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Evaluation of Electrocoagulation for the Removal of Chromium (VI) From Brackish Groundwater

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UAEU College of Engineering

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Department of Chemical and Petroleum Engineering

EVALUATION OF ELECTROCOAGULATION FOR THE REMOVAL OF CHROMIUM (VI) FROM BRACKISH GROUNDWATER

Shaima S. Hamdan

This thesis is submitted in partial fulfillment of the requirements for the Master of Science in Chemical Engineering degree

Under the direction of Professor Muftah H. El-Naas

February 2014

Declaration of Original Work

I, Shaima Subhi Hamdan, the undersigned, a graduate student at the United Arab Emirates University (UAEU) and the author of the thesis titled "Evaluation of Electrocoagulation for the Removal of Chromium (VI) from groundwater", hereby solemnly declare that this thesis is an original work done and prepared by me under the guidance of Prof. Muftah H. El-Naas, in the College of Engineering at UAEU. This work has not been previously formed as the basis for the award of any degree, diploma or similar title at this or any other university. The materials borrowed from other sources and included in my thesis have been properly acknowledged.

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Abstract

Electrocoagulation (EC) has been evaluated for the removal of Cr (VI) from brackish groundwater using three different bench-scale EC reactors, namely batch stirred tank reactor (BSTR), continuous stirred tank reactor (CSTR) and a continuous electrocoagulation column (ECC). Batch EC process was experimentally examined at room temperature and the results indicated that Fe-Fe electrode pair was the most efficient arrangement and was able to achieve 100 % Cr removal at an electrocoagulation time of 5 minutes, a current density of 7.94 mA/cm^2, and pH of 8. A kinetic study of batch EC was then performed using both pseudo-first-order and pseudo-second-order models. It was confirmed that removal of chromium by EC follows pseudo-first-order models. In all conditions SSE was minimized below 3.696. The generated sludge was characterized using EDS, X-ray fluorescence (XRF) and FE-SEM. The analysis confirmed the formation and precipitation of $Fe(OH)_3$ and $Cr(OH)_3$ as solids. The efficiency of different inlet flow rate was also assessed for both continuous CSTR and ECC, and indicated that 90 mL/min was the most efficient flow rate when continuous stirred EC (CSTR) reactor is used, and 30 mL/min using continuous column EC (ECC), at Fe/Fe pairs and room temperature 25 ^{0}C. The study affirmed that the new innovative ECC process improves the removal efficiency of chromium with lowest estimated energy consumption of 0.75 kWh/m^3 and dissolved iron of 0.185 mg/l with an electrical cost of 0.030 US \$/m^3 of treated groundwater. Overall, the study affirmed that electrocoagulation is a reliable, environmentally compatible technique for the purification of groundwater.

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Dedication

This thesis is dedicated to:

My parents, Subhi Hamdan and Mona Abduljabaar,

My sisters, Rana, Hiba and Essra,

My brothers, Abdulatife and Mohammed,

and to all those who supported me during this journey.

List of Publications and Oral Presentations

Journal Papers	Hamdan, S. S., **M. H. El-Naas,** Characterization of the removal of Chromium (VI) from groundwater by electrocoagulation, *Journal of Industrial and Engineering Chemistry,* DOI 10.1016/j.jiec.2013.11.006
	Hamdan, S. S., **M. H. El-Naas**, Assessment of a continuous Electrocoagulation Column (ECC) for the purification of groundwater, Separation and Purification Technology, Under review.
Conference Proceedings	**El-Naas, M. H.** and S. S. Hamdan, Assessment of Electrocoagulation for the Removal of Cr (VI) from Groundwater, The *2nd International Conference on Chemical Engineering and Applications (CCEA 2011)*, Male, Maldives, November 2011.
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	Hamdan, S. S., and **M. H. El-Naas**, Removal of Cr(VI) from Brackish Groundwater Using Electrocoagulation, *The 1st International Conference on Desalination and Environment,* Abu Dhabi, UAE, November 2011.

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List of Symbols and Abbreviations

ACD	Applied Current Density (mA/cm^2)
[CC]	Pollutant concentration
C_0	Initial chromium concentration (mg/L)
C_f	Final chromium concentration (mg/L)
CSTR	Continuous stirred reactor
DC	Direct current
EC	Electrocoagulation Process
ECC	Electrocoagulation Column Process
EDS	Energy Dispersive X-ray Spectroscopy
EEC	Electrical Energy Consumption (kWh/m^3)
F	Faraday's constant (96,500 C/mol)
FE-SEM	Field Emission Scanning Electron microscope
I	Operating current (A)
K	Conductivity (μs/cm)
M	Molecular weight of sacrificial anode (g/mol)
m	Amount of electrode material dissolved (g of metal/cm^2)
q_{air}	Air flow rate (L/min)
q_L	Influent flow rate (m^3/h)
$-r_{cr}$	Removal rate of chromium (mg/L.min)
T	Reaction time (h)
TDS	Total dissolved suspended particles (g/L)
t_{EC}	Electrolysis time (second)
V	Operating voltage (kV)
v	Volume of wastewater (m^3)
X	Chromium removal ($x = [C_0 - C_f]/C_0$).
XRF	X-ray Fluorescence
Z	Number of electrons in oxidation/reduction reaction
ZSV	Zone settling velocity

Chapter One

Introduction

"Try to learn something about everything and everything about something"

Thomas Huxley, (1825-1895)

In most parts of the world, there is always a need for large quantities of water with different levels of quality that may be used for drinking, irrigation, industrial applications or other domestic uses. On the other hand, main water sources such as surface water and groundwater are being constantly polluted through the accumulation of hazardous contaminants and dangerous heavy metals from industrial effluents as well as other natural processes. The treatment and re-use of wastewater has become an absolute necessity. There is, therefore, an urgent need to develop effective and inexpensive techniques to purify different water sources.

Chromium compounds that have harmful effects on all living forms are extensively used in chrome plating, leather tanning, and manufacturing of cement [1-3]. Chromium occurs primarily in two states: hexavalent Cr(VI) and trivalent Cr(III), that are characterized by different chemical behaviors and toxicity. Hexavalent chromium Cr(VI) is certainly more harmful to humans and animals. It has severe risks in terms of toxicity, including skin irritation, and kidney failure , in addition to the carcinogenic effect [4]. To meet environmental regulations, effluent of wastewater contaminated with chromium compounds must be treated before discharge. One of the most underexploited treatment technologies is the electrocoagulation (EC), which has established itself as a convenient, efficient, economical and compact alternative to conventional chemical and other traditional methods. A major advantage of EC is the low occurrence of secondary pollution by in-situ generation of coagulants [5]. Also, EC is characterized by high separation efficiency due to the generation of oxygen and hydrogen bubbles in a compact frame [6]. Such features make this technology especially attractive for use in facilities where purifications in limited space are desired.

During the last decade, considerable amount of research has been focused on understanding the mechanisms of chromium removal from different sources of wastewater by electrocoagulation processes. The extensive experimental work carried out using this technique has so far confirmed the effectiveness of EC for chromium removal from industrial, electroplating, textile and synthesized wastewater. However, no one had studied the chromium removal from groundwater by EC process, with very little had been done to establish the kinetics of the EC process.

From that point of view, the present research herein aims to address the performance of electrocoagulation process for the treatment of chromium contaminated groundwater. Three different bench-scale EC reactor configurations were experimentally tested. First, the efficiency of batch stirred EC process was examined for the removal of chromium from groundwater for different operating parameters and the results were analyzed in order to establish the kinetics of chromium removal by the EC process. The study was then further extended to the continuous mode to assess flow dynamics and evaluate removal efficiency at different flow conditions. Finally, an innovative electrocoagulation column (ECC) reactor was tested for the removal of chromium at different feed flow rates and operating conditions. The flow behavior and chromium removal efficiencies were then compared for the two flow reactors.

The results of this research represent an important contribution to knowledge as they offer a better understanding of the chromium removal and its kinetics from groundwater in an electrocoagulation process. In addition, the study assesses a new reactor design (EEC) for the treatment of wastewater that is believed to be more efficient than conventional electrocoagulation cells. The effect of initial pH, applied current density (ACD), initial chromium concentration, and electrode types on the removal of chromium were analyzed for all reactors, in addition to the effect of influent flow rate, temperature and air mixing flow rate for the continuous EC processes.

Chapter Two

Literature Review

"Life is a succession of lessons which must be lived to be understood"

Helen Keller, (1880-1968)

2. Literature review on Electrocoagulation

In this chapter, the fundamentals of electrocoagulation and EC reactor design are introduced. The concepts and reactions occurring in such system, process mechanisms, parameters affecting EC and interpretation are explained. This section starts with a brief discussion about the sources of chromium exposure and its concentrations indifferent aqueous sources, including environmental restrictions by means of both water quality and wastewater disposal. This is followed by a brief comparison between electrocoagulation and other conventional methods that have been used to remove chromium from different types of wastewater. At the end of this section, the specific chromium reactions that occurs in-situ by EC reactions have been explained, relevant operational parameters, advantages and disadvantages of the process.

2.1. Chromium species in Aqueous Solution

Chromium is an inorganic metallic element that generally exists in water with two stable oxidation states: trivalent chromium Cr (III) and hexavalent chromium Cr (VI), which are characterized by different chemical behaviors and toxicity. Hexavalent chromium is known to be highly toxic and carcinogenic, with high solubility in aqueous medium [2, 7]. On the other hand, trivalent chromium Cr (III) is much less toxic, has low solubility in aqueous solutions and readily precipitates as $Cr(OH)_3$ at pH values greater than 4, and would be a concern in drinking water only at very high concentrations. Therefore, chromium reduction is the main phenomenon to eliminate it from polluted aqueous medium ,since it converts toxic mobile Cr(VI) into less toxic immobile Cr(III) [7].

2.1.1. Sources of Chromium Exposure

Chromium compounds are found naturally in rocks, plants, soil and volcanic dust, humans and animals. Human beings can be exposed to chromium by breathing air, drinking water, or eating food contaminated with chromium, or through skin contact with chromium compounds. The occurrence of chromium forms in aqueous systems, especially groundwater is often attributed to industrial disposal that associated with industrial activities. Occupational sources of chromium exposure (with chemical forms of interest shown by checked mark) are shown in Table 2.1.

Table 2.1.Sources of chromium compounds in wastewater by industrial activities [2, 4, 8].

Industrial activity	**Hexavalent chromium**	**Trivalent chromium**
Stainless steel welding	✔	
Ferrochrome industry	✔	✔
Chrome pigments	✔	✔
Leather tanning		✔

2.1.2. Environmental Regulations

There is a growing environmental concern for new water treatment technologies as fresh water sources are polluted. These concerns are attributed to the presence of pollutants, such as carcinogenic chemicals, organic matter and oils, which have adverse impacts once the contaminated water is discharged into the environment.

Unlike most organic pollutants, metals are particularly problematic because they are not biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain. Although at low doses some heavy metals are essential micronutrients for plants and animals, in higher doses they can detrimentally affect the health of most living organisms [9, 10]. Due to the harmful effects of chromium compounds, described in Section 2.1, governments apply enhanced regulation for chromium species. Worldwide authorities have fixed more stringent requirements concerning their presence in drinking water (Table 2.2). Fortunately, the remarkable growth in economics and living standards has accelerated the development of water and wastewater purification technologies.

Table 2.2 International regulation criteria.

Country	Total Cr in drinking water (mg/L)	Reference
US	0.1	US EPA [11]
International	0.05	WHO [12]
Canada	0.05	HC [13]

The natural total chromium content of different water sources are shown in Table 2.3. As it was reported in government documents, chromium concentration in groundwater is approximately in the range from 0.0002 mg/L to 0.148 mg/L. Even though these concentrations are in dilution range the treatment still required to reduce chromium below international regulations.

Table 2.3 Natural total chromium concentrations of various water sources.

Country	Water source	Chromium concentration (mg/L)	References
UAE/ Al Ain	Groundwater	0.0004 – 0.148	[14]
USA	Surface water	0.084	[15]
USA	Groundwater	0.0002-0.05	[16]
Canada	Surface water	0.0002-0.044	[12]
India	Groundwater	<0.0002	[17]

2.2. Electrocoagulation Versus other Cr(VI) Reduction Methods

Researchers have been striving to develop advanced technologies for the removal of toxic chromium species from wastewater. Various methods have been proposed and applied toward the attainment of this goal (Table 2.4), including ion exchange [18-20], Adsorption [21-24], chemical precipitation [25-28], biological reduction via bacteria [29, 30], membranes [31-33], solvent extraction [34] and chemical precipitation [35]. Although each of these techniques has its own distinct advantages, the high treatment cost and low efficiency in one or more areas does not completely resolve the outstanding environmental problems. Even thought the cost of adsorption by activated carbons seems to be low, the process still suffers from high operation cost due to regular regenerations [36].

Table 2.4 Electrocoagulation for Cr(VI) reduction versus other methods.

Method	Cost Per 1,000 gal	Treatment efficiency	Reference
Electrocoagulation	$ 1.69	100 %	[1]
Chemical coagulation	$ 14.18	-	[37]
Ion exchange	$ 6685 – 13370	>98.5 %	[20]
Adsorption/ Activated carbon	$ 0.7-1.2 per pound of activated carbon	70%-99%	[23, 24]
Ultrafiltration	-	93 %	[38]
Nanofiltration	-	88 %	[39]

As documented by Chen and Hung [40], using electricity to treat water was first proposed in England in 1889, and the application of electrolysis in mineral beneficiation was patented by Elmore in 1904. Electrochemical technologies can be regarded nowadays as established technologies due to their versatility and environmental compatibility, which makes the treatments of water possible.

Electrochemical processes categorized to electrocoagulation (EC), electroflotation (EF) and electrodissolution. Among these methods, the electrocoagulation technique has attracted a renewed interest in the search for cost-effective alternative to conventional technologies. Hence, ideal electrocoagulation strategies seeking low-cost electrode materials and easier sludge handling methods must be considered to make electrocoagulation more economically competitive [41].

2.3. Electrocoagulation Wastewater Treatment

Electrocoagulation (EC) with aluminum and iron electrodes was patented in the United States in 1909. At that time, because of the relatively large capital investment and the expensive electricity supply, electrocoagulation wastewater technologies did not find wide application worldwide. With the ever increasing standard of drinking water supply and the stringent environmental regulations regarding the wastewater discharge, electrocoagulation technology has regained its importance worldwide during the past two decades. The electrocoagulation (EC) process can be defined as a wastewater treatment technique that works through destabilizing suspended or dissolved contaminants in an aqueous medium by introducing a current into the medium whereas indirect electrolysis occur as dissolved redox reagent is generated in-situ from an appropriate anode material (Aluminum , or Iron) [42]. A schematic diagram of the simplest bench-scale EC reactor is shown in Fig. 2.1.

Electrocoagulation has been applied for the treatment of a broad range of wastewaters with various contaminants. Typical examples include: oily wastewater

[43, 44], fluorination of water [5, 45], heavy metal containing solution such as Ne, Cr, Cu [46, 47], dye and textile wastewater [3, 48], chemical oxygen demand [49, 50], synthetic detergent effluents [5] and potable water [51, 52].

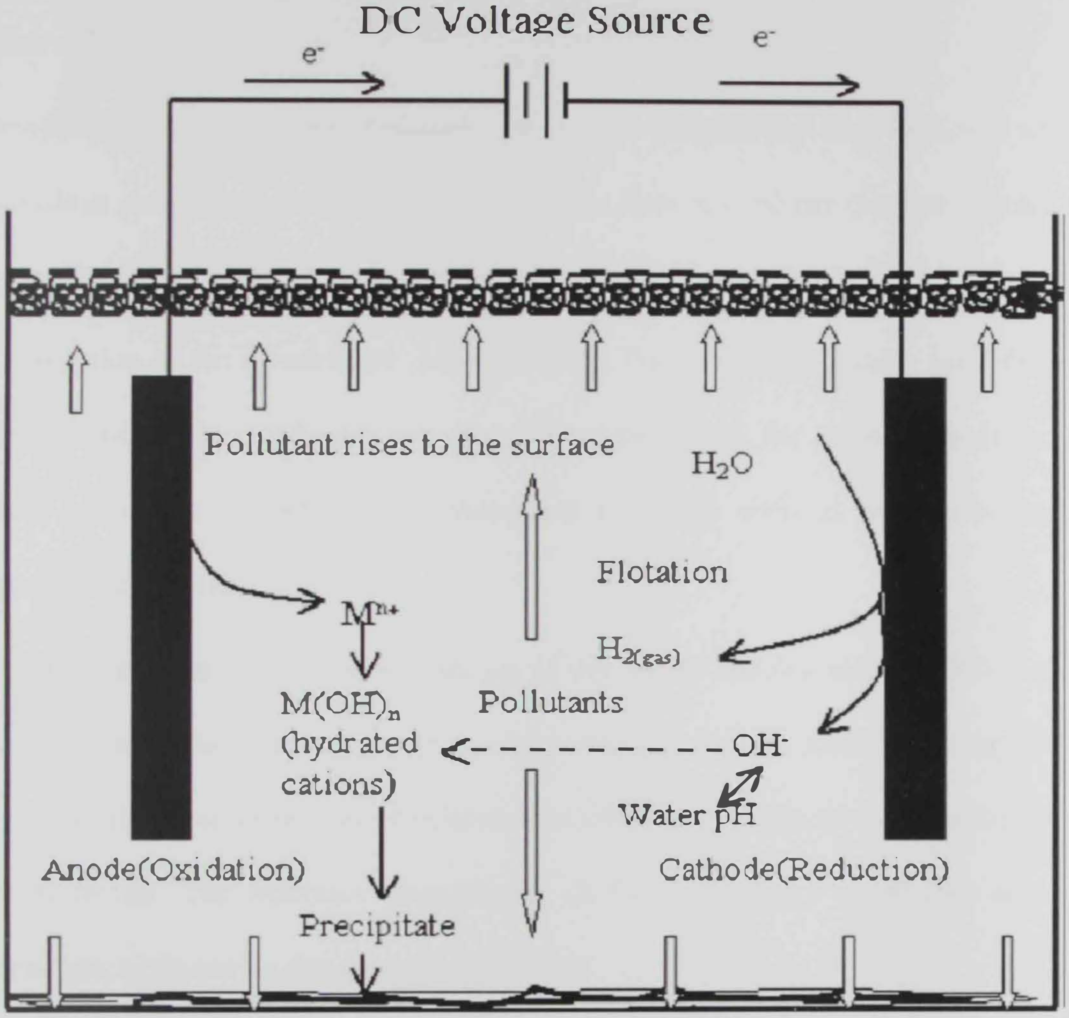


Fig.2.1 A schematic diagram of a bench-scale electrocoagulation (EC) [5].

2.3.1. General Mechanism of Electrocoagulation

As mentioned previously, electrocoagulation (EC) is a complex process involving chemical and physical mechanisms operating simultaneously using consumable electrodes (sacrificial) to supply coagulation ions in-situ [53]. As the current passed through the electrodes, sacrificial metal anode (Al and/or Fe) is dissolved generating the respective metal ions, which immediately undergo the destabilization mechanism of particulate suspension that take a place in an EC reactor as follows [5]:

- Destabilization of the contaminants, particulate suspension and breaking of emulsions as compression of the diffuse double layer around the charged species by the interactions of ions generated by oxidation of the sacrificial anode
- Aggregation of the destabilized phases to form floc, creating a sludge cake that entraps and bridges colloidal particles still remaining in the aqueous medium. They are then removed by the subsequent processes such as sedimentation, filtration or flotation.

The simplest EC reactor is made up of one anode and one cathode. When a direct current is applied from an external power source, the anode material undergoes oxidation, while the cathode will be subjected to reduction or reductive deposition of elemental metals. The reactions occurring in an EC cell with a metal (M) as a sacrificial electrode can be summarized as follows:

At the cathode:

$$2H_2O_{(l)}+2e^- \rightarrow H_{2(g)}+2OH^- \qquad \textbf{(2.1)}$$

At the anode:

$$M_{(s)} \rightarrow M_{(aq)}{}^{n+}+ne^- \qquad \textbf{(2.2)}$$

$$2H_2O_{(l)} \rightarrow 4H_{(aq)}^{+} + O_{2(g)} + 4e^{-} \quad (2.3)$$

2.3.2. Chromium Reduction by Electrocoagulation

In spite of the success of electrocoagulation for treating different types of wastewater, its application as a possible technique for the treatment of contaminated groundwater is rather scarce in the literature. Therefore, the major objective of this study is to evaluate the potential of utilizing EC for the removal of Cr (VI) for brackish groundwater and optimize the operating conditions to reduce Cr (VI) concentration to be within the acceptable limit of 0.05 mg/L. Since Cr(III) is relatively innocuous and immobile, the reduction of Cr(VI) to Cr(III) and the formation of insoluble chromium precipitates are essential steps in remediating the Cr(VI) contaminated groundwater. Both iron (Fe) and aluminum (Al) can be used as sacrificial electrodes.

I- Iron electrode

The reactions taking place in an electrochemical cell when iron metal (Fe) used as sacrificial electrode can be described by the following equations [2]:

Anode reaction:

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^{-} \quad (2.4)$$

$$Fe^{2+}_{(aq)} + 2OH^{-}_{(aq)} \rightarrow Fe(OH)_{2(s)} \quad (2.5)$$

When the pH of the wastewater is between 6 and 8, Fe^{2+} ions form insoluble species onto which Cr(VI) ions are adsorbed and removed from the solution.

Direct electrochemical Cr (VI) reduction to Cr (III) and water electrolysis occurs at the Cathode:

$$Cr_2O_7^{2-} + 6e^- + 7H_2O \rightarrow 2Cr^{3+}_{(aq)} + 14OH^- \quad (2.6)$$

Moreover, there are several reactions occurring in the bulk solution. The Fe^{2+} dissolved at the anode reduces Cr (VI) to Cr (III):

$$Cr_2O_7^{2-} + 6Fe^{2+} + 7H_2O \rightarrow 2Cr^{3+}_{(aq)} + 6Fe^{3+} + 14OH^- \quad (2.7)$$

Subsequently, the hydroxide ions formed at the cathode increase the pH of the wastewater and may induce precipitation of Cr (III) in the form of its corresponding hydroxide in-site:

$$Cr^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Cr(OH)_{3(s)} \quad (2.8)$$

II- Aluminum electrodes

On the other hand, aluminum anodes are used to produce aluminum cations which form hydroxide species. The pollutants present in aqueous solution are destabilized and then adsorbed on the $Al(OH)_3(s)$ produced. The reactions involved during the electrocoagulation using Al electrode are as follows:

Anodic reaction:

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^- \quad (2.9)$$

Cathodic reaction:

$$3H_2O + 3e^- \rightarrow 3OH^-_{(aq)} + 3/2H_{2(g)} \quad (2.10)$$

Overall reaction in bulk solution:

$$Al^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Al(OH)_{3(s)} + 3/2H_{2(g)} \quad (2.11)$$

2.4. Factors Affecting Electrocoagulation

In general, the overall efficacy of an electrocoagulation technique is highly dependent on the chemistry of the aqueous medium, the type and amounts of pollutants, metal dissolution of sacrificial electrodes, flow rate and pH of the wastewater, electric current density, temperature of the solution and specific energy consumption.

2.4.1. Type of Electrodes

The electrode material has considerable effects on the performance of the electrocoagulation reactor. According to the literature, iron (Fe) and aluminum (Al) are the most widely used as sacrificial electrodes in EC process, due to low-cost and effectiveness to treat various types of wastewater [43, 54, 55]. In addition, these materials lower the dissolution potential of the anode and minimize the passivation of the cathode [47]. Depending on the pollutants of the wastewater, one of them is preferred.

As explained in Section (2.3.1), the generated metal ions immediately undergo further spontaneous reactions to produce the corresponding hydroxides. These compounds have strong affinity for dispersed particles as well as counter ions to cause coagulation. As shown in Table 2.5, the efficiency of using both aluminum and iron as sacrificial electrodes has been reported for the removal of chromium from different wastewater sources. The most effective chromium removal by EC technology was with Fe electrodes, and to reach a complete cleaning, it would need too much time including the possibility of metal re-dissolution, and enhanced power consumption. Whereas, using aluminum electrodes lower the removal rates and increased the power consumption [46, 56].

