THE INNOVATIVE USE OF ELECTROCOAGULATION-MICROWAVE TECHNIQUES FOR THE REMOVAL OF POLLUTANTS FROM WATER

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ABSTRACT

Electrocoagulation (EC) is an effective water and wastewater treatment technology; where the coagulants are generated in-situ by electrolytic oxidation of a sacrificial anode. In this technique, pollutant removal is done without adding chemicals; therefore, it remarkably reduces the sludge produced, and consequently reduces the cost of sludge handling. This method has been efficiently used to remove, up to 99%, of a wide range of pollutants such as heavy metals, oil, dyes, and fluoride. However, the EC technology still has a deficiency in the variety of reactor design, and its performance is highly influenced by the chemistry of the water being treated, especially the presence of organic matter (OM), as this inhibits heavy metal removal due to the formation OM-heavy metals complexes.

The presence of heavy metals and OM in water resources is one of the most problematic pollutants in Hilla River, Babylon city, Iraq, which inhibits the application of the EC method in that area. Thus, the current study has been devoted to develop a new hybrid EC rector that can be applied to treat water drawn from Hilla River especially, and to treat water containing OM-heavy metals complexes.

The aims of this study are therefore; firstly to examine the removal of heavy metals from drinking water in the presence of OM-heavy metal complexes using a new hybrid treatment method that utilises a combination of microwave-electrocoagulation (MW assisted-EC method). Secondly, to present a new configuration for an electrocoagulation reactor (FCER) that employs perforated plate flow columns (which are widely used in the chemical industry) to achieve water mixing, aeration, and temperature control processes. Additionally, the development of statistical models for the EC performance, recovery of hydrogen gas, and the removal of biological pollutants are other targets in the present project.

Initially, the performance of the new flow column EC reactor (FCER) was validated in terms of water mixing efficiency, water aeration, and temperature controllability. The results were compared to those of traditional EC reactors. Then, the ability of the FCER to work as an EC unit was validated by treating different pollutants such as fluoride, nitrate, iron, and reactive black 5 (RB-5) dye from drinking water. Then, the ability of the new MW assisted-EC method to remove OM-heavy metal complexes was experimentally proved by treating synthetic water samples contain iron (Fe^{2+}) ions and ethylenediaminetetraacetic acid (EDTA) ($C_{10}H_{16}N_2O_8$) (as organic matter).

The results obtained showed that FCER achieved a complete water mixing efficiency, and increased the dissolved oxygen (DO) concentration by 110.6% within 10 min, and kept the temperature of water being treated within the range of 22-28 ^{o}C for 30 min of electrolysing. While the traditional reactors achieved water-mixing efficiency of 96.5%, increased the DO by 52.2%, and the temperature increased to about 32 ^{o}C over the same treatment period. Additionally, FCER was able to reduce fluoride, iron, nitrate, and RB-5 dye concentrations by 98%, 99.6%, 95.2%, 98.6%, respectively.

In terms of OM-heavy metal complex removal (the novelty of the present work), the results obtained demonstrated that this novel method removes 92% of this refractory complex within 35 min of treatment at a power of 100 W, temperature of 100 ^{o}C, initial pH of 6, ID of 5 mm, and CD of 1.5 mA/cm^2. While, the traditional treatment (EC only) removed only 69.6% of this complex under the same operating conditions. It is noteworthy to mention, the new MW assisted-EC method achieved 100% removal of culture-able activated sludge microorganisms *ASM* from drinking water, which could eliminate the need for costly separated biological treatment units.

Statistically, empirical models were developed to reproduce the performance of FCER in terms of fluoride, nitrate, RB-5 dye, iron, and iron-EDTA complex removal. The R^2 value for the models of fluoride, nitrate, RB-5 dye, iron, and iron-EDTA complex removal were, respectively, 0.823, 0.848, 0.798, 0.868, and 0.923.

Economically, it has been found that the preliminary operating cost of the MW assisted-EC method is 0.628 US \$/m^3. Additionally, it has been found that the generated hydrogen gas from this new method could be used to reproduce about 2.82 kW/m^3 of power, which is a promising amount of power on field scale plants.

In conclusion, according to the obtained results, the new MW assisted-EC method is a safe promising alternative to the complicated, expensive, and time consuming traditional treatment methods, as it removes heavy metals in the presence of OM in a relatively short time without the need for chemical additives. Economically, the MW assisted-EC method reduces the need for separated biological treatment unit that require space, money, equipment, and time, because drinking water will be sterilised as it passes through the microwave field. The latter merit makes this new method a cost-effective alternative. Additionally, FCER reduces the need for external mixing and aeration devices that require extra power to work, which makes FCER a cost-effective alternative for traditional lab-scale EC units.

DECLARATION

I, Khalid Safaa Hashim, declare that this thesis, submitted in fulfilment of the requirements for awarded of Doctor of Philosophy, in the school of the Civil Engineering, Liverpool John Moores University, is my own work, except where otherwise referenced or acknowledged. This thesis was completed under the supervision of Prof. Andy Shaw, Prof. Rafid Al Khaddar, and Dr. Ortoneda Pedrola, Montserrat, and has not been submitted for qualification at any other academic institution.

Khalid Safaa Hashim

May 2017

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This project would not have been completed without the support of my great family, especially my brother Hamza for his continuous support during the course of my study.

Last but not least, special thanks to my friends Hassnen, and Anmar and their respective wives for their support.

DEDICATION

This thesis is dedicated to my family.

To the memory of my first teacher my father, Safaa Hashim, who unfortunately did not stay in this world long enough to see his son follows his steps.

To the great woman, my mother, who spent her life to raise five children by herself after the death of my father.

To my wife, for her continuous support, and sacrifice over these years.

To my sisters and brother for their support.

To my son Zain Al-Abedeen who makes the world a much happier place.

AWARDS

The following awards are the results of this thesis (Appendix B):

No.	Award	Event and awarding body	Year
1	Best Elevator Pitch	Liverpool John Moores University, Faculty of Engineering and Technology	2015
2	3MT Runner up	3MT competition, Founded by the University of Queensland, Australia.	2016
3	The best Paper with the best potential impact.	Liverpool John Moores University, Faculty of Engineering and Technology	2016
4	The Best presentation	ICCGE 2016: 18th International Conference on Civil and Geological Engineering. Paris, France.	2016
5	Medal of excellence	Awarded by the Iraqi Minster of Higher Education and Scientific Research in the Iraqi Cultural Attaché in London.	2017
6	Certificate of Excellence	Awarded by the Ambassador of the Republic of Iraq in the UK, and the Iraqi Student Society in the UK.	2017
7	Recognition Award and appreciation certificate	Awarded by the executive Dean of the Faculty of Engineering and technology, LJMU, during the Faculty research week.	2017
8	3MT Runner up for the Faculty of Engineering and Technology, LJMU	3MT competition, Founded by the University of Queensland, Australia.	2017

CONTENTS

LIST OF SYMBOLS AND ABBREVIATIONS

Symbol	Definition
ABS	Absorbance (for spectrophotometer).
Al	Aluminium
ARPANSA	Australian Radiation Protection and Nuclear Safety Agency
ASM	Activated Sludge Microorganisms.
bar	A pressure unit equal to the atmospheric pressure at sea level
BOD	Biochemical oxygen demand
BRH	US Bureau of Radiological Health
°C	Celsius
$C_{0(EDTA)}$	Initial concentration of EDTA
C_0	Initial concentration (mg/L)
CD	Current density (mA/cm^2)
cfu/mL	Colony Forming Unit per millilitre
C_{MW}	The consumed power by the MW unit (kWh/m^3)
COD	Chemical oxygen demand (mg/L)
COO_1	Cook’s Distance
C_t	Final concentration of a pollutant (mg/L)
DBPs	Disinfection by-products
DLVO theory	Derjaguin, Landau, Vervey, and Overbeek theory
DO	Dissolved oxygen (mg/L)
DV	Dependant variable.
EC	Electrocoagulation
EDL	Electrical double layer
EDTA	Ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency
F	Faraday’s constant
F/m	Farads per meter
FCER	Flow column electrocoagulation reactor
Fe	Iron
FR	Flow rate (mL/min)
HAA	Halo-acetic acids
hrs	Hours
I	Electrical current (Milliampere)
ID	Inter-electrode distance (mm)
IEC	International Electrotechnical Commission
IVs	Independent variables.
J/kg. °C	Joule per kilogram per degree Celsius
K	Kurtosis

kg/m^3	Kilogram per cubic meter
kJ	Kilojoule
kJ/g	Kilojoule per gram
kPa	Kilopascal
kWh	Kilowatt hour
m	Molecular weight (kg/mol)
m	Number of independent parameters.
mA/cm^2	Milliampere /square centimeter
mg/dm^3	Milligrams per cubic decimeter
mg/L	Milligram per litre
mg/m^3	Milligrams per cubic meter
min	Minute
mL	Millilitre
MPN/dm^3	Most probable number per cubic decimeter
mS/cm	Millisiemens per meter
MW	Microwave
MW assisted-EC	Microwave assisted-Electrocoagulation
MW/H_2O_2	Microwave/hydrogen peroxide
MW/SPS	Microwave / sodium persulfate
N	Sample size
NHMRC	National Health and Medical Research Council
nm	Nanometer
NOM	Natural organic matter
O.S	Ordinary steel
OD$_{525}$	Optical density at a wavelength of 525 nm.
OM	Organic matter
pfu/mL	Plaque-forming unit per millilitre
pH	Logarithmic measure of hydrogen ion concentration
ppm	Part per million
PSI	Pounds per square inch
PVC	Polyvinyl chloride
R^2	Coefficient of determination
RB5	Reactive black 5 dye
RDD	Red drain dye
Re%	Removal efficiency (%)
rpm	Revolutions per minute
S	Skewness
S_k	Standard error for kurtosis
S_s	Standard error for skewness
S.S.	Stainless steel
SAR	Specific absorption rate (W/kg)

SE	Concentration of supporting electrolyte (mg/L)
Sec	Second
SS_{reg}	Sum of squares for regression
SS_y	Total sum of squares
t	Treatment time (min)
T	Temperature (^{o}C)
TCLP	Toxicity Characteristic Leaching Procedure
THM	Tri-halo-methane
Ti/MnO_2	Titanium per manganese dioxide
Ti/PbO_2	Titanium per lead dioxide
Ti/Pt	Titanium per platinum
To.	Tolerance
USEPA	United States Environmental Protection Agency
UV	Ultra violet
UV/TiO_2	Ultraviolet irradiation and photocatalyst titanium dioxide
V cell	Potential inside the EC cell
V/m	Volt per meter
VFA	Volatile fatty acid
Vol.	Volume of treated water
W	Watt
W/kg	Watt per kilogram
W/mL	Watt per millilitre
WHO	World Health Organisation.
Z	Number of electron
Z_P	Zeta potential
µg/L	Microgram/ litre
λ_{max}	A spectrophotometric wavelength (nm) (at the maximum
Ω	Ohm

LIST OF FIGURES

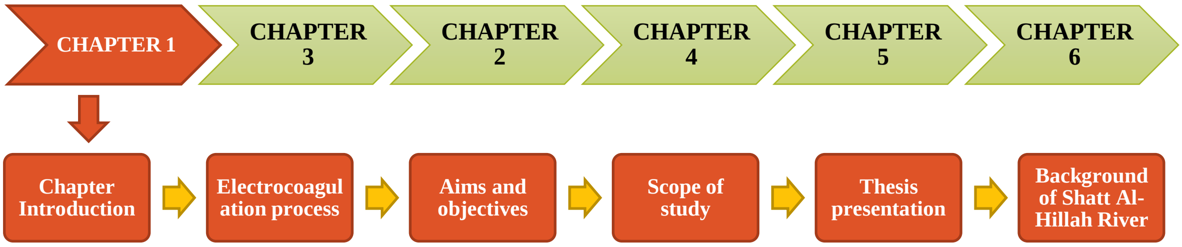
LIST OF TABLES

LIST OF APPENDICES

CHAPTER 1

Introduction

CHAPTER 1: INTRODUCTION



1.1 Chapter Introduction

Water is the most essential element to ensure the reliability and sustainability of the ecosystem of our planet. Although 1400 million cubic kilometres of water covers 71% of the earth surface, less than 2.5% of this huge amount is fresh water (Fogden and Wood, 2009). A vast amount of this fresh water is captured in glaciers, snowy mountain ranges, and groundwater, which leaves less than 1% safe for drinking purposes (Fogden and Wood, 2009; Kuokkanen, 2016). Moreover, with the increasing population and industrial growth that generate billions of litres of polluted wastewater every day, fresh water resources are becoming limited and/or contaminated (Holt *et al.*, 2005; Linares-Hernández *et al.*, 2009). According to the WHO/Unicef (2000), at the turn of the last century, about 1.1 billion people were without access to a safe drinking water source. Furthermore, some forecasting studies confirm that by 2050 the world's population will experience severe drinking water scarcity (Emamjomeh, 2006; Fogden and Wood, 2009). It is believed that by 2050 more than 50% of the world's population will not have an access to safe drinking water sources (Fogden and Wood, 2009).

To reverse this downward trend, a wide spectrum of treatment methods have been practised to treat water and wastewater such as chemical precipitation, biological treatment, electrocoagulation, ion exchange, ultrasound, photo-degradation and membrane filtration (El-Naas *et al.*, 2014; Katal *et al.*, 2014; Swelam *et al.*, 2015).

Amongst these methods, the electrocoagulation (EC) method has recently gained increasing popularity as a promising alternative to treat polluted water and wastewater because it bears many environmentally and economically attractive merits (Mollah *et al.*, 2004; Emamjomeh, 2006; Khandegar and Saroha, 2013; Kuokkanen, 2016).

1.2 Problem Statement

Electrocoagulation – the process of applying electric current through metallic electrodes to remove pollutants from an aqueous media without adding chemicals – is a century old technology gaining increasing interest as a promising alternative to remove pollutants (especially metals) from water and wastewater (Emamjomeh, 2006; Heffron, 2015). In addition to the previously mentioned merits of this method (for instance, ease of installation and operation, and it does not require chemical additives) (Zodi *et al.*, 2009; Chaturvedi and Dave, 2012), it removes very fine particles due to the attraction force of the electric field (Mollah *et al.*, 2004; Butler *et al.*, 2011). Thus, this method has been widely used to purify water from different pollutants such as nitrate (Lakshmi *et al.*, 2013), pathogens (Ricordel *et al.*, 2014), and heavy metals (Srithanrat *et al.*, 2015).

However, the EC technology has some drawbacks such as its performance is considerably influenced by operating parameters such as the chemistry of the solution being treated (Wan *et al.*, 2011). It is well documented that the ability of this technology to remove heavy metals from solutions is highly influenced by the presence of OM (Pallier *et al.*, 2011; Mohora *et al.*, 2014). This negative influence is attributed to the ability of the OM to chelate the heavy metals in water forming complexes (OM-heavy metals complex) that resist coagulation, which in turn negatively influences pollutants removal (Chen *et al.*, 2012; Khelifa *et al.*, 2013; Xu *et al.*, 2015; Huang *et* *al.*, 2016). In fact, OM will not only form complexes less prone to coagulate, but it reacts with chlorides, which is important to enhance water conductivity and to inhibit the formation of the anodic layer, forming toxic by-products (Khandegar and Saroha, 2013; Pivokonsky *et al.*, 2015). Moreover, it increases the energy consumption due to promoting the growth of an oxide layer on anode's surface (Mohora *et al.*, 2014). The influence of OM on the EC method is described in detail in Chapter 2. The deficiency in the variety of reactor design is another drawback of EC technology; where most of the EC reactors have parallel plate monopolar or bipolar electrode configuration systems (Un *et al.*, 2013). Moreover, no sufficient models to reproduce the performance of the EC method exist (Kuokkanen, 2016). Although construction of models is an academic issue, availability of models is vital to enhance the design of the EC units and to reproduce their performance.

The mentioned defects highlight an urgent need to develop EC technology to remove such hazardous complexes safely and efficiently, and to investigate new designs for EC reactors that enhance their performance and reduce the operational costs. In addition, these defects highlight the need to develop empirical models that simulate pollutants removal by EC technology to meet both academic and industrial needs.

The purpose of the present project is therefore to fill a part of these gaps in literature by developing a novel microwave (MW) assisted-EC method that enhances the removal of heavy metals from drinking water in the presence of OM. In addition, it presents a new configuration for the EC units that utilises the flow column concepts to conduct water mixing, aeration, and temperature control process. Four empirical models will also be developed, in this thesis, to reproduce the performance of the new reactor (FCER) in terms of fluoride, nitrate, iron, and RB-5 dye removal from drinking water.

In fact, the present project is designed to achieve more useful targets, as explained in the following section.

1.3 Aims and objectives

The aim of this project is to suggest a new, safe, and cost-effective water treatment method that utilises a combination of microwave irradiation and electrocoagulation technologies. This new hybrid method aims to remove refractory OM-heavy metal complexes from drinking water. The specific objectives of the current project are:

1- Review the previous works for information and data on the applications of the EC and MW technologies for pollutants (especially the OM, and heavy metals), and for better understanding of the fundamentals of the MW and EC process.

2- Construct, and validate the performance of a new bench scale EC reactor (FCER) that employs perforated plate flow columns (which are widely used the in chemical industry). Performance of FCER will be validated by comparing its water mixing, aeration, and temperature control efficiency with those of five different traditional EC reactors. Additionally, FCER will be applied to remove fluoride, nitrate, RB-5 dye, and iron from drinking water.

3- Propose a new, safe, and cost-effective water treatment method that utilises a combination of microwaves irradiation and electrocoagulation technologies to remove the refractory OM-heavy metal complexes from drinking water. The targeted pollutants were selected according to their availability in the water of the Shatt Al-Hillah River, as explained in section 1.5.

4- Remediate the biological pollutants (a case study of Activated Sludge Microorganisms (ASM)) from drinking water as an additional benefit of applying microwave field.

5- Calculate the recoverable amount of hydrogen gas, the main by-product of the EC units, and estimate the producible energy from this clean gas.

6- Develop empirical models to reproduce the performance of FCER in terms of fluoride, nitrate, RB-5 dye, iron, and iron-EDTA complex removal from drinking water.

1.4 Thesis presentation

This thesis is presented in eight chapters (Figure 1-1); this general introduction is followed by an investigation into the fundamentals and principles of EC, OM, and MW and a literature survey in chapters 2 and 3. Then the research methodology, results and discussion, and the development of models are presented in chapters 4, 5, and 6, respectively. The last chapter highlights the outcomes and conclusions drawn from this project.

- Chapter 1 highlights the objectives of the thesis together with a general background of the EC method. This chapter is divided into 4 key parts, general introduction, aims and objectives, the scope of thesis, and thesis presentation.
- Chapter 2 includes the fundamentals, theory, and a review of previous works related to the applications of the EC method in water and wastewater treatment. It presents a definition of the EC method, its early applications, advantages and disadvantages of this method, and the current obstacles and challenges to EC applications in water treatment. Additionally, this chapter identifies the negative impacts of the OM on the removal of heavy metals by the EC method together with the environmental and health problems associated with the presence of OM. Additionally, the influence of the OM on some traditional treatment methods will be highlighted.

- Chapter 3 presents the fundamentals, theory, and applications (especially in water treatment) of the microwaves. It highlights the advantageous properties of the MW irradiation that can be effectively employed in water treatment, especially that relate to the destruction of OM and remediation of pathogens. Additionally, it gives a brief description of the types of MW ovens, MW generation, mechanism of MW heating, thermal and athermal effects of MW, and emission limitations.

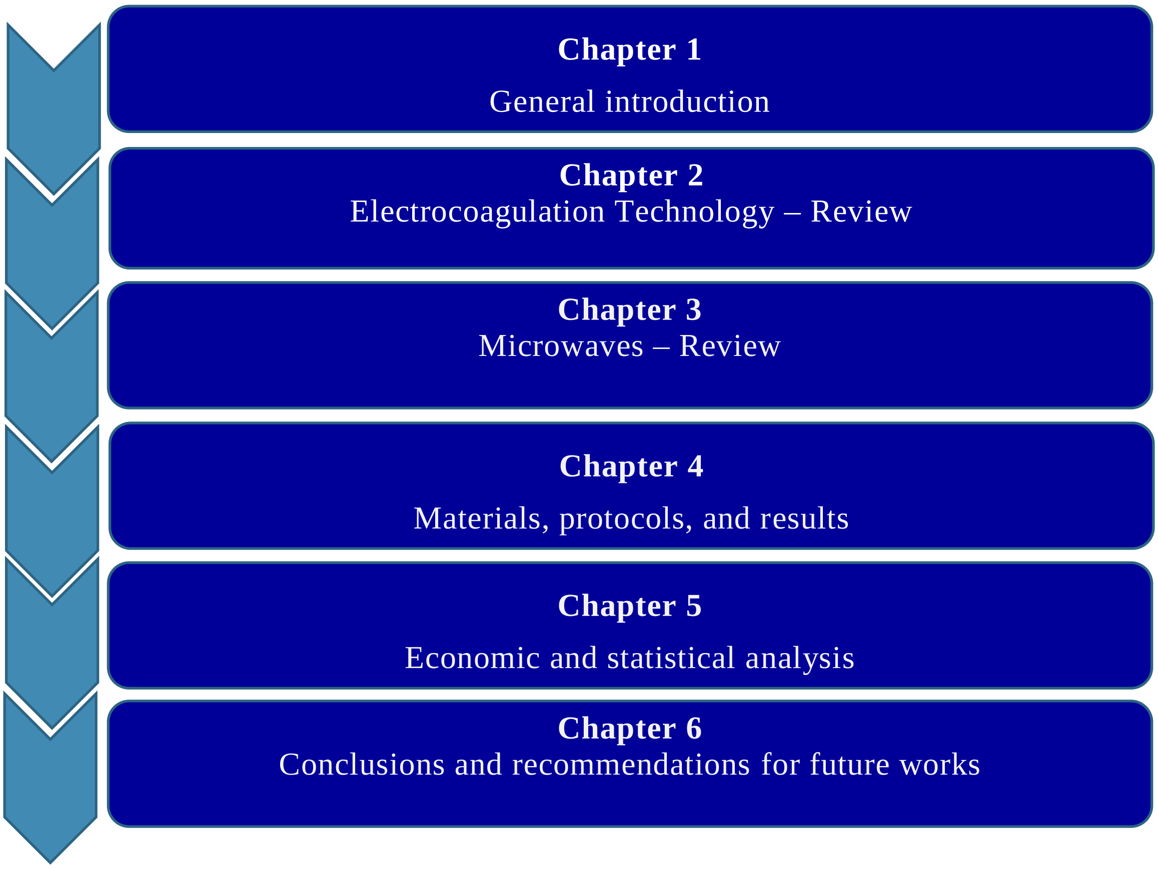


Figure 1-1: Structure of thesis.

- Chapter 4 is entitled the materials, protocols, and results; it is mainly consists of two sections. The first section presents the operational structure of the experimental work in which the objectives of this thesis will be achieved. It outlines the design and construction of the new EC reactor, the succession of the experiments, data collection and analysis, and it gives a precise description of tools, equipment, and chemicals that will be used in this project. Additionally, it provides a justification, with clear reasons, for the choice of the used elements, method or material, in this thesis.

  - While the second section shows the results obtained from the experimental work and gives logical explanations for these data. In general, this section will be divided into six subsections: the advantages of using a flow column in the EC unit, a validation of FCER performance, an investigate the influence of OM on the performance of the EC unit, the application of the MW assisted-EC method to remove OM-heavy metals complex, pathogens removal from drinking water using the new method, and recovery of hydrogen gas.

- Chapter 5 deals with the development of empirical models for the removal of fluoride, nitrate, RB-5 dye iron, and iron-EDTA complex from drinking water using FCER. The main purpose of this part of the project is to gather the influences of the operating parameters (such as the initial pH and current density) on the removal of a pollutant in one equation (model), which in turn could be used to predict the removal of that pollutant under different operating conditions. These models will be developed using SPSS 23 and Minitab 172. Additionally, this chapter includes a preliminary economic study to estimate the cost of pollutant removal using the MW assisted-EC method.
- Chapter 6 summarises the outcomes and conclusions drawn from conducting this thesis together with research limitations. Additionally, it provides suggestions for future works.

For better understanding of the current study, these objectives has been presented, in logical and sequential steps, in Table 1-1.

Table 1-1: Phases of thesis.

Phase	Description	
Phase 1	Conducting a literature survey for information and data on the fundamentals and applications of the EC technology for pollutants removal (especially OM, and heavy metals).	
Phase 2	Reviewing the occurrence of OM in water, its influences on water quality, health issues related to its occurrence in drinking water, and its treatment methods.	
Phase 3	Conducting a literature survey for information and data on the fundamentals and applications of the MW technology in the field of water and wastewater treatment, and its influence on OM.	
Phase 4	Designing and construction of a new flow column EC reactor. Another five traditional reactors will also be constructed for comparison purposes.	
Phase 5	Investigate the advantages of using a flow column in the EC unit in terms of water mixing, aeration, and temperature control processes, and compare the results with those of traditional ones.	
Phase 6	Validate the ability of the new reactor to work as an EC unit by applying it to remove the following pollutants from synthetic drinking water samples; taking into considerations the influence of key operating parameters such as initial pH, CD, ID, and C_0 of the targeted pollutant :	
	Fluoride	In batch flow pattern.
	Nitrate	In batch flow pattern.
	Iron	In batch flow pattern.
	RB-5 dye	In continuous flow pattern.
Phase 7	Prove, experimentally, the existence of the targeted problem (influence of OM on heavy metal removal by the EC method) by treating water samples containing EDTA-iron complex using FCER.	
Phase 8	Apply the new treatment method (MW assisted-EC method) into EDTA-iron complex containing water samples. For validation purposes, iron removal using the new method will be compared with that of the EC method.	
Phase 9	Remediate the biological pollutants using the new MW assisted-EC method / ASM as a case study.	
Phase 10	Calculate the recoverable amount of hydrogen gas and the yieldable energy from this eco-friendly fuel.	
Phase 11	Development of empirical models that could be used to predict the performance of FCER in terms of fluoride, nitrate, RB-5 dye, iron, and iron-EDTA complex removal from drinking water. Additionally, a preliminary economic study will be carried out to estimate the cost of pollutants removal using MW assisted-EC method.	

1.5 Background of Shatt Al-Hillah River

Babylon city, which was built in 2300 BC, is one of the most ancient cities in the world; it situated about 100 km to the north of the Iraqi capital, Baghdad (Khalidy *et al.*, 2012). This city occupies about 5315 km^2 in area and is considered as a home for 1,974,490 inhabitants. Its land is fertile as the Shatt Al-Hillah River passes through the city dividing it into two parts (Khalidy *et al.*, 2012; Chabuk *et al.*, 2015).

Indeed, the Shatt Al-Hillah River represents the lifeline of Babylon city, as the water demands for domestic, commercial, industrial, and municipal uses are supplied from this river (Salman *et al.*, 2015). This river, which branches off from the Euphrates River at the district of Sadat Al-Hindiah in the north of Babylon, has a total length of 103 km and a discharge of 250 m^3/sec (Hassan *et al.*, 2008; Chabuk *et al.*, 2015), Figure 1-2. Unfortunately, discharging of the municipal, agricultural, and industrial effluents of Babylon and upstream cities into this river left it with a broad spectrum of pollutants. Recent studies revealed that the water of Shatt Al-Hillah River is polluted with lead, iron, zinc, cadmium, nitrate, organic compounds, and different textile dyes such as methylene blue and reactive black 5 (RB-5) (Al-Syad, 2014; Baqir *et al.*, 2014; Salman *et al.*, 2014; Salah *et al.*, 2015; Hassan *et al.*, 2016). Moreover, the discharge of the Shatt Al-Hillah River has recently been decreased by almost 30% due to construction of dams on the Euphrates River, in Turkey, which in turn intensified the pollution levels (Salman *et al.*, 2015).

The current project therefore; has been devoted to developing a new hybrid treatment method to remove the OM-heavy metal complexes from water, which could be used to treat the water of the Shatt Al-Hillah River. Additionally, the performance of the new

EC unit (FCER) was validated by treating pollutants that widely existed in the water of the Shatt Al-Hillah River.

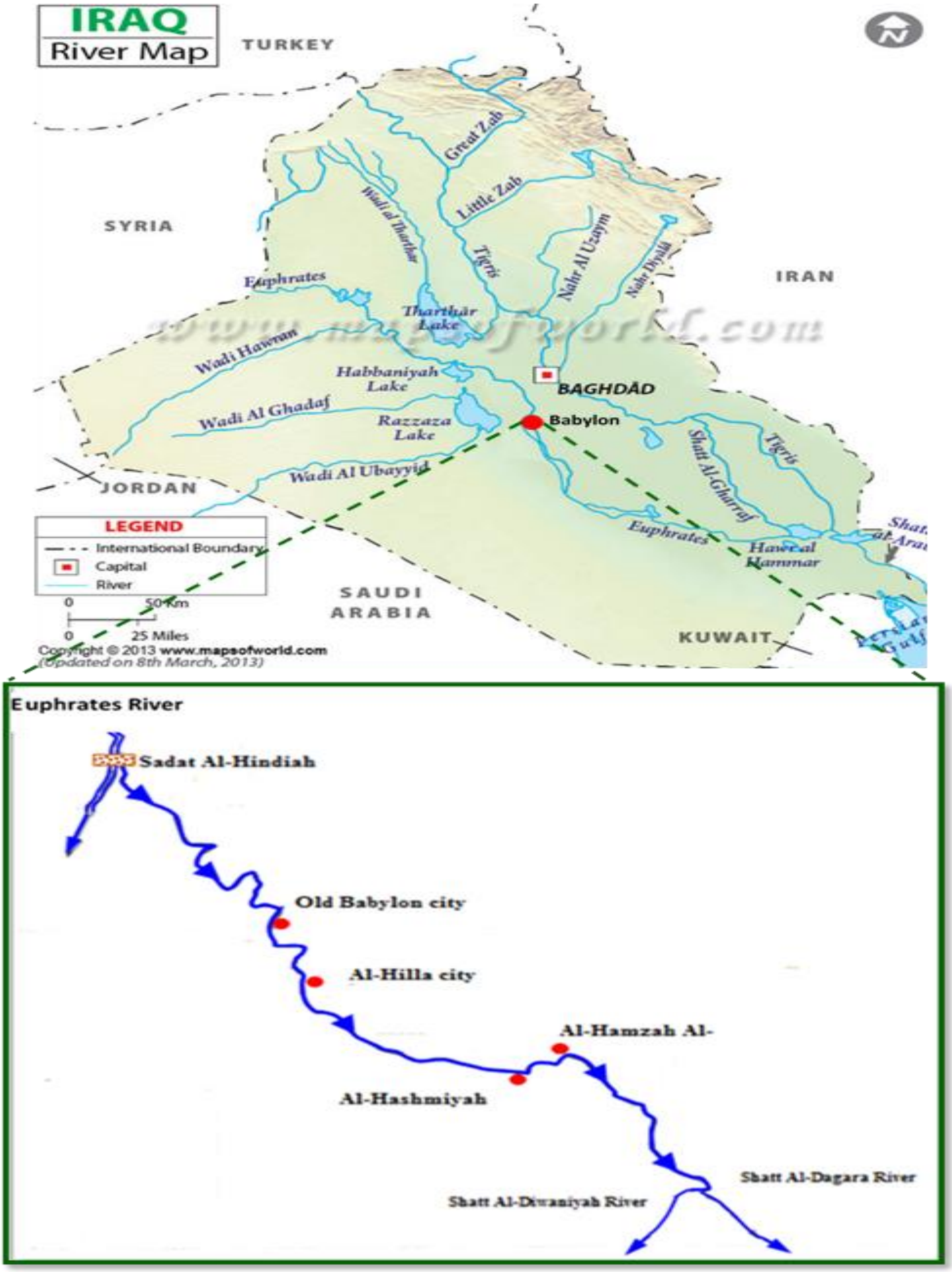
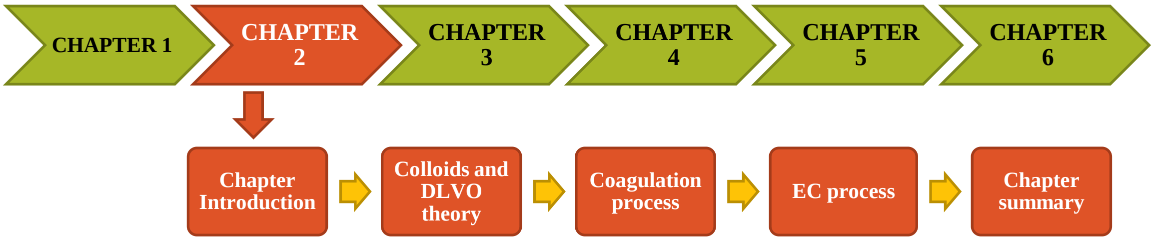


Figure 1-2: Shatt Al-Hillah River.

CHAPTER 2

ELECTROCOAGULATION TECHNOLOGY - REVIEW

CHAPTER 2: ELECTROCOAGULATION TECHNOLOGY – REVIEW



2.1 Chapter introduction

This chapter has been devoted to present the principles of coagulation theory, impacts of size and charge of particle on their removal mechanisms, and the possible methods to destabilise colloids. This chapter will also present the fundamentals, history, applications, limitations, advantages and disadvantages of the EC method, the role of key operating parameters on the performance of the EC reactors, and highlight the differences between the traditional coagulation process and EC technology. More importantly, this chapter will highlight the defects of EC technology that need to be enhanced.

Additionally, this chapter identifies the negative impacts of the OM on the removal of heavy metals by the EC method together with the environmental and health problems associated with the presence of OM. Furthermore, the influence of the OM on some traditional treatment methods will be highlighted.

2.2 Colloids and DLVO theory

Water pollutants are generally divided, depending on their sizes, into large (suspended) particles, and colloids. Large pollutants, such as sand and remains of plants, are easy to be removed from water by physical settling due to their large size (greater than

10 µm). Whilst, the colloids are exceptionally small in size, ranging in diameter from 10 µm to 10 nm, and do not settle due to gravity (Wang, 2003; Koohestanian *et al.*, 2008). The presence of colloids in water causes turbidity and inhibits the removal of microorganisms (Hesami *et al.*, 2013). More importantly, because colloids are exceptionally small and their surface area to weight ratio is extremely high (2.25×10^9 m^2/kg for a 10 µm particle), the influence of other molecules in their vicinity keeps them in a continuous jiggling (Brownian) motion, which in turn keeps these colloids suspended in water for years, as shown in Table 2-1, (Engelhardt, 2010).

Table 2-1: Relationship between size and settling time of particles with specific gravity of 2.65, (Engelhardt, 2010).

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Colloids in water are classified into two groups: hydrophilic and hydrophobic. Hydrophilic colloids, such as detergents and microorganisms, are affinitive for water and known for their solubility and stability in water (Wang, 2003; Hong, 2016). Whilst, hydrophobic colloids, such as clay and gold particles, are unstable, tend to repel water, and known for their non-affinity for water (Koohestanian *et al.*, 2008). Generally, OM are hydrophilic colloids, while inorganic pollutants are categorised as hydrophobic colloids (Wang, 2003).

Since most colloids in water are negatively charged, they attract the positively charged ions forming a strongly bound layer called the stationary or Stern layer. More positively charged ions are still attracted to the negative colloid but are repulsed by the fixed layer; at the same time, the fixed layer attracts negative ions but the colloids repel them. Therefore, another loose layer (so-called diffuse layer) consisting of positive and negative ions will be formed around the fixed layer, the contact line between the fixed and diffuse layers is called the shear plane (Wang, 2003; Engelhardt, 2010). The number of positively charged ions in the diffuse layer decreases as the distance from the colloid increases, i.e. the potential decreases with the increase of distance from the surface of the colloid, as shown in Figure 2-1. The potential at the contact line between the fixed and diffuse layers called Zeta potential (Z_P), which represents the required energy to bring two colloids to contact (Engelhardt, 2010). The influence of these two layers is known as electrical double layer (EDL) (Kuokkanen, 2016).

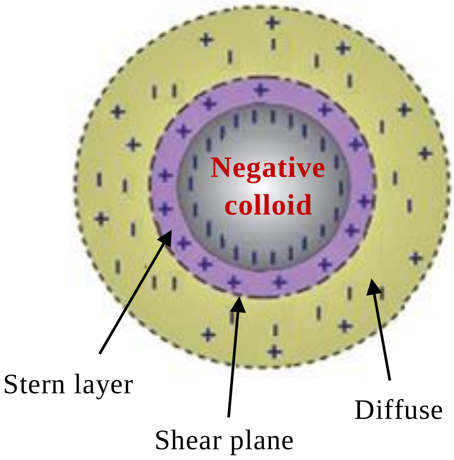

Figure 2-1: Stern and diffuse layers (Pritchard *et al.*, 2010).
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According to the theory of Derjaguin, Landau, Vervey, and Overbeek (DLVO theory), colloidal particles in water influence each other with two opposite forces. Van der Waals forces work to bring particles together. While, a repulsive force resulting from the influence of the ionic layers works to repel particles, as shown in Figure 2-2, (Kuokkanen, 2016). In fact, the repulsive force between two colloids is greater than the attraction forces, Therefore, adhesion between particles to form large flocs will not happen, and consequently colloids remain suspended in the water (Wang, 2003; Kuokkanen, 2016). To remove colloids therefore, they must be chemically destabilised, the latter can be achieved by the coagulation process.

Figure 2-2: Attraction and repulsive energies (Kuokkanen, 2016).

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2.3 Coagulation process

Coagulation is defined as a process of destabilising colloids by reducing the negative charge (zeta potential) that allows van de Waals forces to coalesce colloids together forming small flocs, the latter can be separated from a solution by different methods such as sedimentation or flotation (Koohestanian *et al.*, 2008). This process is achieved by adding coagulants that are defined as positively charged chemicals used to neutralise the negative charges of colloids that strongly decreases the electrostatic repulsion force among them. Coagulants aggregate colloids together to form flocs, as shown in Figure 2-3, (Wang, 2003; Emamjomeh, 2006). The coagulation process consists of three stages: coagulant addition or formation, destabilisation of colloids, and flocs formation (Wang, 2003). Addition of a proper coagulant, such as aluminium or iron salts, is achieved either chemically or electrically to the water being treated (Emamjomeh, 2006).

Chemically, the coagulation process is achieved by direct adding of coagulants such as $FeCl_3, Fe_2(SO_4)_3, AlCl_3$, and [$Al_2(SO_4)_3, H_2O$] into solution being treated, these positively charged coagulants destabilise negatively charged colloids by promoting the attraction forces among them. Consequently, the colloids start the aggregation process forming larger flocs that can be separated from the solution by precipitation, flotation, or filtration process (Wang, 2003; Emamjomeh, 2006; Kuokkanen, 2016). In this method of coagulation (direct addition of coagulants), the required amount (dose) of a coagulant is a function of the chemistry of water being treated such as pH, hardness, ionic strength, and water temperature (Emamjomeh, 2006). The electrical addition of coagulants, which is known as electrocoagulation process, will be explained in the following section.

Figure 2-3: Coagulation process (Jiang and Graham, 1998).

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2.4 EC process

2.4.1 Definition of EC process

Electrocoagulation is a process of in-situ generation of coagulants by passing an electric current through metallic electrodes to destabilise suspended pollutants in an aqueous media (Emamjomeh, 2006; Heffron, 2015). This method consists of three main stages: generation of coagulant agents (destabilising agents), destabilisation of pollutants, and flocs formation (Heffron, 2015). Initially, the destabilising agents (such Al and Fe) are electrochemically generated from the sacrificial electrodes, these agents destabilise pollutants due to providing an opposite electrostatic charge. Once charged, the pollutants start the bridging process forming flocs that can easily be separated from the solution (Emamjomeh, 2006; Heffron, 2015). Therefore, it can be said that the EC method utilises the advantages of three traditional treatment methods: traditional chemical coagulation, flotation, and electrochemistry (Kuokkanen, 2016). Figure 2-4 summaries the EC method.

Figure 2-4: Summary of basic reactions in the EC cell (Heffron, 2015).

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2.4.2 History of EC method

The EC technology is an old water and wastewater treatment process gaining a recent growing interest as an effective option for pollutants (especially metals) removal from aqueous media (Heffron, 2015). lectricity was introduced for the first time as a possible wastewater treatment method in the UK in 1889 (Chen, 2004). This trial was followed by several studies to apply this new approach in water treatment until an EC cell was patented in 1906 by Dietrich to treat wastewater from ships, another EC cell supplied with aluminium and iron electrodes was patented in the United States in 1909 by J.T. Harries to treat wastewater (Casillas *et al.*, 2007). Two years later, EC wastewater treatment plants were operated in Oklahoma and Santa Monica (Heffron, 2015). In fact, applications of this technology were limited to wastewater treatment until 1925, when Russian scientists applied this method for the first time to treat drinking water in Moscow using iron electrodes (Heffron, 2015). However, EC technology did not attract enough attention at that time for several reasons; firstly and most importantly is the high operating cost at that time in comparison with other treatment methods, no minimum federal limitations for the secondary treatment of wastewater that reduced the need for advanced treatment methods (Holt *et al.*, 2005; Heffron, 2015). Additionally, the ready availability and cost-effectiveness of traditional alternatives (such as traditional chemical coagulation) gave them an edge over EC technology (Kuokkanen, 2016). For the reasons mentioned, water and wastewater treatment companies started to abandon the EC technology gradually during the 1920s of the last century until all EC wastewater treatment plants, in the United States, were decommissioned by the 1930s (Holt *et al.*, 2005).

During the 1970s, with the recent application of strict contemporary limitations and regulations on water and wastewater quality and the availability of affordable energy sources (such as solar energy), using the EC method has recently seen a resurgence as an efficient and portable alternative for water and wastewater treatment (Heffron, 2015). Recent successful applications of the EC method to treat a broad spectrum of polluted water and wastewater, such as effluents from slaughterhouses (Asselin *et al.*, 2008), paper mills (Bellebia *et al.*, 2012), petroleum refineries (Ben Hariz *et al.*, 2013), and the textile industry (Khandegar and Saroha, 2013), evidenced the reliability and efficiency of this technology. Where the EC method has removed 95 to 99% of a wide range of pollutants such as fluoride (Emamjomeh and Sivakumar, 2009), arsenic (Wan *et al.*, 2011; Kobya *et al.*, 2014), iron (Chaturvedi and Dave, 2012), bacteria (Ricordel *et al.*, 2014), nickel (Srithanrat *et al.*, 2015), nitroanilines (Tamne *et al.*, 2015), and dyes (Vidal *et al.*, 2016).

With the recent advancements in the production of alternative clean energies such as windmill and solar, the use of the EC method became possible even in rural areas, where sufficient energy can be driven from a windmill or an attached solar panel (Chaturvedi and Dave, 2012; Deokate, 2015; Kuokkanen, 2016). Additionally, these advancements in the production of alternative clean energies, scalability and the easy deployment of EC units make this technology a favourable water treatment option especially in the event of disasters and emergencies (Bagga *et al.*, 2008; Heffron, 2015; Symonds *et al.*, 2015). The contemporary applications of the EC method will be highlighted later (in section 2.4.8).

2.4.3 Principles of the EC process

The principle of the EC process is the application of an electrical current to the solution being treated through sacrificial metallic electrodes to form in-situ coagulating ions (Essadki *et al.*, 2009; Chaturvedi, 2013; Heffron, 2015). Selection of the material of the metallic electrodes is dependent on several key parameters such as material availability, cost-effectiveness, oxidation potential, toxicity, and the properties of the targeted pollutant (Chaturvedi and Dave, 2012; Kuokkanen, 2016). The literature shows that several materials, such as stainless steel(Abuzaid *et al.*, 2002), diamond (Cañizares *et al.*, 2008), iron (Malakootian *et al.*, 2010), zinc (Vasudevan *et al.*, 2012a), graphite (Raju *et al.*, 2008), and aluminium (Vidal *et al.*, 2016), were used as electrodes in EC units. However, it is well documented that aluminium is a very effective and efficient, as an electrode material, to remove different pollutants at suitable operating conditions (Emamjomeh, 2006; Essadki *et al.*, 2009; Chaturvedi and Dave, 2012; Heffron, 2015).

As the electrical current starts to flow through the immersed electrodes, the anode starts to dissolve forming coagulating ions, while the cathode generates hydroxide (OH^-) ions and hydrogen (H_2) gas (Chen, 2004; Essadki *et al.*, 2009; Mechelhoff *et al.*, 2013; Heffron, 2015). The EC reactions are determined by several operating parameters such as the initial pH, applied current, electrolysing time, solution conductivity, and electrode material (Bard and Faulkner, 2001; Emamjomeh, 2006; Kobya *et al.*, 2014); the influence of these parameters will be discussed later (in chapter 5).

In the case of using aluminium (Al) as an electrode material, the anode liberates $\mathrm{Al}^{3+}_{(aq)}$ ions, while the cathode produces H_2 gas (Essadki *et al.*, 2009; Chaturvedi, 2013); these reactions are represented in the following equations (Chen, 2004; Essadki *et al.*, 2009; Heffron, 2015):

At the anode:

$$Al_{(s)} \rightarrow Al^{3+} + 3e^{-} \qquad \textbf{(1)}$$

At the cathode:

$$2H_2O + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}$$

(2)

After dissolution, the $\mathrm{Al}^{3+}_{(aq)}$ ions undergo a series of sequential reactions to yield different monomeric and polymeric substances such as $\mathrm{Al(OH)^{2+}}$, and $\mathrm{Al_{13}O_4(OH)_{24}^{7+}}$, which in turn readily coagulate pollutants forming flocs (Adhoum *et al.*, 2004; Essadki *et al.*, 2009; Heffron, 2015). In fact, speciation of aluminium (hydrolysation of dissolved ions) is highly governed by the pH of the solution being treated, where $\mathrm{Al(OH)^{2+}}$ is the prevailing species of aluminium for pH range of 5 to 6, $\mathrm{Al(OH)_4^-}$ is the predominant species for pH above 9, while $\mathrm{Al(OH)_3}$ is predominant in neutral or slightly alkaline pH (Vasudevan *et al.*, 2009; Heffron, 2015). Generally, aluminium speciation is modelled as follows (Holt *et al.*, 2002; Heffron, 2015):

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+ \quad \textbf{(3)}$$

$$Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+ \quad \textbf{(4)}$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3^0 + H^+ \quad \textbf{(5)}$$

$$Al(OH)_3^0 + H_2O \rightarrow Al(OH)_{4\,(aq)}^- \quad \textbf{(6)}$$

2.4.4 Pollutants adsorption and precipitation in EC method

Since the electrolysing process started, an electrophoretic immigration of negatively charged ions started towards the anode and positive ions move towards the cathode. This electrophoretic movement works to concentrate the negatively charged colloids near to the anode, which in turn greatly increases their collision rate with the coagulant species, and aggregates formation consequently (Den and Huang, 2005; Chaturvedi, 2013; Shim *et al.*, 2014). Colloids in the EC method are aggregated by adsorbing them into the freshly formed flocs, and/or chemical transforming (Zhu *et al.*, 2007; Essadki *et al.*, 2009; van Genuchten *et al.*, 2014). Aluminium and iron hydroxides have a high affinity for dispersed negatively charged colloids, especially metallic ones, that leads them to coagulate forming large aggregates (Gomes *et al.*, 2007; Ferreira *et al.*, 2013; Heffron, 2015). Positively charged metallic ions can bond themselves to $\mathrm{OH^-}$, such as $\mathrm{Cu(OH)_2}$ and $\mathrm{Cu(OH)_2}$, leading to coagulation and forming, with aluminium hydroxide, large flocs whose separation is easily obtained (Ferreira *et al.*, 2013). In addition, colloids and hydroxides may also co-precipitate by replacing ions in the floc structure (Essadki *et al.*, 2009; Heffron, 2015).

For instance, fluoride ions readily react with Al^{3+} ions forming AlF_6^{3-} (Mameri *et al.*, 1998; Zhu *et al.*, 2007; Essadki *et al.*, 2009) according to the following equation:

$$Al^{3+} + 6F^- \rightarrow AlF_6^{3-} \qquad \textbf{(7)}$$

Which could undergo more reactions, in the presence of sodium ions, to form salt as follows:

$$AlF_6^{3-} + 3Na^+ \rightarrow Na_3AlF_6 \qquad \textbf{(8)}$$

Chromium removal using iron electrodes is another good example of the high affinity of iron hydroxides metallic ions, where dichromate ions are readily reduced by ferrous ions according to the following equation (Heffron, 2015):

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \qquad \textbf{(9)}$$

During the final stage of the electrocoagulation process, the formed aggregates will be separated from the liquid being treated by either flotation or sedimentation. Flotation is a process for separating particles from liquid by electrolytic gas; while the bubbles are moving upwards, aggregated colloids adhere to them and float to the surface to be skimmed later (Holt *et al.*, 2005; Emamjomeh, 2006; Butler *et al.*, 2011). While sedimentation takes place when the weight of the aggregated colloids become big enough to settle to the bottom of the EC unit due to the gravity, and this will be removed later as sludge (Emamjomeh, 2006; Chaturvedi and Dave, 2012). The dominant one of these two removal paths is determined by the magnitude of the applied current density; sedimentation is the dominant path at low current densities, while flotation is the predominant path at high current densities (Holt *et al.*, 2005; Chaturvedi and Dave, 2012). The number of bubbles produced in the EC unit explains this shift in removal mechanism, lower current densities produce an insufficient number of bubbles to float aggregates, making sedimentation predominant. As the current density increases, the number of bubbles increases, leading to aggregates floating to the surface, i.e. it gives the flotation path an edge over sedimentation (Holt *et al.*, 2005; Maximova and Dahl, 2006; Chaturvedi and Dave, 2012).

The pollutants removal efficiency (Re%) can be calculated using the following formula (Un *et al.*, 2013):

$$Re\% = \frac{C_0 - C_t}{C_0} \times 100\% \tag{10}$$

Where C_0 and C_t are the initial and final concentrations of the studied pollutant.

2.4.5 Energy consumption of EC units

Energy consumption is one of the most important parameters in water treatment as it determines the operating cost of any method, which in turn determines its applicability (Bayramoglu *et al.*, 2004; Ozyonar and Karagozoglu, 2011). Power consumption for EC units, which highly depends on the gap between the electrodes and conductivity of liquid being treated, can be calculated using the following Equations (Emamjomeh, 2006; Un *et al.*, 2013):

$$\boldsymbol{Power}\ (Watts) = V_{cell} \,.\, I \tag{11}$$

Where V_{cell} and I are the cell potential (volts) and the applied electric current (amperes).

$$\boldsymbol{Power\ consumption}\ (C_{energy})(kWh) = \frac{\mathrm{I}\,.V_{cell} \cdot t}{1000} \tag{12}$$

Where t is the treatment time (hours).

The consumed power per cubic meter of treated solution is:

$$C_{energy}\ (kWh/m^3) = \frac{I\,.V_{cell} \cdot t}{1000.\ Vol.} \tag{13}$$

Where $Vol.$ Is volume of treated liquid (m^3).

