إقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

Nitrate removal from groundwater using continuous flow electrocoagulation reactor

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وإن هذه الرسالة ككل، أو أي جزء منها لم يقدم من قبل لنيل درجة أو لقب علمي أو بحثي لدى أية مؤسسة تعليمية أو بحثية أخرى.

DECLARATION

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification

Student's name: Tamer M. S. Tabash

اسم الطالب: تامر محمد سالم طبش

Signature:

التوقيع:

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The Islamic University-Gaza.

Deanery of High Studies

Faculty of Engineering

Civil Engineering Department

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Presented by:

Tamer M. S. Tabash

Supervised by:

Dr. Fahid Rabah

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Nitrate removal from groundwater using continuous flow electrocoagulation reactor

وبعد المناقشة العلنية التي تمت اليوم السبت 27 شعبان 1434هـ، الموافق 2013/07/06م الساعة الواحدة ظهراً بمبنى طيبة، اجتمعت لجنة الحكم على الأطروحة والمكونة من:

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د. عبد المجيد رمضان نصار	**مناقشاً داخلياً**	....
د. يونس خليل المغير	**مناقشاً خارجيًا**	....

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أ.د. فؤاد علي العاجز

DEDICATION

To my parents for their kindness…

To my brothers and sisters

To My Friends and Colleagues …

To all knowledge seekers…

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ABSTRACT

Nitrate contamination of groundwater is a major concern due in large part to excessive use of nitrate-based chemical fertilizers. It can be noticed that all countries and organizations restricted nitrate concentration in drinking water within the range 45-50 mg-NO_3/L.

The purposes of this study is nitrate removal from aqueous solution by Electrocoagulation process.Then find the best operating conditions and apply to the northern Gaza water samples.

A laboratory continuous flow electrocoagulation reactor was designed to investigate the effects of different parameters on the removal of nitrate from aqueous solution. Influence of process parameters such as initial nitrate concentration (C_i), hydraulic retention time (HRT), distance between electrodes (D), applied voltage (V) and effective area of anode (A_{eff}).

The best operating conditions for nitrate removal for the aqueous solution were found to be at HRT 2, 2.5 and 2.5hours, applied voltage 40V, distance between electrode 3cm and effective area of electrode 47.1, 47.1 and 61.4 cm^2, when initial nitrate concentration were 100, 150 and 200 mg-NO_3/L, respectively. Moreover, obtained best conditions were tested on original groundwater sample from the northern of Gaza water distribution system. It was found that the nitrate removal efficiency was reached to 80 % at the best conditions: V = 40V, HRT = 2.5hours, D = 3cm and A_{eff} = 61.4cm^2, when TDS_i and C_i were 1000 mg/L and 200mg-NO_3/L , respectively. Therefore, this process is suggested as an efficient alternative technique on nitrate removal from aqueous solution. And also it was possible to remove nitrate from groundwater below the limit of the drinking water standard using this method. And also there are many side benefits that can be achieved when using EC, such as that the alkalinity, total hardness concentration and TDS were decreased when using the EC in groundwater.

الملخص

ازدياد تركيز النترات في المياه الجوفية يسبب العديد من المضار الصحية وهو مدعاة للقلق ويرجع ذلك للاستخدام المفرط للأسمدة الكيميائية في الزراعة. حيث أن جميع البلدان والمنظمات وضعت معيار لتركيز النترات في مياه الشرب وهو 45-50 ملغم-نترات/لتر .

الغرض من هذه الدراسة هو إزالة ملوث النترات من محلول مائي بواسطة عملية التخثر كهربي (Electrocoagulation) والعثور على أفضل الظروف التشغيلية لإزالة النترات من مياه الشرب وتطبيقها علي عينات من المياه شمال قطاع غزة.

وقد تم تصميم جهاز التخثر الكهربائي المستمر الجريان في المختبر وذلك للتحقيق في أثر بعض المتغيرات المختلفة وتأثيرها على ازالة النترات من المحلول المائي. ومن هذه المتغيرات تركيز نترات الأولية، HRT، المسافة بين الأقطاب، فرق الجهد ومساحة المنطقة الفعالة من الآنود (المغمورة في الماء).

ومن النتائج أن أفضل الظروف التشغيلية لإزالة النترات من المحلول المائي قد تحققت عندما كانت المتغيرات كالتالي: فرق الجهد قدره 40 فولت و المسافة بين الأقطاب كانت 3 سم و مساحة المنطقة الفعالة من الآنود تساوي (47.1، 47.1، 61.4 سم^2) و HRT يساوي (2، 2.5، 2.5 ساعة) عندما كانت تركيز النترات الأولية (100 ، 150 ، 200 ملغم-نترات/لتر)على التوالي . وقد تم بعد ذلك استخدام تلك الظروف التشغيلية على عينة مياه حقيقية من آبار المياه الجوفية في المنطقة الشمالية لقطاع غزة و قد وصلت كفاءة إزالة النترات الى 80 % .عندما كان تركيز النترات الأولية 200 ملغم-نترات/لتر و تركيز المواد الصلبة الذائبة 1000 ملغم/لتر عند الظروف التشغيلية التالية :(فرق الجهد قدره 40 فولت و المسافة بين الأقطاب 3 سم و مساحة المنطقة الفعالة من الآنود 61.4 سم^2 و HRT 2.5 ساعة). لذلك يقترح أن تكون هذة الطريقة طريقة فعالة لإزالة النترات من محلول مائي وأيضا من الممكن استخدامها في المياه الجوفية لإزالة النترات وايصالها الى الحد المطلوب حسب معايير مياه الشرب الدولية . وأيضا هناك العديد من الفوائد الجانبية التي يمكن تحقيقها عند استخدامها في معالجة المياه الجوفية مثل انخفاض تركيز كل من القلوية المائية و عسر المياه و أيضا المواد الصلبة الذائبة .

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List of Abbreviations

Notation	**Abbreviation**	**Unit**
°C	Celsius	
A	Amber	
A_{eff}	Effective area of anode	cm^2
Al	Aluminum electrode	
Al_3^+	Aluminum ions	
BAT	Best Available Technologies	
CC	Chemical coagulation	
cm	Centimeter	
cm^2	Square centimeter	
COD	Chemical oxygen demand	mg/L
D	Distance between the electrode	cm
EC	Electrocoagulation	
ECF	Electrocoagulation/flotation	
ED	Electrodialysis	
EDR	Electrodialysis reversal	
EF	Electroflotation	
EO	Electrooxidation	
EPA	Environmental protection agency	
Fe	Iron electrode	
Fe_3	Ferric ions	
FTU	Formazine Turbidity Unit	
g	Grams	
H+	Hydrogen ions	
HCl	Hydrochloric acid	
hr.	Hour	
HRT	hydraulic retention time	hour
I	Current	A
IX	Ion exchange	
KNO_3	Potassium nitrate	
m^2	square meter	
m^3	Cubic meter	
MAC	Maximum acceptable concentrations	
MCL	Maximum contaminant level	
mg/L	Milligram per Liter	
mg-NO3/L	Milligram Nitrate per Liter	
mg-NaCl/L	Milligram NaCl per Liter	
mL/hr.	Melliliter per hour	
mL/hr.	Milliliter	
N_2	Nitrogen gas	
NaCl	Sodium chloride	

NaOH	Sodium Hydroxide	
NH_4^+	Ammonia	
NO_2	Nitrite	
NO_3	Nitrate	mg-NO_3/L
NOM	Natural organic matter	
NTU	Nephelometric Turbidity Unit	
OH−	hydroxyl ion	
pH	(solvated) hydrogen ion	
ppm	Part per million	mg/L
PS	poultry slaughterhouse	
RO	Reverse osmosis	
SAC	Strong acid cation	
SBA	Strong base anion	
T_i	initial temperature	°C
TDS_i	Initial total suspended solid	mg/L
TDO	Total Dissolved Oxygen	mg/L
TSS	Total suspended solids	mg/L
USEPA	United states environmental protection agency	
WAC	Weak acid cation	
WBA	Weak base anion	
WHO	World Health Organization	

CHAPTER 1: Introduction

1.1 Background

One of the biggest concerns is the increase of nitrate in the receiving waters. High nitrate concentrations have contributed to negative effects on human health and on the environment. Common treatment methods for nitrate removal include several physicochemical and biological processes, but few of them have been found effective and economically for application to groundwater treatment systems. However, electrochemical has potential as a possible treatment method to remove nitrate in ground water.

1.2 Nitrate

Nitrate is naturally occurring ions that are part of the nitrogen cycle. The nitrate ion ($NO3^{-}$) is the stable form of combined nitrogen for oxygenated systems. Although chemically unreactive, it can be reduced by microbial action. Chemical and biological processes can further reduce nitrite to various compounds or oxidize it to nitrate (WHO, 2011) .

Table 1.1: Physicochemical properties of nitrate .

Property	Nitrate
Acid	Conjugate base of strong acid HNO3; pKa = −1.3
Salts	Very soluble in water
Reactivity	Unreactive

NO_3^- and nitrite (NO_2^-) are naturally occurring inorganic ions, which are part of the nitrogen (N) cycle. Microbial action in soil or water decomposes wastes containing organic nitrogen first into ammonia, which is then oxidized to NO_2^- and NO_3^- . Because NO_2^- is easily oxidized to NO_3^-, NO_3^- is the compound predominantly found in groundwater and surface waters under oxidizing conditions. Contamination with N-containing fertilizers, including anhydrous ammonia, as well as animal or human natural organic wastes, can raise the concentration of NO_3^- in groundwater. NO_3^- containing compounds in the soil are generally soluble and readily migrate into groundwater. (Shomar, et al., 2008)

Nitrate is used mainly in inorganic fertilizers. It is also used as an oxidizing agent and in the production of explosives, and purified potassium nitrate is used for glass making. Nitrate is sometimes also added to food to serve as a reservoir for nitrite (WHO, 2011) .

Nitrate pollution of surface and groundwater's has become a major problem in some agricultural areas (Meyer, et al., 2005) .

Nitrate can reach both surface water and groundwater as a consequence of agricultural activity (including excess application of inorganic nitrogenous fertilizers and manures), from wastewater treatment and from oxidation of nitrogenous waste products in human and animal excreta, including septic tanks. Nitrite can also be formed chemically in distribution pipes by Nitrosomonas bacteria during stagnation of nitrate-containing and oxygen-poor drinking-water in galvanized steel pipes or if chloramination is used to provide a residual disinfectant and the process is not sufficiently well controlled.

1.2.1 Effects of Nitrate

Several health problems may be caused by excess nitrate in water sources. Nitrate Ions in groundwater have many adverse effects on human. In humans, water contaminated with nitrate has been related to outbreaks of infectious diseases, childhood diabetes and decrease iodine uptake, but the current studies are incomplete. Other studies indicates that high nitrate uptake can lead to abortion in animals such as cattle .

Nitrate is hazardous to infants and pregnant women due to the risk of methaemoglobinaemia , also called the "blue-baby syndrome". Reduction of nitrate to nitrite in the stomach of infants occurs, where nitrite will bind to haemoglobin and form methaemoglobin in the red bloodcells (eq 1.1).

$$\textit{haemoglobin}\ (Fe^{2+}) \xrightarrow{NO_2^-} \textit{methaemoglobin} \quad \ldots\ldots\ldots\ldots\ldots \quad \textit{eq 1.1}$$

Metaemoglobin binds up oxygen and prevents oxygen transport. When the levels of it exceed 10 %, there is risk for cyanosis (blue-baby syndrome) where the infants are suffocated. Most of the nitrate in the body will oxidize to nitrate, but there will be residual that can react with the haemoglobin. The risk is greater for bottle-fed-infants than adults and children, due to the infant's body weight and limited ability to produce repairing enzymes. In studies reported by the World Health Organization (WHO), 97% of the cases where symptoms of cyanosis were observed occurred in infants that were mostly under 3 months old, and the nitrate concentration in the water was over 50 mg/L. Methaemoglobinaemia is normally seen as a result of high nitrate concentrations in drinking water, even though it has been found in infants that are related to high nitrate consumption from vegetables.

In drinking water, nitrate may cause different types of cancer in humans who are exposed to high amounts (WHO, 2011) .

Another health concern, which has been under study for many years, is nitrate contaminated drinking water’s link to non-Hodgkin’s lymphoma and stomach cancer. Although this link is very tenuous and controversial, research and surveys are ongoing in an attempt to document the connection. The United States National Research Council found some suggestion of an association between high nitrate intake and gastric and/or oesophageal cancer. However, individual exposure data were lacking, and several other plausible causes of gastric cancer were present. Connections exists between nitrate intake and several disorders and adverse effects, however there is still a lack of compelling evidence (WHO, 2011) .

1.3 Electrocoagulation historical background

As documented by (Chen & Hung, 2007) using electricity to treat water was first proposed in England in 1889. The application of electrolysis in mineral beneficiation was patented by Elmore in 1904. Electrocoagulation (EC) with aluminum and iron electrodes was patented in the United States in 1909. The EC of drinking water was first applied on a large scale in the United States in 1946. At that time because of the relatively large capital investment and the expensive electricity supply, electrochemical water or wastewater technologies did not find wide application worldwide. However, in the United States and former USSR extensive research during the following half century has accumulated abundant amount of information. With the ever increasing standard of drinking water supply and the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide during the past two decades and processes such as electrochemical metal recovery, EC, electroflotation (EF) and electrooxidation (EO) can be regarded nowadays as established technologies.

In the environmental field, electrocoagulation is one of the main applications of electrochemical reactor technology for the treatment of water and wastewater. EC is a complicated process that involves many chemical and physical phenomena using consumable electrodes (Fe/Al) to supply ions into the water stream. During the late nineteenth century, EC was applied in several large-scale water treatment plants in London (Matteson, et al., 1995), while electrolytic sludge treatment plants were operated as early as 1911 in various parts of the United States (Vik, et al., 1984) .

1.4 Statement of the problem

One of the main processes that should be applied in the water treatment is nitrate removal, which is complex and expensive. However, nitrate removal is essential to achieve the minimum accepted level for safe drinking .

In general, basic problems are related with most of nitrate removal techniques. Reverse osmosis (RO) can effectively separate nitrate from well water. However, RO cannot separate nitrate selectively. It can be seen that the RO effluent average nitrate concentration was less than the maximum allowable concentration. On the other hand, RO rejection brine concentration is high and disposal of regenerant brine can pose a problem. However, resulting brine with high nitrate content cannot be discharged into a river or a deep well. Nitrate ions can be removed from the water on an anion exchange resin. However, it may be cost prohibitive when targeting nitrate due to the high cost of waste disposal. In biological treatment, microbiological contamination of water is possible and the control and the effectiveness of the method has its limitations. Biological de-nitrification, however, shows some drawbacks in process control and output water quality.

The EC is a promising technique in the field of water treatment that is proposed to have a great role in nitrate. However, the characteristics and mechanism of nitrate removal from groundwater by EC is still unknown, which are the basic step for utilizing EC in nitrate removal from groundwater.

1.5 Objectives

The main goal of this research is to investigate the characteristics of nitrate removal from groundwater using continuous flow electrocoagulation reactor. Moreover, this research is supposed to achieve the following objectives:

A. To investigate the combined effects of applied voltage (V), initial nitrate concentration (C_i), distance between electrode (D), effective area of anode (A_{eff}) and hydraulic retention time (HRT) on the efficiency of EC for the removal of nitrate from aqueous solutions using continuous flow reactor .

B. To study the matrix effect using real water sample from the northern area from Gaza Strip .

Matrix effect : The effect of the electrocoagulation process on the other chemicals existing in the water during the removal of nitrate and the possible production of other chemicals during the process .

1.6 Methodology

To achieve the objectives of this study, an assessment of the characteristics of removing nitrate from drinking water using electrocoagulation is investigated.
The following methodology was applied:

a. Literature review:

Including revision of:-

- Scientific papers, reports in the fields of EC applications in water treatment.
- Books and websites in the fields of nitrate removal methods

b. Laboratory experiments:

- **Water Samples**

Lab experiments were applied on both synthetic and real groundwater samples.

1- **Aqueous solution groundwater :** The samples (nitrate solution) were prepared in lab using potassium nitrate (KNO_3)
2- **Real groundwater samples**

- **Experimental Procedures(in chapter 3)**

The following chart illustrates the proposed methodology:

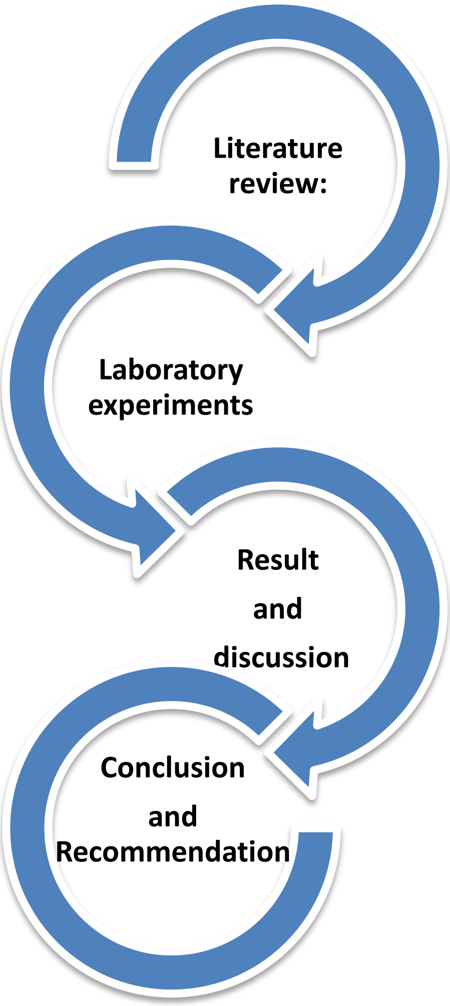


Figure 1.1: Methodology

1.7 Thesis structure

The structure of the thesis consists of five chapters arranged carefully, to make the research clear and understandable. This section presents a concise description of these chapters.

Chapter (1) is a briefly introduction, which presents a general background about water, nitrate and electrocoagulation. In addition, statement of problem, objectives, scope of work and methodology are given.

Previous researches and studies about nitrate removal techniques and standard limits are illustrated in **Chapter (2).** This chapter gives a general overview of relevant previous researches concerning electrocoagulation technology applications in several fields including water treatment.

Details of the apparatus and analysis procedures of EC processes are discussed in **Chapter (3)**. Experimental methods used to determine the concentration of nitrate ions, as well as the materials are also discussed.

Chapter (4) outlines the electrocoagulation continuous reactor experiment, with the related results and analyses. Factors affecting nitrate removal are studied during this chapter. These factors include hydraulic retention time (HRT), initial nitrate concentration (C_i), distance between electrodes (D) and effective area of anode (A_{eff}).

The conclusion derived from experimental results is presented in **Chapter (5).** Finally, the recommendations for the present study and other further studies are also provided in this chapter.

CHAPTER 2: Literature review

2.1Introduction

The excessive application of fertilizers, the intense exploitation of farms and the ubiquity of other agriculture-related industries have increased the nitrogen load discharged into waterways. This growth in the nitrogen load has resulted in a decrease in water quality and has even let to health problems related to oxidized forms of nitrogen. The removal of nitrogen can be carried out by using either biological or physico-chemical methods (Lacasa, et al., 2011) .

Pollution of ground and surface waters by nitrates is a wide spread and serious problem (Koparal & Ogutveren, 2002) **.**

2.2 Nitrate in Groundwater

Nitrate is a natural part of the environment and the nitrogen cycle. In oxygenated water systems it is the stable form of nitrogen. In all plants, nitrate can be found at different concentrations, and the nitrate itself is an essential nutrient for the plant. However, nitrate can pollute surface waters and ground waters, especially areas with agricultural activity nearby where there is excessive use of fertilizers. Other sources for nitrate are animal waste, sewer lines, land discharges from wastewater and atmospheric deposition (WHO, 2011) (Shrimali & Singh, 2001) (Bhatnagar & Sillanpää, 2011) . Nitrate has a relatively high solubility and does not bind readily to soil, which makes it susceptible to leaching and a wide spread contaminant (Bhatnagar & Sillanpää, 2011) . A common scenario for nitrate formation is the process occurring with urine from animal waste, which contains nitrogen as urea ($(NH_2)_2CO$). Degradation of this product results in formation of ammonia which can be oxidized to nitrite and nitrate by the aerobic process of nitrification. The process is mediated by bacteria such as *Nitrosomonas* and *Nitrobacter*, as shown in the eqn. 1 and eqn. 2. Oxygen consumption during these processes may have a harmful effect on the environment if the levels of oxygen consumed are sufficiently high.

$$2NH_3 + 3O^2 \xrightarrow{Nitrosomonas} 2NO_2^- + 2H^+ + 2H_2O$$ --------------------- eqn. (2.1)

$$2NO_2^- + O_2S \xrightarrow{Nitrobacter} 2NO_3^-$$ -- eqn. (2.2)

At the same time, nitrite and nitrate can be converted to nitrogen gas and nitrogen monoxide during the denitrification process mediated by denitrifying bacteria under anaerobic conditions (eqn. 3)

$$\frac{NO_2^-}{NO_3^-} \xrightarrow{\text{Denitrifiers}} N_2 + 2H^+ + N_2O$$ -- eqn. (2.3)

2.2.1 Nitrate standard limits

Despite conflicting research findings, standards have been set for nitrate in drinking water. The U.S. Environmental Protection Agency (USEPA) maximum contaminant level (MCL) for nitrate is 10 mg NO_3^--N/L (USEPA, 2009), whereas the World Health Organization (WHO) and the European Community have set an MCL of 50 mg NO_3^-/L which is equal to 11.3 mg NO3$^-$-N/L (WHO, 2011) . Ontario Ministry of the Environment and Health Canada have set the maximum acceptable concentrations (MAC) of nitrate in drinking water of 45 mg NO3$^-$/L (10 mg NO3$^-$-N/L) (Ontario Ministry of the Environment, 2006) (Health Canada, 2012) . The MAC of nitrate as regulated by the National Health and Medical Research Council and Engineering Services Division Ministry of Health Malaysia are also 50 mg NO_3^-/L (11.3 mg NO3$^-$-N/L) (Health Australia, 2004) (Health Malaysia, 2004) .

The organizations concerned with drinking water quality and many governments have paid a great attention for nitrate limitation in the drinking water. Table (2.1) lists some international standards of nitrate concentration in drinking water according to some international water quality guidelines. It can be noticed that all countries and organizations restricted nitrate concentration in drinking water within the range 45-50 mg/l as NO3$^-$ or 10-11.3 mg NO3$^-$- N/L , which indicates that nitrate is a matter of concern that should be treated well.

Table (2.1) International standards of nitrate concentration in drinking water

Country/Organization	Nitrate concentration	Reference
WHO	50 mg/l as NO_3^-/L	(WHO, 2011)
The USEPA	10 mg NO_3^--N/L	(USEPA, 2009)
Canada	45 mg/l as NO_3^-/L	(Health Canada, 2012)
Ontario Ministry of the Environment	10 mg NO_3^--N/L	(Ontario Ministry of the Environment, 2006)
Australia	50 mg NO_3^-/L	(Health Australia, 2004)
Malaysia	50 mg NO_3^-/L	(Health Malaysia, 2004)

2.2.2 Nitrate removal techniques

Several techniques for the removal of nitrate from drinking water have been adopted based on scientific developments. A brief overview of some techniques is presented in this literature review.

Nitrate is a stable and highly soluble ion with low potential for coprecipitation or adsorption. Thus conventional treatment technologies cannot be used. This reviews various techniques in terms of their effectiveness, ease of operation and cost.

At high nitrate concentrations, water must be treated to meet regulated concentrations. But, it is almost impossible to remove nitrate by conventional drinking water treatment methods such as coagulation and filtration due to its high stability and solubility, as well as its low potential for coprecipitation or adsorption in water (Luk & Au-Yeung, 2002) .

Therefore, other technologies including biological denitrification, ion exchange (IX), reverse osmosis (RO), electrodialysis (ED), and chemical denitrification have been studied or applied to remove nitrate from drinking water (Luk & Au-Yeung, 2002) (Kapoor & Viraraghavan, 1997) (Samatya , et al., 2006) Among these methods, the first four have been applied at full-scale. WHO has suggested biological denitrification and IX as nitrate removal methods. (WHO, 2011) while IX, RO, and ED are approved by EPA as Best Available Technologies (BAT) for removing nitrate (USEPA, 2004) .

2.2.2.1 Reverse Osmosis For Denitrifaction

RO is a pressure-driven membrane separation process in which feed water passes through a semipermeable membrane due to a pressure difference at the opposite sides of the membrane (Darbi, et al., 2003) (Symons, et al., 2001) (MWH, 2005). For a pressure driven membrane process, the concentrated solution containing substances that do not pass through the membrane is called the reject water or concentrate. (Symons, et al., 2001) .The main application of RO is desalination of seawater and brackish water, and the first commercial RO desalination plant was built in Goalinga, California in 1965 (MWH, 2005).

However, RO membranes can be used for the removal of natural organic matter (NOM), microorganisms, inorganic contaminants such as arsenic, nitrate, nitrite, selenium, barium, and fluoride, and for softening (Symons, et al., 2001) (MWH, 2005) .