Table 2.5 Batch electrocoagulation for Cr(VI) reduction.

Wastewater Source	**Reactor capacity// $[Cr_o]$**	**Reactor type**	**Electrode Materials**	**Current density/ Voltage**	**Treatment efficiency**	**Reference**
Simulated wastewater heavy metals	2000 mL //10-50 mg/L	Batch bipolar	Al plates	0.3–1 mA/cm^2	70 %	[57]
Simulated Drinking water	900 mL// 5-25 mg/L	Batch	Al–stainless steel	0.01-0.05 mA/cm^2	98.2%	[58]
Simulated wastewater	560 mL//100 mg/L1	Batch	Al plates	2.3-20.7 V	49.6%	[59]
Metal plating	650 mL // 44.5 mg/L	Batch monopolar	Fe-Al	2.5-10 mA/cm^2	100%	[1]
Plating wastewater	400 mL//500 mg/L	Batch	Fe plates	10-40 mA/cm^2	>99%	[60]
Simulated wastewater	1200 mL//10-50 mg/L	Batch bipolar	Fe-steel	0.2-3 A	100%	[2]

2.4.2. Current density

Operating current density is very important in electrocoagulation because it is the only operational parameter that can be directly controlled. The amount of electrodes metal dissolved or deposited is dependent on the quantity of electricity passed through the electrolytic solution. The amount of metal dissolved (g of M cm^{-2}) can be derived from Faraday's law:

$$m = \frac{ACDt_{EC}M}{1000\ zF} \qquad \textbf{(2.12)}$$

Where m is the amount of electrode material dissolved (g of metal/cm^2); ACD is the applied current density (mA/cm^2); t_{EC} is the electrolysis time (second); M is the molecular weight of the electrode connected (g/mol); z is the number of electrons in oxidation/reduction reaction; and F is the Faraday's constant (96,500 C/mol).

From that, current density directly determines both coagulant dosage and bubble generation rates and strongly influences both solution mixing and mass transfer at the electrodes. In order for the electrocoagulation system to operate for a long period of time without maintenance, its applied current density is suggested to be 2 – 2.5 mA/cm^2 unless there are measures taken for a periodical cleaning of the surface of electrodes [61].

The electrical energy consumption (EEC) of the batch EC process can be determined by the equation given below [60]:

$$\mathrm{EEC}(^{\mathrm{kWh}}/_{\mathrm{m}^3}) = VIt/v \qquad (2.13)$$

Where V is the operating voltage (kV), I is the operating current (Ampere), t is the time of reaction (h) and v is the volume of wastewater (m^3).

Whereas for the continuous EC process, the electrical energy consumption can be determined by the equation given below:

$$\mathrm{EEC}(^{\mathrm{kWh}}/_{\mathrm{m}^3}) = \mathrm{VI}/q_L \qquad (2.14)$$

Where V is the operating voltage (kV), I is the operating current (Ampere), q_L is the influent flow rate (m^3/h). In addition, electrical energy costs were estimated for all applied current densities, based on the electrical costs in the UAE (0.15 Dhs/kWh).

2.4.3. pH of the Wastewater

According to the pH of the bulk solution, metal ions and hydroxide ions could be generated at the electrode surface forming various hydroxides and build up polymeric chemicals (Section 2.3.1). The solubility of these complex compounds also has a considerable influence on the performance of the electrocoagulation process. It has been established that the pH selection should be selected with other operating parameters such as electrode types, current density as well as flow rate to ensure high removal rate.

2.4.4. Temperature of the Solution

Although electrocoagulation has been around for over 100 years, the effect of temperature on this technology was not very much investigated, with only few studies on the effect of temperature on the performance of electrocoagulation process [62].

They reported a direct relation between the solubility of formed coagulant and the temperature, thus higher temperature increases the solubility and therefore decreases the removal efficiency, in spite of the fact that the temperature increase speeds up the destructive reaction of the oxide layer on the electrode surface and increases the current efficiency [63].

2.4.5. Inlet Flow Rate

The flow rate parameter is related to the residence time, which is the time that the wastewater stream is treated inside a continuous EC reactor, and thus it is related to the amount of dissolved electrode metal and the EC performance efficiency. At high influent flow rate, EC process provides short reaction time between the contaminant ions present in the wastewater and the sacrificial anode [64], thus giving less time to adsorb the flocs which tends to slow down the rate of anodic reactions [65]. In addition, enhancing the turbulence of the wastewater can reduce the effect of concentration over-potential, which is caused by the difference on electro-active species concentration between the bulk solution and electrode surface.

2.5. Advantages and Disadvantages of Electrocoagulation Process

EC system suffers from some drawbacks, such as the passivation of electrodes, limiting their performance and requiring regular replacement. The concentration of aluminum or iron ions in the effluent will most likely be increased, requiring careful pH control. In addition, high conductive wastewater is required [37]. Despite these drawbacks, electrocoagulation is still applicable for the treatment of wide range of wastewaters.

The most important advantage of EC treatment of metal ion pollutants is avoiding any addition of chemical substances hence reducing the possibility of secondary pollution [5, 47]. In addition to the following [5, 6, 42, 47]:

- The formed oxygen and hydrogen bubbles increase the efficiency of the separation process through flotation, by destabilizing suspended particles.
- Control of stream pH can be electrochemically achieved. Such control can avoid some side reactions or promote the production of desired products (for example, the production of $Cr(OH)_3$ during Cr(VI) reduction).
- Sludge production is minimized.
- Removal of a particular metal ion in mixtures of metal ions may be achieved in some cases.
- Operating costs are much lower when compared with most of the conventional technologies.
- The corresponding anodic reaction can be advantageously used; for example, undesirable agents such as cyanide may be destroyed at the anode of the same cell.
- Simple equipment, thus requiring less maintenance and easy automation. It is also environmentally compatible, and energy efficient.

Because of these advantages, EC system has been widely used to treat wastewater from different industries, such as municipal wastewater [54], textile [3], laundry [66], and refinery [43].

It is worth noting here that most studies in the literature on the removal Cr (VI) from wastewater have been carried out using synthetic water [2, 56, 67]; consequently, their results can differ with respect to those obtained with real wastewater due to the complexity of species present in the wastewater and their interference with the removal process [7]. In terms of chromium removal from groundwater, no studies have been reported in the literature so far in spite of the importance of groundwater as a source of drinking water.

Chapter Three

Materials & Methodology

"Believe you can and you're halfway there"
Theodore Roosevelt, (1848-1919)

3.1. Analytical Techniques

The groundwater samples used in this study were collected from farm wells (350 m in depth) located in Al-Ain, UAE. The characteristics of the collected groundwater samples (pH, conductivity, TDS, TSS, sulphate, chloride ions and chromium concentration) are presented in Table 3.1. The concentrations of different metals and ions: chromium (Cr), strontium (Sr), magnesium (Mg), cadmium (Cd), manganese (Mn), copper (Cu), zinc (Zn) and iron (Fe) were measured using Varian ICP Optical Emission Spectrometer, Model 710 ES.A HACH UV Spectrophotometer, Model DR-5000 HACH, Germany, was used for measuring the concentration of the photometric sulphate. The sulphate and Cr (VI) were measured according to US EPA Method (375.4) and Method (7196), respectively. A JENWAY bench conductivity/ TDS meter, Model (4510 JENWAY, UK) was used for the conductivity and TDS measurements of the samples. The pH of all samples were measured before and after the treatment using HANNA Checker pH meter (HI 98103, USA). The collected samples were classified as brackish groundwater due to the high conductivity (5,930 μs/cm) and high TDS (3.57 g/L).

Table 3.1 Characterization of groundwater.

Characteristic	**Cr (mg/L)**	**Sulfate (mg/L)**	**Cl- (mg/L)**	**κ (μs /cm)**	**TDS (g/L)**	**TSS (g/L)**	**pH**
Value	0.2	376	181	5,930	3.57	0.02	8

During experiments, samples were withdrawn from the reactor at distinct time intervals, filtered using Whatman filter paper (Grade 40) and then analyzed. In addition, zone settling velocity (ZSV) test of 250 ml of treated groundwater after electrocoagulation column (ECC) was conducted in graduated cylinder. The height of the interface between the sludge and clear water was plotted against time; (ZSV) was then calculated from the initial slope of the graph [68].

Different initial chromium concentrations were prepared by adding a specific mass of potassium dichromate to a set volume of groundwater and then treated in the EC reactor. Percentage chromium removal efficiency was calculated as follows:

$$\%\,\text{Chromium removal efficiency} = (C_o - C_f)/C_o * 100 \qquad (3.1)$$

Where C_o and C_f are the initial and final chromium concentrations in (mg/L), respectively.

To remove the thin passivation layer formed at the surface of the electrodes, electrodes surfaces were abraded with sand paper, washed with nitric acid then rinsed with distilled water, dried and weighted before and after each experiment. All experimental runs were repeated twice or three times and the average values are reported here.

3.2. Sludge Characterization

The sludge generated by the electrocoagulation of groundwater was filtered, dried at 60 ^{0}C for 24 h in an oven to avoid any phase modification. After that, the dried sludge was grinded to produce homogeneous powder, which was then coated with carbon using the auto carbon coater (JEC 560) to reduce the surface charge. The coated samples were characterized by Field Emission Scanning Electron Microscope FE-SEM (JSM-7001F) to evaluate the surface morphology with high resolution images. In situ qualitative and quantitative measurements of the coated samples were also carried out by energy dispersive X-ray spectroscopy (EDS) to determine the chemical composition. In addition, X-ray fluorescence (XRF) was used to determine the elemental composition of the powder.

3.3. Process Kinetics

In the process investigated, electrocoagulation kinetic models, namely, pseudo-first-order and pseudo-second-order were tested. The best-fit model was selected according to the linear regression correlation coefficient value, SS. Transient state was chosen to test these models. The experimental conditions where only two points of transient stage can be found were terminated from the models.

3.3.1. Pseudo-First-Order Model

Initially, the experimental data of all conditions were analyzed with pseudo-first-order model, given by the following equation [69]:

$$\frac{dx}{dt} = k_1(1 - x) \qquad \textbf{(3.2)}$$

Where k_1 is rate constant (min^{-1}), and x is chromium removal ($x=[C_0-C_f]/C_0$). Integrating Eq. (3.2), with initial boundary conditions and rearranging to obtain the following time dependence formula:

$$\ln\frac{1}{1-x} = k_1 t \qquad \textbf{(3.3)}$$

The value of $\ln\frac{1}{1-x}$ versus t was plotted, from which k_1 can be determined by the slope of the plot.

3.3.2. Pseudo-Second-Order Model

The kinetic data were also fitted to the pseudo-second-order model. The pseudo-second-order equation is given by Eq. (3.4) [69]:

$$\frac{dx}{dt} = k_2(1 - x)^2 \qquad (3.4)$$

Where x is removal of chromium, and k_2 is rate constant (min^{-1}). Integrating Eq. (3.4), the value of $\frac{x}{(1-x)}$ vs. t was plotted for each parameter and the value of rate constant for each parameter was founded.

Chapter Four

Results and Discussion

"All life is an experiment. The more experiments you make the better"
Ralph Waldo Emerson, (1803-1882)

Performance of the electrocoagulation process is highly dependent upon the electrolyte dosage and solution resistance potential. In the EC cell, as the current pass through the metal electrodes it creates resistance causing a voltage drop known as IR-drop [70], which can reduce the performance of the EC. In order to limit the IR-drop, conductivity of the solution should be sufficiently high [71]. It has been reported that chloride anion and sulphate could enhance the conductivity of the solution [1, 72] which in turn influences the current density, voltage and power consumption. In addition, the percent of chloride anions could significantly reduce the adverse effects of other anions, such as HCO_3^-. Indeed, the existence of carbonate anion would lead to the precipitation of Ca^{2+} ion that can form an insulating layer at the surface of the cathode, thus could increase the Ohmic resistance of the electrocoagulation cell and consequently affect removal efficiency [48].

As shown in Table 3.1, the collected groundwater samples can be characterized as brackish water with high electrical conductivity of 5,930 µs/cm thus plays a key role in enhancing the current flow. At the same time, the presence of sulphate and chloride ions improves the dissolution of a sacrificial anode by pitting corrosion and avoids the anode passivity which consequently improves EC performance at short operation time [72].

4.1. Batch Process

The performance of batch electrocoagulation process has been widely tested to remove different types of contaminant. Balla et. al. [73] studied a combined system consist of electrocoagulation/flotation reactor to remove COD and color from synthetic and real textile wastewater. Lacasa et. al. [74] treated groundwater from nitrate by stirrer EC. Others were interested in removing of chromium from synthesized wastewater as shown in Table 2.5 [58]; others have evaluated the removal of chromium combined with different heavy metals such as copper, zinc, and nickel from synthetic wastewater [67] and metal plating [1], respectively.

No studies were reported in the literature on the treatment of contaminated groundwater by batch EC process. It was therefore thought prudent to investigate the removal of Cr(VI) from groundwater by bench-scale EC using two electrodes. In this section, the effect of operating parameters such as electrode materials, pH, ACD and initial concentration of the solution on Cr(VI) removal performance was experimentally studied. Then, removal kinetic models were tested and rate coefficients and removal rate were obtained for the selected model.

4.1.1. Batch EC Procedure

The electrocoagulation experiments were conducted using a batch Plexiglas cylindrical reactor (ID = 150 mm; H = 150 mm) with a total volume of 2,649 ml. The total volume of the treated groundwater in each experiment was 1000 ml; two materials of rectangular metal electrodes (Fe and/or Al) were used with dimensions of

63 mm X 50 mm X 2 mm and a total anode surface area of 6300 mm^2 (63 cm^2). The metal electrodes were placed at fixed distance between the electrodes in the middle of the reactor and connected to a DC power supply (Popular PE-23005). A schematic diagram of the experimental set-up is shown in Fig.4.1. All experiments were carried out at room temperature (25 ^{0}C).

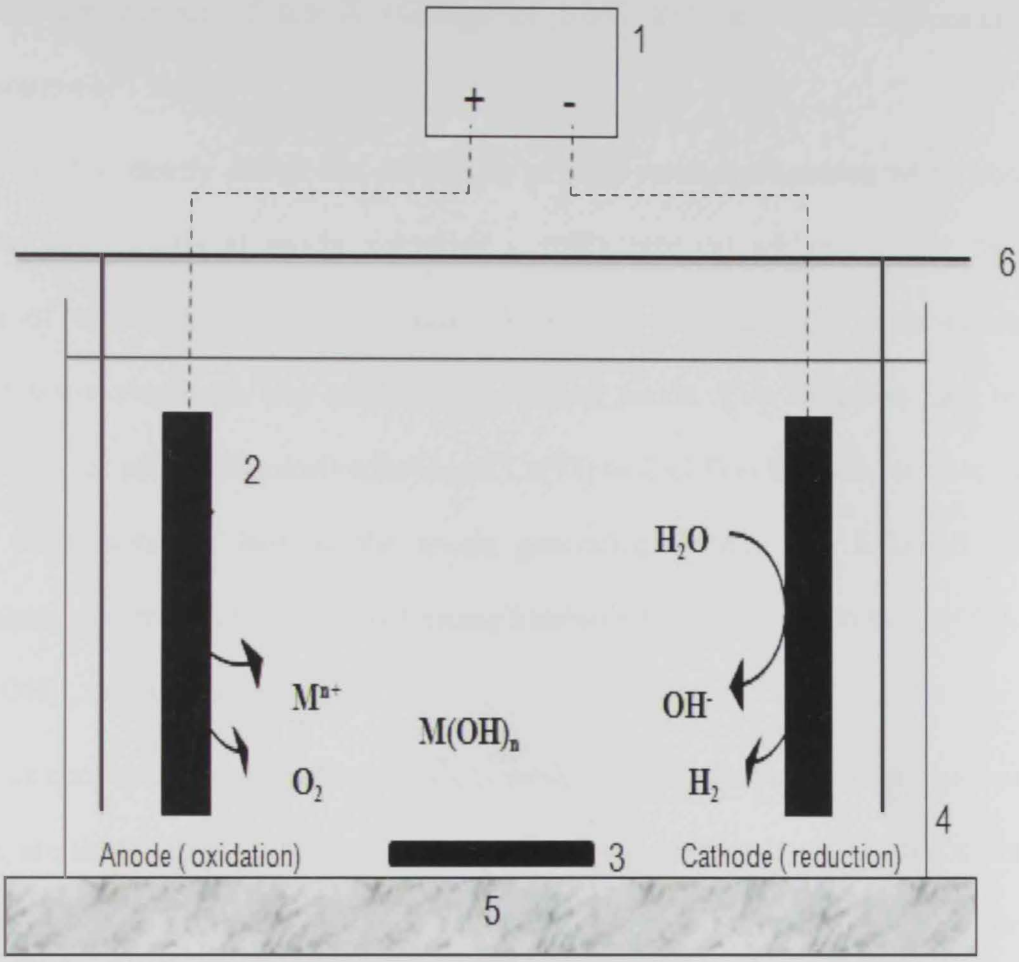


Fig.4.1. A schematic diagram of the batch electrochemical apparatus: 1- DC power supply, 2- Metal electrodes, 3- Magnetic bar stirrer, 4- Plexiglas beaker, 5- Magnetic stirrer, 6-Plexiglas cover.

4.1.2. Effect of Electrode Material

To get deep understanding on the reduction mechanism of Cr (VI) from groundwater using iron and/or aluminum electrodes, different anode/ cathode configurations: Fe/Fe, Al/Al, and Fe/Al were used in this section to carry out electrocoagulation test. Each experiment, with 63 cm^2 electrode area, was conducted at a constant current of 0.5 A (voltage of 0.007 kV) and initial chromium concentration of 1 mg/L.

Fig.4.2. clearly shows that chromium removal was instantaneous when iron was used as a sacrificial anode, achieving a 100% removal within the first few minutes of operation. During the same coagulation time, the EC performance declined when aluminum was used as a sacrificial anode. This behavior may be attributed to the electrochemical reduction of Cr(VI) to Cr(III) at the cathode as well as the dissociation of iron at the anode generating Fe(II) ions, followed by electrochemical reaction with Cr(VI) forming insoluble hydroxide products ,$Cr(OH)_3$ and $Fe(OH)_3$, in situ (Section 2.3.2.).

In contrast, when aluminum anode is used, the chromium ions in the aqueous solution are destabilized only by the electrochemical reduction reaction that takes place directly at the cathode (Eq. 2.6) [22]. The reactions involved in the electrocoagulation process, using Al electrode, are as follows:

Anodic reaction:

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^- \qquad (2.9)$$

Cathodic reaction:

$$3H_2O + 3e^- \rightarrow 3OH^-_{(aq)} + 3/2H_{2(g)} \qquad (2.10)$$

Overall reaction in bulk solution:

$$Al^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Al(OH)_{3(s)} + 3/2H_{2(g)} \qquad (2.11)$$

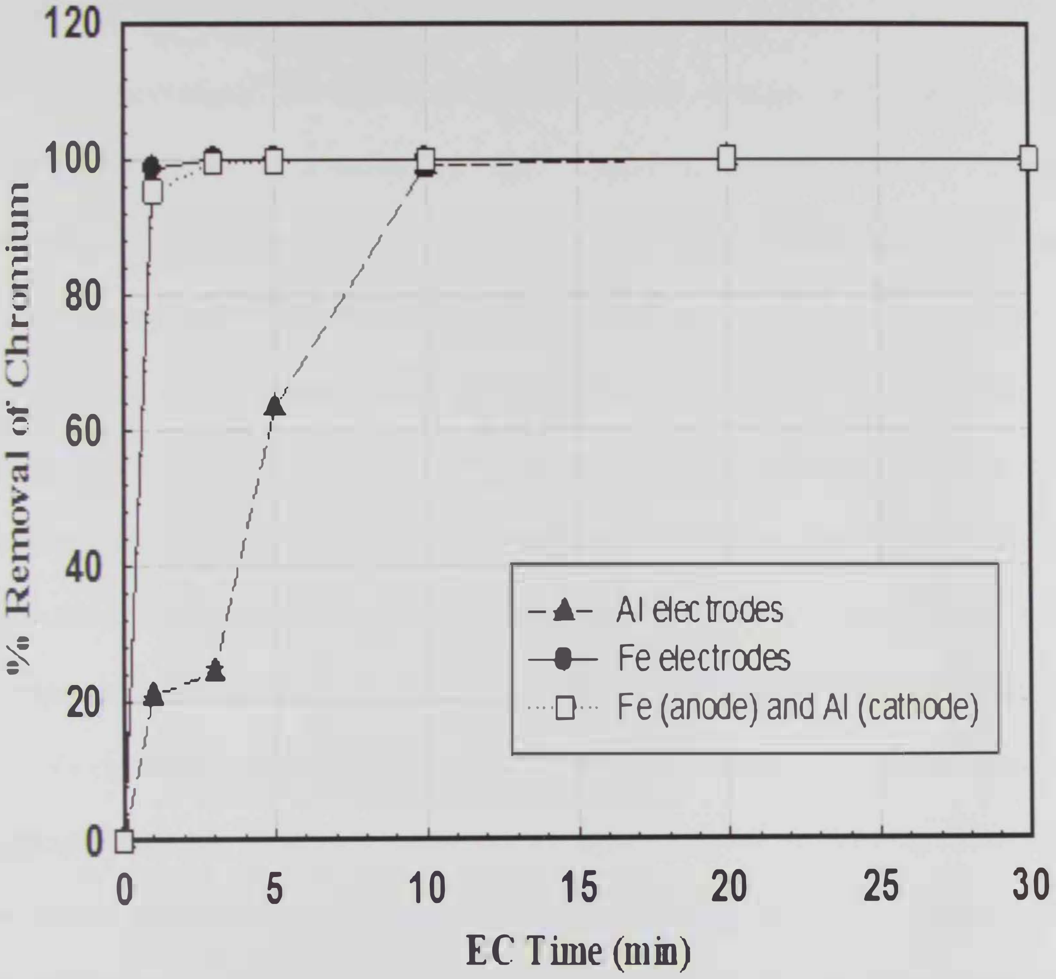


Fig.4.2. Influence of electrode material on the removal of chromium from groundwater by batch EC at 0.5 A and initial chromium concentration of 1mg/L.

4.1.3. Effect of Applied Current Density

Applied current density (ACD) is one of the main operating parameters that directly affect the process performance and operating cost. According to Faraday's law (Eq. 2.12), ACD not only determines the coagulant production dosage, but also the microscopic bubbles size, which consequently have significant effect on the removal rate of the pollutants [5].

To investigate the effect of applied current density on the removal of chromium, a series of experiments were conducted on groundwater samples containing a constant chromium concentration of 1 mg/L at wide range of current density varying from 1.59 to 15.87 mA/cm^2 (voltage ranging from 0.019 to 0.016 V) by controlling a DC current source at fixed surface area equal to 63 cm^2 and an average initial pH value of 8 ± 0.1. Fig.4.3 indicates that chromium removal rate increases with increasing ACD. As the applied current density is raised from 1.59 to 7.94 mA/cm^2, the electrocoagulation performance was enhanced from 33 % up to 98 %, respectively within the first minute and 100% within three minutes of operation for Fe-Fe electrode pairs. A further increase in the ADC up to 15.87 mA/cm^2 was not beneficial, since the chromium concentration seemed to be the limiting factor and most of the added energy would be transferred to heating the reactor content. This behavior can be explained according to Faraday's law (Eq.2.12), where increasing the applied current cause an increasing in the amount of sacrificial anode dissolved (i.e. iron ions) and its hydroxide ions formed in situ at constant electrolysis time, which improves the reduction rate by iron ions and increases the coagulant dosage by forming insoluble compounds; $Cr(OH)_3$ and $Fe(OH)_3$ [75].

