

University Constantine 3 Salah Boubnider Faculty of Process Engineering Department of Pharmaceutical Engineering

N° of series: N° of order:

TREATMENT OF INDUSTRIAL WASTEWATER BY ELECTROCHEMICAL AND MEMBRANE PROCESSES: EXPERIMENTAL STUDY AND MODELING

THESIS

Submitted in Partial Fulfilment of the Requirements for the Degree of Doctorate in Process Engineering
Option: Pharmaceutical Engineering

By Abir HASNAOUI

Before the Examination Committee Composed of:

MEROUANI Slimane	President	Professor	University Constantine 3 Salah Boubnider
CHIKHI Mustapha	Supervisor	Professor	University Constantine 3 Salah Boubnider
BENAISSA Akila	Examiner	Professor	University Constantine 3 Salah Boubnider
DERBAL Kerroum	Examiner	Professor	ENP of Constantine
MAMMERI Lamia	Examiner	AP	University Constantine 1
LAID Nassima	Examiner	AP	University Constantine 1
ARRIS Sihem	Invited	Professor	University Constantine 3 Salah Boubnider

Academic Year 2024–2025

Table of Contents

List of figures	xiii
List of tables	xvi
List of abbreviations	xvii
List of figures	xiv
List of tables	xvii
List of abbreviations	xviii
Abstract	xx
Résumé	xxii
الملخص	xxiv
GENERAL INTRODUCTION	1
CHAPTER I: LITERATURE REVIEW	5
1.1 Water pollution overview	5
1.2 Synthetic dyes in industrial effluents	6
1.2.1 Methylene Blue	6
1.2.2 Direct Violet 51 dye	7
1.3 Pharmaceutical pollutants: Ketoprofen	8
1.4 Industrial wastewater: Orange juice wastewater contamination	9
1.5 Overview of conventional and advanced wastewater treatment methods	9
Conventional wastewater treatment methods	10
1.5.1 Physical treatment methods	10
1.5.2 Chemical treatment methods	10
1.5.3 Biological treatment methods	11
1.5.4 Limitations of conventional methods	11
1.6 Advanced wastewater treatment methods	11
1.6.1 Electrocoagulation (EC)	12
1.6.1.1 Evolution of electrocoagulation process	12
1.6.1.2 Electrocoagulation process	15
1. Current density: the primary control parameter in electrocoagulation	17
2. Electrode spacing optimization	18
3. Solution pH	19
4. Supporting electrolytes in electrocoagulation	20
5. Impact of reaction time on electrocoagulation process performance	21

1.6.1.3 Electrode materials for electrocoagulation	22
1.6.1.4 Valorization strategies for electrocoagulation sludge	24
1.6.2 Advanced oxidation processes (AOPs)	24
1.6.3 Electro-advanced oxidation processes (EAOPs)	25
1.6.3.4 Electro-Fenton and Photoelectro-Fenton	25
1.6.3.5 Electrodes commonly used in electro-fenton an possible aluminum scrap as cathode material	25
1.6.3.5 Heterogeneous Photo-Electro-Fenton (Hetero-PEF): A step forward	27
1.6.3.6 Green chemistry in nanotechnology	28
1.6.3.7 Oudneya Africana	29
1.6.3.8 The mechanisms and efficiency iron nanoparticles in heterogeneous PEF	30
1.6.4 Membrane filtration process overview	31
1.6.4.1 Microfiltration (MF)	32
1.6.4.2 Ultrafiltration (UF)	33
1.6.4.3 Nanofiltration (NF)	33
1.6.4.4 Reverse Osmosis (RO)	34
1.6.4.5 Membrane materials: polymeric and ceramic	35
1.6.4.6 Integration of Treatment Technologies	37
1.6.4.7 Emerging Trends and Innovations	38
1.7 Comparative analysis of conventional and advanced methods	
1.7.1 Efficiency and effectiveness	38
1.7.2 Sustainability and environmental impact	39
1.7.3 Economic considerations	39
1.7.4 Scalability and practical implementation	39
1.8 Conclusion	39
CHAPTER II: MATERIAL AND METHODS	40
2.1 Introduction	40
2.2 Wastewaters and pollutants	40
2.2.1 Target pollutants	40
2.2.2 Industrial wastewater	41
2.3 Chemicals	42
2.4 Instrumentation	43
2.5 Materials preparation	44
2.6 Experimental Procedures	44
2.6.1 Electrocoagulation treatment process	44

