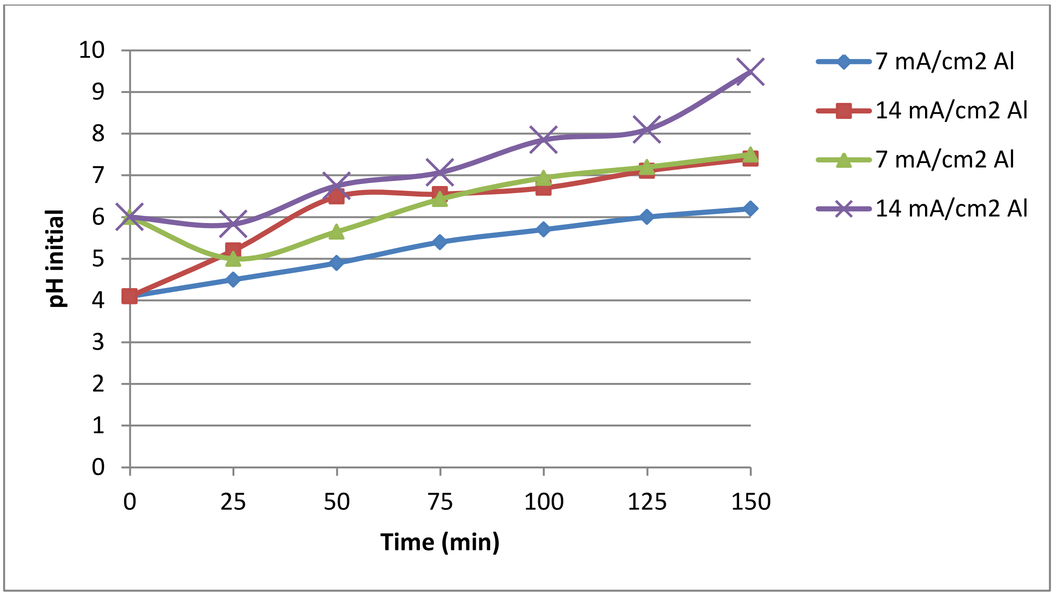

Figure 4.7 (a) Change of pH values during electrocoagulation process using aluminum electrodes

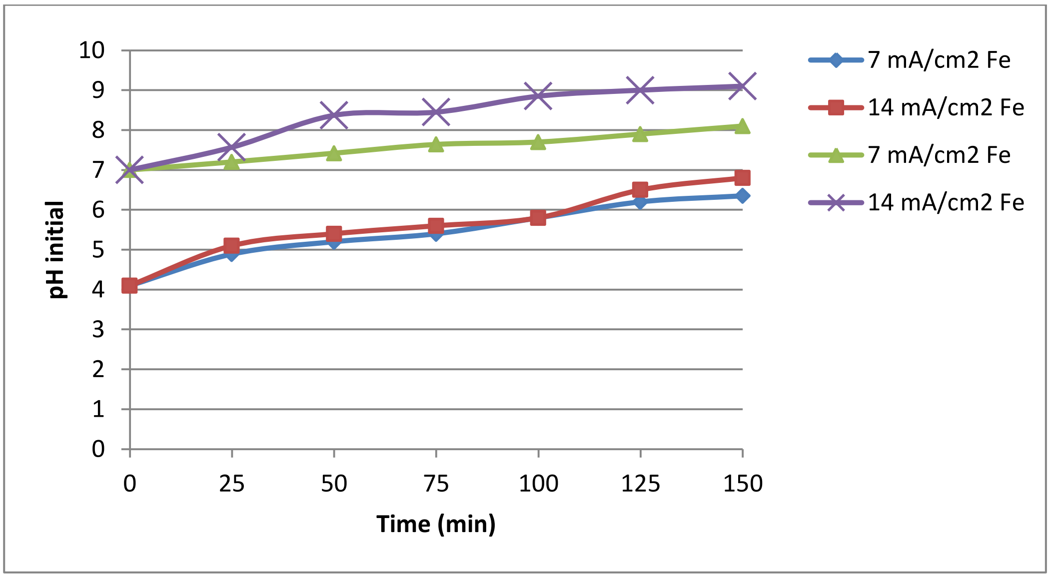

Figure 4.7 (b) Change of pH values during electrocoagulation process using iron electrodes

4.2.4 Effect of wastewater conductivity on the specific energy consumption

Usually, sodium chloride is employed to increase the electrical conductivity of the wastewater to a suitable level. Wastewater conductivity affects faradic yield, cell voltage and thus energy consumption in EC cells. Sodium chloride was chosen because of its low toxicity at moderate levels, its reasonable cost, and because the chloride species avoids inhibition phenomena at the surface of sacrificial anodes [37]. However, an excessive concentration of sodium chloride was proved to be detrimental to process efficiency [42]. According to our results, already, it has established that increasing the conductivity of wastewaters had not a considerable effect on pollutants removal efficiency. Figure 4.8.a and b show the Variation of tannery wastewater conductivity vs. electrocoagulatiom time.

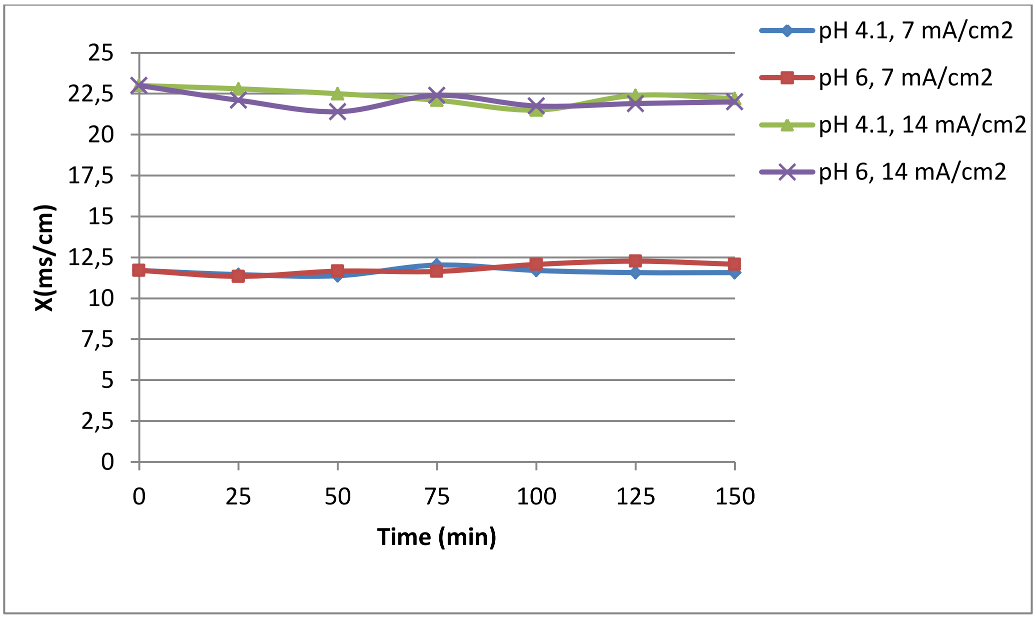

Figure 4.8 (a) Variation of wastewater conductivity vs. electrocoagulatiom time (min) using aluminum electrodes

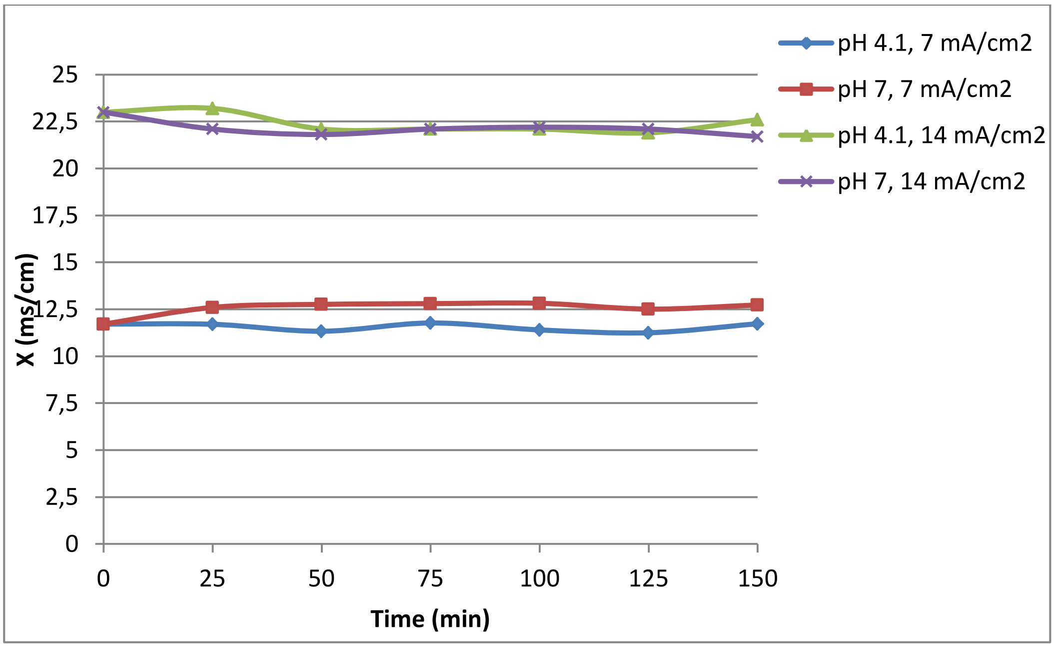

Figure 4.8 (b) Variation of wastewater conductivity vs. electrocoagulatiom time (min) using iron electrodes

However, it must be pointed out that the absence of supporting electrolyte is never the optimum situation from an energetic point of view. In this work, the conductivity of wastewater was adjusted using 4 g NaCl/L for the current density 14 mA/cm^2. This is illustrated by Figure 4.9.a and b that report the evolution of specific energy consumption as a function of NaCl addition in terms of Y_{COD}. The electrical energy consumed, expressed as kWh/m^3 of the tannery wastewater treated. Energy consumption in kWh/m^3 of wastewater has been obtained from the data generated at cell current 6 A. figures 5.8 a indicated that at optimum condition of COD_f (125 min), COD_f of 0.756 Kg was noted at the energy consumption of 3.7 kWh/m^3 in the case of aluminum electrodes. The corresponding COD removal efficiency was 73%. However, in the case of iron electrodes figure 5.8 b indicated that the energy consumption of COD_f of 4.0 kWh/m^3, when the COD_f of 0.924 Kg and the corresponding removal efficiency was 67%. On the other wards, it is obvious from that electrolyte addition was beneficial for the continuous EC process and constitutes a good way for minimizing operating costs.