Moreover, the amount of micro bubbles, generated during the EC process, is highly dependent on the applied current. The bubble size, is inversely proportional, while the bubble amount is directly proportional to the ACD [76], which improves the flotation of the aggregated sludge formed through the EC process. Nevertheless, these parameters should be kept at a level to achieve low-cost operation at low energy consumption.

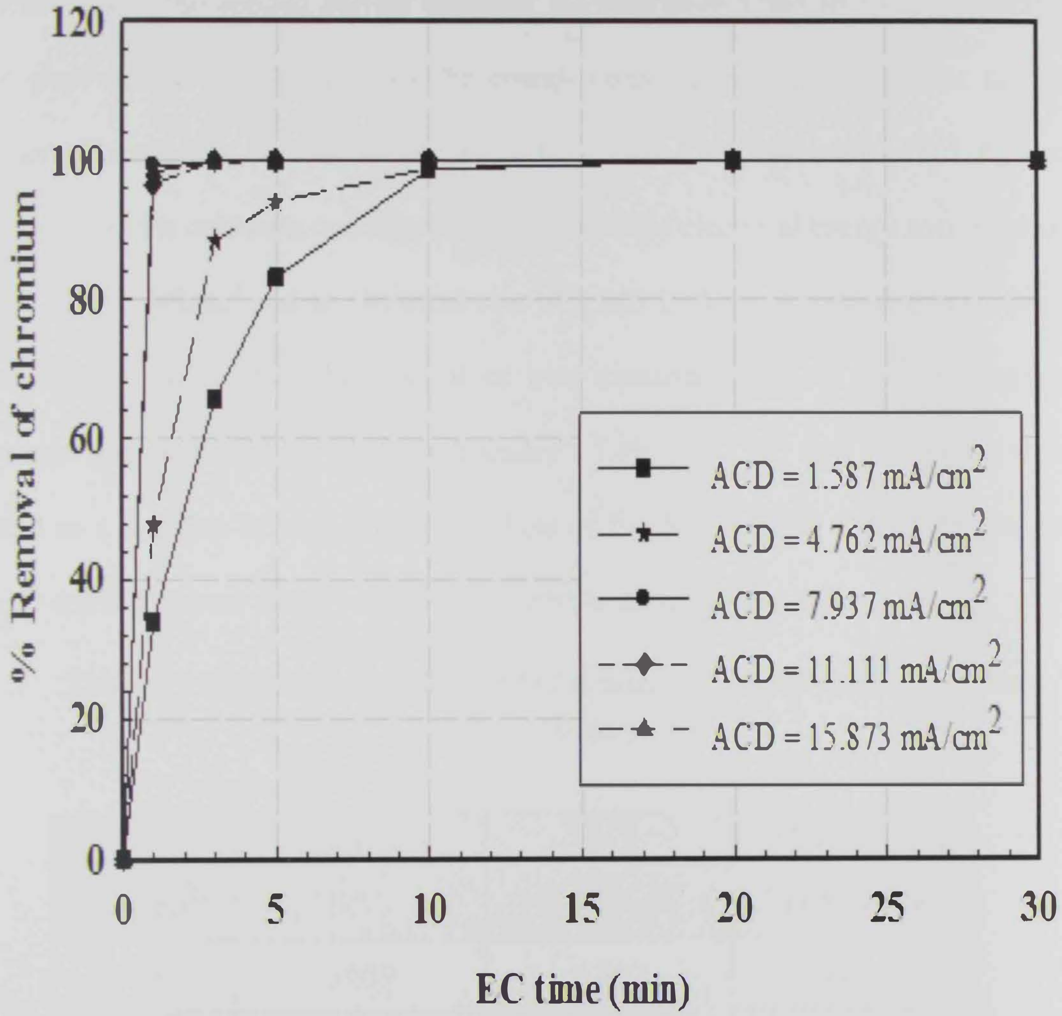


Fig.4.3. Influence of different applied current density on the performance of batch EC removal of chromium from groundwater using iron electrodes at initial chromium concentration of 1 mg/L.

Raising the current density from 1.59 to 15.87 mA/cm^2 (voltage ranging from 0.019 to 0.016 kV) increases the electrical energy consumption from 0.032 to 2.733

kWh/m^3 (Eq.2.13) of treated groundwater, respectively as depicted in Fig.4.4. Electrical costs were estimated for the applied current densities and indicated significant increase from 0.001 to 0.111 US $ for each one cubic meter of treated groundwater as the applied current densities increase from 1.587 to 15.873 mA/cm^2. At higher current density, part of the energy consumption is lost to heat up the solution. Therefore a current density equal to 7.94 mA/cm^2 (current of 0.5 A) was considered as the optimum condition with a reasonable electrical energy consumption (EEC) of 0.6 kWh/m^3 and an electrical cost of 0.025 US$/m^3 of treated groundwater. At this optimum current, the amount of iron dissolved from 63 cm^2 rectangular electrode was estimated by applying Faraday's Law (Eq.2.12) and the results were plotted as a function of time. From the slope of Fig.4.5, the iron electrodes erosion rate, at applied current density of 7.94 mA/ cm^2, is about 8.7 mg/min.

Table 4.1 Electrical costs of batch EC at different applied current densities (t_{EC} = 10 min).

ACD (mA/cm^2)	**Voltage (kV)**	**EEC (kWh/m^3)**	**Electrical cost (US $/m^3)**
1.587	0.019	0.032	0.001
4.762	0.004	0.210	0.009
7.937	0.007	0.600	0.024
11.111	0.012	1.412	0.057
15.873	0.016	2.733	0.111

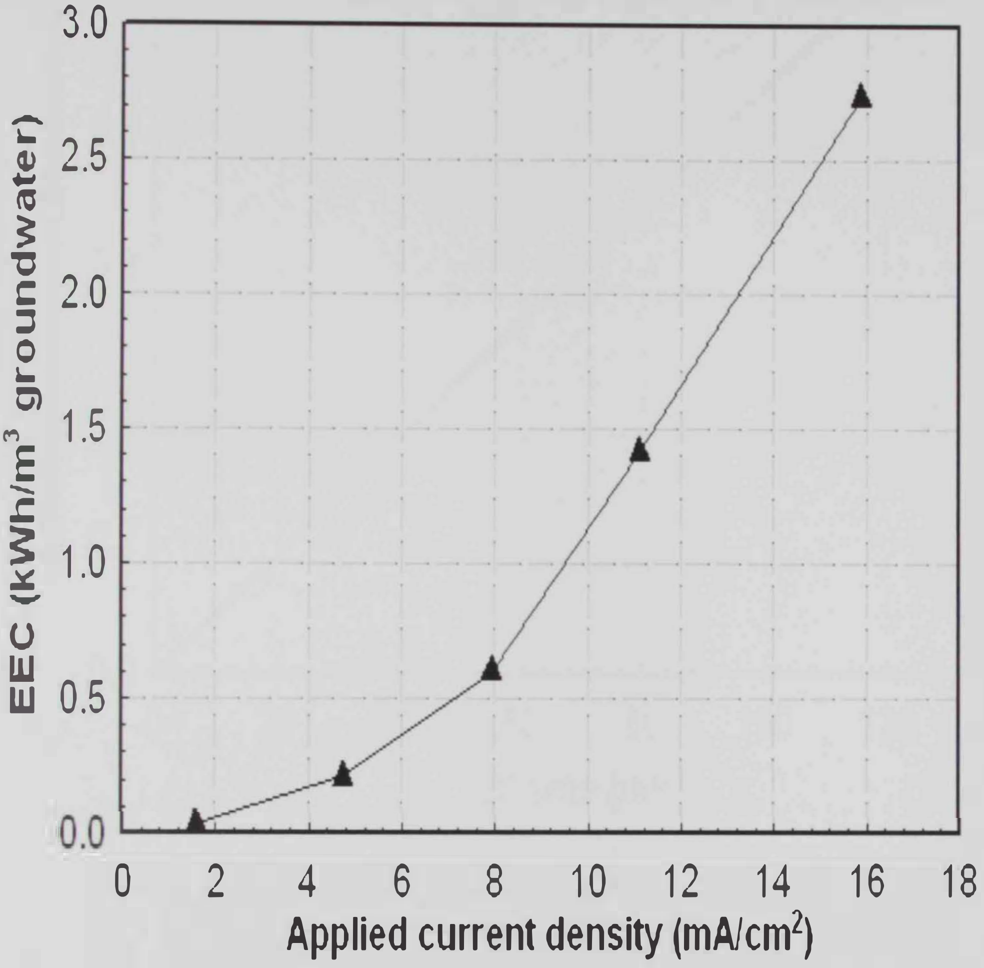


Fig.4.4. The energy consumption of different current densities using iron electrodes at initial chromium concentration of 1 mg/L, electrolysis time 10 min.

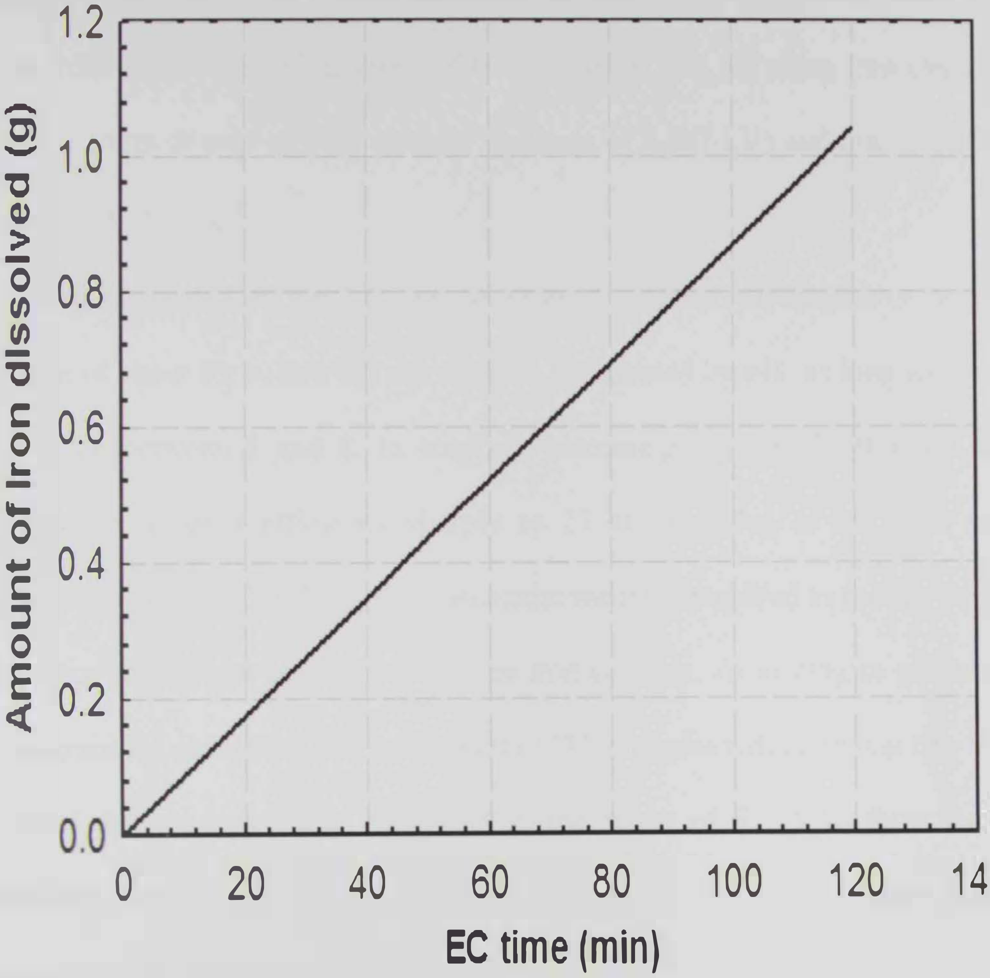


Fig.4.5. Amount of Iron electrode dissolved with time for applied current density of 7.94 mA/cm^2.

4.1.4. Effect of Initial pH

In order to improve the efficiency of chromium removal in aqueous solution, several reactions must be performed in situ (as explained earlier in Section 2.3.2): a reduction of hexavalent chromium to trivalent chromium, and an oxidation of Fe^{2+} to Fe^{3+}, followed by formation of insoluble $Cr(OH)_3$ and $Fe(OH)_3$. The formation of these products and there solubility is highly dependent on the solution pH. For this reason, the dependence of Cr(VI) reduction on initial pH was investigated for pH ranging from 2 to 10 by adding drops of HCl or NaOH (0.1 M) using iron electrode at optimum current density of 7.94 mA/cm^2 (voltage of 0.007 kV) and initial chromium concentration of 1 mg/L.

As illustrated in Fig.4.6, the percentage removal of chromium reached a maximum of about 99 % and did not seem to be affected by pH, as long as it is kept in the range between 5 and 8. In contrast, increasing the initial pH more than 8 decreases the removal efficiency sharply to 27 at pH value of 10. This can be explained by Eq. (2.4, 2.6, 2.7) where an acidic media is required to reduce Cr(VI) to Cr(III) once the current passed through the iron cathode. According to predominant zone diagram for chromium and iron species [77], once the reduction reaction occurs, the pH of the aqueous media increased in the range of 5 - 8 to form insoluble compounds $Cr(OH)_3$ and $Fe(OH)_3$ as shown in Eq. (2.5-2.7). These insoluble compounds will constitute the sludge.

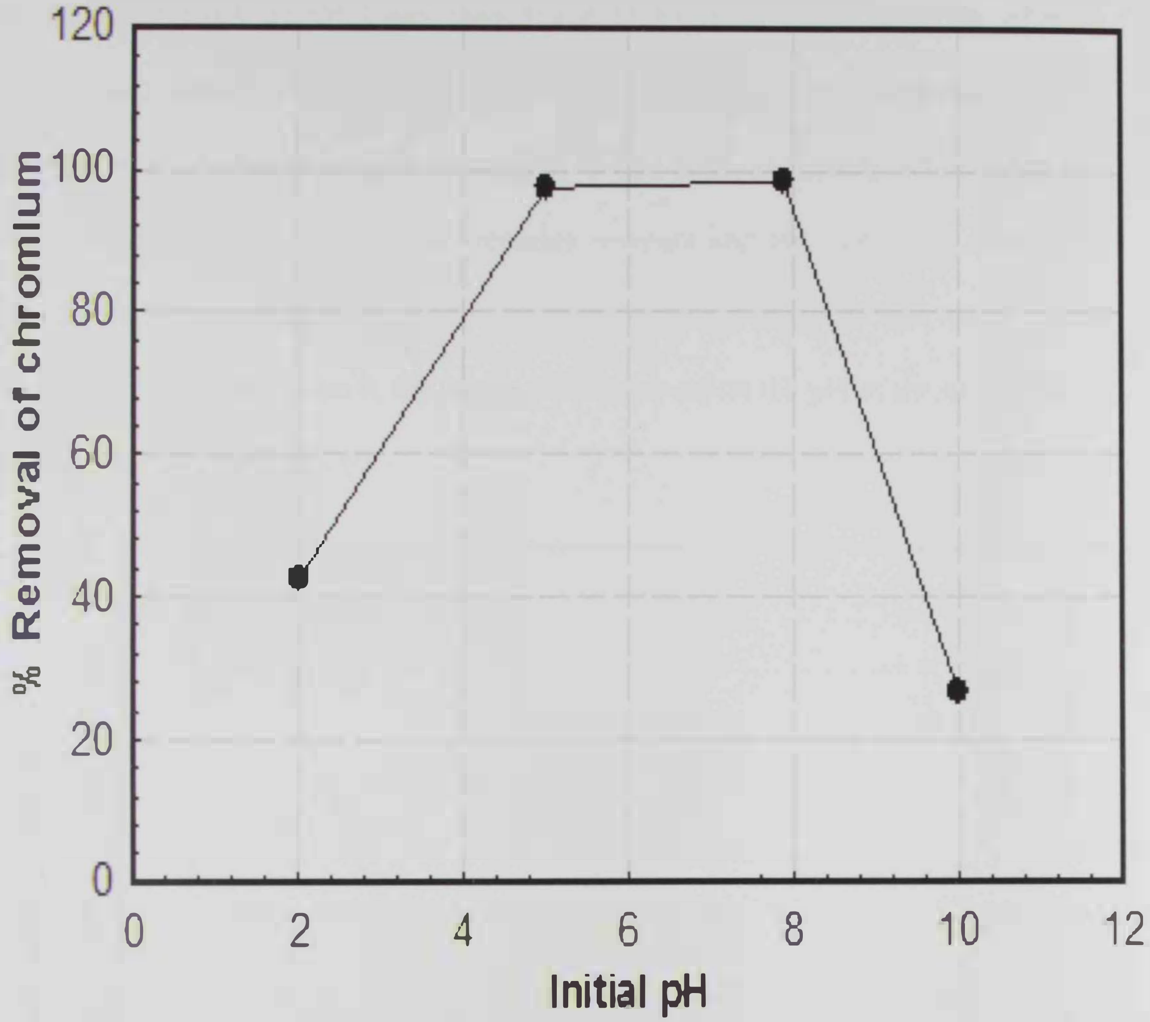


Fig.4.6. Influence of initial pH on the performance of batch EC removal of Cr(VI) from groundwater using iron electrodes at an applied current density of 7.94 mA/cm^2.

The total iron dissociated from sacrificial electrode was measured after treating the groundwater with batch electrocoagulation process, and the results presented in Fig.4.7. As the pH of the solution increased from 2 to 10, the iron concentration sharply decreased. This behavior is directly related to the pH of the aqueous media, as the pH value kept in the range between 5 and 10, the excess amount of Fe(III) ions generated in site is precipitated in the form of $Fe(OH)_3$ [77].

On the other hand, at pH lower than 5 and higher than 8 the solubility of both $Cr(OH)_3$ and $Fe(OH)_3$ increased. Furthermore, the corrosion rate of iron electrodes in aqueous media decreasing at pH lower than 5 due to H_2 evolution; while at the pH range of 5 to 10, the corrosion rate remains constant and low due to O_2 adsorption [78]. Since 99 percentage removal of chromium from groundwater was reached with the original initial pH value 8, there was no need to adjust the pH of the groundwater for the rest of the experiments.

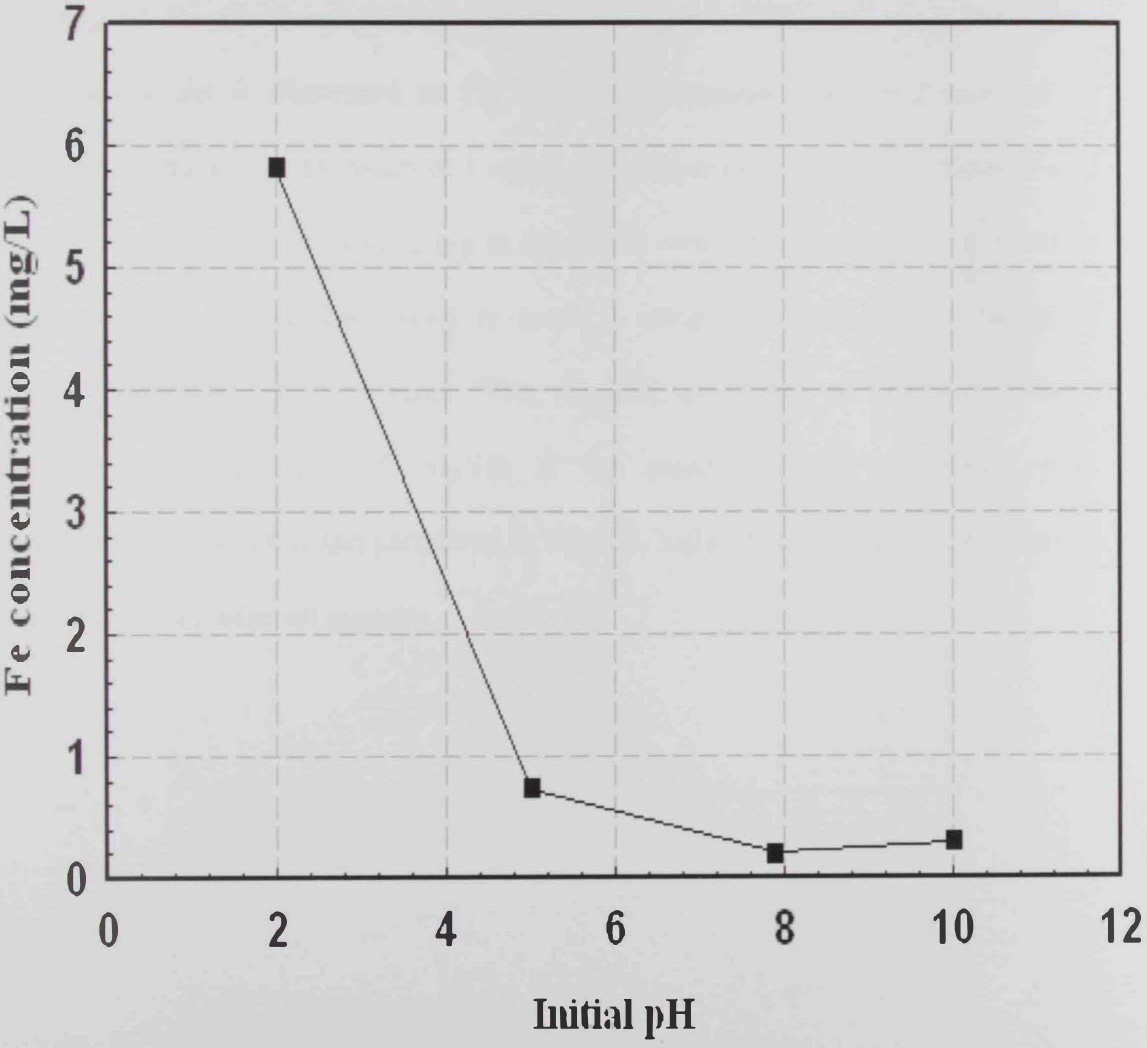


Fig.4.7. Influence of different pH values on the dissolved Fe concentration.

4.1.5. Effect of Initial Chromium Concentration

It has been established that the initial chromium concentration has a considerable influence on the performance of electrocoagulation process via the coagulant dosage. Most researchers studied high initial chromium concentration parameter reaching a maximum concentration of 100 mg/L [1, 2, 56, 59]. In this work, a wide range of initial concentrations, from 0.2 mg/L to 100 mg/L, were treated on a batch EC using Fe/ Fe electrodes, at optimum ACD and pH. Generally, the efficiency of the electrocoagulation process decreased with increasing the initial concentration. As it illustrated in Fig.4.8, a spontaneous completed removal of chromium at initial concentration of 1 mg/L was achieved at an interval time of one minute; however, a further increasing in the initial concentration from 5 to 20 mg/L required a longer electrolysis time to reach a complete steady-state removal of chromium from 3 to 20 minutes. The removal efficiency for extremely high chromium concentration (100 mg/L); at the same previous conditions, was experimentally evaluated and presented in Fig.4.8; only 86 percentage of chromium could be removed after 60 minutes.