2.4.6 Dissolving rate of anode

The dissolved mass (dose) of the sacrificial anode is governed, as previously mentioned, by several operating parameters such as the magnitude of the applied current and treatment time. In fact, the applied current and treatment time are the most significant parameters in the anodic dissolving process as they determine the number of liberated ions from the metallic anode (Bayramoglu *et al.*, 2004; Emamjomeh, 2006; Pallier *et al.*, 2011; Vidal *et al.*, 2016). Theoretically, the dissolved amount of the anode can be calculated using Faraday's second Law (Ozyonar and Karagozoglu, 2011; Un *et al.*, 2013; Kobya *et al.*, 2014; Vidal *et al.*, 2016):

$$C_{material} = \frac{I\,.t\,.\,m}{Z\,.\,F.\,Vol.} \qquad \textbf{(14)}$$

Where $C_{material}$, t, m, Z, and F represent the dissolved mass from the anode (g/L), treatment time (second), molecular weight (g/mol) (26.98 for Al), number of electrons (3 for Al), and Faraday's constant (96,500 C/mol).

Experimentally, the consumed mass of electrodes can be calculated by measuring the difference between the anode before and after each run.

2.4.7 Operating cost (OC) of EC units

The operating cost of EC process consists of operating and fixed costs; the operating cost includes the cost of energy, material (electrodes), chemicals, labour, maintenance, and sludge handling, while the cost of other parts of the EC plant, costs of equipment and construction, represent the fixed costs (Bayramoglu *et al.*, 2004; Ghosh *et al.*, 2008; Dalvand *et al.*, 2011) . However, the operating cost of bench scale EC units (Lab work) includes the costs of energy and materials (Ghosh *et al.*, 2008; Kobya *et al.*, 2010; Ozyonar and Karagozoglu, 2011; Chopra and Sharma, 2012). In the present study therefore, the following equation, which was suggested by Kobya *et al.* (2010), will be used to estimate the operating cost of the electrocoagulation process:

$$OC = \gamma_1 \, C_{energy} + \gamma_2 \, C_{electrodes} + \gamma_3 \, C_{chemicals} \qquad \textbf{(15)}$$

Where C_{energy} (kWh/m^3), $C_{electrodes}$ (kg/m^3), and $C_{chemicals}$ (kg/m^3) are the consumed energy, electrode material, and chemicals respectively. While γ_1, γ_2 and γ_3 represent the unit price of power, electrode material, and chemicals respectively.

2.4.8 Applications of EC method in the treatment of water and wastewater

It is well documented that the EC technology has widely been applied in the water and wastewater treatment field to remove different pollutants such as heavy metals, dyes, oil, and bacteria (Genc and Bakirci, 2015; Wan *et al.*, 2011; Ricordel *et al.*, 2014; Vidal *et al.*, 2016). Overall, EC technology is able to remove as much as 95-99% of the targeted pollutants within a relatively short treatment time (Gomes *et al.*, 2007; Gao *et al.*, 2010; Butler *et al.*, 2011; Ricordel *et al.*, 2014; Vidal *et al.*, 2016). However, the performance of this technology is influenced by several parameters such as the chemistry of the liquid being treated, chemical properties and concentration of the targeted pollutant, material of the electrodes, and the operating parameters (Golder *et al.*, 2007; Dubrawski and Mohseni, 2013; Wan *et al.*, 2011; Kenova *et al.*, 2015).

Therefore, this section is devoted to presenting a quick review of earlier applications of EC technology in water and wastewater treatment, especially those applications which are related to the topic of the present thesis (heavy metals and OM removal). This literature survey provides important information and data on the applications of the EC technology, which can be used as a guide to conduct the experimental work of the present study. The applications of EC technology discussed here were divided into the following five groups:

2.4.8.1 Removal of dyes

Treatment of water or wastewater containing deys using EC method has become one of the most attractive methods during the last few decades due to its high efficiency and cost-effectiveness (Kim *et al.*, 2002; Daneshvar *et al.*, 2006; Aoudj *et al.*, 2010; Naje *et al.*, 2016). For instance, Ogutverena *et al.* (1992) used a bipolar packed bed EC cell supplied with soluble electrodes to remove Acilan Blau dye from wastewater, taken into considerations the influence of several operating parameters such as initial pH, current density, and dye concentration. A complete dye removal efficiency of 98-100%, was achieved within 3-5 min and the power consumption was 2.24 kW/m^3. Jia *et al.* (1999) treated more than 20 types of dyes; such as sulfur brilliant green GB, Vat red F3B, and Vat blue RSN, using electrodes made from active carbon fibre. Overall, 90% of the studied dyes were removed within 60 min of electrolysing at voltage of 25 V and 0.5 g/L of Na_2SO_4. Suncion Blue P-3R, Suncion Yellow H-E4R, Suncron Blue RD-400 and Suncron Yellow 3GE- 200 dyes-containing wastewater was treated by Kim *et al.* (2002) using three different types of electrodes (Al, Fe), and stainless steel (SS), taking into consideration the influences of different operating parameters such as flow rate, concentration of the electrolyte, pH, and current density. The obtained results showed that the removal of dyes is more efficient (about 99%) by Al electrodes. Daneshvar *et al.* (2007) investigated the influence of dye concentration, initial pH, current density, and duration of electrocoagulation on the removal of Acid yellow 23 dye. The findings of this study showed that the highest removal efficiency (98%) was achieved after 5 min of electrolysing at an initial pH of 6, current density of 11.25 mA/cm^2, and initial dye concentration of 50 mg/L. Another study conducted by Aoudj *et al.* (2010) to remove direct red 81 dye from water using EC technology. The highest removal efficiency, using Al electrodes, was 98% at initial pH of 6, and current density of 1.875

mA/cm^2. Direct red 81 dye containing water was treated by Zodi *et al.* (2013) using a continuous flow EC reactor (aluminium electrodes), the results showed that 90.2% of dye was removed after 7.3 min at a current density of 20 mA/cm^2, initial pH of 7.5, and flow rate = 10 L/H. Naje *et al.* (2016) investigated the removal of Imperon violet KB dye from textile wastewater using a rotated bed EC unit (made from aluminium). 98.5% of this dye was removed after 10 min of treatment at a current density of 4 mA/cm^2, initial pH of 4.57, and water temperature of 25 ^{o}C. In fact, there is a vast amount of literature regarding the application of the EC method to remove dyes from water and wastewater, which is impossible to be summarised in a few pages. Therefore, appendix C is devoted to provide some of the recent applications of the EC method to treat dye-containing water and wastewater.

2.4.8.2 Removal of heavy metals

Application of the EC method to treat water and wastewater containing heavy metals has gained substantial interest during the last few years, and removal efficiencies of 95 to 100% have been documented (Öğütveren *et al.*, 1994; Mills, 2000; Yilmaz *et al.*, 2007; Vasudevan *et al.*, 2011; Heffron, 2015).

Öğütveren *et al.* (1994) used a bipolar packed bed EC reactor with steel ring electrodes to treat water containing 100 mg/L chromium, taking into account the influences of some operating parameters such as time of treatment, and the applied potential. A complete removal of chromium (100%) was achieved after 20 min of electrolysing at a current of 160 mA, power consumption of 33.33 kW/m^3, and 0.25 mole/L of NaCl (as electrolyte). In another study, Mills (2000) treated leachate from a landfill site to remove iron using a continuous flow EC reactor, the latter consists of a ladder series of electrolytic cells made from iron (as anodes) and stainless steel (as cathodes). The outcomes of this study showed that the iron concentration was reduced from 130 mg/L to 0.015 mg/L at a current density of 1.1 mA/cm^2, 1.5 mm gap between electrodes, and 24 min retention time. Kumar *et al.* (2004) used three different types of electrodes, namely iron, aluminium, and titanium, to treat water containing 2 mg/L arsenic, III and V. The results of their study showed that the most efficient electrode to remove arsenic was iron followed by aluminium and titanium, where, 99% of arsenic was removed using iron electrodes at a current density of 1.53 mA/cm^2, for a pH range 6-8. Yilmaz *et al.* (2005) investigated the removability of boron from wastewater by EC. To achieve that, a batch flow EC reactor, having a volume of 1024 cm^3 and aluminium electrodes, was employed to treat wastewater containing 100 mg/L of boron at different operating parameters. The highest removal efficiency was obtained at an initial pH of 8, current density of 3 mA/cm^2, and 0.015 mole/L of $CaCl_2$ (as an electrolyte). A batch flow EC unit supplied with aluminium electrodes was employed by Ghosh *et al.* (2008) to remove iron, 25 mg/L, from tap water. A complete iron removal was achieved after 35 min of electrolysing at a current density of 0.004 mA/cm^2, with an initial pH of 7.5, and ID of 5 mm. The simultaneous removal of two heavy metals, zinc and copper, from water using the EC method was investigated by Nouri *et al.* (2010). In this study, a batch flow EC cell with four aluminium electrodes was applied to treat 5 mg/L of zinc and 5 mg/L of copper at different operating parameters such as initial pH and the applied potential. The results obtained from this study showed that EC was able to remove 90.2% zinc and 97.7% of copper after 15 min at an initial pH of 7, and cell voltage of 30V. Ouaissa *et al.* (2013) used an EC unit supplied with aluminium electrodes to investigate the ability of the EC method to remediate chromium Cr (VI) from synthetic water samples. The highest removal efficiency of 97% for initial Cr (VI) concentration of 100 mg/L was achieved at a current density of 4.03 mA/cm^2, with an initial pH of 3 to 6. Another study, conducted by Lekhlif *et al.* (2014), showed that 88% removal of nickel was achieved using EC at an initial pH of 8 to 9, cell voltage of 12 V, and initial nickel concentration of 16.3 mg/L.

More applications of the EC method in heavy metal removal from water and wastewater are listed in appendix D.

2.4.8.3 Removal of organic matter

Since the 1970s, EC technology has been practised in the treatment of organic-rich waters and wastewaters (Deng and Englehardt, 2007), such as the wastewater from coke plants, tanneries, and slaughterhouses, landfill leachate, seawater, and drinking water (Chiang *et al.*, 1995; Tsai *et al.*, 1997; Rao *et al.;* Kobya *et al.*, 2006c; Labanowski *et al.*, 2010; Hakizimana *et al.*, 2016). For instance, Chiang *et al.* (1995) used EC technology to treat wastewater from a coke plant containing 2143 mg/L of COD (chemical oxygen demand). The obtained results showed that the COD decreased from 2143 to 226 mg/L (89.5% removal efficiency) after 120 min of electrolysing using an EC cell supplied with a lead dioxide coated titanium anode. Tsai *et al.* (1997) employed a batch EC reactor, with two different pairs of electrodes (iron (anode) – copper (cathode)) and (aluminium (anode) – copper (cathode)), to eliminate soluble organic matter from municipal landfill leachates. The obtained results showed that the highest removal efficiency, about 50%, was achieved after 20 min of electrolysing at 2.0 V using iron– copper electrodes. Remediation of the organic content of tannery wastewater is another application of the EC technology; Rao *et al.* (2001) treated samples of tannery wastewater collected from the effluent of a treatment plant for 85 tanneries in India using a batch EC cell. The electrolysing process used three different pairs of electrodes, titanium/platinum(Ti/Pt), titanium/lead dioxide$(\mathrm{Ti/PbO_2})$, and titanium/manganese dioxide$\mathrm{Ti/MnO_2}$. The obtained results showed that the order of removal efficiency was $\mathrm{Ti/Pt > Ti/PbO_2 > Ti/MnO_2}$, where the COD concentration decreased from 515 to 189 g/m^3 (which the highest removal efficiency) after 240 min of electrolysing using Ti/Pt electrodes.

Wastewater from the student canteen, with COD concentration of 500 to 1500 mg/L, in the Zhejiang University was subjected to the EC process to remove the organic matter. In this study, Xu and Zhu (2004) reported that the collected samples were electrolysed for 30 min using 5 L batch EC cell supplied with iron electrodes at a current density range of 0.2-1.8 mA/cm^2, and pH of 3-10. The optimum removal efficiency of 95% was achieved at current density of about 1.4 mA/cm^2, conductivity of 0.72 mS/cm, and initial pH of 7. Kobya *et al.* (2006c) investigated the applicability of the EC method to remediate the organic matter in the effluents of slaughterhouse plants. To perform this investigation, wastewater samples were collected from a local poultry slaughterhouse plant, in Turkey, and treated using two different electrodes, Al and Fe. The obtained results revealed that the optimum removal of COD (93%) was achieved after 25 min using the Al electrodes at a current density of 15 mA/cm^2, and initial pH of 2 to 3. Tchamango *et al.* (2010) used a batch EC cell with aluminium electrodes to treat synthetic samples of dairy wastewater. The outcomes of this study showed that 61% of the initial COD was removed after 30 min of electrolysing at a current density of 4.3 mA/cm^2, and initial pH of 6.88 to 7. Ulu *et al.* (2014) studied the treatability of water containing humic acid (16.17 mg/L COD) by EC using two different types of electrodes Al and Fe, at different operating parameters. The outcomes of this study showed that the optimum COD removal efficiency (87.5%) was achieved using Al electrodes at a current density of 1.2 mA/cm^2, treatment time of 25 min, and initial pH of 4. Aswathy *et al.* (2016) conducted an investigation about the removability of organic matter from synthetic bilge water using the EC method. Synthetic bilge water samples with initial COD of 2.1120 g/L was treated using an EC cell supplied with Al electrodes and magnetic stirrer at different initial pHs (3 to 10), voltages (5 to 10 V), and gaps between electrodes (1 to 5 cm). The obtained results indicated that the 85% of the COD was removed after 120 min of electrolysing at initial pH of 7, with a mixing rate of 300 rpm, an applied voltage of 10V, and a gap between electrodes of 1 cm. Some of the recent applications of the EC method in the treatment of water and wastewater containing OM are listed in appendix E.

2.4.8.4 Removal of organisms and pathogens

Beside the acknowledged efficiency of the EC technology to coagulate and remove colloids from water and wastewater, it has been found that this technology can eliminate several types of biological pollutants such as bacteria and algae (Chen, 2004; Ricordel *et al.*, 2010; Kuokkanen, 2016). Several trials have been made over the last four or five decades to use the EC method as a disinfection tool for water and wastewater. For instance, Sandbank *et al.* (1974) applied the EC technology to remove algae from algal ponds effluents. In this study, an EC unit having graphite and iron electrodes was used to treat pond effluents containing 100-400 mg/L of algae. The outcomes of this study indicated that about 83% of the algae was removed after 10 min of electrolysing at current density of 16.6 mA/cm^2, and initial pH of 6.0. Later, during the 90s and 2000s, a number of studies were carried out to employ the EC method in densification of water and wastewater. Matsunaga *et al.* (1994) developed a new EC reactor using activated carbon fibre as electrodes to remediate *Escherichia coli* (*E.*coli) bacteria from drinking water. Water samples containing 22 cells of *E.coli*/L were treated using this type of electrodes at different voltages and durations, the obtained results showed that a complete removal of *E.coli* was achieved after 8 hrs of treatment at voltage of 0.8V. Nakayama *et al.* (1998) used another new type of electrodes, made from titanium nitride, to conduct the electrochemical disinfection process. These electrodes were applied to remove 420000 cells/cm^2 of marine bacteria, *Vibrio alginolyticus*, from seawater. The findings of this study showed that 98.7% of the *Vibrio alginolyticus* cells were rendered inactive after 30 min of treatment at 0.8 V. The ability of the EC technology to removal algae from water was investigated by Alfafara *et al.* (2002), the researchers used an EC reactor supplied with an aluminium anode and a titanium cathode to treat lake water containing *Chorophyll*. The experimental work was conducted under different flow patterns (batch and continuous flow), taking into account the influence of several operating parameters such as algae loading rate (from 2.4 to 22.9 mg/dm^3. H), applied power (60 to 155 W/dm^3). The results showed that, under flow pattern conditions, algae removal efficiency was about 50%. Sarkka *et al.* (2008) applied the EC technology to de-activate three types of paper mill bacteria (*Deinococcus geothermalis*, *Pseudoxanthomonas taiwanensis* and *Meiothermus silvanus*). After 3 min of electrolysing, using an EC unit with stainless steel and mixed metal oxides electrodes, at current density of 50 mA/cm^2, these three types of bacteria were efficiently de-activated (> 2log). Gao *et al.* (2010) treated synthetic water samples $1.2 - 1.4 \times 10^9$ cells/L of *M. aeruginosa* (algae) using aluminium and iron electrodes with a current density range of 0.5-5 mA/cm^2, and initial pH from 4 to 10. The obtained results demonstrated that 100% of algae was removed using the aluminium electrodes after 45 min at current density of 1 mA/cm^2, initial pH of 4-7, and power consumption of 0.4 kW/m^3. Another study about the removal of *E.coli* from water by the EC method was conducted by Castro-Rios *et al.* (2014). In this study, a 500 mL batch EC cell having aluminium electrodes was used to treat synthetic water samples containing 10^5 to 10^6 cfu/mL of *E.coli*. The outcomes of this investigation confirmed that a current density of 2.27 mA/cm^2 at initial pH of 4 and 2.5 mg/L of Na_2SO_4 was enough to reduce the *E.coli* number by 1-log and 1.9-log after 40 min and 90 min respectively. More of the recent applications of the EC method in the treatment of organic matter containing water and wastewater are listed in appendix F.

2.4.8.5 Removal of other pollutants

Beside the mentioned applications of EC, the literature survey showed that this technology has been applied to remove a vast number of other pollutants. For instance, Emamjomeh and Sivakumar (2009) applied EC to remove fluoride from tap water. In this study, a continuous flow lab scale EC reactor with aluminium electrodes was used to treat tap water samples with fluoride content of 5 to 25 mg/L. The removal process was performed under different operating conditions, current density of 1.25-5 mA/cm^2, initial pH (4 - 8) and flow rate (150 – 400 mL/min). The obtained results demonstrated that fluoride removal of 99% can be achieved at current density of 5 mA/cm^2, 150 mL/min, final pH of 6-8, and initial fluoride concentration of 10 mg/L. Another study about fluoride removal was conducted by Un *et al.* (2013) using a batch EC reactor with aluminium electrodes for defluoridation of 5 mg/L fluoride-containing water. To obtain the best removal efficiency, the current density was changed between 0.5 to 2 mA/cm^2, the initial pH range between 4 to 8, and electrolyte concentration between 0.01 to 0.03 moles of Na_2SO_2. The highest removal efficiency of 97.6% was achieved after 30 min of electrolysing at current density, initial pH, and electrolyte concentration of 2 mA/cm^2, 4, and 0.01 mole respectively.

Additionally, the EC method was efficiently used to remove phosphate and nitrate from water and wastewater. Behbahani *et al.* (2011) studied phosphate removal from synthetic water samples using EC technology. In this study, phosphate removal was performed using two different types of electrodes (Al and Fe) taking into accounts the effects of the initial pH (3 to 10), current density(8.33 to 2.5 mA/cm^2), treatment time (0 to 40 min), and the initial concentration of phosphate (25 to 400 mg/L). The results showed that after 40 min of treatment at pH of 3, current density of 25 mA/cm^2, and initial concentration of phosphate of 400 mg/L, the aluminium electrodes achieved a removal efficiency of 100%, while the iron electrodes achieved 84.7%.

Govindan *et al.* (2015) used a batch flow EC cell, supplied with two different types of electrodes Al-Fe (anode – cathode) and Fe-Fe, to denitrify synthetic drinking water samples containing 100 mg/l of nitrate. The denitrification process was optimised for different current densities (0 to 25 mA/cm^2), treatment time (0 to 180 min), and electrolyte concentration (0 to 500 ppm). The outcomes showed that, after 180 min of electrolysing at 25 mA/cm^2 and with 100 ppm of NaCl, the nitrate removal was 92% for Al-Fe electrodes, and 80% for Fe-Fe electrodes.

2.4.9 Influence of liquid chemistry on the EC method.

In spite of the proven efficiency of the EC technology to remove a vast number of pollutants from aqueous media, its performance is highly influenced, negatively or positively, by the chemistry of the liquid being treated. It has been found that the presence of chloride or magnesium ions in water being treated enhances the performance of the EC units (Huang *et al.*, 2009; Heffron, 2015). Chloride inhibits the formation of the inert metallic film of the anode surface and accelerates anode dissolution rate by pitting corrosion, which enhances both generation of coagulants and current efficiency (Huang *et al.*, 2009). While, the presence of magnesium to a certain level enhances the performance of EC units by making the flocs bigger and denser, which greatly facilitates their precipitation (Heffron, 2015).

Conversely, it has been well documented that the presence of some competitive ions (such as phosphate, silica, or organic matter) and/or the initial pH of liquid being treated can significantly decrease the efficiency of the EC cells (Hu *et al.*, 2003; Heffron, 2015; You and Han, 2016). For instance, Hu *et al.* (2003) found, during defluoridation of water samples using an EC cell with aluminium electrodes, that the presence of sulphate ions in water decreases the fluoride removal efficiency. The same negative impact of sulphate on the performance of the EC units was observed by Huang *et al.* (2009), where the latter noticed, during cadmium removal from water, that no reaction took place during 10 min of electrolysing due to the presence of sulphate ions in the water being treated. The authors believed that sulphate ions inhibit the corrosion of Al electrodes, which in turn decreases the removal efficiency. Silicate and phosphate play a very negative role in the electrochemical removal of other pollutants such as arsenic (Roberts *et al.*, 2004; Wan, 2010). Where, during the electrolysing of 0.5 mg/L arsenic containing water using iron electrodes, (Roberts *et al.*, 2004) found that the presence of 30 mg/L of silicate in water reduces arsenic removal by 90%. Moreover, the authors found that the presence of 3 mg/L of phosphate cause the same influence as 30 mg/L of silicate. Similar findings were obtained by Wan (2010), the latter found that the presence of 4 mg/L of phosphate, during the electrolysing of 0.1 mg/L of arsenic containing water, inhibits arsenic removal. The authors explained this decrease in removal efficiency by competition between arsenic ions and phosphate and silicate ions to occupy the active sites on the surface of freshly generated coagulants.

The presence of organic matter (OM) represents one of the major challenges for water treatment, not because it reduces the efficiency of EC units only, but because it possesses the ability to chelate inorganic pollutants or to react with water disinfectants forming toxic compounds (Ghernaout *et al.*, 2009; Ben-Sasson *et al.*, 2011; Khandegar and Saroha, 2013). For instance, You and Han (2016) conducted an investigation about the influence of OM on the treatability of arsenic-containing water using an EC cell. The obtained results showed that, in the absence of OM, the EC method required only 15 min to remove 100% of arsenic. But, the presence of 20 mg/L of OM was enough to drop the removal efficiency from 100% to only 35%. Another study was conducted by Farrokhi *et al.* (2013) to investigate the influence of OM on the cyanide oxidising process. In this study, water samples with a cyanide content of 100 mg/L were treated for 120 min at a pH of 7, and 1 g/L of titanium dioxide (UV/TiO_2). The obtained results showed that the presence of 100 mg/L of OM decreased the removal efficiency by about 40%.

In fact, the presence of OM significantly reduces the performance of the EC units through several combinations of reasons. A broad body of experimental evidence proved that OM promotes the formation of a passive metallic layer on the surface of the anodes, maximises energy consumption, and negatively influences the properties of the generated flocs (Matilainen *et al.*, 2010; Ben-Sasson *et al.*, 2011; Pallier *et al.*, 2011; Khandegar and Saroha, 2013). Therefore, the following section has been allocated to highlight the influence of OM on the performance of water treatment methods, especially the EC units.

2.5 Impact of organic matter on water treatment process

Organic matter (OM), which is a grouping of carbon containing compounds, is a major component of the aquatic environment, where it can be found in all surface, ground, and reservoir waters, industrial effluents, and agricultural wastewater (Pettit, 2004; Matilainen *et al.*, 2010; Zheng *et al.*, 2013; Pivokonsky *et al.*, 2015). The occurrence of this pollutant in water is a result of the interaction between the hydrological cycle and the geosphere and biosphere. Chemically, the structure of the OM contains carbon atoms along with different elements such as hydrogen, nitrogen and oxygen depending on its origin. The quantity and chemical composition of the OM vary significantly depending on the origins of water or wastewater (Särkkä *et al.*, 2015; Ulu *et al.*, 2015). For instance, phenols, pesticides, and aliphatic compounds can be found in industrial and agricultural wastewater (Zheng *et al.*, 2013), while the natural organic matter (NOM) that derives from the residuals of plants and animals, and humic substances, are result from the surrounding environment (Ghernaout *et al.*, 2009; Pivokonsky *et al.*, 2015). Furthermore, the quantity and composition of the OM may seasonally vary in the same location within the aquatic environment (Matilainen *et al.*, 2010; Pivokonsky *et al.*, 2015). This variation in quality and quantity of OM exerts significant influences on selection, design and performance of treatment methods (Teixeira and Nunes, 2011; Särkkä *et al.*, 2015). Moreover, the worldwide increasing trend in the quantity of OM represents a challenge to water treatment utilities (Ghernaout *et al.*, 2009; Särkkä *et al.*, 2015). For instance, nowadays the global refining industry produces about 40 billion litres of polluted water every day (Esmaeilirad *et al.*, 2015).

It is noteworthy that the concentration of OM in water is generally measured by either biochemical oxygen demand (BOD) or chemical oxygen demand (COD) (Attiogbe *et al.*, 2007; Tchobanoglous and Burton, 1995). BOD is defined as the required quantity of oxygen, usually expressed by either mg/L or parts per million (ppm), for the bacteria to oxidise organic matter in water. Usually, this test is conducted at room temperature (20 ^{o}C) for a specific period (usually 5 days) (Attiogbe *et al.*, 2007; Dhillon *et al.*). While, the COD is defined as "as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant" (Dhillon *et al.*). In fact, the COD test has many advantages, for instance it is simple and takes a much shorter time (about 2 hrs) in comparison to the BOD test that normally requires 5 days (Attiogbe *et al.*, 2007; Dhillon *et al.*, 2013).

2.5.1 Influence of OM on quality and treatability of water

The presence of OM in water has significant negative impacts on organoleptic properties and treatability of water (Matilainen *et al.*, 2010). For instance, it promotes the microbial growth, increases coagulants consumption, reduces the effect of water disinfectants, and it possesses the ability to react with most of the chemical pollutants in nature forming pollutants that are less prone to coagulate, and it produces unwanted colour, taste, and odour (Ghernaout *et al.*, 2009; Pivokonsky *et al.*, 2015). Even worse, a broad body of evidence has shown that OM causes serious health problems, such as cancer, due to its ability to react with water disinfectants, especially chlorine, forming toxic disinfection by-products (DBPs) such as trihalomethanes (THM) and haloacetic acids (HAA) (Ghernaout *et al.*, 2009; Matilainen *et al.*, 2010).

Due to these serious impacts, the US Environmental Protection Agency (USEPA) and the European countries strictly regulate OM and its by-products in drinking water. For instance, the European Union countries recently limited BOD and THM in drinking water to 6 mg/L and 0.1 mg/L, respectively, while the USEPA limits THM and HAA in drinking water to 0.08 and 0.06 mg/L (Ghernaout *et al.*, 2009; Ulu *et al.*, 2015; Yasin *et al.*, 2015).

2.5.2 OM treatment methods

To meet the mentioned strict limitations for OM and its by-products in drinking water, a wide range of treatment technologies have been suggested to eliminate OM from drinking water, such as coagulation, adsorption on activated carbon, membrane filtration, and EC (Ulu *et al.*, 2015; Matilainen *et al.*, 2010). Unfortunately, no single treatment method alone can completely treat the OM matter because of the high variation in the quantity and chemical composition of OM (Särkkä *et al.*, 2015). For instance, OM is responsible for the fouling of the membranes that negatively influences the efficiency of the membrane filtration process (Huang *et al.*, 2008; Al-Amoudi, 2010). It negatively influences the coagulation process by reacting with most of the chemical pollutants to form complexes less prone to coagulate, and it increases the coagulants demand (Pallier *et al.*, 2011).

Furthermore, OM negatively influences the adsorption process due to blocking the adsorption sites on the surface of adsorbents, which in turn significantly reduces removal efficiency (Teixeira and Nunes, 2011).

Additionally, Farrokhi *et al.* (2013) reported that using nano-oxidants to remove cyanide from water is high influenced by the presence of OM, where they found that the presence of 100 mg/L of OM decreased the removal efficiency by about 40%.

The influence of OM on the EC technology is explained in the following section.

2.5.3 Impacts of OM on EC technology

In spite of the acknowledged advantages of EC technology to treat a wide spectrum of pollutants from water and wastewater, its efficiency is considerably influenced by some parameters such as the chemistry of the solution being treated (Wan *et al.*, 2011). Due to the high reactability of OM with most of the chemicals found in the water forming different complexes (Ghernaout *et al.*, 2009), and thereby changing the chemistry of water, OM significantly influences the performance of the EC method. For instance, Fan *et al.* (2016) used carbon electrodes to treat 0.2 mg/L arsenic-containing water samples. The latter reported that the presence of 20 mg/L of OM was enough to reduce arsenic removal efficiency by about 45%.

Generally, the impacts of the OM on the EC method can be summarised as follows:

- OM chelates some of the target inorganic pollutants forming a complex that is difficult to remove, which in turn reduces the removal efficiency (Chen *et al.*, 2012; Xu *et al.*, 2015; Huang *et al.*, 2016).
- In iron-based electrodes, OM tends to react rapidly with the freshly generated ferrous coagulation ions, a process that disables flocs formation (Ben-Sasson *et al.*, 2011; Heffron, 2015).
- OM coats the inorganic pollutants that inhibits their coagulation (Ghernaout *et al.*, 2009).
- It promotes the growth of the passive oxide film on the anode that decreases the number of cations at the anode, and consequently minimises the rate of floc formation and the adsorption of pollutants (Khandegar and Saroha, 2013; Mohora *et al.*, 2014) .
- OM reacts with chlorides, which is important to enhance water conductivity and to inhibit the formation of the anodic layer, forming toxic by-products (Khandegar and Saroha, 2013; Pivokonsky *et al.*, 2015).
- The presence of OM reduces the size of the formed flocs because of the more negative zeta potential, which in turn negatively influences the coagulation process (Pallier *et al.*, 2011; Mohora *et al.*, 2014).
- OM competes for active adsorption sites on flocs decreasing the removal of the targeted pollutants (Matilainen *et al.*, 2010; Mohora *et al.*, 2014).

- Fractionation of high molecular weight organic compounds during EC produces hydrophilic and low molecular weight compounds, leading to a poor coagulation process (Ghernaout *et al.*, 2009; Pallier *et al.*, 2011).
- OM increases the energy consumption of the EC units due to promoting the growth of an impermeable oxide layer on the anode, which in turn resists the electric current (Matilainen *et al.*, 2010; Khandegar and Saroha, 2013).

A good example of the OM impacts on the EC method is the heavy metals removal from drinking water in the presence of OM. For instance, using EC technology, Kobya *et al.* (2014) reduced arsenic concentration in drinking water from **150 to 6.3** µg/L (96%) in less than 6 min retention time at a current density of 0.25 mA/cm^2, and A/V (electrodes area/volume of water) of 0.24 cm^{-1}. However, in the presence of $9.31 \pm 0.51\ \mathrm{mg/L}$ of organic matter, Mohora *et al.* (2012) needed, with the same A/V, 90 min of electrolysis at a current density of 5.78 mA/cm^2 to reduce the arsenic concentration from only **45 to 6.2** µg/L (85%). Furthermore, Mohora *et al.* (2012) added an additional $60\ \mathrm{mg/L}$ of $\mathrm{Cl^-}$ to an EC unit in order to breakdown the anodic oxide layer that was promoted by the presence of the OM. This example reveals that the presence of OM increased the required retention time and the consumed energy by 15 and 23-fold respectively, to remove 1/3 of the arsenic concentration that was removed in the absence of OM. Moreover, Mohora *et al.* (2012) used high chloride concentration to enhance the performance of the EC unit, which gives a high probability of forming toxic by-products.

Due to the mentioned significant impacts of the OM on water treatability and performance of treatment methods, this study focuses on the development of a new, cost effective, and environmentally friendly hybrid method to remove heavy metals from water in the presence of OM. This method is a combination of microwave and EC technologies (microwave assisted- EC). For better understanding of MW effects on the removal of water pollutants, it would be necessary to allocate the following chapter to explain the fundamentals, theory, and applications of MW in water and wastewater treatment.

2.6 Advantages and disadvantages of the EC technology

2.6.1 Advantages

- The EC method does not produce secondary pollutants as it does not required chemical additives, which makes it a green technology (Chaturvedi and Dave, 2012; García-García *et al.*, 2015).
- In comparison with the traditional coagulation process (such as adding $FeCl_3$ followed by sodium hydroxide or lime dose), the flocs formed by the EC method have very low water content that significantly reduces the volume of the sludge produced (Olmez, 2009; Zodi *et al.*, 2009). It has been found that the EC units produce about 50% less sludge than traditional coagulation processes (Barrera-Diaz *et al.*, 2011). This significant reduction in sludge volume greatly reduces the cost of sludge dewatering and handling, which in turn reduces the operating cost of the EC units (Olmez, 2009).
- The EC method forms large and dense flocs that accelerate the settling process (Larue *et al.*, 2003). These properties greatly enhance the filterability of the produced solution, which is very advantageous for the filtration units that followed the EC units (Al-Shannag *et al.*, 2013).

- It has a large treatment capacity and a relatively short treatment time, where adsorption of hydroxide on coagulants in EC technology is 100 times greater than in the traditional coagulation process (Mollah *et al.*, 2004).
- In comparison with traditional chemical and biological treatment methods, the EC units are able to remove very small particles, as the fine charged particles are more easily attracted to the electric field (Mollah *et al.*, 2004).
- Selectivity is another important advantage of the EC method (Mollah *et al.*, 2004), for instance nitrate reduction can be controlled by the chemical composition of electrodes and the operating parameters such as the initial pH, and current density (Reyter *et al.*, 2006).
- The EC treatment plant is relatively small in size as it does not require rapid mixing or dilution tanks, large sedimentation pools, and chemical storage (Zhu *et al.*, 2005; Kuokkanen, 2016). In addition, the required simple and easy to use equipment, makes it a cost effective alternative (Mollah *et al.*, 2004; García-García *et al.*, 2015).
- Using solid electrodes, such as aluminium and magnesium, makes the EC units more transportable and incorporable (into packaged plants), which in turn makes this method suitable for emergency water supply (Zhu *et al.*, 2005).
- Due to the low electricity consumption, using the EC method becomes possible in rural areas as the required energy can be driven from windmills or an attached solar panel (Chaturvedi and Dave, 2012; Deokate, 2015; Kuokkanen, 2016).
- The sludge produced by the EC units has higher dry and hydrophobic solids than that formed by the tradition coagulation process (Martínez-Huitle and Brillas, 2009), and tends to be stable in a non-hazardous form as metallic oxides/hydroxides (Mollah and Schennach, 2001; Barrera-Diaz *et al.*, 2011; Kuokkanen, 2016). It has been proved that heavy metals leaching from the EC sludge, according to the

Toxicity Characteristic Leaching Procedure (TCLP), was within the permissible limits of the Environmental Protection Agency (EPA) (Addy *et al.*, 2011). These facts makes the EC sludge one of the favourable additives for construction materials, for instance EC sludge was successfully used in the production of concrete (Barrera-Diaz *et al.*, 2011), and cement mortar (Banerjee and Chakraborty, 2005).

- One of the main by-products of the EC units is hydrogen gas (Nasution *et al.*, 2011; Lakshmi *et al.*, 2013), which is categorised as an environmentally friendly and high energy fuel ($122\ kJ/g$) (Eker and Kargi, 2010). Therefore, recovery of hydrogen gas is considered to be one of the important advantages of the EC technology, where Phalakornkule *et al.* (2010) reported that about 5.8 to 13% of the required electrical energy to operate the EC unit can be produced from the generated hydrogen gas.
- It requires less maintenance as it consists of metallic plates and source of power (Emamjomeh, 2006; Hashim *et al.*, 2017a).
- Finally, EC technology has the ability to treat a wide range of pollutants efficiently such as heavy metals, oil, dyes, bacteria, and fluoride (Zhu *et al.*, 2007; Yehya *et al.*, 2014; Genc and Bakirci, 2015). This efficient performance makes EC technology suitable to treat different types of industrial wastewater such as tannery, paper mill, and textile effluents (García-García *et al.*, 2015).

2.6.2 Disadvantages

EC technology, like any other treatment technology, has some drawbacks that could influence its performance. For instance:

- The electrodes should be periodically replaced as they dissolve into the solution due to the oxidation process (Emamjomeh, 2006; Tamne *et al.*, 2015).

- The formation of an oxide film on the surface of the anode during the electrolysing process reduces the anode dissolution, which in turn reduces the pollutants removal efficiency (Mansour *et al.*, 2013). Moreover, this film maximises energy consumption (Heffron, 2015), and limits hydrogen recovery (Yang *et al.*, 2015). However, the negative influence of this film could be reduced by different techniques such as using an alternating current technique (Mansour *et al.*, 2013), adding (at least) 60 mg/L of chloride to the solution being treated (Heffron, 2015), avoiding large inter-electrode distances (Ghosh *et al.*, 2008). The addition of anti-passivation agents (Mechelhoff *et al.*, 2013), aeration or increasing the turbulence (Mohora *et al.*, 2014), and periodically cleaning electrodes (Kuokkanen, 2016) can control the growth of the oxide film.
- The EC method requires sufficient conductivity to perform; thus the conductivity of natural water or low conductivity wastewater must be increased by adding a supporting electrolyte (Mollah and Schennach, 2001; Kuokkanen, 2016). However, industrial effluents usually have high enough conductivity that eliminates the need for supporting electrolytes (Kuokkanen, 2016).
- The EC technology still has a deficiency in the variety of reactor design (Un *et al.*, 2013); where most of the EC reactors have parallel plate monopolar or bipolar electrode configuration systems.
- The probability of toxic chlorinated-organic compounds formation; it has been reported that treating chlorides and organic matter containing water using the EC method could form toxic compounds (Kabdaşlı *et al.*, 2012; Kuokkanen, 2016). Therefore, high chloride concentration should be avoided.
- The performance of the EC units, in terms of heavy metals removal, is highly influenced by the presence of OM in the water being treated (Pallier *et al.*, 2011;

Mohora *et al.*, 2014). It has been shown that OM possess the ability to chelate the heavy metals in water forming complexes that resist coagulation (Chen *et al.*, 2012; Xu *et al.*, 2015; Huang *et al.*, 2016).

In addition, there is a real deficit in the modelling of EC performance, which is very important to design, optimise, and reproduce the performance of the EC units (Kuokkanen, 2016).

The last two disadvantages of the EC technology reveal the significant impact of the OM on the performance of the EC units and the quality of treated water. Moreover, with the wide occurrence of OM and heavy metals in water and wastewater (Nanseu-Njiki *et al.*, 2009; Matilainen *et al.*, 2010; Phadke, 2014; Särkkä *et al.*, 2015), it is expected that all EC treatment plants are exposed to these negative influences. Thus, the current project has been devoted to enhance the performance of EC, in terms of heavy metal removal in the presence of OM, by applying a MW field.

2.7 Chapter summary

The following table summarises the influence of OM on the performance of some widely used treatment methods along with the main advantages and disadvantages of these methods.

Table 2-2: Advantages, disadvantages, and influence of OM on the performance of some widely used treatment methods.

Method	Advantages	Disadvantages	References
Chemical coagulation	• It reduces the time required to settle out suspended particles, which enhances the performance of other treatment units. • Chemical coagulation efficiently reduces odour and turbidity. • It is one of the effective methods to remove microorganisms, such as protozoa, bacteria and viruses.	• Produces large volume of sludge, which increases sludge handing cost. • The generated sludge may require further treatment before disposal due to non-biodegradability of synthetic polymer. • High sensitivity of inorganic coagulants to pH level limits its applicability. • Possibility of pollution of treated water with traces of toxic synthetic polymeric or residual iron and aluminium ions. • It is difficult to maintain an accurate dosing rate, because the latter depends on water quality that may vary rapidly.	(Cristina *et al.*, 2007; Borchate *et al.*, 2014; Sorlini *et al.*, 2015)
Reverse osmosis (RO)	• It is a reliable treatment method. • RO efficiently removes almost all microorganisms, such as the viruses, bacteria and protozoa. • It possess the ability to remove several pollutants simultaneously (jointly removal).	• High operating cost in comparison with other method. • It requires pre-treatment units to protect the membrane from obstruction of the pores. • Re-mineralisation of produced water is required as this technique removes salts and minerals.	(Amer, 2004; Sorlini *et al.*, 2015; Golder, 2009)

		• Presence of high concentrations of OM causes membrane fouling, therefore it requires pre-treatment.	
Biological methods (Aerobic and anaerobic)	• High treatment capacity in comparison with other methods. • No secondary pollution. • Efficient reduction of odours. • Production of biogas, which can be recovered to produce energy. • It efficiently stabilises both soluble and solid organic matter. • Effective stabilisation of nitrogen. • Co-fermentation by taking up other organic wastes.	• Bacteria is very sensitive to oxygen concentration, therefore biological treatment plants could fail due to the lack of oxygen. • Very sensitive to environmental parameters, such as ambient temperature. • It requires a long starting time. • Its performance is highly limited by the chemical composition of water being treated, as strong chemicals kill the bacteria. • Biological reduction of azo dyes under anaerobic conditions forms aromatic amines, which categorised as carcinogens.	(Danesh *et al.*, 2000; Chan *et al.*, 2009; Koboević and Kurtela, 2011; Lourenço *et al.*, 2015).
Ultra Violet (UV)	• UV efficiently inactivate microorganisms. • UV units can be designed to fit any size of drinking water treatment need.	• Its efficiency is highly influenced by the presence of natural organic matter (NOM). • Direct exposure to UV causes serious health problems.	(Steven and William, 2006; Hijnen *et al.*, 2006; Vilhunen *et al.*, 2009)

	• Its performance is independent of water temperature and pH. • In contrast to traditional disinfection methods, UV treatment units do generates toxic disinfection by-products	• The penetration of UV light is highly limited by the cloudiness of water being treated, where the UV light will not penetrate highly turbid or coloured water. • It has a short-lasting disinfection effect, as it is unable to provide a residual.	
Ozonation	• An effective disinfectant. • Ozonation is an eco-friendly technology. • Ozone is exceptionally faster and more powerful disinfectant in comparison with chemical ones. • It efficiently remediates taste, odour, colour and other mineral compounds. • Ozone oxidation is less dependent on pH than for other oxidants.	• The reactivity of OM (such as EDTA) with ozone is greatly weakened as a result of metal complexation. • Ozone disinfection could be accompanied by the formation of bromate, which increases with increasing ozone dose. • Some chemical additives (such as ammonia) or expensive procedures are required to control bromate formation. • High ozone dosages make the removal of NOM more difficult due to breaking down it into smaller molecular weight.	(Bollyky, 2002; Gad, 2010; Fang *et al.*, 2013; Dastan and Masoodi, 2015; Huang *et al.*, 2016)
Electrocoagulation (EC)	• A cost effective method in comparison with traditional ones. • It does not produce secondary pollutants.	• The electrodes should be periodically replaced. • Formation of oxide film on the surface of the anode during the electrolysing process reduces	(Chaturvedi and Dave, 2012; García-García *et al.*, 2015; Olmez, 2009;

	• It does not required chemical additives. • The sludge produced by the EC units is small in size and has higher dry and hydrophobic solids than that formed by the tradition methods. • It has a large treatment capacity and a relatively short treatment time. • EC units are able to remove very small particles. • Selectivity is another important advantage of the EC method. • EC units are more transportable and incorporable, which makes it suitable for emergency water supply. • EC units produce hydrogen gas, which is high-energy fuel, as by-product. Recovery of this gas could provide a considerable amount of energy. • It requires less maintenance	the anode dissolution, which in turn reduces the pollutants removal efficiency. Moreover, this film maximises energy consumption. • The EC method requires a sufficient conductivity to perform. • The EC technology has a deficiency in the variety of reactor design. • The performance of the EC units, in terms of heavy metals removal, is highly influenced by the presence of OM in the water being treated.	Zodi *et al.*, 2009). (Larue et al., 2003). (Mollah et al., 2004) (Reyter et al., 2006). (Zhu et al., 2005; Kuokkanen, 2016). (Nasution et al., 2011; Lakshmi et al., 2013),

CHAPTER 3

MICROWAVES – REVIEW

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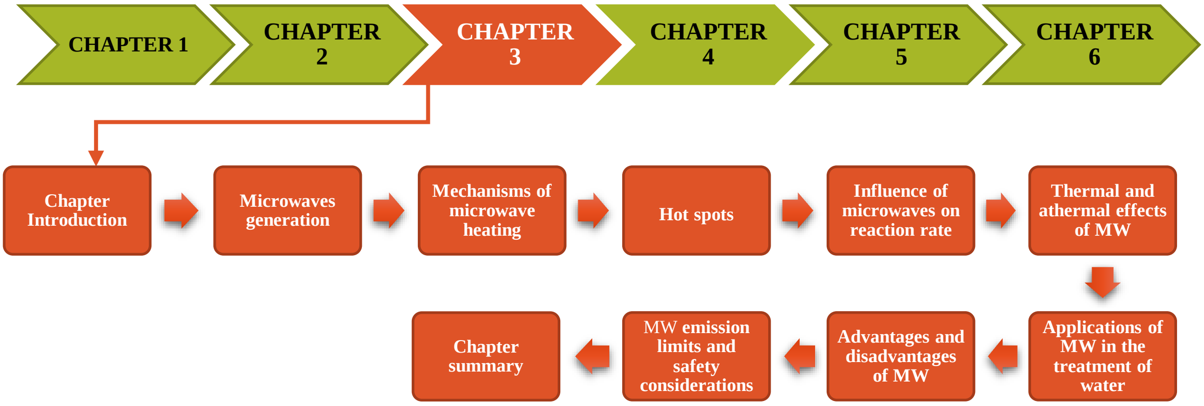

3.1 Chapter introduction

Microwave (MW) is a form of electromagnetic waves with a frequency range between 300 MHz and 300 GHz and a wavelength range between 1m at 300 MHz to 1 mm at 300 GHz (Wong and Gupta, 2015). This wide range of frequencies is divided into three major microwave bands: the ultra-high frequency (UHF) (300 MHz to 3 GHz), the super high frequency (SHF)(3 GHz to 30 GHz), and the extremely high frequency (EHF) (30 GHz to 300 GHz) band (Scott, 2005). Although the fundamentals of the electromagnetic theory were introduced by Maxwell in 1873 (Pozar, 2012), microwaves were technically introduced for the first time in 1932 by Nello Carrara to describe the electromagnetic wave band above 1 GHz (Sorrentino and Bianchi, 2010). Microwave technology attracted substantial interest during the 1940s due to the urgent military demand for enhanced communications and radars, and this period became synonymous with the innovation of viable radar technology (in 1941) (Bassyouni *et al.*, 2011; Wong and Gupta, 2015).

The heating ability of the microwaves was accidently discovered during the Second World War (in 1945) by Percy LeBaron Spencer, when the latter noticed that his candy had melted while he was testing a radar magnetron (Hayes, 2002; Bijanzad *et al.*, 2015).

Percy Spencer, who was an engineer in Raytheon, patented microwaves' applicability for food processing that led to the manufacture of the microwave oven in 1947, however this oven was limitedly used due to its high cost, heavy weight (about 317 kg), and large size (about 1.8 m tall) (Bassyouni *et al.*, 2011; Wong and Gupta, 2015). The intensive investigations, during the period 1960 and 1975, into microwave applications led to the manufacture of a smaller and affordable microwave ovens, and by 1978 the first laboratory microwave was produced and marketed by CEM (Bassyouni *et al.*, 2011; Wong and Gupta, 2015).

3.2 Microwaves generation

Although microwave systems are available in different configurations each designed for specific applications, they mainly consist of two basic elements, a microwave generator (such as magnetron) to produce microwave power, and a transmission line (such as the waveguide) to transmit microwave energy (Scott, 2005).

A magnetron is a high power microwave generator consisting, basically, of a cathode surrounded by a vacuum anode tube (Darwish, 2012; Pozar, 2012). Although magnetrons produce high output noise and do not maintain a stable output frequency, they have many advantages such as moderate average power, high peak power, high efficiency (about 80%), and low cost (Scott, 2005; Pozar, 2012). In operation, the magnetron generates a rotating cloud of electrons around its cathode, then the energy can be transferred from the electron beam to radio frequency (Pozar, 2012). The generated microwaves are conveyed from one point to another using microwave guiding structures such as waveguides (Orfanidis, 2002). A waveguide can be defined as a hollow metal pipe with a rectangular, oval, or circular cross section that works in a similar way to a water pipe; microwaves travel from one component to the next through the waveguide (Scott, 2005). These two basic parts can be connected to other components to produce different configurations each offering performance characteristics designed for specific applications such as communications, heating, and radars.

3.3 Mechanisms of microwave heating

Traditionally, the heating process is conducted by transferring heat from an external source, passing through the walls of the container, to the targeted substance (Wong and Gupta, 2015). This makes the temperature of the container higher than that of substance until they attain the equilibrium state, which may take hours (Hayes, 2002; Wong and Gupta, 2015). This heating process is considered as uncontrollable because, conductive heat inhibits the operator's control over the chemical reaction. Thus, a cooling process must be conducted after removing the external source of heat to reduce the bulk internal temperature, i.e., it does not follow "instant on-instant off", and the heat transfer rate is influenced by the thermal conductivity of container material (Hayes, 2002).

Microwave heating, in contrast, is vitally different from the traditional heating process as the MW energy couples with the molecules of the substance being heated, which means the heat is generated from within the mixture without heat transfer (Hayes, 2002; Bassyouni *et al.*, 2011). MW heat is independent of the thermal conductivity of the container because it is generated through the direct absorption of MW energy by the targeted substance (Wong and Gupta, 2015). Therefore, MW results in a rapid superheating of the substance that produces enormous accelerations in many chemical reactions, which cannot be produced by traditional heating. In fact, MW heating helps to perform some chemical reactions that are impossible to occur by the traditional heating (de la Hoz *et al.*, 2005). Additionally, MW heating enables operators to control reactions as the heating process instantaneously stops when the MW energy is switched off, i.e. it is described as “instant on-instant off” (Hayes, 2002).

The magnitude of MW energy that is absorbed by a mass unit of the substance being heated can be calculated using equation 16 (Lee *et al.*, 2012):

$$P_{abs} = 2\pi f \in_0 \in''_{eff} E^2 \qquad \textbf{(16)}$$

where, $f, \in_0, \in''_{eff},$ and E^2 represent the MW frequency in Hz, the permittivity of MW in the space (8.854 x 10^{-12} in F/m), the complex component of the relative permittivity of the dielectric, and the electric field (V/m), respectively (Lee *et al.*, 2012). In addition, P_{abs} can be calculated using equation 17:

$$\frac{\Delta T \,.\rho \,.C_p}{\Delta t} = P_{abs} \qquad \textbf{(17)}$$

where $\Delta T, \rho, C_p,$ and Δt are the change in substance temperature (^{o}C), density of the substance (kg/m^3), the specific heat of the substance in (J .kg^{-1} .^{o}C^{-1}), and heating duration (sec).