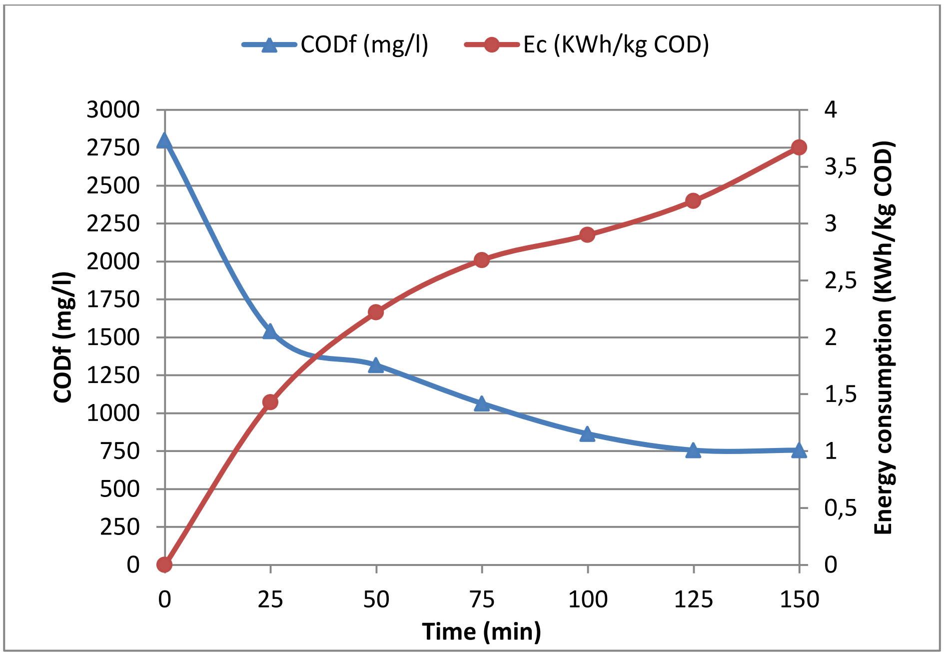

Figure 4.9 (a) Effect of NaCl addition on energy consumption Y COD for current density j = 14 mA/cm2, COD_i = 2800 mg/L, pH 6, and five pairs of aluminum electrodes.

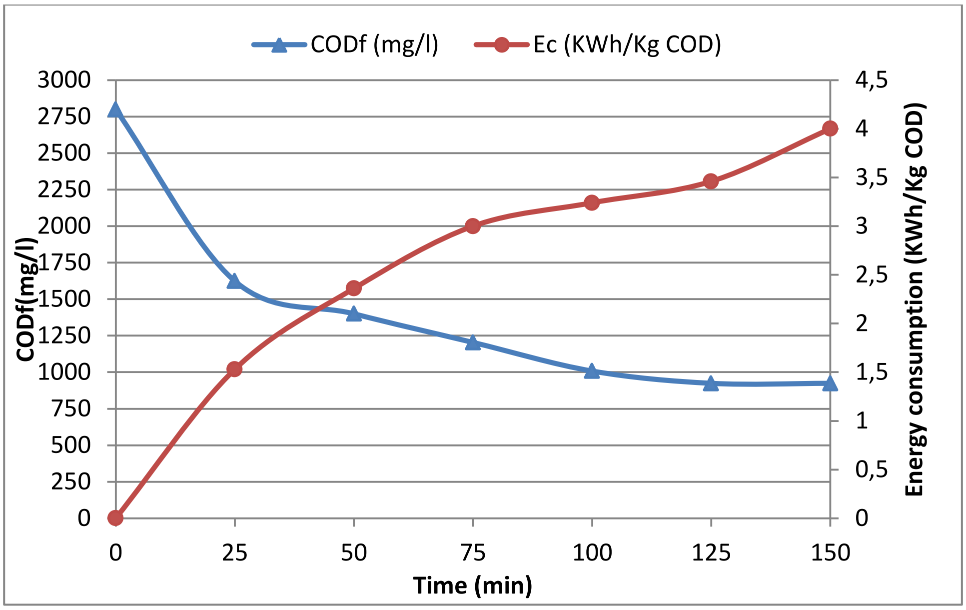

Figure 4.9 (b) Effect of NaCl addition on energy consumption Y COD for current density j = 14 mA/cm2, CODi = 2800 mg/L, pH 7, and five pairs of iron electrodes.

4.2.5 Recovery of hydrogen experimental and theoretical hydrogen yields

The effluent of tannery wastewater was supplied continuously to the bottom of the electrochemical reactor. As the wastewater is moved to the top, gas bubbles also moved up to the top together with upward effluent. The gas flowed out at the gas outlet located at the top of the gas separation tank, and water flowed out at a water outlet located near the top of the tank. With high liquid flow rates, only small amounts of solids accumulated in the gas separation tank. The amount of total gas produced was determined by water displacement method. The cumulative hydrogen gas production was determined by using the following equation (4.5):

$$VH_{2,i} = VH_{2,i-1} + V_{TG} + V_{G,i} - V_{G,i-1} \qquad (4.5)$$

Where $V_{H2,i}$ and $V_{H2,i\text{-}1}$ are the volumes of cumulative hydrogen (ml) calculated after the ith and the previous measurement; V_{TG} is the total gas volume measured by the water displacement method (ml); $V_{G,i}$ and $V_{G,i\text{-}1}$ are the volumes of the gas in the headspace of the reactor for the ith and the previous measurement (ml).

Figure 4.10.a shows hydrogen gas evolution coupled with electrocoagulation of different current densities (7 and 14 mA/cm^2) and pH values (4.1 and 6) for aluminum electrodes versus electrolysis time (min). As can be seen from Figure 4.10.a, the hydrogen gas production rates coupled with current density (7mA/cm^2) and

electrocoagulation time (150 min) were 332 and 380 ml at pH values 4.1 and 6, respectively.

While, the hydrogen gas production rates coupled with current density (14mA/cm^2) and electrocoagulation time (150 min) were 632 and 720 ml at pH values 4.1 and 6, respectively. As mentioned above, in the case of aluminum electrodes, the optimum current density and inlet out flow or electrocoagulation time seemed therefore to be 14 mA/cm^2, pH 6 and 20 ml/min or 125 min, respectively, as it can be considered that Y_{COD} = 73 %, and also, at these conditions it can be concluded that the hydrogen gas production rate was 582 ml.

However, in the case of iron electrodes an investigation of hydrogen production coupled with electrocoagulatoin of two values of current density (7 and 14mA/cm^2) and pH (4.1 and 7) versus electrolysis time (min) was conducted. As can be seen from Figure 4.10.b the hydrogen gas production rates coupled with current density (7mA/cm^2) and electrocoagulation time (150 min) were 328 and 336 ml at ph values 4.1 and 7, respectively. Thus, the hydrogen gas production rates coupled with current density (14mA/cm^2) and electrocoagulation time (150 min) were 612 and 668 ml at pH values 4.1 and 7, respectively.

For iron electrodes, as it can be considered that Y_{COD} =67 %, corresponds to the minimum acceptable value for EC process. The optimum conditions were seemed therefore to be 14 mA/cm^2, pH 7 and 20 ml/min or 125 min, at these conditions it can be attained about 546 ml of hydrogen gas. It should be pointed out that the amount of ammonia gas has been taken into consideration.

Ultimately, it could be explained that the hydrogen gas production increased when current density increased for each electrolyte, this is because that more protons released from the anode reaction which is agree with the COD removal [165]. Beyond that, the experiments with aluminum electrodes clearly indicated that hydrogen gas production from tannery wastewater was satisfactory than iron electrodes, this is due to high free electron density and high electrical conductivity of aluminum [166].

However, the theoretical amount of hydrogen gas generated is calculated by faraday law;

$$\eta_{H_2} = \frac{I.t}{F} \ .H \qquad (4.6)$$

Where, η_{H_2} is the amount of hydrogen generated (mole), I is the supplied current (Ampere), t is the electrocoagulation time (s), F is Faraday's constant (96,500 C per mole of electrons), H is the number of hydrogen molecules generated per electron involved in the redox reactions. The value of H is independent of the type of anode; i.e. iron or aluminum. That is, H is equal to 1/2 in both cases.

Table 4.3 compares the experimental hydrogen yield from the harvested hydrogen product and the electrical energy requirement of the electrocoagulation process. The experimental energy yield from the harvested hydrogen was calculated based on the energy yield of hydrogen of 67.4 kcal/ H_2. (h)/ Volume (m^3).

The results show that the energy yield of harvested hydrogen can reduce the electrical energy consumption of the electrocoagulation process by 20 % for current density 7 mA/cm^2 and 30 % for current density 14 mA/cm^2, (Assuming 50% efficiency in hydrogen to electricity conversion). It has been noted that the choice of current densities, electrocoagulation time, pH and the type of electrodes, the estimated hydrogen produced is always of the same order of magnitude, ranging between 0.93 and 2.00 kWh m^{-3}. Besides an energy source, hydrogen can be used as a reactant in hydrogenation process to produce low molecular weight compounds, or to remove some of pollutants such a sulfur and nitrogen compound [167].