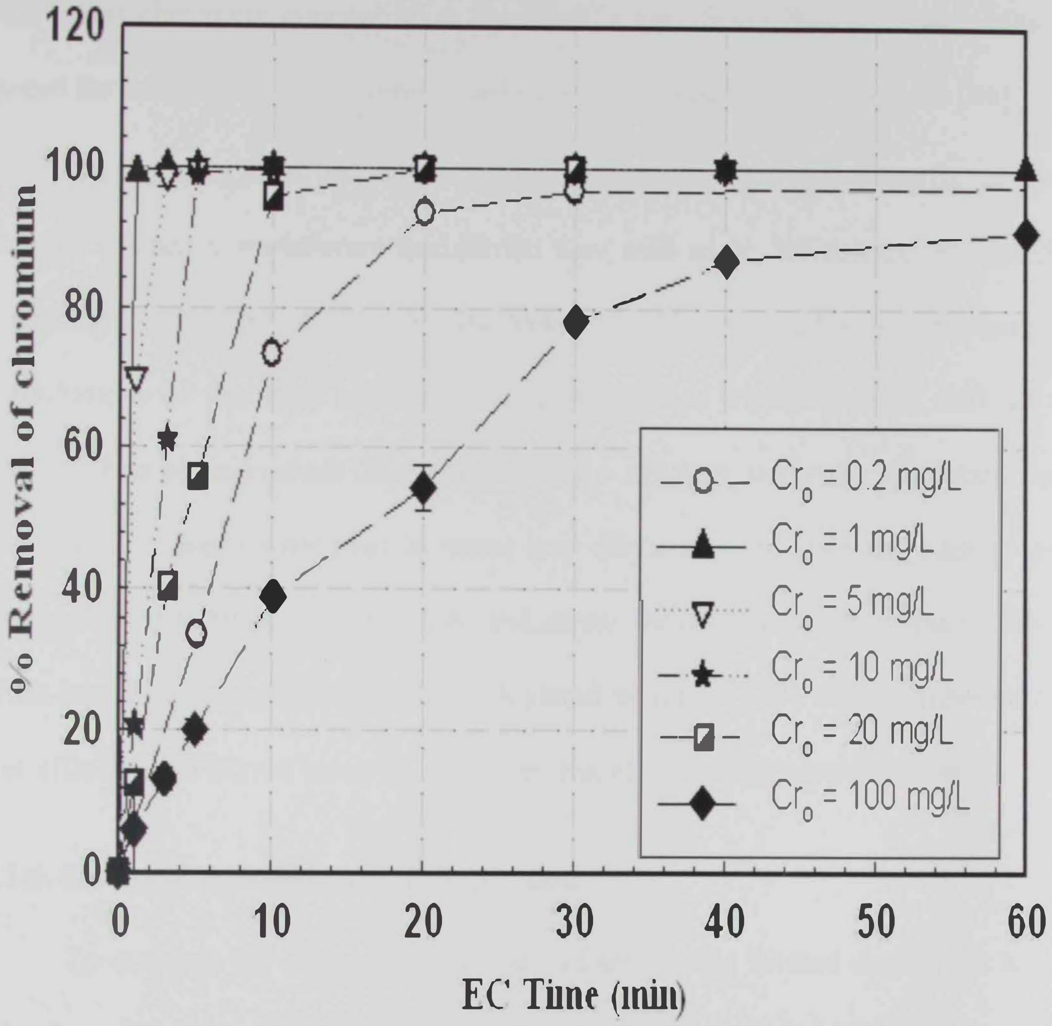


Fig.4.8. Influence of different initial concentrations on the performance of batch EC removal of chromium from groundwater using iron electrodes at ACD of 7.94 mA/cm^2 and initial pH of 8.

Faraday's law given in Eq.2.12, explained the concept of constant amount of iron ion dosage generated in site from the anode material dissociation at constant applied current, which increases with increasing the electrolysis time. These generated ions get involved in increasing the reduction rate of hexavalent chromium, forming insoluble chromium and iron hydroxide compounds Eq. (2.4-2.8). Therefore, as the initial chromium concentration increases, a significant dosage of iron ions is required for longer electrolysis time to reduce forming insoluble compounds [56].

On the other hand, in case of dilute concentration (less than 1 mg/L) removal efficiency of chromium behaves in different way with some difficulties, particularly when using standard flat plate electrodes (as used in this work). This can be related to the limitations of this type of electrodes, as high mass transfer rate is difficult to achieve. When plating metals dissolved forming a solution, the layer of solution next to the cathode becomes depleted in metal ions. Since there is fewer chromium ions present in dilute solution, diffusion into and across the depleted layer is much slower and the layer becomes thicker and more depleted with time [79] which explained the lower efficiency of stirred batch EC at diluted initial chromium concentration.

4.1.6. Sludge Morphology and Composition

To evaluate the surface morphology of the sludge formed during the batch electrocoagulation, a field emission scanning electron microscope analysis was carried out. As illustrated in Fig.4.9, the FE-SEM images depict the presence of irregular flak-shaped aggregates at 25x magnification range with a diameter size ranged from 30 to 180 µm. The size of the generated sludge particles is expected to depend on the applied current density, efficiency of mixing and the initial chromium concentration.

Fig.4.9. FE-SEM micrographs of sludge powder: 25X.

4.1.6.1. Energy Dispersive X-ray Spectroscopy Analysis

Chemical composition analysis of the coated powder samples was performed by EDS at 15 kv accelerating voltage and 1,000x magnification at four different spots as shown in Fig.4.10. A qualitative and semi-quantitative analysis of the spots indicates that the major chemical compositions in sludge sample are oxygen and iron with 53.73 and 22.24 average mass %, respectively; however a small amount of chromium appear in the analysis due to the small chromium concentration in groundwater. Other elements appear in the sludge with low average mass include Na, Mg, Si, and Ca, which indicates that these ions could not be fully removed by the electrocoagulation process. Thus, infinitely soluble matter ions with molecular weights smaller than Ca^{+2} or Mg^{+2} cannot be fully removed from aqueous medium by electrocoagulation process [79].

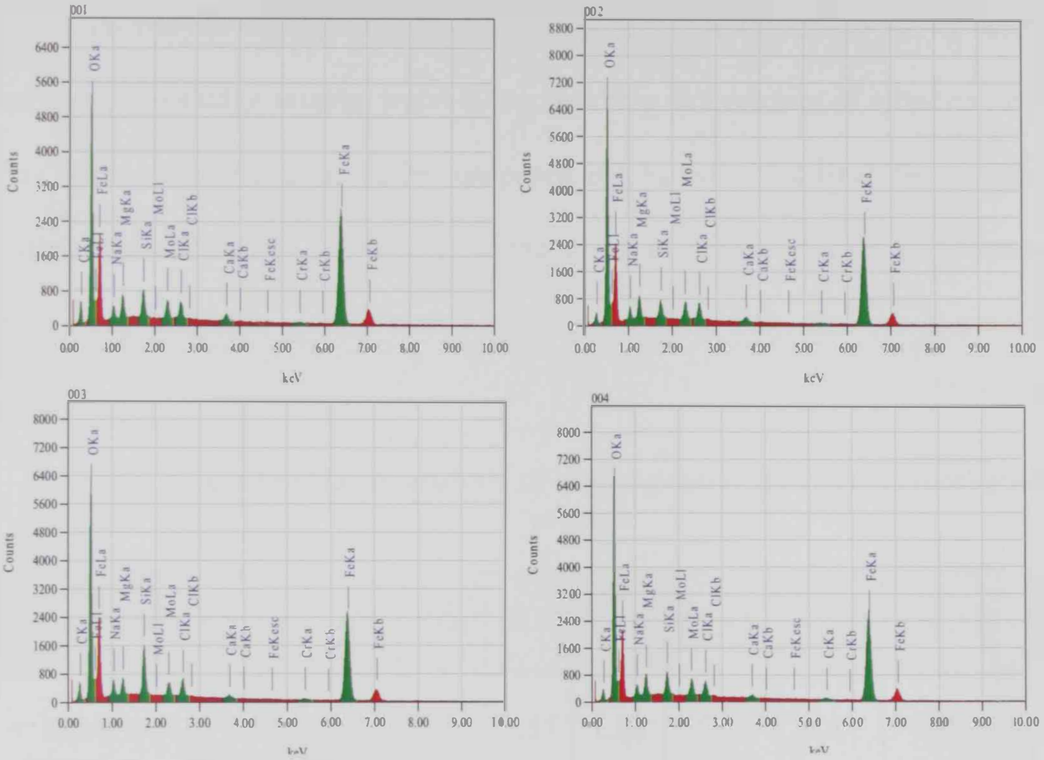


Fig.4.10. EDS spectrum of the sludge powder at four different spots.

4.1.6.2. X-Ray Fluorescence

Sludge samples were also analyzed by XRF to quantify the elemental composition. The results in Table 4.2 indicate that the sludge consists of different forms of element oxides with a dominant appearance of iron oxide with 84.1 mass% in the form of Fe_2O_3 which is resulted from thermal decomposition of $Fe(OH)_3$ [80]. The rest are SiO_2, SO_3, MgO, CaO, Cl^-, Cr_2O_3, MnO, SrO, P_2O_5 and K_2O in descending order to minimum appearance of 0.0547 mass% of K_2O. The lower percentage mass of Cr_2O_3 (0.616) in the sludge samples can be attributed to the low initial chromium concentration in the water. As it was mentioned earlier in Section 2.3, formation of the insoluble hydroxides by electrocoagulation process generates a significant amount of coagulant. Once the coagulant is heated above 50 ^{0}C; during the preparation of sludge sample, water is lost resulting in a mixture of metal oxides [82]. This finding confirmed the earlier proposed mechanisms that once the contaminant material destabilized by applying a current, it can be separated from the groundwater by forming insoluble species such as $Fe(OH)_3$ and $Cr(OH)_3$ that are present in the sludge.

Table 4.2 Compositional analysis of sludge generated from electrocoagulation process.

Composition	**MgO**	**SiO_2**	**SO_3**	**Cl^-**	**CaO**	**Cr_2O_3**	**MnO**	**Fe_2O_3**	**SrO**
Mass %	2.78	4.55	3.85	1.85	1.88	0.62	0.19	84.1	0.095

4.1.7. Process Kinetics

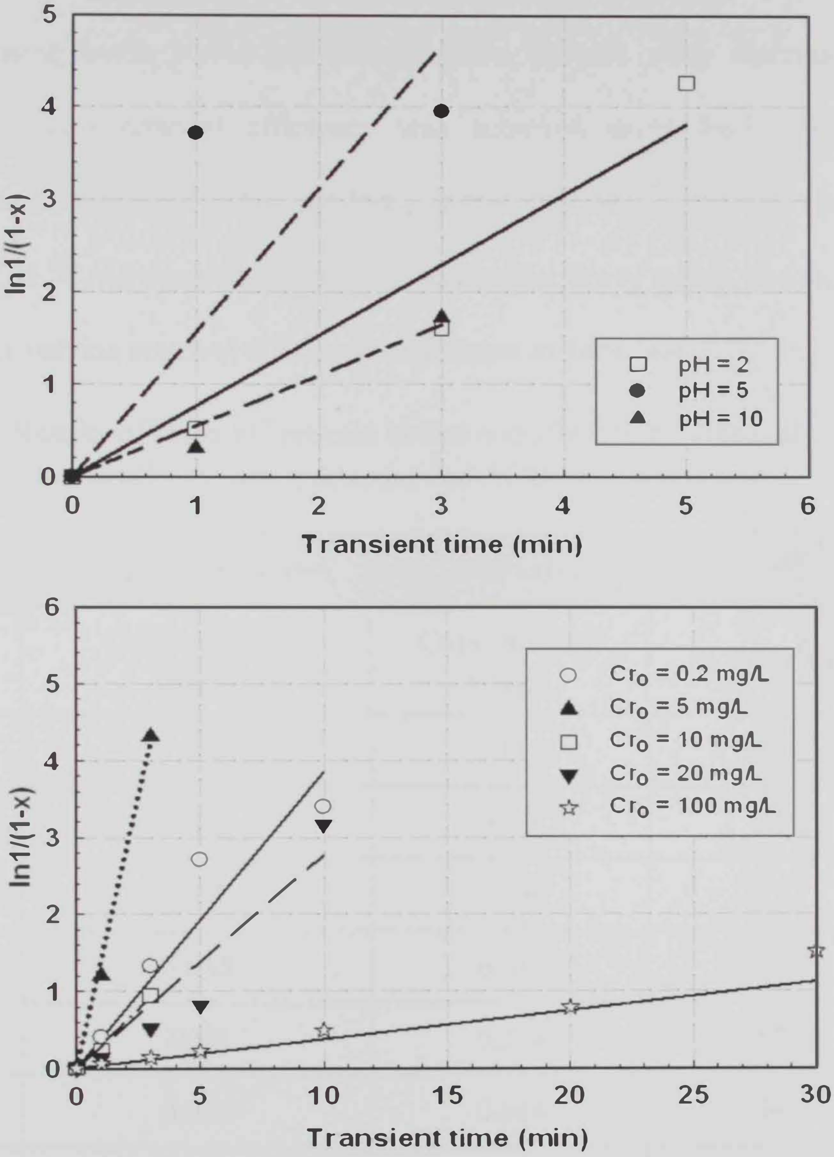
The kinetics of chromium removal from groundwater by batch electrocoagulation was tested by applying pseudo first-order (Eq.3.3) and pseudo second-order models (Eq.3.4) [69].

The results of both models are presented in Table 4.3. By statistical analysis it was determined that the plot of pseudo first-order reaction model was found to be linear, for all conditions studied, with acceptable correlation coefficients. This implies that the best equation representing chromium removal from groundwater is a pseudo fist-order homogeneous model. The initial removal rate was predicted from the slope of the plot of chromium concentration versus time for all the conditions examined.

The plot of $\ln 1/(1-x)$ vs. t is given in Fig.4.11, as a function of different initial pH and initial chromium concentration. As seen from the figure, there was a linear relationship between $\ln 1/(1-x)$ and t; the plots for other parameters also exhibited linear variation.

Table 4.3 Kinetics parameters adjusted from the experimental data of batch EC.

		Pseudo-first order model			**Pseudo-second order model**	
Parameter		$-r_{cr}$ (mg/L.min)	k_1 (min^{-1})	SSE	k_2 (min^{-1})	SSE
Initial pH	2	0.197	0.8343	0.6068	0.1335	979.004
	5	0.327	1.1480	3.6964	15.470	341.065
	10	0.274	0.5920	0.0444	1.6110	0.8706
Initial Cr (mg/L)	0.2	0.0110	0.3526	0.7225	3.073	23.863
	5	1.6445	1.4560	0.0352	26.270	320.70
	10	2.0392	0.3212	0.0043	0.5440	0.0443
	20	2.2312	0.3151	0.4247	0.2572	0.0089
	100	1.4444	0.0353	0.1892	0.1114	0.9841
Electrode material	Al/Al	0.127	0.1812	0.0782	0.3155	0.3424
	Fe/Al	0.332	1.6820	1.0403	71.100	1461.8



(I)

(II)

Fig.4.11. Plot of ln1/(1-X) versus time for: I) initial pH, II) initial chromium concentration.

4.1.8. Optimum Operation Conditions for Batch EC

Optimum operation conditions for the removal of chromium from brackish groundwater using batch stirred electrocoagulation process were determined. A maximum chromium removal efficiency was achieved using Fe/Fe electrodes arrangement, with ACD of 7.94 mA/cm^2, initial pH of 8, and an operating temperature of 25 ^{0}C. At these optimum conditions, other heavy metals and ions were also removed at varying removal efficiencies as shown in Table 4.4.

Table 4.4 Results of batch EC process before and after the treatment at optimum conditions: initial pH = 8, Iron electrodes and ACD of 7.94 mA/cm^2.

	Feed groundwater	**Treated groundwater**	
Metals	Concentration (mg/l)	Concentration (mg/l)	% Removal
Cr	5	0	100
Mg	110.8	86.5	22
Sr	18.4	15.6	15
Cd	0.018	0.016	11
Mn	0.66	0.318	52
Cu	0.066	0.044	34
Zn	0.141	0.062	56
Fe	-	0.243	-

4.2. Continuous Electrocoagulation Process

The performance of continuous electrocoagulation reactors for the treatment of wastewater was rarely investigated, with the exception of limited studies on the reduction of COD [41, 48, 83, 84], removal of petroleum contaminants [85], and removal of arsenic from synthetic wastewater [86] (Table 4.5). The possibility of reducing electrode performance, due to passivation of the electrodes over time has limited the usage of continuous electrocoagulation as a mainstream wastewater treatment technology. However, strict environmental regulations on industrial effluent wastewater have re-evaluated the usage of continuous EC. Chromium reduction has only been reported using a batch EC process [57, 58, 60, 87].

Table 4.5 Continuous electrocoagulation process.

Wastewater source	Reactor capacity //[CC]	Reactor type and connection	Electrode materials	Retention time/ flow rate	Treatment efficiency	Reference
Groundwater	200 mL// petroleum hydrocarbon [64mg/L]	Continuous	St-Fe	2 - 60 min	67.2% - 93.4%	[85]
MSG fermentation wastewater	COD [3000mg/L]	Continuous bipolar	Fe	1 – 3 L/min	68%	[41]
Synthetic wastewater	COD [120 mg/L]	Continuous	Al	10 - 28 L/h	71.5% - 90.2%	[83]
Synthetic wastewater	3.1 L// COD [25-200 mg/L]	Continuous	Al	28 – 78 L/h	95%	[48]
Dyeing wastewater	1.65 L// COD [870 mg/L]	Continuous monopolar	Al	50 – 200 mL/min	95% >	[84]
Synthetic drinking water	As [2 mg/L]/ N [300 mg/L]	Continuous bipolar	Steel	2 L/ h	70% / 80%	[86]

The prime objective of this part of the study was to assess the performance of electrocoagulation in a continuous stirred mode (CSTR) for the removal of hexavalent chromium from brackish groundwater. In this chapter, the following operational parameters have been experimentally investigated: electrode materials, influent flow rate (Q_L), applied current density (ACD), influent pH and influent chromium concentration (C_0).

4.2.1. Continuous Stirred Electrocoagulation Procedure

An electrocoagulation reactor with similar configuration to that used for the batch process (Section 4.1) was utilized for the continuous stirred tank reactor (CSTR) experiments. At the beginning of each continuous experiment, EC reactor was filed with an effective volume of 1000 mL of groundwater, achieving complete metal electrode coverage with surface area of 63 cm^2. Both electrodes were connected to the middle of the Plexiglas cover as shown on the schematic diagram of the experimental set-up in Fig.4.12. This design was retained to decrease the passivation of anode by enhancing the mixing between the inter surface of the cover and anode electrode [61]. The contaminated inlet flow rate was controlled by a peristaltic pump (MasterFlex7553-79). Thus, the treated groundwater leaves the EC reactor by continuous spilling and gently enters a settling container. A continuous stirring at 300 rpm was applied to homogenate the liquid at both feed container and EC reactor. The treated groundwater samples were collected from the settling container at constant time intervals.

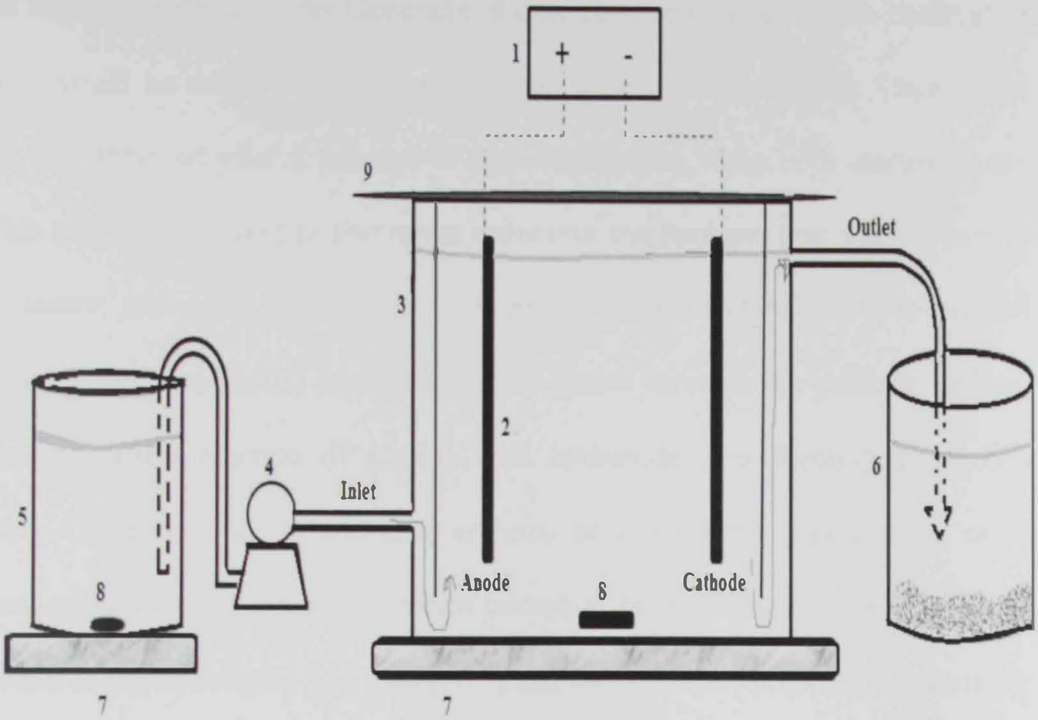


Fig.4.12. A schematic diagram of continuous stirred EC process: 1- DC power supply; 2- Metal electrodes; 3-Plexiglass cylindrical; 4- Feed pump; 5-Feed container; 6-Settling container; 7- Magnetic stirrer; 8- Magnetic bar stirrer; 9-Plexiglass cover.

4.2.2. Effect of Electrode Material

As in the batch process, two electrode materials were used: iron (Fe) and aluminum (Al) at different arrangements. Four sets of experiments were carried out using four different electrode arrangements (Fe/Fe, Al/Al, Fe/Al, and Al/Fe) using fixed influent flow rate of 90 mL/min, initial chromium concentration of 5 mg/L and a current of 0.5 A (voltage of 0.009 kV). These arrangements refer to the materials used and the placement of the electrode (Anode/Cathode).

The experimental results, shown in Fig.4.13, prove that the chromium removal efficiency of the continuous EC reactor is significantly affected by the material of the sacrificial anode. Generally, it was observed that complete removal of chromium could be achieved when iron is used as an anode material. Thus 100% removal was achieved after 5 minutes of electrolysis time when both electrodes are iron. This may be attributed to chromium reduction mechanisms that take a place in the EC reactor. According to Eq.2.6 and 2.8, hexavalent chromium Cr(VI) is reduced to trivalent chromium Cr(III) once the current passes through the cathode surface, followed by in-situ reaction of Cr(III) with hydroxide ions forming chromium hydroxide $Cr(OH)_3$ solid. In the case of iron as a sacrificial anode, one more additional reduction reaction of chromium occurs in the bulk media (Eq.2.7) due to the reaction of the dissociated iron ions (Fe^{2+}) and the chromium ions Cr(VI), forming insoluble products, $Cr(OH)_3$ and $Fe(OH)_3$, in-situ [8, 77]. Therefore the contribution of the two mechanisms to Cr(VI) reduction by iron as a sacrificial anode facilitates chromium removal at a short operation time (electrolysis time = 5 min).

On the other hand, for aluminum sacrificial anode, limitations on chromium removal were observed, with only 40 % of the chromium could be removed (electrolysis time = 30 minutes) when both electrodes were made of aluminum. In this case, both electrochemical reduction of Cr(VI) at the cathode surface and adsorption of chromium on $Al(OH)_3$ floc (Eq. 2.9-2.11) [88] take place. Replacing the cathode with iron electrode, seems to have more detrimental effect on the removal efficiency as shown in Fig. 4.13. This could be attributed to the fact the chromium removal mechanism in this case is only limited to the electrochemical reduction of chromium [56].