The main factors that should be considered in designing an RO system are membrane type, feed water characteristics, pre-treatment, post-treatment, blending, residual disposal, recovery, and energy recovery (MWH, 2005) .

Nitrates could be removed by RO cells under pressures ranging from 300 to 1,500 psi to reverse the normal osmotic flow of water. Membranes used were made of cellulose acetate, polyamides and composite materials. Problems associated with reverse osmosis membranes included fouling, compaction and deterioration with time. These problems resulted from deposition of soluble materials, organic matter, suspended and colloidal particles, and other contaminants, pH variations and chlorine exposure; thus the RO process required pretreatment (Archna, et al., 2012)

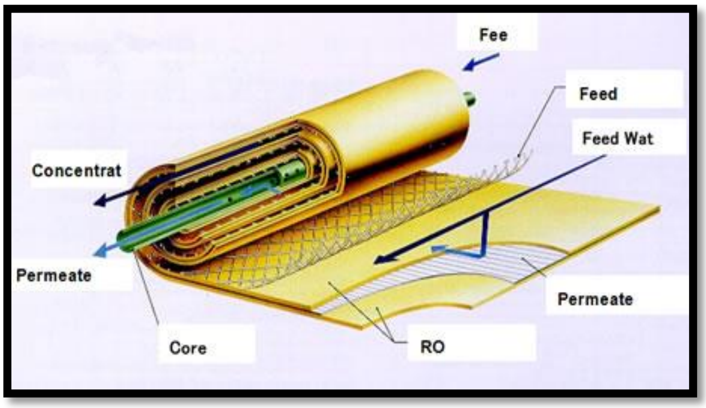


Figure 2.1:- Reverse Osmosis membrane.

2.2.2.2 Ion Exchange Process

IX is a reversible chemical process in which ions from an insoluble permanent solid medium (the ion exchanger-usually a resin) are exchanged for ions in a solution or fluid mixture surrounding the insoluble medium. The direction of the exchange depends on the selective attraction of the ion exchange resin for the specific ions present and the concentration of the ions in the solution. Both cation and anion exchange are used to remove hardness or contaminants. Cation exchange is commonly used for water softening (Symons, et al., 2001) .

Ion exchange resin is a bead-like material that removes ions from water. Synthetic ion exchange resin is a manufactured ion exchange resin, commonly made with cross-linked polymers having exchangeable functional groups (Symons, et al., 2001) . Strong acid cation (SAC), and weak acid cation (WAC) are the two general types of resins that can exchange cations. Strong base anion (SBA) and weak base anion (WBA) are used for removing anions such as nitrate (MWH, 2005) . Ion exchange resins exchange ions in a selective order based on the chemical and physical properties of both resin and ions. This characteristic is called selectivity and for regular SBA resins is found to be as follows:

$$SO4_2^- > ClO_4^- > I^- > NO_3^- > Br^- > Cl^- > HCO_3^- > OH^- \quad \text{(MWH, 2005)}$$

Several factors influence practicality and efficiency of nitrate removal by IX. These factors can be categorized into four main groups including operating conditions, feed water characteristics, type of resin, and finally regeneration and waste disposal.

Ion exchange process was found to be five times more economical in comparison to RO process. A process was developed in which regeneration and exhaustion were performed in the same direction and reduced nitrate concentrations from 15.8 to 5.7 mg/L. The Carbon dioxide regenerated ion exchange resins (CARIX) process for removing nitrate, sulfate, and hardness from water was based on ion exchange principles (Archna, et al., 2012) .

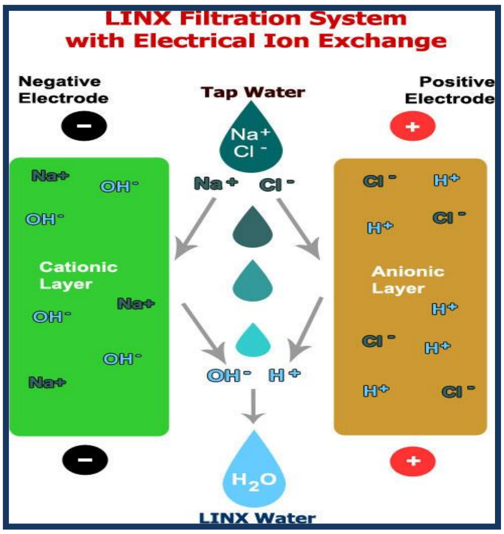


Figure 2.2 :- Ion Exchange system.

2.2.2.3 Electrodialysis (ED) For Denitrification

ED is a desalting process driven by an electrical potential difference between oppositely charged electrodes. Ions are transferred by electric current flow through cation and anion membranes, depending on ion charge, from a less concentrated solution to a more concentrated one, leaving a demineralized stream (Symons, et al., 2001).

Similar to RO, water treatment by ED is also limited to soft waters due to membrane scaling problems. Therefore, this technology also needs pre-treatment. To minimize membrane scaling and reduce the need for pre-treatment, use of a modified ED method known as electrodialysis reversal (EDR) was investigated (Kapoor & Viraraghavan, 1997) (Rautenbach, et al., 1987) .

EDR is an electrodialysis process in which the electrical polarity of the electrodes is reversed on a set time cycle, thereby reversing the direction flow of ions in the system providing fouling control (Symons, et al., 2001). However, operating EDR is more complicated and needs close monitoring (Kapoor & Viraraghavan, 1997) (Rautenbach, et al., 1987) .

The principle of ED (Hell, et al., 1998)

The principle of ED involves the removal of ionic components from aqueous solutions through ion exchange membranes using the driving force of an electric field. The water to be treated is pumped through a membrane stack ،which consists of alternately placed anionic and cationic selective membranes. Separated by gasket frames and spacers, the membranes are fixed between two end plates, which contain the electrodes producing the electric field. In order to transfer the electric current and to remove gases produced by the electrode reactions, the electrode chambers are rinsed with an electrolyte solution In the compartments of the membrane stack, the ion content is diluted or concentrated according to the ion penetration through the membranes (Figure 2.3)

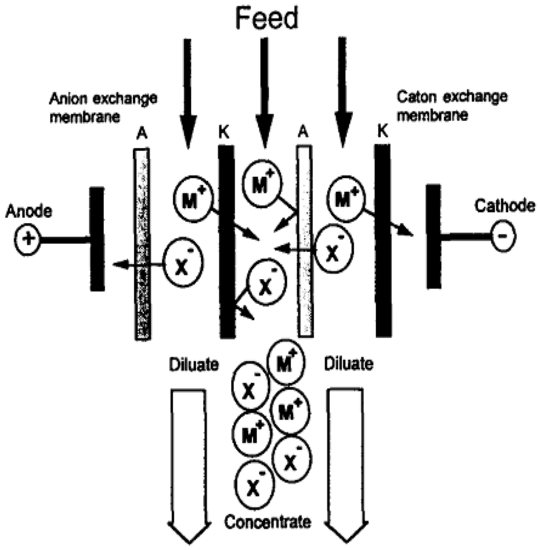


Figure 2.3 : The electrodialysis principle (Hell, et al., 1998)

(Elmidaoui, et al., 2001) to conclude some advantages in terms of Technically and Economically . Technically, the electrodialysis process is more simple to conduce in comparison with the conventional denitrification processes. Economically, the operating cost is not high. The membrane replacement and electricity constitute the greater part of the operating cost. Chemical and spare parts costs are not significant. The investment cost depends on the capacity of the industrial plant. This investment decreases when capacity increases.

2.2.2.4 Biological Denitrification

Biological denitrification is an important alternative which actually removes nitrate from the drinking water sources. This process reduces nitrate to innocuous nitrogen gas rather than to ammonia which exerts an adverse impact on drinking water quality by combining with chlorine (utilized as disinfectant) to form chloramine and nitrogen trichloride. These may be responsible for the obnoxious taste and odor in drinking water. Under the anoxic conditions (free from molecular oxygen), denitrifying bacteria are capable of using the chemically bound oxygen in nitrate as a terminal electron acceptor. The microorganisms which utilize inorganic carbon (CO2 or HCO_3^-) for their growth are classified as the autotrophic microorganisms, while those utilizing complex organic compounds are termed as the heterotrophic microorganisms and the denitrification processes are termed as autotrophic and heterotrophic, respectively. Biological denitrification is the only process that directly targets nitrate and does not shift the concentration of other ions. For these reasons, biological treatment represents a cost-effective technique for removing the nitrate ion from the contaminated water (Shrimali & Singh, 2001).

However, potential contamination of the treated water with these microorganisms and their metabolic byproducts are the drawbacks of this technology (Shrimali & Singh, 2001) (Samatya , et al., 2006) .

These problems result in increased disinfectant demand or the need of post-treatment of the product water by filtration. In addition, low production rates and cold temperature restrictions can also be considered as a disadvantage of biological denitrification (Samatya , et al., 2006) (Kapoor & Viraraghavan, 1997)

Processes based on IX, RO and ED have a lower efficiency if compared with biological denitrification, but they seem to be very interesting for medium and small applications (Schoeman & Steyn, 2003) .

Nitrate removal by means of biological denitrification is usually the preferred solution for nitrate removal because it is transformed in gaseous nitrogen with a very high yield and low process cost. Biological denitrification, however, shows some drawbacks in process control and output water quality. Nitrites are formed if insufficient carbon or energy is available and substrate is in excess. This problem, especially when random changes in the feed composition occur, can also be complicated by the presence of excess biomass (bacteria) or dead biomass in the final water. Therefore, post-treatment, disinfection and oxygenation of product water are generally needed. Biological treatment is preferred for large plants (Schoeman & Steyn, 2003) .

2.2.2.5 Chemical Denitrification

The electron-donating tendency of zero-valent metals can reduce several anions. So these metals have been investigated as developing water treatment technologies to remove contaminants such as nitrate. Iron and aluminum powder are considered as effective zero- valent metals for the chemical process of nitrate removal from drinking water, known as chemical denitrification (Shrimali & Singh, 2001) (Luk & Au-Yeung, 2002) .

a- Nitrate Reduction with Iron

Zero-valent iron has been widely used to reduce nitrate (NO_3^-). Iron is oxidized to ferrous ion (Fe^{2+}), and nitrate is reduced to ammonia or nitrogen gas (N_2). Oxidation of Fe^0 to Fe^{2+} is the anodic half-reaction, in the process, and H^+ or dissolved oxygen, as electron acceptors, are involved in the cathodic half-reaction in anaerobic and aerobic systems respectively. The final products of chemical reduction of nitrate by iron are N_2 or NH_3, depending on the experimental conditions (Cheng, et al., 1997) (Yang & Lee, 2005) (Kumar & Chakraborty, 2006). Pathways for nitrate reduction by zero-valent iron proposed by various researchers are listed in Table 2-5.

The large demand of iron and its relative costs, long reaction time, pH constraints, and need of post-treatment to remove ammonia are the main drawbacks that limit the use of this technology (Luk & Au-Yeung, 2002) (Kumar & Chakraborty, 2006) .

Table 2.2 : Proposed pathways for nitrate reduction by zero-valent iron.

Proposed pathway(s)	Reference
$6NO_3^- + 10Fe^0 + 3H_2O \rightarrow 5Fe_2O_3 + 3N_2(g) + 6OH^-$ $NO_3^- + Fe^0 + 2H^+ \rightarrow Fe^{2+} + NO_2^- + H_2O$	(Siantar, et al., 1996)
$NO_3^- + Fe^0 + 2H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3\,H_2O$	(Cheng, et al., 1997)
$NO_3^- + Fe^0 + 2H^+ \rightarrow Fe^{2+} + NO_2^- + H_2O$ $2\,NO_3^- + 5Fe^0 + 6\,H_2O \rightarrow 5\,Fe^{2+} + N_{2(g)} + 12OH^-$	(Choe, et al., 2000)
$NO_3^- + 2.82\,Fe^0 + 0.75Fe^{2+} + 2.25H_2O \rightarrow NH_4^+ + 1.19Fe_3O_4 + 0.5OH^-$	(Huang & Zhang, 2002)
$NO_3^- + 4Fe^0 + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O$ $NO_3^- + 8Fe^0 + 10H^+ \rightarrow 8Fe^{2+} + NH_4^+ + 3H_2O$	(Huang & Zhang, 2004)

b- Nitrate Reduction with Aluminum

Powdered zero-valent aluminum can also be used to reduce nitrate to nitrite, and eventually to ammonia or nitrogen gas. The nitrate to ammonia reduction process is described by the following chemical reactions (Murphy, 1991) (Kapoor & Viraraghavan, 1997) (Luk & Au-Yeung, 2002) :

$$3NO_3^{-}+2Al^{0}\ +3H_2O \rightarrow 3NO_2^{-}+2Al(OH)_3\downarrow$$
$$NO_2^{-}\ +2Al^{0}\ +5H_2O \rightarrow NH_3\ (g)\ +2Al(OH)_3\downarrow+OH^{-}$$

Overall:

$$3NO_3^{-}+8Al^{0}+18H_2O \rightarrow 3NH_3\ (g)\ +8Al(OH)\ 3\downarrow+3OH^{-}$$

And the nitrate to nitrogen reduction process is described by the following chemical Reactions (Murphy, 1991) (Kapoor & Viraraghavan, 1997) (Luk & Au-Yeung, 2002) (Kumar & Chakraborty, 2006):

$$3NO_3^{-}+2Al^{0}\ +3H_2O \rightarrow 3NO_2^{-}+2Al(OH)_3\downarrow$$
$$2NO_2^{-}+2Al^{0}+4H_2O \rightarrow N_2\ (g)\ +2Al(OH)_3\downarrow+2OH^{-}$$

Overall:

$$6NO_3^{-}+10Al^{0}\ +18H_2O \rightarrow 3N_2(g)\ +10Al(OH)_3\downarrow+6OH^{-}$$

Disadvantages of this technique include its low efficiency especially for removing nitrate from waters with high original nitrate concentrations, p^H constraints, and the need for post treatment to remove ammonia (Kapoor & Viraraghavan, 1997) (Luk & Au-Yeung, 2002) (Kumar & Chakraborty, 2006) .

2.2.3 Conclusion and Comparison between techniques for the removal of nitrate from drinking water

The treatment processes that have been applied full-scale for nitrate removal include ion exchange, biological de-nitrification and reverse osmosis. The other methods discussed have limited potential for full-scale application.

Removal of nitrates from drinking water is an important and developing area of research. Technology development has occurred in this area, but further optimization of current technologies is required. Biological denitrification reactor operation in regard to microbiological characteristics of biologically denitrified water demands attention. RO and ED performance data for nitrate removal is limited and the impact of rapid advances in these technologies should be examined.

The techniques discussed above and their attributes are summarized according to some advantages and disadvantages to different Nitrate Removal Technologies in drinking water in Table 2.3.

Table 2.3 : Comparison of Nitrate Removal techniques .

Method	IX	RO	ED	Chemical	Biological
Advantages	• short time period • simple and effective relatively • low cost • selectivity • it is stable, fast and easily automated in process control • small and medium-sized treatment plants • medium operational cost	• short time period • hardness reduction • Better economics • larger automation possibilities • lower level in feed • process parameters control • no need for extensive post-treatment • very low chemical demand	• simple separation • hardness reduction • selectivity • low chemical demand	• High efficiency • No other residual constituents, such as chlorides and bicarbonates	• it is transformed in gaseous nitrogen with a very high yield. • low process cost • medium operational cost • IX, RO and ED have a lower efficiency if compared with biological denitrification • very selective reduction
Disadvantages	• disposal problems • Necessity for re-generation chemicals. • fairly high in capital and operating costs • high residual constituents such as chlorides and bicarbonates in the treated water	• high pressure • need for pre treatment • and post-treatment • disposal problems • expensive • limiting its applications to mainly specialized industrial application • High operational cost	• need for pre-treatment • close monitoring • expensive • disposal problems	• post treatment for ammonia • expensive • pH constraints • lime softening • High operational cost	• contamination • post treatment, • low reaction rate, • temperature constraints • large plants • very costly • requires extensive maintenance • require biomass waste disposal
reference	(Samatya , et al., 2006) (Hell, et al., 1998) (Luk & Au-Yeung, 2002) (Bhatnagar & Sillanpää, 2011)	(Schoeman & Steyn, 2003) (Hell, et al., 1998) (Shrimali & Singh, 2001) (Luk & Au-Yeung, 2002) (Bhatnagar & Sillanpää, 2011)	(Hell, et al., 1998) (Rautenbach, et al., 1987)	(Yang & Lee, 2005) (Ruangchainikom, et al., 2006) (Luk & Au-Yeung, 2002) (Bhatnagar & Sillanpää, 2011)	(Schoeman & Steyn, 2003) (Luk & Au-Yeung, 2002) (Bhatnagar & Sillanpää, 2011)

2.3 Electrocoagulation (EC)

Treatment of wastewater by EC has been practiced for most of the 20th century with limited success and popularity. In the last decade, this technology has been increasingly used in South America and Europe for treatment of industrial wastewater containing metals. It has also been noted that in North America EC has been used primarily to treat wastewater from pulp and paper industries, mining and metal-processing industries. In addition, EC has been applied to treat water containing foodstuff wastes , oil wastes , dyes, suspended particles , chemical and mechanical polishing waste , organic matter from landfill leachates , defluorination of water , synthetic detergent effluents , mine wastes and heavy metal-containing solution . Typically, empirical studies are done on EC to define major operating parameters for broad classes of contaminated water or waste streams (Mollah, et al., 2001) .

2.3.1 Theory of EC

EC processes a direct current source between metal electrodes immersed in wastewater. The electrical current causes the dissolution of metal electrodes commonly iron and aluminum into water. The dissolved metal ions, at an appropriate pH, can form wide ranges of coagulated species and metal hydroxides that destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants. (Katal & Pahlavanzadeh, 2011)

This technique is based on the in situ formation of coagulant as the sacrificial anode (usually aluminum or iron) corrodes due to an applied current (Figure 2.4). Aluminum and iron materials are usually used as anodes, the dissolution of which produces hydroxides, oxy-hydroxides and polymeric hydroxides. In EC, settling is the most common option, while flotation may be achieved by H2 (electroflotation) or assisted by air injection (Essadki, 2012) .

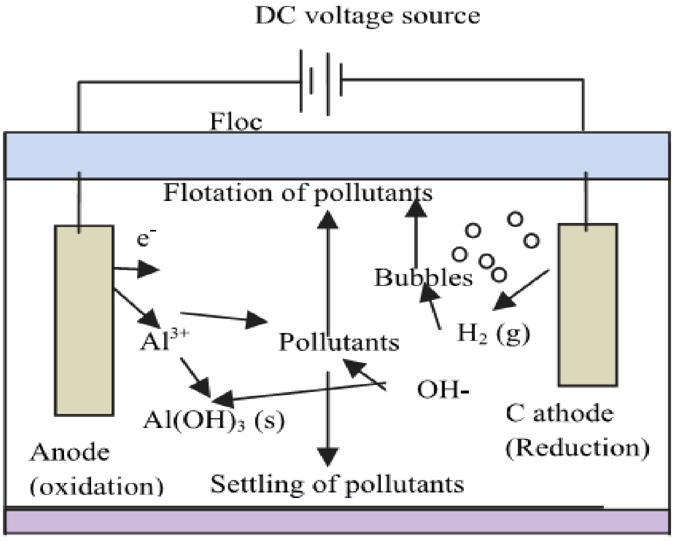


Figure 2.4 : Schematic diagram of two-electrode EC cell (Essadki, 2012).

Three successive stages occur during EC (Essadki, 2012) :

i. Formation of coagulants by electrolytic oxidation of sacrificial anode
ii. Destabilization of the pollutants, particulate suspension and breaking of emulsions
iii. Aggregation of the destabilized phases to form flocs.

The pollutants can be in form of (Essadki, 2012) :

- Large particles easy to separate them from water by settling.
- Colloids.
- Dissolved mineral salt and organic molecules.

It is impossible to use the decantation as a technique to eliminate the maximum of particles. This remark is especially valid for colloids. Thus, colloids are organic or mineral particles in which the size is between some nanometers and approximately 1 µ responsible for color and turbidity (Essadki, 2012) .

Generally, six main processes occur during EC (Katal & Pahlavanzadeh, 2011):

1. Migration to an oppositely charged electrode (electrophoresis) and aggregation due to charge neutralization;
2. The cation or hydroxyl ion (OH^-) forms a precipitate with the pollutant;
3. The metallic cation interacts with OH^- to form a hydroxide, which has high adsorption properties thus bonding to the pollutant (bridge coagulation);
4. The hydroxides form larger lattice-like structures and sweeps through the water (sweep coagulation);
5. Oxidation of pollutants to less toxic species;
6. Removal by electroflotation or sedimentation and adhesion to bubbles .

2.3.2 Mechanism of EC

The mechanisms of EC for water and wastewater treatment are very complex. It is generally believed that there are three other possible mechanisms involved besides EC, i.e. electroflotation, electrochemical oxidation and adsorption (Kobya, et al., 2011)

The main electrochemical reactions at the electrodes during EC process (Katal & Pahlavanzadeh, 2011) :

At the cathode, H_2 gas is liberated:

$$3H_2O + 3e^- \rightarrow (3/2)H_2 + 3OH^- \qquad \text{Eqn. (2.4)}$$

The metal cathode (M) may be chemically attacked by OH^- especially at high pH values:

$$2M + 6H_2O + OH^- \rightarrow 2M(OH)_4^- + 3H_2 \qquad \text{Eqn. (2.5)}$$

At the anode, sacrificial metal (M), Al or Fe, is dissolved :

$$M \rightarrow M^{3+} + 3e \qquad \text{Eqn. (2.6)}$$

In the case of Fe electrode, the anodic reaction also occurs:

$$Fe \rightarrow Fe^{2+} + 2e \qquad \text{Eqn. (2.7)}$$

In conclusion, the formation of metal hydroxide flocs proceeds according to a complex mechanism which may be simplified as:

$$M^{3+} \rightarrow \text{monomeric species} \rightarrow \text{polymeric species} \rightarrow \text{amorphous } M(OH)_3 \qquad \text{Eqn. (2.8)}$$

In the case of Al electrode ; monomeric species such as $Al(OH)^{2+}$, $Al(OH)^{2+}_{2}$, $Al_2(OH)^{4+}_{2}$, $Al(OH)^{4-}$ and polymeric species such as $Al_6(OH)^{3+}_{15}$, $Al_7(OH)^{4+}_{17}$, $Al_8(OH)^{4+}_{20}$, $Al_{13}O_4(OH)^{7+}_{24}$, $Al_{13}(OH)^{5+}_{34}$ are formed during the EC process .

In the case of Fe electrode; $Fe(OH)^{2+}$, $Fe(OH)^{2+}$,$Fe_2(OH)^{24+}$,$Fe(OH)^{4-}$, $Fe(H_2O)^{2+}$, $Fe(H_2O)_5OH^{2+}$, $Fe(H_2O)_4(OH)^{2+}$, $Fe(H_2O)_8(OH)^{24+}$, $Fe_2(H_2O)_6(OH)^{42+}$ are produced. Formation rates of these different species depend on pH of the medium and types of ions present, and play an important role in the EC process .

2.3.2.1 EC using iron electrodes (Ni'am, et al., 2006)

EC is based on the fact that the stability of colloids, suspensions and emulsions is influenced by electric charges. Therefore, if additional electrical charges are supplied to the charged particles via appropriate electrodes, the surface charge of particles is neutralized and several particles combine into larger and separable agglomerates (Koparal & Ogutveren, 2002) .

In EC with electrical current flowing between two electrodes, coagulant is generated in situ by electrolytic oxidation of the anode material. With an iron anode, Fe(OH)n with n = 2 or 3 is formed at the anode. Simplified oxidation and reduction mechanisms at the anode and cathode of the iron electrodes are represented by :

a- Mechanism 1:

Anode: $Fe\ (s) \rightarrow Fe^{2+}\ (aq) + 2e^-$ Eqn. (2.9)

$Fe^{2+}\ (aq) + 2OH^-\ (aq) \rightarrow Fe(OH)_2\ (s)$ Eqn. (2.10)

Cathode: $2H_2O\ (l) + 2e^- \rightarrow H_2\ (g) + 2OH^-\ (aq)$ Eqn. (2.11)

Overall: $Fe\ (s) + 2\ H_2O\ (l) \rightarrow Fe(OH)_2\ (s) + H_2\ (g)$ Eqn. (2.12)

b- Mechanism 2:

Anode: $4\ Fe\ (s) \rightarrow 4\ Fe^{2+}\ (aq) + 8\ e^-$ Eqn. (2.13)

$Fe^{2+}(aq) + 10H_2O\ (l) + O_2\ (g) \rightarrow 4Fe(OH)_3\ (s) + 8H^+\ (aq)$ Eqn. (2.14)

Cathode: $8\ H^+\ (aq) + 8\ e^- \rightarrow 4\ H_2\ (g)$ Eqn. (2.15)

Overall: $4\ Fe\ (s) + 10\ H_2O\ (l) + O_2\ (g) \rightarrow 4\ Fe(OH)_3\ (s) + 4\ H_2\ (g)$ Eqn. (2.16)

The generation of iron hydroxides (Fe(OH)n) is followed by an electrophoretic concentration of colloids (usually negatively charged) in the region close to the anode. Particles interact with the iron hydroxides and are removed either by surface complexation or electrostatic attraction.