Substitution of Eq. (16) in Eq. (17) yields the following equation that can be used to calculate the magnitude of MW energy that absorbed by a mass unit of the substance per time unit:

$$\frac{\Delta T \,.\rho \,.C_p}{\Delta t} = 2\pi f \in_0 \in''_{eff} E^2 = 5.563 \text{ x } 10^{-11} f \in''_{eff} E^2 \qquad \textbf{(18)}$$

Indeed, there are two basic mechanisms to heat substances that are subjected to the MW field; dipolar polarization and ionic conduction (Collins, 2010; Darwish, 2012; Schwenke *et al.*, 2015).

Dipolar polarization is a phenomenon of polar (dipole) molecules agitation due to the influence of MW field; where these molecules will be change their direction in a rotational motion to orient themselves with the swiftly oscillating electric field. This ultrafast rotational motion, about 2.45 billion times/sec for MW frequency of 2.45 GHz, of molecules rapidly elevates the temperature of the targeted substance due to molecular friction (Collins, 2010; Veitía and Ferroud, 2014; Schwenke *et al.*, 2015). This mechanism is responsible for the majority of MW heat generation (Darwish, 2012).

The second mechanism, ionic conduction, occurs if the targeted substances have free ions, where, these free ions will be set in an ionic motion when the molecules start the rotational motion (previously mentioned), which produces extra MW heat (Hayes, 2002; Collins, 2010; Schwenke *et al.*, 2015). Figure 3-1 shows the difference between traditional and MW heating processes.

In fact, besides the previously mentioned two mechanisms, there is another important thermal phenomenon that occurs during the MW heating process called "hot spots" that significantly influences the degradation of organic pollutants and the reaction rate (Xu *et al.*, 2014; Wang and Wang, 2016).

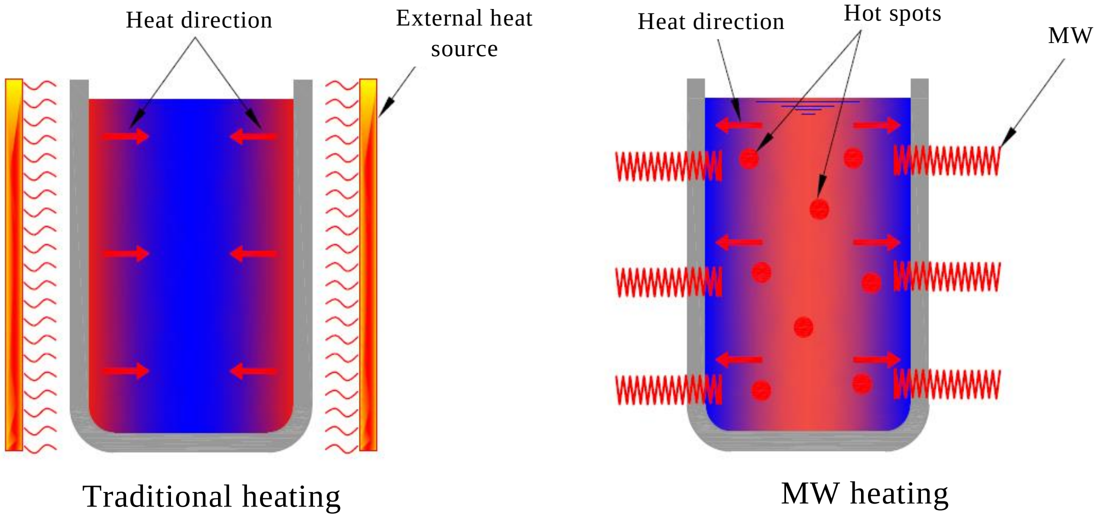

Figure 3-1: Schematic of traditional and MW heating processes.

3.4 Hot spots

A broad body of authors proved that MW heating is accompanied by the generation of some extremely hot microscopic zones (called hot spots) within the substance being heated. The temperature in these spots is significantly higher than those of other zones (de la Hoz *et al.*, 2005; Zhang *et al.*, 2007; Sánchez, 2008; Xu *et al.*, 2014; Wang and Wang, 2016). Where the temperature in these microscopic spots, 100 µm in size, is about 100 – 200 ^{o}C higher than the bulk temperature (de la Hoz *et al.*, 2005), and can reach 1000-1200 ^{o}C on the absorbent surface (Zhu *et al.*, 2007; Fu *et al.*, 2010; Xu *et al.*, 2014).

Hot spots are formed by the inhomogeneity of the MW magnetic field, by the difference in conductivity properties of materials, or by volumetric dielectric heating under MW environments (de la Hoz *et al.*, 2005). These extremely hot points greatly enhance the degradation of organic pollutants (Xu *et al.*, 2014), accelerate the chemical reactions (de la Hoz *et al.*, 2005), and help chemists to avoid the decomposition of thermally unstable compounds (Bassyouni *et al.*, 2011). It is noteworthy that using multimode or commercial MW ovens without stirring probably raises the temperature of the hot spot to explosion limit (Sánchez, 2008). However, intermittent stirring or rotation of a sample being heated prohibits the generation of hot spots (Sánchez, 2008; Dankovich, 2014).

Therefore, MW irradiation is described as a selective, volumetric, and controllable heating method (Schwenke *et al.*, 2015). For the mentioned reasons, MW heating has been substantially used in a broad spectrum of applications such as organic water and wastewater treatment, chemical applications, polymers industries, and treatment of polluted soils (Wang and Wang, 2016).

3.5 Influence of microwaves on reaction rate

Typically, a reaction starts with reactants that have an amount of energy less than that required to start the transformation process; therefore, these reactants need extra energy (E_a, the activation energy) to collide in a geometrically right orientation and start the transformation (reach the transition state), Figure 3-2 (Hayes, 2002). Once this additional amount of energy, which must be absorbed from the reaction environment, becomes available, the reaction starts rapidly yielding the final products (with low energy) (Bassyouni *et al.*, 2011). Usually, in such reactions, the required energy is driven from external heat sources such as MW or traditional heat sources. MW irradiation, in comparison with the traditional heating, rapidly provides the required momentum to complete the reaction without influencing the activation energy (Hayes, 2002). Furthermore, as previously mentioned, the MW heating process will not decompose the thermally unstable compounds that might be present in the reaction environment.

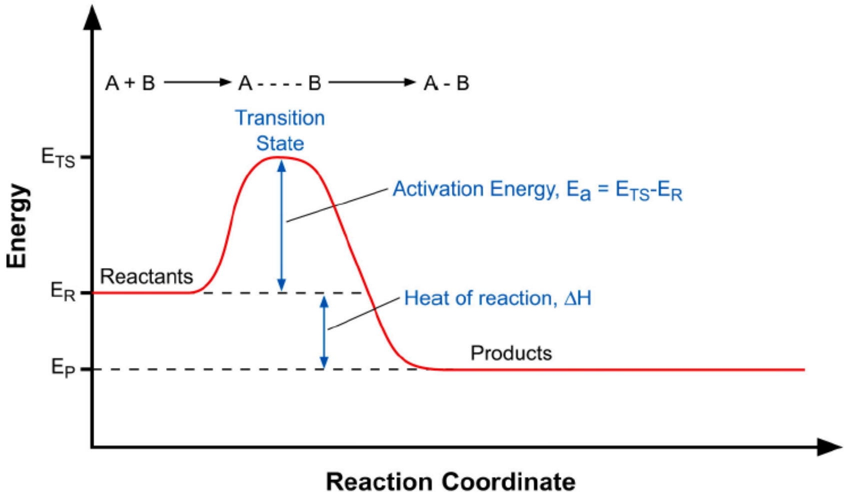

Figure 3-2: Typical reaction coordinate (Bassyouni *et al.*, 2011).
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In fact, the enhancement or acceleration of the chemical reactions by the MW irradiation cannot be explained by rapid heating alone (de la Hoz *et al.*, 2005; Lin *et* *al.*, 2009b). A large number of authors have extensively investigated the nature of MW influence on the different substances considering the properties of the microwaved medium, and found that the MW influence is a combination of thermal and athermal effects (Lin *et al.*, 2009b; Yang *et al.*, 2014; Wang *et al.*, 2014; Mawioo *et al.*, 2016).

3.6 Thermal and athermal effects of MW

The observed acceleration in chemical reactions during MW exposure is a combination of thermal (high bulk temperature and extremely hot microscopic spots) and athermal effect (molecular motion and polarizing fields) (de la Hoz *et al.*, 2005). Thermal effects of the MW field are related to the dissipation of MW energy into heat as a result of direct absorption of MW energy by the substance being irradiated (Yu *et al.*, 2010).

While the term athermal effects of MW refer to any effect that is not associated with temperature increase, i.e. the chemical, physical, or biochemical changes in the behavior of the substance being microwaved when the system temperature remains constant (Lin *et al.*, 2009b; Yu *et al.*, 2010; Yang *et al.*, 2014).

In fact, the existence of athermal MW effects was experimentally proved by heating a certain substance, such as ammonia-containing wastewater (Lin *et al.*, 2009b), at identical conditions, using traditional and MW heating sources, the obtained results were different in terms of products distribution and/or quantity (Obermayer *et al.*, 2009; Lin *et al.*, 2009b).

The athermal effects of the MW field are originated from several origins such as the increase in polarization of the dipolar transition state (Veitía and Ferroud, 2014), and the interaction between the MW field and the materials (de la Hoz *et al.*, 2005). The athermal MW effects increase the vibration and wriggle of the polar chains of molecules that leads to the breaking or weakening of the chemical bonds, which in turn accelerates the reactions and enhances the removal of organic and biological pollutants (Tyagi and Lo, 2012; Mawioo *et al.*, 2016; Wang and Wang, 2016).

The athermal MW effects were beneficially used in several applications such as increase biogas production (Eskicioglu *et al.*, 2007), ammonia removal from a soft drinks-plant wastewater (Lin *et al.*, 2009b), volatile fatty acid removal from landfill leachate (Yang *et al.*, 2014), and the enhancement of organic pollutant decomposition by photo-assisted reactions (Horikoshi and Serpone, 2014). Although the ability of athermal MW effects to improve and accelerate numerous reactions has been verified, a broad body of evidence has proved that the thermal MW effects play the major role in microwave applications and athermal MW effects play a supporting role to some extent (Lin *et al.*, 2009b; Eskicioglu *et al.*, 2007).

3.7 Applications of MW in the treatment of water and wastewater

The unique heating mechanism of the MW irradiation and its ability to penetrate different media such as water, sludge, and activated carbon makes it an attractive alternative for the traditional water and wastewater treatment methods (Darwish, 2012). MW technology has recently been applied, separately or integrated with other methods, to remove a broad spectrum of pollutants from water or wastewater (Mishra *et al.*, 2010; Zalat and Elsayed, 2013; Li *et al.*, 2015). Additionally, MW technology is considered as an effective disinfectant due to the combined influence of the thermal and athermal MW effects. Where, the athermal MW effects significantly increase the vibration and wriggle of the polar chains of molecules that leads to break hydrogen bonds leading to rupture the cells wall and death of the pathogens (Tyagi and Lo, 2013; Mawioo *et al.*, 2016). Another application of the MW technology in the treatment of water and wastewater is the treatment of sludge, it has been found that application of the MW field to fresh sludge can increase the quantity of the produced biogas (Eskicioglu *et al.*, 2007), and significantly reduces its volume and pathogen content (Mawioo *et al.*, 2016).

The application of the MW technology in the treatment of water and wastewater was conducted either as a separated treatment method or integrated with other methods.

3.7.1 MW irradiation as a separated treatment method

According to the literature survey, MW irradiation alone was efficiently used to disinfect water (kill pathogens), remove algae, decompose organic matter, and remove volatile and semi-volatile pollutants (Kim *et al.*, 2009; Zalat and Elsayed, 2013; Wang and Wang, 2016).

For instance, water samples containing endospores from *Bacillus megaterium*, *B. stearothermophilus*, *Clostridium sporogenes* and *Thermoanaerobacterium thermosaccharolyticum* were sterilised by Vaid and Bishop (1998) using a 600 W microwave field under controlled conditions (pressure of 14 bar, irritation time 2 to 14 min, and temperatures of 60 to 200 ^{o}C). The obtained results indicated that a complete fragmentation of the targeted endospores was achieved after 12 min of microwaving at 600 W and 140 ^{o}C. In addition, the results indicated that traditional heating, even when prolonged, did not achieve the defragmentation of spores that achieved by MW field. Kim *et al.* (2009) brought to boiling point *Bacillus licheniformis spores* containing water samples using 0.5 kW, 2 kW, and traditional heating process. The obtained results showed that, after 3 min, 2 kW, 0.5kW, and traditional heating killed 99.45%, 92.8%, and 5.4% respectively. Moreover, the obtained results revealed that the killing mechanism of MW irradiation is significantly different from traditional heating. It was found that MW ruptured the spore cortex and membranes leading to the leakage of protein of spores, while the traditional heating process did not alter the spore cortex. Lin *et al.* (2009b) investigated the ability of MW irradiation to remove ammonia nitrogen from wastewater. The findings of this study showed that microwaving wastewater samples (300 mL) containing a 500 mg/L ammonia at 750 W for 3 min was enough to remove as much as 98% of ammonia. In addition, they confirmed that athermal MW effects contribute to ammonia removal, where they brought ammonia nitrogen-containing wastewater samples to boiling point using MW irradiation and traditional heat source. The obtained results showed that the MW irradiation increased ammonia removal by about 25% more than that of traditional heating, which indicates that the presence of athermal MW effects. Pyridine removal from wastewater using MW technique was investigated by Zalat and Elsayed (2013) taking into account the influence of different operating parameters such as irradiation time, and the initial concentration of pyridine. The latter found that 5 min of irradiation, at 850 W and initial pH of 9, was enough to reduce pyridine concentration from 20 to 0.5 ppm (97.5%). Remediation of volatile fatty acid (VFA) from landfill leachate by MW irradiation, taking into account the influence of different operating parameters such as irradiation time (2 to 10 min) and MW power (100 to 750 W), was investigated by Yang *et al.* (2014). The outcomes of this investigation showed that 30.7% of VFA was removed after 8 min of microwaving at 625 W. Additionally, the authors used a traditional heating source to bring landfill leachate samples to boiling point to figure out whether the athermal MW effects contributed to the removal of VFA or not. The results showed that the MW heating achieved a removal efficiency of about 28% in comparison with 22% using traditional process, which proved that the athermal MW effects played an essential role in the removal of VFA.

3.7.2 MW as an assistance treatment method

Although MW irradiation alone was efficiently used to destroy pathogens, decompose organic matter, and remove volatile and semi-volatile pollutants, it is not able to remove other types of pollutants such as azo dyes, pesticides, and organic base compounds (Wang and Wang, 2016). Therefore, combination methods with MW technology have recently been studied, such as MW- Fenton, MW-sonolysis, and MW-oxidant (Mishra *et al.*, 2010; Asgari *et al.*, 2014; Wang and Wang, 2016).

For instance Zhang *et al.* (2007) used a combination of activated carbon and MW methods to treat water containing congo red dye. In this study, the influence of activated carbon amount (2 and 3.6 g/L), MW irradiation time (0.5 to 2.5 min), and dye concentration (10 to 90 mg/L) on degradation of dye were investigated. The results showed that 87.79% of dye was removed after 1.5 min of MW irradiation at 800 W, initial dye concentration of 50 mg/L, and 2 g/L of activated carbon. Additionally, it was found that increasing activated carbon amount from 2 to 3.6 g/L, at the same operating condition, increased the removal efficiency from 87.79% to 96.49%, while increasing MW irradiation time from 1.5 to 2.5 min was enough to degrade the dye completely. An advanced MW-activated persulphate oxidation method, with and without activated carbon, was applied by Shiying *et al.* (2009) to remove azo dye acid orange 7 from water. This advanced oxidation method depends on the sulphate radical ($SO_4^{\cdot-}$) to remove dye. The obtained results showed that, in the absence of activated carbon, microwaving water samples containing 1g/L dye for 5-7 min at 800 W and sodium persulphate/dye molar ratio of 10:1 was required for a complete dye removal. Additionally, it was found that adding of 1 g/L of activated carbon (as a catalyst) reduced the required MW irradiation time, to achieve 100% dye removal, from 5-7 to

3 min. Another study about the combination of MW irradiation and activated carbon methods to remove dyes from water was conducted by Fu *et al.* (2010). The latter applied a 800 W MW field in the presence of different dosages of activated carbon (5-30 g/L) to remove Active Brilliant Red X-3B dye from water. The influence of some operating parameters, such as irradiation time (0-10 min) and initial concentration of dye (0.2-1.2 g/L), were taken into account. The obtained results showed that 99% of the initial concentration of dye (0.8 mg/L) was removed after 8 min of microwaving in the presence of 20 g/L of activated carbon. Additionally, the researchers found the COD was decreased by 66% during this process. Asgari *et al.* (2014) used two different MW assisted methods, hydrogen peroxide (MW/H_2O_2) and sodium persulfate (MW/SPS), to eliminate 100 mg/L of pentachlorophenol from water. To achieve the optimum removal efficiency, the influence of different factors, such as MW power (200 to 600 W), SPS concentration (0.01 to 0.05 mol/L), and H_2O_2 concentration (0.01 to 0.3 mol/L), was investigated. The obtained results showed that the maximum removal efficiency, 97%, was achieved using (MW/SPS) method at MW power of 600 W, and SPS of 0.02 mole/L. While the MW/H_2O_2 method achieved a removal efficiency of 87% at the same condition with H_2O_2 concentration of 0.2 mole/L. Two different MW-assisted treatment methods, namely MW-sonolysis and MW-photolysis, were applied by Gole and Gogate (2014) to eliminate brilliant green dye from water. These bench scale experiments were performed using an ultrasonic source at 20 kHz and actual power dissipation of 39 W, a 160 W domestic microwave, two 11 W UV tubes with wavelength of 350-450 nm. For a dye concentration of 20 ppm and initial pH of 6, the maximum dye removal efficiency, 93.2%, was obtained using the MW-sonolysis method. While, the MW-photolysis achieved 84.5%. Lin *et al.* (2015) applied a MW field to enhance the performance of the Fenton method to remove some copper–EDTA and copper-nickel-

EDTA complexes from water. In this investigation, water samples were irradiated at a MW power of 240 W, temperature of 80 ^{o}C, and in the presence of 4.8 mL of H_2O_2. The obtained results showed that the highest copper removal was 97% in copper-nickel-EDTA, and 94.4% in copper-EDTA after 15 min of microwaving. While the highest nickel removal was 94.5% in copper-nickel-EDTA after about 8 min of microwaving.

3.8 Advantages and disadvantages of MW technology

3.8.1 Advantages

An enormous number of applications such as the acceleration of chemical reactions, activation of catalysis, drug industries, and decomposition of organic matter made a clear shift towards the MW synthesis because the latter bears unique beneficial merits (Lin *et al.*, 2009a; Solanki *et al.*, 2010; Bassyouni *et al.*, 2011; Wang and Wang, 2016) such as:

1- Fast heat elevation, in comparison with other heating processes, due to the direct delivery of MW energy into the substance being heated, which in turn greatly reduces heating time (Wang and Wang, 2016). For instance, densification of transparent alumina using traditional heating processes lasts for several hours to reach the optimum density, while it takes only 45 min using MW heating (Oghbaei and Mirzaee, 2010).

2- The uniform distribution of MW heat makes the temperature equilibrium state easy to reach, which in turn results in homogenous reaction and products (Sánchez, 2008; Lin *et al.*, 2009a; Bijanzad *et al.*, 2015). For instance, irradiation of organic wastewater with MW increased ammonia removal by 35% compare to traditional methods (Lin *et al.*, 2009a).

3- MW heating processes are highly controllable as the heat generation instantaneously responds to switching on /off of the irradiation. This important property greatly enhances the quality of reaction products (Hayes, 2002; Schwenke *et al.*, 2015).

4- MW energy consumption provides a precise monitoring tool for the MW-heated reactions by tracking the consumption of MW-energy during the reaction, thereby the heat capacity and transformation point can be tracked (Schwenke *et al.*, 2015).

5- One of the most important properties of MW heating is the selectivity that allows users to mix more than one absorber in the solution being heated, i.e., MW rapidly and intensely heats polar substances while the nonpolar substances in the same solution remain unheated (Oghbaei and Mirzaee, 2010; Tyagi and Lo, 2012). This advantage is particularly significant in the decomposition of organic matter, and for catalyst activation. For instance de la Hoz *et al.* (2005) mentioned that applying MW heat to organic matter-containing water increased the temperature of aqueous and organic phases to 50 and 110 ^{o}C respectively.

6- Hot spot formation is very important advantage of the MW heating, because it significantly accelerates the oxidation of organic pollutants due to the extreme increase in temperature in these points (Zhu *et al.*, 2007). Where, the temperature in these microscopic spots, 100 µm in size, is about 100 – 200 ^{o}C higher than the bulk temperature (de la Hoz *et al.*, 2005), and can reach 1000-1200 ^{o}C on the absorbent surface (Fu *et al.*, 2010; Xu *et al.*, 2014). In addition, it helps to avoid the disintegration of thermally unstable compounds (Bassyouni *et al.*, 2011).

7- MW heat is independent of the thermal conductivity of the container and energetic barriers as it is generated through the direct absorption of MW energy by the targeted substance. This feature is very beneficial in synthetic chemistry as it allows chemists to control the reaction rate by controlling the amount of the delivered MW energy (Sánchez, 2008; Wong and Gupta, 2015).

8- The athermal MW effect is an attractive characteristic of the MW technology as it increases the vibration of the polar chains of molecules that leads to breaks and weakens the chemical bonds. Consequently, it accelerates the reactions and enhances the removal of organic and biological pollutants (Tyagi and Lo, 2012; Mawioo *et al.*, 2016; Wang and Wang, 2016).

9- MW is considered as an effective and safe sterilization method because of the rapid increase of solution temperature efficiently deactivates bacteria and enzymes in water and wastewater without the need for chemical disinfectants (Lin *et al.*, 2009a).

10- MW units are easy to be integrated with water and wastewater treatment methods such as Fenton oxidation (Li *et al.*, 2015), photolysis and sonolysis (Gole and Gogate, 2014), and the adsorption method (Wang and Wang, 2016).

11- MW heating process can be combined with pressure vessels that enable chemists to perform reactions under controllable heat-pressure conditions (Collins, 2010).

12- Because the MW heating process can use water as a solvent and it does not generate combustion products, it is considered an environmentally friendly method (Lin *et al.*, 2009a; Bassyouni *et al.*, 2011).

13- Economically, the MW technology is of great interest to different industries as it reduces the total cost due to acceleration of the reaction rate that reduces the size of production lines and the required space (Sánchez, 2008; Tyagi and Lo, 2012).

14- Last but not least, nowadays MW heat is considered as a clean heating source (Saikia *et al.*, 2012). Therefore, it has been substantially used in pharmaceutical industries and scientific labs as a clean heating and drying source, where it does not contaminate the products like traditional heating sources with combustion waste such as oil remains or gases. In addition, it possess the ability to dry microstructures (Solanki *et al.*, 2010)**.**

3.8.2 Disadvantages

Although MW technology has an enormous number of advantageous aspects, there are still some drawbacks such as:

1- Solution heating using MW source without proper stirring could raise the temperature of the hot spot to the explosion limit (Sánchez, 2008). Thus, security and safety is a crucial issue for the workers. However, intermittent stirring or rotation of the sample being heated prohibits the generation of hot spots (Sánchez, 2008; Dankovich, 2014).

2- Capital cost of equipment for MW generation is relatively high (Sánchez, 2008).

3- The elevated temperature reduces the lifetime of glassware that is usually used in the microwave cavity, hence the glassware must be replaced periodically (Lin *et al.*, 2009a).

3.9 MW emission limits and safety considerations

Since microwave were introduced for the first time as a heating source, a question has been raised that requires an answer. This is whether the MW irradiation can be used as a safe reaction-heating source. The answer is yes, but only when the MW equipment is correctly selected and used. In addition, when the properties of reactants and reagents, and emission rate were precisely addressed (Hayes, 2002), the following aspects must be taken into consideration to ensure the safety of the operators of MW units:

3.9.1 Emission level

According to the regulations of the US Bureau of Radiological Health (BRH), MW emission level must not exceed $5\ \mathrm{mW/cm^2}$ at 5 cm, the National Health and Medical Research Council (NHMRC) and the International Electrotechnical Commission (IEC) adopted the same limitation (Bangay and Zombolas, 2003; Darwish, 2012). In addition, the Australian Radiation Protection and Nuclear Safety Agency (ARPANSA) limits the specific absorption rate (SAR), spatial peak, of MW to 2 and 4 W/kg for the head/torso and limbs respectively (Bangay and Zombolas, 2003).

3.9.2 MW unit

Using the correct MW unit for the targeted purpose is imperative for the safety of the MW unit operators, for instance using a domestic MW oven for laboratory purposes could result in a serious explosion. This is because the ordinary MW ovens are not designed to bear the prolonged usage or explosive force, and not provided with pressure, temperature, and power controlling systems (Hayes, 2002). For laboratory usage, the MW ovens should be supplied with ventilation systems, reinforced doors and corrosion resistant stainless steel tunnel/cavity to resist possible explosion force and also be supplied with pressure, temperature, and power controlling systems, and auto-turning off safety system (Hayes, 2002).

3.9.3 Chemical properties

The properties of a chemical being heated in the MW oven is a vital safety issue, in fact the operators must have a knowledge about the potential kinetics of the reaction to be performed and the stability of their reagents at elevated temperatures. This is because some reagents decompose under the influence of prolonged heating at elevated temperatures into hazardous elements, moreover some chemicals cause explosion when heated such as azide and nitro groups (Hayes, 2002; Pradhan *et al.*, 2012). In addition, exothermic reactions must be conducted (heated) cautiously as these reactions are uncontrolled and produce pressure and heat at an alarmingly quick rate, which could cause an explosion (Hayes, 2002).

3.10 Chapter summary

Microwave (MW) is a form of electromagnetic waves with a frequency range between 300 MHz to 300 GHz, and a wavelength range between 1m at 300 MHz to 1 mm at 300 GHz. This technology has recently received increasing interest from water and wastewater treatment industries due to its unique heating mechanism. Where the MW heating is vitally different from the traditional heating processes is that the MW energy couples with the molecules of the substance being heated, which means the heat is generated from within the mixture without heat transfer. In addition, MW heating has many other unique merits such as it enables operators to control reactions as the heating process is instantaneously stopped when the MW energy is switched off. It is independent of the thermal conductivity of the container because it is generated through the direct absorption of MW energy by the targeted substance. Additionally, MW heating is accompanied by the generation of some extremely hot microscopic zones (called hot spots) within the substance being heated, the temperature in these microscopic spots, 100 µm in size, is about 100 – 200 ^{o}C higher than the bulk temperature. Therefore, MW results in a rapid superheating of the substance that produces enormous accelerations in many chemical reactions, which cannot be produced by traditional heating.

Beside these unique MW thermal effects, the athermal MW effects increase the vibration of the polar chains of molecules that leads to the breaking or weakening of the chemical bonds, which in turn accelerates the reactions and enhances the removal of organic and biological pollutants.

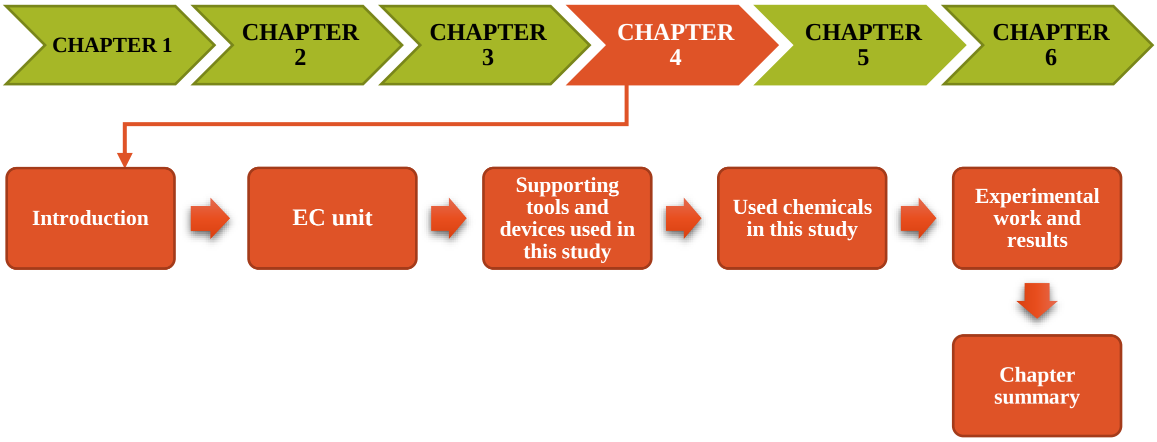
Due to these unique merits, the MW technology has been efficiently applied, separately or integrated with other methods, to remove a wide range of pollutants from water and wastewater, such as algae, volatile and semi-volatile pollutants, and to decompose organic matter. Additionally, due to its superheating, the MW technology is categorised as an efficient water disinfectant (kills pathogens).

As a result of the mentioned attractive merits of the MW, along with those advantages mentioned in section 3.8.1, the MW technology has been selected as a supporting method to enhance the performance of the EC unit in terms of iron removal from drinking water in the presence of OM matter.

CHAPTER 4

MATERIALS, PROTOCOLS, AND RESULTS

CHAPTER 4: MATERIALS, PROTOCOLS, AND RESULTS



4.1 Chapter introduction

The current chapter is devoted to present both the operational structure of the experimental work in which the objectives of this thesis will be achieved and the results obtained from the experimental work. It outlines the design and construction of the new EC reactor, the succession of the experiments, data collection and analysis, and it gives a precise description of tools, equipment, and chemicals that will be used in this project. Additionally, it provides a justification, with clear reasons, for the choice of the studied pollutants, methods, and material, in this thesis.

4.2 The Traditional EC units

For comparisons purposes, five traditional EC reactors, with different shapes and electrodes, were constructed in the labs of Liverpool John Moores University (LJMU) (Figure 4-1). These types of EC reactors, namely EC1, EC2, EC3, EC4, and EC5, were selected according to their availability in the Iraqi markets.

1- EC1: is a cylindrical reactor, made from Perspex, having dimensions of 25 cm in height and 10.5 cm in diameter. It was supplied with perforated discoid electrodes that are made from aluminium, with a diameter of 10.4 cm. Each electrode contains nine holes (10 mm in diameter) distributed radially around the centre of the electrode.

2- EC2: is similar to the EC1 but with solid discoid electrodes.

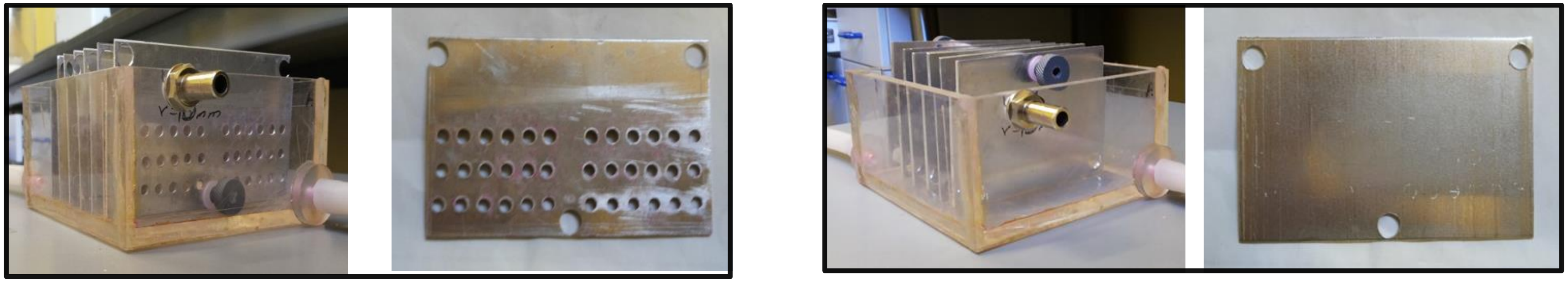
3- EC3: This traditional reactor consisted of a Perspex made rectangular container, $10 \times 9.5 \times 7$ cm, with parallel-perforated rectangular electrodes made from aluminium. Each electrode,(6×9.4 cm), has 36 holes (5 mm in diameter) distributed in three rows (1.2 cm centre to centre).

4- EC4: similar to EC3 but supplied with solid rectangular electrodes.

5- EC5: a traditional rectangular reactor with solid rectangular electrodes, 6×8 cm, arranged in a zigzag arrangement (spiral flow pattern).

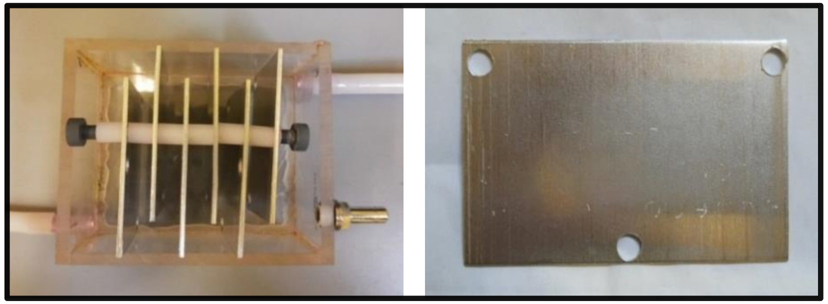
A) **EC1 and its electrodes**

B) **EC2 and its electrodes**



C) EC3 and its electrodes

D) EC4 and its electrodes



E) EC5 and its electrodes

Figure 4-1: The studied electrocoagulation reactors and their electrodes.

4.3 The new EC unit (FCER)

In this study, a new cylindrical electrocoagulation reactor, FCER (Figure 4-2), has been designed with the innovative use of a perforated-plate flow column, which is widely used in chemical industries, to create high mixing efficiency. This reactor consisted of a Perspex cylindrical container having dimensions of 25 cm in height and 10.5 cm in diameter. It was supplied with a flow column that consisted of perforated discoid electrodes that are made from aluminium, 99.5% purity provided by LJMU laboratories, with a diameter of 10.4 cm and thickness of 1 mm. In this study, aluminium was selected as the electrode material because of its cost effectiveness, ready availability, and it requires comparatively less oxidation potential (Ghosh *et al.*, 2008). Additionally, aluminium produces flocs with large surface areas, which are favourable for pollutants removal (Aoudj *et al.*, 2010).

Each electrode has 48 small holes (0.5 cm in diameter) distributed radially at an angle of 45^0, with a 1 cm diameter closable central hole for aeration (if needed). These perforated electrodes were vertically installed inside the reactor; each electrode was rotated horizontally by an angle of 22.5^0 from the one above it. This is to ensure that the water will follow a convoluted path, thereby efficiently mixing the water being treated. Additionally, this convoluted path increases the contact time between water drops and the ambient air, enhancing evaporation that dissipates water temperature and increases the concentration of dissolved oxygen. These electrodes have been held in the required position inside the reactor by using three 0.5 cm in diameter PVC (Polyvinyl chloride) supporting rods. While the required distance between electrodes was controlled using 1 mm in thickness PVC fixation washers (PVC rods and washers were supplied by purity provided by LJMU laboratories). The whole flow column is movable which enables the user to shake or rotate the electrodes, manually or mechanically, to expel the accumulated air bubbles on the electrodes during the treatment process.

Figure 4-2: The new EC reactor (FCER).

This reactor was connected to a rectifier (HQ Power; 0–30 V) to supply the required electrical current. A peristaltic pump (Watson Marlow type, model: 504U) was used to flow water through the reactor was conducted using a, while the temperature of the water being treated was controlled using a 22L manual thermostat Clifton water bath (Ne1 Series). The whole unit is shown in Figure 4-3. This bench-scale EC unit was provided with a thermometer, a pH sensor, and a conductivity meter (Hanna; Model: HI 98130).

Although the efficiency of this flow column, as a water mixer was investigated and proved by (Hashim *et al.*, 2015b; Hashim *et al.*, 2015a), its performance, in the current study, has been reinvestigated and compared with that of the traditional reactors.

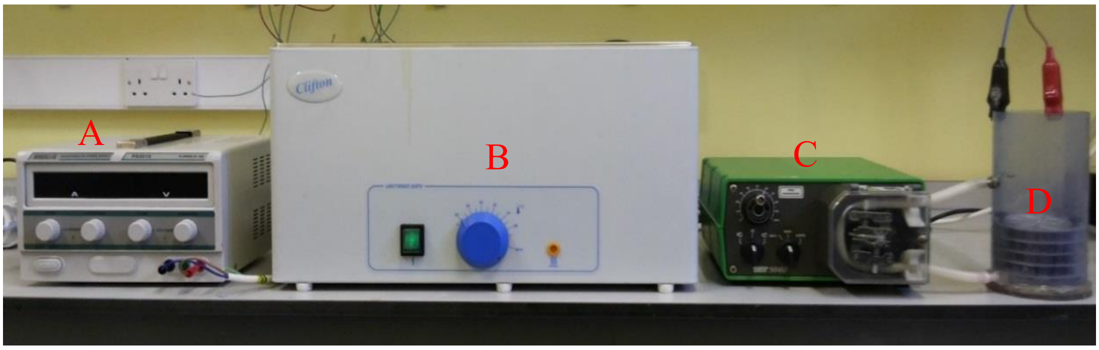


Figure 4-3: Experimental set-up: (A) power supply, (B) water bath, (C) peristaltic pump, (D) FCER.

4.4 Supporting tools and devices used in this study

In addition to the EC unit, several tools and devices were used in this project to monitor the progress of the pollutant removal process. Firstly, an accurate camera (type: HUE HD) was used to record the mixing process over the treatment period inside each reactor in order to locate the unmixed areas. Then, camera records were separated into many frames in order to calculate the unmixed areas by using Auto CAD- 2014 software. Concentrations of effluent red drain dye (RD dye), fluoride, nitrate, reactive black 5 dye (RB5), and COD were measured using a Hach Lange spectrophotometer (Model: DR 2800). For COD, heating block Hach Lange dry thermostat (model: LT200) was used to incinerate, at 148 ^{o}C for 120 min, COD cuvettes. While, the residual concentration of iron was measured using a Thermo atomic absorption spectrophotometer (Model: ICE 3300). The weight of the chemicals used was measured using three digits accuracy KERN precise scale (model: PCB-A02).

For aeration efficiency of the FCER, an air pump (type: Hailea; model: ACO-9630) was used to increase the concentration of dissolved oxygen, the latter was measured using a Hach Lange DO meter (Model: 5130).

MW irradiation was conducted using a lab-scale CEM device (model: discovery – SP W/ACTIVENT), Figure 4-4. A SRI – 8610C gas chromatograph was used to calculate the amount of hydrogen gas. Finally, a Memmert incubator (model BM 400) was used to incubate the agar plates during the course of experiments of biological pollutants removal. The agar plates were supplied by Thermo Scientific.

Figure 4-4: CEM microwave unit.

4.5 Chemicals used in this study

All chemicals used in this study and their suppliers are listed in Table 4-1.

Table 4-1: Used chemicals and their suppliers.

No.	Chemical	Assay	Supplier
1.	Sodium fluoride NaF	≥ 97%	Acros organics
2.	Potassium Nitrate KNO_3	≥ 99%	Sigma-Aldrich
3.	Iron(II) Sulphate Heptahydrate	≥ 99%	Sigma-Aldrich
4.	Reactive black 5 dye (RB-5 dye)	55% dye content	Sigma-Aldrich
5.	Ethylenediaminetetraacetic (EDTA)	≥ 98.5%	Sigma-Aldrich
6.	Red Drain Dye	-----	J S & F Entwisle
7.	Sodium sulphite	≥ 99%	Sigma-Aldrich
8.	Sodium chloride	99.5%	Fisher Scientific
9.	HCL	35-38%	VWR Chemicals
10.	NaOH	98%	Fisher Scientific
11.	Fluoride cuvette test LCK 323.	-----	Hach-Lange
12.	COD cuvette test LCI 400.	-----	Hach-Lange
13.	NitraVer 5 Nitrate Reagent Powder Pillows	-----	Hach-Lange
14.	Nutrient agar	------	Thermo fisher

4.6 Experimental work and results

In order to highlight the novelty of the current project and to explain the results obtained from the experimental work in a clear and understandable way; this section has been divided into six main phases.

PHASE I

4.6.1 Influence of the flow column on the performance of the EC units

The influence of using a flow column in the FCER will be investigated by comparing its efficiency in terms of water mixing, aeration, and temperature control with those of traditional EC reactors. These three parameters have been selected as comparison indicators because they play important roles in the EC process; as is explained in the following sections.

4.6.1.1 Water mixing efficiency

I. Methodology

Water mixing is a key factor in the electrocoagulation process because it helps to create a good homogenisation of coagulants and pollutants inside the EC reactor, which in turn helps to create big enough flocs to settle (Al-Baiani, 2003; Adhoum and Monser, 2004; Un *et al.*, 2013). Traditionally, EC reactors usually use either mechanical agitators (Un *et al.*, 2013; You and Han, 2016) or magnetic stirrers (Yilmaz *et al.*, 2007; Ulu *et al.*, 2014) to achieve the required degree of mixing, such devices require power to work. While in the present work, a flow column has been used to achieve the water mixing process without the need for extra power.

To assess the ability of the flow column to mix water, a coloured stock solution was prepared by dissolving red drain dye (RD dye) in deionised water to have an initial dye concentration of 2000 mg/L. Samples of lower RD dye concentrations were prepared by diluting a proper volume of the stock solution.

Before starting the electrocoagulation process, it was essential to prepare a calibration curve for RD dye. The first task was selecting the best wavelength for RD dye; therefore, a 3 mL coloured water sample (with a known concentration) was tested by using a Hach Lange spectrophotometer at different wavelengths ranging between 400 and 600 nm (a visible colour region) and the corresponding absorption value was recorded. It was found that the best wavelength is 525 nm; which gave the maximum absorption value. Then, 55 coloured water samples with different concentrations of RD dye (varying between 0 mg/L to 2000 mg/L) were used to find the corresponding spectrophotometric optical density (OD_{525}) (or the spectrophotometric absorbance ABS). A direct relationship between the absorption values and RD dye concentrations was noticed in the region from 0 up to 600 mg/L of RD dye, but after this region the curve sharply spiked making the relationship unclear; which means the sensitivity of the Hach Lange

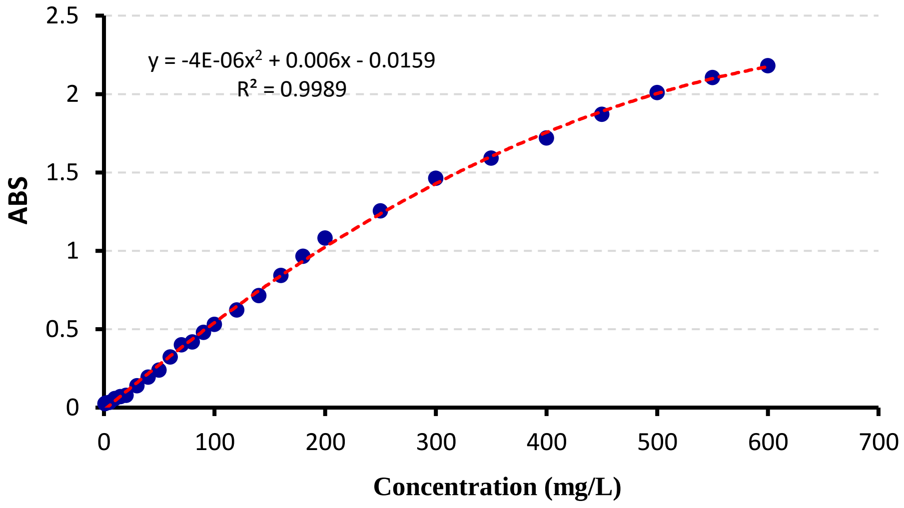


Figure 4-5: Spectrophotometric absorption values for RD dye.

spectrophotometer for RD dye concentrations became very low. Therefore, the mixing process will be investigated, in chapter 5, within the range of 0 up to 600 mg/L of RD dye, Figure 4-5.

Water mixing efficiency of the studied EC reactors (new and traditional reactors) was calculated by filling each reactor with 500 mL of deionised water. Then, a peristaltic pump was used to pump the coloured water, which was stored in a plastic container near to the reactor, continuously to the reactor for 10 minutes. Water pumping was conducted in direct and back flow modes at different flow rates (80, 180, 280, and 380 ml/min). These flow rates agree with most of the studied flow rates, for bench scale units, by the previous researchers; such as those of (Kim *et al.*, 2002), (Zhu *et al.*, 2005), (Mollah *et al.*, 2010), (Amrose *et al.*, 2013), and (Mohora *et al.*, 2014).

5 mL samples were collected of the effluent water at 20 seconds intervals during the course of the experiment; and they were filtered with 0.25 µm Whatman filters (supplied by Sigma-Aldrich). The effluent dye concentration was calculated using a Hach Lange spectrophotometer according to the pre-prepared calibration curve. Optimum mixing efficiency (100%) occurs when the influent and effluent RD dye concentrations became equal.

For more accuracy, a visible tracing for water mixing process across the reactor was conducting using an accurate HUE HD camera. This camera was installed as close as possible, at 30 cm, to the studied reactors to give a clear view of the mixing process during the 10 minutes of treatment. Video records help to check if there is an unmixed area inside the reactor (stagnation zones). The camera records then were separated into frames using VirtualDub software. The unmixed areas, on these frames, were calculated using Auto CAD- 2014 software.

II. Results and discussion

As mentioned before, water mixing is a key factor in the electrocoagulation process creating a good homogenisation of coagulants and pollutants inside the EC reactor, which in turn helps to create big enough flocs to settle. In the current study, a flow column (which is widely used in chemical industries) has been innovatively used in the design of the FCER to achieve the water mixing process.

The ability of the FCER, along with five other different traditional EC reactors, was investigated in continuous flow mode taking into account the influence of flow mode and flow rate, as follows:

A. Influence of flow mode

Measurement of water mixing efficiency was initiated by filling each reactor with clear deionised water and then water with an initial concentration of RD dye of 400 mg/L, which was pumped continuously into the reactor by a peristaltic pump. Water pumping was conducted in direct and back flow modes at flow rates of 80, 180, 280, and 380 mL/min.

Initially, sets of continuous flow experiments were carried out at a constant flow rate, 80 mL/min, to investigate the influence of flow mode on water mixing efficiency of the studied reactors. All experiments were carried out at room temperature.

The obtained results, Figure 4-6, demonstrated that the maximum mixing efficiency was achieved by FCER under back flow conditions, where, it was found that the effluent and influent concentrations of RD dye became equal (100% mixed) after 9 minutes of water pumping through the FCER. While, the other reactors EC1, EC2, EC3, EC4, and EC5 achieved a mixing efficiency of 96.7%, 87.6%, 96.3%, 91.9%, and 87.9% respectively.

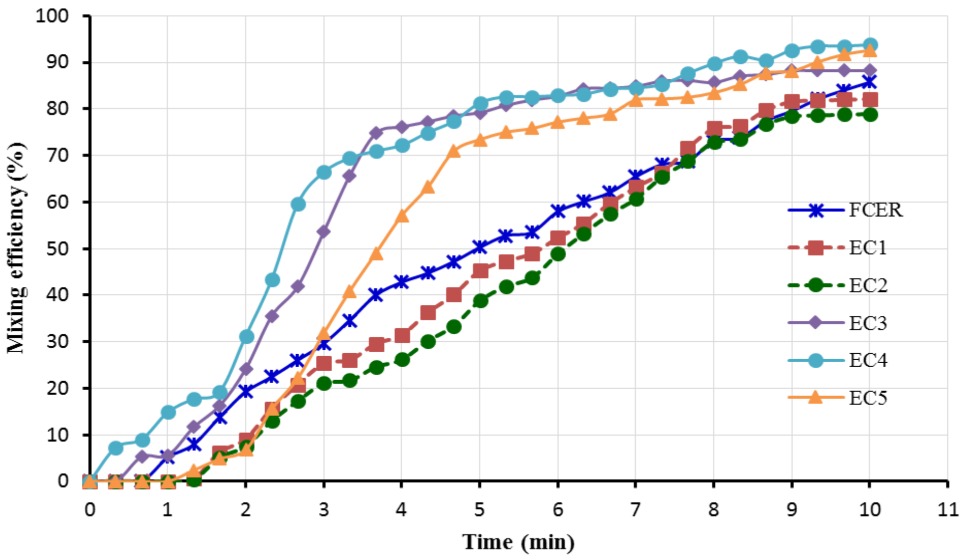


Figure 4-6: Mixing efficiency of the selected reactors under direct flow conditions.

Then, dyed water was continuously pumped through the studied EC reactors in direct flow mode. The obtained results, Figure 4-7, showed that the mixing efficiency of the studied EC reactors decreased under the direct flow conditions. For instance, after 10 minutes of continuous pumping, the highest mixing efficiency of FCER was 85.7%.

In order to validate the results, the mixing process was recorded using a camera. Then, the obtained images were examined, according to the procedures discussed in the previous section, to check if there are unmixed areas inside the studied reactors.