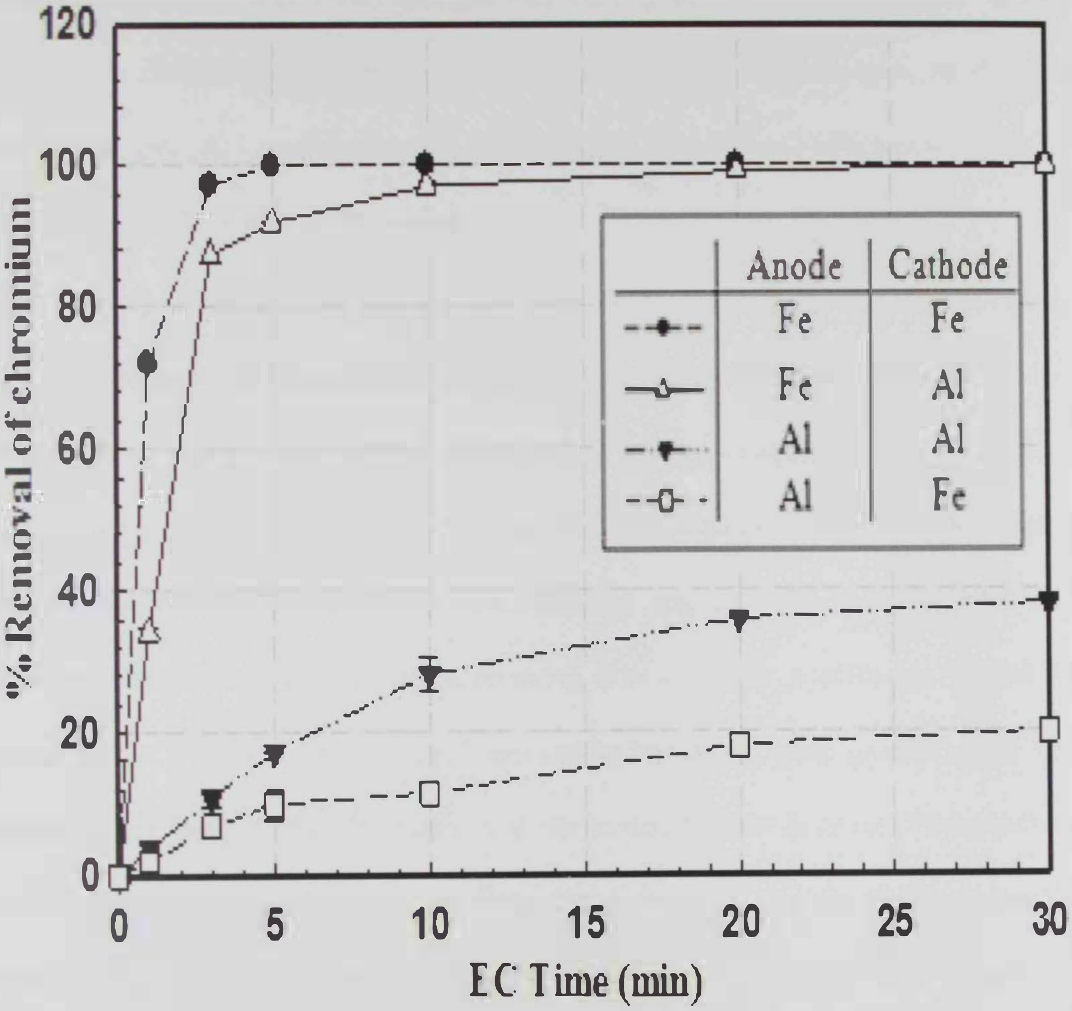


Fig.4.13. Influence of electrode material on continuous stirred EC at Q_L = 90 ml/min, and Cr_0 = 5 mg/L.

4.2.3. Effect of Inlet Flow Rate

The effect of inlet flow rate on the performance of EC CSTR with iron electrodes was evaluated using three different flow rates 30, 90 and 150 mL/min, at an initial chromium concentration of 5 mg/L. Both current density and initial pH were kept constant at 7.94 mA/ cm^2 and 8, respectively. The experimental results are shown in Fig.4.14. After three minutes of electrolysis reaction, chromium removal efficiency is decreased from 99% at 90 mL/min to 72% at 150 mL/min. At the same electrolysis time, EC performance is slightly reduced (removal efficiency = 90%) at the lowest inlet flow rate of 30 ml/min.

The inverse relation between the inlet flow rate and the removal efficiency (for Q_L of 90 and 150 ml/min) can be related to the residence time inside the reactor; low inlet flow rate provides longer reaction time between the chromium ions present in the water and the iron ions released from the anode surface [64], thus giving more time to destabilize chromium ions and thereby improve the removal rate [89]. However, the decline in chromium removal efficiency by continuous stirred EC process at low flow rate (Q_L = 30 mL/min) can be attributed to the generation of large amount of gas bubbles that is observed at the surface of the cathode. These bubbles reduced the interface surface area between chromium ions and the electrode causing reduction in the removal rate of the chromium [65]. At an inlet flow rate of 30 ml/min, the solution turbulence in the reactor is lower compared with 90 ml/min, thus affecting chromium ions destabilization process and leading to lower chromium removal.

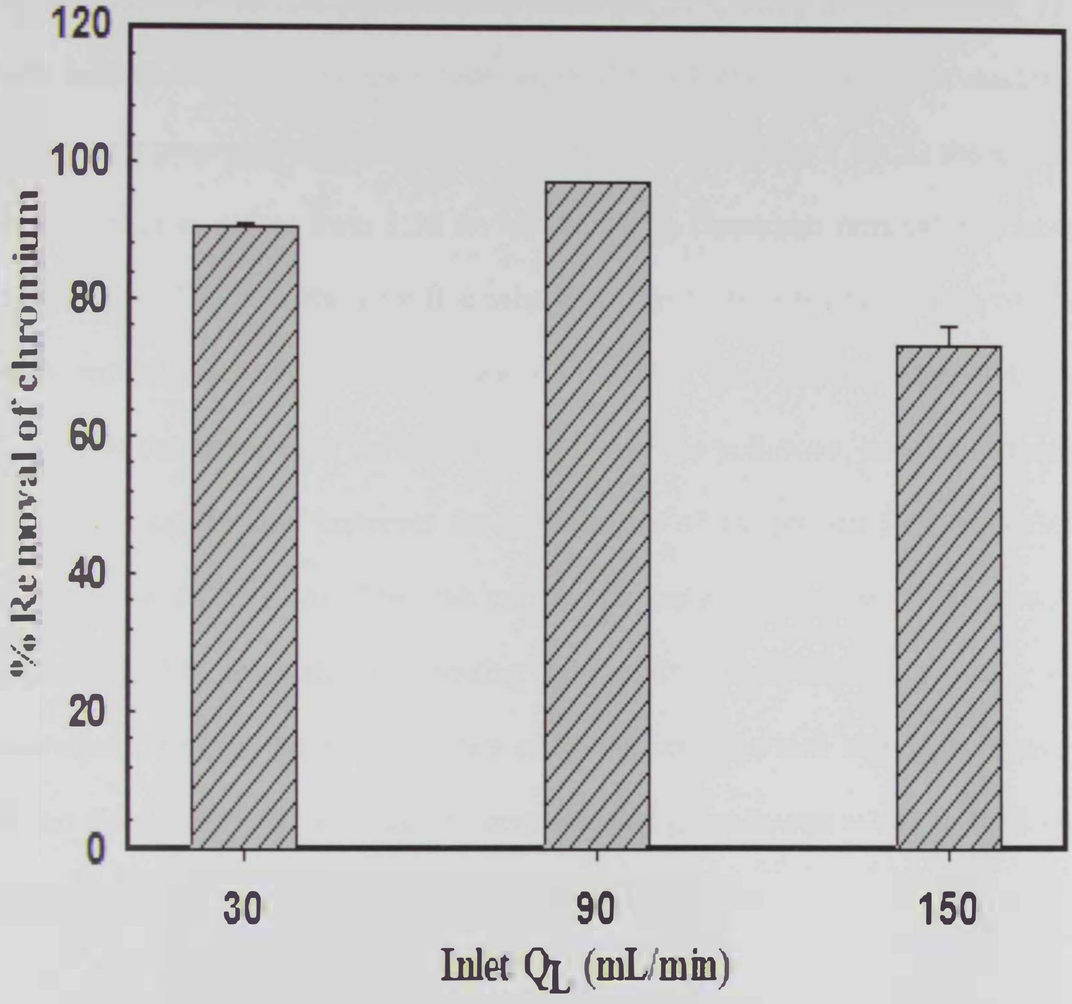


Fig.4.14. Influence of inlet flow rate in removal efficiency of chromium in continuous stirred EC process using iron electrodes.

4.2.4. Effect of Applied Current Density

Applied current density (ACD) is directly affecting coagulant dosage and hydrogen evolution rate, as well as mass transfer near the electrodes. The ACD was varied from 1.50 mA/cm^2 to 15.87 mA/cm^2 (voltage ranging from 0.002 to 0.014 kV)to assess its effect on the performance efficiency of the EC CSTR The experimental work was conducted at fixed inlet concentration (C_0= 5 mg/L), inlet flow rate (Q_L = 90 mL/min)and constant initial pH of 8, using iron electrodes. The results indicated that the operation time required to achieve a steady-state condition was inversely proportional to the current density as shown in Fig. 4.15. As the applied current density increases from 1.59 to 7.94 mA/cm^2, chromium removal efficiency increases from 37% to 99%, after five minutes of electrolysis reaction. High current density would accelerate the dissolution rate of Fe^{2+} ions provided by an anode material and therefore raises the destabilizing rate of the pollutants, thus forms larger amount of coagulant and improves the performance of EC process [47]. However, increasing the ACD above 7.94 mA/cm^2 is not justified as most of the energy supplied would be dissipated into heating the reactor content and hence raising the temperature. The high influent flow rate of 90 mL/min provided high mass transfer between the electrode surfaces and the contaminated groundwater within the cell and thereby increases the removal efficiency of the CSTR EC.

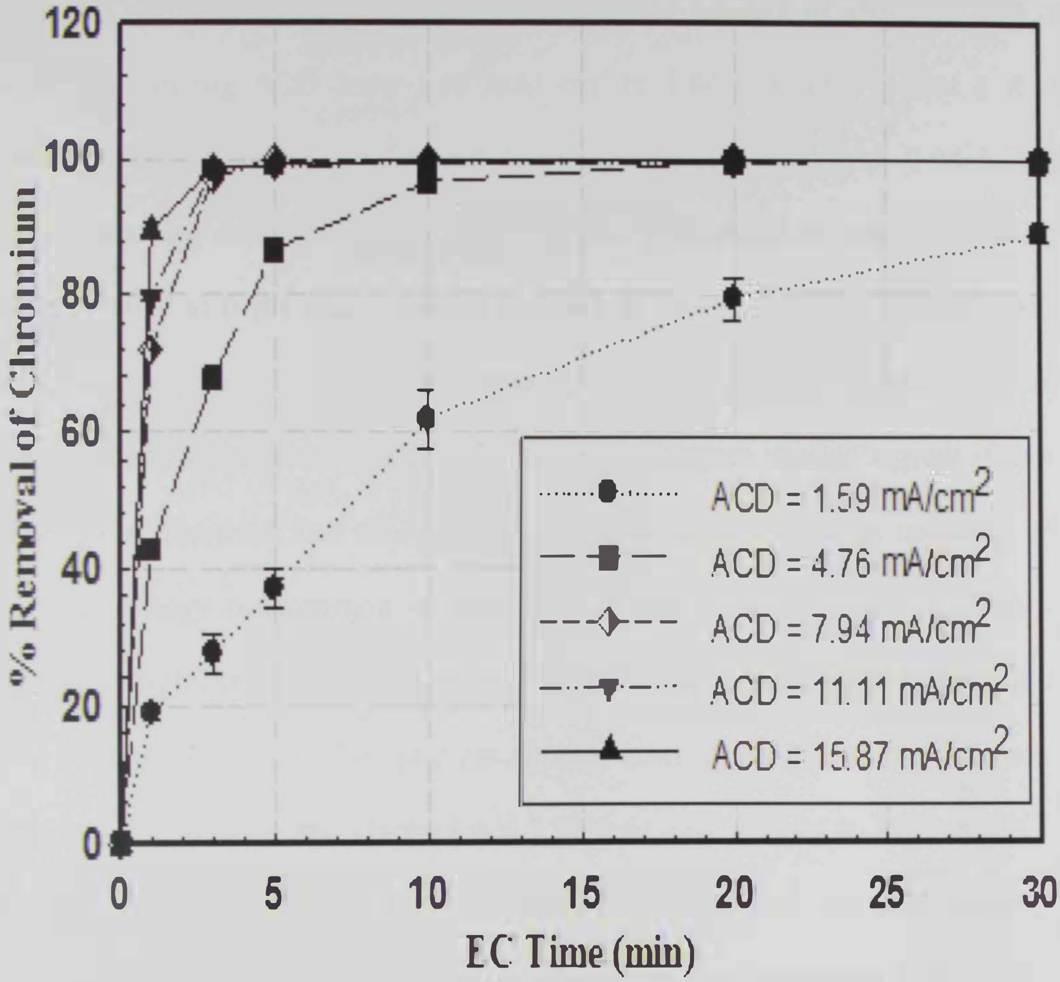


Fig.4.15.Influence of Applied Current Density on the performance of continuous stirred EC at Q_L = 90 ml/min.

When it comes to optimizing the applied current density, three major parameters are essential in evaluating the removal efficiency: the electrical energy consumption (EEC) (Eq. 2.14), the amount of iron ions dissolved from sacrificial anode and the operating electrical costs. Fig.4.16 presents both electrical energy consumption and the amount of dissolved iron, for different values of ACD, with an electrolysis time of 30 min. The results show that increasing the ACD leads to an incremental rise in energy consumption as well as the amount of dissolved iron. In that case, increasing ACD from 1.59 mA/ cm^2 to 7.94 mA/ cm^2 causes a slight increase in the cell voltage and therefore energy consumption from 0.04 to 0.80 kWh/m^3, electrical costs from 0.002 to 0.032 $US\$/m^3$ (Table 4.6) and dissolved iron dose from 0.099 to 0.304 mg/L. Further increase in current density (maximum ACD =15.87 mA/cm^2) brings up the energy consumption significantly to about 2.6 kWh/m^3 (electrical costs equal to 0.106 $US\$/m^3$). At this maximum applied current density, the amount of dissolved iron exceeded the environmental regulations, reaching 1.03 mg/L. The energy consumption is directly attributed to the increase in potential difference at high current density, and most of that energy is converted to heating the reactor content. Therefore, the optimum applied current density for the continuous electrocoagulation using iron electrodes is 7.94 mA/ cm^2 with an acceptable EEC of 0.80 kWh/m^3 and a reasonable electrical cost of 0.032 $US\$/m^3$. At these conditions chromium is completely removed from the contaminated groundwater after a shorter electrolysis time (t_{EC} = 5 min) with an acceptable iron dose of 0.304 mg/L.

Table 4.6 Electrical costs of continuous stirred EC at inlet flow rate of 90 ml/min and different applied current densities.

ACD (mA/cm^2)	Voltage (kV)	EEC (kWh/m^3)	Electrical cost (US $/m^3)
1.587	0.002	0.041	0.002
4.762	0.005	0.253	0.010
7.937	0.009	0.792	0.032
11.111	0.009	1.219	0.049
15.873	0.014	2.611	0.106

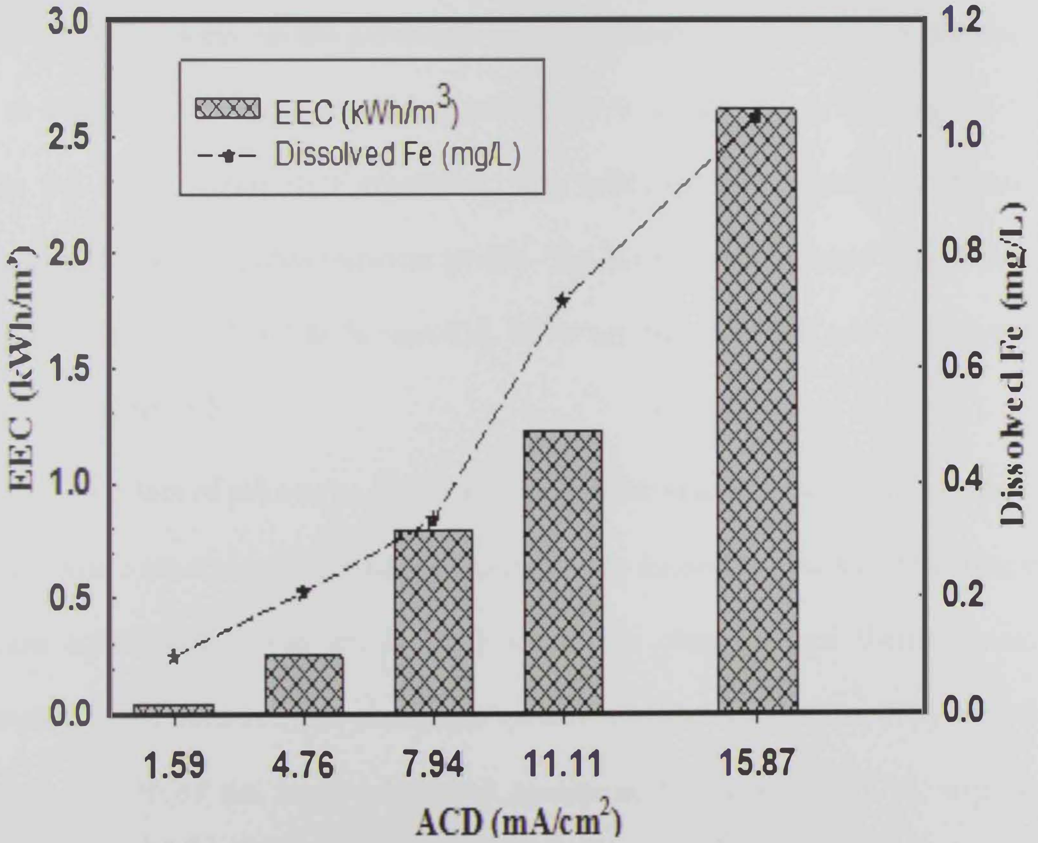


Fig.4.16. Electrical energy consumption and dissolved Fe dose as a function of ACD at inlet flow rate 90 mL/min using iron electrode.

4.2.5. Effect of Initial pH

As presented in Section 2.3, the electrocoagulation process results in the formation of iron and chromium ions, which form metal hydroxides with OH^- species, depending on the pH of the wastewater. Thus metal hydroxides (mainly, $Fe(OH)_3$ and $Cr(OH)_3$) tend to form insoluble coagulants at suitable initial pH, so easily separated by filtration. Therefore, the initial pH is a key operating parameter that influences the performance of EC process. Several experiments were performed by adjusting the initial pH using H_2SO_4 and NaOH at inlet flow rate of 90 mL/min, using iron electrodes. The experimental results, illustrated in Fig.4.17, clearly indicate that the continuous EC process has the capability to remove more than 90 % of the chromium ions as long as the pH of the treated groundwater is maintained in the range of 5 to 10. At this range, steady-state conditions were achieved more rapidly and removal rate was higher in the initial transient period. The highest performance was observed at initial pH of 8, with a 100 % removal. However, the reduction rate of chromium was poor at a pH of 2.

The effect of pH can be explained by complex reactions generated during EC process, which are strongly related to hydroxide ions formed in situ, thus affecting the reaction equilibrium. Di'az et. al. [77] tested the chemical and thermodynamic characteristics of both iron and chromium species in aqueous solutions. They reported that, as the pH of the wastewater was monitored between 4 and 10, iron and hydroxide ions were generated by electrochemical reactions forming various polymeric species such as: $Fe(OH)^+$, $Fe(OH)_2^+$, $Fe(OH)_4^-$, and $Fe(OH)_2$ thus finally transforms into $Fe(OH)_3$ as a predominant insoluble hydroxide though complex polymerization-precipitation kinetics. At the same time, initial pH within the range of 8 to 10 is needed to form insoluble $Cr(OH)_3$ [90]. Thus, there is an overlap with the pH required to reduce and form insoluble metals hydroxide ions. In addition, pH of the wastewater affects the generation rate of gas bubbles [91], which provide both sufficient surfaces area for gas-liquid-solid interface and mixing efficiency toward the aggregation of tiny destabilized particles. In addition, the generated hydroxide ions were affecting the reaction equilibrium. At an acidic pH of 2, low generation of OH^- ions increased the reverse reactions forming soluble chromium and iron ions, thus preventing the formation of insoluble hydroxide compounds and lowering chromium removal efficiency. In contrast, an increasing the chromium reduction efficiency at higher initial pH (pH > 2) is attributed to the generation of large amount of hydroxide ions, thus forming more insoluble hydroxide compounds ($Cr(OH)_3$ and $Fe(OH)_3$).

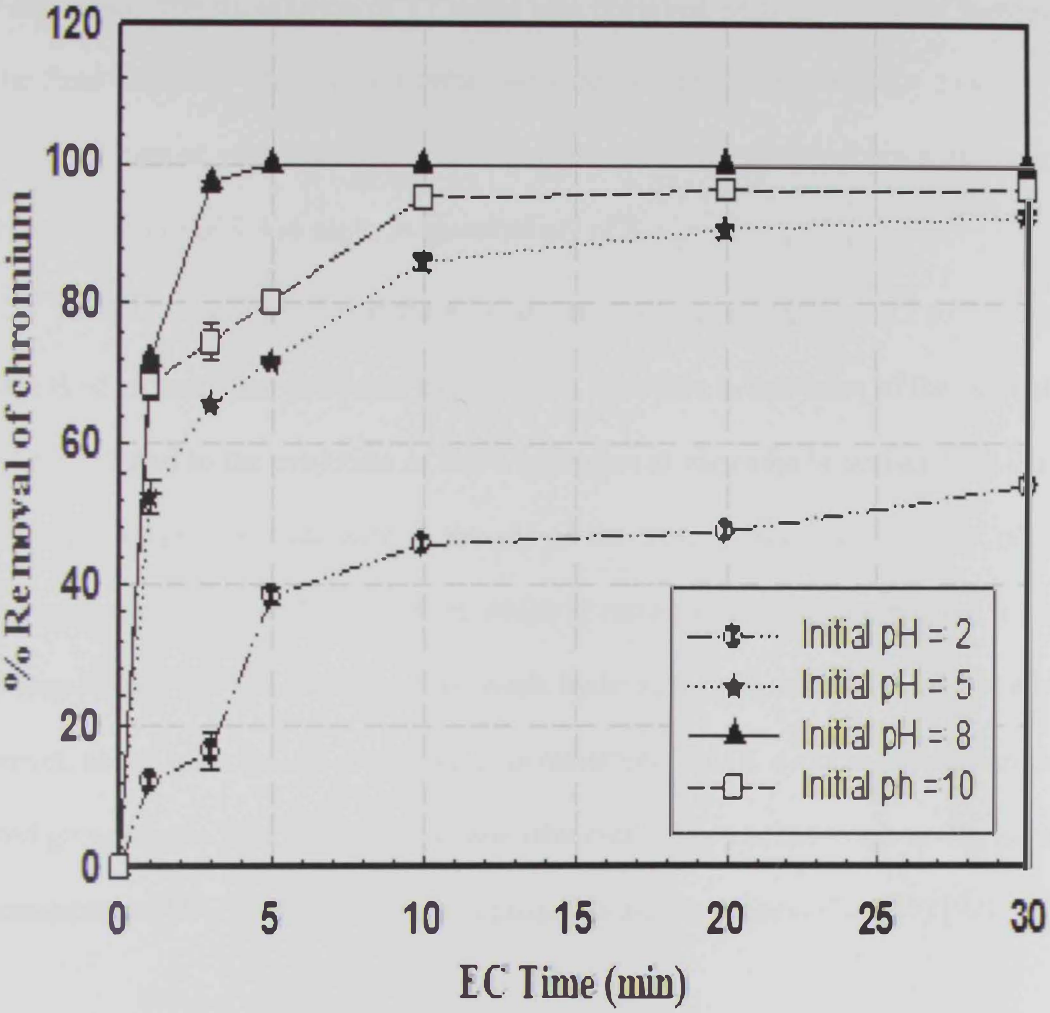


Fig.4.17. Influence of pH at Q_L = 90 ml/min, Cr_0 = 5 mg/L, and ACD = 7.94 mA/cm^2 using iron electrode.

Optimum initial pH must be selected based on the highest chromium removal rate in combination with minimum dissolved iron after the treatment. For this reason, the final pH and the total dissolved iron of the treated groundwater were analyzed and the results are illustrated in Fig 4.18. The results indicated that high initial pH reduced the concentration of dissolved iron ions after the treatment. At an initial acidic pH of

2, a maximum iron dissolution of 17 mg/L was observed with a significant increase on the final pH (final pH = 4.2). Further increases in the initial pH (pH> 2) sharply reduced the amount of dissolved iron in the treated groundwater reaching a minimum iron concentration of 0.304 mg/L at an initial pH of 8.