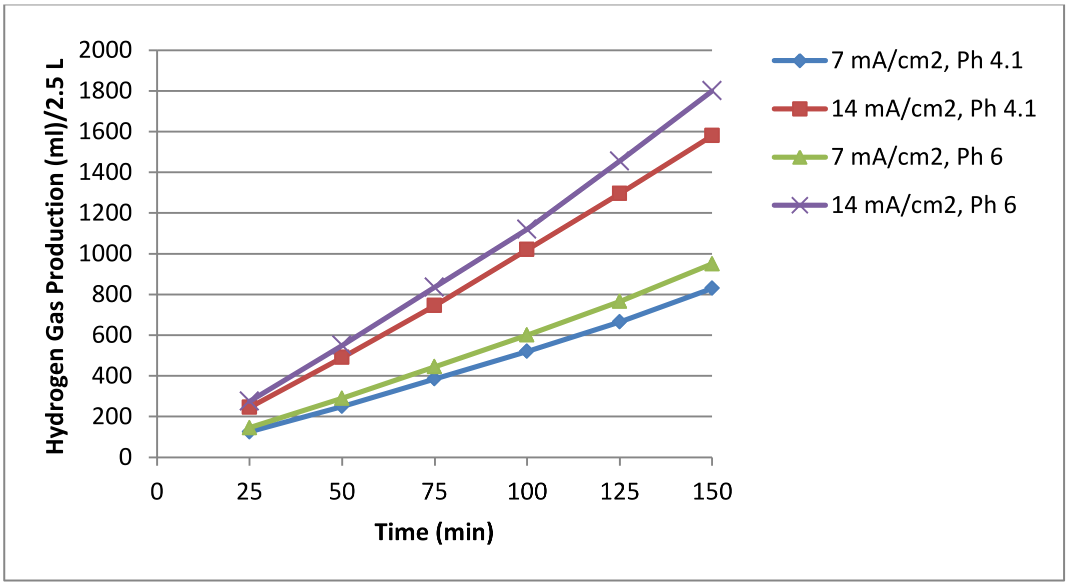

Figure 4.10 (a) Hydrogen gas production with aluminum electrodes

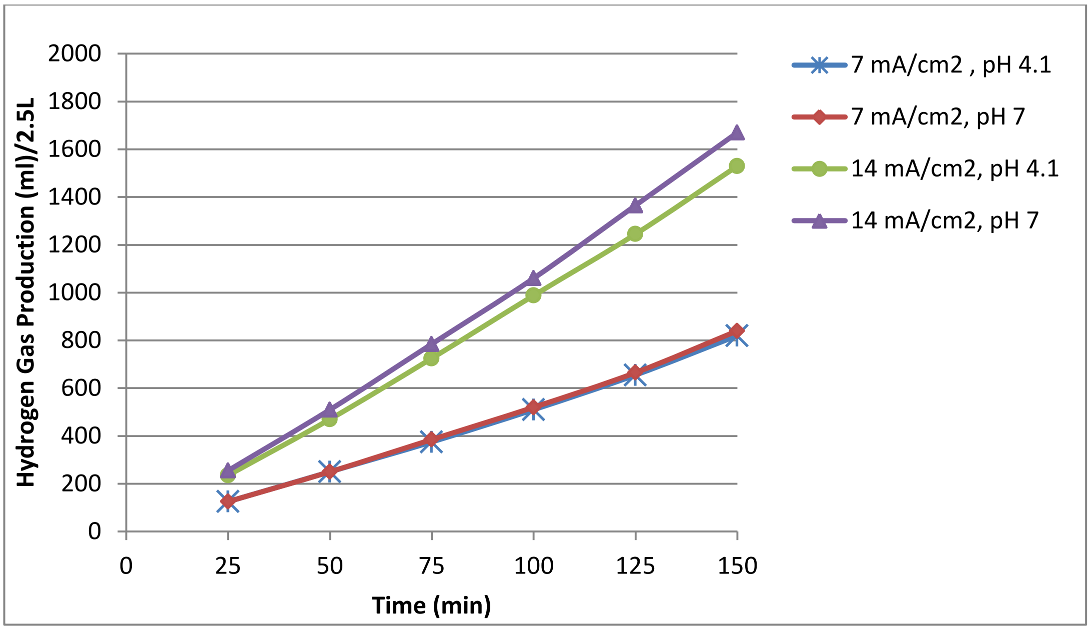

Figure 4.10 (b) Hydrogen gas production with iron electrodes

Table 4.3 Comparison of theoretical energy yield from harvested hydrogen product and energy consumption of the electrocoagulation process

Current density mA/cm^2)/ electrocoagulation time (min)	**pH value**	**Electrode type**	**Experimental energy production (KWh/m^3)**	**Experimental electrical energy requirement of EC process (KWh/m^3)**
7 mA/cm^2/125	4.1	Al	0.93	4.46
14 mA/cm^2/125	4.1	Al	1.80	6.75
7 mA/cm^2/125	6.0	Al	1.10	4.40
14 mA/cm^2/125	6.0	Al	2.00	6.75
7 mA/cm^2/125	4.1	Fe	0.91	4.46
14 mA/cm^2/125	4.1	Fe	1.73	6.75
7 mA/cm^2/125	7.0	Fe	0.93	4.46
14 mA/cm^2/125	7.0	Fe	1.90	6.75

4.2.6 Sludge production

Sludge produced in EC process is separated in clarifiers by sedimentation and flotation. In addition flocs formed by EC settle easy and they are well de-waterable. It can be observed from table 4.4 that the amounts of dried sludge were 0.43 – 0.72 Kg/m^3 in the case of aluminum electrodes while they were 0.38- 0.67 Kg/m^3 in the case of iron electrodes. The amount of sludge produced is related to the amount of pollutants removed. Based on our results in two cases (Al &Fe) we found that removing of 1 Kg of COD produces 0.35 Kg of dried sludge.

Table 4.4 Sludge production by Electrocoagulation process (kg/m^3)

COD removed	**Chromium removed**	**Organic sludge**	**Inorganic sludge**
For aluminum electrodes			
1.26	0.524	0.43	1.40
1.48	0.566	0.50	1.90
1.74	0.568	0.57	2.70
1.93	0.569	0.65	3.20
2.00	0.569	0.70	4.00
2.00	0.569	0.72	4.6
For iron electrode			
1.18	0.564	0.38	1.80
1.40	0.567	0.47	2.75
1.60	0.568	0.58	3.76
1.80	0.569	0.63	4.80
1.88	0.569	0.65	5.65
1.88	0.569	0.67	6.82

4.2.7 Comparison of the aluminum with the iron electrodes currently used in electrocoagulation process

In any electrochemical process, selection of the electrode material is important due to have significant effect on the treatment efficiency. Iron and aluminum were chosen as electrode materials because these are non-toxic, cost effectiveness and easily available. To compare the effect of electrode materials on the treatment efficiency, from our result in this study, it was found that, the optimum conditions have been investigated and determined before. At optimum conditions, the efficiency of both electrode materials (Al & Fe) was compared as shown in Table 4.5.

Table 4.5 Efficiency of tannery wastewater treatment comparing different electrode materials.

Electrode materials	**pH**		**Removal Efficiency (%)**				**Energy cons.**	**Hydrogen gas production**		**Operating costs ($/m^3)**
	B	A	COD	Color	Cr	NH_3-N	(KWh/m^3)	Vol. (ml)	Energy (KWh/m^3)	
Al	6.0	8.1	73	94	>99	51	6.75	582	2.00	1.5
Fe	7.0	9.0	65	93	>99	46	6.75	546	1.90	1.2

Conditions: electrocoagulation continuous mode; five pairs of electrodes; current density14 mA/cm^2; electrocoagulation time 125 min; A: after treatment; B: before treatment.

From the results presented in Table 4.5 it can be resulted that the aluminum electrode was more effective than the iron electrode, thus the different electrode materials had an effect on the effectiveness of water treatment because of its mechanisms which are mentioned before.

4.2.8 Operating costs

The operating cost is considered a vital parameter that affects s the implementation of any method of wastewater treatment. In this paper, the operating costs have been calculated for EC process under optimum conditions. Generally, the operating cost includes material (mainly electrode s) cost, electrical energy cost, as well as labor, maintenance, and other costs. However, in this study, the operating costs were calculated as energy consumption, pH adjustment and electrode material where as consumption quantities per m^3 of wastewater treated. Unit prices, given as Turkish market, 2015, are as follows: electrical energy price 0.1 $/kWh, electrode material price

0.2 \$/kg, for iron and for aluminum 1.5 \$/kg, and also, the cost of the NaOH chemical used in pH adjustment 0.75 \$/kg.

The electrode and energy consumptions in the EC process were calculated via equations: (4.3) and (4.4).

In the case of aluminum electrode, optimum pH value was 6.0. 1.7 ml 6N NaOH/L wastewater solution was used to bring the pH from 4.1 to 6.0. Then, the required NaOH solution per cubic meter should be 1.7 L 6N NaOH/m^3 wastewater. To prepare 1.7 L 6 N NaOH 0.41 kg NaOH chemical is needed. This amount of NaOH per unit cubic meter cost 0.27 \$/m^3. In addition, the electric energy consumption was taken into account for EC continuous system, the required energy amount for optimum reaction time (125 min) was 6.75 KWh/m^3 tannery wastewater, so the cost of EC process per unit cubic meter was 0.51 \$/m^3 tannery wastewater. , the pumping energy was not taken into account on integrating the power consumption. Thus, the cost of electrode material consumption of tannery wastewater treated was 0.83 \$/m^3. The total cost of the EC continuous process was found to be 1.5 \$/m^3 wastewater.

In the case of iron electrodes, optimum pH was 7.0. 2.0 ml 6N NaOH/L wastewater solution was used to bring the pH from 4.1 to 7.0. After that, the required NaOH solution per cubic meter should be 2.0 L 6N NaOH/m^3 wastewater. To prepare 2.0 L 6 N NaOH 0.48 kg NaOH chemical is needed. This amount of NaOH per unit cubic meter cost 0.32 \$/m^3. However, the cost of energy consumption and electrodes consumption were found to be 0.675 and 0.51 \$/m^3 tannery wastewater, respectively at optimum condition (125min). The total cost of the EC continuous process was found to be 1.2 \$/m^3 wastewater.

4.3 Electrodialysis process

4.3.1 Optimization of electrodialysis (ED)

In this work, experimental results with a single membrane and a 25 V electrical voltage were established to be the optimum operation conditions depended on two effluents treated tannery; one is the effluents treated tannery by EC with aluminum electrodes and the other with iron electrodes. Continuously analytical results for the anolyte, catholyte and dilute streams under optimum operating conditions are taken. The conductivity and current are taken into account in order to optimize the electrodialysis process as below:

4.3.1.1 Desalination of tannery wastewater

In this study, tannery effluents treated by EC process with aluminum electrodes (EC_{Al}) was fed into ED process. ED was conducted with a single membrane and 24 electrical voltages. It can be seen from Figure 4.11 that the shift of pollutants was established at the first moment of the experiment. A sharp decreasing in tannery conductivity from 22 to 1.5 mS/cm during the first 25 min was demonstrated. And also, it has decreased to 0.397 ms/cm after 45 min. Over the first 45 min the conductivity was decreased slowly. Moreover, tannery effluents treated by EC with iron electrodes (EC_{Fe}) also imposed to ED process. It can be noticed from figure 6.3 that decreasing of tannery conductivity from 21 to 1.5 mS/cm corresponding to 75 minutes was also occurred. Over the first 75 minutes the decreasing of the conductivity was weakly. In two cases of our experiments this is anticipated as a result of a decrease in current as the conductivity is reduced but removal efficiency of pollutants was increased.

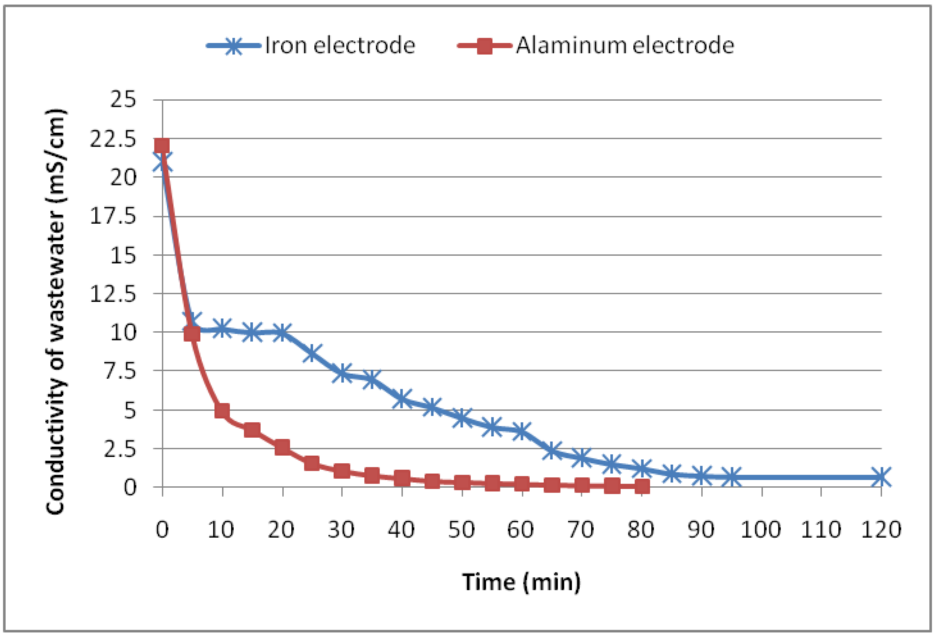

Figure 4.11 Conductivity variations of treated tannery by electrodialysis process

As shown in Table 4.6 a-b the obtained results indicated the removal efficiency of more than 87% for COD in the present effluents. It was clearly observed that the removal efficiency for ammoniacal nitrogen (NH_3-N) and chromium was >99%. Another important positive result obtained with the treatment was a great reduction in color and smell.