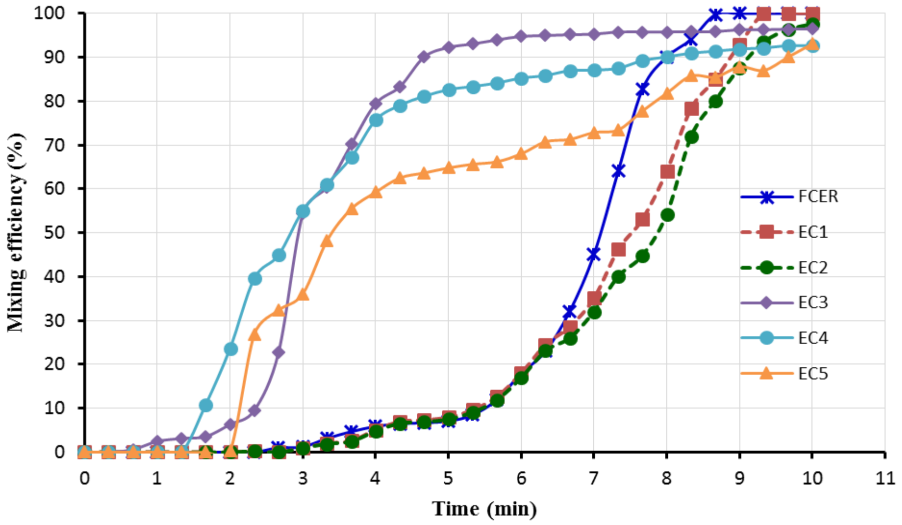
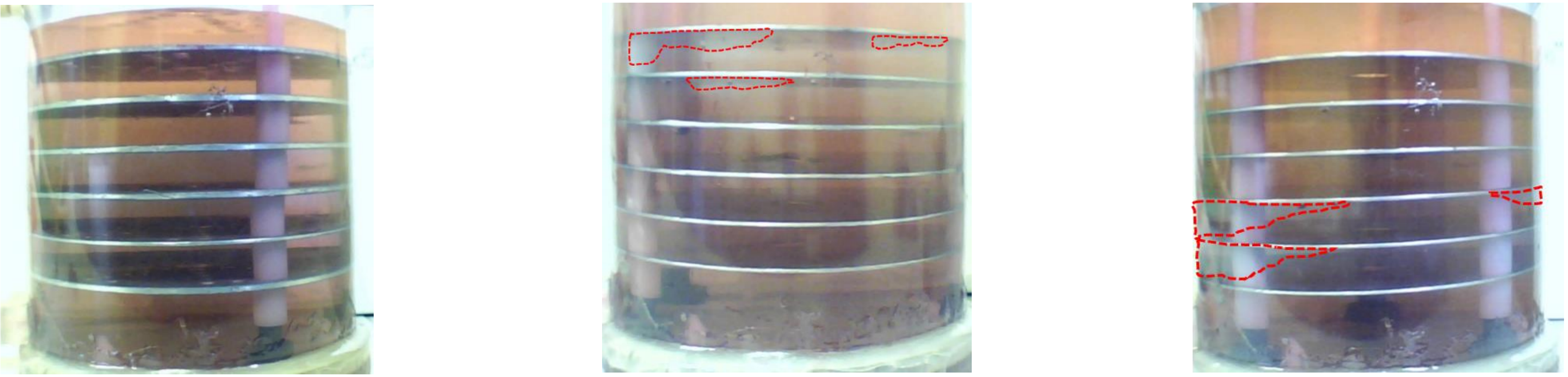
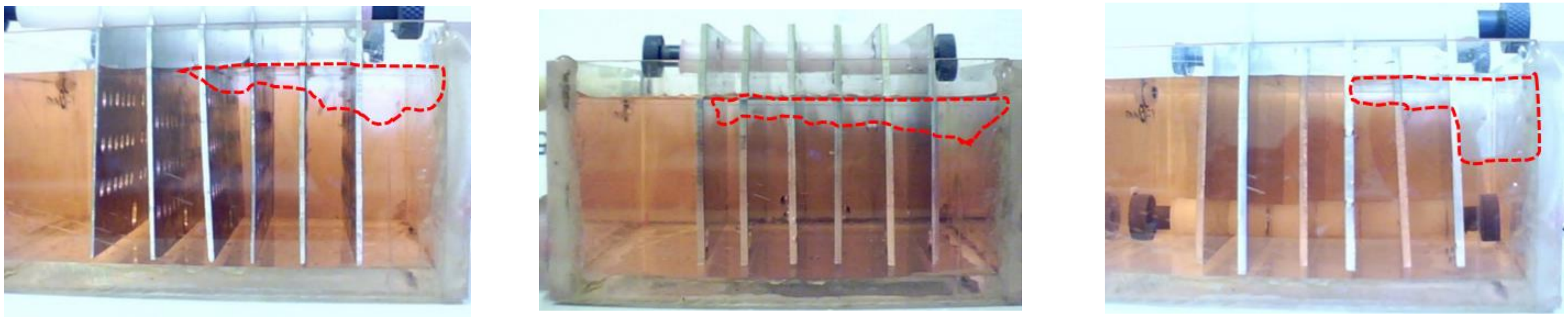


Figure 4-7: Mixing efficiency of the studied EC reactors under back flow conditions.

Camera images, during the back flow pattern, revealed an important phenomenon; they showed that the treated water in all reactors, except the FCER that creates a homogenous colour distribution, was not completely mixed. It can be clearly seen from Figure 4-8 that there are some areas, generally near to the outlets of the reactors, which remain undisturbed. These images indicated that the FCER required only 6 minutes to create a visibly homogenous colour over the entire reactor. While, about 7%, 11%, 9%, 10%, and 11% of the treated water remained undisturbed inside EC1, EC2, EC3, EC4, and EC5, respectively. The results obtained clearly showed that the new FCER reactor achieved the highest mixing efficiency in terms of effluent RD dye concentrations and the visible observations. The FCER gains its high mixing efficiency due to the novel use of a flow column in its design. Where, the disks of the flow column (the electrodes) were designed to utilise the hydraulic flow to achieve water mixing by forcing the water being treated to pass through their small orifices in a convoluted path creating mini fast whirlpools around each electrode. These mini whirlpools work as a hydraulic mixer for the treated water. It was also observed that the mixing efficiency, under the backflow conditions, was better than it was in direct flow. This may be explained by the influence of weight of the water column (water being treated) which works, under back flow conditions, on strengthening the turbulent flow and enhancing the mixing efficiency. Contrarily, under the direct flow mode the gravity works on facilitating water flow through the small orifices, which weakens the turbulent flow and decreases the mixing efficiency.



- FCER, Perforated electrodes.
- EC1, Perforated electrodes (10 mm) electrodes.
- EC2, Solid electrodes.



- EC3, Perforated electrodes.
- EC4, Solid electrodes.
- EC5, Solid electrodes (zigzag arrangement).

Figure 4-8: Unmixed areas after 6 minutes of back flow pumping, red marks represent the unmixed water.

B. Influence of flow rate

The effect of flow rate on water mixing efficiency has been investigated by pumping 400 mg/L RD dye-containing water through the FCER at different back flow rates (80, 180, 280, and 380 mL/min). The results, Figure 4-9, showed a direct relationship between mixing efficiency and water flow rate; it was found that the FCER achieved full mixing efficiency within 9, 5, 3, and 2.2 minutes at back flow rates of 80, 180, 280, and 380 mL/min, respectively. These results highlighted an important fact; that the required time to achieve full mixing is inversely proportional to the flow rate, i.e., mixing time can be reduced by increasing the flow rate. The most likely explanation for this phenomenon is that the increase in flow rate increased the velocity of the mini whirlpools, and consequently improved the mixing efficiency

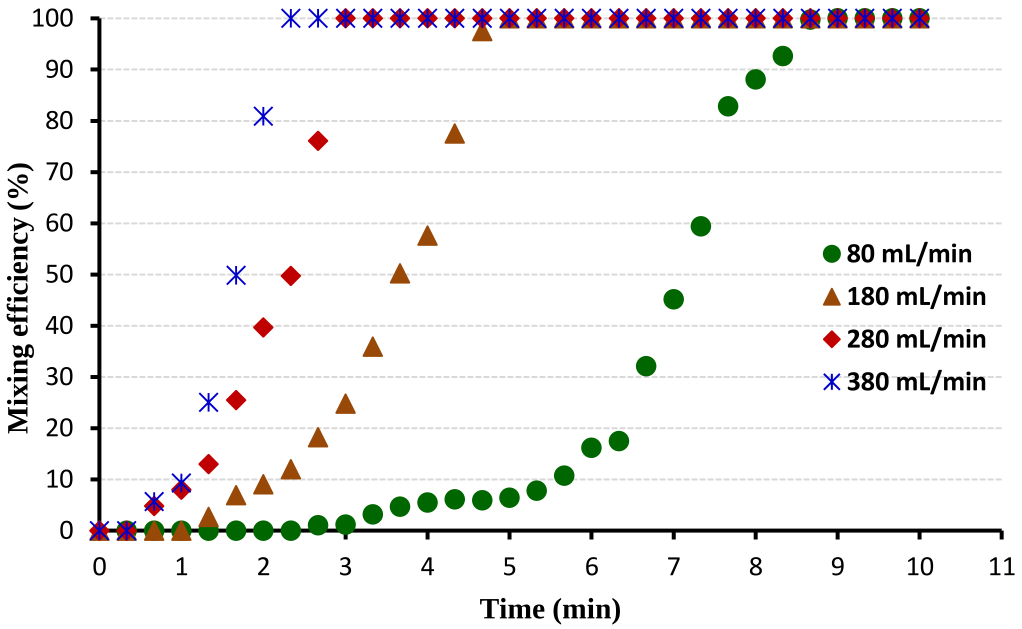


Figure 4-9: Influence of flow rate on mixing efficiency of FCER.

4.6.1.2 Aeration efficiency

I. Methodology

Dissolved oxygen (DO) is an another essential parameter in the EC process because it oxidizes the targeted pollutants, such as heavy metals (Wan *et al.*, 2011; Sun *et al.*, 2009), ammonia (Ilhan *et al.*, 2008), and cyanide (Gao *et al.*, 2013), so that they can be easily removed from the solution being treated. The cathodes of the EC reactors start to produce oxygen species (such as OH) due to the water degradation process according to the following equations (Den *et al.*, 2006; Ben Sasson *et al.*, 2009):

$$2H_2O \rightarrow O_{2(g)} + 4H^+_{aq} + 4e^- \quad \textbf{(19)}$$

Near the cathode:

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \,, \quad \textbf{(20)}$$

The external aeration process is necessary for several applications of EC, for instance Sun *et al.* (2009) demonstrated that the aeration of wastewater is a crucial condition as the DO content of wastewater was depleted within 7 to 30 min of treatment, which could inhibit the treatment process. Additionally, the available concentration of DO in some types of ground water and leachates is too low to accomplish the pollutants oxidation process (Ilhan *et al.*, 2008). Furthermore, Hug and Leupin (2003) stated, according to the influence of 2-propanol, that the *OH cannot be oxidant for As (III). Therefore, traditional EC reactors depend on external aerators, which need extra power to work, to provide the required amount of the DO. The aeration process, in the present work, was achieved using a flow column.

The water aeration mechanism, using a flow column, could be explained by the conversion of the mass water flow into droplets, where, maintaining the water level inside the FCER up to the mid-height of the flow column allows the unsubmerged perforated electrodes (upper part) to work as a water diffuser, Figure 4-10. Thereby, the mass water flow converts into droplets that maximises the contact area between water and the ambient air, and consequently increases the DO concentration.

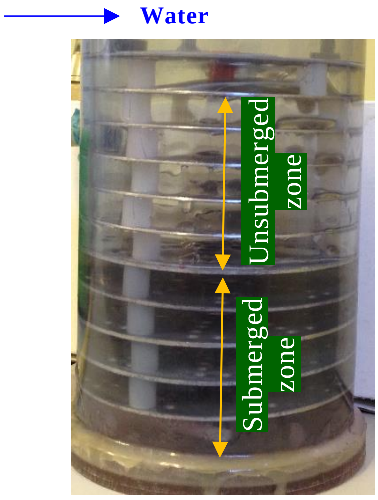


Figure 4-10: Submerged and unsubmerged zones inside FCER.

In order to assess the performance of FCER, in terms of water aeration, 0.5 L water samples with DO concentration of 5 mg/L, measured using a Hach Lange DO meter, were prepared by adding stoichiometric quantities of sodium sulphate Na_2SO_3. The latter reduces and maintains O_2 concentration at the desired level according to the following reaction (Ambasta, 2012):

$$2Na_2SO_2 + O_2 \rightarrow 2Na_2SO_4 \qquad \textbf{(21)}$$

These samples were then circulated inside the reactors for 10 min using a peristaltic pump. To monitor the progress of the DO concentration, 5 mL samples were collected, every 2 min, from the reactors.

For comparison purposes, saturated water samples were prepared by direct pumping of fresh air, using a Hailea air pump, into deionised water samples for 15 min.

The influence of water flow rate on the progress of DO concentration was studied using three different flow rates, 110, 220, and 440 ml/ min. All experiments were performed at room temperature.

II. Results and discussion

Sets of batch flow experiments were carried out to assess the performance of the FCER in terms of enhancement of DO concentration.

Initially, 500 mL water samples with an initial DO concentration of 5 mg/L were pumped through the FCER for 10 min at flow rate of 220 mL/min and ID of 1 cm. Effluent samples were collected at 2-minute intervals during the course of the experiment.

Then, for comparison purposes, water samples with identical properties were treated using EC2 under the same operating conditions.

The results obtained demonstrated that the FCER was able to increase the DO concentration by 110.6% (5.53 mg/L) after 10 min of treatment, Figure 4-11. Where, the DO concentration was increased gradually from 5.0 mg/L to reach 10.53 mg/L after 10 min.

At the same time, the results obtained showed that the traditional reactor, EC2, increased the DO concentration by 66%, where the DO concentration was increased from 5 to 8.3 mg/L after 10 min of water circulation.

This increase in DO concentration could be attributed to the conversion of the mass water flow into droplets by the unsubmerged perforated electrodes, where, the unsubmerged perforated electrodes (in the upper part) work as a water diffuser.

Thereby, the mass water flow converts into droplets that maximises the contact area between water with the ambient air, and consequently increases the DO concentration.

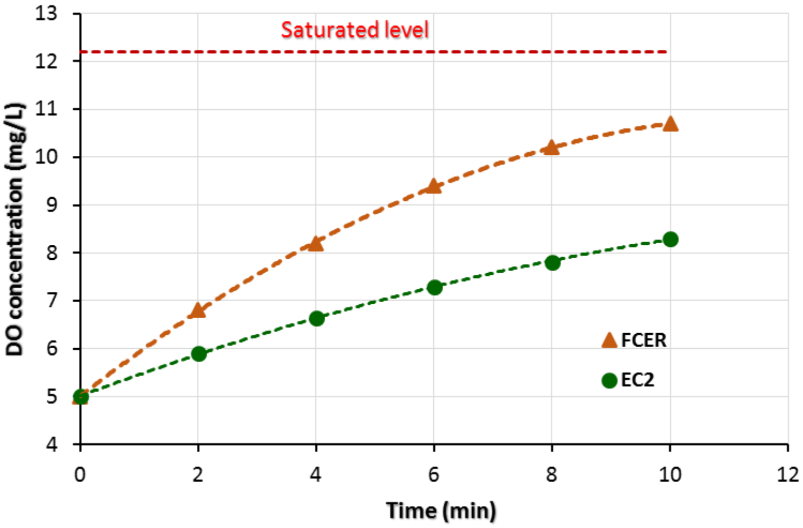


Figure 4-11: Aeration efficiency of FCER and EC2.

Additionally, the influence of water recirculation rate (flow rate) on the DO concentration, using the FECR, was investigated at flow rates of 110, 220, and 440 mL/min. The results obtained, Figure 4-12, indicate that the higher the flow rate, the more rapid the increment of the DO, where, it was found the DO concentration increased from 5.0 to 9.54, 10.53, and 11.0 mg/L, which is equivalent to 90.8%, 110.6%, and 120%, as the flow rate increased to 110, 220, and 440 mL/min respectively.

The reasonable explanation for these results is that increasing the recirculation rates caused higher agitation of water flow over the unsubmerged perforated electrodes, which increased the water-air mixing process, and consequently increased the DO concentration.

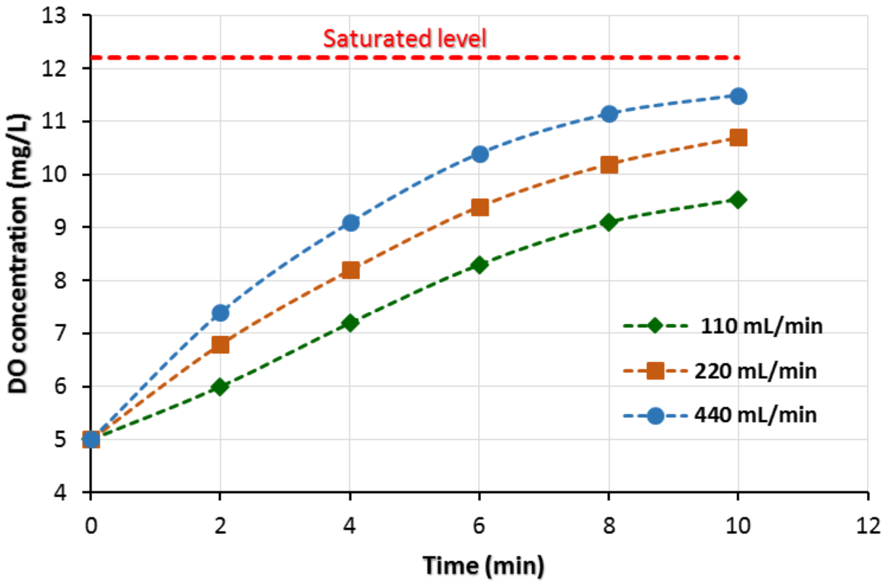


Figure 4-12: Influence of flow rate on DO concentration using FCER.

It is noteworthy to highlight the vital difference between the aeration mechanism using flow column, FCER, and the traditional aeration process. Traditionally, the aeration process is conducted through pumping fresh air directly into the water being treated. This process generates a large number of small air bubbles inside the EC unit, which maximises the electrical resistance, and consequently increases the energy consumption (Gao *et al.*, 2013). While, in the FCER, the aeration process is carried out in the unsubmerged part of the flow column where the perforated electrodes convert the mass flow of water into droplets to increase air-water mixing process. This mechanism inhibits the generation of air bubbles inside the reactor, and consequently reduces energy consumption.

4.6.1.3 Control of water temperature

I. Methodology

The EC process like any other chemical reaction is influenced by the solution temperature, it affects the production rate of hydroxyl radicals, mobility and collision rate of particles, eroding of electrodes, and solubility of the precipitates (Chou and Huang, 2009; Vepsäläinen *et al.*, 2009). In fact, previous investigations show that the solution temperature exerts either a positive or negative impact, depending on several factors such as the properties of the targeted pollutant, on EC removal efficiency (Gao *et al.*, 2010). Generally, the removal efficiency of EC units increases with the increase of solution temperature to a certain extent (Gao *et al.*, 2010; Vasudevan *et al.*, 2012a). However, the ability of EC units to remove some pollutants such as acid red 14 dye (Daneshvar *et al.*, 2004), fluoride (Mameri *et al.*, 1998), and oil (Fouad *et al.*, 2009), decreases at high temperatures as the mobility of particles increases to an extent which reduces the chance to aggregate and form flocs (Daneshvar *et al.*, 2004). Therefore, most of published researchers have either used an external cooler to control the reaction temperature (Vasudevan *et al.*, 2011) or carried out EC experiments at room temperature (Hu *et al.*, 2003; Ghosh *et al.*, 2008; Kobya *et al.*, 2010).

The ability of FCER to dissipate the temperature of water was investigated by treating water samples with different initial temperatures (15 to 35 ^{o}C) at different current densities (0.5 to 3 mA/cm^2). The initial temperatures were either controlled using a Clifton water bath (for high temperatures 20, 25, 30, and 35 ^{o}C) or an ice bath (for the temperature of 15 ^{o}C).

Experimentally, 0.5 L water samples with known initial temperature (from 15 to 35 ^{o}C) were circulated inside the studied reactors using a peristaltic pump for 30 minutes at a certain current density ranging from 0.5 to 3.0 mA/cm^2. This quantity of water was enough to fill FCER to its mid-height that allows the unsubmerged electrodes to work as a water diffuser. Thereby, the mass water flow converts into droplets that maximises the contact area between water with the ambient air, and consequently dissipates the water temperature. To check the influence of flow column usage on the EC reactors, FCER has been used in three different operating modes. Firstly, it was used as a continuous flow unit supplied with five submerged electrodes and five unsubmerged electrodes. Then, it was used as a continuous flow unit without the unsubmerged electrodes. Finally, it was used as a batch flow unit without unsubmerged electrodes.

II. Results and discussion

A. Influence of flow mode

In the current phase of study, the FCER has been used in three different flow modes in order to evaluate the influence of the unsubmerged electrodes on the progress of water temperature. Firstly, it was used as a continuous flow unit supplied with five submerged electrodes and five unsubmerged electrodes. Then, it was used as a continuous flow unit without the unsubmerged electrodes. Finally, it was used as a batch flow unit without unsubmerged electrodes, where the water being treated was circulated through the FCER at the same flow rate for 30 min.

The experimental work was initiated by using the FCER to treat 500 mL water samples with initial temperature of 35 ^{o}C for 30 min at a CD of 1.0 mA/cm^2, σ of 150 mS/cm, and ID of 1 cm. The results obtained, Figure 4-13, showed that when the FCER was used as a continuous flow unit with unsubmerged electrodes, the water temperature decreased from 35 to 27.3 ^{o}C during the first 5 min. Then it increased slowly to the vicinity of 28 °C after 15 min of treatment and remained almost the same level until the end of the treatment time.

It is noteworthy, that the results obtained showed that removing the unsubmerged electrodes increased the temperature of the water being treated by about 2 °C. It can be seen from Figure 4-13 that the temperature initially decreased to about 28.1 °C and then started to increase gradually to reach 29.8 °C by the end of the experiment time.

In batch flow mode, however, the FCER showed a weak performance in terms of water temperature control. Where, the results obtained showed that the water temperature decreased during the first 5 min of treatment to the vicinity of 30 °C then quickly increased over the remaining 25 min of the experiment to reach about 32 °C by the end of the experiment.

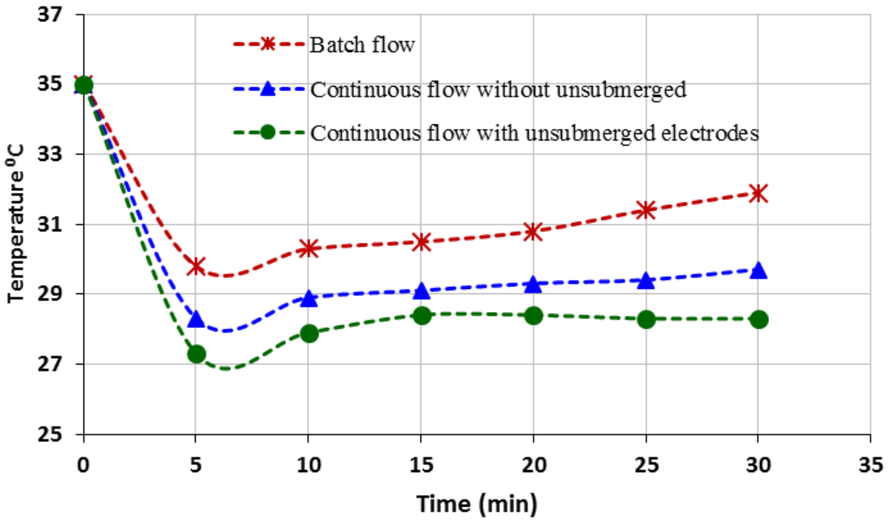


Figure 4-13: Influence of flow mode on the progress of water temperature.

B. Influence of initial water temperature

The influence of the initial water temperature on the ability of the FCER to control the temperature of the water being treated was investigated by changing the initial temperature from 15, to 20, 25, 30, and 35 ^{o}C, while other parameters were kept constant.

The results obtained, Figure 4-14, showed the FCER was able to dissipate the temperature of water being treated from 35 and 30 ^{o}C to the vicinity of 28 ^{o}C after 30 min of water circulation at 180 mL/min. On the other hand, the results obtained showed that lower temperatures (25, 20, and 15 ^{o}C) were increased during intervals during the course of experiments but did not exceeded 27 ^{o}C. It can be seen from Figure 4-14 that the initial water temperature of 25 ^{o}C gradually increased during the first 20 min of experiment to plateau at the vicinity of 27 ^{o}C after 25 min, and kept the same level until the end of experiment. While, the temperatures of 15 and 20 ^{o}C showed a similar trend to reach, by the end of experiments, 25 and 22.1 ^{o}C, respectively.

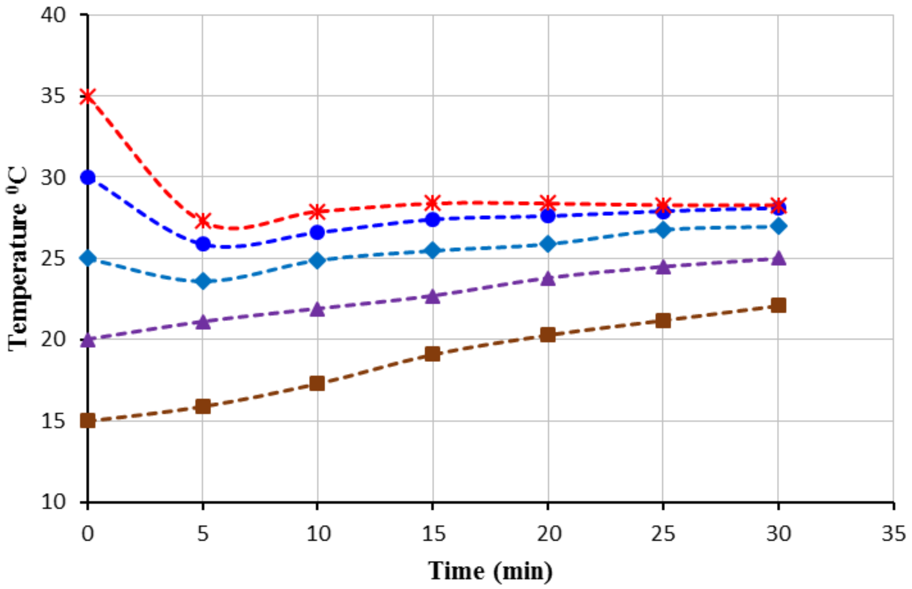


Figure 4-14: Influence of initial temperature of water on the progress of water temperature.

These results confirmed that the FCER has the ability to maintain the temperature of the water being treated in a moderate range (between 22 and 28 ^{o}C). This range of temperature is suitable for the removal of different pollutants such as acid red 14 dye (Daneshvar *et al.*, 2004), fluoride (Mameri *et al.*, 1998), and oil (Fouad *et al.*, 2009).

In this phase of study, the rest of the experiments will be carried out at room temperature (20 ± 1) as the variation in the final temperatures was not big. Additionally, most of the previous studies, such as those of (Mameri *et al.*, 2001); Song *et al.* (2007) ; Essadki *et al.* (2009) ; (Daud *et al.*, 2013) ; and (Pi *et al.*, 2014), were carried out at room temperature.

C. Influence of water conductivity

According to the principle of ohmic heating, the passing of electric currents through a solution will heat it due to the electrical resistance (Castro, 2007; Darvishi *et al.*, 2011). The amount of the heat produced can be calculated according to the equation 22:

$$Q = R.I^2 \tag{22}$$

Where $Q, R,$ and I are the generated heat (joule), electrical resistance (**Ω**), and the applied current (A), respectively.

Therefore, water conductivity plays an important role in the determination of heat generation because it facilitates the passage of current. To explore the influence of water conductivity on the progress of water temperature inside the FCER, water samples with different conductivities (σ) (0.15, 0.3, 0.6, and 1.2 mS/cm) were prepared by dissolving the required amount of NaCl in deionised water. Initial water temperature, CD, treatment time, and ID, were kept constant at 20 ^{o}C, 1 mA/cm^2, 20 min, and 1 cm, respectively.

The results obtained, Figure 4-15, showed a reverse relationship between the conductivity of water and the progress of water being treated, where, water temperature clearly decreased from 23.1 to 21.4, and 20 ^{o}C as the conductivity increased from 0.15 to 0.3 and 0.6 mS/cm, respectively.

However, it was noticed that increasing water conductivity more than 0.6 mS/cm slightly influenced water temperature. It can be seen from Figure 4-15 that increasing the conductivity by twofold, from 0.6 to 1.2 mS/cm, merely reduced the water temperature by 0.3 ^{o}C. This might be explained by the fact that increasing water conductivity to a certain level decreases the resistance that decreases the generated temperature. Beyond this certain level, the solution becomes saturated with ions and the extra amounts of electrolyte will not facilitate the passage of current any more. Thus, in this investigation, water conductivity of 0.6 mS/cm will be used to carry out the rest of experiments.

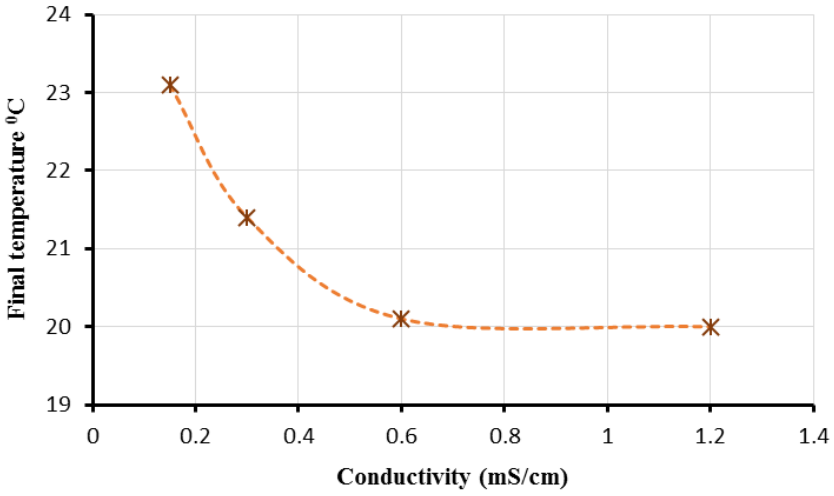


Figure 4-15: Influence of water conductivity on the progress of water temperature.

D. Influence of current density

As mentioned in the last section, the amount of heat generated is in proportion to the square of the applied current and the resistance. Therefore, extra sets of experiments were carried out to investigate the influence of CD on the progress of water temperature, where, 0.5 mL water samples were subjected to four different CDs (0.5, 1.0, 2.0, and 3.0 mA/cm^2) while the conductivity, initial temperature, treatment time, and ID were 0.6 mS/cm, 20 ^oC, 20 min, and 1 cm, respectively.

The obtained results indicated that the higher the current density, the more rapid the increase of water temperature, see Figure 4-16. For instance, as the current density increased from 0.5 to 1, 2, and 3 mA/cm^2, the final water temperature increased from 20 to 20.1, 20.3, 21.4, and 23.2 ^oC, respectively. At the same time, these results confirm that at a conductivity of 0.6 mS/cm, the FCER is able to maintain the temperature of water being treated within a moderate range (20 -25 ^oC) even when the applied CD reaches 3 mA/cm^2.

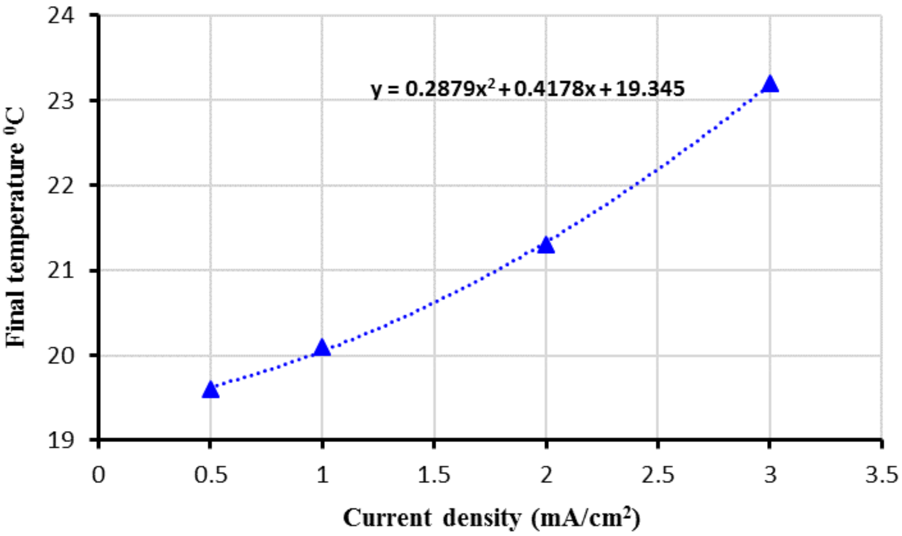


Figure 4-16: Influence of CD on the progress of water temperature.

4.6.1.4 Phase summary.

The results obtained from this preliminary phase of study confirmed that the new flow column EC reactor, FCER, has a very good performance in terms of water mixing, water aeration, and control of water temperature. The FCER was able to achieve a complete water mixing process within 9 min, according to the measured effluent concentration of RD dye and camera records. In terms of water aeration, the outcomes of the experimental work showed that the FCER is able to increase the DO concentration by 110.6% (from 5 to 10.53 mg/L) within 10 min of treatment. Furthermore, it has been noticed that the FCER possesses the ability to maintain the temperature of water being treated within the range of 22-28 ^{o}C even when the initial temperature of influent water and the applied current density were 35 ^{o}C and 3 mA/cm^2, respectively.

It is noteworthy that the FCER reduces the need for external stirring, aeration, or cooling devices that require extra power to work; these devices until now have been commonly used in the EC units (especially laboratory scale ones). Additionally, the aeration mechanism of the FCER takes place in the unsubmerged zone of the flow column that inhibits air bubbles generation inside the water being treated, which enhances energy consumption. Therefore, the FCER could be a cost-effective alternative to traditional EC reactors.

In conclusion, according to the results obtained from the current phase of study and the literature survey, the FCER is a promising cost-effective alternative to the traditional EC reactors; especially to treat pollutants that required moderate treatment temperature or low DO concentration water and wastewater. For instance, the literature survey indicated that the optimum temperature for water defluoridation (Mameri *et al.*, 1998), acid Red 14 dye removal from wastewater (Daneshvar *et al.*, 2004). COD removal from wastewater (Wang and Chou, 2009), sulfate removal from refinery wastewater (El-Naas *et al.*, 2014), polyvinyl alcohol removal from water (Chou *et al.*, 2010), is within the range of 20-28 ^{o}C.

PHASE II

4.6.2 Validation of FCER performance as an EC unit.

The performance of FCER as an EC unit has been validated through examining its ability to remove several pollutants from synthetic water samples, where, FCER has been used to remove fluoride, nitrate, and iron in batch flow pattern, and reactive black 5 dye (RB5) in a continuous flow pattern. The experimental work for each one of these pollutants is explained in detail in the following sections.

All the following experiments were carried out at room temperature (20 ± 1 ^{o}C), except those related to the influence of temperature, and a constant water conductivity (0.32 mS/cm). Water conductivity was adjusted using NaCl.

At the end of each run, electrodes were abraded with sandpaper (400 CW) and dipped for 5 min in an HCl solution (35%), and then carefully rinsed with deionised water to remove the accumulated impurities on the electrodes.

4.6.2.1 Fluoride removal

I. Methodology

Fluoride has been selected as one of the case studies because it is abundantly available in nature with an average concentration, in the earth's crust, ranging between 585 and 6000 mg/kg (Lide, 2008; Arif *et al.*, 2013). Moreover, some industries, such as semiconductor and aluminium plants, produce effluent that contains high concentrations of fluoride which is discharged into the aquatic environment (Zhu *et al.*, 2007; Emamjomeh and Sivakumar, 2009). Fluoride intake above1.5 mg/L causes serious health problems such as skeletal fluorosis and teeth mottling (Mameri *et al.*, 1998; Zhu *et al.*, 2007). Therefore, the World Health Organisation (WHO) limits fluoride in drinking water to 1.2 mg/L (Un *et al.*, 2013).

In this study, FCER has been applied to remove fluoride from drinking water taking into account the effects of initial pH, CD, ID, and initial concentration of fluoride. The first step in the experimental work was the preparation of a concentrated fluoride stock solution, 100 mg/L, by dissolving the required amount of NaF in deionised water. Then, 500 mL samples with different lower concentrations of fluoride (10, 15, and 20 mg/L) were diluted from this stock solution. The initial pH of these samples was adjusted to the desired value (4, 5, 6, 7, and 8) using 1 M HCl or 1 M NaOH solutions. While the CD (1 to 3 mA/cm^2) and ID (5 to 11mm) were manually adjusted to the required value. The electrolysing process was conducting using two electrodes with total effective area (A) of 284 cm^2. Four unsubmerged electrodes were used as water diffusers.

The progress of the defluoridation process was monitored by collecting 5 mL samples from the FCER at 5 min intervals during the course of the experiment. The collected samples were filtered with 0.22 µm filters (Millex syringe filters supplied by Sigma-Aldrich) to remove undesirable solids (Zhu *et al.*, 2007). The residual fluoride concentration was measured using a standard Hach Lange fluoride cuvettes test according to the instructions. 3 mL of the collected filtrate was pipetted into a cuvette and swirled a few times to mix the contents; then it was left for 1 min to react before measuring the fluoride concentration. The latter was measured using a Hach Lange spectrophotometer. The total removal efficiency was calculated using Eq. 10.

II. Results and discussion

The FCER has been applied to difluoride synthetic drinking water taking into consideration the influences of initial pH, CD, ID, and initial concentration of fluoride. Several sets of batch experiments were carried out by varying the initial values of pH from 4 to 8, ID from 5 to 11 mm, CD from 1 to 3 mA/cm^2, and the initial concentration of fluoride from 10 to 20 mg/L. Water conductivity and temperature were 0.32 mS/cm and 20 ± 1 ^{o}C, respectively.

A. Influence of initial pH

A broad body of previous studies evidenced that the influence of initial pH of the solution being treated on the performance of the EC units ranges from slight to significant depending on the targeted pollutants and the material of the electrodes used (Chen, 2004; Emamjomeh, 2006; Gao *et al.*, 2010; Khandegar and Saroha, 2013). The initial pH of solution not only affects the chemistry of solution but it also influences the speciation of the freshly produced coagulants.

Therefore, to investigate the influence of the initial pH of the solution on the performance of the FCER in terms of fluoride (F^-) removal, the initial pH of 0.5 L synthetic water samples containing F^-concentration of 10 mg/L was adjusted to the required value (from 4 to 8) using sodium hydroxide solution and hydrochloric acid. Then, these water samples were electrolysed for 25 min at a current density of 1 mA/cm^2, and an ID of 5 mm.

According to the results obtained from the experimental work, the initial pH of water samples exerted a moderate influence on fluoride removal, where a slight decrease was observed in fluoride removal as the initial pH increased from 4 to 8 to reach the lowest value at pH = 8, as shown in Figure 4-17. For instance, fluoride removal efficiency decreased from about 97% to 94% as the initial pH of water increased from 4 to 8, respectively. This could be mainly attributed to amphoteric characteristics of aluminium hydroxide, where the positively charged aluminium hydroxides that have high adsorption capacity are predominant in the neutral and slightly acidic pHs. While, in alkaline conditions (especially when the pH value exceeds 9), the Al $(OH)^{-}_{4}$, which has low adsorption capacity, becomes the prevailing hydroxide species, causing an obvious decrease in the removal efficiency (Emamjomeh and Sivakumar, 2009; Un *et al.*, 2013). Thus, in the current experimental work, an initial pH of 6.0 was selected to carry out the rest of the experiments.

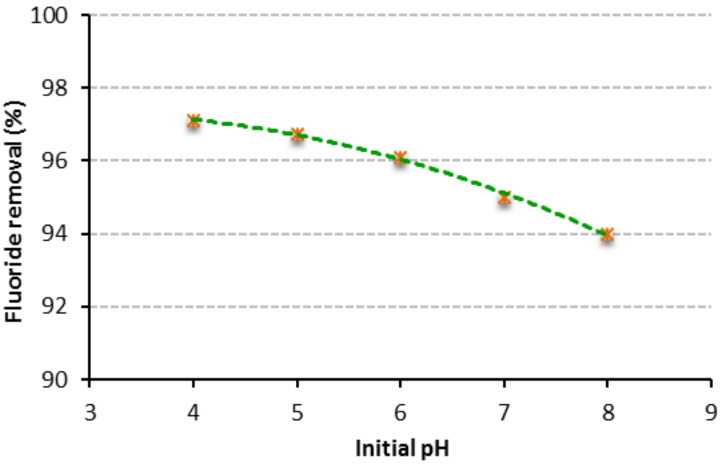


Figure 4-17: Influence of initial pH on fluoride removal.

B. Influence of inter-electrode distance

Inter-electrode distance (ID) was studied as a key parameter in this project as it has a significant influence on ohmic resistance, which greatly influences the energy consumption and the removal efficiency (Mameri *et al.*, 1998; Mohora *et al.*, 2012). Moreover, the optimum ID decreases the formation of the oxide film on the surface of the anode that enhances the anode dissolution (Ghosh *et al.*, 2008), which in turn enhances both the pollutant removal efficiency and the hydrogen gas production (Yang *et al.*, 2015).

To investigate the influence of the ID on fluoride removal and to determine the optimum distance between anodes and cathodes, batch experiments were carried out using a constant current density of 1 mA/cm^2, retention time of 25 min, and initial pH of 6, at IDs of 5, 8, and 11 mm.

The results, shown in Figure 4-18(A), indicated that fluoride removal decreased as the ID increased, where it can be clearly seen that, after 25 min of electrolysing, fluoride removal decreased from 96.3% to 85.2 % as ID increased from 5 mm to 11 mm, respectively.

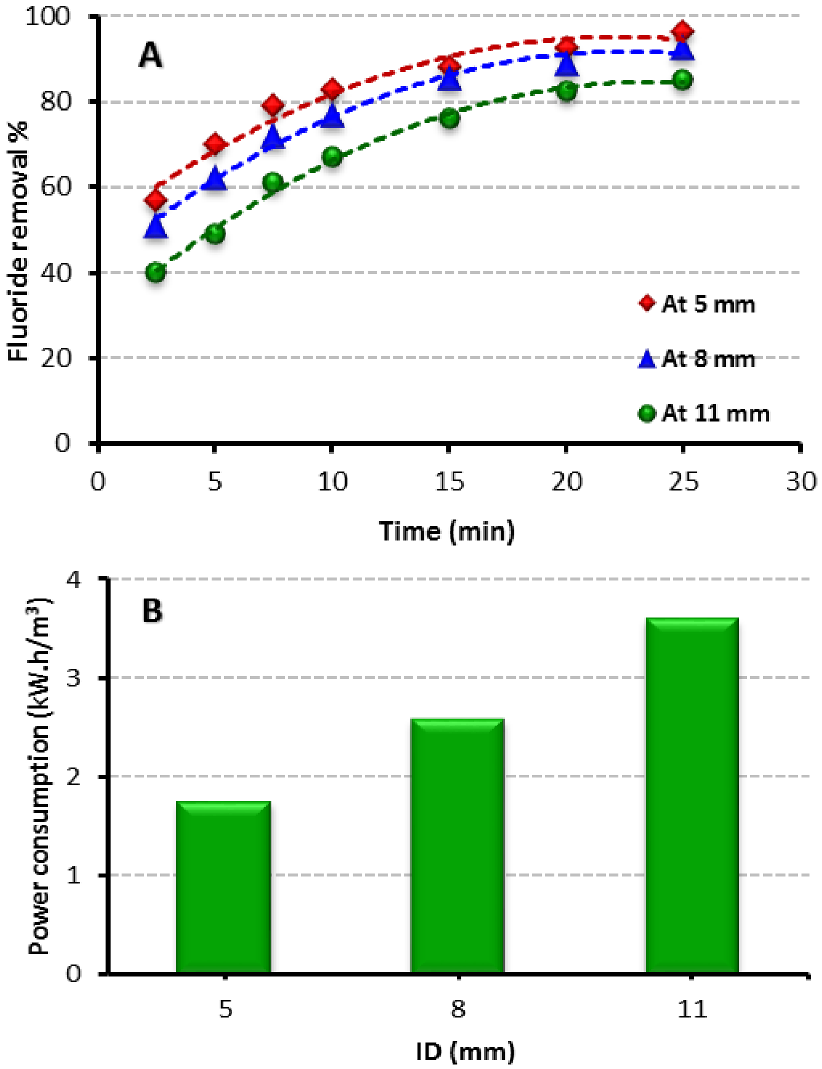


Figure 4-18: (A) Fluoride removal at different IDs, (B) Influence of ID on power consumption.

This could be attributed to the fact that the wide gap between electrodes promotes the formation of a very thin film of metal hydroxides on the anode, which decreases the number of produced coagulants, and consequently decreases the removal efficiency (Ghosh *et al.*, 2008). The effect of this film will be diminished as the inter-electrode distances decreased because the hydrogen gas, which is formed in the vicinity of the cathode, sweeps those fluoroaluminium complexes from the anode surface, and promotes the dissolution of the aluminium anode as a consequence (Mameri *et al.*, 1998). Additionally, widening the gap between the electrodes results in decreasing the electrostatic attraction force that decreases flocs formation, and consequently reduces removal efficiency (Khandegar and Saroha, 2013).

In terms of power consumption, it has been noticed that the power consumption increased as the gap between electrodes increased. Figure 4-18(B) shows that the power consumption increased from 1.75 to 3.6 kW.h/m^3 as the ID increased from 5 to 11 mm, respectively. This could be explained by the fact that if the distance increases then the resistance will also increase. Therefore, the current will decrease and the amount of floc formed will likewise decrease, hence the efficiency will change. The relation between the ohmic potential drop and the ID can be explained the equation 23 (Naje *et al.*, 2015):

$$IR = I \cdot \frac{ID}{A.k} \tag{23}$$

Where $IR, I, ID, A,$ and k represent the ohmic potential drop, current (A), gap between electrodes (m), area of the anode (m^2), and specific conductivity (µS/m) respectively.

However, a very short ID is not recommended as it maximises the electrostatic attraction force that increases the collision rate between the formed flocs, and consequently degrades them (Khandegar and Saroha, 2013). Hence, in the current investigation, the ID will be maintained at 5 mm for the rest of the experiments.

C. Influence of current density

Current density (CD) has a significant influence on the performance and energy consumption of the EC cells as it determines the rate of coagulant dosage, the rate of bubble generation, and size and the floc's growth (Un *et al.*, 2009; Vasudevan *et al.*, 2009; Gao *et al.*, 2010). Therefore, a set of batch experiments, to determine the influence of current density on the performance of the FCER in terms of fluoride removal and power consumption, were carried out using 10 mg/L of fluoride, initial pH of 6.0, ID of 5 mm, and retention time of 25 min, at CDs of 1, 2, and 3 mA/cm^2 .

The results obtained, Figure 4-19(A), indicated that the higher the current density was, the more rapid the fluoride removal was. For instance, 10 min at CD of 3 mA/cm^2 was enough to remove about 92% of the initial concentration of fluoride, while 20 min was required to reach this removal efficiency at CD of 1 mA/cm^2. This could be explained by the fact that the dissolved aluminium ions from the anode increase as the CD increases, and enhances flocs formation and fluoride removal as a consequence (Un *et al.*, 2013).

Although the obtained results proved that fluoride removal was enhanced as the CD increased, increasing the CD also maximised the power consumption, where Figure 4-19(B) shows that when the CD increased from 1 to 3 mA/cm^2, the power consumption exponentially rose from 1.75 to 12.4 kWh/m^3, respectively .Therefore, in this investigation, it might be reasonable to use the current density of 2 mA/cm^2 to perform the rest of experiments.

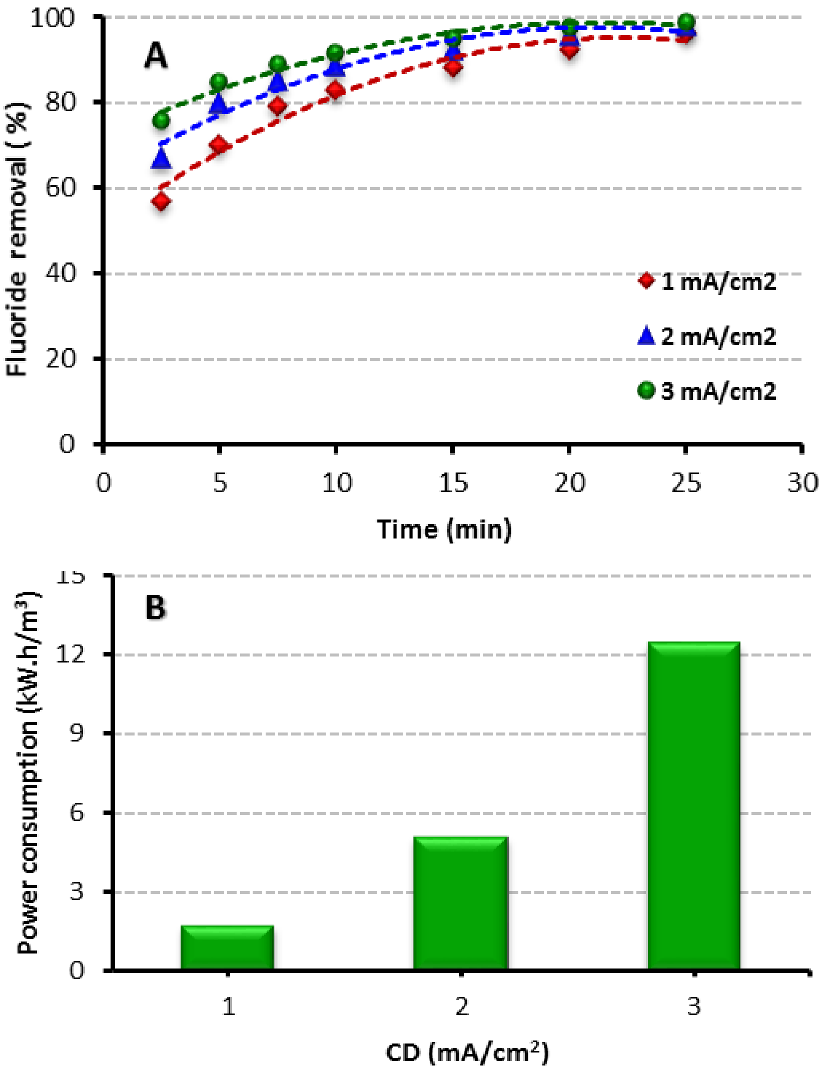


Figure 4-19: (A) Fluoride removal at different CDs, (B) Influence of CD on power consumption.

D. Influence of initial concentration of fluoride

The initial concentration of fluoride was varied from 10 to 15 and 20 mg/L, keeping all other parameters at the optimum values that were obtained from the previous experiments, in order to determine its influence on the performance of FCER. The results obtained, Figure 4-20, indicate that fluoride removal decreased from 98% to 92% as the initial fluoride concentration increased from 10 to 20 mg/L. Moreover, it was found that 13 min of electrolysing was enough to meet the WHO requirements (1.2 mg/L) when the initial fluoride concentration was 10 mg/L, but about 20 min was required when the initial fluoride concentration was 15 mg/L. This could be explained by the fact that the longer electrolysing time, the more coagulation ions were released from the anode (Emamjomeh and Sivakumar, 2009), and consequently the higher fluoride removal efficiency.

In summary, the obtained data from the experimental wok showed that 20 min of electrolysing using the FCER, at the optimum operating conditions, is enough to reduce the fluoride concentration to the permissible limits even when the initial concentration of fluoride is 15 mg/L.

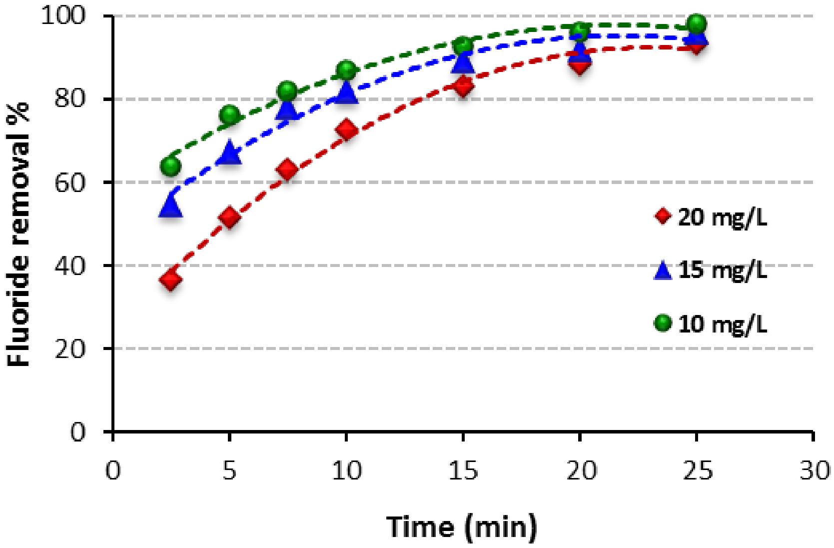


Figure 4-20: Fluoride removal efficiency for different initial concentrations of fluoride.