2.3.2.2 EC using aluminum electrodes (Mouedhen, et al., 2008)

It is well known that in EC process the main reactions occurring at the aluminum electrodes during electrolysis are:

$$Al^{3+} \rightarrow Al^{3+} + 3e^{-} \qquad \text{(anode)} \qquad \text{Eqn. (2.17)}$$

$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-} \qquad \text{(cathode)} \qquad \text{Eqn. (2.18)}$$

when the anode potential is sufficiently high, secondary reactions may occur, especially oxygen evolution Eqn. (2.19):

$$2H2O \rightarrow O2 + 4H^{+} + 4e^{-} \qquad \text{Eqn. (2.19)}$$

Aluminum ions (Al^{3+}) produced by electrolytic dissolution of the anode (Eqn. (2.17)) immediately undergo spontaneous hydrolysis reactions which generate various monomeric species according to the following sequence (omitting coordinated water molecules for convenience):

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^{+} \qquad \text{Eqn. (2.20)}$$

$$Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2^{+} + H^{+} \qquad \text{Eqn. (2.21)}$$

$$Al(OH)_2^{+} + H_2O \rightarrow Al(OH)_3 + H^{+} \qquad \text{Eqn. (2.22)}$$

Hydrolysis reactions [(Eqn. (2.20-22)] make the anode vicinity acidic. Conversely, hydrogen evolution at the cathode (Eqn. (2.18)) makes the electrode vicinity alkali.

2.3.3 The electrode connections (Essadki, 2012):

The electrodes configuration can be divided into three modes:

1- **Monopolar electrodes in parallel connections :**

As observed in Figure 2.5, the parallel arrangement consists of pairs of conductive metals plates placed between two parallel electrodes and DC power source. All cathodes are connected to each other and to negative pole of DC; in the same manner, all sacrificial anodes are connected to each other and to positive pole of DC. The electric current is divided between all the electrodes in relation to the resistance of the individual cells.

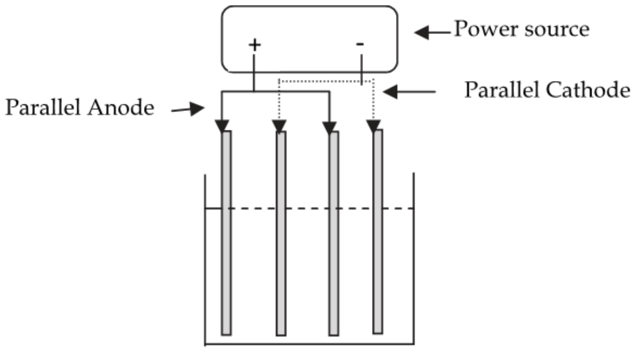


Figure 2.5 Monopolar electrodes in parallel connections.

2- Monopolar electrodes in series connections :

Each pair of sacrificial electrodes is internally connected with each other, and has no inter-connections with the outer electrodes (Figure 2.6). The same current would flow through all the electrodes.

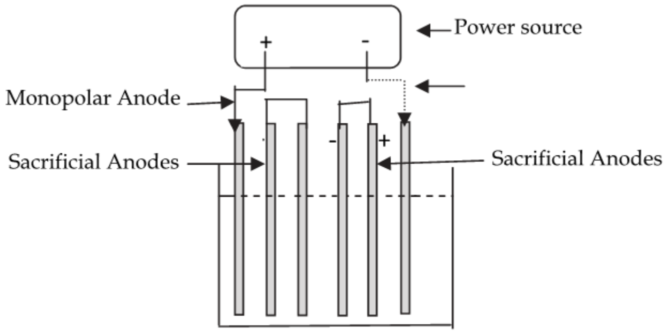


Figure 2.6 Monopolar electrodes in series connections.

3- Bipolar electrodes

The cells are in series. The sacrificial electrodes are placed between the two parallel electrodes without any electrical connection. Only the two monopolar electrodes are connected to the electric power source with no interconnections between the sacrificial electrodes (Figure 2.7).

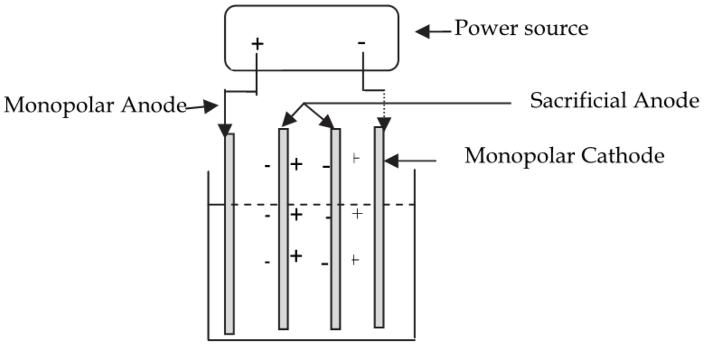


Figure 2.7 Bipolar electrodes in series connections.

2.3.4 Energy and electrode consumption

In an EC experiment, the electrode or electrode assembly is usually connected to an external DC source. The amount of metal dissolved or deposited is dependent on the quantity of electricity passed through the electrolytic solution. The majority of EC studies use aluminum and iron electrodes were employed to treat pollutant in EC reactor. Dissolution of aluminum and iron electrodes depends upon electrolysis time, applied voltage, pH of water. The relationship between amount of aluminum or iron produced to electrolysis time and current could be explained from Faraday's law .

Faraday's law relates the theoretical amount of aluminum or iron ions (M) and hydroxyl ions generated in the reactor to the current flow (I in time t).

$$\mathrm{m} = \frac{\mathrm{I}t_{EC}M_w}{\mathrm{nF}} \ldots\ldots\ldots\ldots\ldots. eqn\ (2.23)$$

Where m is the quantity of electrode material dissolved (g Al or Fe electrode), n is the number of electrons transferred in the reaction at the electrode(for Fe, $n_{Fe} = 2$ and for Al, $n_{Al} = 3$), t_{EC} is the time in seconds (s), M_w is the molecular weight of electrode metal ($M_{w,Fe} = 55.85$ g/mol, $M_{w,Al} = 26.98$ g/mol , I is current flow (A) and F is faraday's constant (96,485 C/mol) .

Energy consumption is a very important economical parameter in the electrocoagulation process. Once the required voltages and the corresponding currents were obtained from the electrocoagulation experimental tests, it was possible to estimate the amount of energy consumed.

The specific electrical energy consumption (C_{energy}) was calculated as a function of applied cell voltage (V):

$$C_{energy}(\mathrm{KWh/L}) = \frac{VIt_{EC}}{v} \ldots\ldots\ldots\ldots\ldots.eqn\ (2.24)$$

Where C_{energy} is The specific electrical energy consumption (KWh/L), V is applied voltage(V), and v is treated potable water (L) .

2.4 Advantages and Disadvantages of EC

The advantages and disadvantages of EC technology are discussed below :

2.4.1 Advantages of EC

Electrocoagulation requires simple equipment and small area as compared to the conventional pond system which causes increase in the greenhouse gases. Electrocoagulation is alternative wastewater treatments that dissolves metal anode using electricity and provide active cations required for coagulation without increasing the salinity of the water (Holt, et al., 1999). Electrocoagulation has the capability to remove a large number of pollutants under a variety of conditions ranging from: suspended solids, heavy metals, petroleum products, colour from dye-containing solution, aquatic humus and defluoridation of water (Holt, et al., 1999). Electrocoagulation is usually recognized by ease of operation and reduced production of sludge (Emamjomeh & Sivakumar, 2009) . Aluminium and iron are suitable electrode materials for the treatment using electrocoagulation (Zongo, et al., 2009) .The removal efficiency of electrocoagulation using Aluminium electrodes was higher than that of using Iron electrodes (Wang, et al., 2009) . Generally, three main processes occur serially during electrocoagulation: (a) electrolytic reactions at electrode surfaces, (b) formation of coagulants in aqueous phase, (c) adsorption of soluble or colloidal pollutants on coagulants, and removal by sedimentation or floatation (Kobya, et al., 2003). The EC process has proven very effective in removing contaminants from water and wastewater and is characterized by reduced sludge production, no requirement for additional chemicals and ease of operation (Emamjomeh & Sivakumar, 2009) (Mollah, et al., 2001) (Sanjeev & Sudha , 2010).

As documented by (Mollah, et al., 2001) summarizing the advantages of EC :

1. EC requires simple equipment and is easy to operate with sufficient operational latitude to handle most problems encountered on running.
2. Wastewater treated by EC gives palatable, clear, colorless and odorless water.
3. Sludge formed by EC tends to be readily settable and easy to de-water, because it is composed of mainly metallic oxides/hydroxides. Above all, it is a low sludge producing technique.
4. Flocs formed by EC are similar to chemical floc, except that EC floc tends to be much larger, contains less bound water, is acid-resistant and more stable, and therefore, can be separated faster by filtration.
5. EC produces effluent with less total dissolved solids (TDS) content as compared with chemical treatments. If this water is reused, the low TDS level contributes to a lower water recovery cost.
6. The EC process has the advantage of removing the smallest colloidal particles, because the applied electric field sets them in faster motion, thereby facilitating the coagulation.
7. The EC process avoids uses of chemicals, and so there is no problem of neutralizing excess chemicals and no possibility of secondary pollution caused by chemical substances added at high concentration as when chemical coagulation of wastewater is used.
8. The gas bubbles produced during electrolysis can carry the pollutant to the top of the solution where it can be more easily concentrated, collected and removed.
9. The electrolytic processes in the EC cell are controlled electrically with nomoving parts, thus requiring less maintenance.
10. The EC technique can be conveniently used in rural areas where electricity is not available, since a solar panel attached to the unit may be sufficient to carry out the process.

2.4.2 Disadvantages of EC (Mollah, et al., 2001)

1. The 'sacrificial electrodes' are dissolved into wastewater streams as a result of oxidation, and need to be regularly replaced.
2. The use of electricity may be expensive in many places.
3. An impermeable oxide film may be formed on the cathode leading to loss of efficiency of the EC unit.
4. High conductivity of the wastewater suspension is required.
5. Gelatinous hydroxide may tend to solubilize in some cases.

2.5 Comparison between EC and Chemical coagulation

Chemical coagulation (CC) and EC have the same phenomenon in which the charged particles in colloidal suspension are neutralized by mutual collision with metallic hydroxide ions and are agglomerated, followed by sedimentation or flotation. The difference between electrocoagulation and chemical coagulation is mainly in the way of which aluminum or iron ions are delivered (Zhu, et al., 2005) (Avsar, et al., 2007).

The comparison between electrocoagulation and chemical coagulation is reported in Table 2.4. (Liu , et al., 2010) .

Table 2.4: Comparison between EC and CC (Liu , et al., 2010)

Electrocoagulation	**Chemical coagulation**
1- The pH neutralization effect made it effective in a much wide pH range (4-9).	1- Final pH always needs to be modulated because the hydrolysis of the metal salt will lead to a pH decrease. The CC is highly sensitive to pH change and effective coagulation is achieved at pH 6-7.
2- Flocs formed by EC are much larger than flocs formed by CC.	2- CC flocs are smaller than EC flocs.
3- EC process can be followed sedimentation or flotation.	3- CC process is always followed by sedimentation and filtration.
4- The gas bubbles produced during electrolysis can help to carry the pollutant to the top of the solution.	4- No bubbles generation.
5-EC is a low-sludge production technique.	5- High sludge production.
6- EC process treats water with low temperature and low turbidity.	6- The CC has difficulty in achieving a satisfying result in case of low temperature and turbidity.
7- EC requires simple equipment and is easy to be operated.	7- High operating problems.

2.6 Previous studies of water , wastewater , seawater and leachate treatment by Electrocoagulation (EC).

2.6.1 Previous studies of water treatment by EC

(Koparal & Ogutveren, 2002) to investigate the feasibility of the removal of nitrate from water by applying electrochemical methods such as electroreduction and electrocoagulation. In electroreduction, removal of nitrate to an allowable concentration has been accomplished at the pH range of 5–7 with energy consumption value of 1 × 10−3 kWh g−1. In electrocoagulation, an allowable concentration of nitrate has been achieved at the pH range of 9–11with energy consumption value of0.5×10−4 kWh g−1. Full removal of nitrate was also possible but with higher energy consumptions for these two methods.

(Holt, et al., 2005) studied in details the future of electrocoagulation as a localized water treatment technology and lack of a systematic approach of electrocoagulation reactor design/operation and issue of electrode reliability.

(Emamjomeh & Sivakumar, 2009) to investigate the effects of different parameters such as electrolysis time, electrolyte p^{H}, initial nitrate concentration, and current rate on the nitrate removal efficiency. The optimum nitrate removal was observed at a pH range of between 9 and 11. It appeared that the nitrate removal rate was 93% when the initial nitrate concentration and electrolysis time respectively were 100 mg-NO3/L and 40 min. The results showed a linear relationship between the electrolysis time for total nitrate removal and the initial nitrate concentration. It is concluded that the electrocoagulation technology for denitrification can be an effective preliminary process when the ammonia byproduct must be effectively removed by the treatment facilities.

An experimental study was conducted by **(Sanjeev & Sudha , 2010)** to evaluate some of the Factors influencing arsenic and nitrate removal from drinking water in a continuous flow electrocoagulation (EC) process. A bench-scale simulation of drinking water treatment was done by adding a filtration column after a rectangular EC reactor. Contaminant removal efficiency was determined for voltages ranging from 10 to 25V and a comparative study was done with distilled water and tap water for two contaminants: nitrate and arsenic(V). Maximum removal efficiency was 84% for nitrate at 25 V and 75% for arsenic (V) at 20 V. No significant difference in contaminant removal was observed in tap water versus distilled water.

(Kobya, et al., 2010) studied the treatment of rinse water from zinc phosphate coating by both batch and continuous electrocoagulation process. In that study the effect of Al and Fe electrodes were investigated. The results showed that the phosphate and zinc removals were more effectively achieved by Al electrode at pH 5 and Fe electrode at pH 3. The highest rates for phosphate and zinc removals were obtained in 25 and 15 of operating time which were 97.7% and 97.8% for Fe electrode, and 99.8% and 96.7% for Al electrodes.

(Malakootian, et al., 2010) studied the Performance evaluation of electrocoagulation process using iron-rod electrodes for removing hardness from drinking water in different circumstances. This study was conducted as a pilot plant. Experimental water sample was taken from water distribution network of Anar City located in northwestern part of Kerman Province, Iran. The indices for calcium and total hardness removal in pH (3.0, 7.0, and 10.0), electrical potential of 6, 12, and 24 V and reaction times of 10, 20, and 30 min were measured. The maximum efficiency of hardness removal which was obtained in pH 10.0, voltage of 12 and reaction time of 60 min are equal to 98.2% and 97.4% for calcium and total hardness, respectively.

(Malakootian, et al., 2011) studied removal efficiency of electrocoagulation on nitrate removal from aqueous solution. In the experiment, the concentrations of nitrate ranged from 100 mg/L to 200 mg/L and they used in the experimental set-up in the study was Batch reactor. They investigated seven factors which were thought to affect nitrate removal were: pH, electrical potential difference, nitrate initial concentration, total dissolved solid (TDS), kind of electrode, electrode connection methods and number of electrode . The experiment results showed that the electrocoagulation process can reach nitrate to less than standard limit. pH, electrical potential difference, total dissolved solids and number of electrodes have direct effect and initial concentration of nitrate has reverse effect on nitrate removal. This study also showed that under optimum condition, nitrate removal from Kerman water distribution system was 89.7 %. According to the results, Electrocoagulation process is suggested as an effective technique in nitrate removal.

2.6.2 Previous studied of wastewater treatment by ECP

(Raju, et al., 2008) concluded that COD would be reduced from 1,316 mg/L to 42.9 mg/L when using electrocoagulation for the purpose of treating textile wastewater. Treatment was completed using graphite and RuO2/IrO2/TaO2 with titanium electrodes. Overall, electrooxidation noticed the effects of electrolyte type within relation to Cl− ions.

(Asselin, et al., 2008) concluded that total suspended solids (TSS) was removed at 89%, turbidity 90%, BOD 86%, and oil and grease 99%, when completing electrocoagulation by combining mild steel or aluminum electrodes for treating slaughterhouse wastewater. In addition, it was identified that the total cost of treatment is 0.71 USD/m3 treated poultry slaughterhouse (PS) effluent, particularly including energy and electrode consumption and chemical and sludge disposal.

The feasibility of boron removal from wastewater by EC using iron and aluminum electrodes was studied by **(Sayiner, et al., 2008)** in this study aluminum and iron were used in the reactor as materials for cathode and anode. The experimental results showed that aluminum electrodes gave better removal efficiency. Their results also noted that EC application needs no chemical reagents. The best removal efficiency exceeded 95%.

(Zongo, et al., 2009) determined that by using electrocoagulation for textile industry wastewater with aluminum and iron electrodes, the authors concluded that that the important parameters—energy consumption where COD, turbidity abatement, electrode material, current efficiency, and cell voltage. Absorbance and COD had similar variations along the treatment, where a model could relate metal dissolution and pollution substance .

(Wang, et al., 2009) to investigate the removal efficiency of COD in the treatment of simulated laundry wastewater in an electrocoagulation/electroflotation cell. The experimental results showed that the removal efficiency was better, reaching to about 62%, when applying ultrasound to the electrocoagulation cell. The solution p^H approached neutrality in all experimental runs. The optimal removal efficiency of COD was obtained by using the applied voltage of 5V when considering the energy efficiency and the acceptable removal efficiency simultaneously. The Cl^- concentration of less than 2500 ppm had a positive effect on the removal efficiency. The performance of the monopolar connection of electrodes was better than that of the bipolar connection in this work. In addition, the removal efficiency of using Al electrodes was higher in comparison with using Fe electrodes in the study. The highest COD removal amount per joule was found to be999mg dm−3 kWh−1 while using two Al electrodes, although the removal efficiency increased with the number of Al plates.

(Aoudj, et al., 2010) conducted a study to investigate the effectiveness of electrocoagulation for color removal of solution containing Direct red81. Their experiments were performed for synthetic solution in batch mode. More than 98% of color removal was obtained at initial pH of 6, current density of 18750 A/m^2, and inter-electrode distance of 1. 5 cm.

(Ilona & Wolfgang , 2010) studied the performance of an electrocoagulation system for Ni, Cu and Cr removal from a galvanic wastewater. Several parameters and their influence on the removal results and on electrocoagulation efficiency were investigated. In this study they indicated that electrocoagulation could be a good alternative to the conventional methods, by treating heavy removal contaminated wastewater in a concentration range up to a few hundred mg/l. The combination of Al-and Fe-electrodes and an initial pH value > 5 led to the removed results.

(Parmar & Murthy, 2011) studied Removal of strontium by electrocoagulation using stainless steel and aluminum electrodes . In the present work, removal of strontium (up to 100 mg/L) from synthetic wastewater by electrocoagulation has been studied. Stainless steel and aluminum electrodes have been used and removal efficiencies have been compared with respect to electrocoagulation time, current density, amount of electrolyte added, solution pH, distance between electrodes, temperature and initial concentration of strontium. Preliminary operating cost estimation has been found out for both electrode materials. The strontium removal data has been used to find adsorption kinetics using pseudo-first-order and pseudo-second-order adsorption kinetics models. Results show that the optimum operating variables values are 50 min of process time, 8 mA/cm2 current density and solution pH 5 for which around 93% and 77% removal efficiency was achieved with using stainless steel and aluminum electrodes, respectively. Pseudo-second-order kinetic model fitted the data better than the pseudo-first-order model.

(Katal & Pahlavanzadeh, 2011) determined that by using aluminum and iron electrodes for electrocoagulation, optimum pH between 5 and 7, current density of 70 mA/cm2 was capable of efficiently treating the wastewater at a low cost. In addition, temperature relationship also poorly affects the performance.

(Al Aji, et al., 2012) In this work, the performance of batch electrocoagulation (EC) using iron electrodes with monopolar configuration for simultaneous removal of copper (Cu), nickel (Ni), zinc (Zn) and manganese (Mn) from a model wastewater was investigated. The influences of current density (from 2 to 25 mA/cm2), initial metal concentration (from 50 to 250 mg/L) and initial pH (3, 5.68, 8.95) on removal efficiency were explored in a batch stirred cell to determine the best experimental conditions. The results indicated that EC was very efficient to remove heavy metals from the model wastewater having an initial concentration of 250 mg/L for each metal under the best experimental conditions. According to initial pH results, high pH values are more suitable for metal removal with EC treatment. At the current density of 25 mA/cm2 with a total energy consumption of _49 kWh/m3, more than 96% removal value was achieved for all studied metals except Mn which was 72.6%.

(Pajootan, et al., 2012) In this study, binary system dye removal by electrocoagulation (EC) process using aluminum electrode was studied in a batch electrochemical reactor. Acid Black 52 and Acid Yellow 220 were used as model dyes. The effect of operating parameters such as conductivity, current density, initial dye concentration and pH on the electrocoagulation process was studied and the electrical energy consumption was calculated. Also the wool dyeing process has been performed and the dye removal from real colored wastewater by the electrocoagulation process has been studied. It was found that the increasing of the current density up to 40 A/m2 had increased the dye removal efficiency and the optimum pH for EC process was 5. The increasing of electrolyte concentration from 0 to 8 g/L had a negligible effect on the color removal but it has decreased the electrical energy consumption.

2.6.3 Previous studies of seawater treatment by EC

(Timmes, et al., 2009) to investigate the use of in-line electrocoagulation (EC) as a pretreatment for seawater prior to ultrafiltration (UF) at the bench-scale and to compare EC with equivalent doses of ferric chloride. UF membrane performance was evaluated by trans membrane pressure (TMP) and hydraulic resistances at sub- and super-critical fluxes, and by flux recovery after hydraulic and chemical cleanings. Modified Atlantic Ocean seawater was used. Constant flux UF operation (50 to about 350 lmh) was used to evaluate short-term performance at sub- and super-critical fluxes, and constant feed-pressure (15psi) experiments were used to investigate filter cake stability under high TMP conditions. In-line EC improved UF membrane performance for all coagulation and flux conditions. Compared to no coagulant pretreatment, ferric chloride improved UF membrane performance under short-term, constant flux conditions that resulted in TMP <8 psi, but produced increased TMP and resistance to filtration at 15psi. EC always resulted in lower resistance and improved flux recovery after cleaning compared to an equivalent dose of ferric chloride.

(Timmes, et al., 2010) to investigated the performance of a pilot-scale electrocoagulation reactor and determined the feasibility of using in-line electrocoagulation as a pretreatment to ultrafiltration (UF) of seawater. This study was conducted at Port Hueneme, CA, using components of a U. S. military water purification system. Iron electrodes were used in that study to the purpose of generating Fe^{2+}. That research indicated that electrocoagulation offers the potential for a feasible and effective pretreatment strategy for mobile ware production facilities.

2.6.4 Previous studied of leachate treatment by EC

(Li, et al., 2011) to investigated the efficiency of electrocoagulation in removing ammonia nitrogen (NH3-N) and chemical oxygen demand (COD) from leachate. The paper studies the factors affecting the efficiency of removing NH3-N and COD of leachate, such as electrode material, current density, electrolysis time, Cl- concentration and pH of solution. Treatment was carried out in a discontinuous system, and the results show that the electrocoagulation can be applied to leachate pre-treatment. The operating conditions were current density of 4.96mA/cm^2, the raw pH, Cl- concentration of 2319 mg/L, operating time of 90 min with Fe electrode, the highest COD and NH3-N removal efficiencies were 49.8% and 38.6%, respectively.

(Ilhan, et al., 2008) to investigated treatment of leachate by electrocoagulation using aluminum and iron electrodes in a batch process. The sample of leachate was supplied from Odayeri Landfill Site in Istanbul. Firstly, EC was compared with classical chemical coagulation (CC) process via COD removal. The first comparison results with 348A/m2 current density showed that EC process has higher treatment performance than CC process. Secondly, effects of process variables such as electrode material, current density (from 348 to 631A/m2), pH, treatment cost, and operating time for EC process are investigated on COD and NH4-N removal efficiencies. The appropriate electrode type search for EC provided that aluminum supplies more COD removal (56%) than iron electrode (35%) at the end of the 30min operating time. Finally, EC experiments were also continued to determine the efficiency of ammonia removal, and the effects of current density, mixing, and aeration. All the findings of the study revealed that treatment of leachate by EC can be used as a step of a joint treatment.

CHAPTER 3: Material and Methods

3.1 Introduction

In this chapter, the materials, equipment, and analysis procedures are described .The experimental work was performed in a continuous mode to remove nitrate from groundwater.

The concept of this model is to remove the nitrate measured in the water streams, using different operating treatment conditions, exposure time and pH. All analytical measurements performed in this study were conducted according to the Standard Methods for the Examination of Water and Wastewater (APHA, 2005). The experimental procedures were applied in the continuous flow technique.

Mild steel electrodes were used in the electrocoagulation cell to form coagulants for the purpose of nitrate removing from water. Experimental work was conducted at the laboratories of the Civil Engineering Department of Islamic University in Gaza (IUG).