4.3.1.2 Current variation

Current value is considered a vital factor in the ED process. In this study, it can be seen from the Figure 4.12 that the changes in the current values were observed to parallel changes in efficiency. Thus, in two cases of effluents EC process (Al & Fe), it can be pointed out that an increased electrical voltage increases current and thus provides faster ion transport. After that the current value was decreased as resistance increased and also electric voltage was remained constant. Moreover, our results for effluent EC process with aluminum electrodes (EC_{Al}-ED) was reached the target conductivity level of 1.5 ms/cm at 25 minutes, while in the second case of (EC_{Fe}-ED) was reached to the same value of conductivity level of 1.5 ms/cm at 75 minutes due to low electrical voltages. As shown in Fig. 6.4 it can be observed that in either case of EC_{Al}-ED and EC_{Fe}-ED, the initial current values of a single membrane with 25 V were 6.5 A and 3.61A, respectively. These current values decreased to 1A and 0.53 A after 25 minutes and to 0.37 A and 0.50 A after 75 minutes respectively. Regard to the flux desalination at optimum conditions, the desalination for 1mS/cm was 414mg of NaCl per one liter. So in the case of aluminum electrodes, the flux was reached to 5.85, 2.23, 0.9 and 0.15 $m^3/m^2.h$ at 5, 10, 25, 45 min respectively. While in the case of iron electrodes, it was reached to 5.0 and 0.3 $m^3/m^2.h$ at 5 and 75 minutes respectively.

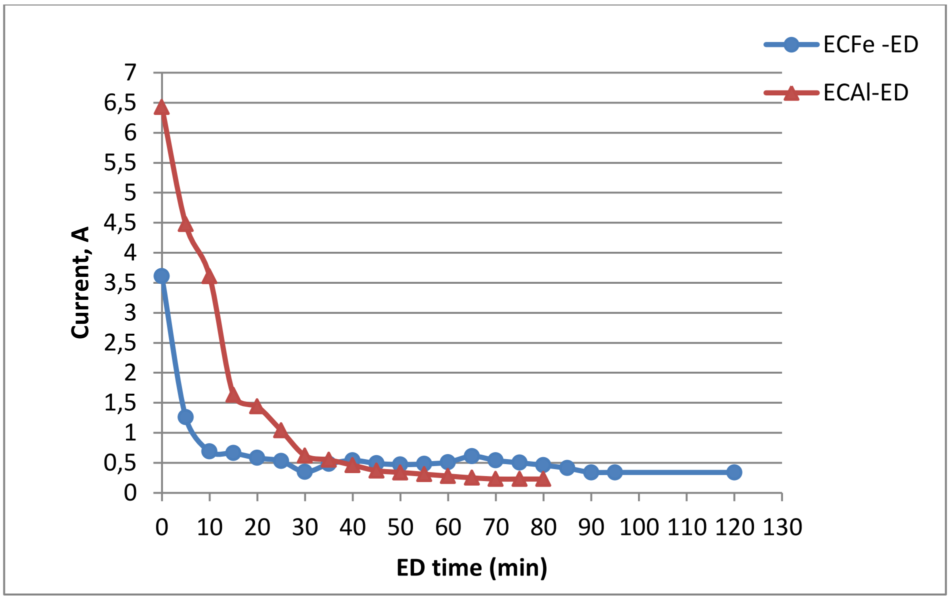

Figure 4.12 Current variations of during electrodialysis process

It can be anticipated that due to low resistance at the starting of the experiment the current value was sufficiently high to obtain rapid treatment, but the rate of decrease in the current values is particularly high. This result can be elucidated by clogging in the process.

4.3.1.3 Economic estimation

As well known ED process has high ion removal efficiency, on the other hand, high operating costs. In this study, ED laboratory scale was conducted with 190 mA/cm^2 current density to continue the treatment of effluent EC process. For EC_{Al}-ED process at 25 minutes the energy requirement was 10 $KWh/m^{3,}$ and also it was 31 KWh/m^3 corresponding to 75 minutes in the case of EC_{Fe}- ED process.

4.3.2 The comparison with EC and EC-ED processes

Table 4.6 a-b shows the values of monitored parameters from effluent tannery wastewater, EC-treated effluent and combined EC-ED treated effluent. As shown in Table 6.3 a-b it was clearly observed that the removal efficiency for of ammonium, color and chromium was >99%. On the other words, it was also found that the effluent treated with combined EC-ED techniques provided water quality values very similar to values of Turkish dischargeable legislation.

It is important to emphasize that the values obtained after EC-ED treatment for critical parameters like COD, chrome, and ammonium comply with present Turkish legislation for effluent discharge standards as presented in Table 4.6.a-b.

In relation to reduction of organic compounds, EC has been shown to be a better option as well as for the heavy metals present in the tannery wastewaters. This result is ascribed to the fact that the extent of anodic dissolution of (aluminum or iron) increases, resulting in a greater amount of precipitate for the removal of pollutants. Moreover, bubble generation rate increases. These effects are both beneficial for high pollutant removal by H_2 flotation.

Table 4.6 a-b Characterization of feed water, effluent treated by EC process, and by EC-ED system, plus removal grade obtained using these techniques

a. In the case of aluminum electrodes

Parameter	**Results**					**Legislation**
	Effluent Tannery wastewater	**Treated effluent (EC)**	**Removal efficiency %**	**Treated effluent (EC-ED)**	**Desalination efficiency %**	
pH	6.0	8.10	-	3.31	-	-
Conductivity	23.0	22.0	-	1.50	-	-
COD	2800	756	73	224	92	300
Total chrome	570	0.1	>99	< 0.1	>99	3.0
NH3-N	180	88.2	51	< 1	>99	5.0
Color	824	49.5	94	< 1	>99	280

b. In the case of iron electrodes

Parameter	**Results**					**Legislation**
	Effluent Tannery wastewater	**Treated effluent (EC)**	**Removal efficiency %**	**Treated effluent (EC-ED)**	**Desalination efficiency %**	
pH	7.0	9.0	-	3.95	-	-
Conductivity	23.0	22.1	-	1.5	-	-
COD	2800	924	67	364	87	300
Total chrome	570	0.1	>99	< 0.1	>99	3.0
NH3-N	180	97.2	46	< 1	>99	5.0
Color	824	58	93	< 1	>99	280

Note: color: (ADMI (10) Pt–Co); conductivity (ms/cm); other parameters: (mg/l); (-) undefined.

4.3.3 Applicability of reuse treated tannery wastewater in irrigation

Nowadays, the increasing water scarcity conduces to a planned reclaimed wastewater (RWW) reuse: irrigation and dischargeable to water bodies. Any of these reuse targets requires a specific quality level. According to this, the environmental impact of the

RWW reuse needs to take into consideration the direct effects of RWW in irrigation reuse (effect on soil, on crops and on the landscape vegetation) or in environmental reuse (ecosystem), and also the hydrological indirect effects of water bodies.

According to EPA, there is a quality criteria required for agricultural reuse treated wastewater in irrigation; it can be highlighted on the chemical quality criteria:

1. Electrical conductivity.
2. Concentration of sodium ions and other cations.
3. Concentration of heavy metals.
4. Suspended solids and organic material.

All of these parameters have been related strongly with the types of food production, climate, soil characteristics, the type of irrigation method (sprinklers, drip, etc). Regard to these parameters there are guidelines to reused TWW in irrigation. Generally the treated wastewater contain essential nutrients for plant mostly ammonium. And also contains toxic ion like chloride, sodium, boron and chrome which can damage indirectly the plant, in the case of above suitable concentration. Sodium may destroy the soil structure which will cause reduction of permeability, also, heavy metals can be toxic to people through food chain. So it is an indispensable to regulate the irrigation process accurately.

Anyway a high concentration of SS makes clog for the irrigation method, so they are recommended that the threshold values are ranged from 5 to 25 mg/l. in addition Salinity leads to change in metabolic processes and physiological process of plants and ultimately inhibits crop production. On the other wards the soil salinity is seen to inhibit plant growth in the form of osmotic stress which is then followed by ion toxicity. TDS limited values were ranged from 500 to 1000 mg/l based on the type of plant or the suitable value of electrical conductivity was 700-3000 μS/cm. And also the value for sodium adsorption ratio (SAR) should be ranged from 3 to 40. Regard to specific ion toxicity it could be pointed that the main ions are sodium, chloride and boron. The concentrations of these ions based on the type of plant that will be irrigated, so the values of sodium ions are ranged from 18 to 102 mg/l and from 178 to 710 mg/l for chloride as well as from 2 to 4 mg/l for boron. Thus for chrome the threshold value is 0.1 mg/l. regard to our results it could be pointed out that the treated tannery wastewater can reuse in irrigation safely.

Based on reviews, the states of Turkey, Palestine and Jordan have guidelines for treated wastewater characteristics according to irrigation. Table 4.7 a-b shows the applicability of treated tannery waste water by a hybrid process (EC-ED) to reuse in irrigation.

Table 4.7 a – b the comparisons with treated tannery effluent and recommended Guidelines for treated wastewater according to different applications

a. in the case of aluminum electrodes (EC_{Al}-ED) process

Quality parameter (mg/l)	**Effluent treated (EC-ED)**	**Guidelines**								
		Turkey			Palestine			Jordan		
		A	B	C	A	B	C	A	B	C
COD	224	400	400	400	250	250	250	500	500	500
Chrome	< 0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
NH_3-N	< 1	40	40	40	50	50	50	45	45	45
Color	< 1	-	-	-	-	-	-	-	-	-
Conductivity mS/cm	1.5	-	-	-	-	-	-	-	-	-

b. in the case of aluminum electrodes (EC_{Al}-ED) process

Quality parameter (mg/l)	**Effluent treated (EC-ED)**	**Guidelines**								
		Turkey			Palestine			Jordan		
		A	B	C	A	B	C	A	B	C
COD	364	400	400	400	250	250	250	500	500	500
Chrome	< 0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
NH_3-N	< 1	40	40	40	50	50	50	45	45	45
Color	< 1	-	-	-	-	-	-	-	-	-
Conductivity mS/cm	1.5	-	-	-	-	-	-	-	-	-

A: dry field crops; B: industrial crops; C: landscape; (-): undefined; color: ADMI (10) Pt–Co)

From table 4.7 a – b, it is noticeable that the effluent treated with combined EC- ED techniques presents very suitable values for irrigation.