It was also observed that the final solution pH increases from 4.2 to 9 as the initial pH of groundwater increases from 2 to 10. This rise in the value of the final pH may be attributed to the evolution of more hydrogen at the cathode surface (Eq. 2.1). In addition, insignificant increase in the pH of the treated groundwater (final pH = 9.1) was obtained at initial pH of 8, in which it remains almost constant due to the buffering capacity of the $Fe(OH)_3$, thus week hydroxide ions were generated in situ. However, as the initial pH of groundwater is maintained at 10, a slight decrease in the treated groundwater pH (final pH = 9) was observed. This phenomenon is due to the accumulation of OH- ions in the aqueous phase during the process (Eq. 2.5) [92].

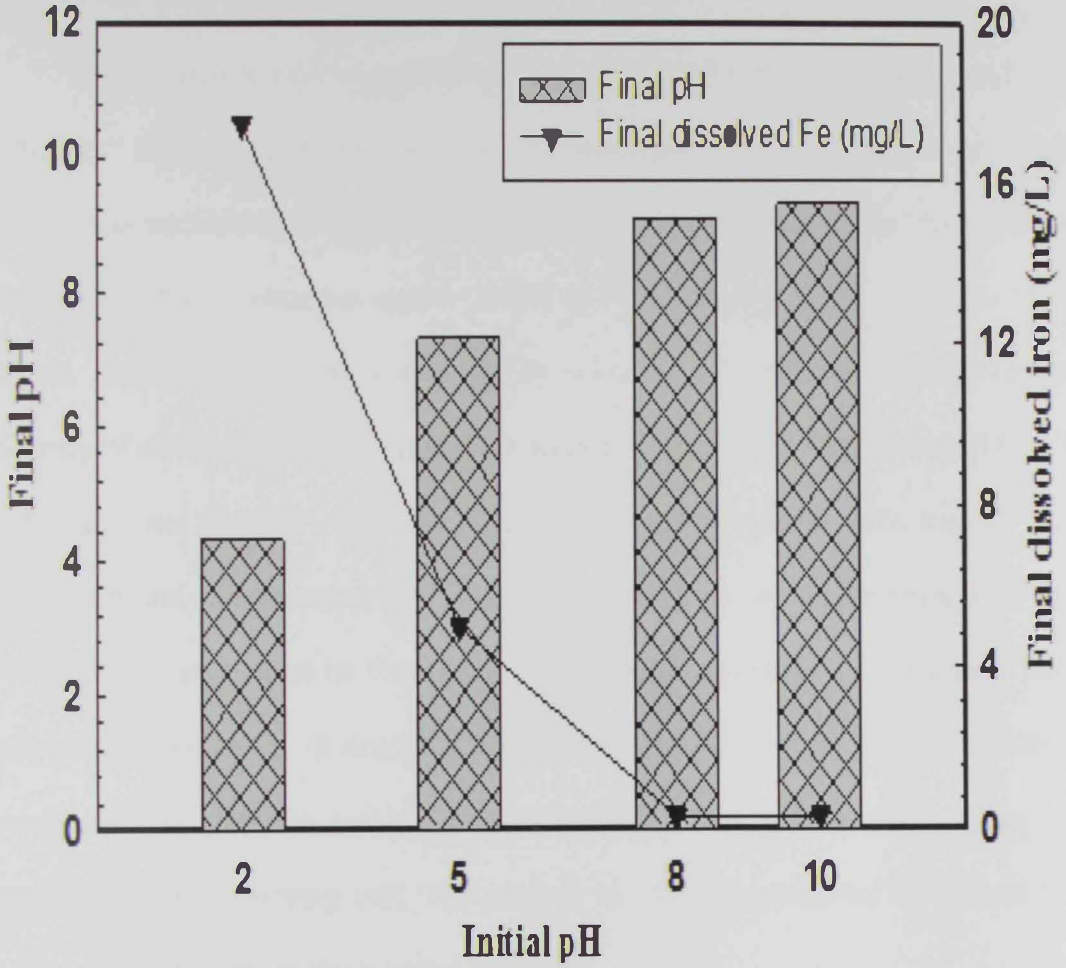


Fig.4.18. Amount of dissolved iron and pH of effluent treated groundwater.

It can be conclude that the optimum pH must be chosen in order to achieve the best removal efficiency with minimum soluble iron content and maintaining a pH value close to neutrality to avoid downstream treatment for pH adjustment. For these reasons, the most favorable initial pH value, within the investigated range, is 8 with the highest removal rate of chromium.

4.2.6. Effect of Initial Concentration

Initial pollutant concentration plays a significant role in the performance of continuous electrocoagulation process. Experiments were conducted at initial chromium concentration ranging between 0.225 and 100 mg/L, using the optimum operating conditions obtained earlier: ACD of 7.94 mA/cm^2, inlet flow rate of 90 mL/min, initial pH of 8 and iron electrode material. Fig. 4.19 shows the removal efficiency of chromium from groundwater samples using CSTR electrocoagulation. It can be seen that removal efficiency of chromium reached 91%, 98% and 97 % at initial chromium concentration of 0.2 mg/L, 1 mg/L and 5 mg/L, respectively (within an electrolysis time equal to 5 min). At these initial concentrations, a steady state could be reached within 10 minute of electrolysis reaction. Higher initial chromium concentration slowed the performance of the CSTR process and decreased the removal efficiency, reaching only 90 % and 67 % chromium removal for 20 and 100 mg/L, respectively (electrolysis time of 30 min).

Faraday's law (Eq. 2.12) shows clearly that at a given applied current, the iron ions dissolved from sacrificial anode are not enough to reduce higher concentration. Whereas longer electrolysis time is required to accumulate iron ions in aqueous solutions and consequently improve the reduction rate forming more coagulants.

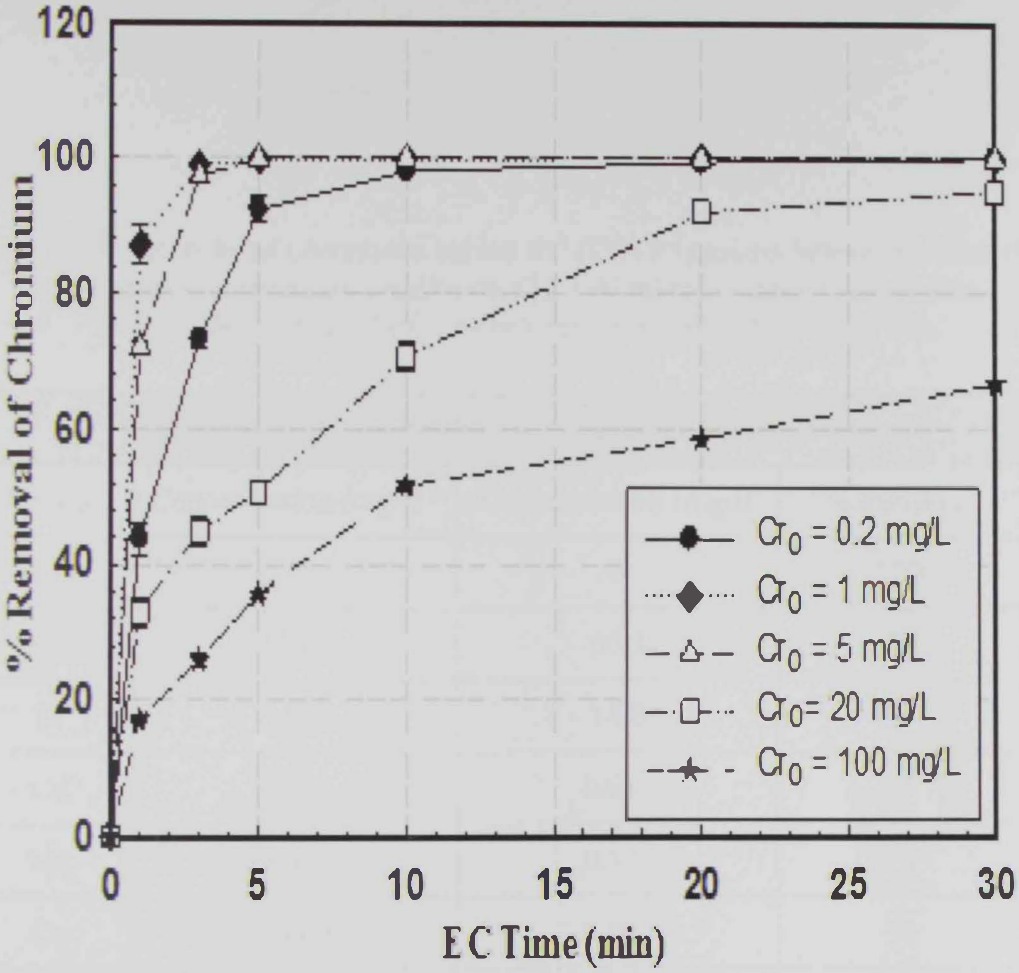


Fig.4.19. Influence of initial chromium concentration at Q_L = 90 mL/min, pH 8 and ACD equal to 7.94 mA/cm^2.

4.2.7. Optimum Operation Conditions for CSTR EC

A chromium removal efficiency of 100% was achieved at inlet flow rate of Q_L = 90 ml/min, initial pH = 8, ACD of 7.94 mA/cm^2 using iron electrodes, at room temperature (T = 25 ^{0}C).These results highlight the potential of applying CSTR EC process for the efficient removal of chromium and other pollutants from groundwater (Table 4.7) at low operation costs.

Table 4.7 Results of continuous stirred EC (CSTR) process before and after the treatment at optimum conditions: Q_L = 90 ml/min, initial pH = 8, Iron electrodes and ACD of 7.94 mA/cm^2, Operation time = 30 min.

	Feed groundwater	**Treated groundwater**	
Metals	Concentration (mg/l)	Concentration (mg/l)	% Removal
Cr	5	0	100
Mg	110.8	80.3	28
Sr	18.4	14.8	19
Cd	0.018	0.015	17
Mn	0.66	0.175	73
Cu	0.066	0.044	34
Zn	0.141	0.025	83
Fe	–	0.304	–

4.3. Continuous EC Column Process

During the past few years, considerable amount of research has been focused on the development of new and more efficient continuous EC processes. Recently the performance of vertical electrochemical column was examined for removing different types of pollutions (Table 4.8) such as: COD, color, turbidity [93, 94] and phenol [95] in addition to the dynamic model of horizontal column for the removal of chromium [96]. Even though these processes could reach high removal efficiency, they are suffering from high cost due to the use of carbon steel as a sacrifice anode.

This part of the study evaluates the performance of a novel electrocoagulation column (ECC) for the removal of chromium from brackish groundwater. To the best of the author' knowledge there is no studies in the open literature that address the removal of chromium from groundwater using ECC system. The aim of the current study is to assess the chromium removal efficiency and estimate the energy consumption as well as sludge generation using this new approach.

Table 4.8 Electrochemical column process

Wastewater Source	Reactor capacity / [CC]	Reactor Orientation	Electrode materials	Mixing type	Residence time	Treatment efficiency	Reference
Simulated wastewater	Cr [1000 mg/L]	Horizontal	Carbon steel wire - rod	No mixing	--*	--*	[96]
Simulated wastewater	1934 L//Phenol [3100 mg/L]	Vertical	Carbon rod- Steel tube	No mixing	10-180 min	42-98%	[95]
Simulated paint wastewater	1774 L//COD [7496 mg/L]// color// turbidity	Vertical	Carbon rod- Steel tube	No mixing	60 - 480 min	44.1% // 86.2% // 87%	[93]
Industrial wastewater	3 L//COD [2100 mg/L]// turbidity// color	Vertical	12 Al horizontal sheets	Air mixing	15, 30, and 60 min	80% // 92% // 94%	[94]

* Simulated data

4.3.1. Column Electrocoagulation Procedure

The electrocoagulation experiments were conducted in a continuous Plexiglas cylindrical column (ID = 6 cm; H = 52 cm) with a total volume of 1470 ml. The EC column was designed with a symmetrical section to produce uniform liquid velocity distribution with a cyclic motion of contaminated water between the electrodes and the internal wall of the reactor, which is generated by an air jet injected through an orifice in the bottom of their actor, thus eliminating any tendency toward bulk circulation [96]. Parallel to the air jet, a feed nozzle was connected to the bottom of the reactor to feed groundwater using a peristaltic pump (Master Flex 7553-79) to control the feed flow rate. The total volume of the groundwater treated in each experiment was about 1100 ml; an iron rod with dimensions of 39 cm X 0.53 cm and a total surface area of 65.6 cm^2 was used as anode. A helical stainless steel cathode of 4 m in length was wrapped around the anode rod, while maintaining a fixed distance between the rod and the helical coil. The electrodes were placed in the middle of the column and connected to a DC power supply (Popular PE-23005). A schematic diagram of the experimental setup is shown in Fig.4.20. A jacket was designed to control the temperature of the groundwater inside the column and achieved homogenous distribution of temperature along the column. The treated groundwater and formed flocs were separated by gravitational settling after the EC column.

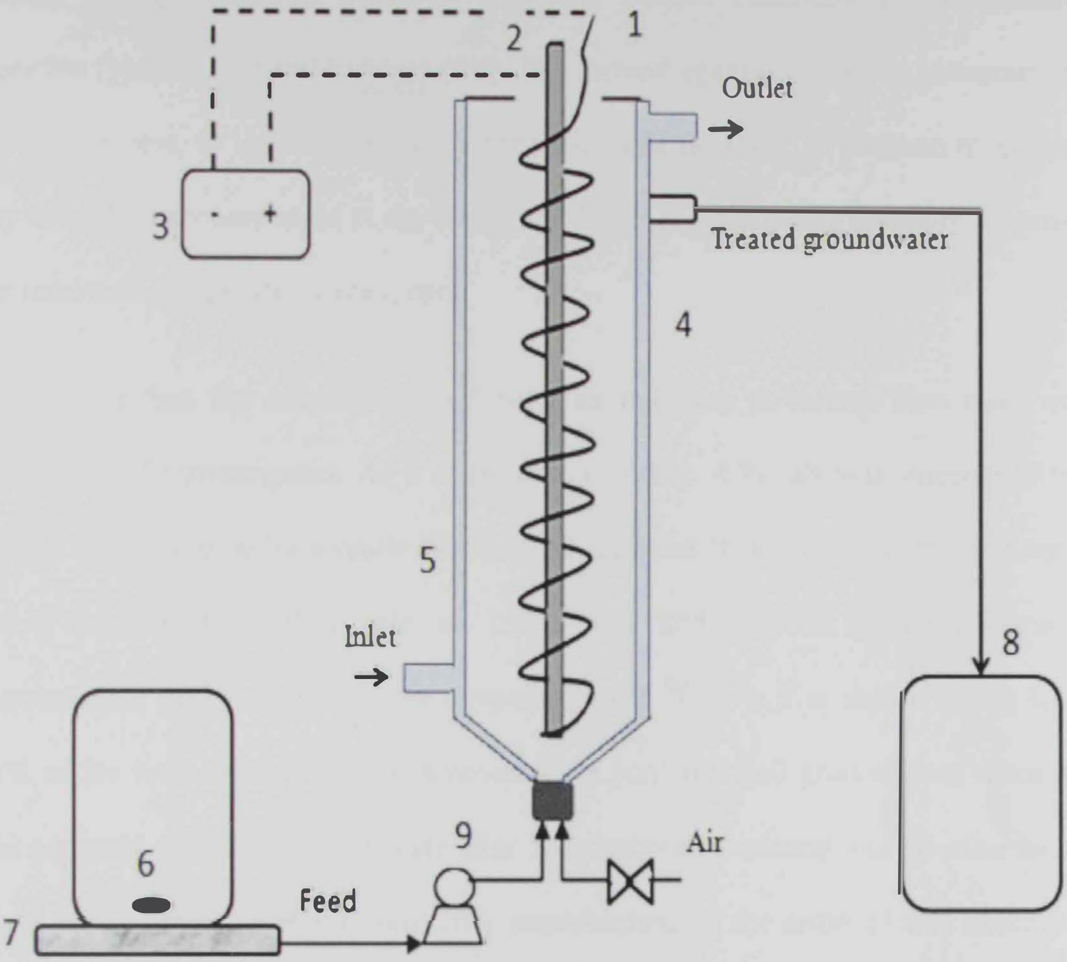


Fig.4.20. A schematic diagram of electrocoagulation column (ECC) system: 1- Helical cathode, 2- Rod anode, 3- DC power supply, 4- Plexiglas column, 5- Water jacket, 6- Magnetic bar stirrer, 7- Magnetic stirrer, 8- Settling tank, 9- Feed Pump.

4.3.2. Effect of Mixing Rate

Mixing characteristics are considered one of the major parameters that affect the removal efficiency, in addition to the hydrodynamic ideality of the column system. It can be created in several ways such as air injection (rising bubbles), solids contact (sludge blanket), hydraulic (jets and baffled channels) and mechanical agitation (paddle, reel and turbine) [56]. The formed agitation by air is necessary, in column process, to induce coagulant's formation and flotation, in addition to prevent any coagulant accumulation at the bottom of the ECC reactor and therefore, improve the removal of a specific contaminant.

For that, the effectiveness of using air injection at various flow rates was experimentally investigated. As it is illustrated in Fig. 4.21, air was injected in the bottom of EC column by a single air nozzle at different flow rates (0 L/min, 2 L/min, and 4 L/min); inlet flow rate of 150 L/min and constant initial chromium concentration of 20 mg/L at room temperature (25 ^{0}C). As it is shown in Fig.4.21, 66% of the total chromium was removed from contaminated groundwater when air was not used, reaching a steady state after 30 minutes of treatment. On the other hand, when air was injected at 2 L/min, 20% improvement in the removal was observed, whereas a maximum chromium removal efficiency of 94 % was achieved after 60 min of electrolysis time at air flow rate of 4 L/min.

High rate of mass transfer between the electrodes surfaces and contaminants in groundwater at the high flow rate of 150 mL/min, explains the high removal without using air (i.e. air flow rate = 0). Nevertheless, as the air flow rate is increased from low (2 L/min) to moderate (4 L/min), the gas–liquid interfacial contact is enhanced due to the speeding up of bubble formation and thus increasing the concentration of dissolved oxygen generated in the system [98]. Therefore, high air flow improves the destabilizing rate of dissolved ions generating insoluble metal hydroxide and increasing coagulant growth size. In addition, using high air flow rate raises the turbulence of liquid phase around the rising bubbles [99]. They are then removed subsequently by flotation. So the optimum air flow was selected at 4 L/min.

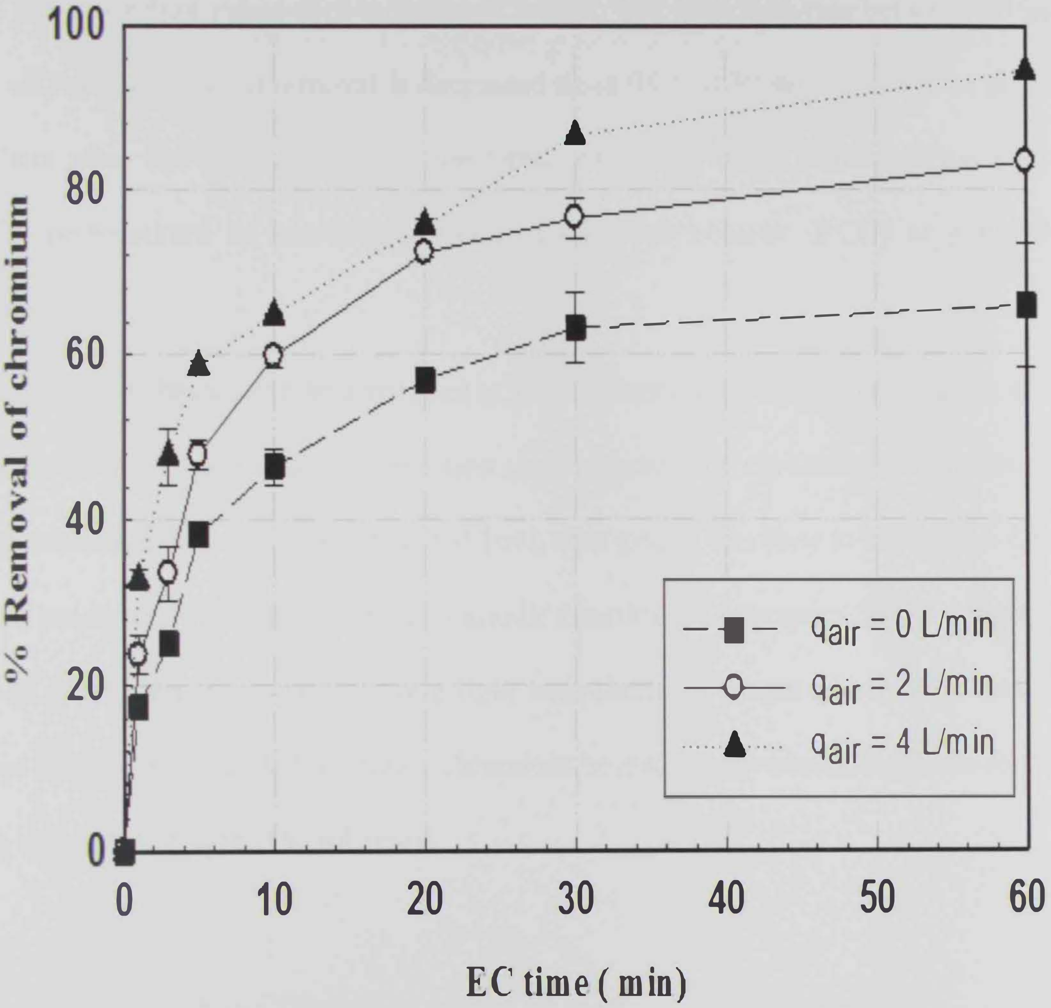


Fig.4.21. Effect of air mixing on the performance of continuous EC column at Q_L = 150 mL/min, Cr_0 = 20 mg/L, pH = 8 and I = 0.5 A.

4.3.3. Effect of Inlet Flow Rate

The effect of feed flow rate on the removal of chromium at two initial chromium concentrations 5 mg/L and 20 mg/L and inlet air flow rate of 4 L/min were experimentally evaluated. The influent flow rate Q_L was progressively increased from 30 mL/min to 150 mL/min, and the results are shown in Fig.4.22. Generally, it was observed that the performance of EC column is inversely proportional to influent flow rate. For a constant initial concentration of 5 mg/L and inlet flow rate between 30 and 150 mL/min, chromium removal is decreased from 93% at 30 mL/min to 43% at 150 mL/min after one minute of operation time. At higher initial concentration of 20 mg/L, performance of continuous electrocoagulation column (ECC) is generally decreased.

This behavior can be attributed to the residence time inside the column; high influent flow rate provides short reaction time between the chromium ion present in the groundwater and the iron anodic rod [64], thus giving less time to adsorb the flocs which tends to slow down the rate of anodic reactions. Consequently, the reduction rate of chromium is reduced forming light coagulants. A longer electrolysis time of about 120 min was needed to reduce chromium below the environmental limit for the high influent flow rate (150 mL/min).