4.6.2.2 Nitrate removal

I. Methodology

There are two main reasons behind the choice of nitrate as a case study in this present work. First of all, the extensive use of nitrogenous fertilisers and recycling of domestic wastewater in rivers, which significantly increases nitrate concentration in water bodies (Emamjomeh and Sivakumar, 2005; Pak, 2015). Secondly, the presence of nitrate in drinking water poses serious threats to human health as it causes several diseases such as blue-baby syndrome (Vasudevan *et al.*, 2010) and gastric cancer (Ghafari *et al.*, 2008).

It is noteworthy to mention that the WHO limits nitrate concentration in drinking water to 50 mg/L and 15 mg/L for adults and infants, respectively (Abdallah *et al.*, 2014; Li *et al.*, 2009).

FCER has been applied for nitrate removal from drinking water taking into considerations the influences of initial pH, CD, ID, initial nitrate concentration, and retention time. Initially, a concentrated nitrate stock solution, 200 mg/L, was prepared by dissolving the required amount of KNO_3 in deionised water. 500 mL samples with different lower concentrations of nitrate (50, 100, and 150 mg/L) were diluted from this concentrated stock solution. The initial pH values of these samples were varied from 4 to 10 using 1 M HCl or 1 M NaOH solutions. The CD was varied from 1 to 3 mA/cm^2, and ID was varied from 3 to 10 mm. Additionally, the influence of electrolysing on nitrate removal was measured lengthening to 70 min.

Nitrate removal experiments were performed using two electrodes with total effective area of 284 cm^2; and other four unsubmerged electrodes as water diffusers.

During the course of the experiments, progressive nitrate removal was monitored by collecting 10 mL samples from the FCER at 5 min intervals. These samples were filtered with 0.45 µm filters (Whatman membrane filters supplied by Sigma-Aldrich) to remove undesirable solids (Abdallah *et al.*, 2014). Content of one NitraVer 5 nitrate reagent powder pillow was added to a standard test cell that contains 10 mL of the collected filtrate; shaken continuously for 1 min and then left for 5 min to react (Hach Lange instructions). Then, nitrate concentration was measured using a Hach Lange spectrophotometer. The total removal efficiency was calculated using Eq. 10.

II. Results and discussion

The FCER has been applied for nitrate removal from drinking water taking into consideration the influences of initial pH, CD, ID, initial nitrate concentration, and retention time.

The influence of the mentioned operating parameters on the performance of the FCER in terms of water denitrification has been investigated as follows:

A. Influence of initial pH

To explore the influence of the initial pH value on the performance of the FCER in terms of nitrate removal from synthetic water samples, the initial pH of 500 mL synthetic water samples, that contain 100 mg/L of nitrate, was adjusted to 4, 5, 6, 7, 8, 9, and 10. Each set of samples were electrolysed for 30 min at CD of 1 mA/cm^2, water conductivity of 0.32 mS/m, and ID of 5 mm.

Figure 4-21 shows the variation of nitrate removal with the initial pH value. According to this figure, the denitrification process using the FCER increased with the increase of the initial pH, where, it can be seen that nitrate removal gradually increased from about 25 % to

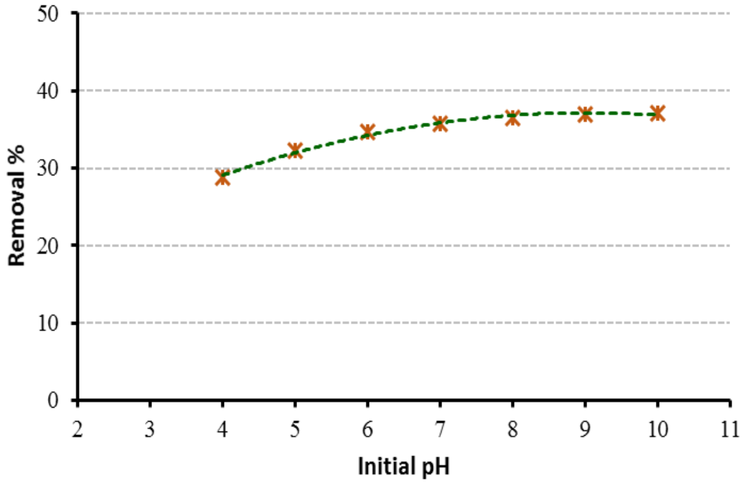


Figure 4-21: Variation of nitrate removal with the initial pH of water.

the vicinity of 35% as the initial pH increased from 4 to 7, then it remained almost at the same level for the rest of studied values.

This change in nitrate removal with the pH value could be mainly attributed to two facts. Firstly, the predominant species of aluminium in the neutral ranges of pH have high adsorption capacity (Ghosh et al., 2008; Emamjomeh and Sivakumar, 2009; Un et al., 2013), which in turn enhances pollutants removal efficiency. Secondly, in the alkaline environment, between 8 and 10, nitrate ions tends to attach to the passivated surface of the Al anodes and erode it. This increases the coagulants production rate and consequently enhances nitrate removal, i.e. compensates the decrease in high adsorption capacity aluminium species (Emamjomeh and Sivakumar, 2005; El-Shazly et al., 2011).

Thus, it might be reasonable, in the current project, to use an initial pH of 7 to carry out the rest of the experiments.

B. Influence of current density (CD)

The applied CD is another important parameter that significantly influences the EC process not only because it determines the amount of the liberated coagulants from the anode, but because it also determines bubbles generation and the floc's growth (Un *et al.*, 2009; Vasudevan *et al.*, 2009; Gao *et al.*, 2010). In order to explore the influence of the CD on the performance of the FCER in terms of nitrate removal and power consumption, 500 mL synthetic water samples containing 100 mg/L of nitrate were electrolysed at three different CDs (1, 2, and 3 mA/cm^2). The electrolysing process was carried out for 30 min at initial pH of 7, ID of 5 mm, and water conductivity of 0.32 mS/m.

Nitrate removal versus the applied CD is shown in Figure 4-22(A). It can obviously be seen from this figure that the higher the CD was, the more rapid the nitrate removal was. For instance, 30 min of electrolysing at 2 mA/cm^2 was required to remove 47% of the initial nitrate concentration, while 17 min was enough to achieve this removal efficiency. Additionally, after 30 min of treatment, nitrate removal efficiency increased from 35.7% to 53.4%, and 66.7% as the CD increased from 1, to 2, and 3 mA/cm^2, respectively. This direct proportion between nitrate removal and the magnitude of the applied CD can be attributed to fact that the CD determines the quantity of the liberated aluminium ions from the anode, thus the pollutant removal efficiency increased with the increase of CD (Vasudevan *et al.*, 2010; Un *et al.*, 2013).

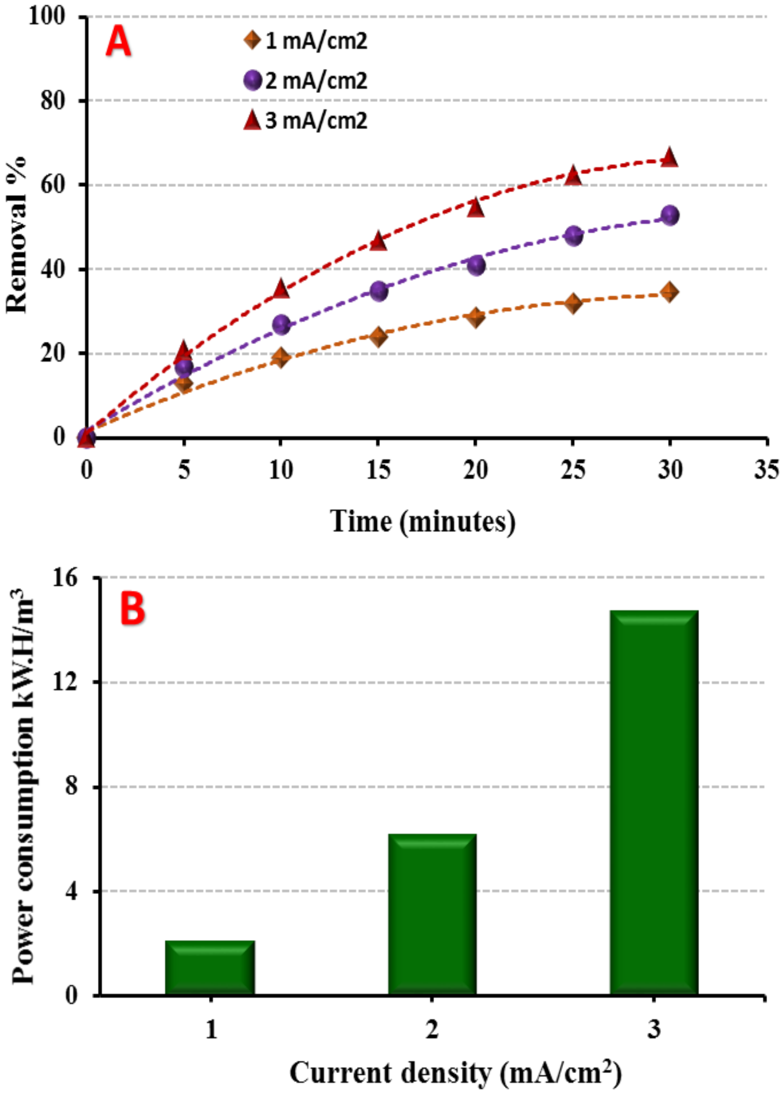


Figure 4-22: Effect of CD on: (A) nitrate removal, (B) power consumption.

At the same time, the results obtained showed that increasing the applied CD remarkably increased the power consumption. It can be seen from Figure 4-22(B) that the power consumption increased from 2.16 to about 14.7 kW.h/m^3 as the CD increased from 1 to 3 mA/cm^2, respectively. Taking into consideration the benefits and drawbacks of increasing the applied CD, the rest of the experiments were performed at CD of 2 mA/cm^2.

C. Influence of inter-electrode distance (ID)

The direct relationship between the electrical resistance of the EC and the gap between electrodes makes the latter an important operating parameter in the electrolysing process (Attour *et al.*, 2014; Sharma and Chopra, 2015). Furthermore, the ID significantly influences the power consumption due to influencing the electrical resistance, which in turn determines the ohmic drop (Hakizimana *et al.*, 2016). Thus, sets of batch experiments have been carried out to investigate the influence of the ID on nitrate removal using the FCER.

Variation of nitrate removal with the IDs was investigated by electrolysing 500 mL samples of synthetic water having 100 mg/L of nitrate at different IDs (3, 5, and 10 mm). The electrolysing process was carried out for 30 min at CD of 2 mA/cm^2, initial pH of 7, and water conductivity of 0.32 mS/m.

The results obtained, Figure 4-23(A), indicated that nitrate removal is inversely proportional to the ID. Nitrate removal decreased from 57.2 % to 46.8% as the ID increased from 3 to 10 mm.

As mentioned before, this could be explained by the fact that long ID promotes the formation of a very thin film of metal hydroxides on the anode, which decreases the number of produced coagulants, and consequently deceases the removal efficiency (Ghosh *et al.*, 2008). The effect of this film will be diminished as the inter-electrode distances decrease because the hydrogen gas, which is formed in the vicinity of the cathode, sweeps those fluoroaluminium complexes from the anode surface, and promotes the dissolution of the aluminium anode as a consequence (Mameri *et al.*, 1998).

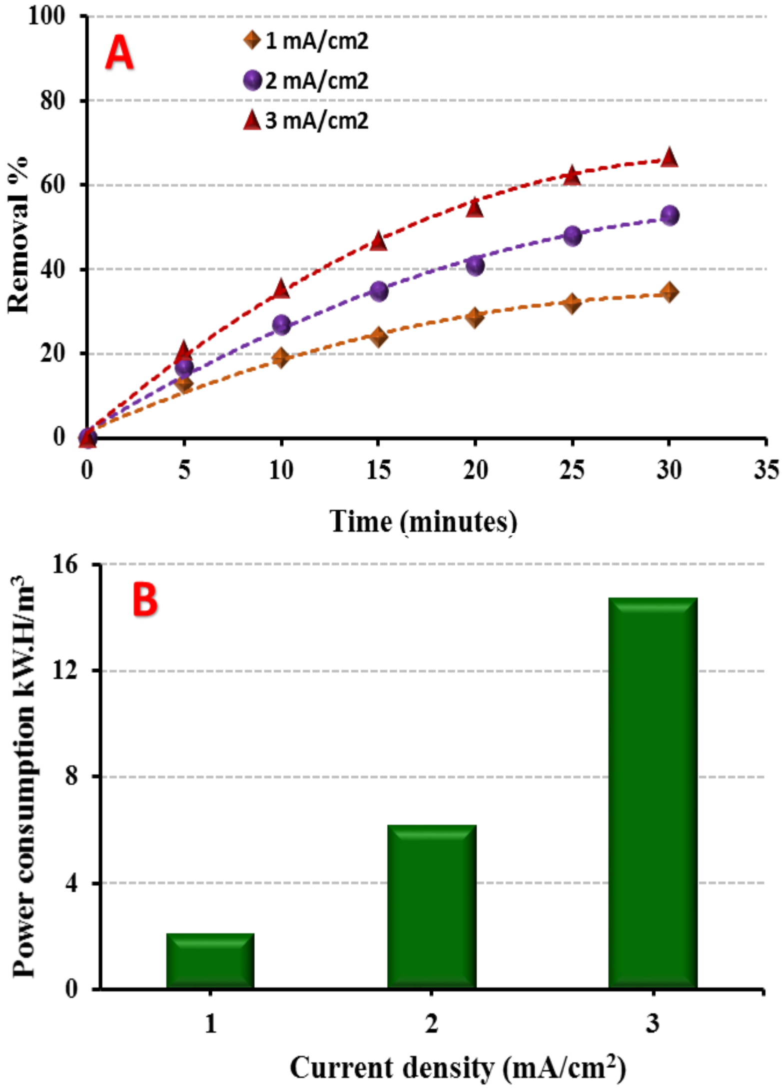


Figure 4-23: A) Variation of nitrate removal with the ID, (B) power consumption versus ID.

Moreover, it was found that increasing the gap between electrodes negatively influenced the power consumption, Figure 4-23(B), where; it was found that increasing the ID from 3 to 10 mm significantly increased the power consumption from 4.9 to 11.5 kW.h/m^3, respectively. Eq. 23 could be used to explain this phenomenon, if the distance increases then the resistance will also increase. Therefore, the current will decrease and the amount of floc formed will likewise decrease, hence the efficiency will change.

However, very short distances are not practical in the EC method (Vasudevan *et al.*, 2013), especially in the FCER as it makes expelling the accumulated air bubbles between electrodes a difficult process, and consequently these bubbles increase the energy consumption (Gao *et al.*, 2013). Therefore, taking into account the results of power consumption and nitrate removal, an ID of 5 mm was used to carry out the rest of the experimental work.

D. Influence of treatment time

The dissolved mass (dose) of the sacrificial anode was determined, as previously mentioned, for several operating parameters such as the applied current, molecular weight of the electrode material, and the electrolysing time. Indeed, the applied current and electrolysing time are the most important parameters in the anodic dissolving process as they determine the number of the liberated ions from the metallic anode (Bayramoglu *et al.*, 2004; Emamjomeh, 2006; Pallier *et al.*, 2011; Vidal *et al.*, 2016).

Therefore, sets of batch experiments have been carried out to investigate the change of nitrate removal over a specific electrolysing period. In this phase of study, 500 mL water samples having 100 mg/L of nitrate were treated for 70 min at initial pH of 7, CD of 2 mA/cm^2, ID of 5 mm, and water conductivity of 0.32 mS/cm. The progress of nitrate removal was monitored by collecting 5 mL samples every 5 min during the course of experiments; and filtered with 0.45µm Whatman filters. The filtrates were tested using a Hach Lange spectrophotometer to determine the residual concentration of nitrate.

The results obtained, Figure 4-24, proved that the pollutant removal increased as the treatment time increased, where, it has been noticed that the nitrate removal increased from about 48% to 95.2% as the treatment time increased from 25 to 70 min, respectively. Additionally, the results obtained showed that the FCER required about 27 min to meet the WHO recommended nitrate concentration (50 mg/L) for adults, and about 55 min to meet the WHO recommended nitrate concentration (15 mg/L) for infants.

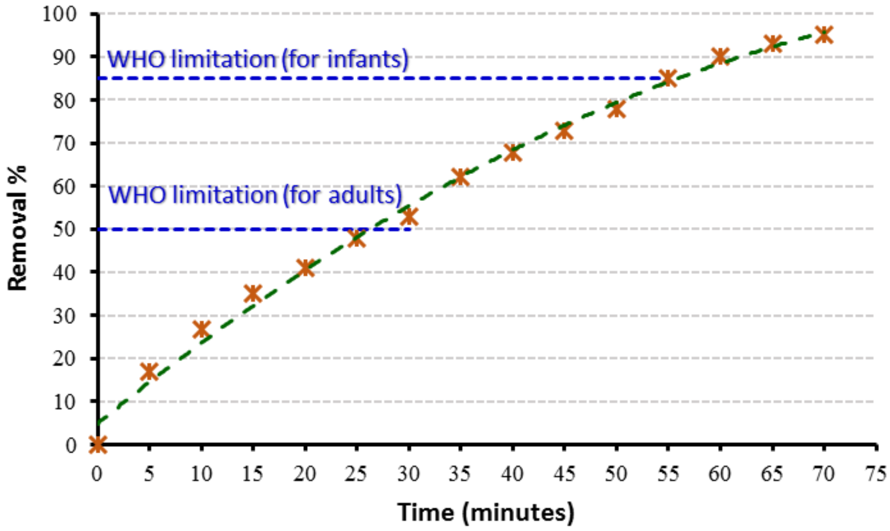


Figure 4-24: Progress of nitrate removal with the treatment time.

The progress of nitrate removal with the progress of electrolysing time is resulting from the increase in the quantity of freshly produced adsorbent (Ganesan *et al.*, 2013; Lu *et al.*, 2015). Moreover, longer electrolysing time gives longer contact time between pollutants and coagulants, which in turn enhances the removal efficiency (Lu *et al.*, 2015).

E. Influence of initial nitrate concentration

To explore the influence of the initial nitrate concentration on the performance of the FCER, synthetic water samples with lower concentrations of nitrate (50, 100, and 150 mg/L) were electrolysed for 70 min at a constant CD of 2 mA/cm^2, initial pH of 7, and ID of 5 mm (the optimum values obtained from the previous experiments).

The results obtained, Figure 4-25, indicated that nitrate removal efficiency is inversely proportional to the initial concentration of nitrate, where, it was found that after 50 min of electrolysing nitrate removal efficiency decreased from 100%, to 79%, and 59% as the initial concentration of nitrate increased from 50, to 100, and 150 mg/L, respectively. Additionally, it was found that the required treatment time to meet the WHO limitations, for adults' consumption, has increased from 27 to 58 min as the initial nitrate concentration increased from 100 to 150 mg/L, respectively.

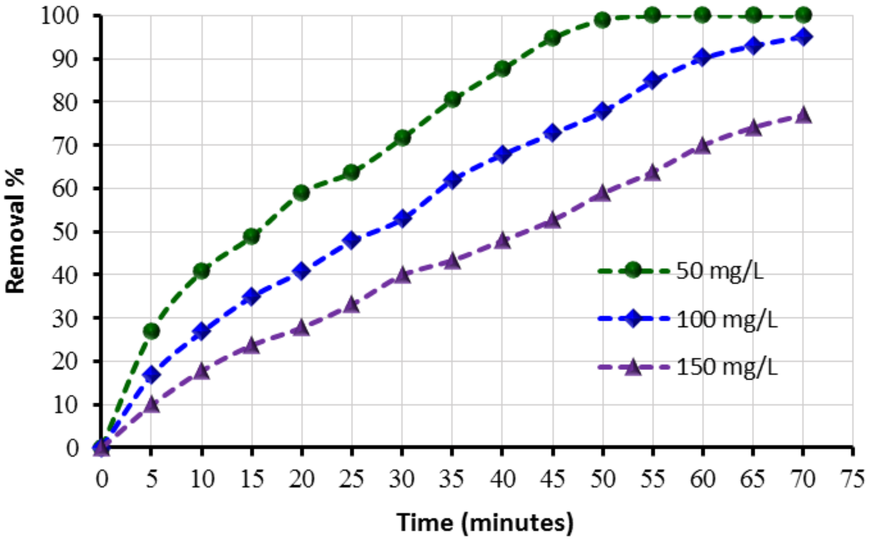


Figure 4-25: Influence of the initial concentration of nitrate on the removal efficiency.

Faraday's law (Eq. 14) explains the decrease of the removal efficiency with the increase of the initial concentration of nitrate. According to this law, a constant amount of coagulation ions is liberated from the sacrificial anode for the same CD and electrolysing time.

Consequently, the same quantity of aluminium ions (coagulants) was produced in the solution. Therefore, the flocs formed at high nitrate concentrations, were not sufficient to absorb all nitrate ions, i.e., the FCER needs longer to remove high nitrate concentrations.

In conclusion, the FCER is efficient to remove as much as 100 mg/L of nitrate from drinking water within 70 min of electrolysing at a CD of 2 mA/cm^2, and initial pH of 7. However, the FCER requires more than 70 min to remove higher concentrations of nitrate (higher than 100 mg/L).

4.6.2.3 Reactive black 5 dye removal

I. Methodology

Reactive black 5 dye (RB-5) is classified as an azo dye because it has a nitrogen double bond in its chemical structure (Salazar and Ureta-Zañartu, 2012), Figure 4-26. Azo dyes account for 60 to 70% of dyes used in textile industry (De Jager *et al.*, 2014). Discharging dyes-containing wastewater into the environment results in serious negative impacts on water quality as: (1) it causes unwanted aesthetic impacts such as colours and odours (Fu *et al.*, 2010); (2) decreases the sun light penetration and oxygen solubility (Santos

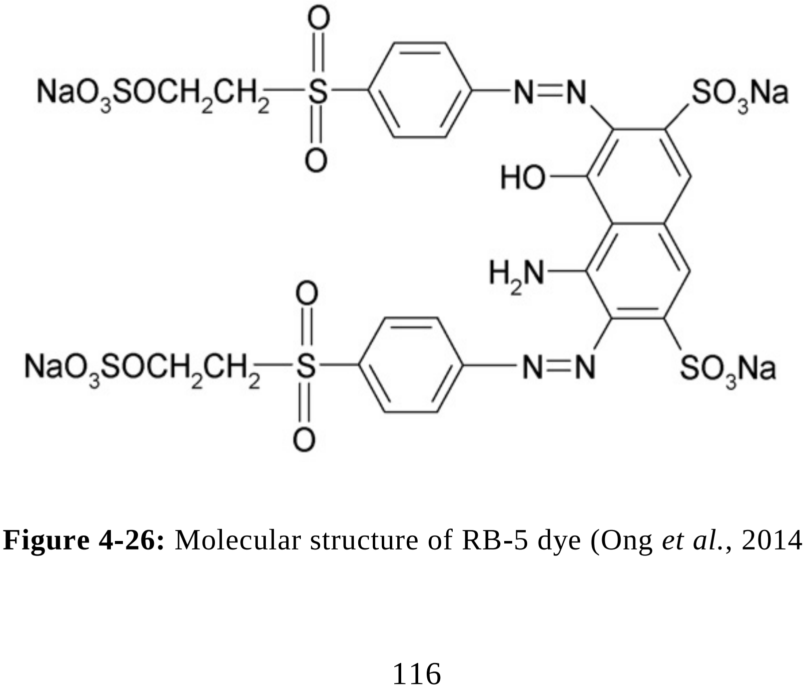


Figure 4-26: Molecular structure of RB-5 dye (Ong *et al.*, 2014).

and Boaventura, 2015; Firmino *et al.*, 2010). (3), several dyes and their decomposition products are carcinogenic(Joshi and Mhatre, 2015). (4), due to the high stability of some dyes’ decomposition products, they can survive in the aquatic life for 46 years at neutral pH water and temperature of 25 ^{o}C (Firmino *et al.*, 2010; Gole and Gogate, 2014). Based on the mentioned considerations, RB-5 has been selected as a case study in the present work.

Before applying the FCER to remove RB-5 dye from water samples, it was necessary to prepare a calibration curve for this dye. Firstly, the best wavelength (λ_{max}) was calculated by testing a 3 mL coloured sample with a known RB-5 dye concentration using a Hach Lange spectrophotometer at different wavelengths ranging between 400 and 600 nm, and the corresponding absorption value was recorded. It was found that the maximum absorption value took place at λ_{max} of 597 nm. Then the calibration curve was prepared by testing 27 water samples with RB-5 dye concentrations ranging between 0 and 25 mg/L, as shown in Figure 4-27.

Then, RB-5 dye removal from synthetic water samples was carried out in continuous flow mode using an FCER that was supplied with four electrodes (with a total effective area of 568 cm^2) and other four unsubmerged electrodes as water diffusers. A synthetic drinking water stock solution, 100 mg/L of RB-5, used in the present study was prepared using deionised water and the required amount of RB-5 dye. Samples with less RB-5 dye concentrations, were diluted from this stock solution. The initial pH value was adjusted to the desired level, in the range of 4 to 10, by using 1 M HCl or 1 M NaOH solutions.

Coloured samples were continuously pumped, at a flow rate of 1 L/h, into the FCER; and were treated at different initial pHs, CDs, IDs, and initial concentrations of dye in order to obtain the maximum removal efficiency.

5 mL water samples were periodically, every 5 min, collected from the outlet of the FCER to monitor the progress of the decolourisation process. The collected samples were filtered with 0.25 µm Whatman filters (supplied by Sigma-Aldrich) (Naje *et al.*, 2016); the residual dye concentration in the filtrate was measured using a Hach Lange spectrophotometer according to the pre-prepared calibration curve. The percentage of dye removal was calculated using Eq. 10.

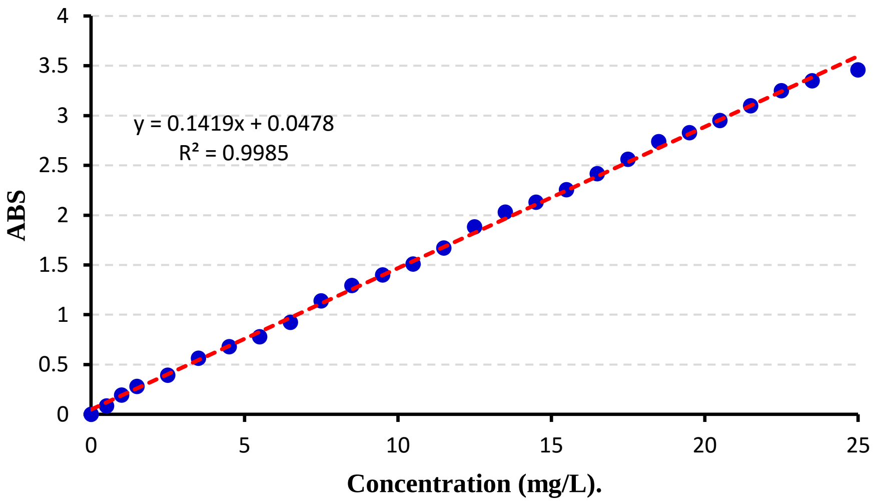


Figure 4-27: Spectrophotometric absorption values for RB-5 dye.

II. Results and discussion

RB-5 dye removal from synthetic water samples was carried out in continuous flow mode using the FCER that was supplied with four electrodes (with a total effective area of 568 cm^2). Coloured samples were continuously pumped into the FCER; and were treated at different initial pHs, CDs, IDs, flow rates, and initial concentrations of dye in order to obtain the maximum removal efficiency.

A. Influence of initial pH

A wide range of previously published works indicated that the initial pH of the solution being treated exerts weak to strong impact on the performance of the EC reactors depending on the targeted pollutants and the material of electrodes used (Chen, 2004; Emamjomeh, 2006; Gao *et al.*, 2010; Khandegar and Saroha, 2013). Where, it was reported that the initial pH could influence the chemistry of the solution, surface charges and speciation of the freshly produced coagulants (Sengil and Ozacar, 2009).

To examine the influence of initial pH on RB-5 removal from drinking water using the FCER, synthetic water samples having 25 mg/L of RB-5 with different initial pHs (4 to 8) were electrolysed for 40 min at flow rates of 1 L/h, CD of 2 mA/cm^2, ID of 4 mm, and water conductivity of 0.32 mS/cm.

Figure 4-28 depicts the influence of the initial pH on RB-5 removal from synthetic water using FCER. It can be seen from this figure that RB-5 removal in a slightly acidic environment was better than it was in a basic environment, where it has been noticed that the removal efficiency decreased from about 99.7% to 98.6%, 94.8%, and 80.3 % as the initial pH increased from 4 to 5, 6, and 8, respectively.

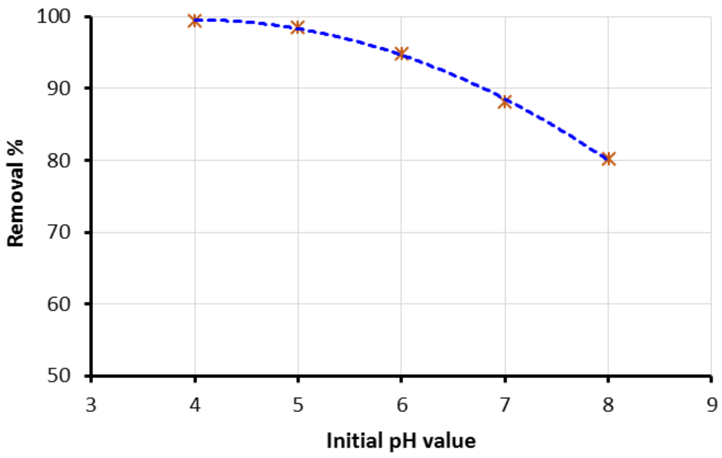


Figure 4-28: Influence of the initial pH on RB-5 removal efficiency.

This could be attributed to amphoteric characteristics of aluminium hydroxide, where the aluminium hydroxides that have high adsorption capacity are predominant in the neutral and slightly acidic pHs. While, in alkaline conditions (especially when the pH value exceeds 9), the $Al(OH)^-_4$, which has low adsorption capacity, becomes the prevailing hydroxide species, causing an obvious decrease in the removal efficiency (Emamjomeh and Sivakumar, 2009; Un *et al.*, 2013). Therefore, in the current work, initial pH of 5.0 will be used to carry out the rest of the experiments.

B. Influence of current density

Influence of CD on the performance of the FCER, in terms of the decolourisation process, has been examined by subjecting synthetic water samples having 25 mg/L of RB-5 for 60 min at different CDs (1,2, and 3 mA/cm^2), flow rate of 1 L/h, ID of 4 mm, initial pH of 5, and water conductivity of 0.32 mS/cm.

The results obtained, Figure 4-29(A), demonstrated that RB-5 removal is positively influenced by increasing CD, where, it has been found that the FCER required 30 min to achieve complete removal efficiency at CD of 3 mA/cm^2, and about 60 min at CD of 2 mA/cm^2 to achieve 98.6%.

Even though the results obtained indicated that RB-5 removal was enhanced as the CD increased, increasing the CD also increased the power consumption, where Figure 4-29(B) shows that as CD increased from 1 to 3 mA/cm^2, the power consumption increased from 4.3 to 10.4 kWh/m^3, respectively .Therefore, in the decolourisation experiments, it might be reasonable to use the current density of 2 mA/cm^2 to carry out the rest of the experiments.

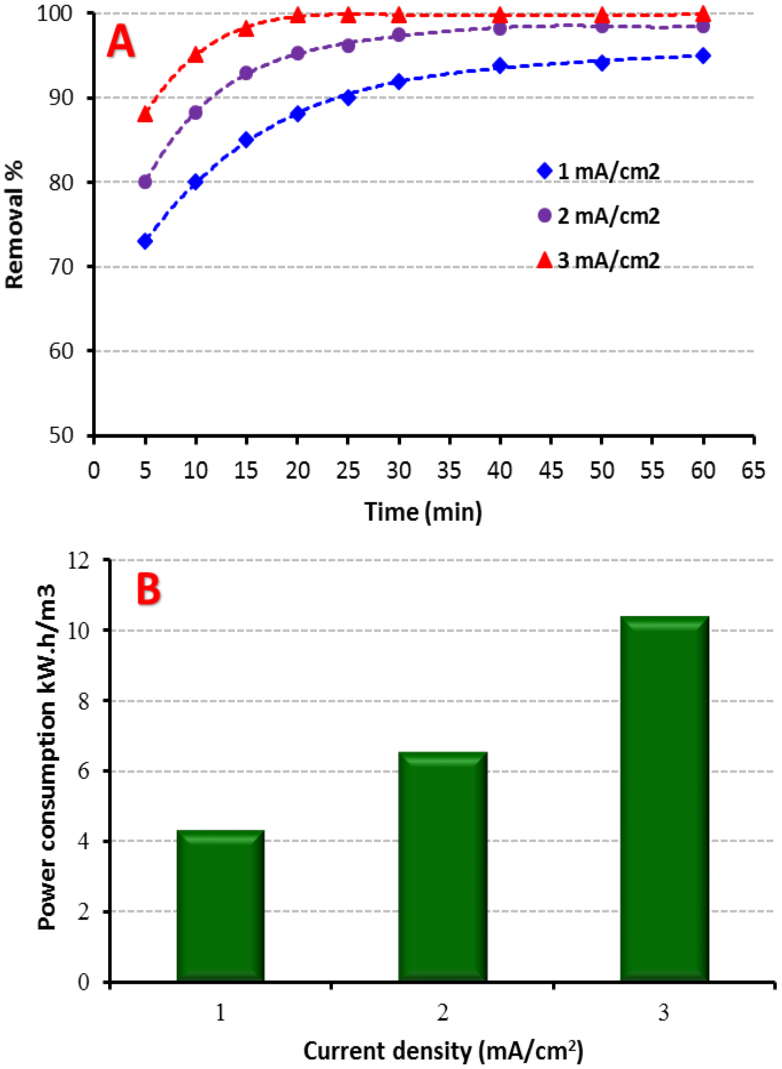


Figure 4-29: (A) RB-5 removal at different CDs, (B) Influence of CD on power consumption.

C. Influence of inter-electrode distance (ID)

In order to explore the influence of the ID on RB-5 dye removal efficiency, synthetic water samples containing 25 mg/L of RB-5 dye were electrolysed at different IDs (4, 8, and 12 mm). The electrocoagulation experiments were carried out for 60 min at a constant water flow rate of 1 L/h, initial pH of 5, CD of 2 mA/cm^2, and water conductivity of 0.32 mS/cm.

The results obtained, Figure 4-30(A), indicated that the wider the ID was, the lower the removal efficiency was. For instance, after 60 min of electrolysing, the removal efficiency decreased from about 98.6%, to 95.6%, and 90.8% as the ID increased from 4, to 8, and 12 mm respectively.

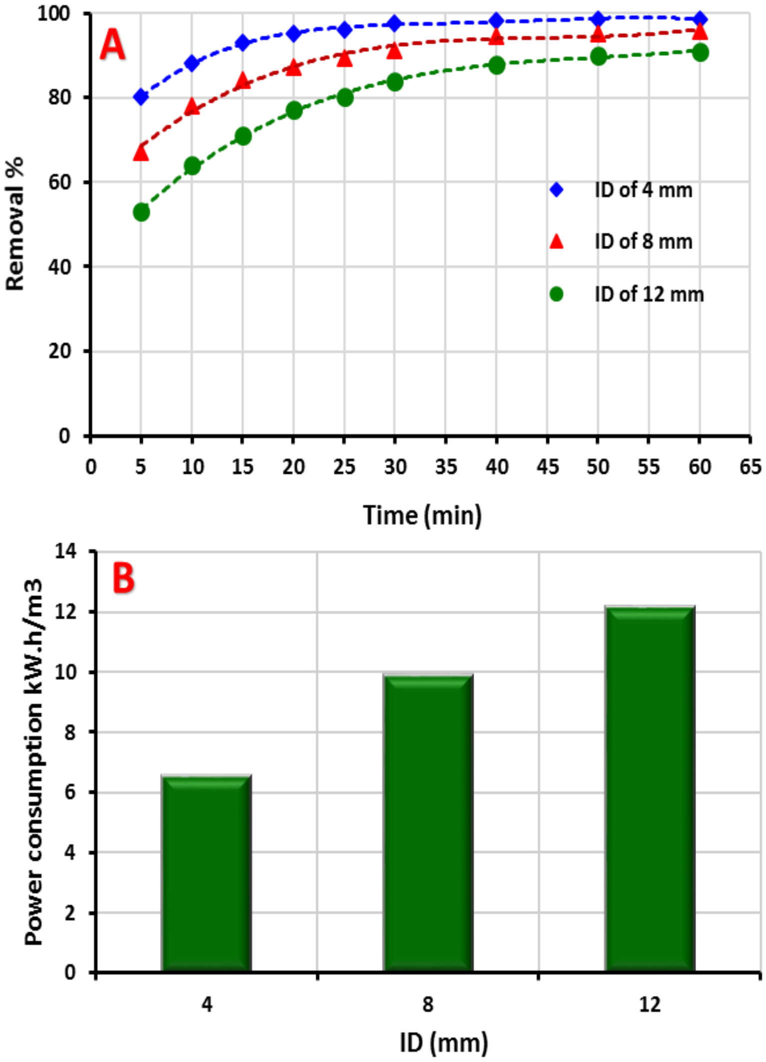


Figure 4-30: (A) RB-5 removal at different IDs, (B) Influence of ID on power consumption.

This behaviour could be attributed to two reasons, firstly; increasing electrodes spacing promotes the formation of the metallic anodic film that reduces the erosion rate of the anode, which in turn slows down the removal process (Mameri *et al.*, 1998; Ghosh *et al.*, 2008). Secondly, increasing the gap between the electrodes results in decreasing the electrostatic attraction force that decreases flocs formation, and consequently reduces removal efficiency (Khandegar and Saroha, 2013).

The influence of the ID on power consumption was examined by electrolysing synthetic water samples containing 25 mg/L of RB-5 dye at three different IEDs (4, 8, and 12 mm), while the CD, water flow, initial pH, and water conductivity were kept constant at 2 mA/cm^2, 1 L/h, 5, and 320 mS/cm, respectively. The results obtained indicated that the power consumption increased as the ID increased. It can be seen from Figure 4-30(B) that the power consumption increased from 6.5 kW.h/m^3 at IED of 4 mm to about 12.5 kW.h/m^3 at ID of 12 mm. This could be explained by Eq.31, increasing the distance between electrodes leads to increase the resistance. Therefore, the current will decrease and the amount of floc formed will likewise decrease, hence the efficiency will change. Thus, in the current project, ID of 4 mm was to carry out the rest of the experiments.

D. Influence of flow rate

The influence of flow rate (FR) on RB-5 removal has been studied by varying the FR from 1 to 1.3, 1.6, 1.9, and 2.2 L/h, while the initial pH, CD, ID, and initial concentration of RB-5 were kept at 5, 2 mA/cm^2, 4 mm, and 25 mg/L, respectively. As is shown in Figure 4-31, the removal of RB-5 dye is inversely proportional to the FR, where it was found that increasing the FR from 1 to 2.2 L/h has decreased the removal efficiency of RB-5 dye from 100% to 71.1%, respectively.

This could be explained by the fact that if the FR increases then the retention time will decrease. Consequently, the quantity of the produced aluminium ions (coagulants) in the solution will decrease and the amount of floc formed will likewise decrease, hence the efficiency will change. According to the results obtained, a FR of 1 L/h will be dependent to perform the rest of experiments.

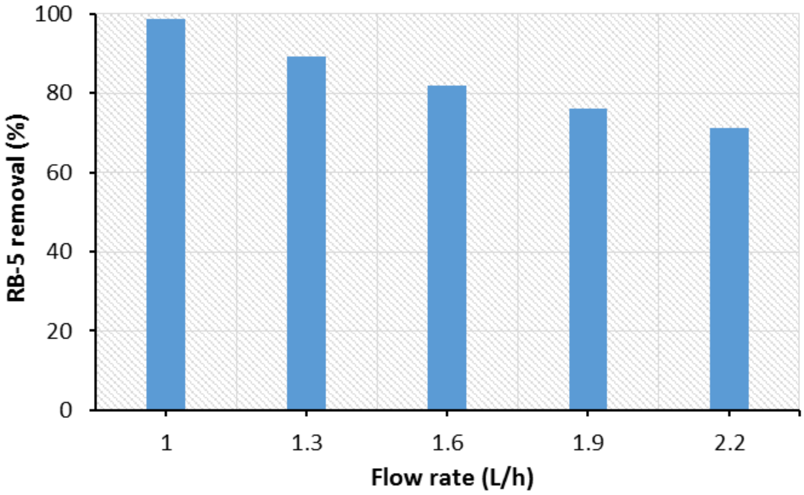


Figure 4-31: Influence of flow rate on RB-5 dye removal.

E. Influence of initial RB-5 concentration

To examine the influence of the initial concentration of dye on the performance of the FCER, synthetic water samples with different initial concentrations of RB-5 (25 to 50) were electrolysed for 60 min at a constant flow rate of 1 L/h, keeping all other parameters at the optimum values.

The results obtained, Figure 4-32, indicate that the higher the initial concentration of RB-5 dye, the slower the RB-5 removal was. For instance, it was found that after 60 min of treatment the RB-5 removal decreased from 98.6% to 91.2% as the initial concentration of RB-5 increased from 25 to 50 mg/L, respectively. Faraday’s law (Eq. 14) could explain this inversely relationship between the initial concentration of dye and the removal efficiency. According to this law, a constant amount of coagulation ions is liberated from the sacrificial anode for the same CD and electrolysing time. Consequently, the same quantity of aluminium ions (coagulants) was produced in the solution. Therefore, the flocs formed, at high RB-5 concentrations, were not sufficient to absorb all RB-5 dye, i.e., the FCER needs longer to remove high RB-5 concentrations.

In summary, the obtained results from the experimental wok showed that 60 min of electrolysing using the FCER, at the optimum operating conditions, is enough to remove as much as 92% of dye from drinking water even when the initial concentration of RB-5 was 50 mg/L.

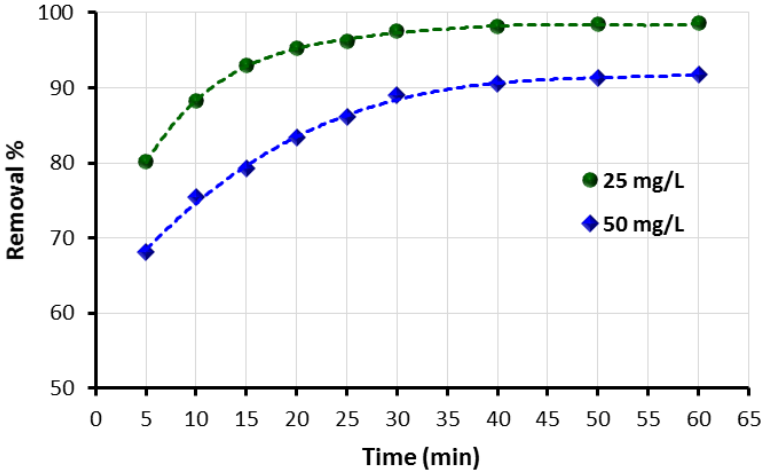


Figure 4-32: Influence of the initial concentration of RB-5 on the removal efficiency.

4.6.2.4 Iron removal

I. Methodology

Iron has been selected as a case study for heavy metal removal using the EC method for several reasons; firstly, it is one of the most abundant naturally occurring elements, which occupies about 5% of the Earth’s crust (Ityel, 2011), and it can be found in fresh waters at a concentration of 0.5 to 50 mg/L (WHO, 2004). Additionally, effluents of some industries, such as steel and iron industries, contain high iron concentrations (Ghosh *et al.*, 2008). Secondly, it can be safely used in the lab, where it is categorised as a secondary pollutant because it is not harmful for human beings (Phadke, 2014). However, the presence of iron in water causes an unpleasant taste and colour, and promotes bacterial growth, which in turn can block the plumbing (Ityel, 2011; Chaturvedi and Dave, 2012; Phadke, 2014). Based on these considerations, iron concentration in drinking water has been limited to 0.3 mg/L (WHO, 2004).

In the present work, iron removal from synthetic drinking water samples was conducted using an FCER that was supplied with two electrodes (with a total effective area of 284 cm^2) and four other unsubmerged electrodes as water diffusers. A concentrated iron stock solution, 300 mg/L, was prepared by dissolving a proper amount of $\mathrm{Fe_2}SO_4.7H_2O$ in deionised water. 500 mL samples with different lower concentrations of iron, ranging from 20 to 60 mg/L, were diluted from this stock solution.

To obtain the maximum removal efficiency, the influence of different operating parameters on iron removal was investigated. Where, the influences of initial iron concentration (20, 40, and 60 mg/L), water temperature (10, 20, and 30 ^{o}C), ID (5, 10, and 20 mm), initial pH (4, 5, 6, 7, and 8), CD (1, 1.5, and 2 mA/cm^2), and retention time (up to 50 min), on iron removal was investigated. Water temperature was adjusted to the desire value using either a water bath (for 20 and 30 ^{o}C) or ice bath (for 10 ^{o}C). While, the initial pH was adjusted to the desired value using 1 M HCl or 1 M NaOH solutions, the rest of the parameters were manually adjusted to the required value.

The progress of the iron electrolysing process was monitored by collecting 10 mL samples from the reactor at 5 min intervals during the course of experiments. These samples were filtered with 0.45 µm filters (supplied by Sigma-Aldrich) to remove undesirable solids (Phadke, 2014); then the residual concentration of iron in the filtrate was measured using an atomic absorption spectrophotometer. The percentage of iron removal was calculated using Eq. 10.

II. Results and discussion

Iron removal from synthetic drinking water samples was carried out using FCER taking into consideration the influence of the initial pH, CD, ID, water temperature, and initial concentration of iron.

A. Influence of initial pH

To find out the influence of the initial pH on iron removal efficiency from drinking water, a series of batch experiments were carried out by changing the initial pH (from 4 to 8) of synthetic water samples containing 20 mg/L of iron. Electrolysing experiments were performed for 20 min at a CD of 1.5 mA/cm^2, ID of 5 mm, and water temperature of 20 ^{o}C.

The results obtained indicated that the best iron removal efficiency occurred in the slightly acidic pH zone (between 6 and 7), where, it can be seen from Figure 4-33 that iron removal efficiency started to increase from 90.1 to the vicinty of 99% as the initial pH increased from 4 to 6, respectively, and slightly decreased to 98.9% as the initial pH increased to 7. Then, it brought a decreasing trend as the initial pH increased from 7 to 8.

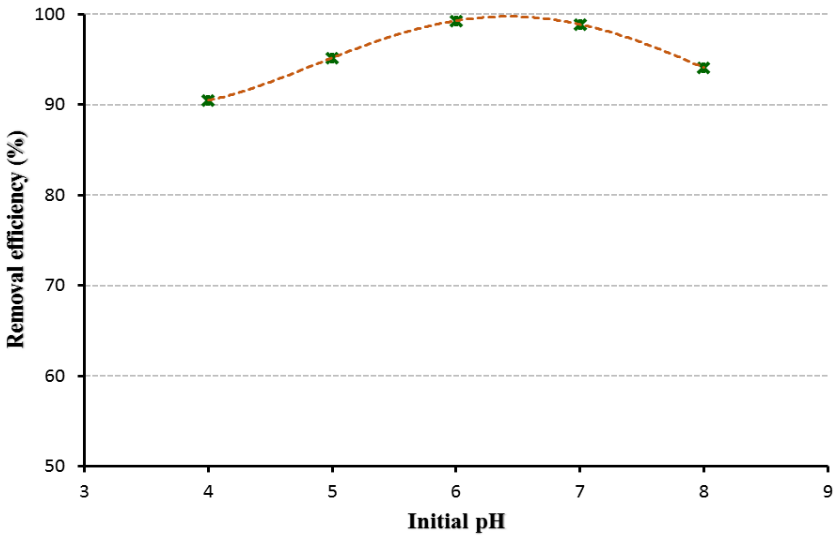


Figure 4-33: Influence of the initial pH on iron removal efficiency.

This could be attributed to the predominance of Al $(OH)_3$ aluminium hydroxides that have high adsorption capacity for iron ions in natural and slightly acidic environments, while in acidic and basic environments the prevailing aluminium hydroxides have low adsorption capacity for iron (Ghosh *et al.*, 2008; Emamjomeh and Sivakumar, 2009; Un *et al.*, 2013).

In the current project, based on the results obtained, it might be reasonable to perform the rest of the experiments at an initial pH of 6.

B. Influence of current density (CD)

Sets of batch experiments have been carried out to examine the influence of CD on iron removal from synthetic water samples. Three different values of the CD (1, 1.5, and 2 mA/cm^2) were applied for 20 min to treat synthetic water samples containing 20 mg/L of iron at ID of 5 mm, initial pH of 6, and T of 20 ^oC.

Figure 4-34(A) shows the iron removal efficiency against electrolysing time for the studied CDs. It can be seen that iron removal was very sensitive for the magnitude of the applied CD. For instance, it has been found that after 15 min of electrolysing the iron removal increased from 87.7% to 98.1%, and 99.1% as the CD increased from 1 to 1.5, and 2 mA/cm^2, respectively. In addition, it was found that at the end of the 20 min, as high as 99.6% of the iron was removed at a CD of 1.5 mA/cm^2, but it decreased to the vicinity of 93 % at a CD of 1 mA/cm^2. This can be attributed to the fact that the higher the current density, the more aluminium ions dissolved from the anode

(Vasudevan *et al.*, 2010; Un *et al.*, 2013), which in turn enhances flocs formation and iron removal.