4.4 Conclusion and recommendations

In this work, Taguchi design experiment (L_{25}) was carried out to optimize the effective parameters on the removal efficiency of tannery wastewater pollutants by EC process. The larger-the-better S/N ratio was used to analyze the result experiments. A confirmation experiment within the optimal process parameters was conducted to assess the usefulness of the Taguchi optimization design technique. In view of our results, the conclusion can be given as follow:

- For iron electrode: current density was the most significant parameter on COD, total chrome, color, and its percentage value was 61.6, 42.4, and 32.5%, respectively. Together with, the second important factor for COD, total chrome and color was electrolysis time and its percentage contribution value was 29, 21.6, and 21%, respectively. Finally, the slightest factor was the initial pH. According to the result statistical analysis, for COD removal, the optimum condition was achieved as: current density 50 mA/cm^2, initial pH 7, and electrolysis time 25 min, for total chrome removal: current density 30 mA/cm^2, initial pH 8, and electrolysis time 25 min, and for color removal: current density 50 mA/cm^2, initial pH 7, and electrolysis time 25 min. In addition, the operating costs for both of COD and color removals were computed as 0.88 \$/m^3, besides, for chrome removal was 0.70 \$/m^3.

- For aluminum electrode: the initial pH was significant parameter on COD and its percentage contribution value was 35.3%, hence both current density and initial pH have the same effect on total chrome and their percentage values were 31.5 and 31.4%, respectively. With regard to color, current density was the most factors and its percentage contribution value was 38%. The second important parameter on COD was the current density with percentage value 33.8%. On the contrary, for color the second important factor was electrolysis time and its percentage value was 32.6%, and also, it can be concluded that the color is independent on the change of initial pH and its percentage value was 19.6%. Electrolysis time for COD and total chrome was the slightest parameter with the same percentage contribution value 29%. As said by the results statistical analysis, the set of optimum condition for COD, total chrome, and color removal was current density 50 mA/cm^2, initial pH 7, and electrolysis time 25 min, whereas operating costs for COD, chrome, and color removals were evaluated as 0.94 $/m^3.

A series of experiments was performed in order to find the effects of operating parameters for tannery wastewater treatment by electrocoagulation of a continuous mode. In addition, the effectiveness of electrocoagulation according to removal pollutants, i.e., COD, NH_3-N, Cr and Color was evaluated. Therefore, the significant amounts of hydrogen gas can be harvested by eclectrocoaulation has been determined. Pollutants removal by electrocoagulation was affected by current density, electrode materials, inlet flow rate, and initial pH.

Our results highlight the opportunity to apply continuous EC process for the efficient removal of pollutants (COD, NH_3-N, Cr, and Color), as well as recovery of hydrogen gas from tannery wastewater at low operating costs. In the case of aluminum electrodes, at optimum conditions the results showed that for tannery wastewater with an influent pH adjusted at about 6, the use of a current density of 14 mA/cm^2, and an EC time of 125 min, gave access to pollutants (COD, NH_3-N, , Cr, and Color) removal efficiency 73, 51, >99 and 94 %, respectively. Thus, Y_{COD} = 73% was achieved when COD_i was 2800 mg/l with a specific energy consumption about 3.2 kWh per kg of COD removed. However, the total cost of the EC continuous process was found to be 1.5 $/m^3 wastewater. With the above-mentioned conditions, it can be harvested a significant amounts of hydrogen gas by EC technology. In this study it can be reported that the hydrogen was lost in the liquid effluent from the gas separation tank. However, the energy yield of harvested hydrogen was 30% of the electrical energy demand of the electrocoagulation process.

In view of our results, the optimum conditions for iron electrodes were determined. With effluent pH adjusted at about 7, , the use of a current density of 14 mA/cm^2, and an EC time of 125 min, gave access to pollutants (COD, NH_3-N, Cr, and color) removal efficiency 67, 46, >99 and 93 %, respectively. Thus, Y_{COD} = 67 % was achieved when COD_i was 2800 mg/l with a specific energy consumption about 3.46 kWh per kg of COD removed. However, the total cost of the EC continuous process was found to be 1.4 $/m^3 wastewater. And also, the energy yield of harvested hydrogen was 28 % of the electrical energy demand of the electrocoagulation process.

The application of an integrated EC-ED process to out flow of tannery wastewater was found to be effective. The efficiency in degrading organic matter by the EC process was proved by the removal of heavy metals and by significant reduction in COD. This pretreatment makes it possible to treat the effluent so that it then does not clog the membranes during ED. The results show significant reductions in all parameters tested. Comparing the values of the effluent treated with the association of EC-ED techniques to the values of Turkish dischargeable legislation and guidelines for irrigation in the states of turkey, Jordan and Palestine. The possibility was documented for directly go to deep sea and to reuse in irrigation. The idea of ‘‘zero effluent technology’’ linked to this process can bring environmental and economic benefits since, besides significantly reducing the volume of effluent discharged, there is also a reduction in the use of feed water.

REFERENCES

[1] Smalley, R.E., Our energy challenge, Available from: http://smalley.rice.edu/Presentations/Columbia, (ppt visited on October 18, 2014 at 3:45 A.m. Central Time). 23 September 2003.

[2] Aboulhassan, A.M., Souabi, S. and Yaacoubi, A., (2008). "Pollution reduction and biodegradability index improvement of tannery effluents", Int. J. Environ. Sci. Tech, 5 (1): 11-16, winter 2008.

[3] Mollah, M.Y.A., Morkovsky, P., Gomes, J.A.G., Kesmez, M., Parga, J. and Cocke, D.L., (2004a). "Fundamentals, present and future perspectives of electrocoagulation", J. Hazard. Mater, B114(5): 199–210.

[4] Espinoza-Quinones, F.R. , Fornari, M.M.T., Modenes, A.N. , Palacio, S.M. , da Silva, F.G. , Szymanski, N. , Kroumov, A.D. , and Trigueros, D.E.G., (2009). "Pollutant removal from tannery effluent by electrocoagulation", Chem. Eng. J., 151(17): 59–65.

[5] Thanikaivelan1, P., Rao, J.R., Nair, B. U. and Ramasami, T., (2004). "Progress and recent trends in biotechnological methods for leather processing", TRENDS in Biotechnology, 22(4): 312-321.

[6] Benhadji, A., Ahmed,M.T. and Maachi, R., (2011). "Electrocoagulation and effect of cathode materials on the removal of pollutants from tannery wastewater of Rouïba", Desalination, 277(28): 128–134.

[7] Lofrano, G., Meriç, S., Zengin, G.E. and Orhon, D., (2013). "Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: A review", Science of the Total Environment, 461(33): 265–281.

[8] Szpyrkowicz,L., Kelsall, G. H., Kaul, S.N. and Faveri, M.D., (2001). "Performance of electrochemical reactor for treatment of tannery wastewaters", Chemical Engineering Science, 56(19): 1579- 1586.

[9] Panizza, M. and Cerisola, A., (2004). "Electrochemical Oxidation as a Final Treatment of Synthetic Tannery Wastewater, Environ", Sci. Technol., 38(3): 5470-5475.

[10] Tunay, O., Kabdasli, I., Orhon, D. and Ates, E., (1995). "Characterization and Pollution Profile of Leather Tanning Industry in Turkey", Wat.Sci.Tech.32 (12):.1-9.

[11] Durai, G., Rajasimman, M. and Rajamohan, N., (2011). "Kinetic studies on biodegradation of tannery wastewater in a sequential batch bioreactor", Journal of Biotech Research [ISSN: 1944-3285], 3(12):19-26.

[12] Costa, R.C. and Olivi, P., (2009). "Effect of chloride concentration on the electrochemical treatment of a synthetic tannery wastewater", Electrochimica Acta, 54(22): 2046–2052.

[13] Sundarapandiyan, S., Brutto, E.P., Siddhartha, G., Ramesh, R., Ramanaiah, B., Saravanan, P. and Mandal, B.A., (2011). "Enhancement of chromium uptake in tanning using oxazolidine", Journal of Hazardous Materials, 190(3): 802–809.

[14] Dogruel, S., Genceli, E.A., Babuna, F.G. and Orhon, D., (2006). "An investigation on the optimal location of ozonation within biological treatment for a tannery wastewater", Chem. Tech no l Biotechn, l81(32):1877–1885.

[15] Ganesh, R., Balaji,G., and Ramanujam, R.A., (2006)."Biodegradation of tannery wastewater using sequencing batch reactor—Respirometric assessment", Bioresource Technology, 97(33): 1815–1821.

[16] Calheiros,C.S.C., Rangel,S.S.O.A. and Castro,L.M.P., (2009). "Treatment of industrial wastewater with two-stage constructed wetlands planted with Typha latifolia and Phragmites australis", Bioresource Technology, 100(3): 3205–3213.

[17] Song, Z., Williams, C.J. and Edyvean, R.G.J., (2004). "Treatment of tannery wastewater by chemical coagulation", Desalination, 164(3): 249-259.

[18] Lofrano, G., Belgiorno, V., Gallo, M., Raimo, A. and Meriç, S., (2006). "Toxicity reduction in leather tanning wastewater by improved coagulation flocculation process", Glob Nest J, 8(11): 151–8.

[19] Menezes, F.M., Amal, R. and Luketina, D., (1996). "Removal of particles using coagulation and flocculation in a dynamic separator", Powder Technol., 88(4): 27–31.

[20] Oller,I., Malato,S. and Sánchez-Pérez,A.J., (2011). "Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination—A review", Science of the Total Environment, 409(5): 4141–4166.

[21] Liu,Z., Wang,F., Li,Y., Xu,T. and Zhu,S., (2011). "Continuous electrochemical oxidation of methyl orange wastewater using a three-dimensional electrode reactor", Journal of Environmental Sciences, 2011, 23(Supplement), S70–S73.

[22] Juttner,K., Galla,U. and Schmieder,H.,(2000)."Electrochemical approaches to environmental problems in the process industry", Electrochimica Acta, 45(36): 2575 – 2594.

[23] Chen,G., (2004). "Electrochemical technologies in wastewater treatment", Separation and Purification Technology, 38(5): 11–41.

[24] Phalakornkule, C., Sukkasem, P. and Mutchimsattha, C., (2010). "Hydrogen recovery from the electrocoagulation treatment of dye-containing wastewater", International journal of hydrogen energy, 35(3): 10934- 1094.

[25] Holt, P., Barton, G. and Mitchell, C., (1999). "Electrocoagulation as wastewater treatment", The Third Annual Australian Environmental Engineering Research Event, 23–26 November, Castlemaine, Victoria, 1999, pp. 23–26.

[26] Chen, B. G., Chen, X. and Yue, P. L., (2000). "Electrocoagulation and electroflotation of restaurant wastewater", J. Environ. Eng., 126 (9): 215-224.

[27] Adhoum, N. and Monser, L., (2004). "Decolourization and removal of phenolic compounds from olive mill wastewater by electrocoagulation", Chem. Eng. Process. Process Intensif., 43(9): 1281–1287.

[28] Tezcan UN, U., Ugur, S., Kopara, A.S. and Bakır Ogutveren, U., (2006)."Electrocoagulation of olive mill wastewaters", .Sep. Purif. Technol., 52(33): 136–141.