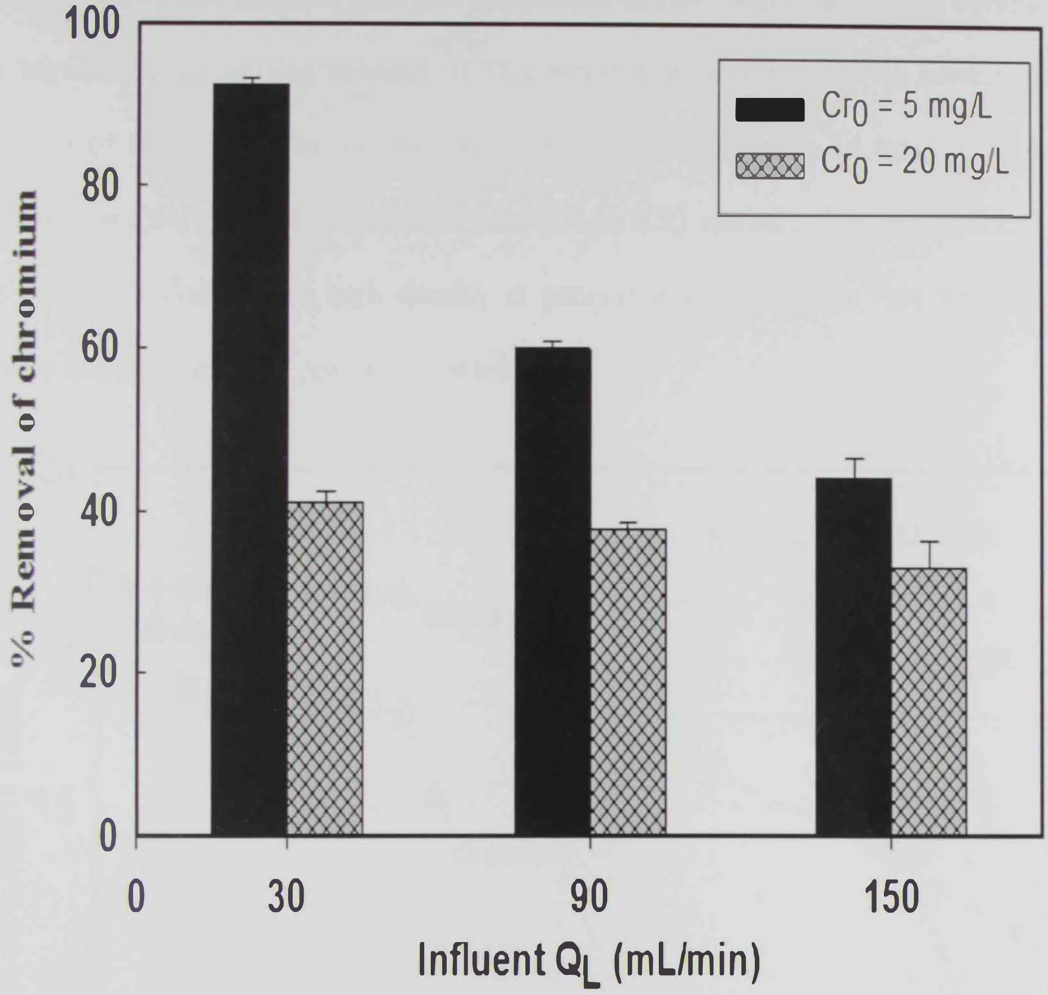


Fig.4.22. Effect of inlet flow rate on chromium removal at electrolysis time of 1 minute, I = 0.5 A, and q_{air} = 4 L/min.

It was experimentally observed that a large amount of sludge was generated as the flow rate decreased, forming larger coagulants size, which directly affected the settling rate and therefore the separation rate in settling tank. In order to predict zone settling velocity (ZSV) of treated groundwater, sludge settling experiments were conducted at room temperature and the results are presented in Fig. 4.23 and the slope of zone settling of each experiment was determined. An inverse relation between settling velocity and influent flow rate at constant initial concentration was obtained. The highest sludge settling velocity of 15 cm/min was obtained for the lowest inlet flow rate of 30 mL/min. In contrast, as the inlet flow rate increased from 90 to 150 mL/min, the ZSV gradually decreased from 2.5 to 0.33 cm/min, thus confirming the fact that large sludge with high density is generated at lower flow rate which can provide fast separation by gravitational settling.

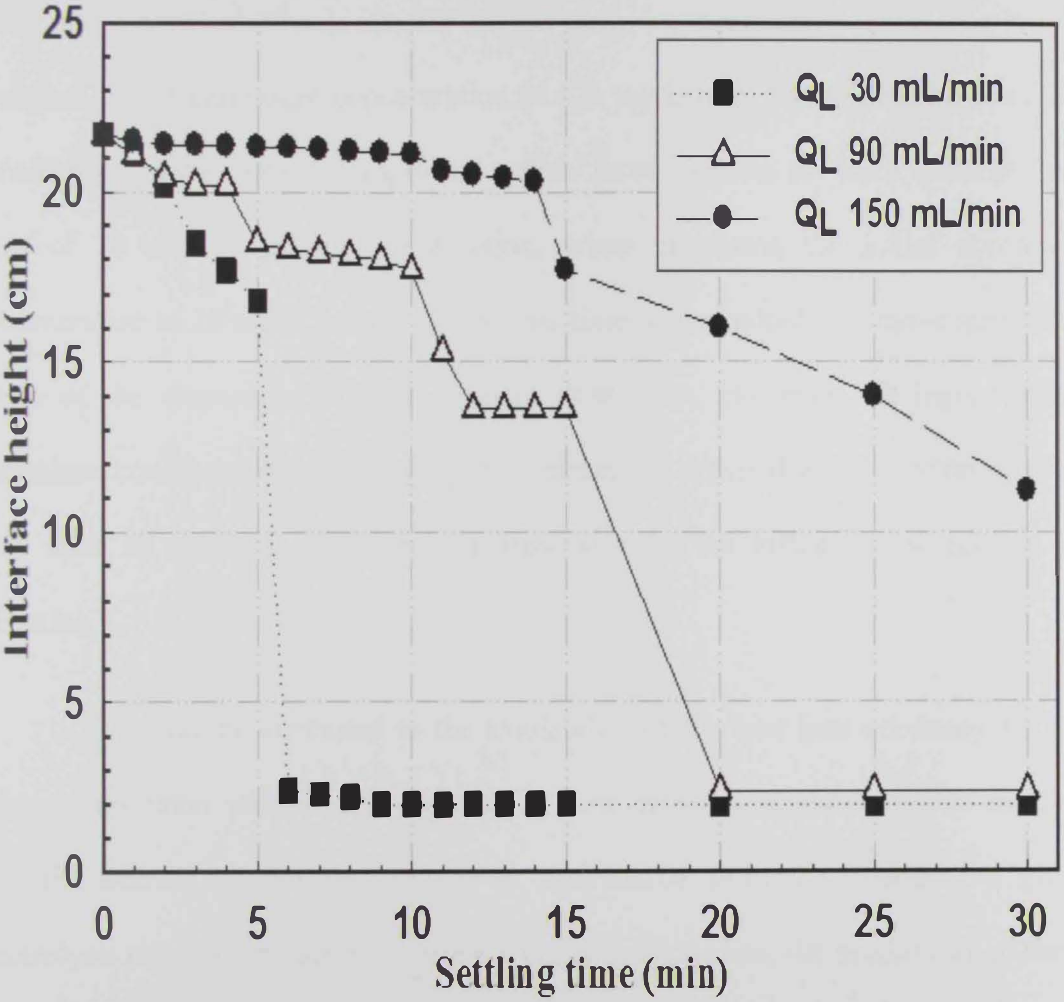


Fig.4.23. Settling profile of treated groundwater as a function of inlet flow rate at C_0= 5 mg/L.

4.3.4 Effect of Initial Concentration

The removal efficiency of chromium from groundwater was investigated as a function of initial concentration ranging from 0.225 to100 mg/L. The obtained results are shown graphically in Fig.4.24 & 4.25 at inlet flow rates of 30 and 90 mL/min, respectively. It was experimentally proved that the removal rate of chromium was faster at Q_L equal to 30 mL/min for all the studied concentration range. For low to moderate initial chromium concentration (0.225 mg/L to 5 mg/L), a quick complete chromium removal was accomplished within three minutes for both influent flow rates of 30 and 90 ml/min. In addition, when increasing the initial chromium concentration to 20 mg/L, longer electrolysis time was required to remove more than 90 % of the chromium for both influent flow rates. However, for higher initial chromium concentration (100 mg/L), the chromium removal efficiency dropped to 60% after 30 minutes of electrolysis treatment for the influent flow rate of 90 mL/min.

This may be attributed to the availability of the iron ions necessary for the electrocoagulation process. At fixed inlet flow rate and applied current density, constant amount of iron ion dosage is dissociated from the anode at a given electrolysis time. As the initial chromium concentration rises, the availability of these ions becomes the limiting factor. This effect is more pronounced for high influent flow rate due to the reduced residence time inside the column. For low feed flow rate, a longer reaction time was provided for the iron ions to react and destabilize the dissolved chromium, forming more flocs [56].

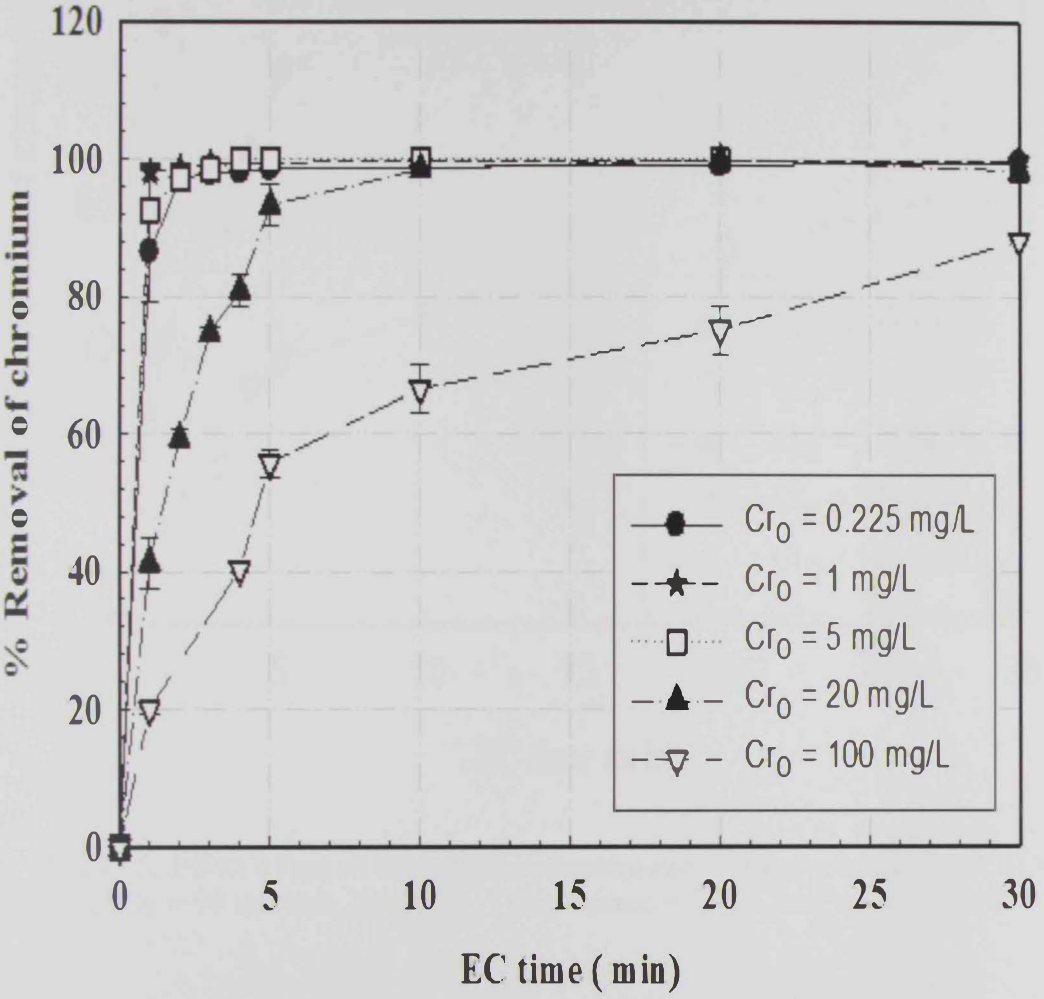


Fig.4.24. Effect of initial chromium concentration on the performance of ECC at Q_L = 30 mL/min, I = 0.5 A, Temperature = 25 ^{0}C, and initial pH = 8.

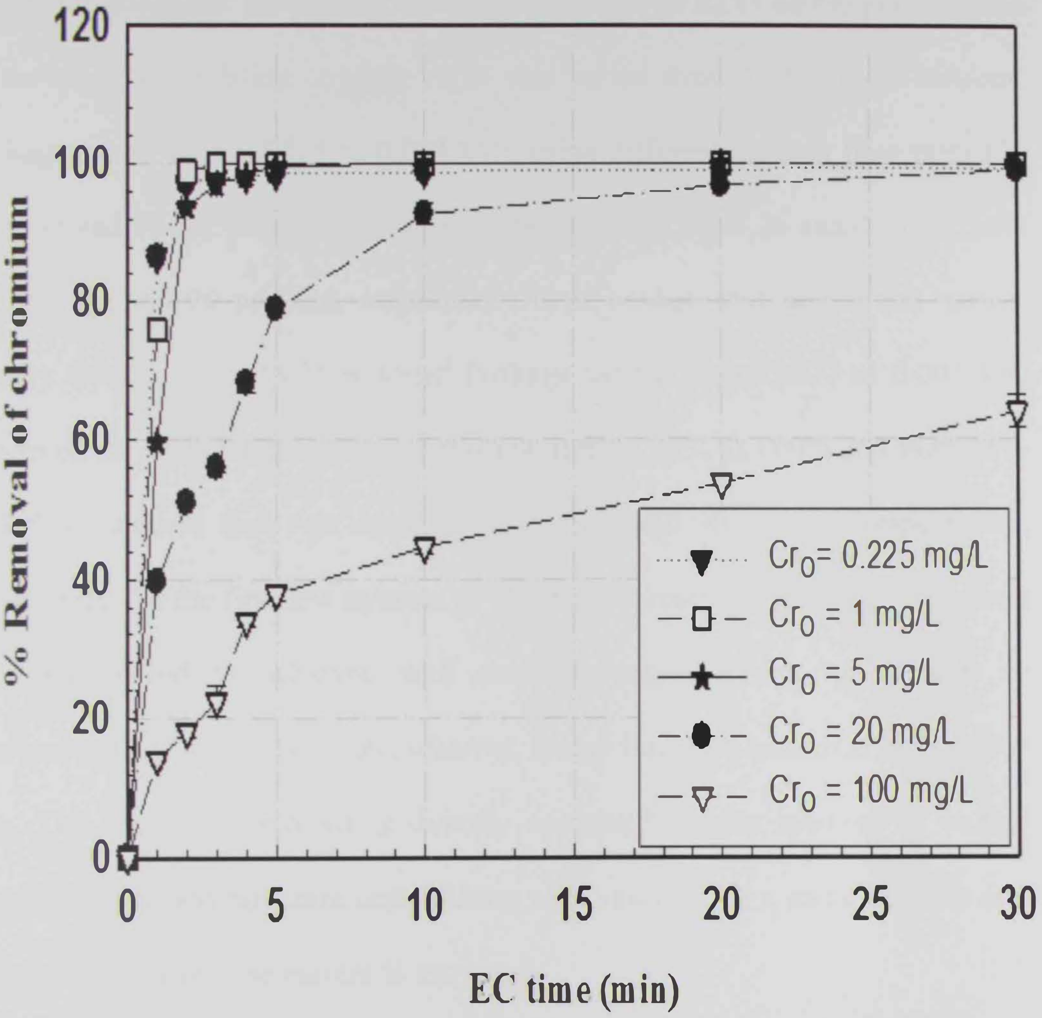


Fig.4.25. Effect of initial chromium concentration on the performance of ECC at Q_L = 90 mL/min, I = 0.5 A, Temperature = 25 ^{0}C, and initial pH = 8.

4.3.5. Effect of Applied Current Density

Applied current density (ACD) is one of the most important parameters that control the performance of continuous electrocoagulation column process [47]. It is well known that ACD determines the removal rate of a specific contaminant, the amount of Fe^{2+} dose achieved within the process, and hence affects the coagulant growth [5]. To study the effect of ACD on the performance of the electrocoagulation column, ACD was varied from 3.04 to15.21 mA/cm^2 (voltage raised from 0.0019 to 0.003 kV), using different influent flow rates (30 mL/min and 90 mL/min). The results are presented in Fig.4.26 and 4.27 for both 30 mL/min and 90 mL/min, respectively. It is evident that raising the current density from 3.04 to 15.21 mA/cm^2 (voltage ranged from 0.002 to 0.003 kV) improved the removal efficiency of chromium from 30% to 100% and from 14% to 90% at influent flow rate equal to 30 mL/min and 90 mL/min, respectively; particularly, for the first few minutes of electrolysis reaction. Indeed, steady-state conditions could be achieved with complete removal after 10 minutes of continuous ECC at low flow rate; whereas, longer time was needed at higher flow rate. This expected behavior is directly explained by the increase of bubble generation rate and pollutant destabilizing rate, resulting in a more efficient and faster removal when the current is increased.

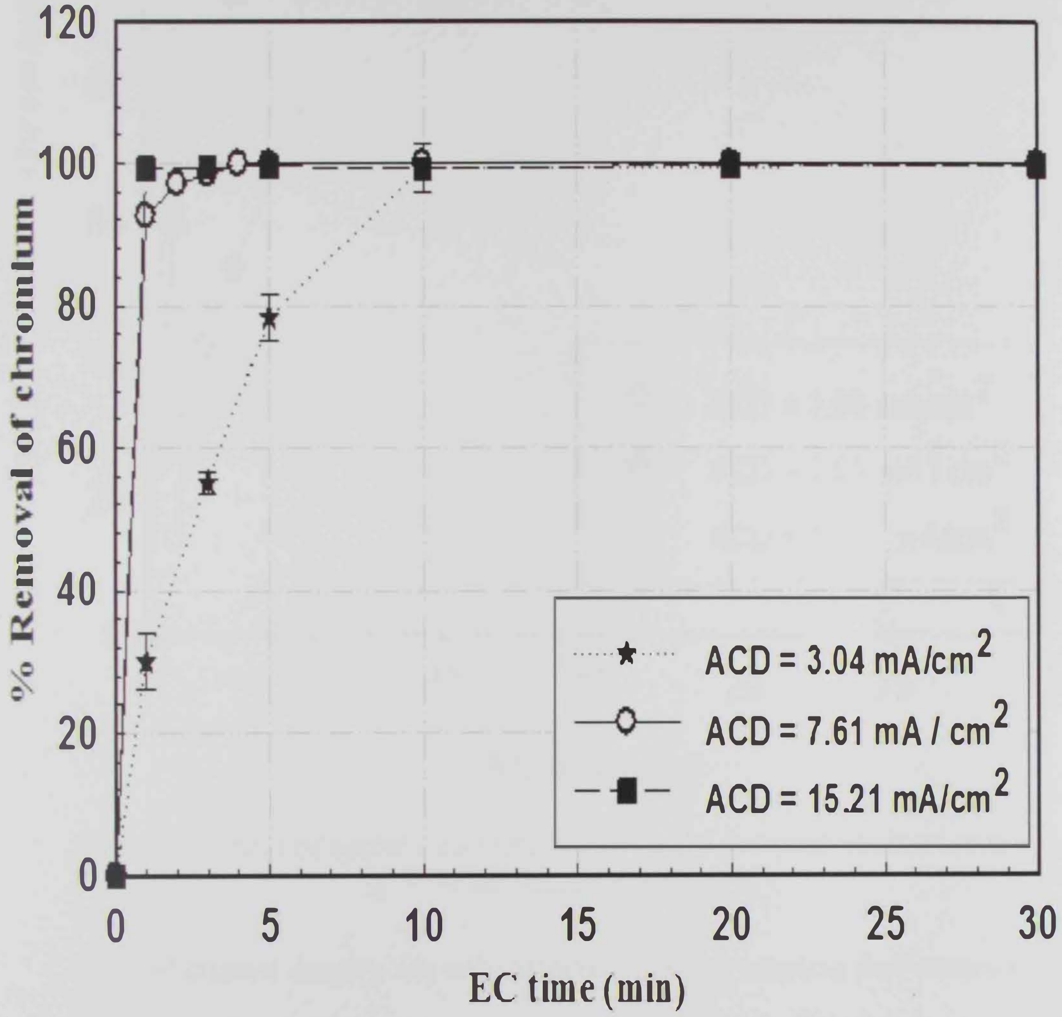


Fig.4.26. Effect of applied current density on chromium removal at $Q_L = 30$ mL/min and $C_0 = 5$ mg/L.

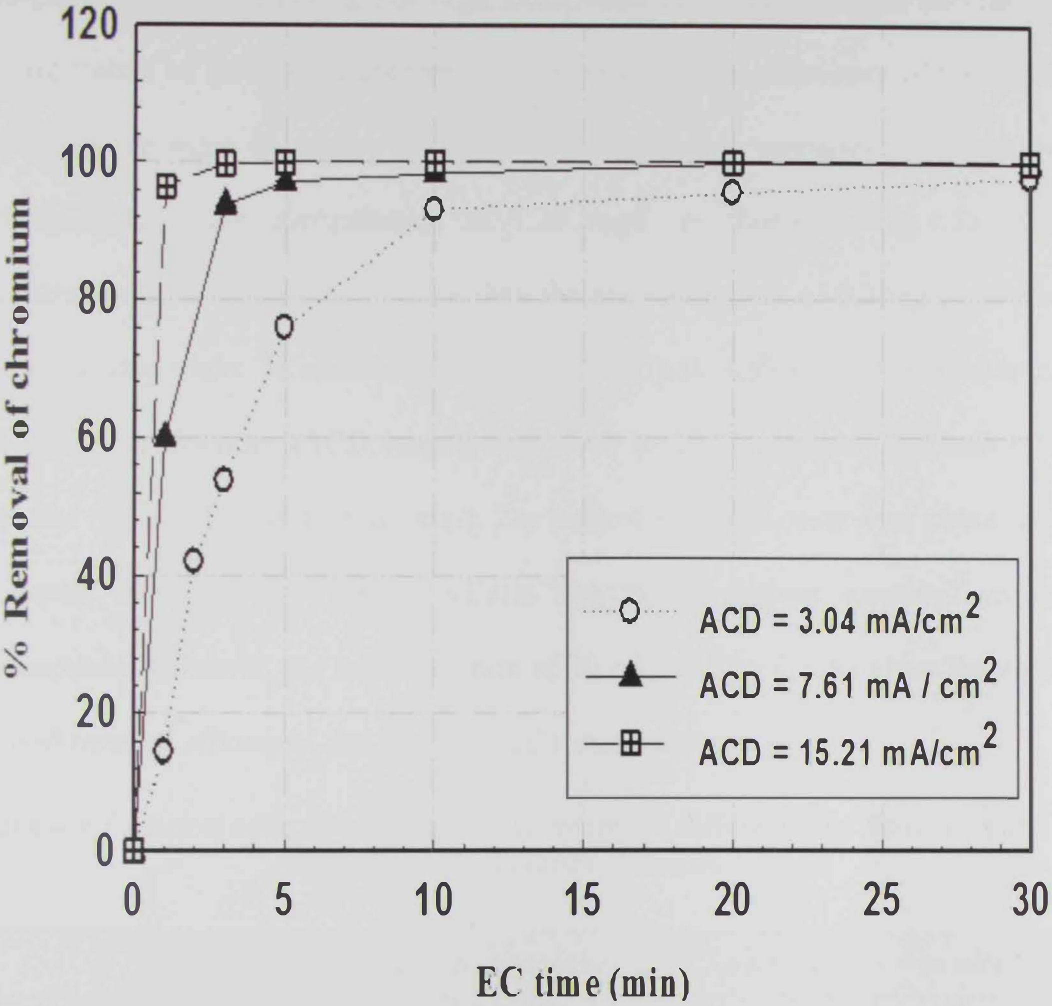


Fig.4.27. Effect of applied current density on the removal of chromium at Q_L = 90 mL/min, C_0 = 5 mg/L.

Applied current density not only affects reduction reaction that occurs in the column, but also controls the amount of iron ions dissociated from the electrodes and consequently affects the electrical energy consumption (EEC). The EEC was calculated using Eq. (2.14) for both flow rates and the results are shown in Fig.4.28. Generally, there is a direct relation between energy consumption and applied current, and an inverse-relation with respect to the influent flow rate. Indeed, maximum EEC of 1.83 kWh/m^3 was obtained for the lowest flow rate (30 mL/min) and the highest

ACD (ACD = 15.21 mA/cm^2). For high ACD, most of the energy goes into raising the temperature of the reactor content and thus reducing the efficiency of the whole process. At the same flow rate, the amount of iron ions is increased considerably, reaching a maximum concentration of 1.39 mg/L as shown in Fig.4.28. This concentration is about six times higher than the allowable limit of 0.3 mg/L for iron ions in drinking water. In addition, electrical costs (Table 4.9) were estimated at the applied current densities (ACD ranged from 3.04 to 15.21 mA/cm^2) for both inlet flow rates (Q_L equal 30 and 90 mL/min). The highest electrical costs were obtained at the lowest inlet flow rate of 30 ml/min due to the highest electrical energy consumptions. However, the inlet flow rate of 30 ml/min (I = 0.5 A) gives favorable for good removal efficiency, and low iron ion concentrations.