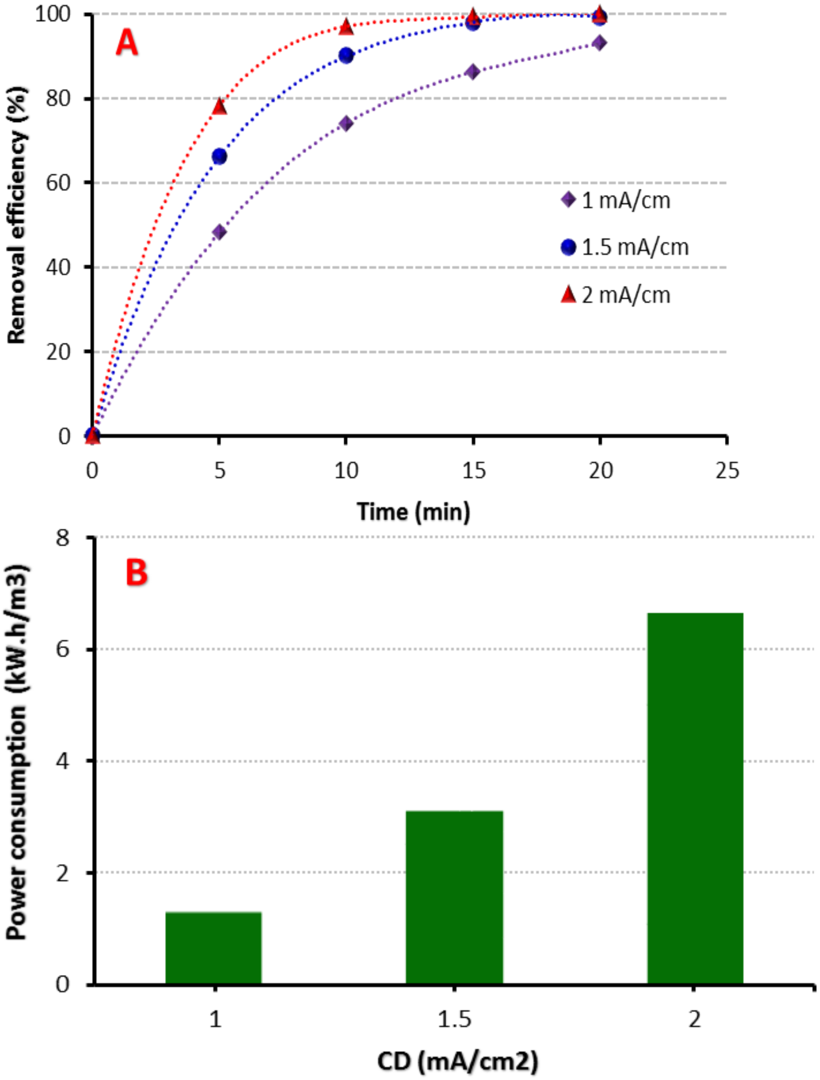


Figure 4-34: (A) Iron removal at different CDs, (B) Influence of CD on power consumption.

However, in terms of power consumption, Figure 4-34(B) indicates that increasing the applied CD negatively influenced the performance of the FCER, where, it has been found that the higher the current density, the higher the power consumption was. For instance, the power consumption was significantly increased from about 1.3 to 6.7 kW.h/m^3 as the CD increased from 1 to 2 mA/cm^2. Thus, taking into accounts the negative and positive influences of the CD on the performance of the FCER, the rest of the experiments will be carried out at a CD of 1.5 mA/cm^2.

C. Influence of inter-electrode distance (ID)

Variation of iron removal with the IDs was explored by carrying out a series of batch experiments, using 500 mL samples of synthetic water having 20 mg/L of iron, at different IDs (5, 10, and 20 mm). The electrolysing process was carried out for 20 min at CD of 1.5 mA/cm^2, initial pH of 6, and water temperature of 20 ^{o}C.

The results obtained, Figure 4-35(A), showed that iron removal is inversely proportional to the ID, where, it was noticed that the residual concentration of iron decreased from 20 mg/l to 0.06, 0.5, and 1.05 mg/L as the ID increased from 5 to 10, and 20 mm, respectively. As mentioned before, this could be explained by the formation of a very thin film of metal hydroxides on the anode at the wider IDs, which decreases the number of coagulants produced, and consequently deceases the removal efficiency (Ghosh *et al.*, 2008). The effect of this film will be diminished as the ID decreases because the hydrogen gas, which is formed in the vicinity of the cathode, sweeps those fluoroaluminium complexes from the anode surface, and promotes the dissolution of the aluminium anode as a consequence (Mameri *et al.*, 1998).

Furthermore, a significant increase was noticed in the power consumption as the ID increased. It can be seen from Figure 4-35(B) that the power consumption increased from about 3.3 to 7.3 kW.h/m^3 as the ID increased from 5 to 20 mm, respectively. According to Eq. 23, if the ID increases then the resistance will also increase. Therefore, the current will decrease and the amount of floc formed will likewise decrease, hence the efficiency will change.

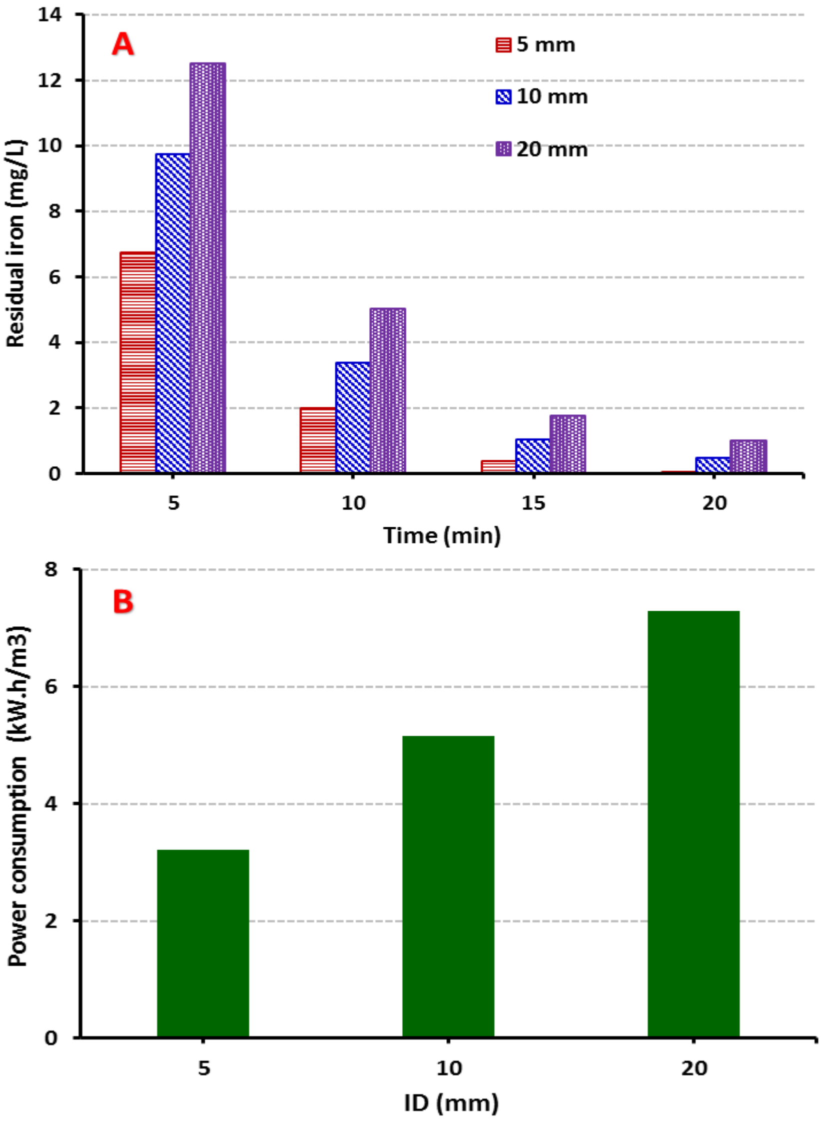


Figure 4-35: (A) Iron removal at different IDs, (B) Influence of ID on power consumption.

Based on the results obtained from iron removal efficiency and power consumption, an ID of 5 mm was used to carry out the rest of the experimental work.

D. Influence of initial water temperature

Like any other chemical reaction, EC reaction is influenced to a certain extent by the temperature of the solution being treated, as the temperature influences the mobility of ions and collision rate (Fouad *et al.*, 2009; and Attour *et al.*, 2014). In addition, it influences the activity of the adsorbent surface (Vasudevan *et al.*, 2012), the dissolving rate of the anode

(Song *et al.*, 2007; and Vepsäläinen *et al.*, 2009), the mass transport (Goa *et al.*, 2013), water conductivity (Zaroual *et al.*, 2009; and Gao *et al.*, 2010), and reducing water viscosity (Fouad *et al.*, 2009; and Goa *et al.*, 2010). In fact, increasing water temperature positively influences the performance of the EC method to a certain extent as the solubility of precipitates increases at high temperatures, which reduces the efficiency of EC units (El-Naas *et al.*, 2009; and Fouad *et al.*, 2009). Moreover, increasing the collision rate between flocs might degrade them (Daneshvar *et al.*, 2004, and Khandegar and Saroha, 2013).

A series of batch experiments have been devoted to examining the influence of water temperature on iron removal by electrolysing 20 mg/L iron-containing synthetic water samples for 20 min at different temperatures (10, 20, 30 and 40 ^{o}C). Experiments in which pH of 6, ID of 5 mm, and CD of 1.5 mA/cm^2 were kept constant indicated that increasing water temperature slightly enhanced iron removal and power consumption. It can be seen from Figure 4-36(A) that water temperature exerted a positive influence on iron removal during the first 10 min of electrolysing, but this influence became negligible after 15 min, where, iron removal increased, during the first 10 min of electrolysing, from 59.6 to 73.2 % as the initial temperature increased from 10 to 40 ^{o}C, respectively. While the difference between iron removal at 10 and 40 ^{o}C became only 3% after 20 min of treatment. As mentioned before, the increment in iron removal that accompanied the increase in water temperature could be attributed to the increase in the anodic dissolving rate, the increase in the collision rate between aluminium hydroxide and colloids, and the enlargement of the pore size on the adsorbent’s surface (Yilmaz *et al.*, 2008; Fouad *et al.*, 2009; Vasudevan *et al.*, 2012b).

In terms of power consumption, the initial temperature of water did not exert a significant influence on the performance of the FCER, Figure 4-36(B), where, it was found that the power consumption decreased, after 20 min of treatment, from 3.4 to 2.5 kW.h/m^3 as the initial temperature increased from 10 to 40 ^{o}C, respectively. The slight decrease in the power consumption could be explained by the fact that water viscosity decreases with the increase of temperature, which increases both the number and speed of ions. Therefore, the conductivity will likewise increase; hence, the power consumption will change (Barron and Ashton, 2005; Fouad *et al.*, 2009; Gao *et al.*, 2010; Zhao, 2012).

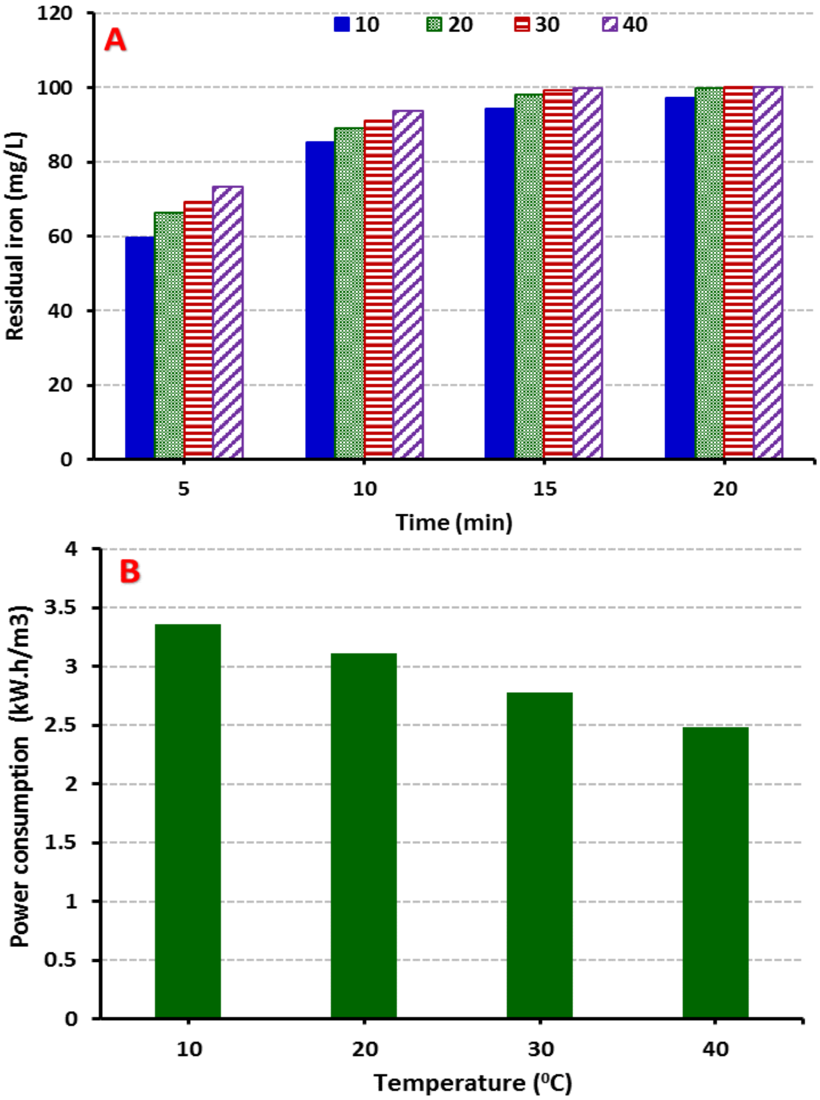


Figure 4-36: Influence of initial water temperature on: (A) Iron removal, (B) power consumption.

It could be concluded from the results obtained that increasing the water temperature greater than 20 °C had not significantly enhanced either iron removal or power consumption. Thus, it is reasonable to adopt the room temperature (20 °C) to carry out the rest of the experiments.

E. Influence of the initial concentration of iron

In order to examine the influence of the initial iron concentration on the performance of the FCER, synthetic water samples with lower concentrations of iron (20, 40, and 60 mg/L) were diluted from the stock solution. These samples were electrolysed for 50 min at a CD of 1.5 mA/cm^2, initial pH of 6, ID of 5 mm, and water temperature of 20 °C (the optimum values that were obtained from the experimental work).

The results obtained, Figure 4-37, show that iron removal increased with the increase of the initial concentration of iron, where, it was found that after 20 min of electrolysing, iron removal decreased from 99.6, to 93.1, and 81.1% as the initial concentration of iron increased from 20, to 40, and 60 mg/L, respectively. Additionally, it was found that the required treatment time to meet the WHO limitations, 0.3 mg/L, has increased from 20 to 41 min as the initial nitrate concentration increased from 20 to 60 mg/L, respectively.

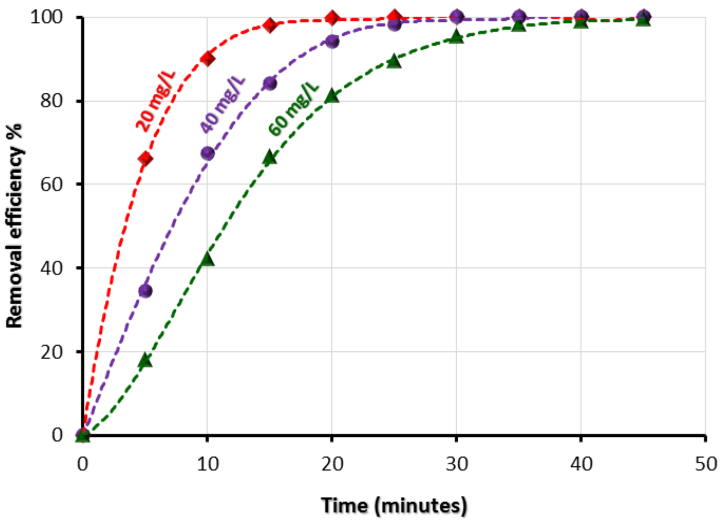


Figure 4-37: Influence of the initial concentration of iron on the removal efficiency.

According to Faraday’s law (Eq. 14), a constant quantity of coagulation ions is dissolved from the sacrificial anode for the same CD and electrolysing time. Accordingly, the same quantity of aluminium ions (coagulants) is produced in the solution. Therefore, the flocs formed at high iron concentrations, were not sufficient to absorb all iron ions, i.e., the FCER needs longer to remove the extra iron concentrations.

In summary, the FCER showed high efficiency in terms of heavy metals removal from drinking water. The results obtained showed that 25 min of electrolysing, at a CD of 1.5 mA/cm^2, and initial pH of 6, was enough for the FCER to meet the WHO limitations even when the initial concentration was 40 mg/L. However, the FCER requires a longer electrolysing time to remove higher concentrations of iron (60 mg/L).

4.6.2.5 Phase summary.

The current phase was allocated to investigate the performance of FCER in terms of the removal of fluoride, nitrate, RB-5 dye, and iron from drinking water. The results obtained proved that this new EC reactor was able to reduce the targeted pollutant to the permissible limits under continuous and batch flow conditions within a reasonable treatment duration. In the batch flow pattern, the FCER required about 20 min, 70 min, and 20 min to remove about 98%, 95.2%, and 99.6% of fluoride, nitrate, and iron respectively. While under the continuous flow pattern, it required about 60 min to reduce the concentration of RB-5 dye by 98.6%.

In fact, the results obtained from the present work were comparable with those in literature, such as the study of Mameri *et al.* (1998), Hu *et al.* (2003), and Un *et al.* (2013) for fluoride removal, Vasudevan *et al.* (2010) for nitrate removal, and Sengil and Ozacar (2009); Naje *et al.* (2016) and (Vidal *et al.*, 2016) for dye removal. However, it is noteworthy that the

FCER reduces the use of external stirring and aeration devices which require extra power to work; these stirrers and aerators until now have been widely used in the EC reactors. Therefore, the FCER could be a cost-effective alternative to the traditional EC reactors (especially lab-scale ones).

PHASE III

4.6.3 Influence of OM on heavy metal removal by EC method.

I. Methodology

This part of the study deals with the experimental proving of the existence of the targeted problem, which is the influence of OM on heavy metal removal by the EC method.

In this study, EDTA has been selected as an OM for two reasons; firstly, it has a strong ability to chelate heavy metal ions forming complexes which resist traditional treatment methods (Chen *et al.*, 2012; Lin *et al.*, 2015). Secondly, it is widely used in different industrial and domestic applications (such as detergents, painting, fertilisers, printed circuit boards, herbicides, and photography and surface treatment industries); thus industrial effluents often contain EDTA complexes with different heavy metals such as lead, nickel, and iron (Babay *et al.*, 2001; Lin *et al.*, 2015; Huang *et al.*, 2016).

Synthetic drinking water samples with different concentrations of EDTA, ranging from 50 to 500 mg/L, were prepared by dissolving the required quantity of EDTA in deionised water. To prepare EDTA-iron complex, 100 mL of pre-prepared iron stock solution (with iron concentration of 100 mg/L) and 400 mL of EDTA solution were placed in 1000 mL container and stirred for 5 min to ensure a homogenous distribution of contents; then stored (refrigerated to avoid the growth of iron-consuming bacteria) for the next use. EDTA-iron complex containing solution was electrolysed using FCER, which was supplied with two electrodes having a total effective area of 284 cm^2 and four other unsubmerged electrodes as water diffusers. To compare iron removal efficiency with and without ETDA, the electrolysing process was carried out under the optimum operating conditions obtained from the iron removal experiments, i.e., under the same values of initial pH, CD, ID, treatment time, water conductivity, and initial concentration of iron.

The progress of iron removal was monitored by collecting 10 mL samples from the reactor at 5 min intervals during the course of experiments. These samples were filtered with 0.45 µm filters (supplied by Sigma-Aldrich) to remove undesirable solids (Vepsäläinen *et al.*, 2012); then the residual concentration of iron in filtrate was measured using an atomic absorption spectrophotometer. The percentage of iron removal was calculated using Eq.10.

II. Results and discussion

This phase of study is a central one as it deals with the experimental proving of the occurrence of the targeted problem, which is the influence of OM on heavy metal removal by the EC method.

In order to investigate the influence of OM on iron removal from drinking water, synthetic water samples containing EDTA concentration ranges from 50 to 500 mg/L were electrolysed, using FCER, under the optimum operating conditions that were obtained from the iron removal experiments.

Figure 4-38 represents experimental evidence on the significant influence of OM on the ability of the EC units to remove heavy metals from water. It can be clearly seen from Figure 4-38 that the iron removal efficiency sharply decreased from 99.6% to

79.8%, 69.6%, and 59.5% as the concentration of EDTA increased from 0 to, 50, 100, and 200 mg/L, respectively. Furthermore, it was noticed that adding 500 mg/L of EDTA was enough to disable the iron removal process, where iron removal plateaued near 25%.

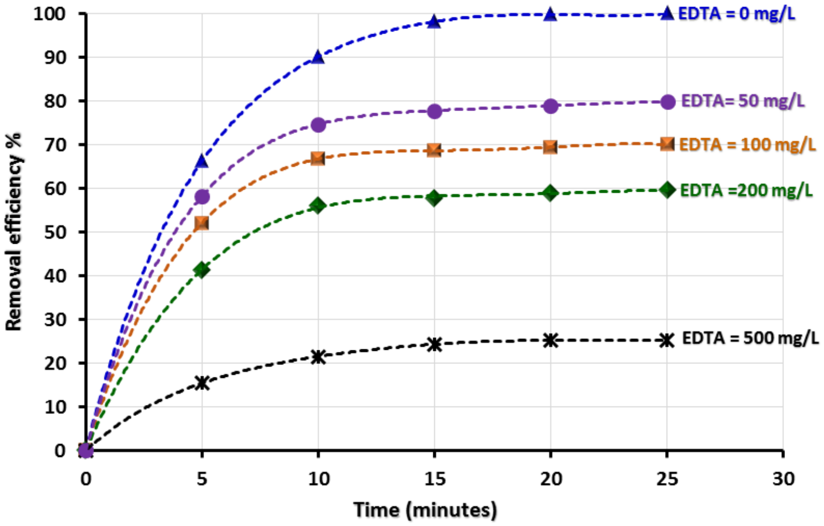


Figure 4-38: Influence of OM (EDTA) on iron removal from water.

The negative influence of EDTA on removal efficiency could be attributed mainly to the ability of EDTA to chelate iron forming a complex that is difficult to remove (Chen *et al.*, 2012; Lin *et al.*, 2015), and its ability (as an OM) to compete for active adsorption sites on flocs, decreasing the removal of the targeted pollutants (Matilainen *et al.*, 2010; Mohora *et al.*, 2014). Additionally, OM promotes the growth of the passive oxide film on the anode that decreases the number of the liberated ions, and consequently minimises the removal efficiency (Khandegar and Saroha, 2013; Mohora *et al.*, 2014).

The results obtained highlighted another negative influence of EDTA on the performance of the EC units, where it was found that the presence of EDTA in the water being treated increased the power consumption. Figure 4-39 shows that the power consumption increased from 3.85 to 4.08, and 4.52 kW.h/m^3 as the concentration of

EDTA increased from 0 to 100, and 500 mg/L, respectively. This could be explained by the fact that OM increases the power consumption of the EC units due to promoting the growth of an impermeable oxide layer on the anode. Therefore, the resistance for the current will increase and the power consumption will likewise increase (Matilainen *et al.*, 2010; Khandegar and Saroha, 2013).

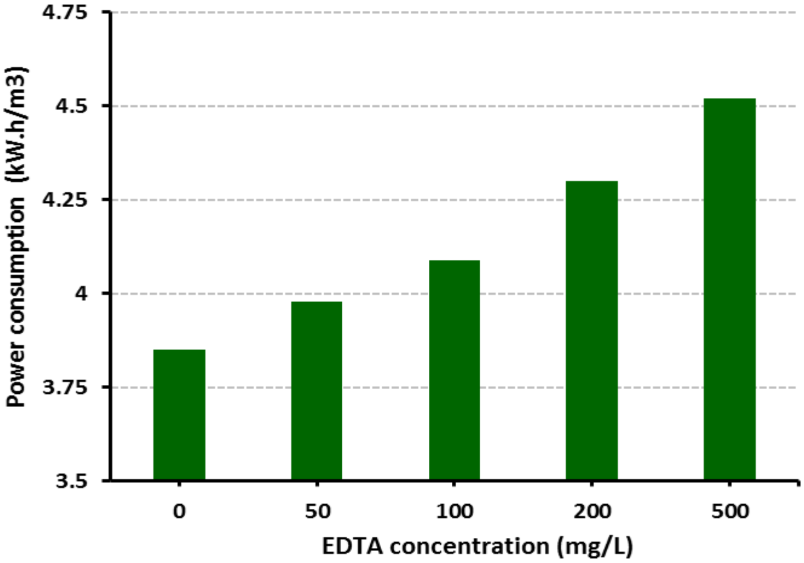


Figure 4-39: Influence of the concentration of OM (EDTA) on power consumption.

III. Phase summary.

The outcomes of this phase of study showed significant impacts of the OM on heavy metal removal from water and on the performance of the EC unit. The results obtained showed that the presence of 100 mg/L of EDTA was enough to reduce the iron removal efficiency by 30%, and increased the power consumption from 3.85 to 4.08 kW.h/m^3.

Therefore, the current project focuses on the application of a new, and environment friendly hybrid method to remove heavy metals from water in the presence of OM. This method is a combination of microwave and EC technologies (microwave assisted-EC unit).

PHASE IV

4.6.4 Application of the MW assisted-EC method to remove iron from water in the presence of OM (EDTA).

This phase of the study represents the main novelty of the present project as it deals with the application of a new MW assisted-EC treatment method to remove OM-heavy metals complex from water.

I. Methodology

OM-heavy metals complex removal using this hybrid method is carried out in two steps; MW irradiation and electrolysing. Initially, 500 mL EDTA-iron complex-containing water samples (contains100 mg/L of EDTA and 20 mg/L of iron) were subjected to MW field at different powers (50 to 300 W), temperatures (50 to 150 ^{o}C), and irradiation time (5 to 15 min). The irradiation process was performed using 35 mL glass vials (to fit the cavity of the MW device); each vial was supplied with magnetic flies to stir water during the irradiation process. During the microwaving process, vials were firmly closed using plastic caps to avoid any spilling inside the MW unit. The maximum allowable (emergency) pressure during sample irradiating was set for 120 PSI. After each run, the irradiated sample was left outside to cool down, to 20 ± 1 ^{o}C; then it was electrolysed at the same optimum conditions that were obtained in the iron removal experiments.

The electrolysing process was carried out at the optimum operating conditions that were obtained in the iron removal experiments. 10 mL samples were collected from the FCER at 5 min intervals during the course of the experiment. The collected samples were filtered with 0.45 µm filters (supplied by Sigma-Aldrich) to remove undesirable solids (Vepsäläinen *et al.*, 2012); then the iron concentration was measured using an atomic absorption spectrophotometer. Iron removal efficiency was calculated using Eq.10.

Extra sets of batch experiments were carried out to investigate whether the enhancement of iron removal was due to the thermal MW effects or due to both thermal and athermal MW effects. To achieve this target, traditional and MW heating sources were used to heat two groups of EDTA-iron complex-containing synthetic water samples (with symmetrical characteristics) to 100 °C for 10 min. The traditional heating process was carried out using a water bath supplied with a plastic cover. Heated samples were left at room temperature to cool down to the range of 20±1 °C. Then, the EC process was carried out at the same optimum conditions that obtained in the iron removal experiments. Additionally, COD removal was calculated using the Hach Lange COD cuvette test. Initially, the COD cuvette was shaken to bring the sediment into suspension; then 2 mL of the collected filtrate was pipetted into the cuvette and inverted two times to mix the contents. Then, immediately, the COD cuvette was heated at 148 °C for 120 min using a pre-heated heating block Hach Lange dry thermostat. At the end of the heating period, the COD cuvette was left in a rack to cool to approximately 60 °C; shaken again a few times and left to cool to room temperature. Then, the COD concentration was measured using a Hach Lange spectrophotometer.

II. Results and discussion

A. Influence of MW power

The influence of MW power on the removal of iron from water was investigated by irradiating 500 mL EDTA-iron complex-containing synthetic water samples for 10 min at three different powers (50, 100, and 300 W) keeping the temperature constant at 50

^{o}C. The irradiated samples were kept at room temperature to cool down to the range of 20±1 ^{o}C. Then, these samples were electrolysed using the FCER at the optimum conditions of iron removal.

The results obtained indicated that the performance of the EC unit (FCER) has enhanced (in terms of iron removal) as the MW power increased. It can be seen from Figure 4-40(A) that microwaving the synthetic samples for 10 min at 50, 100, and 300W has increased iron removal from 69% (non-microwaved) to 71.1% to 74.3%, and 76.2%, respectively. This could be explained by the fact that the higher the MW power, the faster the heating was, which in turn induces rapid molecular motion of ions polar and clusters (Yang *et al.*, 2014). Additionally, the MW field, especially the hotspots,

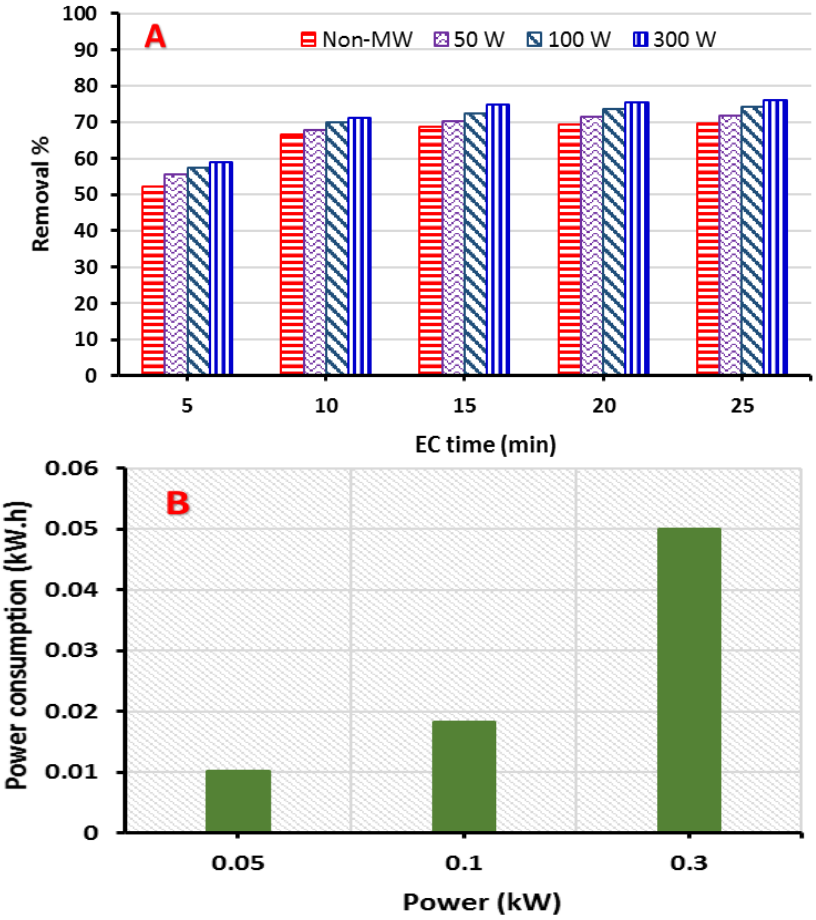


Figure 4-40: Influence of MW power on: (A) Iron removal using EC method, (B) power consumption.

rapidly provides the required temperature to break the chemical bonds without influencing the activation energy (Hayes, 2002).

Although it has been found that the higher the MW power, the better the iron removal was, increasing the MW power negatively influenced the energy consumption. A quick glance at Figure 4-40(B) reveals that increasing the MW power from 50 to 100, and 300 W dramatically increased the power consumption from 0.01, to 0.018, and 0.05 kWh, respectively, i.e., increasing the MW power from 50 to 300W increased the power consumption by about five fold. Thus, in this project, a MW power of 100W will be used to carry out the rest of experiments.

Figures 4-41, 43 show the power, temperature, and pressure profiles during the microwaving process.

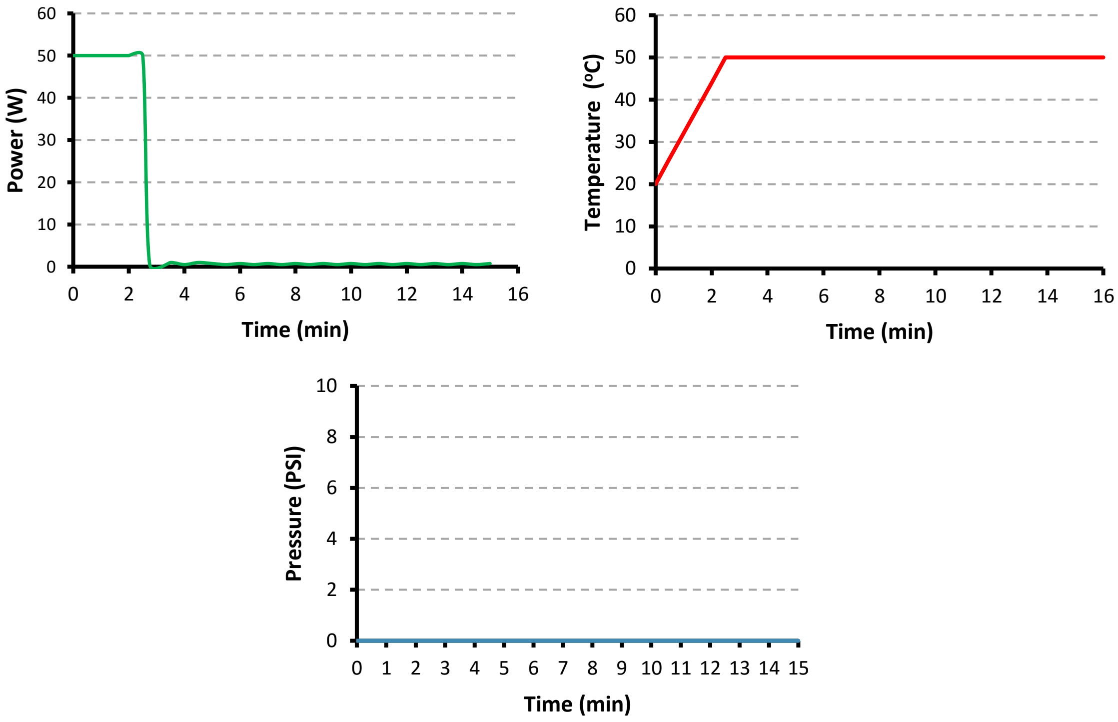


Figure 4-41: Power, temperature, and pressure profiles during microwaving at 50 W.

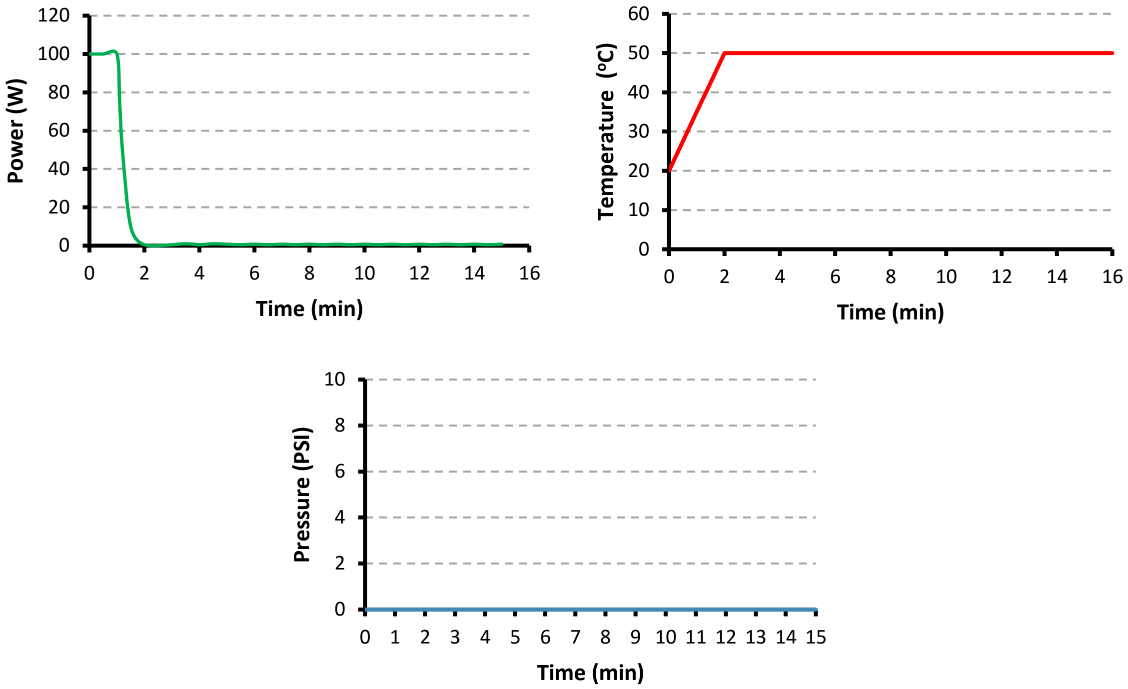


Figure 4-42: Power, temperature, and pressure profiles during microwaving at 100 W.

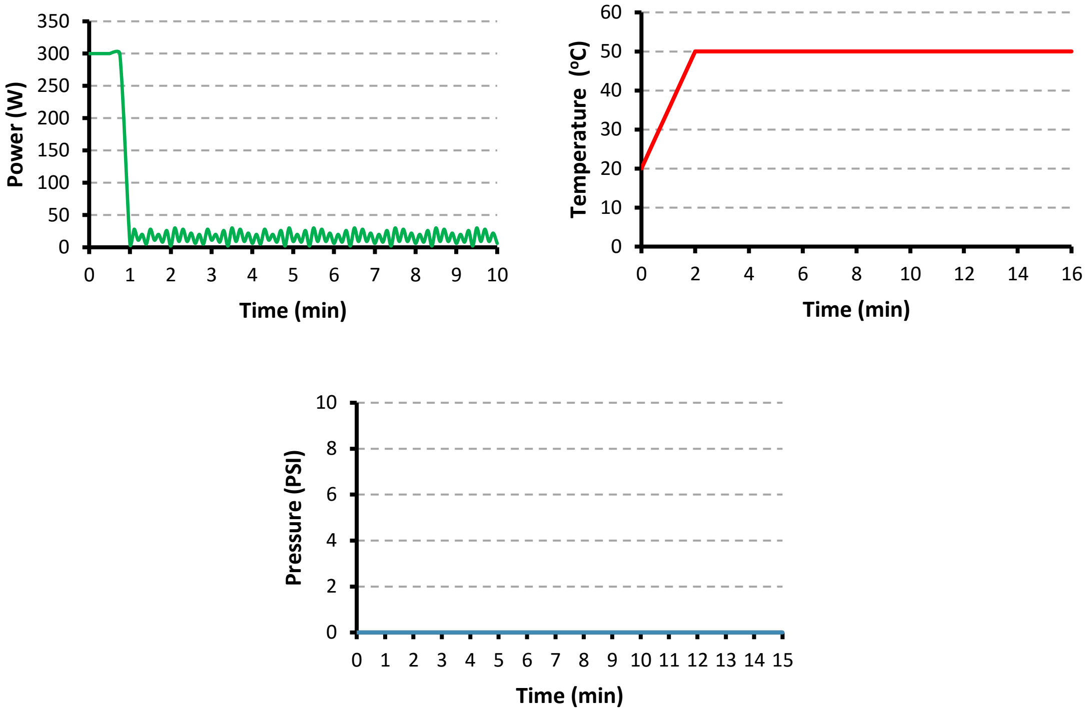


Figure 4-43: Power, temperature, and pressure profiles during microwaving at 300 W.

B. Influence of MW temperature

The heating process plays a central role in the decomposition and removal of pollutants from aqueous media. One of the most effective heating methods is the MW one, as the MW energy couples with the molecules of the substance being heated, which means the heat is generated from within the mixture without heat transfer (Hayes, 2002; Bassyouni *et al.*, 2011). Additionally, MW heat is independent of the thermal conductivity of the container because it is generated through the direct absorption of MW energy by the targeted substance (Wong and Gupta, 2015). Another unique and effective heating phenomenon takes place during the MW heating, which is the hotspots. The temperature in these microscopic spots, 0.1 mm in size, is about 100 – 200 ^{o}C higher than the bulk temperature (de la Hoz *et al.*, 2005), and can reach 1000-1200 ^{o}C on the absorbent surface (Zhu *et al.*, 2007; Fu *et al.*, 2010; Xu *et al.*, 2014). Therefore, MW irradiation results in a rapid superheating of the substance that produces enormous accelerations in many chemical reactions, which cannot be produced by traditional heating. The MW heating technique has been successfully used to remove different pollutants from water and wastewater, such as nitrogenous compounds, pyridine, volatile fatty acid (Lin *et al.*, 2009b; Zalat and Elsayed, 2013; Yang *et al.*, 2014).

In order to investigate the influence of MW heating on the performance of the FCER in terms of iron removal, sets of 500 mL EDTA-iron complex-containing synthetic water samples were microwaved for 10 min at different temperatures (50, 100, and 150 ^{o}C), keeping the MW power constant at 100W. Then, these samples were left at room temperature to cool down to the range 20±1 ^{o}C, and electrolysed at the optimum conditions of iron removal.

The results obtained, Figure 4-44(A), showed the performance of the FCER, in terms of iron removal, enhanced with the increase of MW temperature. It has been found that the iron removal efficiency, increased from 69.6% (for non-microwaved samples) to 74.3%, 92%, and 95.6% as the microwaving temperature increased from 50, to 100, and 150 °C, respectively. As is mentioned in the chapter 4, the increase in iron removal could mainly be attributed to the unique thermal effects of the MW field. If the applied MW temperature increases then the coupled MW energy with the molecules of the substance being heated and the temperature of the hotspots will also increase. Therefore, a rapid superheating of the substance being heated takes place and the decomposition of the EDTA-iron complex will likewise increase, hence the iron removal by the EC unit will increase.

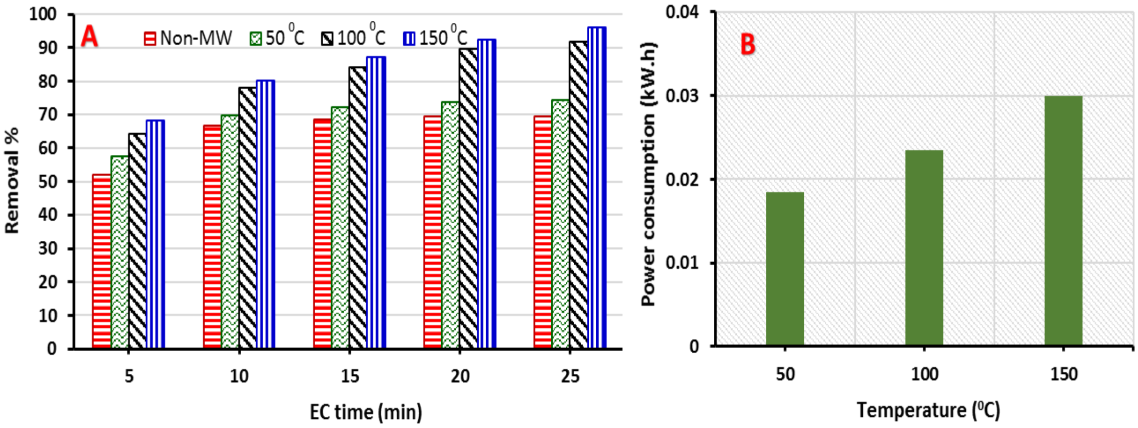


Figure 4-44: Influence of MW temperature on: (A) Iron removal using EC method, (B) power consumption.

However, the results obtained show increasing the MW temperature requires longer duration, which negatively influences the operational cost of the unit due to increasing the power consumption. For instance, figure 4-44(B) shows that increasing the temperature from 50 to 100, and 150 °C has increased the power consumption from 0.018 to 0.023, and 0.03 kWh, respectively. Therefore, a MW temperature of 100 °C will be used to perform the rest of the experiments. Power, temperature, and pressure profiles are shown in Figures 4-45, 47.

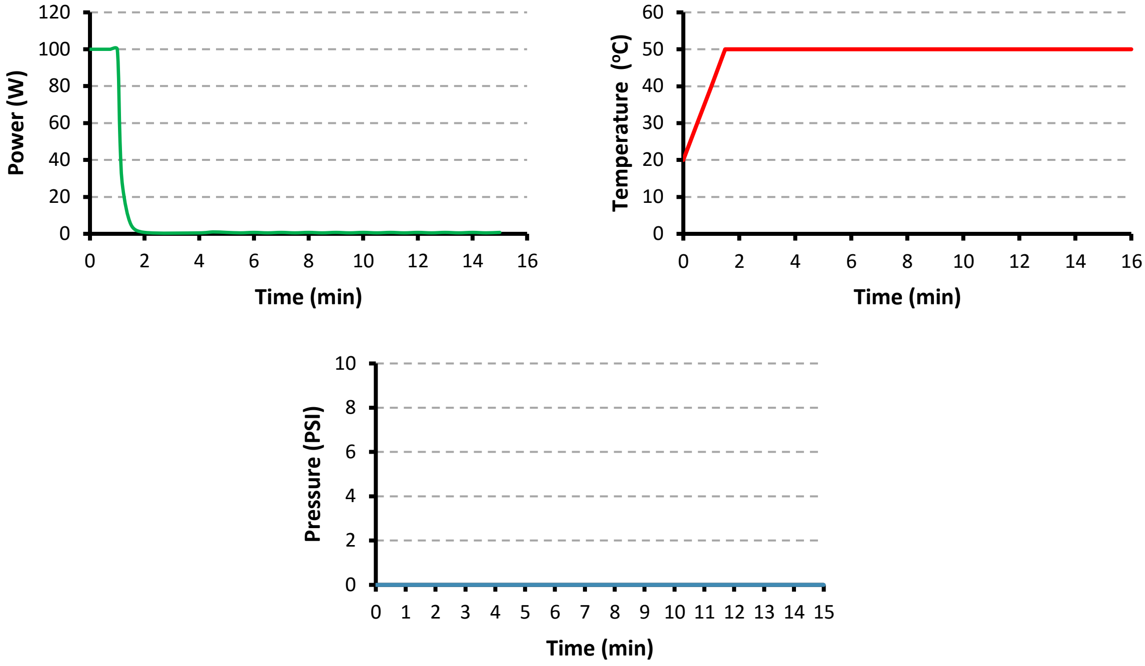


Figure 4-45: Power, temperature, and pressure profiles during microwaving at 100 W and 50 °C.

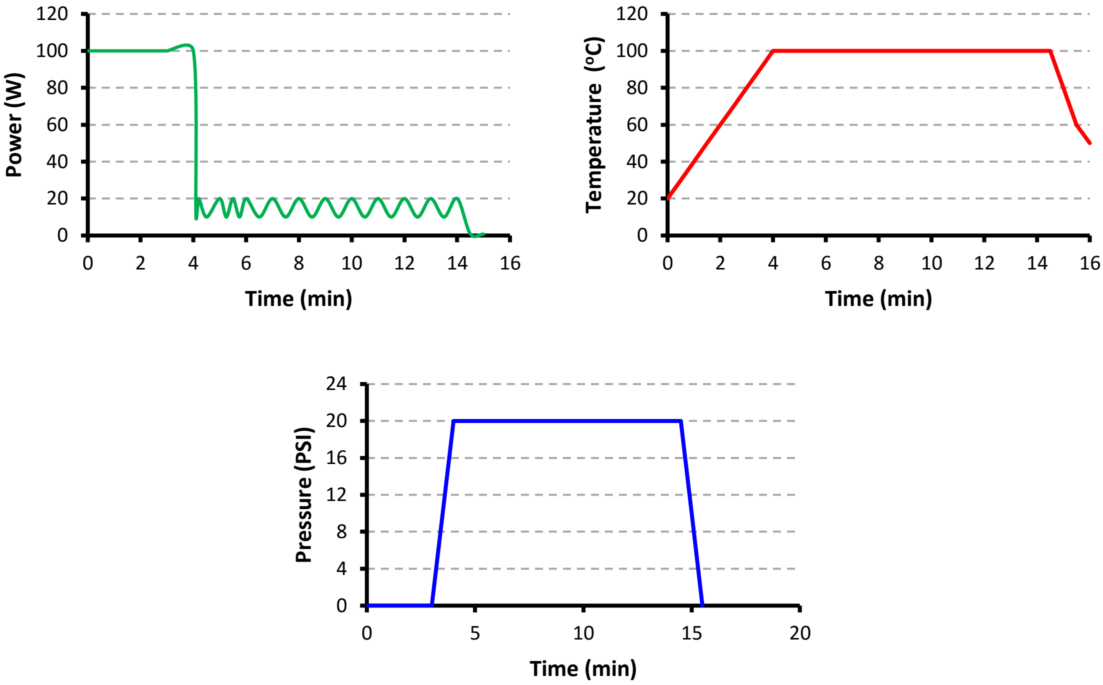


Figure 4-46: Power, temperature, and pressure profiles during microwaving at 100 W and 100 °C.

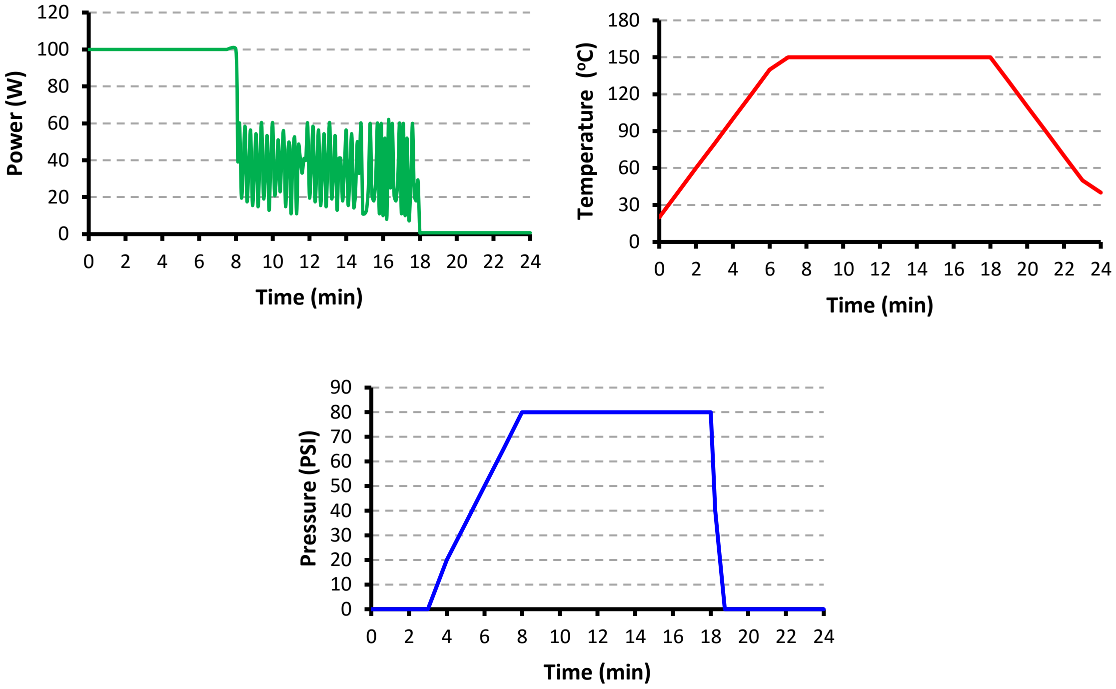


Figure 4-47: Power, temperature, and pressure profiles during microwaving at 100 W and 150 °C.

C. Influence of MW duration

In order to investigate the influence of the irradiation time on the iron removal, a series of batch experiments were conducted by microwaving 500 mL EDTA-iron complex-containing synthetic water samples for different durations (5, 10, and 15 min). The microwaving process was carried out at a constant MW power and temperature of 100W, and 100 °C, respectively. After each microwaving run, samples were left at room temperature to cool down to the range 20±1 °C, and then electrolysed at the same optimum conditions of iron removal.