3.2 Experimental set up

A continuous flow EC reactor was made in the lab from perspex sheet with dimensions of 24 cm × 8 cm × 12 cm and a length to width ratio of 3. It was run at a flow rate of 500 mL/hrs, and a design hydraulic retention time of 3 hrs . All tests were carried out at a pH of 7±0.1 and room temperature (25±3 °C). The electrodes used in the EC process were mild steel of size 13 cm×3 cm×0.3 cm with immersion depth of 7 cm, number of electrodes of two (anode & cathode) and distance of 3 cm between them. The effective area of the iron electrodes is 47.1 cm^2. Before each experiment, the pH of the electrolyte was adjusted with HCL or NaOH solution while the conductivity was adjusted with NaCl.

The change in the hydraulic retention time (HRT) during the operation period was considered to be another indication of the relative performance of the processes. The HRT is defined by the following equation:

$$HRT = \left(\frac{V_r}{Q}\right)$$

Where V_r is the reactor volume (m3) and Q is the flow rate (m^3/s).

In this experiment, flow rate was increased from (750 mL/hour) to (428 mL/hour) corresponding to HRT of 2 to 3.5 hours, respectively.

A schematic of the experimental setup for the EC reactor is shown in **Figure 3.1**. Applied voltage was varied using a transformer which converts AC to DC and the current was measured with multi-meters during the experimental run.

Each run was timed starting with the DC power supply switching on. During the experiments, anodic dissolution occurred and hydrogen gas was produced at the cathode. Each sample was taken from a distance between two electrodes and at fixed depth. pH and turbidity were monitored during the course of each experiment in the influent and effluent. Effluent samples of 30 ml were taken at different times during the experiment to be filtered and then analyzed. The experiment was continued until steady-state concentrations were achieved. In general, each experimental run lasted 4 hrs. All effluent samples were analyzed for pH, turbidity, ammonia, temperature, current rate, total dissolved solids (TDS) and nitrate. After each run, the electrodes were washed and brushed then cleaned by ethanol to remove any solids accumulated on the electrode surface.

3.2.1 Apparatus

The following apparatus was used in the experiments.

1- DC power supply: a laboratory digital DC power supply (type: GWINSTEK GPS 3303) with a voltage ranged from 0-30 V and current ranged from 0-3 A, was used in the experiments.

2- Fe plate electrode.

3- Water pump machine (peristaltic pump).

4- Stirrer.

5- Flexible PVC pipe.

6- Stop watch.

7- CT-2600 Spectrophotometer.

8- pH meter (pH/ORP/ISE Graphic LCD pH Bench top Meter , HANNA instruments)

9- Turbidity meter (HI 93703, Portable Microprocessor Turbidity Meter, HANNA instruments)

10- Small tank 20 liter contained Synthetic Polluted Water Preparation.

11- Glass ware: some glass wares were used in this work such as pipette, beakers, volumetric flasks and others.

12- pH adjustment (HCl 1 mol/L and NaOH 1mol/L)

13- Electronic Balance

14- Multi-meter (type: GWINSTEK GDM -8135)

15- Electrocoagulation cell: A continuous flow EC reactor was made in the lab from Perspex sheet with dimensions of (24 cm length × 8 cm width × 12 cm height) and a length to width ratio of 3.

Figures 3.1 and 3.2 show schematic and photographic pictures for the electrocoagulation system used in this work.

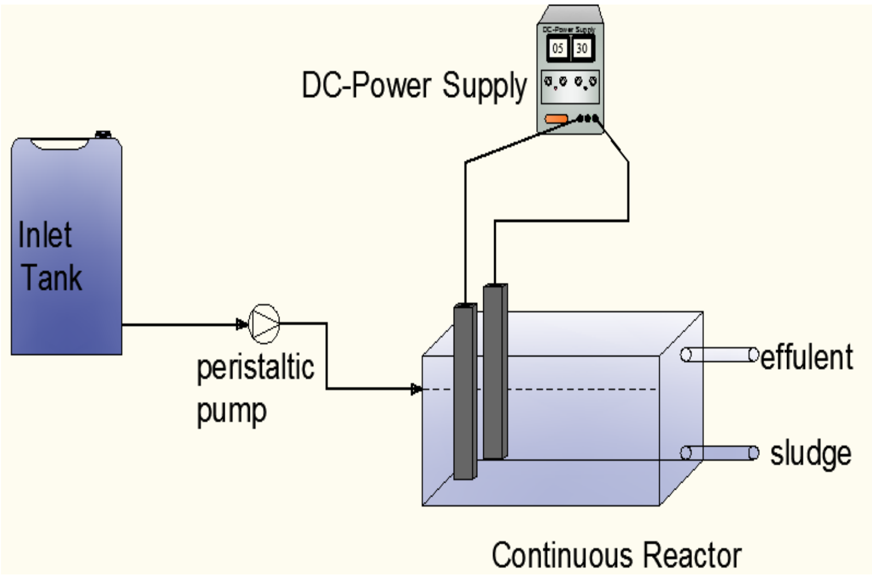


Figure 3.1 : Schematic diagram of the EC continuous flow experiment.

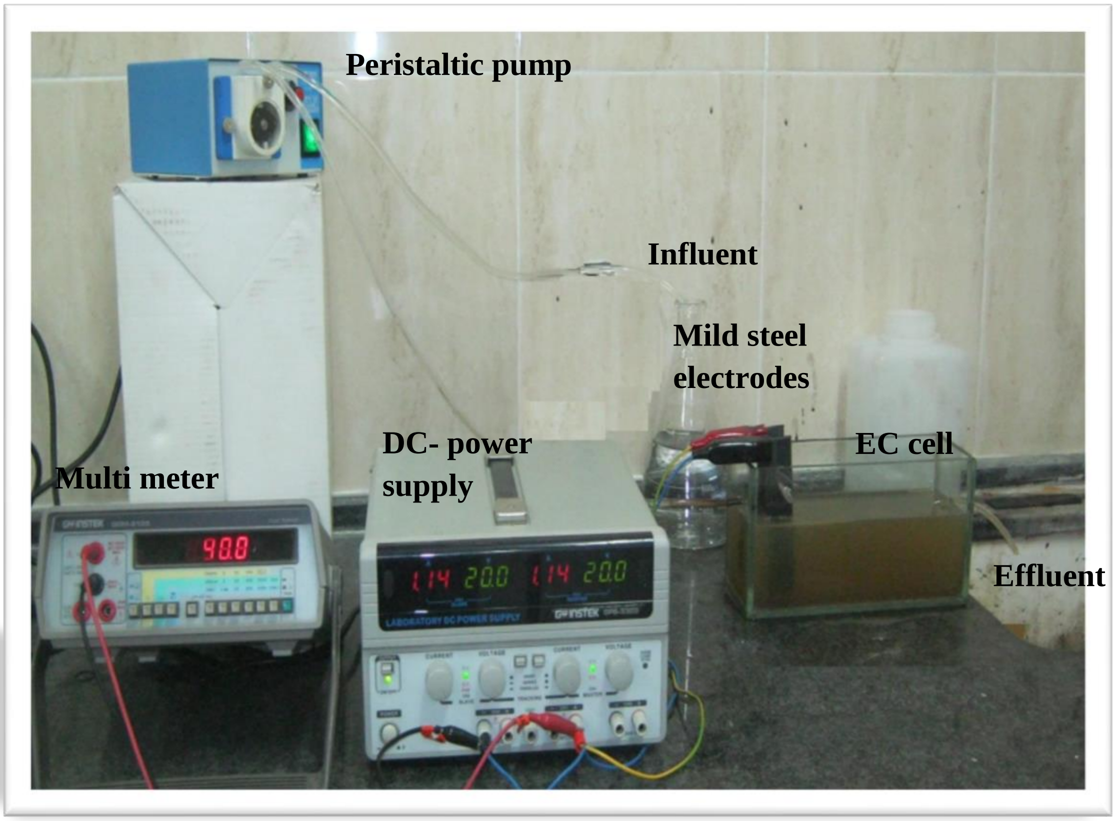


Figure 3.2: photographic pictures for the electrocoagulation system.

3.3 Materials and analytical methods

3.3.1 Materials

The following chemicals were used in the experiments:

1. Potassium nitrate (KNO3), purity equal to 99.5 % wt, produced by: HiMedia Laboratories Pvt. Ltd., India).
2. Sodium chloride (NaCl), purity equal to 99.5 % wt, produced by: HiMedia Laboratories Pvt. Ltd., India).
3. Sodium Hydroxide Pallets Extra Pure , (NaOH) purity equal to 97.5 % wt, product of loba chemie , India)
4. Hydrochloric acid (HCl), 1M and 0.1M.
5. Sodium hydroxide (NaOH), 1M and 0.1M.
6. Buffer solutions with pH= 4, 7 and 11.
7. Conductivity Standard - 1412 µmhos/cm
8. Distilled water.

In the present work, mild steel electrodes were used as anode and cathode. Electrodes design is one of the most important factors that affect the electrocoagulation process. Electrode design affects the release of coagulants in the solution and the bubble type, there by influencing pollutant flotation, mixing, and mass transfer.

Aqueous polluted water preparation

A stock solution of 1000 ppm nitrate was prepared by dissolving potassium nitrate (KNO_3) in distilled water. The amount of KNO_3 required to prepare the stock solution was calculated from the following equation:

$$W = V C_{st} \frac{M_{wt}}{At_{wt}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.\ 1)$$

Where:

W = weight of KNO_3 (g).

V = volume of solution (L).

C_{st} = nitrate concentrations in stock solution (g/l).

M_{wt} = molecular weight of KNO_3 (101.1032 g/mole).

At_{wt} = atomic weight of nitrate (62.0049 g/mole).

To prepare Nitrate stock solution of 1000 ppm (mg-NO3-N/L)

$$W = VC_{st}\frac{M_{wt}}{At_{wt}} = 1 \times 1000 \times \frac{101.1032}{62.0049 * 1000} = \frac{1.6307}{99.5\% \text{ (purity)}}$$

$$= 1.6389 \; gram \; at \; 1 \; liter \; distilled \; water$$

Nitrate stock solution of 1000 ppm was prepared by dissolving 1.6389 g of potassium nitrate in one letter of distilled water. A certain amount of the stock solution was mixed with distilled water to prepare the standard solution of each experiment to the required concentration.

3.3.2 Analytical methods

1- Measurement of NO_3 as N by spectrophotometer Instrumentation

The concentration of nitrate was determined by CT-2600 Spectrophotometer. The instrument was turned on and warmed up for 20 min before starting any sample measurement. The cuvette was cleaned every time before the use by rubbing the inner wall with a detergent-saturated cotton-tipped stick.

Nitrate Determination Method (4500-NO_3^- B. Ultraviolet Spectrophotometric Screening Method)

The method was a modified type of the “Ultraviolet Spectrophotometric Screening Method” . In this method, wavelength settings were 275 nm, 220 nm (275 nm can be eliminated in the nitrate detection; however, it was useful to detect nitrite). According to this standard method, common interfering material, such as bacterial cells, resulted in predictable absorption or scattering at 275 nm and produced absorption at 218 nm two times as much as that at 275 nm. NO_2^- had no absorption at 275 nm but equivalent absorption at 220 nm; dissolved NO_3^- had no absorption at 275 nm but significant absorbance at both 220 nm. Using these data the detection of NO3- was carried out as follows:

a. Deionized water produced a reproducible background absorbance at the wavelengths used. In the experiment, deionized water was used as blank; signals at those three fixed wavelengths were taken.

Table 3.1: Blank (Deionized Water) Absorbance

A275	Absorbance at 275 nm
A220	Absorbance at 200 nm
A1 = A220 – 2*A275	corrected absorption at 220 nm

b. Standards consisting of deionized water, NO_3^- (with concentrations simulating those of realistic samples) was measured at those three wavelengths, and the variables described in the above table were used to get the corrected nitrate absorbance.

c. Samples consisting of deionized water, NO_3^- and/or NO_2^- were used as standards. The highlight was that after these calculation processes, NO_2^-- signal was eliminated and only NO_3^- signal was left (part of NO_3^- signal was also subtracted).

d. Reagents

> ***Stock nitrate solution:*** Potassium nitrate (KNO_3) was dried at 105 °C for 24h. A mass of 0.7218 g was dissolved in 100 mL sterilized deionized water and diluted to the 1000 mL scale in a volumetric flask to prepare stock solution I which contained 100 mg NO3- N /L.

e. Standard Solution Series: Nitrate-containing standards were prepared by the following:

  a- 0, 1.00, 2.00, 4.00, 6.00, 8.00, 10.00 mL of stock I were separately added to 100 mL volumetric flask and diluted to 100 mL. The resulting concentration range was: 0, 1, 2, 4, 6, 8 and 10 mg NO3- N/L.

  b- The signals of those standard solution series, used to establish the linear calibration line.

f. Sample Preparation: 10 mL of water was taken out of the test in experimental and diluted to 50 mL with deionized water (5 dilution times). The diluted sample was filled in a cuvette to full volume. Absorption was measured separately and recorded at 275 nm, 220 nm.

2- Evaluation of Removal Efficiency

Each sample taken from the electrocoagulation cell was filtered and then analyzed using atomic absorption spectrophotometric, model (CT-2600) in the Islamic University of Gaza (IUG).

The removal efficiency of nitrate in synthetic polluted water treated by electrocoagulation is calculated as follows:

$$R\% = \frac{C_o - C}{C_o} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad 3.2$$

$R\%$= nitrate removal efficiency.

C_o = nitrate concentration at initial (mg/l as NO_3).

C = nitrate concentration at any time (mg/l as NO_3).

3.4 Experiments program

A-Treatment of aqueous solution

The operating conditions for each test run are summarized in Table 3.2.

Table 3.2 : Test runs plan summery for operating parameters.

Test run #	Test run description	Voltage (V)	Initial nitrate concentration (mg-NO_3/L)	Hydraulic retention time (HRT) (hour)	Distance between electrode (D) (cm)	Effective area (A_{eff}) (cm^2)
1	Effect of hydraulic retention time	35,40, 45,50	100,150, 200,250	2,2.5,3, 3.5	2,3,4,5	47.1,54 61.4
2	Effect of applied voltage	35,40, 45,50	200	2,2.5,3	3	47.1
3	Effect of initial nitrate concentration	40	100,150, 200,250	2,2.5,3, 3.5	3	47.1
4	Effect of distance between electrode	40	200	2,2.5,3	2,3,4,5	47.1
5	Effect of effective area of anode	40	200	2,2.5,3, 3.5	3	47.1,54 61.4

Initial total suspended solid TDS_i of 1000 mg/L, pH of 7±0.1 and initial temperature T_i of 25±2 °C have kept constant during all the experiments.

B-Treatment of real ground water

In the treatment of real ground water, a groundwater sample was concentration of nitrate and TDS_i are 200 mg-NO_3/L and 700 mg/L. And increase conductivity of the solution by adding electrolyte [100mg to 300mg of NaCl in fixed amount (1L of original ground water sample)] in the solution of real ground water.

The best operating conditions were determined from the result of the aqueous solution as show later. After that, the best conditions were tested on groundwater samples from the northern of Gaza water distribution system.

CHAPTER 4: Results and Discussion

4.1. Introduction

In this chapter, the results of the experiments and the resultant discussions are given. The nitrate removal efficiency was investigated by studying many parameters that affects the electrocoagulation process. These parameters are applied voltage (V), hydraulic retention time (HRT), initial nitrate concentration ($C_{i)}$ in the solution, the distance between electrode (D), initial Total dissolved solid (TDS_i) and effective area of anode (A_{eff}).

4.2. Effect of Hydraulic retention time (HRT)

Among the various operating variables, the Hydraulic retention time (HRT) is an important factor which strongly influences the performance of electrocoagulation.
The effect of HRT on nitrate removal was investigated in the electrocoagulation with the change of other parameters such as: initial nitrate concentration ($C_{i)}$, applied voltage (V), distance between electrode (D) and Area effective of anode (A_{eff}).

4.2.1. The effect of HRT on nitrate removal in relation to initial nitrate concentration (C_i) .

The effect of HRT on nitrate removal was examined with solutions of HRTs ranging from 2–3.5 hour. To investigate the effect of HRT, the initial nitrate concentration (C_i) was fixed at certain value (100, 150, 200 or 250 mg-NO_3/L) while HRT was change to 2, 2.5, 3 and 3.5hours. Figures 4.1 and 4.2 illustrate the effect of HRT on the steady state residual nitrate concentration (C) and the steady state removal nitrate percentage (R), respectively when the V, D and A_{eff} were kept constant at 40 V, 3 cm, 47.1 cm^2, respectively. It was observed from figure 4.1 that at low C_i the increase of HRT resulted in lower nitrate steady state residual concentration (C) (i.e. higher removal efficiency). For example, at a C_i of 100 mg-NO_3/L, when HRT was 2 hour, the final nitrate concentration was 27.8 mg-NO3/L (i.e. R = 72 %).while when HRT was increase to 3.5hour, the final nitrate concentration decreased to 13.14 mg-NO3/L, and removal percentage increased to 86.9 %. The same trend was observed for the other initial nitrate concentrations.
It is noted from this figure that the removal efficiency decreased upon increasing solution flow rate (i.e. decreasing HRT). This reduction in efficiency is explained by the decrease of residence time in the electrocoagulation cell with decreasing HRT. Indeed the amounts of iron and hydroxide ions generated at a given time are constant since the applied voltage is constant. Consequently, the same amount of hydroxide flocs was produced in the aqueous solution.
From Figure 4.1 at can be interpreted that the standard concentration limit of nitrate (i.e. 50 mg-NO_3/L) can be reached at C_i of 100 for all HRT. Consequently, the HRT has no significant effect of residual nitrate concentration (C) . On the other hand for C_i of 150 mg-NO_3/L, the HRT is equal or greater than 2.35 hours. Moreover, for the other C_i (200 and 250 mg-NO_3/L) the HRT should be high than 3.5 hours.

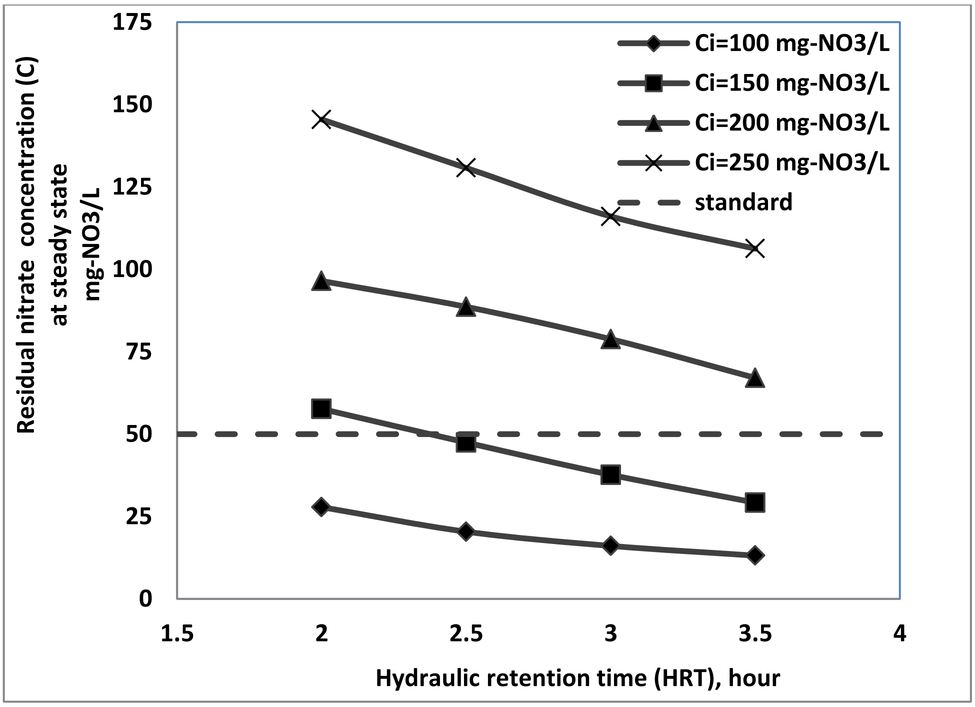


Figure 4.1: Effect of HRT on the steady state residual nitrate concentration (C) at different C_i values.

(pH = 7, V = 40 V, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C and Ar_{eff} = 47.1 cm^2).

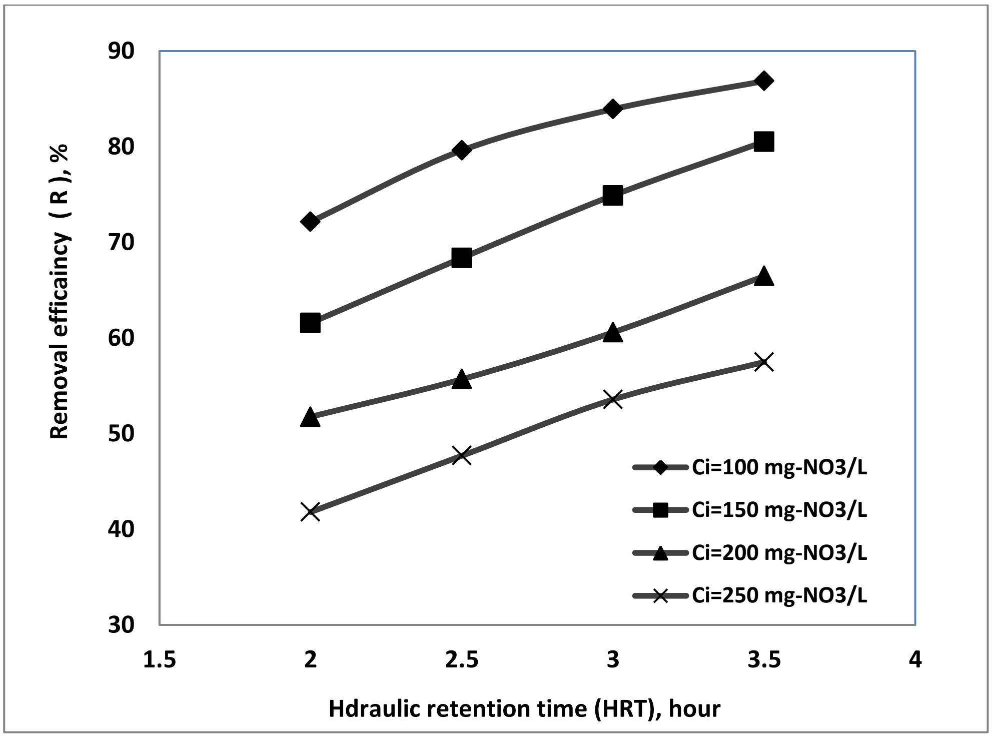


Figure 4.2: Effect of HRT on the nitrate removal efficiency (R) at different C_i values.

(pH = 7, V = 40 V, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C and Ar_{eff} = 47.1 cm^2).

4.2.2. The effect of HRT on Nitrate removal in relation to applied voltage (V).

The effect of hydraulic retention time (HRT) on nitrate removal was examined with solutions of HRTs ranging from 2 – 3.5 hour. To investigate the effect of hydraulic retention time (HRT), the applied voltage (V) was fixed at certain value (35, 40, 45, and 50 V) while HRT was change to 2, 2.5, and 3hours. Figures 4.3 and 4.4 illustrate the effect of hydraulic retention time (HRT) on the steady state residual nitrate concentration (C) and the steady state removal nitrate percentage (R), respectively when the C_i, D and A_{eff} were kept constant at 200 mg-NO_3/L, 3 cm, 47.1 cm^2, respectively. It was observed from Figure 4.3 that at low applied voltage (V) the increase of HRT resulted in lower nitrate steady state residual concentration (C) (i.e. higher removal efficiency). For example, at V of 35 V, when HRT was 2 hour, the final nitrate concentration was 123.9 mg-NO_3/L (i.e. R = 38 %) .while when HRT was increase to 3hour, the final nitrate concentration decreased to 90.6 mg-NO3/L, and removal percentage increased to 54.7 %. The same trend was observed for the other applied voltage. As explained at the end of item 4.6.1.

From Figure 4.3 at can be interpreted that the standard concentration limit of nitrate (i.e. 50 mg-NO_3/L) can be reached at V of 50, and 45 V, the HRT is equal or greater than 2.25 hours and 2.9 hours, respectively. On the other hand for the other V (35 and 40 V) the HRT should be high than 3 hours.