Table 4.9 Electrical costs of continuous EC column at different inlet flow rates and different applied current densities.

		Inlet flow rate = 90 ml/min		**Inlet flow rate = 30 ml/min**	
ACD (mA/cm^2)	**Voltage (kV)**	**EEC (kWh/m^3)**	**Electrical cost $(\text{US }\$/\text{m}^3)$**	**EEC (kWh/m^3)**	**Electrical cost $(\text{US }\$/\text{m}^3)$**
3.04	0.0019	0.0704	0.003	0.211	0.009
7.61	0.0028	0.2593	0.011	0.750	0.030
15.21	0.0033	0.6111	0.025	1.833	0.073

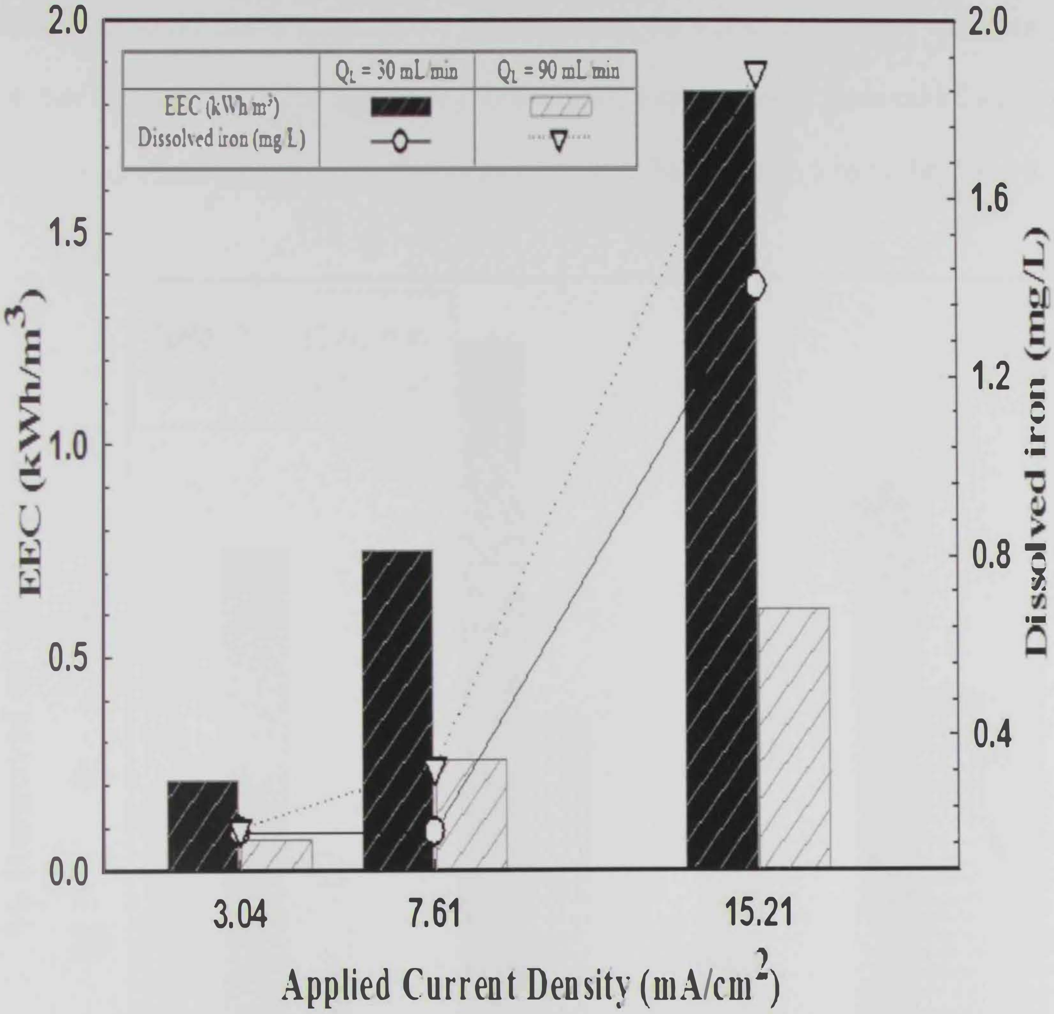


Fig.4.28. Electrical energy consumption and dissolved iron as function of current densities.

4.3.6. Effect of pH

Chromium removal by electrocoagulation has a complicated mechanism that is highly sensitive to the solution pH, since it affects the reaction pathways and the formation of intermediate compounds. The performance of the ECC was examined at initial solution pH ranging between 2 and 10, ACD equals to 7.61 mA/cm^2 and influent flow rates of 30 ml/min and 90 ml/min. As illustrated in Fig.4.29, the highest chromium removal (more than 90 %) was obtained for initial pH ranged between 5 and 8. For the same influent flow rate (30 ml/min), a much lower removal efficiency was achieved when the solution pH was monitored to be less than 5 or higher than 8.

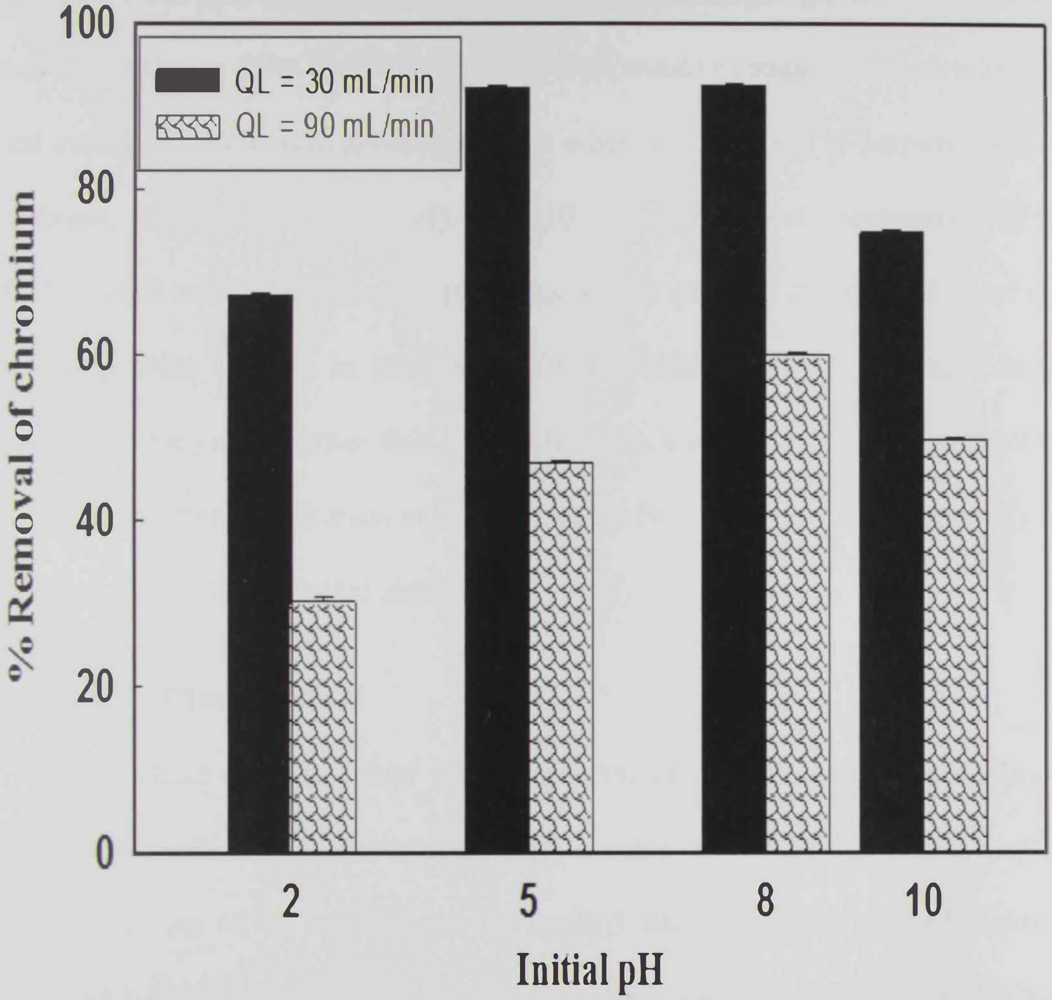


Fig.4.29. Effect of initial pH on the removal of chromium at different inlet flow rates, Cr_0 = 5 mg/L, ACD = 7.61 mA/cm^2; q_{air} = 4 L/min; at electrolysis time of 1 minute.

During the electrocoagulation process, several ions are generated simultaneously as the current passes through the sacrificial electrode rod (Eq. 2.4-

2.11). These ions undergo further spontaneous reactions to produce various metal hydroxide complexes such as $Fe(OH)_3$, and $Fe(H_2O)_4(OH)^{2+}$ in addition to $Cr(OH)_3$ and $Cr(OH)_6$ depending on the solution pH [1]. Diaz et al. [76], studied the formation of chromium and iron compounds as a function of solution pH and reported that iron ions are favorable to form insoluble $Fe(OH)_3$ compounds in addition to precipitate the excess amount of Fe(II) ions generated in site when the initial pH in the range of 5- 8. In addition, the reduction of Cr(VI) to Cr(III) and subsequent precipitation of the $Cr(OH)_3$, are favorable at the same pH range which explains the high efficiency of electrocoagulation column in this range. On the other hand, the decrease in the removal efficiency at pH lower than 5 or higher than 8 was ascribed to an amphoteric behavior of $Fe(OH)_3$ which leads to soluble cations Fe^{3+} , $Fe(OH)_2^+$ (at acidic pH) and monomeric anions $Fe(OH)_4^-$ (at alkaline pH) [3, 4].

4.3.7. Effect of Temperature

The effect of temperature on the removal of chromium from groundwater was evaluated at three different temperatures, namely 10, 25 and 40 ^0C at a constant influent flow rate of 90 ml/min and an applied current density of 7.61 mA/cm^2 (voltage of 0.0028 kV), where the temperature was controlled using a water bath jacket. The results presented in Fig.4.30 show that temperature has an important effect on chromium removal, whereas chromium removal efficiency was more effective at lower temperatures. The removal efficiency was increased by 10 % as the temperature decreased from 40 ^0C to 10 ^0C. It was observed that longer electrolysis time (i.e. more than 2 hours) is required to reach almost complete removal as the temperature increased from 10 ^{0}C to 40 ^{0}C. As explained earlier, high temperature of the solution affects the solubility of generated coagulants temperature thus increased the solubility. Therefore the precipitation of complex iron hydroxides and chromium hydroxides increased as the temperature decreased [100]. Maximum removal efficiency was achieved at 25 ^{0}C.

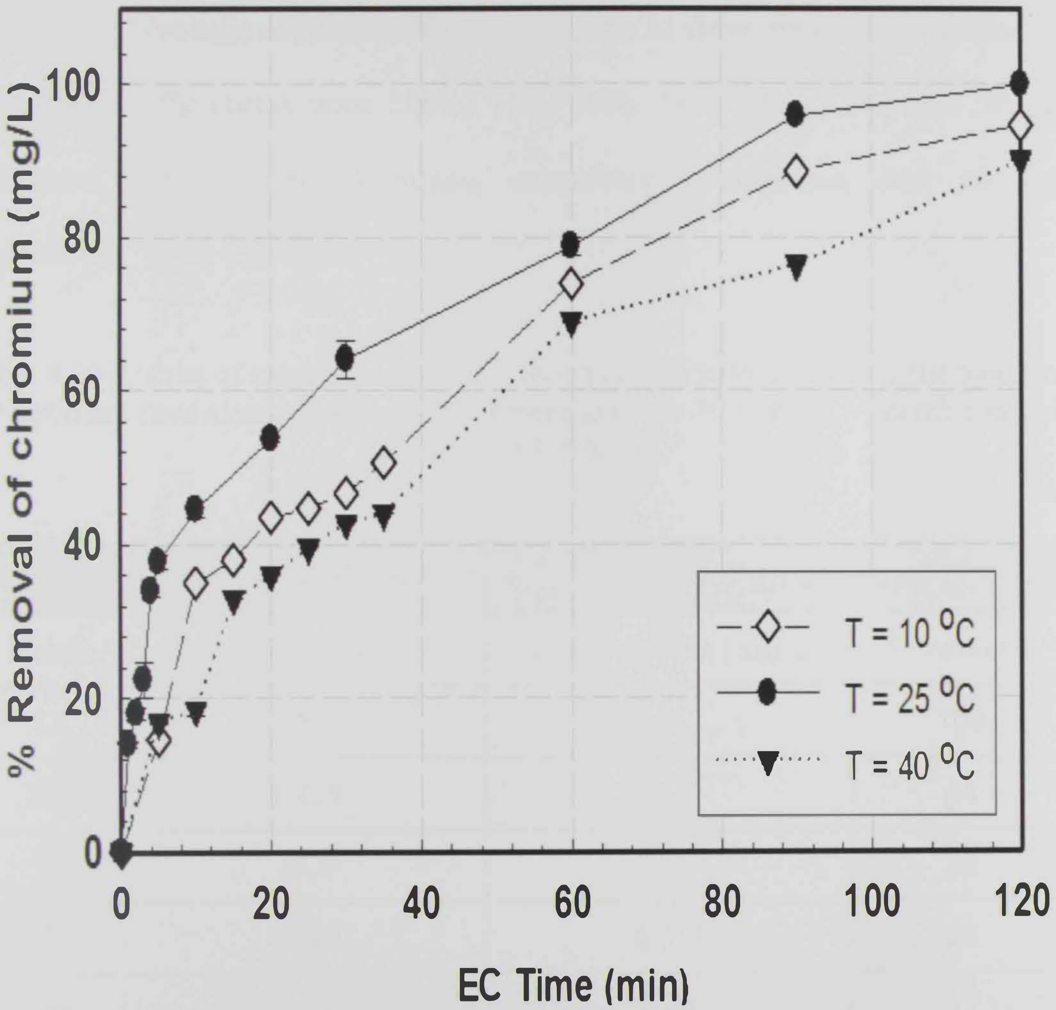


Fig.4.30. Effect of temperature of solution on the removal of chromium, by continuous EC column Cr_0 = 100 mg/L, ACD = 7.61 mA/cm^2; q_{air} = 4 L/min.

4.3.8. ECC Optimum Operation Conditions

A new electrocoagulation column (ECC) was evaluated for the removal of chromium and other ions from brackish groundwater and its performance was optimized for continuous operation. The optimum conditions in terms of initial pH, feed flow rate and Applied Current Density (ACD) were found to be 8, 30 ml/min and 7.61 mA/cm^2 (voltage of 0.0028 kV), respectively. At these optimum conditions, the ion removal efficiencies were 100%, 74%, 70%, 59%, 44%, 33%, and 28% for chromium, copper, zinc, strontium, magnesium, manganese, and cadmium respectively.

Table 4.10 Results of electrocoagulation column (ECC) before and after the treatment at optimum conditions: initial pH = 8; Operation time 30 min; Q_L = 30 ml/min and ACD of 7.61 mA/cm^2.

	Feed groundwater	**Treated groundwater**	
Metals	Concentration (mg/l)	Concentration (mg/l)	% removal
Cr	5	0	100
Mg	110.8	61.7	44
Sr	18.4	7.6	59
Cd	0.018	0.013	28
Mn	0.66	0.44	33
Cu	0.066	0.017	74
Zn	0.141	0.042	70
Fe	-	0.185	-

4.3.8. Comparison of Continuous EC processes

The performance of continuous CSTR EC was compared to that of the continuous column EC at initial chromium concentration of 5 mg/L and current of 0.5 A. The obtained results are presented in (Table 4.11). Faster chromium removal rate was obtained using continuous EC column (ECC), compared to the CSTR EC. Although the same amount of contaminants is treated inside both reactors when using the same inlet flow rate, the efficient air mixing associated with the ECC improves the liquid-gas-solid mass transfer, which consequently enhances the reduction rate of chromium [98]. In addition, using rod as a sacrificial electrode instead of rectangular sheet improved the mixing process inside the column. The continuous EC column (ECC) process was found to be more economical (electrical costs were always lower than 0.030 US $\$/m^3$), compared to the continuous stirred (EC) (electrical cost was equal to 0.096 US $\$/m^3$). The low electrical costs for the ECC are attributed to the small distance between rod and helical electrodes, resulting in lower operating voltages.

Table 4.11 Performance of continuous stirrer and column electrocoagulation processes on chromium removal, at Cr_0 = 5 mg/L, pH = 8, t_{EC} = 10 min, and I = 0.5 A at room temperature.

Reactor type	**Anode type**	**Mixing type**	**Inlet flow rate (mL/min)**	**% Removal efficiency**	**Electrical cost (US \$/m^3)**
Column EC	Rod	Air 4 L/min	30	99.9	0.030
			90	98.4	0.011
			150	96.8	0.006
Stirred EC	Rectangular sheet	Stirrer 300 rpm	30	99.8	0.096
			90	100	0.032
			150	93.8	0.019

Chapter Five

Conclusions & Recommendations

"If we knew what it was we were doing, it would not be called research, would it?"
Albert Einstein, (1879-1955)

5.1. Conclusions

Generally, high conductivity of the collected samples has a significant effect on the performance of electrocoagulation process, which decreases the IR- drop and therefore improves the reduction rate. Chromium removal efficiency by EC process was affected by applied current density, initial pH, initial concentration and electrode material. It was also proved that longer electrolysis time was required to reach 100% chromium removal as the initial concentration increased from few minutes (for diluted concentrations of 1 mg/L) and the electrolysis time extended to more than one hour (at initial chromium concentration of 100 mg/L).

Batch stirred electrocoagulation reactor proved to be a promising treatment method for the removal of chromium from brackish groundwater. The experimental results indicated that batch EC process could reach 100 % removal efficiency of total chromium from brackish groundwater using iron electrodes arrangement, with applied current density of 7.94 mA/cm^2 (voltage of 0.007 kV), stirrer speed of 300 rpm, initial pH of 8, and an operating temperature of 25 ^{0}C. At the same conditions, harmful heavy metals and other ions could significantly be removed through the batch process, at efficiencies of 56%, 52 %, 34%, and 22% for zinc, manganese, copper, and magnesium, respectively. Analysis of the process kinetics indicated that the Pseudo first-order model was correlated with the experimental data to a great extent, yielding a lower SSE than the Pseudo second-order model. Furthermore, sludge generated from EC was analyzed by FE-SEM to study the surface morphology in addition to chemical composition by EDS. The results showed high oxygen and iron content with a small amount of chromium in amorphous and flake-shaped aggregates with an average diameter size of 145 μm. XRF analyzes indicated that the main composition of the sludge was $Fe(OH)_3$ with Cr_2O_3.

The performance of two different continuous electrocoagulation processes, namely continuous stirred tank reactor (CSTR) and continuous electrocoagulation column (ECC) were examined. The experimental results indicated that the highest removal efficiency of chromium was achieved using the ECC with the lowest dissolved iron concentration of 0.185 mg/L at applied current density of 7.61 mA/cm^2 (voltage of 0.0028 kV) and an inlet flow rate of 30 mL/min. Electrical energy consumption was found to be equal to 0.75 kWh/m^3 (electrical cost of 0.03 $US\$/m^3$). Therefore, ECC process is highly recommended for industrial applications.

The effect of temperature on the performance of column reactor was assessed at different temperatures, namely 10, 25 and 40 ^0C. Maximum chromium removal efficiency of 100% was achieved at 25 ^0C, in which maximum precipitation of chromium iron hydroxides takes place. EC treatment of groundwater, using iron electrodes, can achieve significant removal efficiency for other heavy metals and harmful ions.

5.2. Recommendations

Based on the results of this research, it is recommended to evaluate the efficiency of the new ECC in the treatment of different types of contaminants such as organic compounds and other harmful heavy metals (arsenic, lead, strontium, etc). It is also worth developing a more rigorous mathematical analysis of the ECC process.

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ملخص

تعتبر المياه الجوفية من أهم مصادر المياه الطبيعية في دولة الإمارات العربية المتحدة التي تستخدم في أغراض الزراعة وتربية الحيوانات. وقد أثبتت التقارير العلمية عن تلوث بعض الآبار بمركبات الكروميوم بتراكيز تشكل خطورة على حياة الكائنات الحية. تعتبر هذه المركبات من المواد المسرطنة، بالإضافة إلى ذوبانيتها العالية في المحاليل المائية مما يزيد من صعوبة فصلها. عملية التخثير الكهربائي (Electrocoagulation) هي تقنية تساعد على فصل المواد الذائبة عن طريق إستخدام تيار كهربائي يعمل على تكوين جزيئات أكبر يسهل فصلها فيما بعد. تم تقيم أداء تقنية التخثير الكهربائي لازالة مركبات الكروميوم الذائبة في المياه الجوفية على ثلاثة تصاميم مختلفة من المفاعلات الكهروكيميائية وهي: المفاعل الثابت (Batch stirred EC reactor)، والمفاعل المستمر (Continuous stirred EC reactor)، و المفاعل العمودي المستمر (Continuous EC column). أثبتت التجارب العملية على مفاعل التخثير الكهربائي الثابت أن استخدام الواح الحديد كأقطاب كهربائية ساعد على إختزال كل جزيئات الكروميوم وتحويلها إلى مواد صلبة يسهل إزالتها في وقت زمني قصير (5 دقائق) باستخدام كثافة تيار كهربائي بمقدار 7.94 ملي أمبير/سنتيمتر مربع وأس هيدروجيني (pH) يساوي 8. وقد تم إجراء دراسة حول الحركة الكيميائية (Kinetics) لإزالة مركبات الكروميوم على المفاعل. ولإجراء هذه الدراسة تم تقيم معادلات التفاعل من الدرجة الأولى والدرجة الثانية. وقد أثبتت النتائج أنه يمكن تطبيق معادلة التفاعل من الدرجة الأولى على المفاعل الثابت لإزالة الكروميوم من المياه الجوفية. بالإضافة إلى ذلك، تم دراسة تأثير سرعة التدفق الداخل إلى المفاعل على أداء المفاعلات المستمرة، حيث كانت أعلى درجات إختزال الكروميم عند إستخدام المفاعل المستمر (Continuous stirred EC reactor) على سرعة تدفق بمعدل 90 مليليتر/ دقيقة، و سرعة تدفق تعادل 30 مليليتر/دقيقة عند إستخدام المفاعل العمودي المستمر (Continuous EC column). و قد أكدت النتائج المختبرية أن المفاعل العمودي المستمر (Continuous EC column) زاد من كفاءة إزالة أيونات الكروميوم من المياه الجوفية بأقل طاقة مستهلكة (0.75 كيلو واط في الساعة/ ميتر مكعب)، و أقل تركيز لأيونات الحديد الذائبة بمقدار 0.185 مليجرام/ ليتر بتكلفة كهربائية رمزية تقدر ب 0.03 دولار أمريكي/ م^3 من المياه الجوفية المعالجة. بصفة عامة تعتبر تقنية التخثير الكهربائي ملائمة بيئيا و إقتصاديا لمعالجة المياه الجوفية و فعالة لفصل المعادن الضارة بالتقليل من ذوابانيتها بأقل تكلفة ممكنة.

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قسم هندسة الكيمياء والبترول

دراسة حول معالجة المياه الجوفية من مركبات الكروميوم عن طريق التخثير الكهربائي

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رسالة مقدمة لاستكمال متطلبات الحصول على درجة الماجستير في علوم الهندسة الكيميائية

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باشراف البروفيسور مفتاح النعاس

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