Iron removal versus the microwaving time is shown in Figure 4-48(A). It can obviously be seen from the figure that the iron removal efficiency increased with the increase of microwaving time. For instance, iron removal efficiency increased from about 83% to 92%, and 93.2% as the microwaving time increased from 5 to 10, and 15 min, respectively. This could be attributed to the fact that the longer irradiation time allows for the transfer of more heat to the solution being microwaved, which is of great benefit for pollutants removal (Yang *et al.*, 2014).

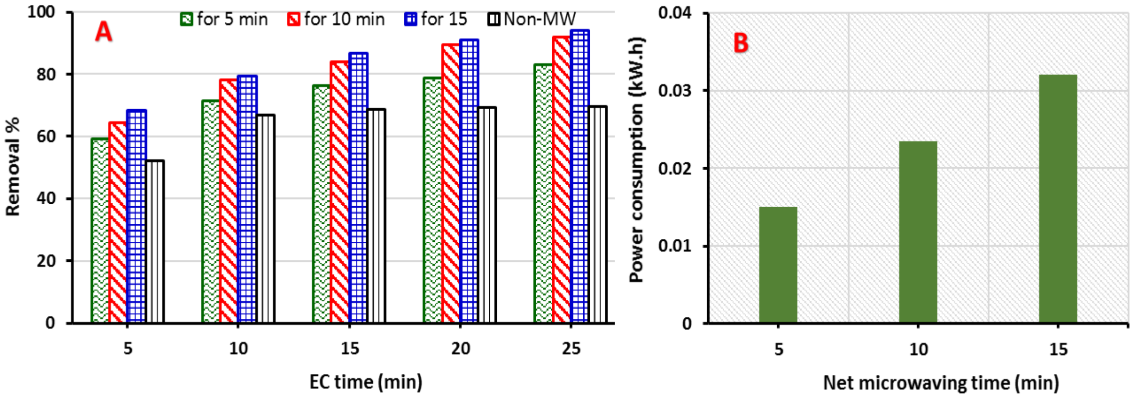


Figure 4-48: Influence of MW time on: (A) Iron removal, (B) power consumption.

However, Figure 4-48(B) shows that increasing the microwaving time has significantly increased the power consumption. For instance, increasing the microwaving time from 5 to 10, and 15 min increased the power consumption from 0.015 to 0.023, and 0.032 kWh, respectively. Power, temperature, and pressure profiles are shown in figures 4-19, 51.

According to the results obtained from this part of the study, it might be reasonable to use a MW field with a power of 100W to produce a temperature of 100 °C for 10 min before the EC process.

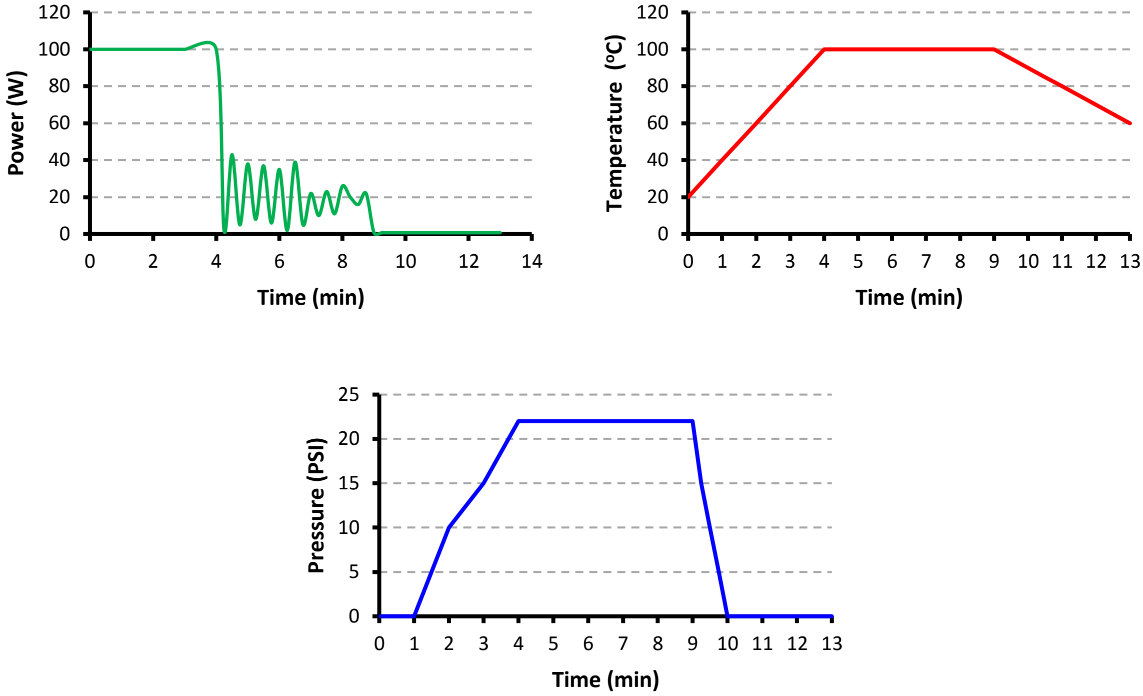


Figure 4-49: Power, temperature, and pressure profiles during microwaving at 100 W for 5 min.

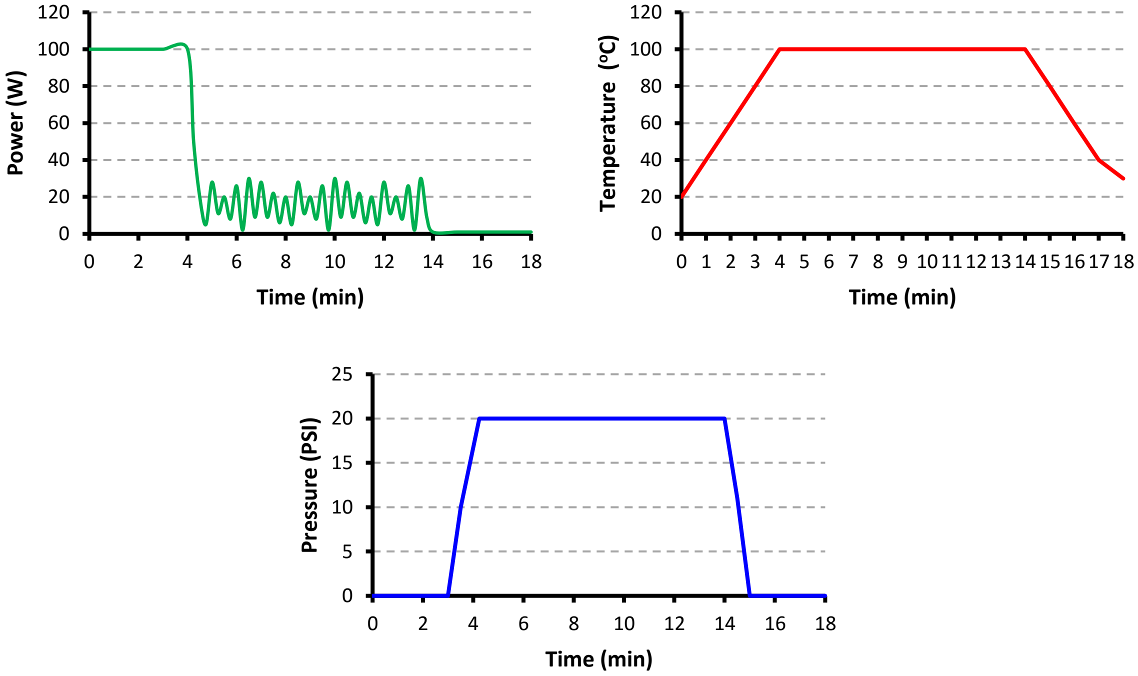


Figure 4-50: Power, temperature, and pressure profiles during microwaving at 100 W for 10 min.

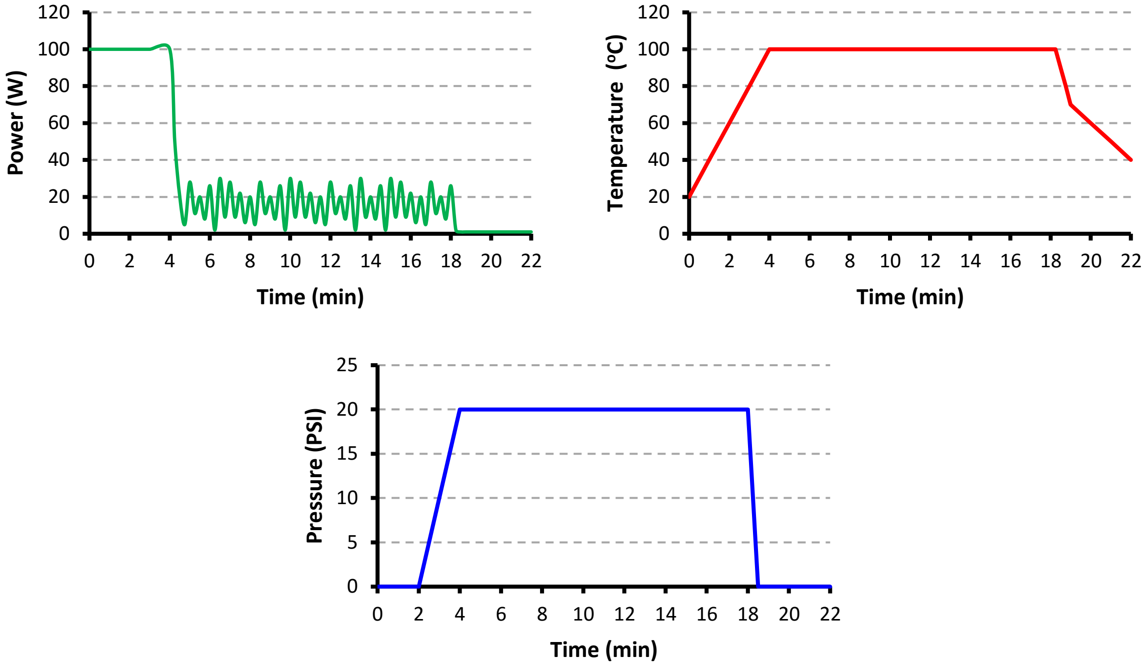


Figure 4-51: Power, temperature, and pressure profiles during microwaving at 100 W for 15 min.

Indeed, a wide body of previous studies claimed that the influence of the MW field on the removal of pollutants is due to its thermal and athermal influences. Therefore, the following section of the project has been devoted to investigate whether the athermal MW effects played a role in the enhancement of iron removal or not.

D. Comparison between the traditional and MW heating

According to the literature survey, the MW heating is more efficient than the traditional ones due to the difference in heating mechanisms. In addition, the MW heating is more effective in the removal of pollutants due to the contribution of athermal MW effects, and the hot spots in the decomposition and removal of pollutants from aqueous media (Lin *et al.*, 2009b; Horikoshi and Serpone, 2014; Yang *et al.*, 2014).

To investigate whether the MW heating or the traditional one is more efficient in iron removal from water in the presence of OM, traditional and MW heating methods were used to heat two groups of EDTA-iron complex-containing synthetic water samples (with identical characteristics) to 100 °C for 10 min. The heated samples were left at room temperature to cool down to the range of 20±1 °C before electrolysing them at the same optimum operating conditions of iron removal.

The results showed that the MW heating was superior to the traditional heating method in terms of iron removal and power consumption. Figure 4-52(A) shows that the iron removal from the microwaved samples was 11% better than that in traditionally heated samples.

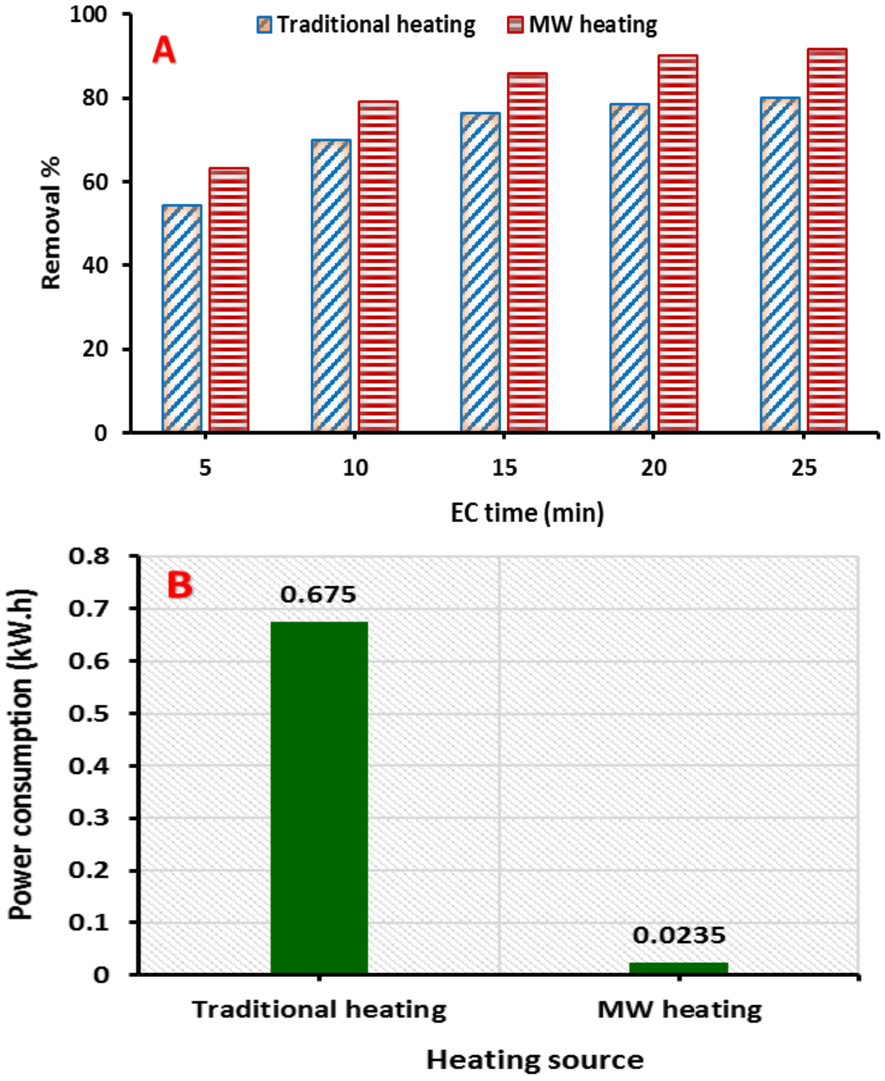


Figure 4-52: Comparison between MW and traditional heating in terms of: (A) Iron removal, (B) power consumption.

This could be explained by the following unique characteristics of the MW heating process. Firstly, the MW energy couples with the molecules of the substance being heated, which means the heat is generated from within the mixture without heat transfer (Hayes, 2002; Bassyouni *et al.*, 2011). Secondly, MW heat is independent of the thermal conductivity of the container because it is generated through the direct absorption of MW energy by the targeted substance (Wong and Gupta, 2015). Thirdly, the formation of super-hot microscopic spots (hotspots) within the solution being microwaved. Therefore, MW irradiation results in a rapid superheating of the substance that produces enormous accelerations in many chemical reactions, which cannot be produced by traditional heating.

Moreover, Figure 4-52(B) shows a significant difference between the MW and traditional heating methods in terms of power consumption, where, it can be seen that the MW heating method required 0.024 kWh to increase water temperature to 100 ^{o}C for 10 min at a power of 100W. While the traditional heating method required 0.675 kWh, i.e., the traditional heating process consumed 28 times the power consumed by the MW method. This difference in power consumption is due to the vital difference between the MW and traditional heating mechanisms, where, traditionally, the heating process is conducted by transferring heat from an external source, passing through the walls of the container, to the targeted substance (Wong and Gupta, 2015). This makes the temperature of the container higher than that of the substance until they attain the equilibrium state, which may take hours (Hayes, 2002; Wong and Gupta, 2015), which in turn maximises the power consumption. While the MW heat, as mentioned before, is independent of the thermal conductivity of the container because it is generated through the direct absorption of MW energy by the targeted substance. In addition, MW heat does not required heat transfer as it couples with the molecules of the substance being heated.

Based on the results obtained, it might be reasonable to use a MW field with a power of 100W, and temperature of 100 °C for 10 min before the electrocoagulation process to enhance the removal (as high as 92%) of iron in the presence of OM (EDTA).

E. Removal of OM

Though the main aim of the current project is to investigate the removal of heavy metals from drinking water in the presence of OM, some experiments were carried out to investigate the influence of MW irradiation on the removal of OM.

The residual concentration of OM was measured by calculating the COD concentration. At the end of some EC runs (after 25 min), 2 mL of the collected filtrate were pipetted into a Hach Lange COD cuvette and inverted twice to mix the contents well. Then, COD cuvette was immediately heated at 148 °C for 120 min using a pre-heated heating block Hach Lange dry thermostat. At the end of the heating period, the COD cuvette was left in a rack to cool to approximately 60 °C; shaken again a few times and left to cool to room temperature. Then, the COD concentration was measured using a Hach Lange spectrophotometer.

The results obtained showed that the MW irradiation has enhanced the removal of OM, Figure 4-53. For instance, it has been found that the removal of OM has increased from about 48% in non-microwaved samples to about 84% in microwaved samples.

This could be explained by the ability of the MW field to break down the chemical bonds within complex chemicals (due to the intensive heat and vibration of the polar chains of molecules) forming smaller intermediates (Tyagi and Lo, 2012; Mawioo *et al.*, 2016; Wang and Wang, 2016), which in turn can be removed by the EC method.

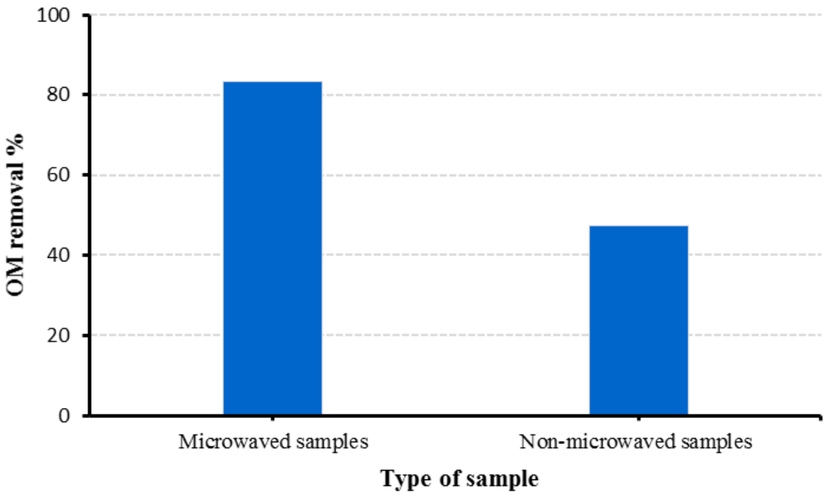


Figure 4-53: Influence of MW irradiation on the removal of OM.

F. Phase summary

The results obtained from the current phase indicated that the removal of heavy metals-OM complex from drinking water, using the EC method, can be significantly enhanced by applying a MW field. Where, it has been found that applying the MW field with a power of 100W to produce a temperature of 100 ^{o}C for 10 min before the EC process, enhanced the removal of iron-EDTA complex by about 22%.

Additionally, it has been found that applying the MW field before the EC process can enhance the removal of OM from drinking water. The obtained results showed that applying MW field has enhanced the removal of OM by about 36%.

PHASE V

4.6.5 Pathogens removal using MW assisted-EC method.

I. Methodology

In fact, the removal of water biological pollutants (Pathogens) is an additional benefit of using the new MW assisted-EC method. According to the literature, subjecting water biological pollutants (Pathogens) to an EC process or a MW field, with the same required conditions to remove iron, is quite enough to remove as much as 99% of these pathogens (Kim *et al.*, 2009; Hakizimana *et al.*, 2016).

To prove this feature, *ASM*-containing synthetic water samples were treated using the MW assisted-EC method at the same optimum conditions obtained in the iron removal experiments. For comparison purposes, similar samples were treated by EC and MW methods.

Bacteria and saline preparation was carried out according to the standard methods mentioned by (Abu Hasan *et al.*, 2016; Nash, 2013). Initially, ready *ASM* solutions were brought from IC lab- LJMU, a 1 mL of this ready sample was mixed with 9 mL of saline solution in a 30 mL glass bottle (concentrated stock). The saline solution was prepared by dissolving 9 g of NaCl in 1 L of deionised water, then autoclaved at 121 ^{o}C for 15 min. Then, five lower concentrations (10^{-1} to 10^{-5}) of *ASM* were diluted from this stock solution. After each dilution process, the caps and top edge of the bottles were sterilised by flame to avoid the pollution with external types of bacteria. The nutrient agar medium was prepared by dissolving 28 g of nutrient agar powder in 1 L deionised water, sterilised in autoclave at 121 ^{o}C for 15 min, and then poured into agar plates to 1/3 of the height of the plate. The prepared plates were allowed to harden and stored at 4 ^{o}C. 0.1 mL of each concentration was dispersed on agar plates, incubated at 37 ^{o}C for 48 hrs, and then the number of the generated colonies were manually calculated (the initial number of colonies, i.e. before any treatment).

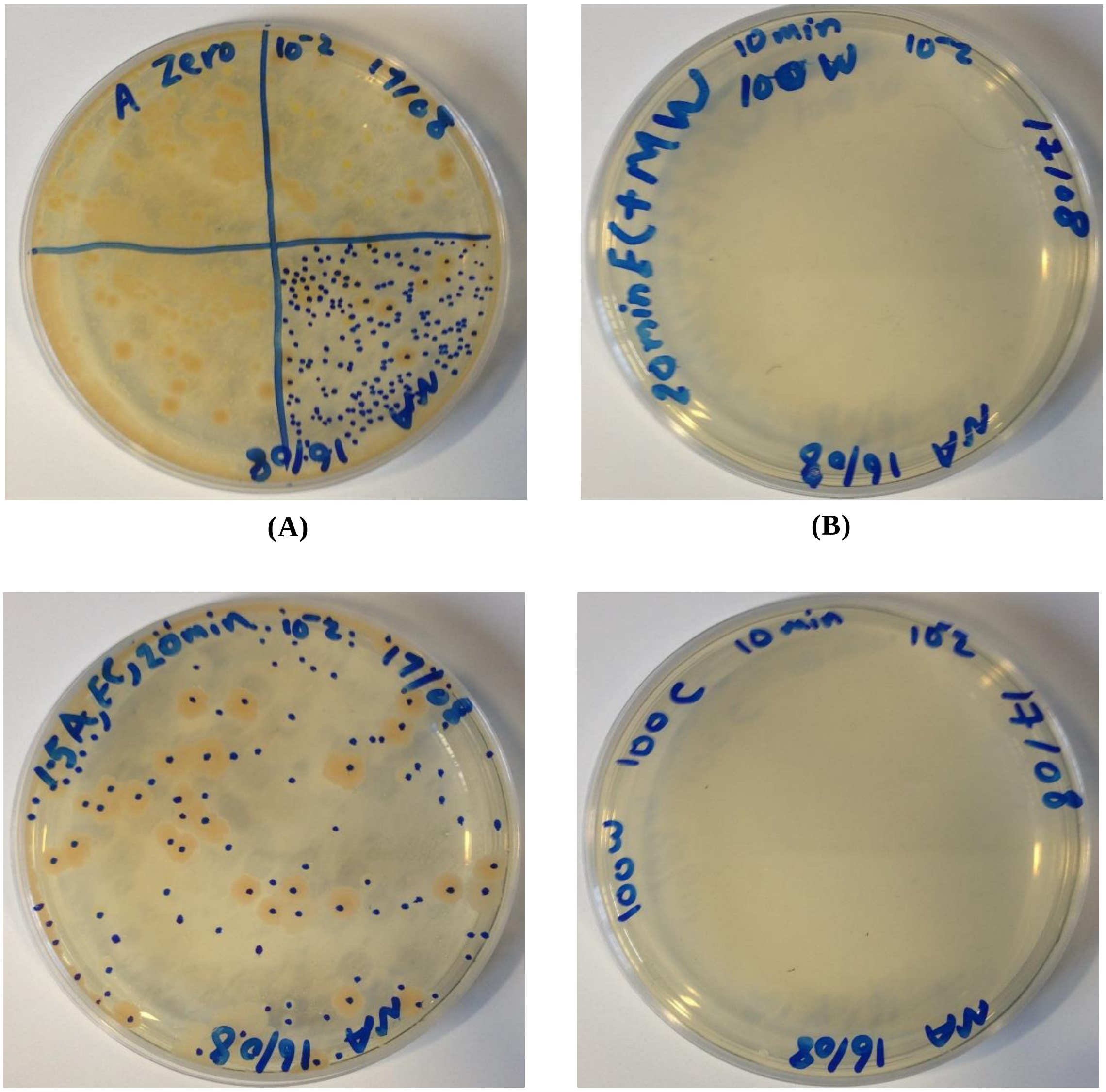
These diluted solutions were treated using EC, MW, and MW assisted-EC methods. Then, the remaining *ASM*, after each run of treatment, were calculated according to the procedures stated above.

II. Results and discussion

To investigate the ability of the new MW assisted-EC method to disinfect water, sets of batch experiments were carried out to remove ASM from drinking water. Initially, 0.5 L water samples, contains 800 to 900 ASM colonies, were microwaved for 10 min at 100 ^{o}C, and 100 W. Then left at room temperature to cool down to 20±1 ^{o}C before being electrolysed for 25 min at CD of 1.5 mA/cm^2, initial pH of 6, and ID of 5 mm (the optimum operating conditions for iron removal). After each run, 0.1 mL of the treated water was dispersed on agar plates, incubated at 37 ^{o}C for 48 hrs, and then the number of the generated colonies were manually calculated.

For comparison purposes, drinking water samples, with identical properties, were treated using EC and MW methods separately. The electrocoagulation process was performed for 25 min at a CD of 1.5 mA/cm^2, initial pH of 6, ID of 5 mm, and T of ^{o}C, while the microwaving process was carried out for 10 min at 100 ^{o}C, and 100W (the optimum operating conditions for iron removal).

The results obtained, Figure 4-4(A-D), showed that the new MW assisted-EC method completely removed culture-able ASM (100% removal efficiency), while the EC method removed about 82.1%. It is noteworthy to highlight that MW alone removed 100% of the culture-able ASM.



(A) (B)

(C) (D)

Figure 4-54: ASM culture-able colonies in: A) Untreated sample, B) Treated sample using MW assisted-EC method, C) Treated sample using EC method, and D) Treated sample using MW irradiation.

PHASE VI

4.6.6 Recovery of hydrogen gas.

I. Methodology

The amount of H_2 gas produced from an EC unit can be calculated using the equation 24 (Phalakornkule *et al.*, 2010):

$$Q_{H_2} = \frac{CD\,.\,A\,.\,t\,.\,H}{F} \tag{24}$$

Where, Q_{H_2}, CD, A, t, H, and F represent the quantity of the produced H_2 gas (mole), applied current density in (A/m^2), effective area of electrodes (m^2), treatment time (sec), number of hydrogen molecules (1/2), and Faraday's constant (96,500 J.mol^{-1}), respectively. The generated amount of hydrogen can be converted into volumetric units using the following ideal gas law (Woody, 2011):

$$pV = nRT \tag{25}$$

Where, p, V, n, R, and T represent pressure (kPa), volume (L), moles of gas, gas constant (8.314 J/kmol at atmospheric pressure), and gas temperature (K), respectively. While the producible energy from the H_2 gas can be calculated using the equation 26 (Nasution *et al.*, 2011):

$$E_{H_2} = m\,(122\,\frac{kJ}{g}) \tag{26}$$

Where E_{H_2}, and m represent the produced energy (kJ), and the produced mass of H_2 gas (g) within a specified time, respectively.

II. Results and discussion

As mentioned in the previous section, the amount of H_2 gas generated from an EC unit can be calculated, using Eq. 24, depending on the magnitude of the applied current density, area of electrodes, and the treatment period.

The amount of H_2 gas produced in the current project, has been calculated at the optimum conditions for iron removal, which are 25 min of electrolysing at CD of 1.5 mA/cm^2. While the total effective area of electrodes was 284 cm^2. Thus, the generated amount of H_2 from the FCER is:

$$Q_{H_2} = \frac{15\ * 0.0284 * 1500 *\ 0.5}{96500} = 0.033 \text{ mole} = 0.793 \text{ L}$$

Taking into account that each one kWh = 3600 kJ (Phalakornkule *et al.*, 2010), and the hydrogen molar mass is 2.016 g/mol, then the reproducible energy from this amount of H_2 gas, according to Eq. 26, is 8.05 kJ, which is equivalent to 2.82 kW/m^3. According to these results, it can be said that the amount of H_2 gas generated from field scale treatment plants can be used to produce a considerable amount of energy.

The results discussed in the current chapter lay a foundation for the modelling of the performance of the new reactor, which is explained in the following chapter.

4.7 Chapter summary

The current chapter presents the results obtained from the experimental part of this project. For better understanding of the sequence of the experimental work, and to highlight the contribution of this project to the knowledge, this chapter has been divided into four main sections. The first part concerns the advantages of using a flow column in EC reactors (FCER), followed by a part relating to the application of the FCER to remove pollutants from drinking water. The third part is devoted to proving, experimentally, the influence of organic matter on heavy metal removal. While the last part includes the novelty of the current project, where it shows the results of applying the MW assisted-EC method to remove heavy metals from drinking water in the presence of OM. In addition, two minor parts have been added to this chapter to show the ability of the new method to disinfect water and to measure the generated amount of hydrogen gas (and the estimated energy) from the EC unit during the treatment process.

The outcomes of the first part indicated that the FCER was able to achieve 100% water mixing process within 9 min, according to the measured effluent concentration of RD dye and camera records. In terms of water aeration, the FCER increased the DO concentration by 110.6% (from 5 to 10.53 mg/L) within 10 min of treatment. Finally, it has been noticed that the FCER possesses the ability to maintain the temperature of water being treated within the range of 22-28 ^{o}C even when the initial temperature of influent water and the applied current density were 35 ^{o}C and 3 mA/cm^2, respectively.

In terms of pollutants removal from drinking water:

1- The FCER removed 98% of fluoride within 20 min, even when the initial concentration of fluoride was 15 mg/L, at initial pH of 6.0, ID of 5 mm, and at CD of 2 mA/cm^2.

2- At a CD of 2 mA/cm^2, initial pH of 7, and ID of 5 mm, 27 min was required by the FCER to reduce nitrate concentration from 100 to 50 mg/L (WHO limitations for adult consumption).

3- In a continuous flow mode, 98.6% of 25 mg/L of RB-5 dye was removed by the FCER after 60 min of electrolysing at an initial pH, DC, ID, and flow rate of 5, 2 mA/cm^2, 4 mm, and 1 L/h, respectively.

4- In terms of iron removal, it has been found that 25 min of electrolysing at pH of 6, ID of 5 mm, CD of 1.5 mA/cm^2 was enough to meet the WHO limitations even when the initial concentration was 40 mg/L.

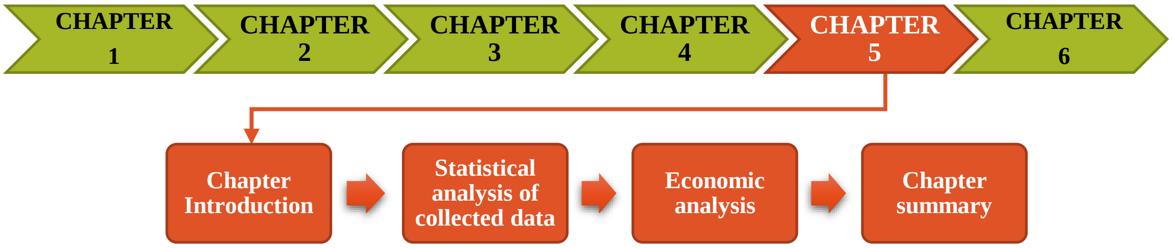
The results of the third part of this chapter represent experimental evidence about the existence of the targeted problem, where, it has been found that the presence of 100mg/L of EDTA (OM matter) was enough to reduce the iron removal from 99.6% to about 69% at the same operational conditions obtained from iron removal experiments. While, the fourth part highlighted the novelty of the current project. Where the result obtained indicated that the new MW assisted-EC method has increased iron removal, in the presence of OM, from 69.6% to 92% after 10 min of microwaving at 100W and 100 ^{o}C, and electrolysing for 25 min at initial pH of 6, CD of 1.5 mA/cm^{2}, and ID of 5 mm.

In terms of microorganisms' removal from drinking water, the fifth phase of the current chapter showed that 100% of the culture-able ASM was removed by the MW assisted-EC method, while the EC method removed about 82.1%. It is noteworthy to highlight that the MW technology removed 100% of the culture-able ASM, which means that the MW field played the central role in the removal of microorganisms. Finally, it has been found, in the sixth phase of this chapter, that the hydrogen gas generated from the MW assisted-EC method could be used to reproduce about 2.82 kW/m^{3} of power, which is a promising amount of power on field scale plants.

CHAPTER 5

ECONOMIC AND STATISTICAL ANALYSIS

CHAPTER 5: ECONOMIC AND STATISTICAL ANALYSIS



5.1 Chapter introduction

The literature highlighted a real deficit in the modelling of EC performance, which is one of the main drawbacks of the EC technology as such models are essential to design, optimise, and reproduce the performance of the EC units (Kuokkanen, 2016). Therefore, the current chapter is devoted to developing some empirical models to reproduce the performance of the FCER in terms of fluoride, nitrate, iron, and dye removal. In the current modelling process, the influences of the operating parameters such as the initial pH, CD, and ID on the removal of a pollutant will be gathered in one equation, which in turn can be used to predict the removal of that pollutant under different operating conditions.

The standard multiple regression technique has been applied to carry out the modelling process because this technique bears several attractive merits. For instance, it enables the operator to explore the relationship between one dependant variable (DV) and a set of independent variables (IVs), and it tells how well a number of IVs is able to predict a certain DV. Additionally, it allows a more sophisticated investigation of the interrelationship among several variables (Pallant, 2005).

In the present study, the initial pH, CD, C_0, t, ID, and T represent the IVs, while the removal efficiency of a pollutant is the DV. The statistical analysis has been performed using SPSS-23 and Minitab 17.2 packages. Additionally, this chapter includes a preliminary economic study to estimate the cost of pollutant removal using the MW assisted-EC method.

5.2 Methodology

5.2.1 Statistical analysis and modelling of FCER performance.

According to the literature survey, there is a real deficit in the modelling of the EC performance, which is one of the main drawbacks of the EC technology as such models are essential to design, optimise, and reproduce the performance of the EC units (Kuokkanen, 2016). Therefore, a part of the present study was devoted to developing some empirical models to reproduce the performance of FCER in terms of fluoride, nitrate, iron, and dye removal.

The standard multiple regression technique has been applied to carry out the modelling process because this technique bears several attractive merits. For instance, it enables the operator to explore the relationship between one dependant variable (DV) and a set of independent variables (IVs), and it shows how well a number of IVs is able to predict a certain DV. Additionally, it allows a more sophisticated investigation of the interrelationship among several variables (Pallant, 2005).

In the present study, the initial pH, CD, C_0, t, ID, and T represent the IVs, while the removal efficiency of a pollutant represents the DV.

The empirical models were developed according to the following steps (Pallant, 2005; Tabachnick and Fidell, 2013; Hashim *et al.*, 2017b):

5.2.1.1 Statistical analysis of the collected data

I. Normality

In order to apply the principles of the multiple regression technique, the collected experimental data must follow a normal distribution. This assumption could be checked by calculating the statistical significance (ρ-value) of the Shapiro-Wilk test. Where it is expected, in normally distributed data, that the ρ-value of the Shapiro-Wilk test is greater than 0.05 (Belgaumkar et al., 2016; Li et al., 2016). Additionally, for normal distribution the z-value of skewness (Z_s) and kurtosis (Z_k) must be within the range of ± 1.96 (Musheer et al., 2016; Shiota et al., 2017). The z-value can be calculated using the equations 27 and 28 (Tabachnick and Fidell, 2013):

For kurtosis

$$Z_k = \frac{K}{S_k} \tag{27}$$

For skewness

$$Z_s = \frac{S}{S_s} \tag{28}$$

Where K, S_k, S and S_s are the calculated kurtosis, the standard error for kurtosis, skewness, and the standard error for skewness, respectively.

II. Generalisability (data size)

Multiple regression techniques cannot be performed on small datasets because the obtained outcomes may not possess the required scientific value and cannot be generalised to other sets of data (Pallant, 2005). Hence, Tabachnick and Fidell (2001) gave the following formula to determine the minimum size of a sample:

$$N > 50 + 8m \qquad \textbf{(29)}$$

Where N is the sample size, and m is the number of independent parameters that will be used in the multiple regression.

III. Multicollinearity

This term refers to the correlation among the IVs, and it occurs when the correlation of the IVs is high, i.e. when the bivariate correlation between two IV_s is ≥ 0.7 (Tabachnick and Fidell, 2001). Multicollinearity is not favourable in the multiple regression as it influences the determinations regarding individual predictors, and it must be eliminated by deleting one of the correlated IVs or by generating a composite variable from the correlated IVs (Pallant, 2005; Field, 2008). The multicollinearity can be detected by calculating the variance inflation factor (VIF) or the tolerance value (O'Brien, 2007):

$$Tolerance = 1 - R^2 \qquad \textbf{(30)}$$

$$VIF = 1/(1 - R^2) \qquad \textbf{(31)}$$

Where R^2 is the coefficient of determination of a regression. Pallant (2005) reported that a small tolerance value (less than 0.1) or a high variance inflation factor (VIF) value (greater than 10) indicates the existence of multicollinearity within the used data.

IV. Outliers

Outliers can be defined as an observation that seems to be incompatible with other observations in the data set (Walfish, 2006). Generally, any observation with standardised residual (SR) greater than 3.3 or less than -3.3 is classified as an outlier (Tabachnick and Fidell, 2001; Pallant, 2005). A screening process must be applied to both DV and IVs to detect the extreme values before performing the multi regression technique, as this technique has high sensitivity to the outliers (Fitrianto and Midi, 2011; Field, 2008). The existence of the outliers in the data used can be detected by different methods, such as determining the SR value from the Scatterplot, or by calculating the Mahalanobis distances, which must be less than the critical values listed in Table 5-1 (Pallant, 2005).

Table 5-1: Critical values for the Mahalanobis distances.

The table originally presented here cannot be made freely available via LJMU Digital Collections because of 'copyright'. The diagram was sourced from Pallant (2005)

V. Normality, linearity, and homoscedasticity of residuals

These terms relate to the nature of the variables' relationship and the scores' distribution, where normality indicates that the residuals are normally distributed around the predicted DV. While linearity means the residuals show a straight relationship with the predicted DV, and homoscedasticity means the variance in the relationship between the IVs and the DV is the same across all magnitudes of the IVs (Pallant, 2005). The scatterplot delivers the required information to check these assumptions (Tabachnick and Fidell, 2001), where it is expected, in normal distribution, that less than 1% of the standardised residual values of the data points exceeds the range of 3.0 to -3.0 (Pallant, 2005).

5.2.1.2 Evaluating the model

The goal of this essential step is to check the ability of the constructed model to explain the variation in the DV. The coefficient of determination (R^2) is a proper tool to achieve this goal, as it is a measure of how many data points fall within the results of the line generated by the regression model (Pallant, 2005; Field, 2008). The R^2 goes on a 0-1 scale: the higher the R^2, the higher the accuracy of the regression model; this coefficient can be calculated using the equation 30 (Tabachnick and Fidell, 2001):

$$R^2 = SS_{reg}/SS_Y \tag{32}$$

Where SS_{reg}, and SS_y are the sum of squares for regression and the total sum of squares respectively.

In fact, it is not necessary that each single IV makes a statistically significant unique contribution to the generated model, where some of IVs can be omitted from the developed models due to their ignorable contribution (Tabachnick and Fidell, 2001; Pallant, 2005). The contribution of each individual IV to the generated model is measured by determining its statistical significance (Sig.). This parameter indicates whether this IV makes a statistically significant unique contribution to the built model or not. Where, any IV with a significance value less than 0.05 makes a significant unique contribution to the multiple regression model, while an IV with significance value greater than 0.05 can be omitted from the model as it does not play a significant role (Pallant, 2005; Field, 2008).

5.2.1.3 Evaluating the contribution of each independent variable.

The contribution of each individual IV to the suggested model is measured by determining its Beta value. This is a measure of how strongly each IV influences the outcomes of the built model (DV) (Tabachnick and Fidell, 2001; Pallant, 2005; Field, 2008). Statistically, the higher the absolute beta value is, the stronger the contribution of the IV to the outcomes of the built model (Pallant, 2005).

In addition, the Sig. value can be used to determine the contribution of each IV to the generated model (Tabachnick and Fidell, 2001; Pallant, 2005; Field, 2008).

5.2.2 Economic analysis.

The operating cost of a treatment method is a vital parameter as it determines the applicability of this method (Ozyonar and Karagozoglu, 2011). Generally, the required cost to operate a treatment method consists of the operating and fixed costs; the operating cost includes the cost of energy, material (such as electrodes in the EC method), chemicals, labour, maintenance, and sludge handling. While, the costs of equipment and construction of a treatment method represent the fixed costs (Bayramoglu *et al.*, 2004; Ghosh *et al.*, 2008; Dalvand *et al.*, 2011).

However, in preliminary economic studies, only the costs of energy and materials are taken into account (Ghosh *et al.*, 2008; Kobya *et al.*, 2010; Ozyonar and Karagozoglu, 2011; Chopra and Sharma, 2012).

In the present study therefore; the operating cost of the MW assisted-EC method will be estimated by adding the energy cost of the MW unit to Eq.15, as follows:

$$OC = \gamma_1\, C_{energy} + \gamma_2\, C_{electrodes} + \gamma_3\, C_{chemicals} + \gamma_1\, C_{MW} \qquad \textbf{(33)}$$

Where C_{MW} (kWh/m^3) is the consumed power by the MW unit.

5.3 Results and discussion

5.3.1 Statistical modelling

5.3.1.1 Statistical analysis of collected data

I. Normality

The normality of the collected data is initially checked by calculating the ρ-value of Shapiro-Wilk test. The results obtained showed that the ρ-values of Shapiro-Wilk test for the studied pollutants were smaller than 0.05, which indicates that the collected data does not follow normal distribution.

Therefore, Johnson transformation has been performed to transform the collected data to normal distribution.

Then, after the transformation, the ρ-value of Shapiro-Wilk test to check the normality of data. The obtained results showed that the ρ-values of Shapiro-Wilk test for the studied pollutants were greater than 0.05, Table 5-2. Additionally, the calculated z-values of skewness and kurtosis for the studied pollutants were within the allowable limit (± 1.96), which indicates that the collected data follows a normal distribution.

II. Generalizability (sample size)

The minimum required data points to develop a reliable model can be calculated according to Eq. 29, which is a function of the operating parameters investigated during the experimental work.

According to the results of Table 5-2, this condition has been met for all the studied pollutants, as the number of experimental data points, collected from the experimental work, is bigger than the required number.

Table 5-2: The minimum required and actual sample size for the studied pollutants.

Pollutant	IVs	Minimum required data points	Experimental data points	ρ-values of Shapiro-Wilk test
Fluoride	5	90	92	0.236
Nitrate	5	90	102	0.257
Iron	6	98	107	0.458
RB-5 dye	6	98	128	0.681
Iron-EDTA	2	66	75	0.158

III. Multicollinearity

The existence of multicollinearity within the studied data can be detected by calculating the variance inflation factor VIF or tolerance (To.) value, where a small tolerance value (less than 0.1) or high VIF value (greater than 10) indicates the existence of multicollinearity within the data used.

According to the results obtained, Table 5-3, from the statistical analysis, VIF values for the studied IVs were less than 10, and the tolerance values were greater than 0.1, which indicates the absence of the multicollinearity in the studied data.

Table 5-3: Summary of statistical analysis results.

Pollutant	IVs	To.	VIF	Max. detected Mahalanobis distance	Std. residual exceeds the acceptable range (3.0 to -3.0)	
					No. of cases	Value
Fluoride	t	1.000	1.000	11.95	2	3.21 3.77
	CD	0.827	1.210			
	C_o	0.880	1.136			
	ID	0.911	1.098			
	pH	1.000	1.000			
Nitrate	t	0.946	1.057	15.17	2	3.05 3.20
	CD	0.942	1.062			
	C_o	1.000	1.000			
	ID	0.988	1.012			
	pH	1.000	1.000			
Iron	t	0.998	1.002	17.1	Non	Non
	CD	1.000	1.000			
	C_o	0.988	1.012			
	ID	0.988	1.012			
	pH	0.998	1.002			
	$T.$	0.998	1.002			
RB-5 dye	t	0.968	1.033	14.07	2	3.84 3.45
	CD	1.000	1.000			
	C_o	0.879	1.138			
	ID	0.878	1.138			
	pH	0.906	1.103			
	FR	0.836	1.196			
Iron-EDTA complex	t	1.000	1.000	5.37	Non	Non
	$C_{0(EDTA)}$	1.000	1.000			
	CD	Constant	Constant			
	Co	Constant	Constant			
	ID	Constant	Constant			
	pH	Constant	Constant			
	T.	Constant	Constant			

IV. Normality, linearity, and homoscedasticity of residuals

The pattern of data distribution plays an essential role in model construction; where it is expected that not more than 1% of the standardised residual values of the data points outside the range 3.0 to -3.0 (Pallant, 2005). Unfortunately, the results of Table 6 indicate that some of the experimental data points exceeded the specified range; for instance 2.2% of fluoride data are beyond the set standards. As was mentioned before, these strange points may influence the outcomes of the developed models.

To check whether these points exert any influence on the results of the developed models as a whole, Tabachnick and Fidell (2001) recommended to calculate the Cook's Distance (COO_1), any case with COO_1 greater than 1.0 is a potential problem.

According to the results of Table 5-4, these detected strange points within the experimental data do not exert a sensible influence on the results of the developed models, as their COO_1 values are less than 1.0.

Table 5-4: COO_1 values for the studied data.

Pollutant	Maximum COO_1
Fluoride	0.341
Nitrate	0.309
RB-5 dye	0.180

V. Outliers

Though an initial screening process has been carried out to omit the strange data points, the presence of outliers within the collected data must be statistically investigated due to their high influence on model reliability. The presence of the outliers in the studied data can be detected, as mentioned before, by calculating the Mahalanobis distances for each data point, which must be less than the critical values listed in Table 5-1.

The results of Table 5-5 indicate the absence of outliers within the studied data as the maximum detected Mahalanobis distances of the studied pollutants were within the permissible limits.

Table 5-5: Mahalanobis distances

Pollutant	Max. detected Mahalanobis distance	Max. allowable Mahalanobis distance
Fluoride	11.95	20.52
Nitrate	15.17	20.52
Iron	17.1	22.46
RB-5 dye	14.07	22.46
Iron-EDTA complex	5.37	13.82

5.3.1.2 Model building and evaluation.

A multiple regression was used to assess the relationship between the removal efficiency of a pollutant (DV) and the operating parameters (IVs), because this technique is suitable to perform a complex investigation of the interrelationship among several variables (Pallant, 2005). The general regression form is (Mustapha and Abdu, 2012):

$$Y = A + B_1X_1 + B_2X_2 + \cdots + B_kX_k + \boldsymbol{\varepsilon} \qquad \textbf{(34)}$$

Where Y is the predicted value of the dependant variable, A represents the Y intercept, B_k are the regression coefficients, X_s are the independent variables, and ($\boldsymbol{\varepsilon}$) is the random error coefficient.

The principles of this technique were applied to the data obtained from fluoride, nitrate, RB-5 dye, and iron removal to develop empirical models, which can be used to reproduce their removal, using the FCER, under different operating conditions.

The removal efficiency of a pollutant, using the EC method, is a function of the influence of several operating parameters such as t, initial pH, CD, T, C_0 and ID (Emamjomeh and Sivakumar, 2005; Fouad *et al.*, 2009; Un *et al.*, 2013; Genc and Bakirci, 2015), which can be expressed by the equation 35:

$$Re\%\ of\ a\ pollutant = f(t, pH, CD, T, C_0, \ldots etc) \quad \mathbf{(35)}$$

In the current project, the influence of t, initial pH, CD, T, ID, C_0 and OM concentration on the performance of FCER in terms of fluoride, nitrate, iron, RB-5 dye, and iron-EDTA complex was investigated. Thus, the removal efficiency of the studied pollutants, in the current project can be expressed as follows:

$$Re\%\ of\ fluoride\ and\ nitrate = f(t, pH, CD, T, C_0) \quad \mathbf{(36)}$$

$$Re\%\ of\ iron = f(t, pH, CD, T, C_0, T) \quad \mathbf{(37)}$$

$$Re\%\ of\ RB - 5\ dye = f(t, pH, CD, T, C_0, FR) \quad \mathbf{(38)}$$

$$Re\%\ of\ iron - EDTA\ complex = f(t, C_{0(EDTA)}) \quad \mathbf{(39)}$$

The multiple regression technique has been applied to the relationships stated above, using the obtained experimental data, to generate empirical models that reproduce the influence of the studied operating parameters on removal of the targeted pollutants.

In fact, it is not necessary that each single IV make a statistically significant unique contribution to the generated model, where some of IVs can be omitted from the developed models due to their ignorable contribution. The contribution of each individual IV to the built model is measured by determining its statistical significance (Sig.). As was mentioned before, any IV with a significance value less than 0.05 makes a significant unique contribution to the multiple regression model, while an IV with significance value greater than 0.05 can be omitted from the built model.

Therefore, during the development of the targeted models, Sig. value of each IV has been calculated using SPSS-23 package. Indeed, the results obtained, Table 5-6, indicated that some of the operating parameters studied could be omitted from the developed models due to their ignorable contribution. For instance, the Sig. values of ID and T in iron data exceeded 0.05, which statistically means these IVs do not make a statistically significant unique contribution to the generated model. The same phenomenon was noticed in nitrate data. Therefore, these IVs were omitted, and the rest of IVs were used to build the targeted models.

Table 5-6: Statistical significance of the studied parameters.