2.6.2 General experimental setup	44
2.6.3 Operating parameters	45
2.6.4 Pollutant-specific details	45
2.7 Dead-end membrane filtration process	46
2.8 Iron oxide nanoparticles phytochemical synthesis	47
2.8.1 Preparation of the plant extract	47
2.8.2 Polyphenol content determination	48
2.8.3 Synthesis of iron oxide nanoparticles	48
2.8.4 Calcination and nanoparticle formation	48
2.8.5 Ion oxide NPs Encapsulation	49
2.8.6 Photo electro-fenton and membrane process setup	50
2.9 Modeling and optimization	52
2.9.1 Electrocoagulation process for DV51 dye removal	52
2.9.2 Photo electro-fenton	52
2.10 Analysis	53
2.10.1 Pollutant removal efficiency	53
2.10.2 Permeate flux	53
2.10.3 Energy consumption	54
2.10.4 Electrode consumption	54
2.10.5 Operational cost estimation	54
CHAPTER III: RESULTS AND DISCUSSION	55
Part A: Electrocoagulation employing recycled aluminum electrodes for methylene blu remediation	
3.A.1 Introduction	
3.A.2 Parameters influencing the EC process	
3.A.2.1 Effect of electrolyte concentration	
3.A.2.2 Effect of current density	
3.A.2.3 Effect of initial dye concentration	
3.A.2.4 Effect of initial pH	
3.A.2.5 Effect of electrolysis time	
3.A.3 Dye removal mechanism	
3.A.4 Characterization of sludge and aluminum electrodes	
3.A.4.1 Analysis of sludge using infrared spectroscopy	
3.A.4.2 Analysis of sludge using scanning electron microscopy	
3.A.4.3 Characterization of the recycled electrodes using scanning electron	
microscopy	64

3.A.4.4 Dispersive Energy Spectroscopy (EDS) of the recycled electrodes	65
3.A.5 Energy consumption, operation cost for the EC process	67
3.A.6 Kinetics of the dye removal	67
3.A.7 Conclusion	69
Part B: Electrocoagulation-based dye removal: modeling and optimization using machilearning and genetic algorithms for cost-effective direct violet 51dye removal using a 3 aluminum waste electrodes	3d
3.B.1 introduction	70
3.B.2 Modeling approaches and statistical analysis	70
3.B.3 Actual (experimental) versus predicted	
3.B.4 Analysis of Variance (ANOVA)	74
3.B.5 Pareto analysis	76
3.B.6 Impact of process parameters on DV51 removal efficiency	77
3.B.6.1 pH impact on the removal efficiency	79
3.B.6.2 Current intensity influence on the EC removal	81
3.B.6.3 Electrolyte concentration impact on the removal efficiency	83
3.B.6.4 Pollutant concentration impact on the EC performance	84
3.B.6.5 The immersed depth impact on the EC process	85
3.B.6.6 The electrode gap impact on the EC performance	87
3.B.7 Optimization of the EC process by GA approach	88
3.B.8 Kinetics study	90
3.B.9 FTIR Analysis of the produced sludge	92
3.B.10 Electrode SEM an EDX analysis	94
3.B.11 Operation cost evaluation	95
3.B.12 Conclusion	97
Part C: Optimization of ketoprofen removal using electrocoagulation with aluminium joinery waste as cuboid electrodes	98
3.C.1 Introduction	
3.C.2 Optimizing Removal Efficiency through Current Density Variations	98
3.C.3 pH-Driven variations in KTF removal	
3.C.4 Impact of KTF concentration on the effectiveness of EC	. 101
3.C.5 The role of NaCl concentration in EC efficiency	
3.C.6 Characterization of EC sludge and KTF	
3.C.7 Kinetics study	
3.C.8 Statistical study	
3 C 8 1 Dataset Descriptive Statistics	106

3.C.8.2 Pearson correlation.	107
3.C.8.3 Polynomial regression	108
3.C.8.4 Deep learning predictive model	109
3.C.9 The cost implications of using aluminum waste	110
3.C.10 Conclusion	111
Part D: Effective COD removal from orange juice wastewater using a combined treat	ıtment
system consisting of electrocoagulation supported re-use of aluminum scraps and membrane processes	112
3.D.1 Introduction	112
3.D.2 Efficiency of the EC across electrode types	112
3.D.3 Current density influence on the OJW treatment	
3.D.4. pH and alkalinity impact on the EC process	116
3.D.5 The salinity influence on EC efficiency	
3.D.6 SEM and EDX characterization for the aluminum scraps	120
3.D.7 The cost implications of using aluminum scraps in the EC process	122
3.D.8 Kinetic study	122
3.D.9 Integrated membrane filtration	124
3.D.10 Conclusion	127
Part E: Green engineering of iron oxide nanoparticles for photoelectro-fenton proces industrial wastewater remediation	
3.E.1 Nanoparticles synthesis results	129
3.E.1.1 Polyphenol quantification	129
3.E.2 FeO NPs Characterization	130
3.E.2.1 Fourier-transform infrared spectroscopy (FTIR)	130
3.E.2.2 X-ray Diffraction (XRD)	131
3.E.2.3 Brunauer–Emmett–Teller (BET) Surface Area Analysis	134
3.E.2.4 UV-Visible Spectroscopy (UV-Vis)	136
3.E.2.5 Thermogravimetric Analysis (TGA)	138
3.E.2.6 Transmission electron microscopy (TEM) analysis	139
3.E.2.7 The pH _p zc (point of zero charge)	141
3.E.3 Encapsulated Iron Oxide Nanoparticles	142
3.E.3.1Morphology and size distribution	142
3.E.3.2 Swelling Behavior of Hematite-Loaded Alginate Beads	
3.E.4 Photoelectrochemical activity of free and the encapsulated iron oxide nanop	
3.E.4.1 Adsorption study in the dark	144