[29] Adhoum, N., Monser, L., Bellakhal, N. and Belgaied, J., (2004). "Treatment of electroplating wastewater containing Cu2+, Zn2+ and Cr (VI) by electrocoagulation", J. Hazard. Mater., 112(3) : 207–213.

[30] Kurt, U., Gonullu, M.T., Ilhan, F. and Varinca, K., (2008). "Treatment of domestic wastewater by electrocoagulation in a cell with Fe–Fe electrodes", Environ. Eng. Sci. 25(2):153–161.

[31] Apaydin, O., Kurt, U. and Gonullu, M.T., (2009). "An investigation on the treatment of tannery wastewater by electrocoagulation", Global Nest J., 11(22): 546–555.

[32] Feng, J., Sun, Y., Zheng, Z., Zhang, J., Li, S. and Tian, Y., (2007). "Treatment of tannery wastewater by electrocoagulation", J. Environ Sci. 19(3): 1409–1415.

[33] Murugananthan, M., Bhaskar Raju,J. and Prabhakar, S., (2004). "Separation of pollutants from tannery effluents by electro flotation", Sep. Purif. Technol., 40(8): 69–75.

[34] Avsar, Y., Kurt, U. and Gonullu, T., (2007). "Comparison of classical chemical and electrochemical processes for treating rose processing wastewater", J. Hazard. Mater. 148(75): 340–345.

[35] Zongo, I., Leclerc, J.-P. , Maıga, H.M., Wethe, J. and Lapicque, F., (2009). "Removal of hexavalent chromium from industrial wastewater by electrocoagulation: A comprehensive comparison of aluminium and iron electrodes", Sep. Purif. Technol. 66(3): 159–166.

[36] Khandegar, V. and Saroha, A.K., (2013). "Electrocoagulation for the treatment of textile industry effluent—A review", J. Environ. Manage. 128(22): 949–963.

[37] Kim, T., Parka, C., Shinb, E. and Kim, S., (2002). "Decolorization of disperse and reactive dyes by continuous electrocoagulation process", Desalination, 150(15): 165-175.

[38] Daneshvar, N., Ashassi-Sorkhabi, H. and Tizpar, A., (2003). "Decolorization of orange II by electrocoagulation method", Sep. Purif. Technol. 31(3): 153–162.

[39] Mameri, N., Yeddou, A.R., Lounici, H., Belhocine, D., Grib, H. and Bariou, B., (1998). "Defluoridation of septentrional of Sahara water of North Africa by electrocoagulation process using bipolar aluminum electrodes", Wat. Res. 32(26): 1604–1612.

[40] Chen, X., Chen, G. and Yue, P.L., (2000). "Separation of pollutants from restaurant wastewater by electrocoagulation", Sep. Purif. Technol. 19(1): 65–76.

[41] Ben Mansour, L., Ksentini, I. and Elleuch, B., (2007). "Treatment of wastewaters of paper industry by coagulation–electroflotation", Desalination 208(3): 34–41.

[42] Merzouk, B., Gourich, B., Sekki, A., Madani, K., Vial, C. and Barkaoui, M., (2009). "Studies on the decolorization of textile dye wastewater by continuous electrocoagulation process", Chem. Eng. J. 149(3): 207–214.

[43] Suthanthararajan, R., Ravindranath, E., Chitra, K., Umamaheswari, B., Ramesh, T. and Rajamani, S., (2004). "Membrane application for recovery and reuse of water from treated tannery wastewater", Desalination. 164(72): 151 –156.

[44] Ahmed, M.T., Taha, S., Chaabane, T., Cabon, J., Maachi, R. and Dorange, G., (2004). "Treatment of the tannery effluents from a plant near Algiers by nanofiltration (NF): experimental results and modeling", Desalination. 165(22): 155–160.

[45] Brites Alves, A.M. and De Pinho, M.N., (2000). "Ultra filtration for color removal of tannery dyeing wastewaters", Desalination. 130(5): 147–154.

[46] Huang, C.H., Xu, T.W., Zhang Y.P., Xue Y.H. and Chen, G.W., (2007). "Application of electrodialysis to the production of organic acids: state-of-the-art and recent developments (review)", J Membr Sci. 288(1):1–12.

[47] Shahi, V. K., Thampy, S.K. and Rangarajan, R., (2001). "The effect of conducting spacers on transport properties of ion exchange membranes in electrodriven separation", Desalination 133(12): 245-258.

[48] Rodrigues, M.A.S., Costa, R.F.D., Bernardes, A.M. and Ferreira, J.Z., (2001). "Influence of ligand exchange on the treatment oftrivalent chromium solutions by electrodialysis", Electrochimica Acta 47 (5): 753–758.

[49] Ilhan, F., Kabuk, H.A., Kurt, U., Avsar, Y., Sari, H. and Gonullu, M.T., (2014). "Evaluation of treatment and recovery of leachate by bipolar membrane electrodialysis process", Chemical Engineering and Processing, 75(33): 67–74.

[50] Wilhelm, F.G., Punt, I., Vegt, N.F.A., Wessling, M. and Strathmann, H., (2001). "Optimization strategies for the preparation of bipolar membranes with reduced salt ion leakage in acid–base electrodialysis", Journal of Membrane Science, 182(10): 13–28.

[51] Rodrigues, M.A.S., Dalla Costa, R.F. and Zoppas Ferreira, J., 1998. "Transport of trivalent and hexavalent chromium through different ion-selective membranes in acidic aqueous media", Separation Science and Technology, 33(8):1135 - 1143.

[52] Gering, K.L. and Scamehorn, J.F., (1998). "Use of electrodialysis to remove heavy metals from water", Separation Science and Technology, 23(11):2231 - 2267.

[53] Mollah, M.Y.A., Schennach, R., Parga, J.R. and Cocke, D.L., (2001). "Electrocoagulation (EC) — science and applications", Journal of Hazardous Materials, B84(3): 29–41.

[54] Parama Kalyani, K.S., Balasubramanian, N. and Srinivasakannan, C., (2009). "Decolourization and COD reduction of paper industrial effluent using electro-coagulation", Chem.Eng. J. 151(9): 97–104.

[55] Jiang, J.Q., Graham, N., André, C., Kelsall, G.H., and Brandon, N., 2002. "Laboratory study of electro-coagulation–flotation for water treatment", Water Res. 36 (16): 4064–4078.

[56] Canizares, P., Martínez, F., Jiménez, C., Lobato, J. and Rodrigo, M.A., (2006). Coagulation and electrocoagulation of wastes polluted with dyes, Environ. Sci. Technol. 40 (20): 6418–6424.

[57] Zhu, B., Clifford, D.A. and Chellam, S., (2005). "Comparison of electrocoagulation and chemical coagulation pretreatment for enhanced virus removal using microfiltration membranes", Water Res. 39 (13):3098-3108.

[58] Aouni, A., Fersi, C., Ali, M.B.S. and Dhahbi, M., (2009). "Treatment of textile wastewater by a hybrid electrocoagulation/nanofiltration process", J. Hazard. Mater. 168 (2 -3): 868 -874.

[59] Raju, G.B., Karuppiah, M.T., Latha, S.S., Parvathy, S., Prabhakar, S., (2008). "Treatment of wastewater from synthetic textile industry by electrocoagulation eelectrooxidation", Chem. Eng. J. 144 (1): 51 -58.

[60] Iaconi, D., Pinto, D., Ricco, G. and Tomei, M., 2002. "Treatment options for tannery wastewater II: integrated chemical and biological oxidation", Ann Chim. 92(15): 531- 539.

[61] Iaconi, D., Bonemazzi, F., Lopez, A. and Ramadori, R., 2004. "Integration of chemical and biological oxidation in a SBBR for tannery wastewater treatment", Water Sci. Technol. 50(3): 107-114.

[62] Naumczyk, J. and Rusiniak, M., (2005). "Physicochemical and Chemical Purification of Tannery Wastewaters", Pol. J. Environ. Stud. 14(22): 789-797.

[63] Kennedy, L.J., Das, K.M. and Sekaran, G., (2004). "Integrated biological and catalytic oxidation of organics/inorganics in tannery wastewater by rice husk based mesoporous activated carbon.—Bacillus sp.", Carbon, 42(5):2399–2407.

[64] Szpyrkowicz, L., Kaul, S.N. and Neti, R.N., (2005). "Tannery wastewater treatment by electro-oxidation coupled with a biological process" J. Appl. Electrochem. 35(12): 381-390.

[65] Rodrigues, M.A.S., Amado, F.D.R., Xavier, J.L.N., Streit, K.F., Bernardes, A.M. and Ferreira, J.Z., (2008). "Application of photoelectrochemical eelectrodialysis treatment for the recovery and reuse of water from tannery effluents", Journal of Cleaner Production". 16(3): 605 -611.

[66] Rao, R. J., Chandrababu, N.K., Muralidharan, C., Unni Nair, B., Rao, P.G. and Ramasami, T., (2003). "Recouping the wastewater: a way forward for cleaner leather processing", Journal of Cleaner Production, 11: 591–599.

[67] Kabdasli, I., Tunay, O. and Orhon, D., (1997). "The treatability of chromium tannery wastes", Wat. Sci. Tech. 28, (2): 97-105.

[68] Lofrano, G., Aydin, E., Russo, F., Guida, M., Belgiorno, V. and Meric, S., (2008). "Characterization, fluxes and toxicity of leather tanning bath chemicals in a large tanning district area (IT)", Water Air Soil Pollut, 8(2):529–542.

[69] Fabiani, C., Ruscio, F., Spadoni, M. and Pizzichini, M., (1996). "Chromium (III) salts recovery process from tannery wastewaters", Desalination, 208(17):183–191.

[70] Munz, G., De Angelis, D., Gori, R., Mori, G., Casarci, M. and Lubello, C., (2009). "The role of tannins in conventional angogated membrane treatment of tannery wastewater", J Hazard Mater, 164(2):733–739.

[71] Cassano, A., Molinari, R., Romano, M. and Drioli, E., (2001). "Treatment of aqueous effluent of the leather industry by membrane processes", J Membr Sci, 181(19):111 –126.

[72] Sundarapandiyan, S., Chandrasekar, R., Ramanaiah, B., Krishnan, S. and Saravanan, P., (2010). "Electrochemical oxidation and reuse of tannery saline wastewater", J Hazard Mater, 180(12):197–203.

[73] Cooman, K., Gajardo, M., Nieto, J., Bornhardt, C. and Vidal, G., (2003). "Tannery wastewater characterization and toxicity effects on Daphnia spp", Environ Toxicol, 18(5):45–51.

[74] Ram, B.P.K. and Bajpai, P.H.K., (1999). "Kinetics of chrome-tannery effluent treatment by the activated sludge system", Process Biochem, 35(4):255–265.

[75] Ates, E., Orhon, D. and Tunay, O., (1997). “Characterization of tannery wastewaters for pretreatment selected case studies”, Water Sci Technol, 36(14):217–223.

[76] Song, Z., Williams, C.J. and Edyvean, G.J., (2000). “Sedimentation of tannery wastewater”, Water Res, 34(3):2171 –2186.