Pollutant	IVs	Sig.	Pollutant	IVs	Sig.
Fluoride	t	0.000	**Iron, (continue)**	ID	0.241
	CD	0.000		pH	0.015
	C_o	0.000		$T.$	0.420
	ID	0.000	**RB-5 dye**	t	0.000
	pH	0.000		CD	0.001
Nitrate	t	0.000		C_o	0.000
	CD	0.000		ID	0.000
	C_o	0.000		pH	0.000
	ID	0.047		FR	0.000
	pH	0.252	**Iron-EDTA complex**	t	0.000
Iron	t	0.000		$C_{0(EDTA)}$	0.000
	CD	0.016		CD, Co, ID, and pH	Constants
	C_o	0.000			

The results obtained indicated that the following equations could be used to reproduce the performance of the FCER in terms of fluoride, nitrate, iron, RB-5 dye, and iron-EDTA complex.

$$Iron\ RE.\% = \left[1 + \frac{2.35 - 10.89\ CD + 0.024\ t\ C_0 + 2.33\ CD\ pH - 0.14\ C_0\ pH}{C_0}\right] * 100 \tag{40}$$

$$Fluoide\ RE.\% = \left[1 - e^{-(0.322 + 0.04\ Cd - 0.007\ C_0 - 0.01\ Id - 0.12\ pH) * t}\right] * 100 \tag{41}$$

$$Nitrate\ RE.\% = 100 - \frac{31.55 - 1.107\ t - 13.756\ CD + 0.753\ C_0 + 0.964\ ID}{0.01\ C_0} \tag{42}$$

$$RB - 5\ RE.\% = \frac{C_0 + 14.83 + 0.1\ t + 1.24\ CD - 0.28\ C_0 - 0.5\ ID - 1.35\ pH - 5.97\ FR}{0.01\ C_0} \tag{43}$$

$$Iron - EDTA\ \ Re.\% = \frac{C_0 - 6.291 + 0.182\ t - 0.025\ OM}{0.01\ C_0} \tag{44}$$

To check the ability of the developed models to explain the variation in the DV with the IVs, R^2 value has been calculated for each model.

According to the results of Table 5-7, R^2 values of the suggested models for RB-5 dye, fluoride, nitrate, iron, and iron-EDTA complex were 0.798, 0.823, 0.848, 0.868, and 0.923, respectively. Though most of the obtained R^2 values were moderated (between 70s% to 80s%), they are categorised as very acceptable values and enough to confirm the applicability of the suggested models to reproduce the performance of the FCER (Pallant, 2005).

Table 5-7: R^2 values for the suggested models.

Model	**R^2 value**
RB-5 dye	0.798
Fluoride	0.823
Nitrate	0.848
Iron	0.868
Iron-EDTA complex	0.923

5.3.1.3 Evaluating the contribution of each independent variable.

As has been explained in section 5.2.1.3, the contribution of each individual IV to the built model is measured by determining its Beta value. The latter is a measure of how strongly each IV influences the outcomes of the built model (DV). Where, the higher the absolute Beta value the stronger the influence of the IV on the accuracy of the built model.

Thus, Beta values for the studied parameters have been calculated in order to measure how strongly each IV influences the outcomes of the built model, Table 5-8.

Table 5-8: Beta values for the studied parameters.

Pollutant	**IVs**	**Beta**	**Pollutant**	**IVs**	**Beta**
Fluoride	t	0.680	**Iron, (continue)**	ID	Omitted
	CD	0.420		pH	0.075
	C_o	0.379		T	Omitted
	ID	0.304	**RB-5 dye**	CD	0.321
	pH	0.181			
Nitrate	t	0.579		C_o	0.687
	CD	0.297		ID	0.319
	C_o	0.669		pH	0.136
	ID	0.046		FR	0.666
	pH	Omitted	**Iron-EDTA complex**	t	0.266
Iron	t	0.519		$C_{0(EDTA)}$	0.923
	CD	0.076		CD, Co, ID, and pH	0.000^{*}
	C_o	0.700			

* These parameters are constants

The results obtained showed that the electrolysing time had the strongest contribution to fluoride removal with a Beta value of 0.68; followed by the current density, initial concentration of fluoride, and inter-electrode distance. While the initial pH had the lowest contribution to the removal of fluoride at a Beta value of 0.181. The influence of the operating parameters followed the order: $\mathrm{C_0 > t > CD > ID}$, on nitrate removal $C_0 > \mathrm{t > CD > pH}$ on iron removal, and $\mathrm{C_0 > FR > CD > ID > pH}$ on RB-5 dye removal. While, in the removal of iron-EDTA complex, the initial concentration of the complex played the strongest role at a Beta value of 0.923, followed by the electrolysing time at a Beta value of 0.266.

5.3.2 Application of the built models.

In this section, the constructed models have been used to predict the removal of the studied pollutants from drinking water at different operating conditions; the obtained outcomes were compared to the real removal values (experimental ones). This step is to ensure that the suggested models possess the ability to simulate the performance of the FCER in terms of pollutant removal within the studied values of the operating parameters.

The suggested model for iron removal prediction, Eq. 40, has been applied to a set of experimental data to investigate the consistency between the measured and predicted removal efficiencies. This set of data consists of 50 experimental observations (at different operating conditions), which were randomly selected from the experimental data, Appendix G. The obtained results, Figure 5-1, indicated that the suggested model possessed an acceptable reproducibility for the performance of the FCER in terms of iron removal, where, R^2 value for the correlation between the predicted and experimental observations was 0.836, which means the suggested model explains 83.6% of the variance in iron removal with the operating parameters.

The same procedures have been repeated in sets of experimental observations (at different operating conditions) to assess the reproducibility of fluoride, nitrate, RB-5 dye, and iron-EDTA complex models. These sets of data consist of 50, 50, 50, and 30 randomly selected experimental observations for fluoride, nitrate, RB-5 dye, and iron-EDTA complex, respectively.

The results obtained, Figures 5-1, 4, indicated an acceptable agreement between the experimental and predicted removal for the studied pollutants, where, R^2 values for these random sets of data of fluoride, nitrate, RB-5 dye, and iron-EDTA complex, were 0.832, 0.866, 0.836, and 0.892, respectively. Statistically, these results, for the random sets of data, indicate that the suggested models are able to describe about 83.2%, 86.6%, 82.4%, and 89.3% of the influences of the operating parameters on the removal of fluoride, nitrate, RB-5 dye, and iron-EDTA complex, respectively.

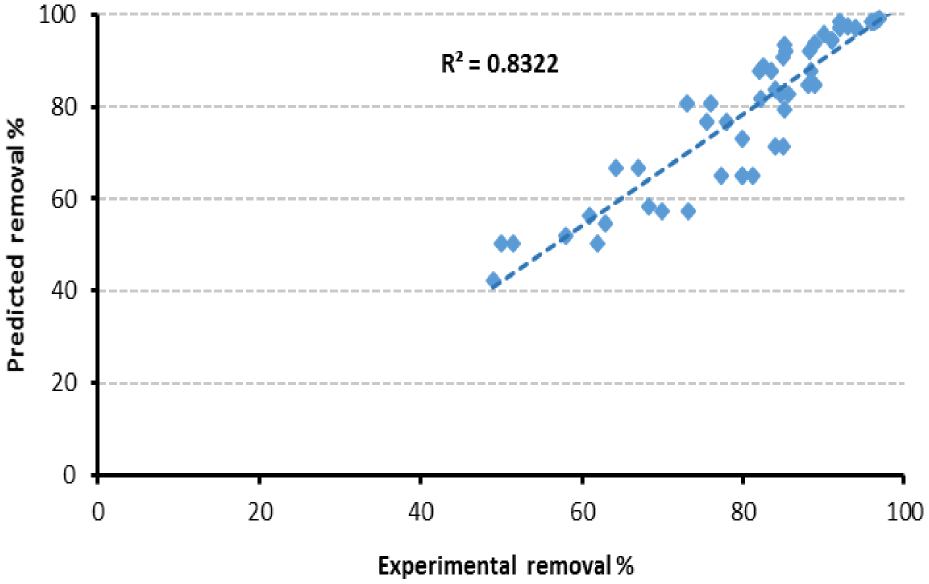


Figure 5-1: Experimental vs predicted fluoride removal for randomly selected data points.

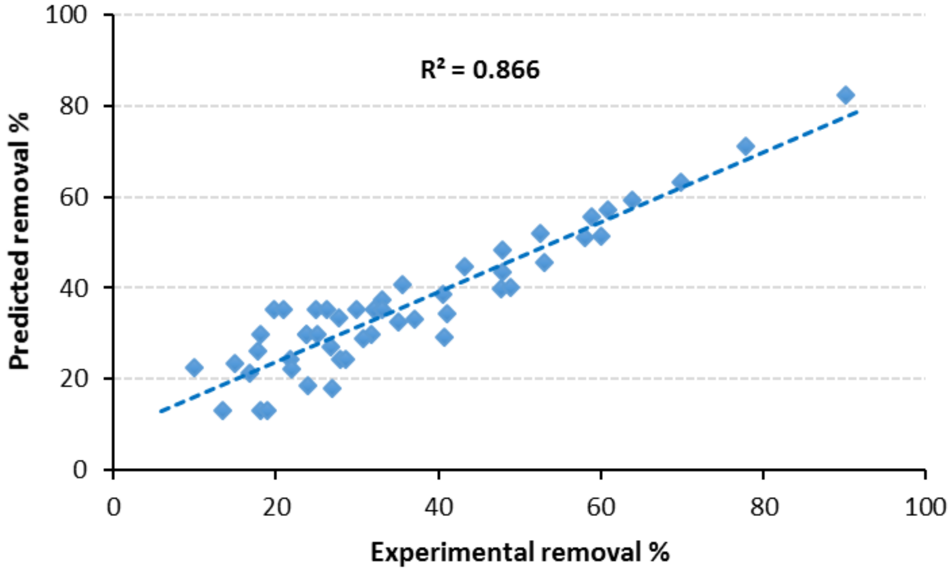


Figure 5-2: Experimental vs predicted nitrate removal for randomly selected data points.

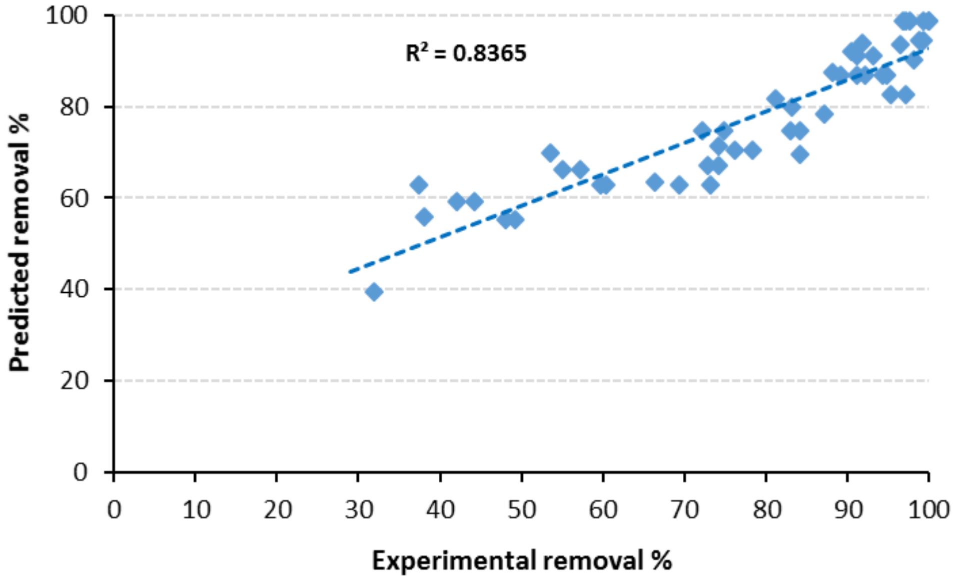


Figure 5-3: Experimental vs predicted RB-5 dye removal for randomly selected data points.

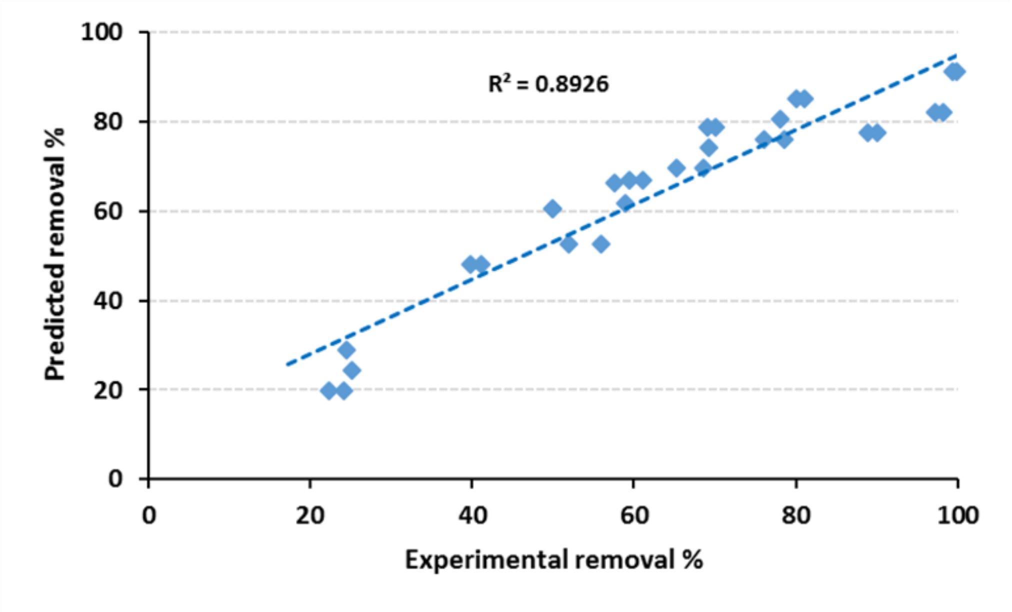


Figure 5-4: Experimental vs predicted iron-EDTA removal for randomly selected data points.

Based on the results obtained from these comparisons, it could be reasonable to consider that the suggested models are reliable enough to reproduce the performance of the FCER in terms of iron, fluoride, nitrate, RB-5 dye, and iron-EDTA complex removal from drinking water

5.3.3 Economic analysis

Applicability of any water or wastewater treatment method is highly determined by the operating cost (Ozyonar and Karagozoglu, 2011). This vital parameter consists of the operating and fixed costs; the operating cost includes the cost of energy, material (such as electrodes in EC method), chemicals, labour, maintenance, and sludge handling. While, the costs of equipment and construction of a treatment method represent the fixed costs.

However, in preliminary economic studies, the costs of energy and materials are taken into account (Ghosh *et al.*, 2008; Kobya *et al.*, 2010; Ozyonar and Karagozoglu, 2011; Chopra and Sharma, 2012).

In the current study therefore; the preliminary operating cost of the MW assisted-EC method will be estimated using Eq. 33, which includes the costs of energy consumption (by WM and EC units), consumed chemicals, and losses in electrodes material.

The operating cost, in the present study, has been calculated at the optimum operating conditions for iron-EDTA complex removal, i.e. 100 W, 10 min of microwaving, 20 min of electrolysing at CD of 1.5 mA/cm^2, initial pH of 6, ID of 5 mm, and water temperature of 20 ^{o}C.

Energy consumption by the FCER and the amount of electrode material consumed have been calculated using equations 13 and 14, respectively. While, the consumed chemicals were measured manually during the experimental work.

Regarding the MW unit, the consumed energy was calculated according to the required microwaving time and device specifications (the operational power).

Unit prices, according to the Iraqi market 2016, were 2.5 cent/kWh of electricity, 1.53 $/kg of aluminium (purity > 99 %), 0.32 $/L of HCl (35%), and 0.2 $/kg of NaCl (purity 99.4% min.). Based on these prices, the operating cost of iron-EDTA removal from drinking water using the MW assisted-EC method is:

$$OC = 0.025 * 4.08 \frac{kWh}{m^3} + 1.53 * 0.113 \frac{kg}{m^3} + 0.02 \frac{\$}{m^3} + 0.025 * 13.33 \frac{kWh}{m^3}$$
$$= 0.628\, USA\, \$/m^3$$

The calculated cost is not cheaper than that of some of traditional treatment methods such as the EC method that costs from 0.36 to 0.61 AUD/m3 (about 0.27 to 0.45 USA$/m3) (Emamjomeh and Sivakumar, 2009) and some of biological methods (Yehya *et al.*, 2014). However, it is still cheaper than many advanced water methods such as membrane filtration that costs about 0.94 $/m^3 and reverse osmosis that requires 0.63 $/m^3 for power alone (Sagle and Freeman, 2004; Alzahrani and Mohammad, 2014). More importantly, the new MW assisted-EC method removes both the refractory heavy metal-OM complex and biological pollutants simultaneously. Additionally, the MW assisted-EC method has many attractive merits that could make it superior to other methods, for instance, it is simple to install and operate, safe as it requires no chemical handling, and it requires a relatively small area.

5.4 Chapter summary

The current chapter has been allocated to develop empirical models that could be used to reproduce the performance of the new EC reactor (FCER) in terms of fluoride, nitrate, RB-5 dye, iron, and iron-EDTA complex from drinking water. Additionally, this chapter presents a preliminary economic study to estimate the required operating cost, of the MW assisted-EC method, to remove iron-EDTA complex from drinking water.

Standard multiple regression technique has been used to explore the relationship between the removal of a pollutant (DV) and a set of critical operating parameters (IVs) such as CD, initial pH, ID, t, C_0, and T. The SPSS-23 package has been used as a statistical tool for both statistical analysis of the collected experimental data and construction of the empirical models.

The results obtained showed that the models possess a good reproducibility for the performance of the FCER, where, it has been found that the R^2 for the models of fluoride, nitrate, RB-5 dye, iron, and iron-EDTA complex removal were, respectively, 0.823, 0.848, 0.798, 0.868, and 0.923. Additionally, data analysis showed that the influence of the operating parameters on the removal of the studied pollutants varied from significant to negligible. For instance, it was found that both t and C_0 of the pollutant played a central role in all built models, while *ID* and *T* were omitted from the iron removal model due to their negligible influence. Generally, the influence of operating parameters followed the order: t > CD > C_0 > ID > pH on fluoride removal,

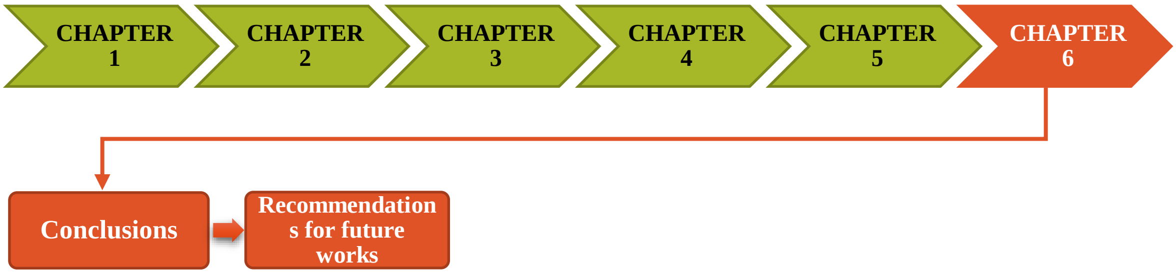
C_0 > t > CD > ID on nitrate removal, t > C_0 > CD > pH on iron removal, C_0 > FR > CD > ID > pH on RB-5 dye removal, and C_0 > t on the removal of iron-EDTA complex.

Results of the preliminary economic study showed that the required cost for removing iron-EDTA complex from drinking water using the new MW assisted-EC method is 0.628 US \$/m^3. This cost was estimated for 10 min of microwaving at 100 ^oC, and MW power of 100 W, and 20 min of electrolysing at CD of 1.5 mA/cm^2, initial pH of 6, ID of 5 mm, and water temperature of 20 ^oC. Though this cost is not cheaper than traditional treatment methods such as biological ones, it still cheaper than most of the advanced ones such as membrane methods. More importantly, the new method shows a good removal of heavy metal-OM complex that cannot to be achieved by traditional methods. Additionally, the MW assisted-EC method has many attractive advantages, such as it possesses the ability to remove pathogens, and it could be recognised as safer than traditional chemical methods as it does not require chemical additives.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORKS

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORKS



6.1 Conclusions

This project shows that the ability of the EC units to remove heavy metals-OM complex from drinking water could be remarkably enhanced by applying a MW field. Additionally, in this project, a new bench scale EC reactor that employs perforated plate flow columns (which are widely used in chemical industries) was suggested, constructed, and tested. The performance of the new EC reactor was validated by determining its efficiency in terms of water mixing, water aeration, control of water temperature, and the removal of some pollutants such as fluoride, nitrate, RB-5 dye, and iron. While the performance of the new treatment method (MW assisted-EC method) was investigated by determining its ability to remove iron-EDTA complex from drinking water. Generally, the following conclusions can be drawn from conducting this thesis:

1. The studied traditional EC reactors have a defect in terms of the water mixing process, where the camera records showed that about 7 to 11% of water being treated remained undisturbed inside these reactors. This defect has been eliminated by using a flow column in the design of a new EC reactor (FCER). The camera records, together with the measurement of effluent dye

concentration, proved that the FCER required only 6 minutes to create a visibly homogenous colour over the entire reactor.

2. Increasing water flow rate enhances the efficiency of the FCER in terms of water mixing and aeration due to increasing both velocity of the mini whirlpools (inside water) and agitation of water over the unsubmerged perforated electrodes.
3. The back flow pattern enhances the water-mixing process, using the FCER, due to the influence of the weight of the water column (water being treated) that works on strengthening the turbulent flow, and consequently enhancing the mixing efficiency.
4. Using a flow column, in the FCER, reduced the need for external stirring, aeration, or cooling devices that require extra power to work; these devices until now have been commonly used in the EC units (especially laboratory scale ones). Thus, the FCER could be a cost-effective alternative for laboratory scale EC units.
5. The aeration mechanism of the FCER takes place in the unsubmerged zone of the flow column that inhibits the formation of air bubbles inside water being treated, which minimises the electrical resistance, and reduces energy consumption consequently.
6. The quantity of the liberated coagulants from the aluminium electrodes is proportional to the combination of current density and electrolysing time.
7. The higher current density, the more rapid the pollutants removal was, due to a faster liberation of aluminium coagulants from the sacrificial anode.
8. Pollutants removal is inversely proportion to the distance between electrodes, as increasing the latter maximises the resistance for current flow, which reduces the generation of coagulants.

9. The residual concentration of a pollutant increases with the increase of its initial concentration because the extra amount of the pollutant required a bigger dosage of coagulants to be removed.
10. Increasing water temperature, to a certain extent, could enhance the efficiency of the FCER due to increasing mobility of ions, collision rate, and dissolving of the anode.
11. In terms of heavy metal removal, the presence of OM significantly reduces the efficiency of the EC method due to chelating the targeted pollutant, competing for active adsorption sites on flocs, and promoting the growth of the passive anodic film.
12. The EC method is not only applicable for the removal of chemical pollutants, but it also removes biological pollutants. The experimental results proved that the FCER has removed about 82.1% of ASM.
13. Using EC units could be made more economical by harvesting its gaseous by-products that mainly consist of hydrogen gas. The results of the current thesis indicated that the hydrogen gas emitted from the FCER could be used to produce power of 2.82 kW/m^3.
14. Applying the MW field before the EC process is of great benefit for the removal heavy metals-OM complex from drinking water. The obtained results from this thesis demonstrate that applying a MW field of 100W for 10 min at 100 ºC, before, the EC process, enhanced the removal of iron-EDTA complex by about 22%.
15. Iron-EDTA complex removal is proportional to the applied MW power because the higher MW power leads to the transfer of more energy to the solution being microwaved.
16. Pollutants removal could be enhanced by increasing irradiation time, as increasing the latter parameter allows the generation of more heat within the targeted solution.

17. Temperature level, during the microwaving process, plays a central role in pollutants removal due to increasing the coupling of the MW energy with the molecules of the substance being heated.
18. Applying the MW field into water helps to decompose the OM; this greatly enhances the removal of this pollutant by the EC unit. The experimental work of this thesis proved that the OM removal was enhanced by about 36% after 10 min of MW irradiation at 100W and 100 ^{o}C.
19. Thermal and athermal effects of the MW field played a vital role in the removal of water microorganisms; it has been found that 100% of culture-able ASM were removed after 10 min of microwaving at 100W and 100 ^{o}C.
20. The performance of EC units is predictable through developing empirical models. The statistical analysis of the collected data from the current thesis revealed that the relation between the removal of a pollutant and the operating parameters is model-able. For instance, the relations between the operating parameters and the removal of fluoride, nitrate, RB-5 dye, iron, and iron-EDTA complex, using the FCER, were modelled with R^2 value of 0.836, 0.848, 0.798, 0.868, and 0.923, respectively.
21. It is not necessary that all operating parameters play a significant role in the removal of the targeted pollutant. The statistical analysis of the experimental data indicated that some operating parameters could be omitted from predicting models due to their negligible statistical significance.
22. The preliminary operating cost of the new MW assisted-EC method was comparable with that of other advanced treatment methods, where it costs about 0.628 USA $ per m^3 of water contains 20 and 100 mg/L of iron and EDTA, respectively.

6.2 Recommendations for future works

In spite of the acknowledged advantages of the EC method to treat a wide spectrum of pollutants from waters and wastewaters, it still has many defects such as reactor design, its sensitivity to solution chemistry, and the removal of complex pollutants. To eliminate these drawbacks, modification and development of this method is required.

The current thesis is one step on this long road, and there is still a wide scope for future work and research in the field and the following recommendations could help to improve water treatment facilities.

1- The results obtained showed that the efficiency of the EC units is negatively influenced by the growth of the passive anodic film. This film does not grow on the cathode due to the formation of hydrogen gas that sweeps those fluoroaluminium complexes. Therefore, the performance of EC units could be enhanced by developing a new design that minimises the growth of this metallic film.

2- Air bubble formation between the electrodes negatively influenced the energy consumption by increasing the electrical resistance. This defect, in the current project, has been minimised by using perforated electrodes. However, a new EC reactor with inclined perforated electrodes may eliminate or greatly reduces this defect. This new design must be optimised for the shape, size, and numbers of holes and the angle of declination (the angle between the electrode centre line and the horizon).

3- Due to the ability of the new EC reactor, FCER, to aerate the solution being treated, it could be effectively applied to treat low dissolved oxygen wastewaters, such as leachate of landfills.

4- According to the previous studies, both the EC method and MW technology are of great benefit for sludge treatment. The EC method reduces the volume of the produced sludge, while the MW technology enhances both sludge dewatering and disinfection. Thus, it might be of great benefit to study the characteristics of the produced sludge from the new MW assisted-EC method as it utilises both EC and MW technologies to conduct the treatment process.

5- Further to the previous point, it is important to conduct an economic study to investigate the cost of sludge treatment (produced from the MW assisted-EC method). It is expected that the required cost will be less than that required to treat the sludge produced from traditional treatment methods. This is because the sludge produced from the MW assisted-EC method is easily to be dewatered and it has a relatively small volume.

6- New designs for the EC units are required to enhance the energy consumption and the removal efficiency, in this context, embedding a number of tubes, made from a conducting material, inside the EC unit. These tubes work as a heat exchanger that can be used to control the reaction temperature or to dissipate the extra temperature (especially from hot industrial effluents), which can be used in other useful applications.

7- The new MW assisted-EC method has been successfully applied to remove iron-EDTA complex from drinking water. There is still a wide scope for further applications of this new method to remove other pollutants such as pesticide, oil, and phenolic compounds. Additionally, it could be applied to remove different heavy metal-OM complexes such as lead-OM, and nickel-OM complex.

APPENDICES

APPENDICES

Appendix A: Publications

The following publications are the results of this thesis:

1- Khalid S. Hashim, Andy Shaw, Rafid Al Khaddar, Montserrat Ortoneda Pedrola, David Phipps, 2017. Energy efficient electrocoagulation using a new flow column reactor to remove nitrate from drinking water - Experimental, statistical, and economic approach. *Journal of Environmental Management*, 196, 224-233.

2- Khalid S. Hashim, Andy Shaw, Rafid Al Khaddar, Montserrat Ortoneda Pedrola, David Phipps, 2017. Iron removal, energy consumption and operating cost of electrocoagulation of drinking water using a new flow column reactor. *Journal of Environmental Management*, 189, 98-108.

3- Khalid S. Hashim, Andy Shaw, Rafid Al Khaddar, Montserrat Ortoneda Pedrola, David Phipps, 2017. Defluoridation of drinking water using a new flow column-electrocoagulation reactor (FCER) - Experimental, statistical, and economic approach. *Journal of Environmental Management*, 197, 80-88.

4- Khalid S. Hashim, Andy Shaw, Rafid Al Khaddar, Montserrat Ortoneda Pedrola, David Phipps, 2017. Influence of electrodes spacing on internal temperature of electrocoagulation (EC) cells during the removal (Fe II) from drinking water. *3rd BUiD Annual Doctoral Research Conference 2017, 13 May 2017*, Dubai, UAE.

5- Khalid S. Hashim, Andy Shaw, Rafid Alkhaddar, Montserrat Ortoneda Pedrola, and David Phipps. 2016. Effect of inter-electrode distance on reactive black 5 (RB-5) dye removal and energy consumption in the electrocoagulation (EC) process. *Research week 2016*, Liverpool John Moores University, UK.

6- Khalid S. Hashim, Andy Shaw, Rafid Alkhaddar, 2016. Enhancement of dissolved oxygen concentration during the electrocoagulation process using an innovative flow column -electrocoagulation reactor. *ICCGE 2016: 18th International Conference on Civil and Geological Engineering,* Paris, France.

7- Khalid S. Hashim, Andy Shaw, Rafid Alkhaddar, Montserrat Ortoneda Pedrola, 2015. Controlling of Water Temperature during the Electrocoagulation Process Using an Innovative Flow Columns - Electrocoagulation Reactor. *17th International Conference on Civil, Environmental and Geological Engineering*, Venice, Italy.

8- Khalid S. Hashim, Andy Shaw, Rafid Alkhaddar, Montserrat Ortoneda Pedrola, 2015. An innovative use of flow columns in electrocoagulation reactor to enhance the water mixing process. *12th international postgraduate research conference*, University of Salford, UK.

Appendix B: Awards.

LIVERPOOL
JOHN MOORES
UNIVERSITY

Faculty of Engineering & Technology

The Award for Paper with Best Potential Impact – winner- at Faculty Research Week 2016 is awarded to:

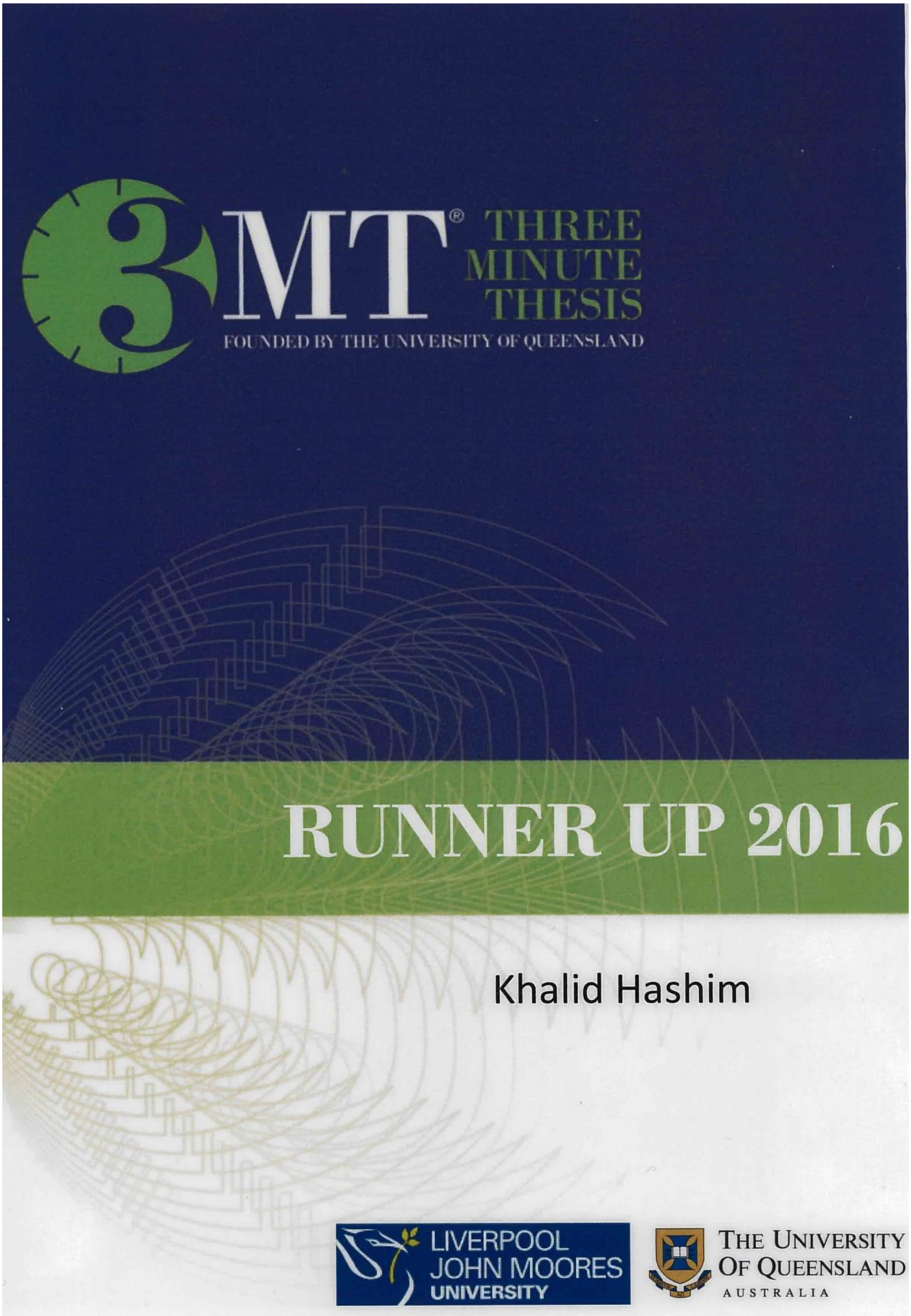
Khalid Hashim

Signed: Executive Dean

13th MAY 2016

Dated

Appendix B - Continue



3MT® THREE MINUTE THESIS

FOUNDED BY THE UNIVERSITY OF QUEENSLAND

RUNNER UP 2016

Khalid Hashim

LIVERPOOL JOHN MOORES UNIVERSITY

THE UNIVERSITY OF QUEENSLAND AUSTRALIA

Appendix B - Continue

CERTIFICATE OF BEST PRESENTATION AWARD

ICCGE 2016 : 18th International Conference on
Civil and Geological Engineering
hereby certifies that
Khalid Hashim
has presented an outstanding work entitled

Removal of Nitrogen Compounds from Industrial Wastewater Using Sequencing Batch Reactor: The Effects of React Time
Ali W. Alattabi, Khalid S. Hashim, Hassnen M. Jafer, Ali Alzeyadi

INTERNATIONAL SCIENTIFIC RESEARCH AND EXPERIMENTAL DEVELOPMENT

PARIS, FRANCE

Authorized Signature

JULY 25-26, 2016

Appendix B – Continue

LIVERPOOL
JOHN MOORES
UNIVERSITY

Faculty of Engineering & Technology

The Award for Best Elevator Pitch at
Faculty Research Week 2015
is Awarded to:

Khalid Hashim

Signed:

9th MAY 2016
Dated

Appendix B – Continue

LIVERPOOL
JOHN MOORES
UNIVERSITY

Faculty of Engineering & Technology

Certificate of Appreciation and Recognition Award for Achievements while studying at LJMU with regards to research, publication and promoting LJMU is awarded to:

Khalid Hashim

Signed: Executive Dean

26th MAY 2017

Dated

Appendix C: Some of the recent applications of EC method to treat dye-containing water and wastewater.

Type of dye	**Material of electrodes**	**Type of reactor**	**Optimum operating conditions**	**Optimum removal**	**Authors**
Acid Orange II	Granular activated carbon	Batch	Time = 30 min, cell voltage = 20V, air flow = 0.1m3/L, gap between electrodes = 14 mm.	87%	Xiong *et al.* (2001)
Acid Red 14	Iron anode and steel cathode.	Batch	Time = 4 min, current density = 8 mA/cm^2, pH = 6-9, gap between electrodes = 4 mm.	83%	Daneshvar *et al.* (2004)
Eosin yellowish	Mild steel	Batch	Time = 15 min, current density = 1.61 mA/cm^2, Power consumption = 1.5 KWh/m^3, pH = 6.8, gap between electrodes = 12 mm.	97%	Golder *et al.* (2005)
Acid yellow 36	Iron	Batch	Time = 6 min, current density = 12.78 mA/cm^2, pH = 8, gap between electrodes = 25 mm.	83%	Kashefialasl *et al.* (2006)
Levafix orange E3 GA	Aluminium	Batch	Time = 12 min, current density = 10 mA/cm^2, Power consumption = 35 kWh/kg dye, pH = 6.4, gap between electrodes = 11 mm.	95%	Kobya *et al.* (2006a)
Red dye (2-naphthoic acid and 2-naphtol)	Aluminium	Continuous	Time = 14 min, current density = 31.25 mA/cm^2, Power consumption = 3.2 kWh/kg dye, flow rate = 37.2 L/h, pH = 6-9, gap between electrodes = 10 mm.	85%	Merzouk *et al.* (2009)
Reactive Black 5	Iron	Batch	Time = 5 min, current density = 4.575 mA/cm^2, Power consumption = 4.96 kWh/kg dye, pH = 5, gap between electrodes = 25 mm.	98.8%	Sengil and Ozacar (2009)
Orange II	Aluminium	continuous	Time = 7.3 min, current density = 16 mA/cm^2, Power consumption = 3.2 kWh/kg dye, pH = 6.5, flow rate = 350 mL/min, gap between electrodes = 6 mm.	94.5%	Mollah *et al.* (2010)
Direct red 81	Aluminium	Batch	Time = 60 min, current density = 1.875 mA/cm^2, pH = 6, gap between electrodes = 15 mm,	98%	Aoudj *et al.* (2010)
Reactive Red198	Aluminium	Batch	Time = 30 min, cell voltage = 20V, pH = 5.5, Power consumption = 1.303 kW/m^3, gap between electrodes = 10 mm,	98.6%	Dalvand *et al.* (2011)
Acid Yellow 220	Aluminium	Batch	Time = 7.5 min, current density = 4 mA/cm^2, pH = 5, Power consumption = 950 kWh/m^3, gap between electrodes = 10 mm.	97%	Pajootan *et al.* (2012)
Direct red 81	Aluminium	Continues	Time = 7.3 min, current density = 20 mA/cm^2, Power consumption = 3.2 kWh/kg dye, pH = 7.5, flow rate = 10 L/H, gap between electrodes = 10 mm.	90.2%	Zodi *et al.* (2013)
Methylene blue	Iron	Batch	Time = 24 min, current density = 5 mA/cm^2, Power consumption = 3.8 kWh/m^3 , pH = 9, gap between electrodes = 10 mm.	100%	Alizadeh *et al.* (2015)

Imperon violet KB	Aluminium	Batch	Time = 10 min, current density = 4 mA/cm^2, Power consumption = 4.66 kWh/m^3 , pH = 4.57, gap between electrodes = 10 mm.	98.5%	Naje *et al.* (2016)

Appendix D: Some applications of the EC method in heavy metal removal from water and wastewater.

Metal	Material of electrode	Type of reactor	Optimum operating conditions	Optimum removal	Authors
Lead	Steel	Batch	Time = 12 min, current = 1 A, pH = 5.5-7, initial concentration of lead = 100 mg/L, gap between electrodes = 10 mm.	99%	(Thaveemaitree *et al.*, 2003)
Arsenic	Carbon steel	Continues	Time = 1.5 min, current density = 3.7 mA/cm^2 , pH = 8.3, water flow rate= 800 mL/min, air flow rate= 600 mL/min, gap between electrodes = 6 mm.	99.77%	(Parga *et al.*, 2005)
Zinc, copper, chromium, and nickel	Iron	Continues	Time = 9 min for zinc and 6.4 min for the rest, current density = 1.35 mA/cm^2 , pH = 7, gap between electrodes = 2 mm.	99%	(Anbari *et al.*, 2008)
Arsenic	Iron	Continues	Time = 0.75 min, current density = 4.5 mA/cm^2, flow rate = 0.875 L/min, pH = 8.06, gap between electrodes = 3 mm.	99%	(Garcia-Lara *et al.*, 2009)
Mercury	Iron and aluminium	Batch	Time = 15 min for iron electrodes and 25 min for aluminium ones, current density = 25 mA/cm^2, pH = 3-7, gap between electrodes = 30 mm.	99%	(Nanseu-Njiki *et al.*, 2009)
Iron	Magnesium (anode), and galvanized iron (cathode)	Batch	Time = 35 min, current density = 0.6 mA/cm^2, pH = 6, gap between electrodes = 5 mm.	98.4%	(Vasudevan *et al.*, 2009)
Cadmium and nickel	Iron	Batch	For cadmium, time = 30 min, current = 3 mA/cm^2, pH = 8-10, power consumption = 11.65 kW/m^3, gap between electrodes = 10 mm. For nickel, time = 80 min, current density = 6 mA/cm^2, pH = 8-10, power consumption = 11.94 kW/m^3, gap between electrodes = 10 mm.	99.4% for cadmium, 99.1% for nickel	(Kobya *et al.*, 2010)
Arsenic	Iron and aluminium	Batch	For iron electrodes: time = 2.5 min, current = 0.25 mA/cm^2, pH = 6.5, power consumption = 0.014 kW/m^3, gap between electrodes = 13 mm. For aluminium electrodes: time = 4 min, current density = 0.25 mA/cm^2, pH = 7, power consumption = 0.025 kW/m3, gap between electrodes = 13 mm.	94.1% using iron electrodes. 93.5% using aluminium electrodes.	(Kobya *et al.*, 2011)
Chromium	Aluminium alloy	Batch	The highest removal achieved using aluminium electrodes at	98.2%	(Vasudevan *et al.*, 2011)

			time = 30 min, current density = 2 mA/cm^2, pH = 7, gap between electrodes = 5 mm.		
Strontium	Iron	Batch	Time = 30 min, current = 0.49 A, pH = 7-8, 1 g/l of NaCl as electrolyte, gap between electrodes = 5 mm.	95%	(Parga *et al.*, 2012)
Copper, zinc and nickel	Aluminium and iron	Batch	The highest removal efficiency was achieved using aluminium electrodes at: time = 60 min, current density = 1.4 mA/cm^2, pH = 6-7.7, water conductivity = 0.35 mS/cm, power consumption = 0.067 kW/m^3, gap between electrodes = 15 mm.	95%	(Ferreira *et al.*, 2013)
Cadmium (Cd), copper (Cu), and nickel (Ni)	Iron	Batch	Time = 90 min, current density = 30 mA/cm^2, pH = 7, 0.05 mole/L of Na_2SO_4 as electrolyte, power consumption = about 22.5kW/m^3, gap between electrodes = 16.5 mm.	99.7% for Cd 99.9% for Ni 98.9% for Cu	(Un and Ocal, 2015)

Appendix E: Some of the recent applications of the EC method in the treatment of OM containing water and wastewater.

Type of water or wastewater	Material of electrode	Type of reactor	Optimum operating conditions	Removal efficiency	Authors
Olive mill wastewater	Aluminium	Batch	Time = 25 min, current density = 75 mA/cm^2, initial pH = 4-6, initial COD = 75.1 g/L, power consumption = Not given, gap between electrodes = 20 mm.	76% of COD	(Adhoum and Monser, 2004)
wastewater of potato chips plant	Aluminium and iron	Batch	The best removal by Al electrodes, time = 40 min, current density = 20 mA/cm^2, initial pH = 4, initial COD = 2.2-2.8 g/L, power consumption = 4 kWh/m^3, gap between electrodes = 11 mm.	60% of COD	(Kobya *et al.*, 2006b)
synthetic waters	Iron cast	Batch	Time = 70 min, applied voltage = 50V, initial pH = 9, initial concentration of humic acid = 200 mg/L, power consumption ≈ 10 kWh/m^3, gap between electrodes = 50 mm.	92.69% of COD	(Yildiz *et al.*, 2007)
Wastewater of agro-industry	Mild steel and aluminium	Batch	Time = 60 min, current density = 5 mA/cm^2, final pH =7.6, power consumption = up to 51.6 kWh/m^3 (according to the type of wastewater), gap between electrodes = 15 mm.	About 85% of COD using bipolar mild steel electrodes	(Drogui *et al.*, 2008)
Wastewater of paper mill	Aluminium and iron	Batch	Time = 7.5 min, current density = 4.8 mA/cm^2, initial pH =7.6, initial concentration of phenol and lignin is 0.535 and 13.514 mg/L respectively, power consumption = 95.52 Kw/m^3, gap between electrodes = 20 mm.	Al electrode were 80% of lignin, and 98% of phenol. Fe electrodes 92% of lignin, and 93% of phenol.	(Ugurlu *et al.*, 2008)
Wastewater of vegetable oil refinery	Aluminium	Batch	Time = 90 min, current density = 35 mA/cm^2, initial pH =7, power consumption = 42.6 kWh/kg of COD, gap between electrodes = 8 mm.	98.9% of COD	(Un *et al.*, 2009)
Hospital wastewater	Fe-Fe Al-Al Al-Fe	Batch	Time = 60 min, applied voltage = 30V, initial pH =3, power consumption = 30.6 kWh/m^3, gap between electrodes = 20 mm.	87.1% of COD	(Dehghani *et al.*, 2012)
Wastewater of petroleum refinery	Iron as anode and aluminium as a cathode	Batch	Time = 30 min, current density = 12.2 mA/cm^2, initial pH =9, initial COD = 72,450 mg/L, power consumption = not given, gap between electrodes = 10 mm.	80% of COD	(Ben Hariz *et al.*, 2013)

Wastewater of distillery industries	Iron and aluminium	Batch	Iron electrodes gave the highest removal efficiency at time = 150 min, applied voltage = 25V, initial pH =3, initial COD = 110-190 g/L, power consumption = not given, gap between electrodes = not given.	85.7% of COD	(Wagh *et al.*, 2015)
Seawater	aluminium	Batch	Time = 40 min, current density = 22.4 mA/cm^2, initial pH =3, initial COD = 1.34 mg/L, power consumption = not given, gap between electrodes = 10 mm.	70.8% of COD	(Hakizimana *et al.*, 2016)
Synthetic oil refinery wastewater	Iron as anode and aluminium as a cathode	Batch	Time = 40 min, applied voltage = 10.5V, initial pH =7, initial diesel concentration = 3.5 g/L, power consumption = 6.47 kWh/m^3, gap between electrodes = 20 mm.	98% of COD	(Safari *et al.*, 2016)

Appendix F: Some of the recent applications of EC method to disinfect water and wastewater.

Organism/ pathogen	Material of electrode	Type of reactor	Optimum operating conditions	Removal efficiency	Authors
Total *bacteria* and *coliform* from drinking water	stainless steel	Batch	Time = 10 min, current = 0.26 A, initial pH = 7.8, initial concentration of total bacteria and coliform = 980 and 1100 cuf/cm^3 respectively, power consumption = Not given, gap between electrodes = 10 mm.	83% for total bacteria, and 58% of coliform	(Hassanien, 2004)
MS2 bacteriophage	stainless steel cathode, and iron	continuous	Time = 10 min, current = 0.26 A, initial pH = 7.3, flow rate= 300 mL/min, virus concentration = 106 pfu/mL, iron dosage= 10 mg/L, gap between electrodes = 2 mm.	99.9%	(Zhu *et al.*, 2005)
Algae - *chlorophyll*	Aluminium	Batch	Time = 15 min, power input = 100W/dm^2, initial pH = 7-8, algae concentration = 550 mg/m^3, gap between electrodes = 20 mm.	99.5%	(Azarian *et al.*, 2007)
Fecal coliforms	Aluminium	Batch	Time = 60 min, current = 18.2 mA/cm^2, initial pH = 4, concentration of coliforms = 11000 MPN/dm^3, power consumption = not given, gap between electrodes = not given mm.	99.9%	(Roa-Morales *et al.*, 2007)
Escherichia coli	Stainless steel (S.S), ordinary steel (O.S), and aluminium (Al)	Batch	Aluminium electrodes were the best, time = 10-15 min, current = 1 A, initial pH = 9, power consumption = not given, gap between electrodes = 20 mm.	55% for S.S 97% for O.S 98% for Al	(Ghernaout *et al.*, 2008)
Coliforms	Aluminium, iron, and aluminium + iron	Batch	Aluminium + iron achieved the highest removal, time = 60 min, current = 3.787 mA/cm^2, initial pH = 8, concentration of coliforms = 11000 mg/dm^3, power consumption = not given gap between electrodes = 20 mm.	99%	(Linares-Hernández *et al.*, 2009)
Chlorella Vulgaris	Aluminium as (anode), graphite (cathode)	Batch	Time = 60 min, current density = 2 mA/cm^2, initial pH = 6-8, concentration of algae = 10^8 cell/L , power consumption = 1.84 kW/m^3, gap between electrodes = 15 mm.	100%	(Tumsri and Chavalparit, 2011)
Chlorella sorokiniana	Non-sacrificial carbon electrode	Batch	Time = 60 min, current = 1 mA/cm^2, initial pH = not given, concentration =2 g/L, power consumption = 1.6 kWh/kg, gap between electrodes = 60 mm.	94.5%	(Misra *et al.*, 2014)

Heterotrophic Bacteria	Aluminium	Batch	Time = 20 min, current = 11.2mA/cm^2, initial pH =8, concentration = not given, power consumption = 4-5 kWh/m^3, gap between electrodes = 20 mm.	100%	(Hakizimana *et al.*, 2016)

Appendix G: Experimental and predicted iron-EDTA complex removal efficiency under different operating conditions.

No.	*t min*	*CD mA/cm^2*	*C_0 mg/L*	*ID mm*	*pH*	*T ^{o}C*	*EDTA mg/L*	*Experimental Efficiency*	*Predicted Efficiency*
1.	25	1.5	20	5	6	20	100	69	78.80
2.	=	=	=	=	=	=	50	81	85.05
3.	=	=	=	=	=	=	0	90.1	77.65
4.	=	=	=	=	=	=	200	41.2	48.10
5.	=	=	=	=	=	=	0	98.1	82.20
6.	=	=	=	=	=	=	100	68.6	69.70
7.	=	=	=	=	=	=	0	99.9	91.30
8.	=	=	=	=	=	=	50	61.1	66.85
9.	=	=	=	=	=	=	500	25.2	24.25
10.	=	=	=	=	=	=	50	78.5	75.95
11.	=	=	=	=	=	=	200	56	52.65
12.	=	=	=	=	=	=	0	88.8	77.65
13.	=	=	=	=	=	=	100	69.3	74.25
14.	=	=	=	=	=	=	100	70	78.80
15.	=	=	=	=	=	=	200	39.8	48.10
16.	=	=	=	=	=	=	500	22.3	19.70
17.	=	=	=	=	=	=	200	59	61.75
18.	=	=	=	=	=	=	0	97.2	82.20
19.	=	=	=	=	=	=	100	50	60.59
20.	=	=	=	=	=	=	50	78.1	80.49
21.	=	=	=	=	=	=	500	24.1	19.70
22.	=	=	=	=	=	=	100	50	60.60
23.	=	=	=	=	=	=	50	76.1	75.95
24.	=	=	=	=	=	=	500	24.5	28.80
25.	=	=	=	=	=	=	0	99.3	91.30
26.	=	=	=	=	=	=	50	59.4	66.85
27.	=	=	=	=	=	=	200	52	52.65
28.	=	=	=	=	=	=	50	80	85.05
29.	=	=	=	=	=	=	200	57.6	66.30
30.	=	=	=	=	=	=	100	65.2	69.70

= means constant at the same previous value

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