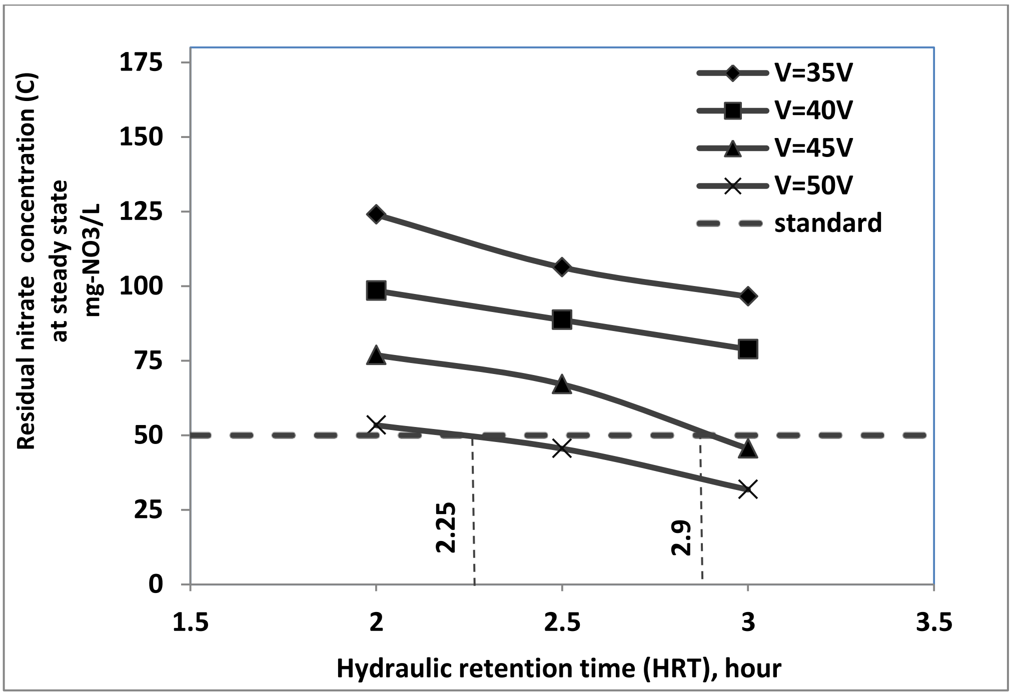


Figure 4.3: Effect of HRT on the steady state residual nitrate concentration (C) at different V values .

(pH = 7, C_i = 200 mg-NO3/L, TDS_i = 1000 mg/l, D = 3cm, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

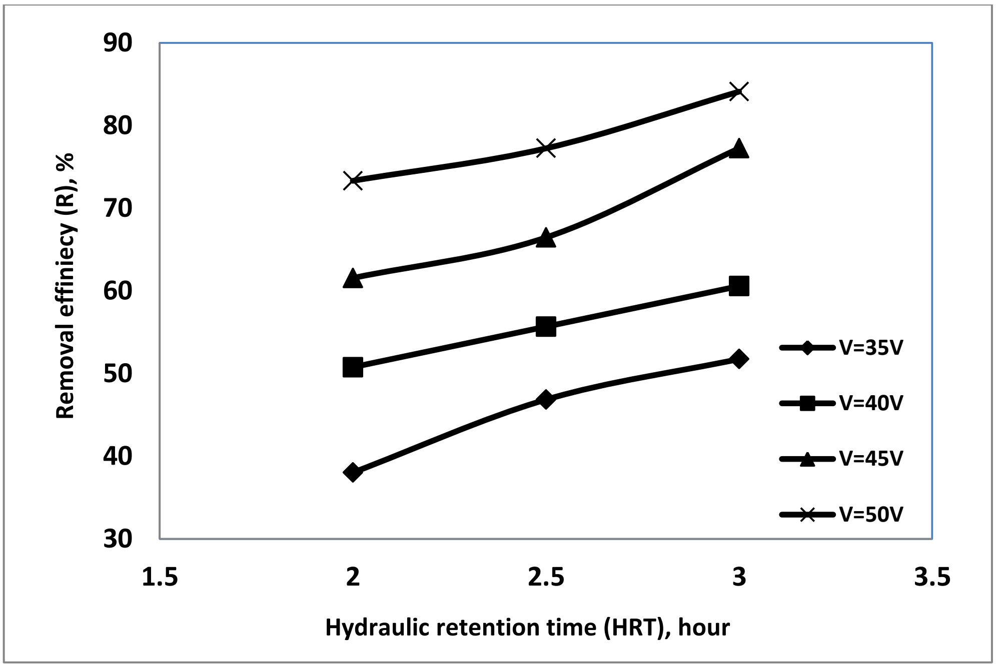


Figure 4.4: Effect of HRT on the nitrate removal efficiency (R) at different V values.
(pH = 7, C_i = 200 mg-NO3/L, TDS_i = 1000 mg/l, D = 3cm, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

4.2.3. The effect of HRT on Nitrate removal in relation to distance between electrodes (D).

The effect of hydraulic retention time (HRT) on nitrate removal was examined with solutions of HRTs ranging from 2–3.5 hour. To investigate the effect of hydraulic retention time (HRT), the distance between electrodes (D) was fixed at certain value (2, 3, 4, and 5 cm) while HRT was change to 2, 2.5, and 3hours. Figures 4.5 and 4.6 illustrate the effect of hydraulic retention time (HRT) on the steady state residual nitrate concentration (C) and the steady state removal nitrate percentage (R), respectively when the C_i, V and A_{eff} were kept constant at 200 mg-NO_3/L, 40 V, 47.1 cm^2, respectively. It was observed from Figure 4.5 that at low distance between electrodes (D) the increase of HRT resulted in lower nitrate steady state residual concentration (C) (i.e. higher removal efficiency). For example, at D of 2 cm, when HRT was 2 hour, the final nitrate concentration was 71 mg-NO_3/L (i.e. R = 64.5 %) .while when HRT was increase to 3hour, the final nitrate concentration decreased to 40 mg-NO3/L, and removal percentage increased to 80 %. The same trend was observed for the other distance between electrodes. As explained at the end of item 4.6.1.

From Figure 4.5 at can be interpreted that the standard concentration limit of nitrate (i.e. 50 mg-NO_3/L) can be reached at D of 2 cm, the HRT is equal or greater than 2.75 hours . On the other hand for the other D (3, 4 and 5 cm) the HRT should be high than 3 hours.

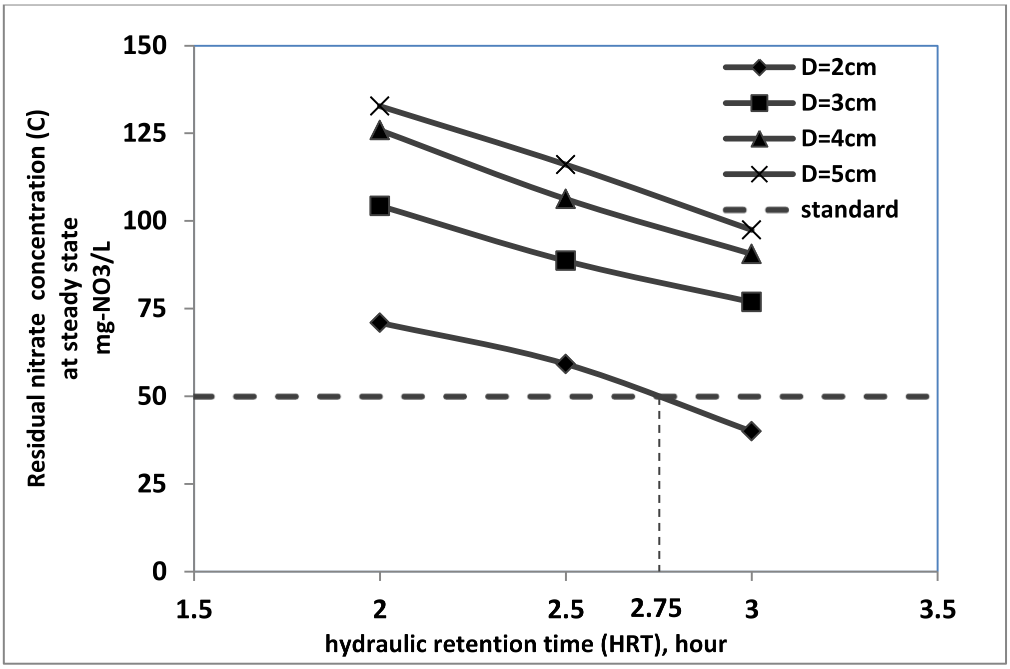


Figure 4.5: Effect of HRT on the steady state residual nitrate concentration (C) at different D values.

(pH = 7, C_i = 200 mg-NO3/L, TDS_i = 1000 mg/l, V = 40 V, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

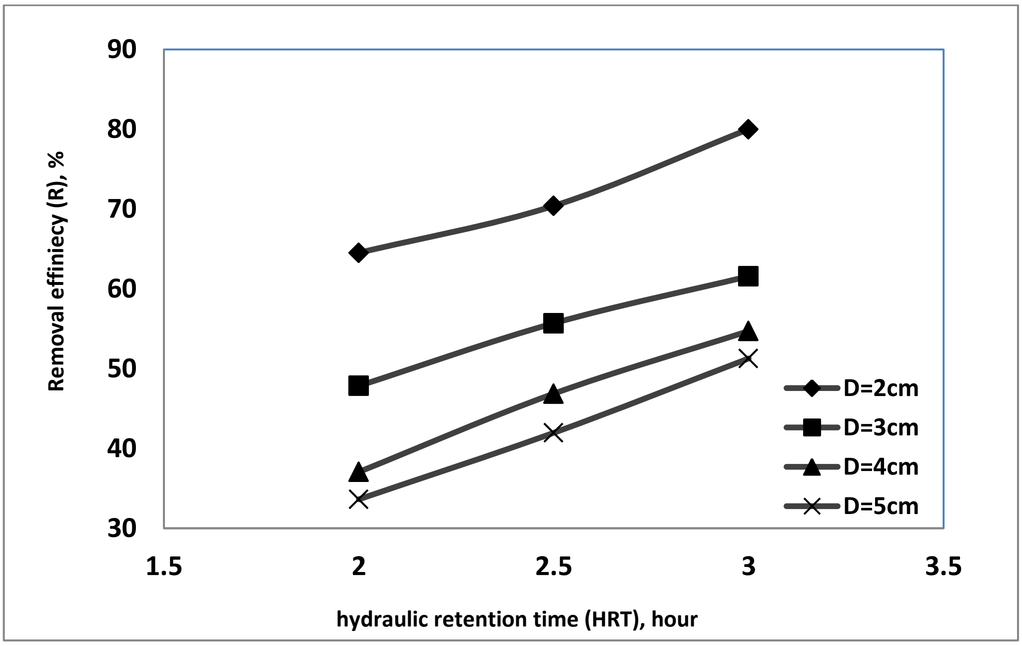


Figure 4.6: Effect of HRT on the nitrate removal efficiency (R) at different D values .

(pH = 7, C_i = 200 mg-NO3/L, TDS_i = 1000 mg/l, V = 40 V, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

4.2.4. The effect of HRT on Nitrate removal in relation to an effective area of anode (A_{eff}).

The effect of hydraulic retention time (HRT) on nitrate removal was examined with solutions of HRTs ranging from 2 – 3.5 hour. To investigate the effect of hydraulic retention time (HRT), the effective area of anode (A_{eff}) was fixed at certain value (47.1, 54 or 61.4 cm^2) while HRT was change to 2, 2.5, 3, and 3.5 hours. Figures 4.7 and 4.8 illustrate the effect of hydraulic retention time (HRT) on the steady state residual nitrate concentration (C) and the steady state removal nitrate percentage (R), respectively when the C_i, V and D were kept constant at 200 mg-NO_3/L, 40 V, 3 cm, respectively. It was observed from Figure 4.7 that at low effective area of anode (A_{eff}) the increase of HRT resulted in lower nitrate steady state residual concentration (C) (i.e. higher removal efficiency). For example, at A_{eff} of 47.1 cm^2, when HRT was 2 hour, the final nitrate concentration was 96.5 mg-NO_3/L (i.e. R = 51.8 %) .while when HRT was increase to 3.5hour, the final nitrate concentration decreased to 67 mg-NO3/L, and removal percentage increased to 66.5 %. The same trend was observed for the other effective area of anode.

From Figure 4.7 at can be interpreted that the standard concentration limit of nitrate (i.e. 50 mg-NO_3/L) can be reached at A_{eff} of 54cm^2 and A_{eff} of 61.4cm^2 , the HRT is equal or greater than 2.4 hours and 2.95 hours, respectively. On the other hand for the other A_{eff} (47.1 cm^2) the HRT should be high than 3.5 hours.

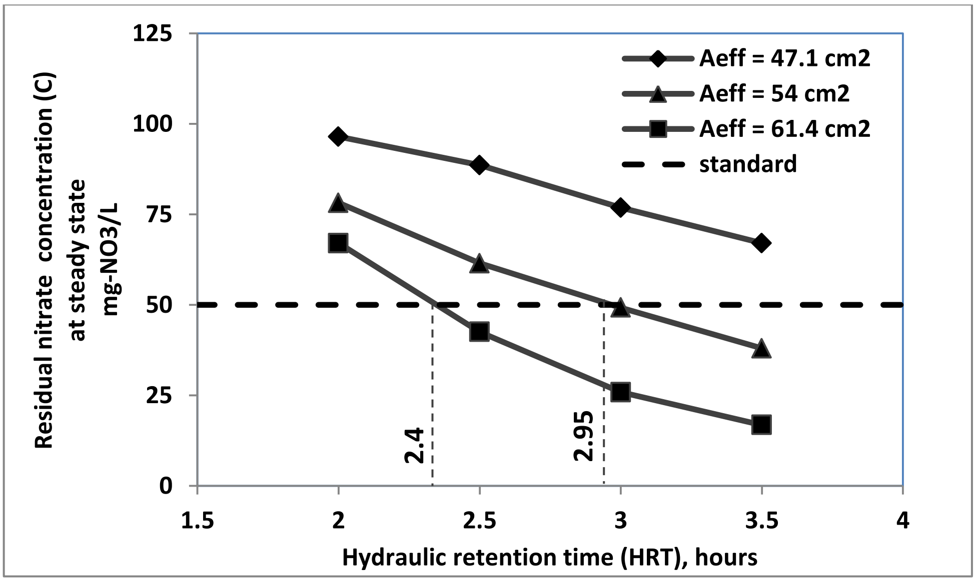


Figure 4.7: Effect of HRT on the steady state residual nitrate concentration (C) at different A_{eff} values.

(pH = 7, C_i = 200 mg-NO3/L, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C and V=40 V).

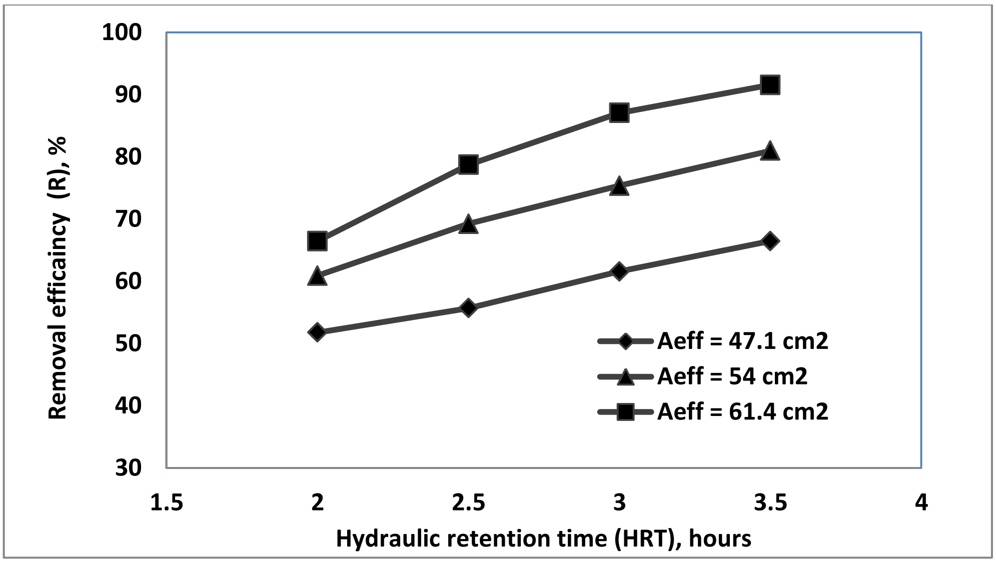


Figure 4.8: Effect of HRT on the nitrate removal efficiency (R) at different A_{eff} values.

(pH = 7, C_i = 200 mg-NO3/L, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C and V=40 V).

4.3. Effect of applied voltage

The effect of applied voltage on nitrate removal was examined with solutions of applied voltages ranging from 35 - 50 V. Figure (4.9), (4.10) and (4.11) show the relation between the value of residual nitrate concentration (C) and the experiment running time (t) for different applied voltages for HRTs of 2, 2.5 and 3hours, respectively. It was observed that the nitrate residual concentration (C) decreased with time at the beginning of each experiment and the reached a steady state value after 3 - 4 hours in all experiments.

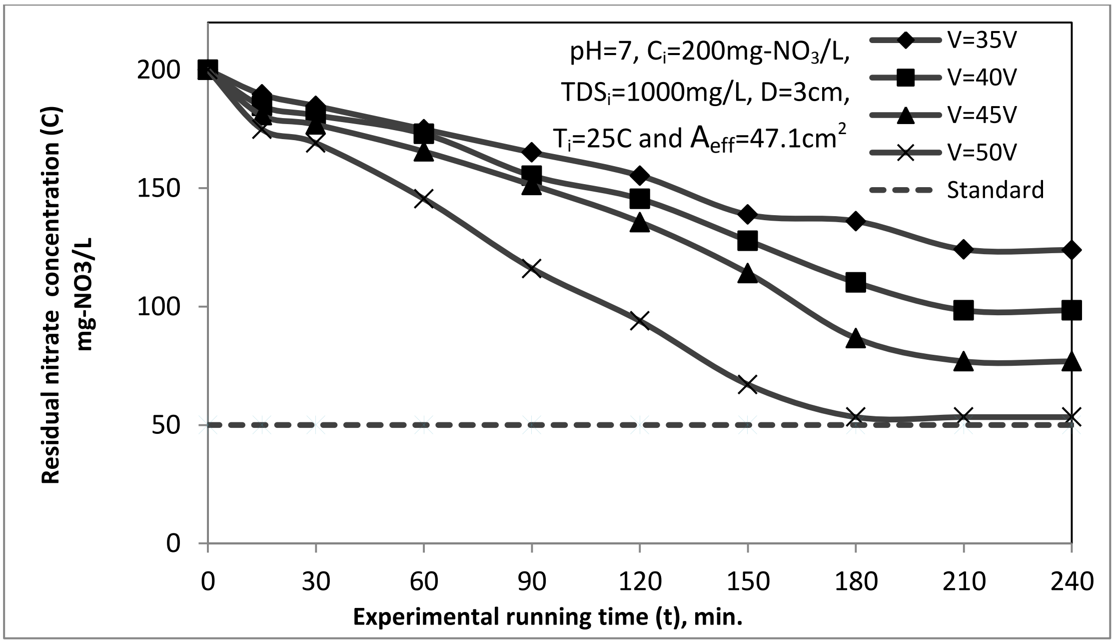


Figure 4.9: Effect of applied voltage on residual nitrate concentration with time at HRT = 2 hrs.

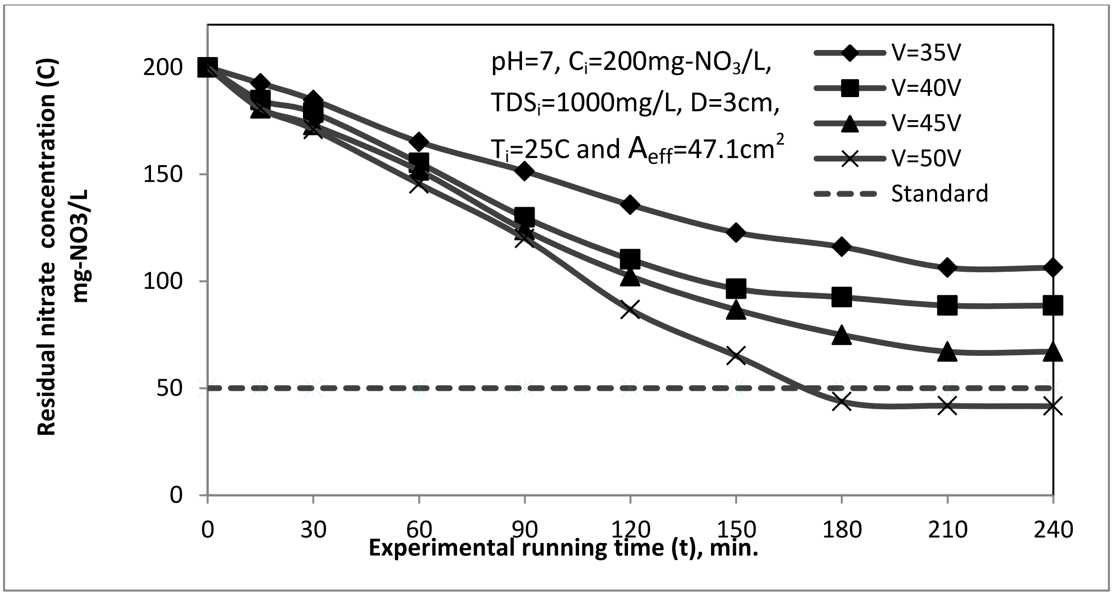


Figure 4.10: Effect of applied voltage on residual nitrate concentration with time at HRT = 2.5 hrs.

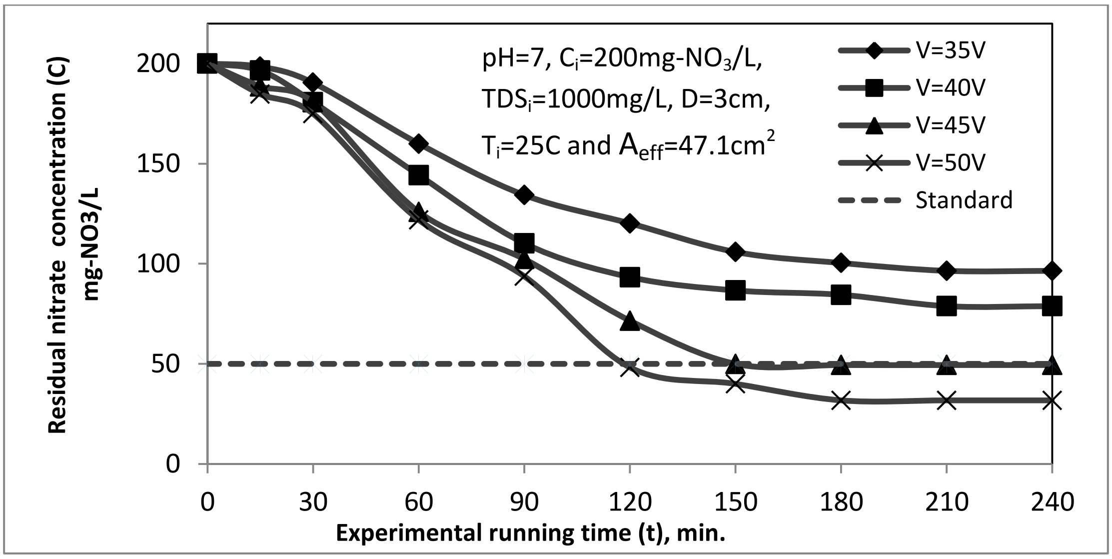


Figure 4.11: Effect of applied voltage on residual nitrate concentration with time at HRT = 3 hrs.

To investigate the effect of applied voltage (V), the HRT was fixed at certain value (2, 2.5, 3 or 3.5 hrs.) while V was changed to 35, 40, 45 and 50 V. Figures 4.12 and 4.13 illustrate the effect of applied voltage (V) on the steady state residual nitrate concentration (C) and the steady state removal nitrate percentage (R), respectively , when D, C_i and A_{eff} were kept constant at 3 cm, 200 mg-NO_3/L, 47.1 cm^2, respectively. It was observed that when the applied voltage (V) increased, the removal percentage (R) also increased and the residual nitrate concentration (C) decreased. For example, at a HRT of 2 hours, when V was 35V, the final nitrate concentration was 124 mg-NO_3/L (i.e. R = 38 %), while when V was increased to 50 V, the final nitrate concentration decreased to 53.3 mg-NO_3/L, and removal percentage increased to 73.33 %. The same trend was observed for the other HRTs.

From Figure 4.12 at can be interpreted that the standard concentration limit of nitrate (i.e. 50 mg-NO_3/L) can be reached at HRT 2.5 and 3 hours for applied voltage that are equal or greater than 45, and 48 V, respectively. On the other hand for the other HRT (2 hours) the applied voltage should be high than 50 V.

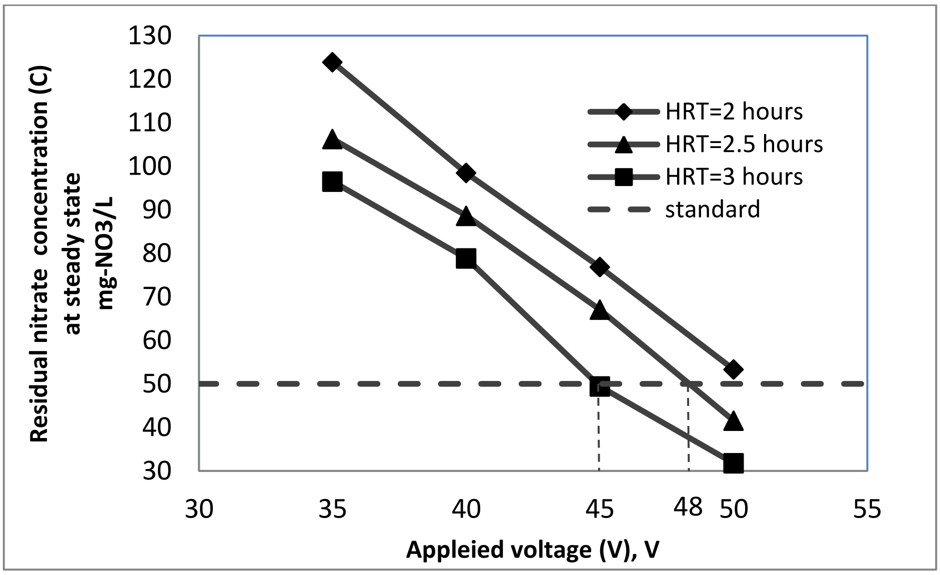


Figure 4.12: Effect of applied voltage (V) on the steady state residual nitrate concentration (C).