[77] Kurt, U., Apaydin, O. and Gonullu, M.T., (2007). “Reduction of COD in wastewater from an organized tannery industrial region by Electro-Fenton process”, J Hazard Mater, 143(9): 33–40.

[78] Karahan, O., Dogruel, S., Dulekgurgen, E. and Orhon, D., (2008). “COD fractionation of tannery wastewater—particle size distribution, biodegradability and modeling”, Water Res, 42(3): 1083–1092.

[79] Mandal, T., Dasgupta, D., Mandal, S. and Datta, S., (2010). “Treatment of leather industry by aerobic biological Fenton oxidation process”, J Hazard Mater, 180(22):204–211.

[80] Kongjao, S., Damronglerd, S. and Hunsom, M., (2008). “Simultaneous removal of organic and inorganic pollutants in tannery wastewater using electrocoagulation technique”, Korean J Chem Eng, 25(5):703–709.

[81] Mannucci, A., Munz, G., Mori, G. and Lubello, C., (2010). “Anaerobic treatment of vegetable tannery wastewaters: a review”, Desalination, 264(33):1 –8.

[82] Lefebvre, O., Vasudevan, N., Torrijosa, M., Thanasekaran, K. and Moletta, R., (2006). “Anaerobic digestion of tannery soak liquor with an aerobic post-treatment”, Water Res, 40(7): 1492–1500.

[83] Dantas, T.L.P., Josè, H.J. and Moreira, R.F.P.M., (2003). “Fenton and Photo-Fenton oxidation of tannery wastewater”, Acta Sci Technol, 25(10):91 –105.

[84] Orhon, D., Ates, E. and Sozen, S., (2000). “Experimental evaluation of the nitrification kinetics for tannery wastewaters”, Water SA, 26(12):43–55.

[85] Deghles, A. and Kurt, U., (2015). “Treatment of raw tannery wastewater by electrocoagulation technique: optimization of effective parameters using Taguchi method”, Desalination, 78(3): 1-12.

[86] El-Sheikh Mahmoud, A., Hazem, I., Saleh, J., Flora, R., Mahmoud, R. and Abd El-Ghany., (2011). “Biological tannery wastewater treatment using two stage UASB reactors”, Desalination, 276(19): 253–259.

[87] Stasinakis, A.S., Mamais, D., Thomaidis, N.S. and Lekkas, T.D., (2002). “Effect of chromium (VI) on bacterial kinetics of heterotrophic biomass of activated sludge”, Water Res., 36(8):3342–3350.

[88] Farabegoli, G., Carucci, A., Majone, M. and Rolle E., (2004). “Biological treatment of tannery wastewater in the presence of chromium”, J Environ Manage, 71(22):345–359.

[89] Görgün, E., Insel, G., Artan, N. and Orhon, D., (2007). "Model evaluation of temperature dependency for carbon and nitrogen removal in a full-scale activated sludge plant treating leather-tanning wastewater", J Environ Sci Health A Tox Hazard Subst Environ Eng, 42(36):747–756.

[90] Zupančič, G.D. and Jemec, A., (2010). "Anaerobic digestion of tannery waste: semi-continuous and anaerobic sequencing batch reactor processes", Bioresour Technol, 101(15): 26–33.

[91] Tadesse, I., Green, F.B. and Puhakka, J.A., (2004). "Seasonal and diurnal variations of temperature, pH and dissolved oxygen in advanced integrated wastewater pond system® treating tannery effluent", Water Res, 38(16):645–654.

[92] Calheiros, C.S.C., Quitério, P.V.B., Silva, G., Crispim, L.F.C., Brix, H. and Moura S.C., (2012). "Use of constructed wetland systems with Arundo and Sarcocornia for polishing high salinity tannery wastewater", J Environ Manage, 95(3):66–71.

[93] Dotro, G., Castro, S., Tujchneider, O., Piovano, N., Paris, M. and Faggi, A., (2015). "Performance of pilot-scale constructed wetlands for secondary treatment of chromium-bearing tannery wastewaters", J Hazard Mater, 32(15): 142–151.

[94] Ashraf, C.M., Ahmad, S. and Malik, M.T., (1997). "Supported liquid membrane technique applicability for removal of chromium from tannery wastes", Waste Manag, 17(22):211 –218.

[95] Labanda, J., Khaidar, M.S. and Llorens, J., "Feasibility study on the recovery of chromium (III) by polymer enhanced ultrafiltration", Desalination, 249(35):577–581.

[96] Fabiani, C., Ruscio, F., Spadoni, M. and Pizzichini, M., (1996). "Chromium (III) salts recovery process from tannery wastewaters", Desalination, 208(11):183–191.

[97] De Pinho, M.N., (2009). "Membrane-based treatment for tanning wastewaters", Can J Civ Eng., 36(12):356–362.

[98] Suganthi, K.V., Mahalaksmi, M. and Balasubramanian., (2013). "Development of hybrid membrane bioreactor for tannery effluent treatment", Desalination, 309(13):231–246.

[99] Schrank, S.G., José, H.J., Moreira, R.F.P.M. and Schroder, H.F., (2004). "Elucidation of the behaviour of tannery wastewater under advanced oxidation conditions", Chemosphere, 56(25): 411–423.

[100] Costa, C.R., Botta, C.M.R., Espindola, E.L.G. and Olivi, P., (2008). "Electrochemical treatment of tannery wastewater using DSA® electrodes", J Hazard Mater, 153(25):616–627.

[101] Lofrano, G., Meric, S., Belgiorno, V. and Napoli, R.M.A., (2007a). "Fenton's oxidation of various based synthetic tannins (syntans)", Desalination, 211(22):10–21.

[102] Lofrano, G., Meriç, S., Inglese, M., Nikolaou, A.D. and Belgiorno V., (2010b). "Fenton oxidation treatment of tannery wastewater and tanning agents: synthetic tannin and nonylphenol ethoxylate based degreasing agent", Desalin Water Treat., 23(1):1 –8.

[103] Sundarapandiyan, S., Chandrasekar, R., Ramanaiah, B., Krishnan, S. and Saravanan, P., (2010). "Electrochemical oxidation and reuse of tannery saline wastewater", J Hazard Mater., 180(17):197–203.

[104] Lofrano, G., Meriç, S., Belgiorno, V., Nikolaou, A. and Napoli, R.M.A., (2007b). "Fenton and photo-Fenton treatment of a synthetic tannin used in leather tannery: a multi approach study", Water Sci Technol., 55(3):53–61.

[105] Modenes, A.N., Espinoza-Quinones, F.R., Borba, F.H. and Manenti, D.R., (2012). "Performance evaluation of an integrated photo-Fenton-electrocoagulation process applied to pollutant removal from tannery effluent in batch system", Chem. Eng. J., 197(2): 1 -9.

[106] Houshyar, Z., Khoshfetrat, A.B. and Fatehifar, E., (2012). "Influence of ozonation process on characteristics of pre-alkalized tannery effluents", Chem Eng J., 191(33):59–65.

[107] Sengil, A.I., Kulac, S. and Ozacar, M., (2009). "Treatment of tannery liming drum wastewater by electrocoagulation", J Hazard Mat., 167(92):940–956.

[108] Pokrywiecki Sauer, T., Casaril, L., Bertoldi Oberziner, A.L., Jose, J., Peralta, H. and Muniz Moreira, R., (2006). "Advanced oxidation processes applied to tannery wastewater containing Direct Black 38—elimination and degradation kinetics", J Hazard Mater., B135(2):274–289.

[109] Gogate, P.R. and Pandit, A.B., (2004). "A review of imperative technologies for wastewater treatment II: hybrid methods", Adv Environ Res., 8(27):553–597.

[110] Nidheesh, P. V., Gandhimathi, R., (2012). "Trends in electro-Fenton process for water and wastewater treatment: An overview", Desalination 299(18): 1 –15.

[111] Holt, P. K., Barton, G. W., Wark, M. and Mitchell. C. A., (2003). "A quantitative comparison between chemical dosing and electrocoagulation", Colloids and Surfaces A: Physicochem. Eng. Aspects, 211(41): 233 -248.

[112] Holt, P. K., Barton, G. W. and Mitchell. C. A., (2005). "The future for electrocoagulation as a localized water treatment technology", Chemosphere, 59(11):355–367.

[113] Daneshvar, N., Oladegaragoze, A. and Djafarzadeh, A., (2006a), "Decolonization of basic dye solutions by electrocoagulation an investigation of

the effect of operational parameters" Journal of Hazardous Materials, B129(3):116-122.

[114] Can, O.T., Bayramoglu, M. and Kobya, M., (2003). "Decolonization of reactive dye solutions by electrocoagulation using aluminum electrodes". Ind Eng Chem Res., 42(5):3391–4006.

[115] Merzouk, B., Madani, K. and Sekki, A., (2010). "Using electrocoagulation - electroflotation technology to treat synthetic solution and textile wastewater, two case studies", Desalination 250 (5): 573 -577.

[116] Bayramoglu, M., Kobya, M., Can, O.T. and Sozbir, M., (2004). "Operating cost analysis of electrocoagulation of textile dye wastewater", Sep. Purif. Technol. 37 (2): 117 - 125.

[117] Hanay, O. and Hasar, H., (2011). "Effect of anions on removing Cu2 +, Mn2 + and Zn2 + inelectrocoagulation process using aluminum electrodes", J. Hazard. Mater. 189 (1-2): 572 -576.

[118] Kobya, M., Demirbas, E. and Sozbir, M., (2010). "Decolorisation of aqueous reactive dye Remazol Red 3B by electrocoagulation", Color Technol. 126 (5): 282-288.

[119] Fu, F. and Wang, Q., (2011). "Removal of heavy metal ions from wastewaters: a review", J. Environ. Manage. 92 (3): 407 -418.

[120] Babu, R.R., Bhadrinarayana, N.S., Meera, K.M., Begum, S. and Anantharaman, N., (2007). "Treatment of tannery wastewater by electrocoagulation", J. Univ. Chem. Technol. Metall. 42 (2): 201 - 206.

[121] Coskun, T., Ilhan, F., Demir, N.M., Debik, E. and Kurt, U., (2012). "Optimization of energy costs in the pretreatment of olive mill wastewaters by electrocoagulation", Environ. Technol. 33 (2): 801- 807.

[122] Zodi, S., Potier, O., Lapicque, F. and Leclerc, J.P., (2010). "Treatment of the industrial wastewaters by electrocoagulation: optimization of coupled electrochemical and sedimentation processes", Desalination 261 (1-2): 186-190.

[123] Mollah, M.Y.A., Gomes, J.A.G., Das, K.K. and Cocke, D.L., (2010). "Electrochemical treatment of Orange II dye solution d use of aluminum sacrificial electrodes and floc characterization", J. Hazard. Mater. 174 (3): 851-858.

[124] Phalakornkule, C., Polgumhang, S., Tongdaung, W., Karakat, B. and Nuyut, T., (2010). "Electrocoagulation of blue reactive, red disperse and mixed dyes, and application in treating textile effluent", J. Environ. Manage. 91 (4): 918 -926.