3.E.4.2 Electro-Fenton process with iron oxide nanoparticles
3.E.4.3 Electro-Fenton process with encapsulated nanoparticles
3.E.4.4 Reusability of green hematite catalyst in photo-electro-fenton process 146
3.E.5 Optimization of a white light-led assisted photo electro-fenton process using green iron oxide catalyst for enhanced degradation of orange juice wastewater using a boxbehnken design approach
3.E.5.1 Model Statistics
3.E.5.2 Normal probability
3.E.5.3 Analysis of variance (ANOVA)
3.E.5.4 Catalyst impact on the process
3.E.5.5 Electrolyte concentration impact on the process
3.E.5.6 The current density impact on the process
3.E.5.7 Interaction effects of catalyst, NaCl, and current density on cod removal efficiency
3.E.5.8 Optimization of Operating Conditions
3.E.5.9 Membrane filtration integrated process
3.E.6 Conclusion
General conclusion
References
Appendix A: Green Chemistry Principles and Quantitative Assessment Parameters 181
Appendix B: Statistical Experimental Design: Central Composite and Box-Behnken Methodologies



Name and Surname: Abir Hasnaoui

Title: Treatment of industrial wastewater by electrochemical and membrane processes: experimental study and modeling

Submitted in Partial Fulfilment of the Requirements for the Degree of Doctorate in Process Engineering Option: Pharmaceutical Engineering

Abstract

The work presented in this thesis focuses on the study and optimization of electrochemical and membrane processes for the treatment of water and industrial liquid wastes, with particular emphasis on electrocoagulation and photo-electro-Fenton techniques. The main objective is to improve the efficiency of treating organic pollutants while optimizing the processes for industrial application. Throughout the work, three-dimensional (3D) prismatic aluminum electrodes, made from recycled materials, were used. These electrodes, derived from reclaimed materials, not only offer a large active surface area that promotes electrochemical reactions, but they also significantly reduce operating costs and add value to metal waste, thus contributing to a more sustainable and circular approach to water treatment.

In the first phase, methylene blue, a synthetic dye, was treated by electrocoagulation using recycled aluminum electrodes obtained from a local carpentry workshop. Process parameters such as pH, current density, pollutant concentration, and NaCl concentration were optimized, achieving a 96% removal efficiency within two hours. Electrode characterization analyses were performed using SEM and EDX. This phase was followed by the optimization of the treatment of Direct Violet 51 through an experimental design based on a response surface methodology generated using Python. Process modeling was carried out with artificial intelligence algorithms, and a genetic algorithm achieved a 99% removal of the dye in 30 minutes. Finally, an economic assessment and a life cycle analysis were conducted to evaluate the industrial viability of the process.

A third part of this thesis addressed the treatment of Ketoprofen, a pharmaceutical drug, using electrocoagulation with optimization of key parameters such as pH, NaCl concentration, and current density. Deep Learning modeling was used to complement the statistical analysis of this treatment, allowing for a better understanding of the removal mechanisms.

In a fourth study, electrocoagulation was applied to the treatment of wastewater from orange juice production from a local industry in Turkey. Recycled 3D aluminum electrodes were used, and their performance was compared with that of other electrodes such as iron, steel, and commercial aluminum. The recycled aluminum showed superior performance, and after optimizing the parameters, a pollutant removal of 62.81% was achieved. Subsequently, ultrafiltration and nanofiltration membranes were tested, with the nanofiltration (NF 270) showing the best results with an 84.98% removal and a COD concentration reduced to 896 mg/L.

The final part of the thesis examines the innovative photo-electro-Fenton process using a green catalyst, iron oxide, which was synthesized from an endemic plant – Oudneya Africana – known for its antioxidant properties. The obtained material underwent a comprehensive series of physicochemical characterizations to determine its structural, morphological, textural, and optical properties. The effectiveness of the photo-electro-Fenton process was tested for the removal of Direct Violet 51, and the encapsulation of nanoparticles in alginate and calcium chloride was performed to facilitate their recovery and reduce agglomeration due to the magnetic effects of iron oxide. This catalyst was then tested in the treatment of industrial wastewater from the BIFA (Didouche Mourad, Constantine) orange juice production facility, achieving a 55.09% reduction in COD within two hours. To further improve the process efficiency, a ceramic membrane manufactured in the laboratory was integrated into the system, enabling a total COD removal of 72.41%. Overall, the work conducted in this thesis demonstrates the effectiveness and relevance of electrochemical and hybrid processes in the treatment of contaminated waters. The use of recycled materials, such as aluminum wastes or locally manufactured ceramic membranes, as well as the green synthesis of catalysts, underscores a sustainable and eco-friendly approach.

Keywords: Industrial wastewater, Water treatment, Electrocoagulation, Photo Electro-fenton, membrane filtration processes, Sustainability.

Supervisor: Mustapha CHIKHI, University Constantine 3 Salah Boubnider

Academic Year 2024–2025