(pH = 7, C_i 200 mg-NO3/L, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

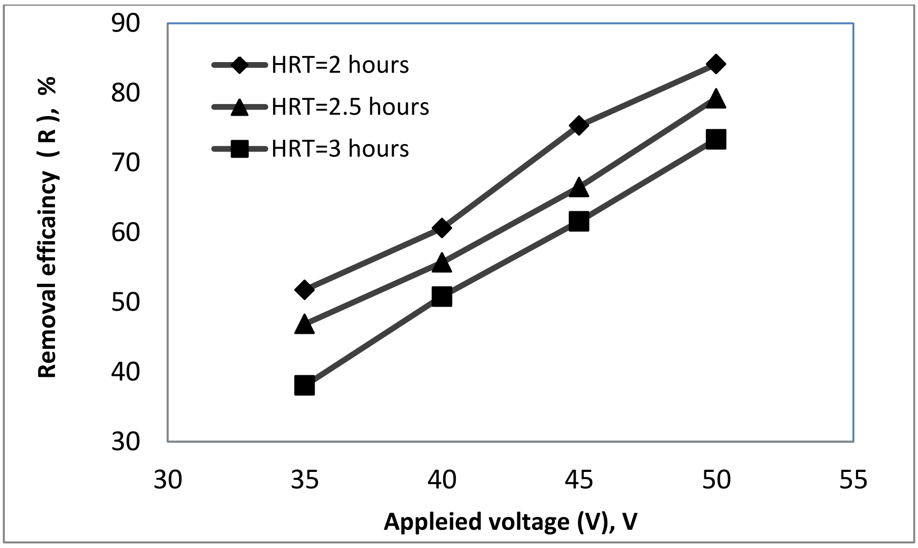


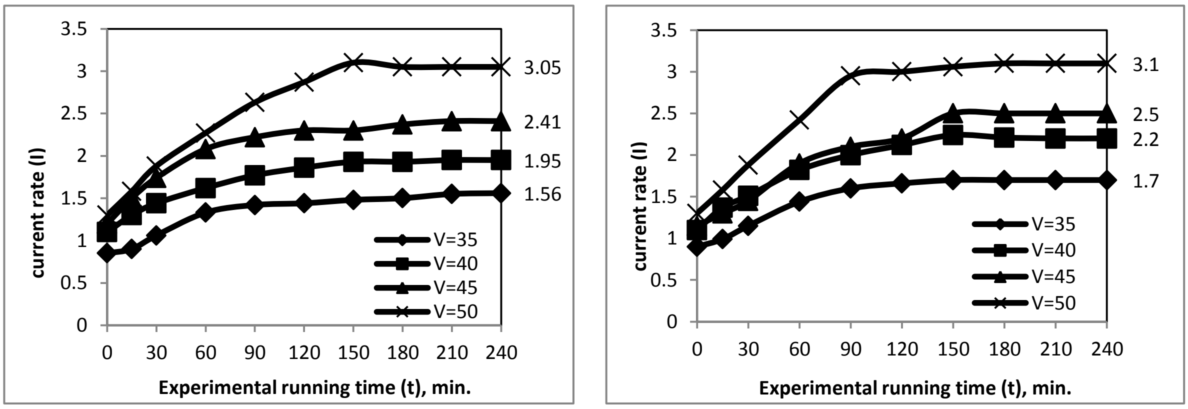
Figure 4.13: Effect of applied voltage (V) on the nitrate removal efficiency (R).

(pH = 7, C_i 200 mg-NO3/L, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

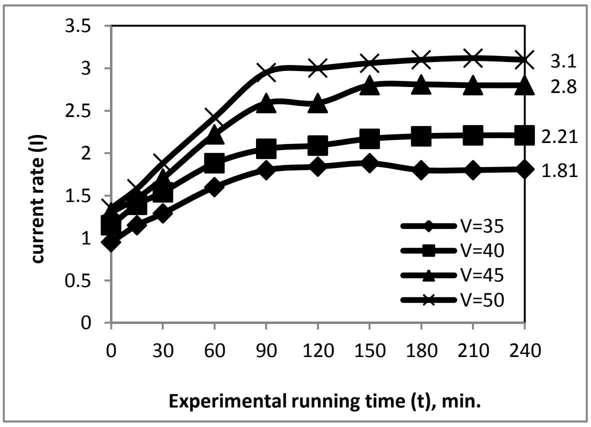
In high voltages, size and growth rate of produced flocs increase and this in turn affects the efficiency of the process. By electrical voltage increase the amount of oxidized iron increases and consequently hydroxide flocs with high adsorption rate increase and this leads to an increase in the efficiency of nitrate removal. Higher current is expected to generate larger amounts of iron, which in turn will trap more pollutant and enhance removal efficiency. Increasing applied voltage with decreasing in residual nitrate concentration (C) and also decreases in time required to achieve steady state concentration in the continuous system.

During the course of each experimental run, it was observed that the TDS of the solution increased with time as a result of which there was an increase in cell current. The increase in TDS is attributed to the dissolution of the anode metal, i.e., elemental Fe is converted to ferrous and ferric ions on the anode and deposition of metal oxides on the cathode.

It was observed from figure 4.13(a, b, c) that the current increase during the experiment and reach steady state value generally after 90 min. Moreover the steady state current increase with increase of applied voltage. For example, for HRT of 2.5 hours, the steady state current was 1.7, 2.2, 2.5 and 3.1 Amber when the applied voltages were 35, 40, 45 and 50V, respectively.



(a) At HRT = 2 hr. **(b) At HRT = 2.5 hr.**



(c) At HRT = 3 hr.

Figure 4.14: Effect of applied voltage on current rates with time (t)

From Table 4.14 (a, b and c), it is evident that all the parameters increased in proportion to the applied voltage due to increase in coagulant generation. pH increased because water is converted to hydrogen gas (from protons generated) and hydroxyl ions. Steady state of current rate (I) and Steady state of temperature also increased with the increase in the applied voltage. It was observed that the nitrate residual concentration decreases when the current intensity is increased at steady state and also temperature is increased. For example, at a HRT of 2 hours, when V was 35V, the final nitrate concentration, steady state current and steady state temperature were 124 mg-NO_3/L, 1.56 A, and 41^{o}C,respectively. while when V was increased to 50 V, the final nitrate concentration , steady state current and steady state temperature decreased to 53.3 mg-NO_3/L, 1.95 A, and 68^{o}C, respectively. The same trend was observed for the other HRTs.

Summary of operating parameters for different applied voltage for nitrate removal C_i = 200 mg-NO3/L, $[TDS]_i$= 1000ppm, D = 3cm, experimental run= 4h (these parameters were constant for all runs).

Table 4.1 : Summary of operating parameters for different applied voltage for nitrate removal

(a) At HRT = 2 hr.

Applied voltage (V)	C_e at steady-state (mg/L)	Initial pH	Final pH Before filt-ration	Initial turbi-dity (NTU)	Final turbidity (NTU) Before filtration	Final turbidity (NTU) After filtration	Current (I) at steady-state (Amber)	Final Temp. at steady-state (C^o)
35	124	7.01	11.65	0.2	51	3.5	1.56	41
40	98.5	7.01	11.54	0.56	54	3	1.95	48
45	76.8	7.01	11.67	0.5	50	3	2.41	58
50	53.3	7.01	11.6	0.5	62	3.8	3.05	68

(b) At HRT = 2.5 hr.

Applied voltage (V)	C_e at steady-state (mg/L)	Initial pH	Final pH Before filt-ration	Initial turbi-dity (NTU)	Final turbidity (NTU) Before filt-ration	Final turbidity (NTU) After filt-ration	Current (I) at steady-state (Amber)	Final Temp. at steady-state (C^o)
35	106.7	7.01	11.8	0.5	54	4.8	1.7	46
40	88.6	7.01	11.6	0.5	55	3	2.2	55
45	67	7.01	11.5	0.5	56	3	2.5	63
50	41.8	7.01	11.6	0.5	62	3.2	3.1	75

(c) At HRT = 3 hr.

Applied voltage (V)	C_e at steady-state (mg/L)	Initial pH	Final pH Before filt-ration	Initial turbi-dity (NTU)	Final turbidity (NTU) Before filtration	Final turbidity (NTU) After filtration	Current (I) at steady-state (Amber)	Final Temp. at steady-state (C°)
35	106.7	7.01	11.8	0.5	54	4.8	1.7	46
40	88.6	7.01	11.6	0.5	55	3	2.2	55
45	67	7.01	11.5	0.5	56	3	2.5	63
50	41.8	7.01	11.6	0.5	62	3.2	3.1	75

4.4. Effect of initial nitrate concentration

The effect of initial nitrate concentration on nitrate removal was examined with solutions of nitrate concentrations ranging from 100 - 250 mg/l as NO_3^- .The value of the nitrate concentrations were based on the characteristics of real water of the northern of the Gaza strip. Figure (4.15), (4.16), (4.17) and (4.18), show the relation between the residual nitrate concentration (C) and the experiment running time (t) for different initial nitrate concentrations at 2, 2.5, 3, 3.5 hours HRT, respectively. It was observed that the nitrate residual concentration (C) decreased with time at the beginning of each experiment and reached a steady state value after 3-3.5 hours in all experiments.

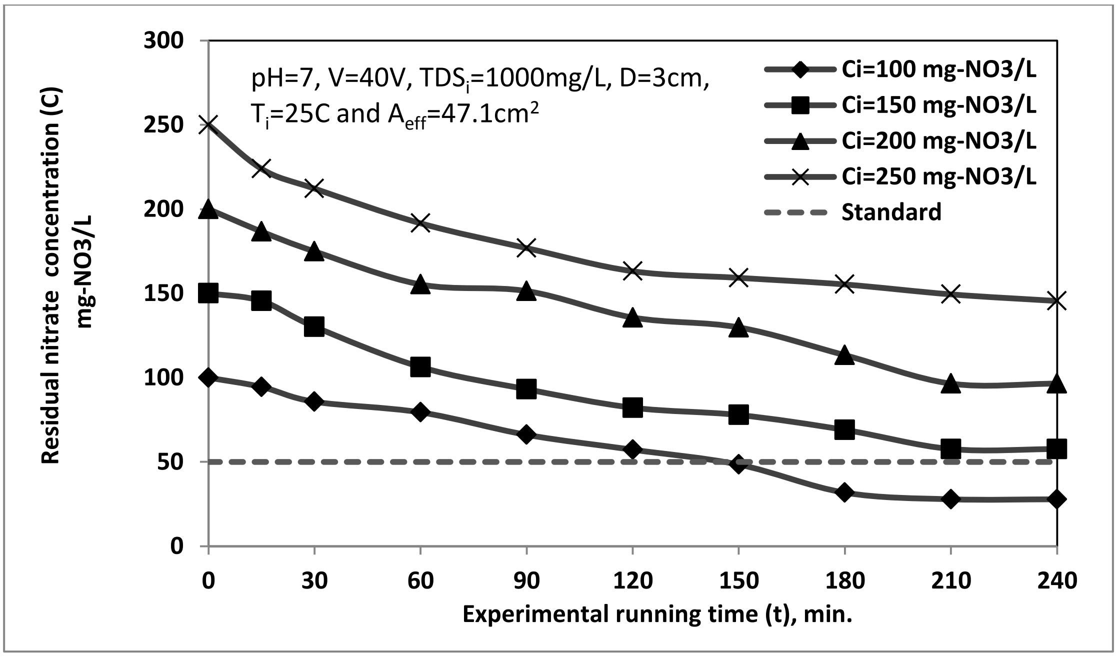


Figure 4.15: Effect of initial nitrate concentration on residual nitrate concentration with time at HRT = 2 hrs.

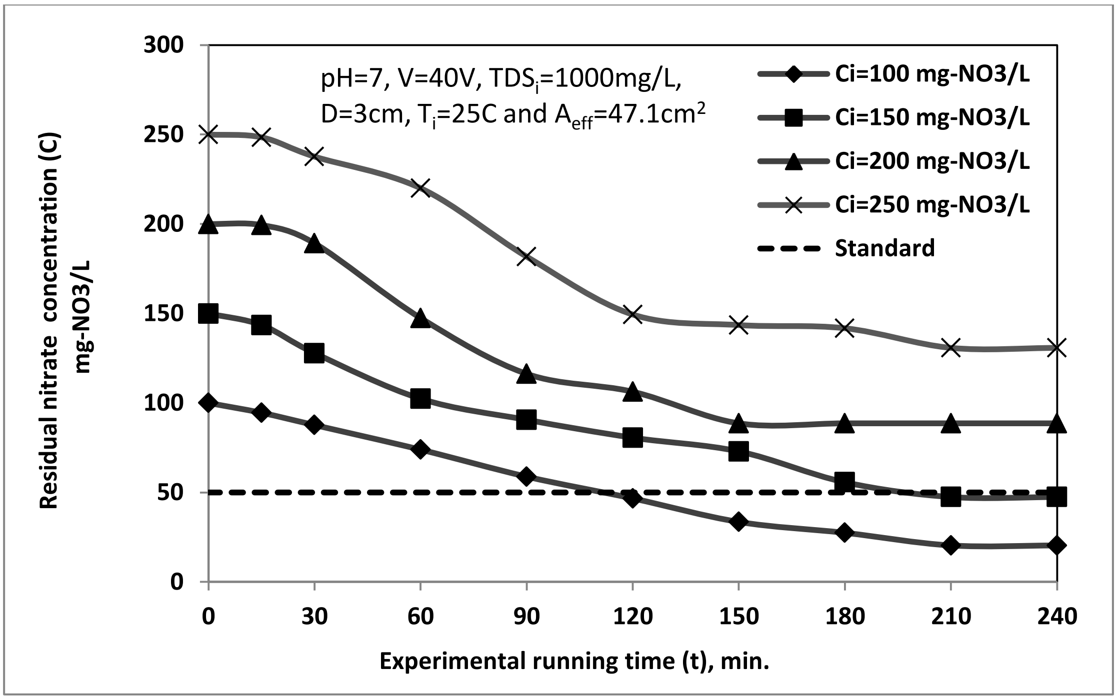


Figure 4.16: Effect of initial nitrate concentration on residual nitrate concentration with time at HRT = 2.5 hrs.

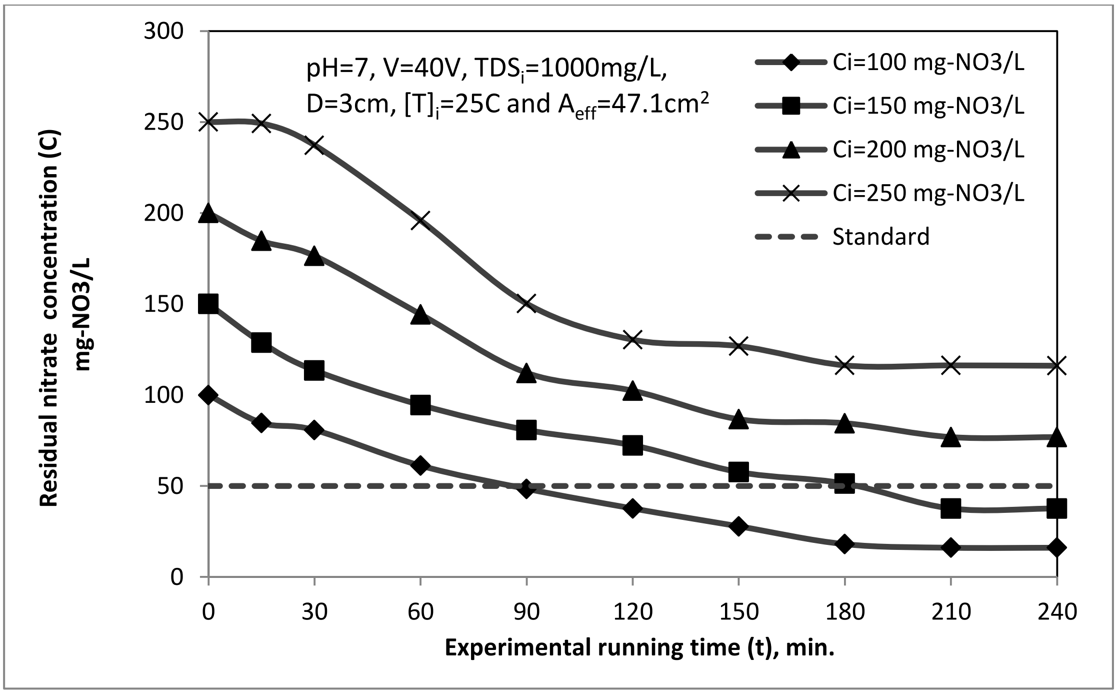


Figure 4.17: Effect of initial nitrate concentration on residual nitrate concentration with time at HRT = 3 hrs.

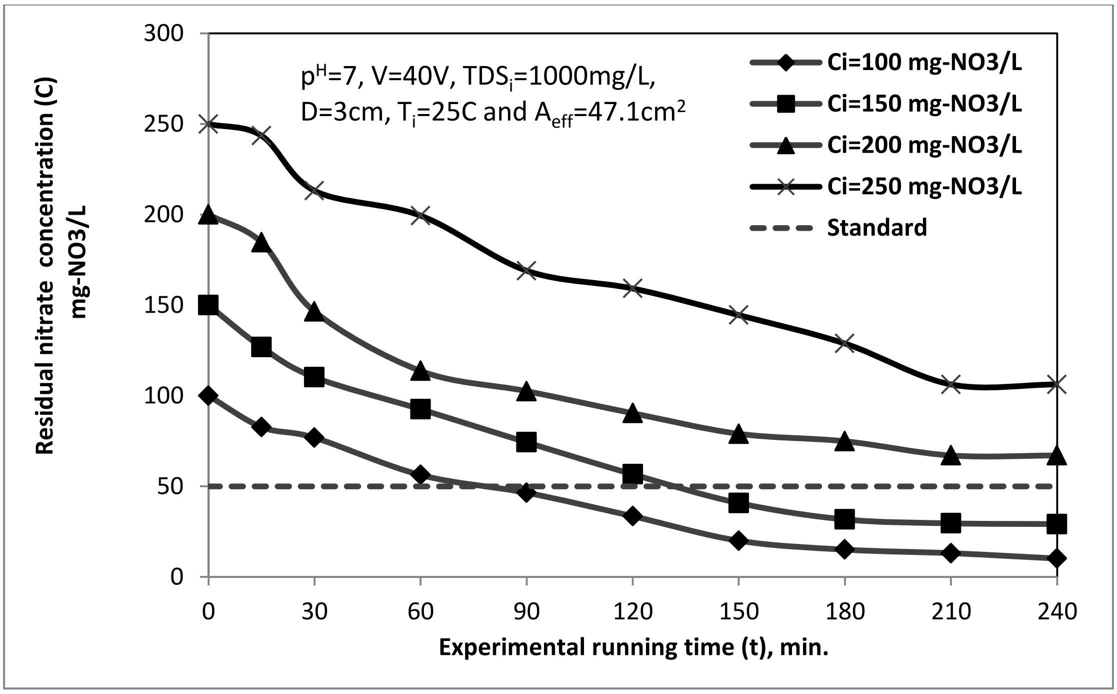


Figure 4.18: Effect of initial nitrate concentration on residual nitrate concentration with time at HRT = 3.5 hrs.

To investigate the effect of initial nitrate concentrations (C_i), the HRT was fixed at certain value (2, 2.5, 3 or 3.5) while C_i was change to 100, 150, 200 & 250 mg-NO_3/L. Figures 4.19 and 4.20 illustrate the effect of initial nitrate concentration (C_i) on the steady state residual nitrate concentration (C) and the steady state removal nitrate percentage (R), respectively when the V, D and A_{eff} were kept constant at 40 V, 3 cm, 47.1 cm^2, respectively. It was observed that when initial nitrate concentration (C_i) increased, the residual nitrate concentration (C) also increased and the removal percentage (R) decreased. For example, at a HRT of 2 hours, when C_i was 100 mg-NO_3/L, the final nitrate concentration was 27.8 mg-NO_3/L (i.e. R = 72 %) .while when C_i was increase to 250 mg-NO_3/L, the final nitrate concentration increased to 145.5 mg-NO_3/L, and removal percentage decreased to 41.8 %. The same trend was observed for the other HRTs.

From Figure 4.19 at can be interpreted that the standard concentration limit of nitrate (i.e. 50 mg-NO_3/L) can be reached at HRT 2, 2.5, 3 and 3.5 hours for nitrate concentration that are equal or less than 138, 153, 167 and 178 mg-NO_3/L, respectively.

In fact, coagulation process sweeps and precipitates the NO_3^- ions by flocs formed. The NO_3^- ions were effectively removed from water owing to aggregation of the colloidal particles by means of Fe^{2+} / Fe^{3+} produced during electrolysis. These ions react with the colloids form settable flocs that can be easily separated from solution.

The decrease of nitrate removal efficiency when the initial nitrate concentration was increase is attributed to the lack of the formed iron oxide flocs in solution, more iron oxides were needed to decrease the dissolved nitrate concentrations. Nitrate removal is consequently limited by the production rate of iron oxides .

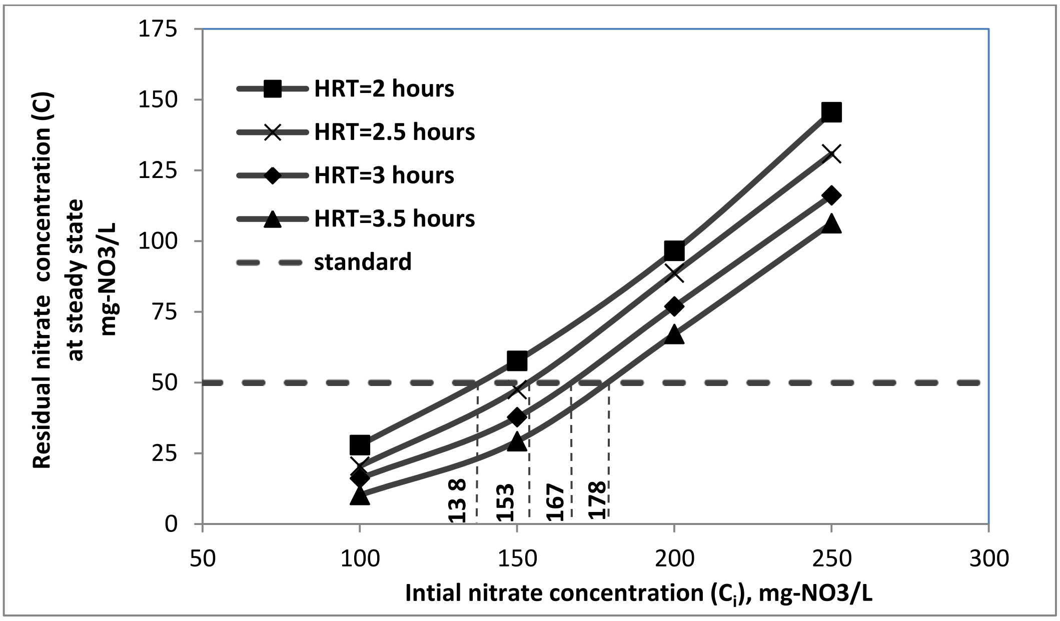


Figure 4.19: Effect of initial nitrate concentration (C_i) on the steady state residual nitrate concentration (C)

(pH = 7, V = 40 V, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C, and A_{eff} = 47.1 cm^2).

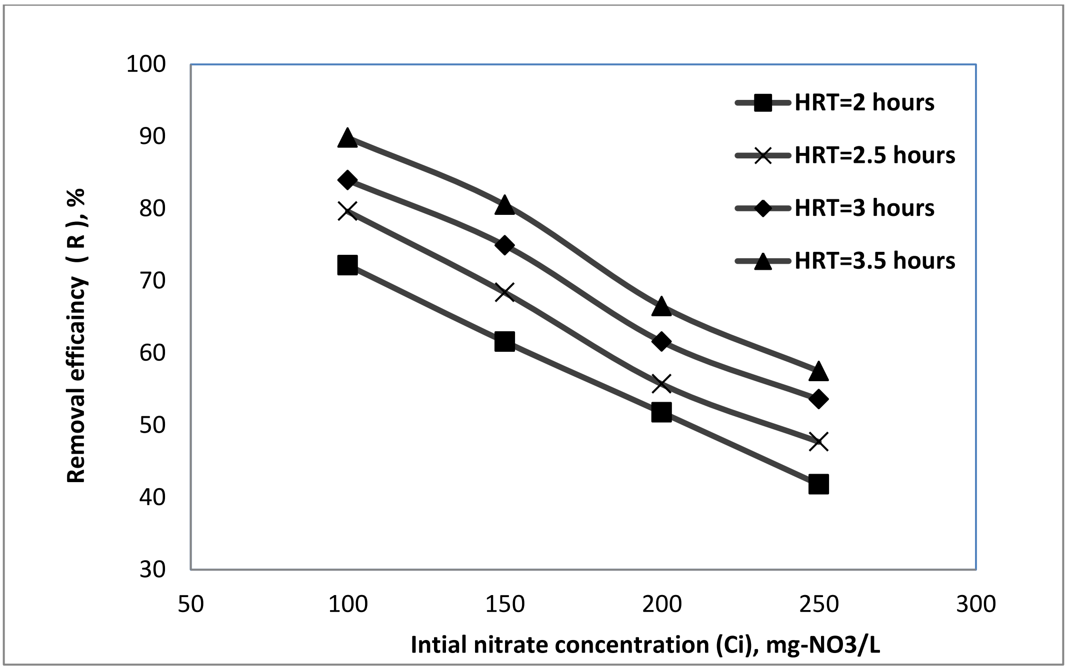


Figure 4.20: Effect of initial nitrate concentration (C_i) on the nitrate removal efficiency (R) .