[125] Verma, S.K., Khandegar, V. and Saroha, A.K., (2013). "Removal of chromium from electroplating industry effluent using electrocoagulation", J. Hazard. Toxic. Radio. Waste, 17 (2): 146 -152.

[126] Kumar, N.S. and Goel, S., (2010). "Factors influencing arsenic and nitrate removal from drinking water in a continuous flow electrocoagulation (EC) process", J. Hazard. Mater. 173 (3): 528-533.

[127] Feng, Q.Y., Li, X.D., Cheng, Y.J., Meng, L. and Meng, Q.J., (2007b). "Removal of humic acid from groundwater by electrocoagulation", J. China Univ. Min. Technol. 17 (4): 513 -515, 520.

[128] Kobya, M., Ulu, F., Gebologlu, U., Demirbas, E. and Oncel, M.S., (2011). "Treatment of potable water containing low concentration of arsenic with electrocoagulation: different connection modes and Fe-Al electrodes", Sep. Purif. Technol. 77 (3): 283-293.

[129] Ghosh, D., Solanki, H. and Purkait, M.K., (2008). "Removal of Fe (II) from tap water by electrocoagulation technique", J. Hazard. Mater. 155 (2): 135 -143.

[130] Zhu, J., Zhao, H. and Ni, J., (2007). "Fluoride distribution in electrocoagulation defluoridation process", Sep. Purif. Technol. 56 (2): 184-191.

[131] Irdemez, S., Demircioglu, N., Yildiz, Y.S. and Bingul, Z., (2006). "The effects of current density and phosphate concentration on phosphate removal from wastewater by electrocoagulation using aluminum and iron plate electrodes", Sep. Purif. Technol. 52 (2): 218 -223.

[132] Valero, D., Ortiz, J.M., Garcia, V., Exposito, E., Montiel, V. and Aldaz, A., (2011). "Electrocoagulation of wastewater from almond industry", Chemosphere 84 (9):1290 - 1295.

[133] Lin, S.H. and Wu, C.L., (1996). "Electrochemical removal of nitrite and ammonia for aquaculture", Water Res. 30 (3): 715-721.

[134] Filho, D.S., Bota, G.B., Borri, R.B. and Teran, F.J.C., (2012). "Electrocoagulation/flotation followed by fluidized bed anaerobic reactor applied to tannery effluent treatment", Desalin. Water Treat. 37 (3): 359 -363.

[135] Yahiaoui, O., Lounici, H., Abdi, N., Drouiche, N., Ghaffour, N., Pauss, A. and Mameri, N., 2011. "Treatment of olive mill wastewater by the combination of ultrafiltration and bipolar electrochemical reactor processes", Chem. Eng. Process. 50 (1): 37 -41

[136] Raju, G.B., Karuppiah, M.T., Latha, S.S., Parvathy, S. and Prabhakar, S., (2008). "Treatment of wastewater from synthetic textile industry by electrocoagulation -electrooxidation", Chem. Eng. J. 144 (1): 51 -58.

[137] Bellebia, S., Kacha, S., Bouyakoub, A.Z. and Derriche, Z., (2012). "Experimental investigation of chemical oxygen demand and turbidity removal from cardboard paper mill effluents is using combined electrocoagulation and adsorption processes", Environ. Prog. Sust. Energy 31 (3): 361 -370.

[138] Wang, C.T., Chou, W.L. and Kuo, Y.M., (2009). “Removal of COD from laundry wastewater by electrocoagulation/electroflotation”, J. Hazard. Mater. 164 (1): 81 -86.

[139] Shen, F., Chen, X., Gao, P. and Chen, G., (2003). “Electrochemical removal of fluoride ions from industrial wastewater”, Chem. Eng. Sci. 58 (6): 987 -993.

[140] Asaithambi, P., Susree, M., Saravanathamizhan, R. and Matheswaran, M., (2012). “Ozone assisted electrocoagulation for the treatment of distillery effluent”, Desalination 297 (3): 1 - 7.

[141] Ouaissa, Y.A., Chabani, M., Amrane, A. and Bensmaili, A., (2012). “Integration of electro coagulation and adsorption for the treatment of tannery wastewater e the case of an Algerian factory”, Procedia Eng. 33 (1): 98 -101.

[142] Can, O.T., Kobya, M., Demirbas, E. and Bayramoglu, M., (2006). “Treatment of the textile wastewater by combined electrocoagulation”, Chemosphere 62 (2), 181 -187.

[143] Song, S., Yao, J., He, Z., Qiu, J. and Chen, J., (2008). “Effect of operational parameters on the decolorization of C.I. Reactive Blue 19 in aqueous solution by ozone enhanced electrocoagulation”, J. Hazard. Mater. 152 (1): 204 -210.

[144] Akbal, F. and Camci, S., (2010). “Comparison of electrocoagulation and chemical coagulation for heavy metal removal”, Chem. Eng. Technol. 33 (10): 1655 -1664.

[145] Khandegar, V. and Saroha, A.K., (2012). “Electrochemical treatment of distillery spent wash using aluminum and iron electrodes”, Chin. J. Chem. Eng. 20 (3): 439 -443.

[146] Sadrzadeh, M., Razmi, A. and Mohammadi, T., (2007). “Separation of different ions from wastewater at various operating conditions using electrodialysis”, Separation and Purification Technology, 54(2): 147–156.

[147] Strathmann, H., (2004). “Ion exchange membrane separation process”, Elsevier, Amsterdam, Netherlands. 25(3): 16-25.

[148] Nagarale, R.K., Gohil, G.S. and Shahi, V.K., (2006). “Recent developments on ion exchange membranes and electro-membrane processes”, Advance on colloid and interface science, 119(3): 97-130.

[149] Mier, M.P. and Ibanez, R., Ortiz, I., (2008). “Influence of ion concentration on the kinetics of electrodialysis with bipolar membranes”, Separation and Purification Technology, 59(18): 197–205.

[150] Lindstrand, V., Sundstrom, G. and Jonsson, A.S., (2000b). “Fouling of electrodialysis membranes by organic substances”, Desalination, 128(1): 91-102.

[151] Kim, D.H., Moon, S.H. and Cho, J., (2000). Investigation of the adsorption and transport of the natural organic matter (NOM) in ion exchange membranes", Desalination, 151(1): 11-20.

[152] Elleuch, M., Sistat, P., Pourecelly, G. and Amor, M. B., (2006b). "Brackish water desalination by electrodialysis: opposing scaling", Desalination, 200(3): 752-753.

[153] Grossman, G. and Sonin, A.A., (1973). "Membranes fouling in electrodialysis: a models and experiments", Desalination, 12(1): 107-125.

[154] Turek, M., Dydo, P., Trojanowksa, J. and Bandura, B., (2007a). "Electrodialysis treatment of boron containing wastewater", Desalination, 205(3): 185-191.

[155] Turek, M., Dydo, P., Ciba, J., Trojanowksa, J. and Kluzaka, J.P.-K., B., (2005). "Electrodialysis treatment of boron containing wastewater with univalent permselective membranes", Desalination, 185(1): 139-145.

[156] Zeni, M., Riveros, R., Melo, K., Pirimeiri, R. and Lorenzini, S., (2005). "Study on fluoride reduction in aretisian well-water from electrodialysis process", Desalination, 185(3): 241.

[157] Amor, Z., Bariou, B., Mameri, N., Taky, M., Nicolas, S. and Elmidaoui, A., (2000). "Fluoride removal from brackish water by electrodialysis", Desalination, 133(3): 215-223.

[158] Elmidaoui, A., Elhannouni, F., Taky, M., Chay, L., Menkoushi Sahli, M.A., Echihabi, L. and Hafsi, M., (2002). "Optimization of nitrate removal operation from ground water by electrodialysis", Separation and purification technology, 29(3): 235-243.

[159] Menkoushi Sahli, M.A., Annouar, S., Mountadar, M., Soufiane, A. and Elmidaoui, A., (2008). "Nitrate removal of brackish underground water by chemical adsorption and by electrodialysis", Desalination, 277(1-3): 327-333.

[160] Lambert, J., Avila-Rodriguez, M., Durand, G. and Rakib, M., (2006). "Separation of sodium ions form trivalent chromium by electrodialysis using monovalent cation selective membranes", Journal of Membrane Science, 280(1-2): 219-225.

[161] Gokkus¸ O., Yıldız, Y.S. and Yavuz, B., (2012). "Optimization of chemical coagulation of real textile wastewater using Taguchi experimental design method", Desalin. Water Treat. 49(2): 263–271.

[162] Ozyonar, F. and Karagozoglu, B., (2014). "Investigation of technical and economic analysis of electrocoagulation process for the treatment of great and small cattle slaughterhouse wastewater", Desalin. Water Treat. 52(31):74–87.

[163] Engin, A.B., zdemir, O. O., Turan, M. and Turan, A.Z., (2008). “Color removal from textile dyebath effluents in a zeolite fixed bed reactor: Determination of optimum process conditions using Taguchi method”, J. Hazard. Mater. 159(42): 348–353.

[164] APHA, AWWA, EF, Standard Methods for the Examination of Water and Wastewater, twentieth ed., American Public Health Association, Washington, DC,1998.

[165] Masahiro T., (2012). “Extraction of hydrogen into vacuum by electrochemical hydrogen pump for hydrogen isotope recovery”, Fusion Engineering and Design 87(31): 1065–1069.

[166] Kargi, F. and Ebru C.C., (2011). “Hydrogen gas production from olive mill wastewater by electrohydrolysis with simultaneous COD removal”, international journal of hydrogen energy, 36 (22): 3457-3464.

[167] Das, D. and Nejat Veziroglu, T., (2001). “Hydrogen production by biological processes: a survey of literature”, International Journal of Hydrogen Energy 26 (3): 13–28.

CURRICULUM VITAE

PERSONAL INFORMATION

Name Surname	: Abdalhadi DEGHLES
Date of birth and place	: 20/12/1975 - Palestine
Foreign Languages	: English , Turkish
E-mail	: daghlas2014@gmail.com

EDUCATION

Degree	**Department**	**University**	**Date of Graduation**
Master	Environmental Engineering	Al-Najah National University	2005
Undergraduate	Agriculture Engineering	Al-Najah National University	2000
High School	Scientific	Burqa Secondary School	1995

WORK EXPERIENCE

Year	**Corporation/Institute**	**Enrollment**
2014-Till Now	Al-Istiqlal University	Instructor
2006-2014	National Agriculture Research Center (NARC)	Director of Natural Resources Research

2005-2006 Al-Quds Open University Part-Time Lecturer

PUBLISHMENTS

Papers

1. Deghles, A. and Kurt, U., (2015). “Treatment of raw tannery wastewater by electrocoagulation technique: optimization of effective parameters using Taguchi method”, Desalination, 78(3): 1-12.

2. Houshia, O.J., Abueid, M., Deghles, A., Zaid. M., Zaid, O. and Souqia, N., (2012), “ Characterization of Grey water from Country-Side Decentralized Water Treatment Stations in Northern Palestine”, Journal of Environment & Earth Science; 2(22):12-21 , April 2012.