(pH = 7, V = 40 V, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C, and A_{eff} = 47.1 cm^2).

4.5. Effect of distance between electrodes

To investigate the effect of distance between electrode (D), the HRT was fixed at certain value (2, 2.5, & 3 hrs.) while D was changed to 2, 3, 4 and 5cm. Figures 4.21 and 4.22 illustrate the effect of distance between electrode (D) on the steady state residual nitrate concentration (C) and the steady state removal nitrate percentage (R), respectively when the V, C_i and A_{eff} were kept constant at 40 V, 200 mg-NO_3/L, 47.1 cm^2, respectively. It was observed that when the distance between electrodes (D) increased, the residual nitrate concentration (C) also increased and the removal percentage (R) decreased. For example, at a HRT of 2 hours, when D was 2cm, the final nitrate concentration was 71mg-NO_3/L (i.e. R = 64.5 %), while when D was increase to 5 cm, the final nitrate concentration increased to 132.75 mg-NO_3/L, and removal percentage decreased to 33.6 %. The same trend was observed for the other HRTs and also the general observed trend was that C increases nonlinearly with a decreasing rate when the distance between electrodes was increased for all the HRTs.

It can be interpreted from Figure 4.21 that to achieve the standard concentration limit (50 mg-NO_3/L) at the experiment conditions mention below the figure and for HRT of 3hours, the distance between electrodes should be around 2 cm. For other HRTs (2, 2.5 hours) the distance between electrodes should between 1 and 2cm.

Show in figure 4.22 the removal efficiency decreased with the increase of distance between electrodes. The highest removal efficiency of 80 % was obtained at distance between of electrode of 2 cm when HRT was 3hour.

This can be explained that decreasing the distance between electrodes results in low resistance through the solution which in effect results in increasing the current and consequently the rate of iron dissolution and Fe^{2+} releases and consequently leads to more nitrate removal from the solution.

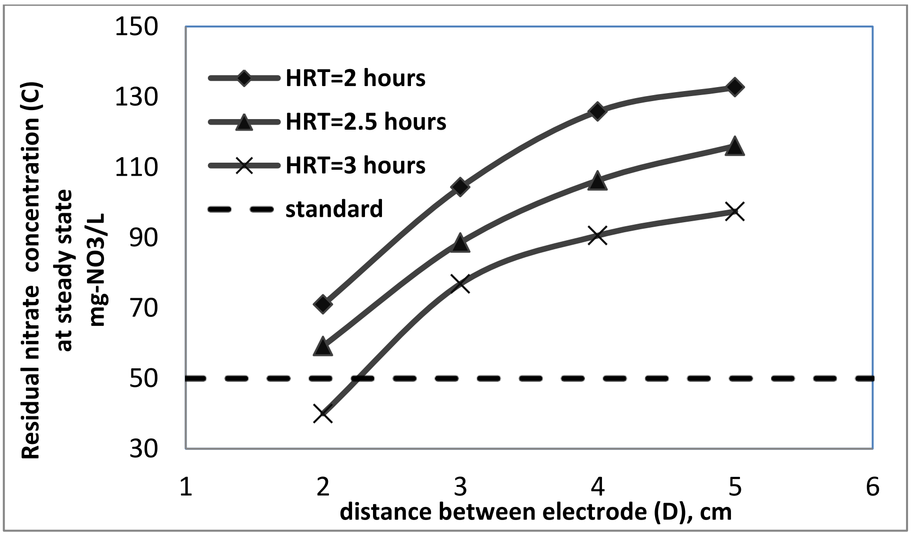


Figure 4.21: Effect of distance between electrode on the steady state residual nitrate concentration (C).

(pH = 7, C_i = 200 mg-NO3/L, V = 40 V, TDS_i = 1000mg/l, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

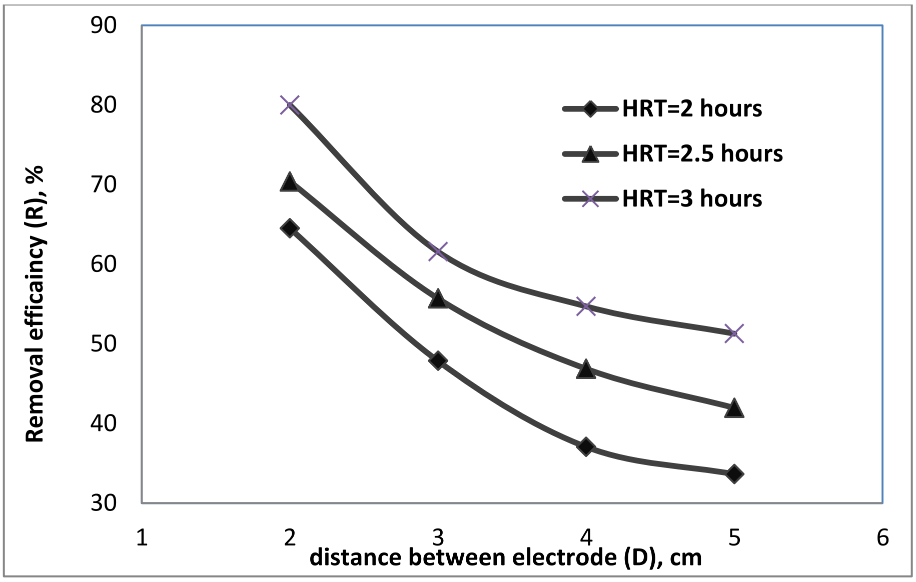


Figure 4.22: Effect of distance between electrodes on nitrate removal efficiency (R).

(pH = 7, C_i = 200 mg-NO3/L, V = 40 V, TDS_i = 1000mg/l, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

4.6. Effect of effective area of anode

To investigate the effect of distance between electrode (D), the HRT was fixed at certain value (2, 2.5, or 3 hrs.) while A_{eff} was changed to 47.1, 54, and 61.4cm^2. Figures 4.23 and 4.24 illustrate the effect of effective area of anode (A_{eff}) on the steady state residual nitrate concentration (C) and the steady state removal nitrate percentage (R), respectively when the V, C_i and D were kept constant at 40 V, 200 mg-NO_3/L, 3 cm, respectively. It was observed that when the effective area of anode (A_{eff}) increased, the removal percentage (R) also increased and the residual nitrate concentration (C) decreased. For example, at a HRT of 2 hours, when A_{eff} was 47.1cm^2, the final nitrate concentration was 96.5mg-NO_3/L (i.e. R = 51.8 %), while when A_{eff} was increase to 61.4 cm, the final nitrate concentration decreased to 67 mg-NO_3/L, and removal percentage decreased to 66.5 %. The same trend was observed for the other HRTs.

The explanation of these phenomena as follows: In high effective area of electrode, growth rate of produced flocs increase and this in turn affects the efficiency of the process. By effective area of electrode increase the amount of oxidized iron increases and consequently hydroxide flocs with high adsorption rate increase and this leads to an increase in the efficiency of nitrate removal. On the other hand, higher effective area of electrode is expected to generate larger amounts of iron, which in turn will trap more pollutant and enhance removal efficiency.

From Figure 4.23 it can be interpreted that the standard concentration limit of nitrate (i.e. 50 mg-NO_3/L) can be reached at HRT 2.5, 3 and 3.5hours for effective area of anode that are equal or greater than 51, 54, and 58cm^2, respectively. On the other hand for the other HRT (2 hours) the effective area of anode should be higher than 61.4 cm^2, to achieve the standard limit.

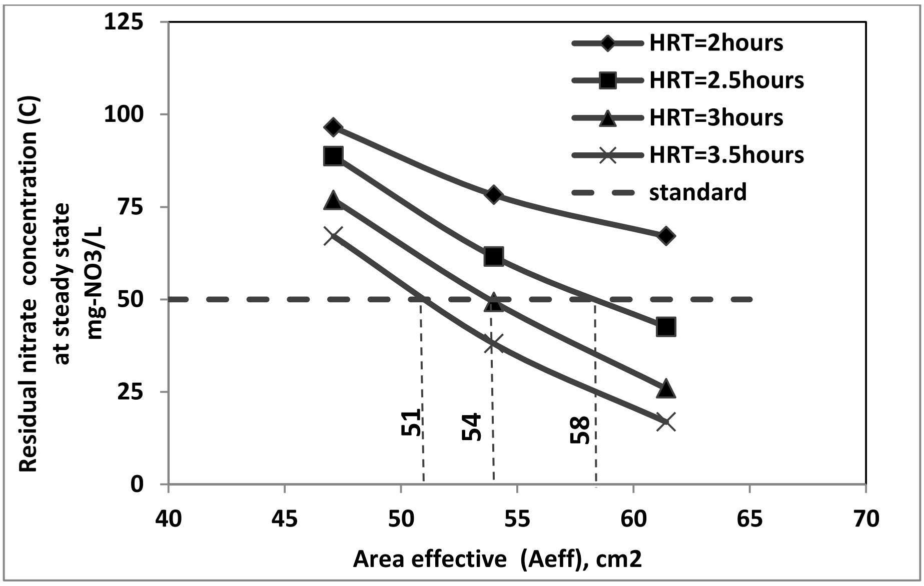


Figure 4.23: Effect of effective area of anode (A_{eff}) on the residual nitrate concentration (C) at steady state.

(pH = 7, C_i = 200 mg-NO_3/L, TDS_i = 1000mg/l, V = 40 V, T_i = 25 ^{0}C and D=3cm).

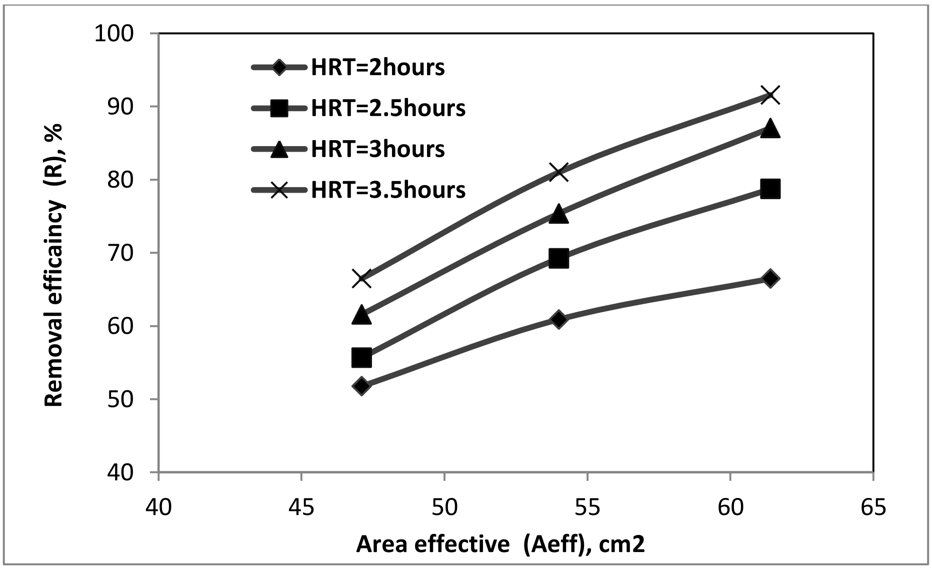


Figure 4.24: Effect of effective area of anode (A_{eff}) on nitrate removal efficiency (R) .

(pH = 7, C_i = 200 mg-NO_3/L, TDS_i = 1000mg/l, V = 40 V, T_i = 25 ^{0}C and D=3cm).

4.7.Treatment of real groundwater

From the experimental studies conducted, the best operating conditions for treatment was chosen based on minimum HRT, distance between electrode, minimum applied voltage and effective area of electrode. The criteria behind the selection of optimum point lay in efficient treatment of solution with minimal time, WHO standards for nitrate and energy consumption. The best operating conditions for nitrate removal for the aqueous solution were found to be at HRT 2, 2.5 and 2.5hours, applied voltage 40V, distance between electrode 3cm and effective area of electrode 47.1, 47.1 and 61.4 cm^2, when initial nitrate concentration were 100, 150 and 200 mg-NO_3/L, respectively.

In order to confirm the results obtained from the synthetic water experiments, a similar experiment was applied on real groundwater sample, that was collected from the groundwater well in the north of Gaza Strip. The sample was collected in Mar. 17th, 2013, and the initial nitrate concentration was 200 mg-NO_3/L. It was noticed that nitrate concentration in the north of Gaza Strip reaches above 50 mg-NO_3/L, which is higher than the standard level. Table 4.2 presents the main characteristic of groundwater sample.

Table 4.2 characteristic of the groundwater sample

Parameter	Unit	Sample (1)
Nitrate	(mg-NO3/L)	200
Chloride	(mg/L)	201
TDS	(mg/L)	709
pH	----	7.23
Electrical conductivity	µs/cm	1417
Turbidity	FTU	1.2
Total hardness	(mg/L)	600
Alkalinity	(mg/L CaCO3)	215
Sodium	(mg/L)	73

The conductivity of the solution depends on the number of ions present. Increase in the concentration of the electrolyte results in increase in number of ions. So, ultimately solution becomes more conductive, which results in passage of more number of electrons per unit time. NaCl has been chosen in the present experiments.

Electrolyte is a substance which is responsible for increasing the conductivity of the solution. The motion of the ions can be measured by measuring the resistance R, of the solution. The conductance G of the solution is the inverse of the resistance.

$$G = \frac{\kappa A}{l} \dots\dots\dots\dots\dots\dots..eqn\ (4.1)$$

where κ is the conductivity.

In the present study without adding electrolyte only 51.8% removal efficiency was achieved for the original sample ground water. 100mg to 300mg of NaCl in fixed amount (1L of original ground water sample) has been added in the solution and removal efficiencies have been observed. We can see from Figure 4.25 that the nitrate removal efficiency increases with the increase of initial total dissolved solid.

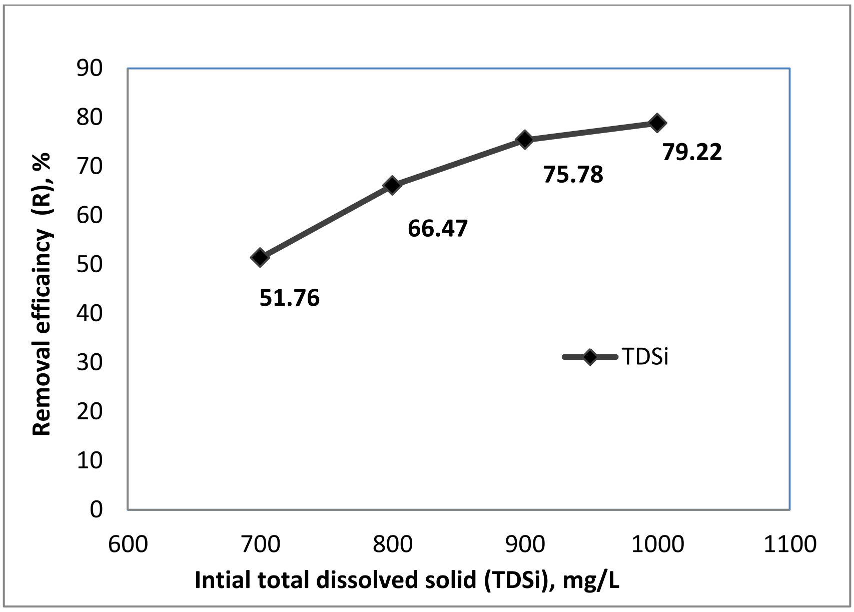


Figure 4.25: Effect of TDS_i on the nitrate removal efficiency (R).

($V=40$ V, HRT=2.5hour, D = 3cm, $A_{eff}=61.4cm^2$, and $T_i = 25\ ^0C$).

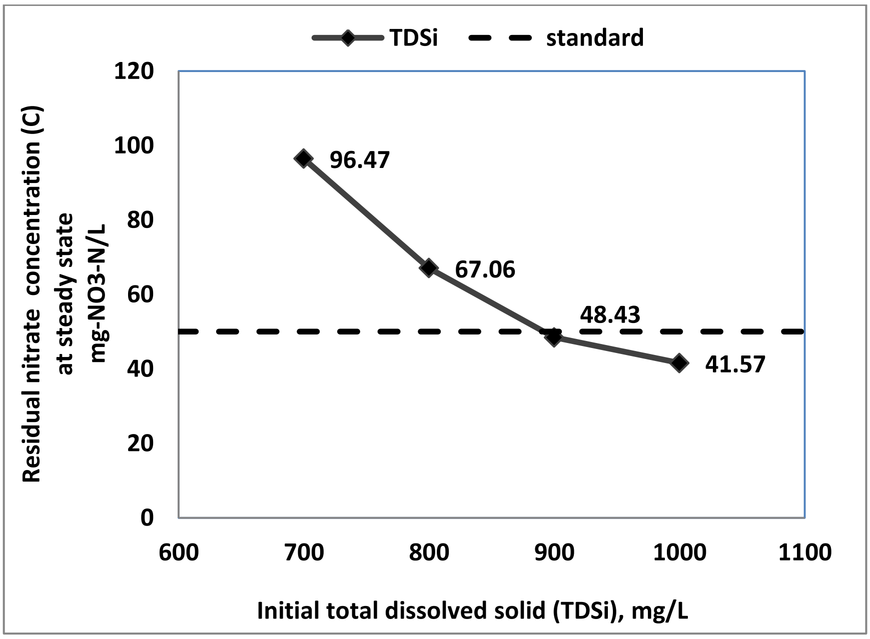


Figure 4.26: Effect of TDS_i on the steady state residual nitrate concentration(C).

($V=40$ V, HRT=2.5hour, D = 3cm, $A_{eff}=61.4cm^2$, and $T_i = 25\ ^0C$).

Figure 4.26 shows the residual nitrate concentration as a function of different initial total dissolved solid within optimum operation conditions.

From Figure 4.26, it can be indicated that a TDS$_i$ equal 900 mg/L gives final nitrate concentration of 47.5 mg-NO_3/L which effectively reduces nitrate concentration to less than 50 mg-NO_3/L which is acceptable to be used as potable water according to WHO. However, although the maximum removal efficiency was obtained at higher NaCl concentrations, subsequent experiments were carried out with 200 mg-NaCl/L (Original sample) in order to minimize the addition of excess Cl^- ions in solution as well as to keep the treated water fresh.

The water quality parameter before and after treatment at operating conditions is presented in Table 4.2 and Table 4.3. Nitrate was reduced below the limit of drinking water standard (50 mg-NO_3/L) when TDS was 900 mg/L and 1000 mg/L. The alkalinity and total hardness concentration were also reduced which may be due to the transport of ions to the anode compartment.

A decrease in TDS was noticed with a corresponding decrease in electrical conductivity, which may be due to the decrease in alkalinity and total hardness concentration.

Table 4.3 characteristic of groundwater sample after treatment [condition for electrocoagulation: V = 40 V, D=3cm, A_{eff}=61.4cm^2, HRT=2.5hours and T_i = 25 ^{0}C]

Parameter	**Unit**	**Original sample**	**Adding 100 mg-NaCL/L$_{\text{(Original sample)}}$**	**Adding 200 mg-NaCL/L$_{\text{(Original sample)}}$**	**Adding 300 mg-NaCL/L$_{\text{(Original sample)}}$**
		TDS$_i$= 700 mg/L	TDS$_i$= 800 mg/L	TDS$_i$= 900 mg/L	TDS$_i$= 1000 mg/L
Nitrate	(mg-NO3/L)	96.5	67	48.43	41.57
Chloride	(mg/L)	130	206	240	320
TDS	(mg/L)	505	596	656	892
pH	----	7.4	7.7	7.84	8.4
Electrical conductivity	µs/cm	790	1150	1292	1550
Turbidity	FTU	4.3	4.45	4	3.5
Total hardness	(mg/L)	97	76	59.5	44
Alkalinity	(mg/L CaCO3)	100	80	52	39
Sodium	(mg/L)	73	113	163	220

4.8. Electrodes Passivation

As a result of the oxidation process, the anode material will under-go electrochemical corrosion, whereas the cathode will be subjected to passivation. Figures 4.27 show photographical pictures of Fe anode after several treatment runs. As explained at the **item 2.3.4** in literature review.

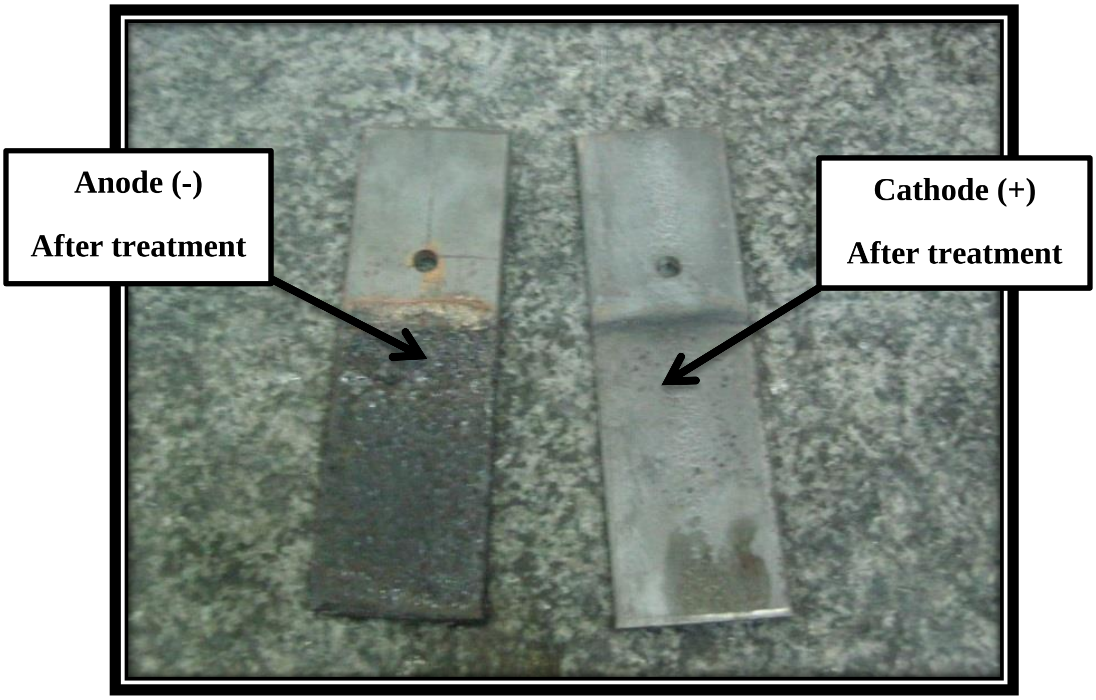


Figure 4.27: Photographical picture for anode and cathode after several treatment runs.

CHAPTER 5: Conclusion and recommendations

5.1 Conclusion

Continuous flow experiments were designed to investigate the effects of the different parameters including applied voltage (V), initial nitrate concentration (C_i), hydraulic retention time (HRT), and effective area of anode (A_{eff}) on the nitrate removal efficiency by electrocoagulation from synthetic aqueous solutions. Then the optimal operating conditions were determined and applied to the northern Gaza water samples.

The main conclusions obtained from this work are:

- The electrocoagulation process is successfully applied to remove nitrate from aqueous solution. The nitrate removal efficiency was found to be dependent on the initial nitrate concentration, distance between electrodes, area effective of anode and the applied voltage.
- The results showed that applied voltage, TDS_i, effective area of anode and HRT are directly proportional to nitrate removal efficiency, while initial nitrate concentration, and distance between electrodes are inversely proportional to nitrate removal efficiency.
- The best operating conditions for nitrate removal by EC are :
    - For C_i of 100mg-NO_3/L: V=40V, HRT=2hours, D=3cm, and A_{eff}=47.1cm^2.
    - For C_i of 150mg-NO3/L: V=40V, HRT=2.5hours, D=3cm, and A_{eff}=47.1cm^2.
    - For C_i of 200mg-NO_3/L: V=40V, HRT=2.5hours, D=3cm, and A_{eff}=61.4cm^2.

  During the three cases TDS_i, pH, and T_i were kept constant at 1000mg/L, 7±0.1, and 25±2ºC and the criteria behind the selection of best point lay in efficient treatment of solution with minimal time, WHO standards for nitrate, and energy consumption.
- The highest nitrate removal efficiency at aqueous solution was obtained for C_i =200 mg-NO_3/L , V=40V, HRT=3.5hours, D=3cm, and A_{eff}=61.4cm^2 when the parameters : TDS_i, pH, and T_i were kept constant at 1000mg/L, 7±0.1, and 25±2ºC and the nitrate removal efficiency was reached to 91.6 %.
- The effectiveness of this process on nitrate removal from the northern of Gaza water distribution system showed that the nitrate removal efficiency was 80 % at the optimal conditions: V = 40V, HRT = 2.5hours, D = 3cm and A_{eff} = 61.4cm^2, when TDS_i and C_i were 1000 mg/L and 200mg-NO_3/L , respectively. Therefore, this process is suggested as an efficient alternative technique for nitrate removal from aqueous solution. And also it was possible to remove nitrate from groundwater below the limit of the drinking water standard using this method.

- This study generated important information on the best conditions of several variables that influence electrocoagulation. It was found that the alkalinity, total hardness concentration and TDS were decreased when using the EC technology in groundwater. For example, TDS_i of 900 mg/L and C_i of 200mg-NO_3/L, when the optimal conditions: V was 40V, HRT was 2.5hours, D was 3cm, and A_{eff} was 61.4cm^2, the removal percentage of alkalinity , total hardness, and TDS were 75.8, 90 and 34.4%, respectively.

5.2 Recommendations

The following recommendations may be considered for further studies.

1. Investigating the influence of: length to width ratio of the continuous flow reactor, energy consumption, the ratio of surface area of the electrode to volume of water in the reactor (A_s/V), and electrode passivation.
2. Investigating the use of horizontal cathode (placed at the bottom of the cell) to enhance the flotation process by generating more distributed bubbles.
3. Initiating a pilot project study in one of north Gaza wells using an inline pipe reactor to investigate the feasibility of this method in the removal of nitrate from groundwater (i.e. inline treatment of nitrate pollution).

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Appendices

Appendix (A)

- **Continuous experiment : Synthetic aqueous solutions**

Table (A.1): residual nitrate concentrations as a function of different C_i values at HRT = 2 hour

(pH = 7, V = 40 V, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C, and A_{eff} = 47.1 cm^2)

Time	C_i=100	C_i=150	C_i=200	C_i=250
0	100.0	150.0	200.0	250.0
15	94.5	145.5	186.7	223.9
30	85.7	130.2	174.9	212.2
60	79.4	106.3	155.3	191.6
90	66.1	93.1	151.4	176.9
120	57.3	82.2	135.7	163.1
150	48.4	77.8	129.8	159.2
180	31.8	69.0	113.3	155.3
210	27.8	57.6	96.5	149.4
240	27.8	57.6	96.5	145.5

Table (A.2): residual nitrate concentrations as a function of different C_i values at HRT = 2.5 hour

(pH = 7, V = 40 V, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C, and A_{eff} = 47.1 cm^2)

Time	C_i=100	C_i=150	C_i=200	C_i=250
0	100.0	150.0	200.0	250.0
15	94.5	143.5	199.4	248.4
30	87.6	127.8	189.2	237.6
60	73.9	102.4	147.5	220.0
90	58.8	90.6	116.3	181.8
120	46.7	80.6	106.3	149.4
150	33.5	72.9	88.6	143.5
180	27.5	55.7	88.6	141.8
210	20.4	47.5	88.6	130.8
240	20.4	47.5	88.6	130.8

Table (A.3): residual nitrate concentrations as a function of different C_i values at HRT = 3 hour

($pH = 7$, $V = 40$ V, $TDS_i = 1000$mg/l, $D = 3$cm, $T_i = 25\ ^0C$, and $A_{eff} = 47.1\ cm^2$)

Time	C_i=100	C_i=150	C_i=200	C_i=250
0	100.0	150.0	200.0	250.0
15	84.7	128.8	184.7	249.2
30	80.8	113.5	176.5	237.3
60	61.2	94.5	144.3	195.9
90	48.4	80.8	112.2	150.2
120	37.6	72.4	102.4	130.4
150	27.8	57.6	86.7	126.9
180	18.0	51.4	84.5	116.3
210	16.1	37.6	76.9	116.3
240	16.1	37.6	76.9	116.1

Table (A.4): residual nitrate concentrations as a function of different C_i values at HRT = 3.5 hour

($pH = 7$, $V = 40$ V, $TDS_i = 1000$mg/l, $D = 3$cm, $T_i = 25\ ^0C$, and $A_{eff} = 47.1\ cm^2$)

Time	C_i=100	C_i=150	C_i=200	C_i=250
0	100.0	150.0	200.0	250.0
15	82.7	126.9	184.7	243.5
30	76.9	110.2	146.5	213.1
60	56.3	92.5	113.7	199.4
90	46.5	74.3	102.5	169.0
120	33.5	56.7	90.4	159.2
150	20.0	40.8	79.0	144.5
180	15.1	31.8	74.9	128.8
210	13.1	29.6	67.1	106.3
240	10.2	29.2	67.1	106.3

Table (A.5): residual nitrate concentrations as a function of different (D) values at HRT = 2 hour

(pH = 7, C_i = 200 mg-NO3/L, V = 40 V, TDS_i = 1000mg/l, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

Time	D=2cm	D=3cm	D=4cm	D=5cm
0	200.0	200.0	200.0	200.0
15	184.7	194.5	171.4	184.7
30	179.2	188.6	156.1	169.0
60	172.9	176.3	143.9	145.3
90	160.6	169.4	132.4	135.1
120	126.1	145.9	131.8	133.3
150	100.4	127.5	125.9	132.7
180	76.9	110.2	125.9	132.7
210	71.0	104.3	125.9	132.7
240	71.0	104.3	125.9	132.7

Table (A.6): residual nitrate concentrations as a function of different (D) values at HRT = 2.5 hour

(pH = 7, C_i = 200 mg-NO3/L, V = 40 V, TDS_i = 1000mg/l, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

Time	D=2cm	D=3cm	D=4cm	D=5cm
0	200.0	200.0	200.0	200.0
15	192.5	199.4	184.7	184.7
30	184.3	189.2	171.0	175.7
60	174.9	147.5	150.4	157.3
90	125.9	116.3	132.7	151.4
120	107.3	106.3	129.8	136.5
150	76.9	88.6	124.9	124.9
180	65.1	88.6	114.3	116.1
210	59.2	88.6	106.3	116.1
240	59.2	88.6	106.3	116.1

Table (A.7): residual nitrate concentrations as a function of different (D) values at HRT = 3 hour

(pH = 7, C_i = 200 mg-NO3/L, V = 40 V, TDS_i = 1000mg/l, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

Time	D=2cm	D=3cm	D=4cm	D=5cm
0	200.0	200.0	200.0	200.0
15	192.4	196.5	192.4	180.8
30	184.7	176.5	176.9	169.0
60	173.9	144.3	133.7	151.4
90	120.0	110.2	116.5	127.8
120	86.7	95.3	95.3	114.3
150	52.4	92.0	92.0	112.2
180	40.4	82.2	90.6	106.7
210	40.2	76.9	90.6	97.5
240	40.0	76.9	90.6	97.5

Table (A.8): residual nitrate concentrations as a function of different (V) values at HRT = 2 hour

(pH = 7, C_i 200 mg-NO3/L, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

Time	V=35V	V=40V	V=45V	V=50V
0	200.0	200.0	200.0	200.0
15	189.6	184.7	180.8	174.9
30	184.7	180.8	176.9	169.0
60	174.9	172.9	165.5	145.5
90	165.1	155.3	151.4	116.1
120	155.3	145.5	135.7	93.9
150	138.8	127.8	114.1	67.1
180	136.1	110.2	86.7	53.3
210	124.1	98.4	76.9	53.3
240	123.9	98.4	76.9	53.3

Table (A.9): residual nitrate concentrations as a function of different (V) values at HRT = 2.5 hour

(pH = 7, C_i 200 mg-NO3/L, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

Time	V=35V	V=40V	V=45V	V=50V
0	200.0	200.0	200.0	200.0
15	192.5	184.7	180.8	180.8
30	184.7	178.8	172.9	171.0
60	165.1	155.3	151.8	145.5
90	151.4	129.8	123.9	120.0
120	135.7	110.2	102.4	86.7
150	122.7	96.5	86.7	65.1
180	116.1	92.5	74.9	47.5
210	106.3	88.6	67.1	45.5
240	106.3	88.6	67.1	45.5

Table (A.10): residual nitrate concentrations as a function of different (V) values at HRT = 3 hour

(pH = 7, C_i 200 mg-NO3/L, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

Time	V=35V	V=40V	V=45V	V=50V
0	200.0	200.0	200.0	200.0
15	198.4	196.5	188.6	184.7
30	190.4	180.8	180.8	174.9
60	160.0	144.3	125.9	122.0
90	134.3	110.2	102.4	93.7
120	120.2	93.3	71.6	48.2
150	105.9	86.7	50.0	40.0
180	100.4	84.5	49.4	31.8
210	96.5	78.8	49.4	31.8
240	96.5	78.8	49.4	31.8

Table (A.11): residual nitrate concentrations as a function of different (A_{eff}) values at HRT = 2 hour

(pH = 7, C_i = 200 mg-NO_3/L, TDS_i = 1000mg/l, V = 40 V, T_i = 25 ^{0}C and D=3cm).

Time	A_{eff}=47.1cm^2	A_{eff}=54 cm^2	A_{eff}=61.4 cm^2
0	200.0	200.0	200.0
15	189.8	188.2	186.7
30	174.9	177.0	179.0
60	155.3	163.7	172.2
90	135.7	149.4	163.1
120	125.9	140.1	154.3
150	116.1	121.1	126.1
180	102.4	99.4	96.5
210	96.5	84.7	72.9
240	96.5	78.2	67.1

Table (A.12): residual nitrate concentrations as a function of different (A_{eff}) values at HRT = 2.5 hour

(pH = 7, C_i = 200 mg-NO_3/L, TDS_i = 1000mg/l, V = 40 V, T_i = 25 ^{0}C and D=3cm).

Time	A_{eff}=47.1cm^2	A_{eff}=54 cm^2	A_{eff}=61.4 cm^2
0	200.0	200.0	200.0
15	184.7	187.3	189.8
30	174.9	178.3	181.8
60	147.5	157.3	167.1
90	125.9	140.7	155.5
120	116.1	125.3	134.5
150	106.3	98.5	90.8
180	98.4	83.1	67.8
210	88.6	66.7	44.7
240	88.6	61.5	42.5

Table (A.13): residual nitrate concentrations as a function of different (A_{eff}) values at HRT = 3 hour

(pH = 7, C_i = 200 mg-NO_3/L, TDS_i = 1000mg/l, V = 40 V, T_i = 25 ^{0}C and D=3cm).

Time	A_{eff}=47.1cm^2	A_{eff}=54 cm^2	A_{eff}=61.4 cm^2
0	200.0	200.0	200.0
15	180.8	182.7	184.7
30	161.2	168.0	174.9
60	135.7	144.8	153.9
90	112.2	116.1	120.0
120	102.4	96.8	91.2
150	86.7	79.6	72.5
180	84.5	67.0	49.4
210	76.9	55.9	34.9
240	76.9	49.3	25.9

Table (A.14): residual nitrate concentrations as a function of different (A_{eff}) values at HRT = 3.5 hour

(pH = 7, C_i = 200 mg-NO_3/L, TDS_i = 1000mg/l, V = 40 V, T_i = 25 ^{0}C and D=3cm).

Time	A_{eff}=47.1cm^2	A_{eff}=54 cm^2	A_{eff}=61.4 cm^2
0	200.0	200.0	200.0
15	184.7	183.6	182.5
30	146.5	151.6	156.7
60	113.7	125.7	137.6
90	102.5	108.5	114.5
120	90.4	88.6	86.9
150	79.0	67.2	55.3
180	74.9	59.2	43.5
210	67.1	46.3	25.5
240	67.1	38.0	16.9

Table (A.15): Residual nitrate concentrations as a function of different HRT values at C_i = 100 mg-NO_3/L

(pH = 7, V = 40 V, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

Time	HRT=2	HRT=2.5	HRT=3	HRT=3.5
0	200.0	200.0	200.0	200.0
15	186.7	199.4	184.7	184.7
30	174.9	189.2	176.5	146.5
60	155.3	147.5	144.3	113.7
90	151.4	116.3	112.2	102.5
120	135.7	106.3	102.4	90.4
150	129.8	88.6	86.7	79.0
180	113.3	88.6	84.5	74.9
210	96.5	88.6	78.8	67.1
240	96.5	88.6	78.8	67.1

Table (A.16): Residual nitrate concentrations as a function of different HRT values at C_i = 150 mg-NO_3/L

(pH = 7, V = 40 V, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

Time	HRT=2	HRT=2.5	HRT=3	HRT=3.5
0	150.0	150.0	150.0	150.0
15	145.5	143.5	128.8	126.9
30	130.2	127.8	113.5	110.2
60	106.3	102.4	94.5	92.5
90	93.1	90.6	80.8	74.3
120	82.2	80.6	72.4	56.7
150	77.8	72.9	57.6	40.8
180	69.0	55.7	51.4	31.8
210	57.6	47.5	37.6	29.6
240	57.6	47.5	37.6	29.2

Table (A.17): Residual nitrate concentrations as a function of different HRT values at C_i = 200 mg-NO_3/L

(pH = 7, V = 40 V, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

Time	HRT=2	HRT=2.5	HRT=3	HRT=3.5
0	200.0	200.0	200.0	200.0
15	186.7	199.4	184.7	184.7
30	174.9	189.2	176.5	146.5
60	155.3	147.5	144.3	113.7
90	151.4	116.3	112.2	102.5
120	135.7	106.3	102.4	90.4
150	129.8	88.6	86.7	79.0
180	113.3	88.6	84.5	74.9
210	96.5	88.6	78.8	67.1
240	96.5	88.6	78.8	67.1

Table (A.18): Residual nitrate concentrations as a function of different HRT values at C_i = 250 mg-NO_3/L

(pH = 7, V = 40 V, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

Time	HRT=2	HRT=2.5	HRT=3	HRT=3.5
0	250.0	250.0	250.0	250.0
15	223.9	248.4	249.2	243.5
30	212.2	237.6	237.3	213.1
60	191.6	220.0	195.9	199.4
90	157.3	181.8	150.2	169.0
120	146.5	149.4	130.4	159.2
150	145.5	143.5	126.9	144.5
180	145.5	141.8	116.3	128.8
210	145.5	130.8	116.3	106.3
240	145.5	130.8	116.1	106.3

Table (A.19): Residual nitrate concentrations as a function of different HRT values at V= 35V .

(pH = 7, C_i = 200 mg-NO3/L, TDS_i = 1000 mg/l, D = 3cm, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

Time	HRT=2	HRT=2.5	HRT=3
0	200.0	200.0	200.0
15	189.6	192.5	198.4
30	184.7	184.7	190.4
60	174.9	165.1	160.0
90	165.1	151.4	134.3
120	155.3	135.7	120.2
150	138.8	122.7	105.9
180	136.1	116.1	100.4
210	124.1	106.3	96.5
240	123.9	106.3	96.5

Table (A.20): Residual nitrate concentrations as a function of different HRT values at V= 40V .

(pH = 7, C_i = 200 mg-NO3/L, TDS_i = 1000 mg/l, D = 3cm, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

Time	HRT=2	HRT=2.5	HRT=3
0	200.0	200.0	200.0
15	184.7	184.7	196.5
30	180.8	178.8	180.8
60	172.9	155.3	144.3
90	155.3	129.8	110.2
120	145.5	110.2	93.3
150	127.8	96.5	86.7
180	110.2	92.5	84.5
210	98.4	88.6	78.8
240	98.4	88.6	78.8

Table (A.21): Residual nitrate concentrations as a function of different HRT values at V= 45V.

(pH = 7, C_i = 200 mg-NO3/L, TDS_i = 1000 mg/l, D = 3cm, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

Time	HRT=2	HRT=2.5	HRT=3
0	200.0	200.0	200.0
15	180.8	180.8	180.8
30	176.9	172.9	171.0
60	165.5	151.8	145.5
90	151.4	123.9	120.0
120	135.7	102.4	86.7
150	114.1	86.7	65.1
180	86.7	74.9	47.5
210	76.9	67.1	45.5
240	76.9	67.1	45.5

Table (A.22): Residual nitrate concentrations as a function of different HRT values at V= 50V .

(pH = 7, C_i = 200 mg-NO3/L, TDS_i = 1000 mg/l, D = 3cm, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

Time	HRT=2	HRT=2.5	HRT=3
0	200.0	200.0	200.0
15	174.9	180.8	184.7
30	169.0	171.0	174.9
60	145.5	145.5	122.0
90	116.1	120.0	93.7
120	93.9	86.7	48.2
150	67.1	65.1	40.0
180	53.3	47.5	31.8
210	53.3	45.5	31.8
240	53.3	45.5	31.8

Table (A.23): Residual nitrate concentrations as a function of different HRT values at D= 2cm .

(pH = 7, C_i = 200 mg-NO3/L, TDS_i = 1000 mg/l, V = 40 V, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

Time	HRT=2	HRT=2.5	HRT=3
0	200.0	200.0	200.0
15	184.7	192.5	192.4
30	179.2	184.3	184.7
60	172.9	174.9	173.9
90	160.6	125.9	120.0
120	126.1	107.3	86.7
150	100.4	76.9	52.4
180	76.9	65.1	40.4
210	71.0	59.2	40.2
240	71.0	59.2	40.0

Table (A.24): Residual nitrate concentrations as a function of different HRT values at D= 3cm.

(pH = 7, C_i = 200 mg-NO3/L, TDS_i = 1000 mg/l, V = 40 V, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

Time	HRT=2	HRT=2.5	HRT=3
0	200.0	200.0	200.0
15	194.5	199.4	196.5
30	188.6	189.2	176.5
60	176.3	147.5	144.3
90	169.4	116.3	110.2
120	145.9	106.3	95.3
150	127.5	88.6	92.0
180	110.2	88.6	82.2
210	104.3	88.6	76.9
240	104.3	88.6	76.9

Table (A.25): Residual nitrate concentrations as a function of different HRT values at D= 4cm .

(pH = 7, C_i = 200 mg-NO3/L, TDS_i = 1000 mg/l, V = 40 V, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

Time	HRT=2	HRT=2.5	HRT=3
0	200.0	200.0	200.0
15	171.4	184.7	192.4
30	156.1	171.0	176.9
60	143.9	150.4	133.7
90	132.4	132.7	116.5
120	131.8	129.8	95.3
150	125.9	124.9	92.0
180	125.9	114.3	90.6
210	125.9	106.3	90.6
240	125.9	106.3	90.6

Table (A.26): Residual nitrate concentrations as a function of different HRT values at D= 5cm .

(pH = 7, C_i = 200 mg-NO3/L, TDS_i = 1000 mg/l, V = 40 V, T_i = 25 ^{0}C and A_{eff} = 47.1 cm^2).

Time	HRT=2	HRT=2.5	HRT=3
0	200.0	200.0	200.0
15	184.7	184.7	180.8
30	169.0	175.7	169.0
60	145.3	157.3	151.4
90	135.1	151.4	127.8
120	133.3	136.5	114.3
150	132.7	124.9	112.2
180	132.7	116.1	106.7
210	132.7	116.1	97.5
240	132.7	116.1	97.5

Table (A.27): Residual nitrate concentrations as a function of different HRT values at A_{eff}= 47.1cm^2 .

(pH = 7, C_i = 200 mg-NO3/L, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C and V=40 V).

Time	HRT=2	HRT=2.5	HRT=3	HRT=3.5
0	200.0	200.0	200.0	200.0
15	189.8	184.7	180.8	184.7
30	174.9	174.9	161.2	146.5
60	155.3	147.5	135.7	113.7
90	135.7	125.9	112.2	102.5
120	125.9	116.1	102.4	90.4
150	116.1	106.3	86.7	79.0
180	102.4	98.4	84.5	74.9
210	96.5	88.6	76.9	67.1
240	96.5	88.6	76.9	67.1

Table (A.28): Residual nitrate concentrations as a function of different HRT values at A_{eff}= 54cm^2.

(pH = 7, C_i = 200 mg-NO3/L, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C and V=40 V).

Time	HRT=2	HRT=2.5	HRT=3	HRT=3.5
0	200.0	200.0	200.0	200.0
15	188.2	187.3	182.7	183.6
30	177.0	178.3	168.0	151.6
60	163.7	157.3	144.8	125.7
90	149.4	140.7	116.1	108.5
120	140.1	125.3	96.8	88.6
150	121.1	98.5	79.6	67.2
180	99.4	83.1	67.0	59.2
210	84.7	66.7	55.9	46.3
240	78.2	61.5	49.3	38.0

Table (A.29): Residual nitrate concentrations as a function of different HRT values at A_{eff}= 61.4cm^2.

(pH = 7, C_i = 200 mg-NO3/L, TDS_i = 1000mg/l, D = 3cm, T_i = 25 ^{0}C and V=40 V).

Time	HRT=2	HRT=2.5	HRT=3	HRT=3.5
0	200.0	200.0	200.0	200.0
15	186.7	189.8	184.7	182.5
30	179.0	181.8	174.9	156.7
60	172.2	167.1	153.9	137.6
90	163.1	155.5	120.0	114.5
120	154.3	134.5	91.2	86.9
150	126.1	90.8	72.5	55.3
180	96.5	67.8	49.4	43.5
210	72.9	44.7	34.9	25.5
240	67.1	42.5	25.9	16.9

Appendix (B)

- **Continuous experiment : Real water (ground water sample)**

Table (A.30): Residual nitrate concentrations as a function of different TDS_i values .

Time	TDS_i=700	TDS_i=800	TDS_i=900	TDS_i=1000
0	200.00	200.00	200.00	200.00
15	188.63	194.51	194.51	184.71
30	178.82	184.71	184.71	174.90
60	172.16	176.86	157.06	161.18
90	169.02	165.10	143.53	151.37
120	164.12	155.29	141.57	137.25
150	162.75	145.49	135.69	119.41
180	149.41	130.78	121.96	101.18
210	140.59	125.88	106.27	76.27
240	117.84	110.78	96.47	59.22
300	99.80	86.67	70.86	46.08
360	98.43	76.86	59.14	45.57
420	96.47	67.06	48.43	41.57
480	96.47	67.06	48.43	41.57

Appendix (C)

Figures

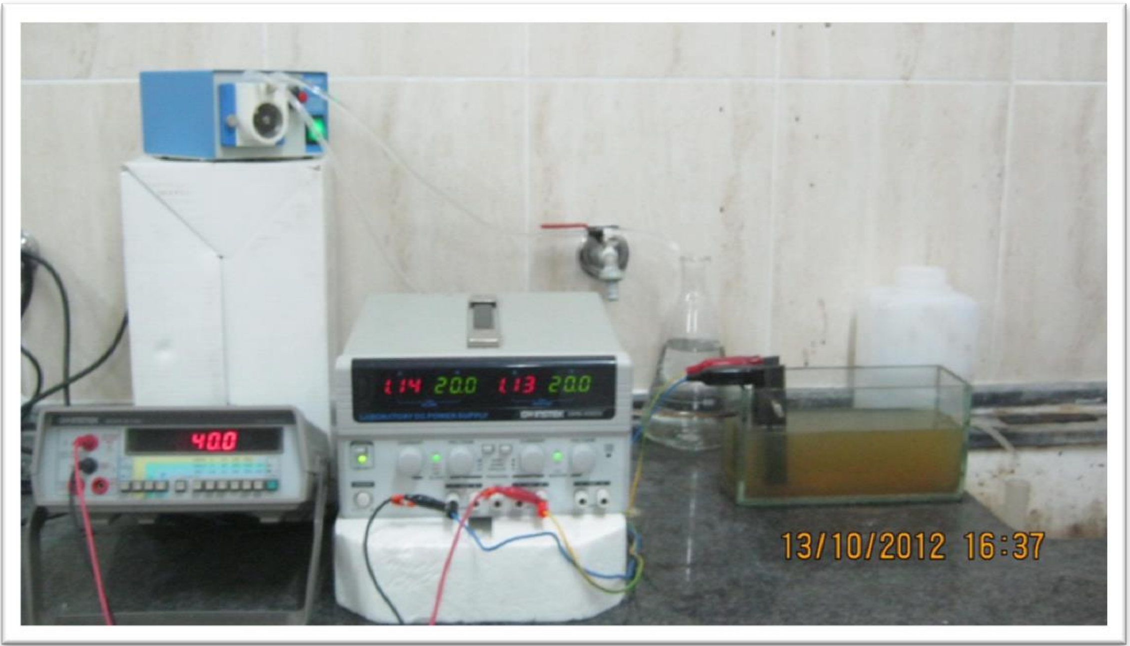

Fig. (A.2) Electrocoagulation cell

Fig. (A.2) Peristaltic pump

Fig. (A.3) DC-Power supply

(GWINSTEK GPS 3303 0-60V 0-3A)

Fig. (A.4) Multi-meter

(GWINSTEK GDM -8135)

Fig. (A.5) CT-2600 spectrophotometer

Fig. (A.6) pH meter

(HI 3221 pH/OP/ISE) Meter

Fig. (A.7) EC Meter

(BDDS-307W MICROPROC ESSOR CONDUCTIVITY METER)

Fig. (A.8) Turbidity meter

(HI 93703 MICROPROCESSOR TURBIDITY METER)

Fig. (A.9) Laboratory chemicals