DOKUZ EYLUL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

ARSENIC REMOVAL FROM DRINKING WATERS BY ELECTROCOAGULATION AND FILTRATION

by
Ceren UCAR

June, 2011
IZMIR

ARSENIC REMOVAL FROM DRINKING WATERS BY ELECTROCOAGULATION AND FILTRATION

“A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylul University
In Partial Fulfillment of the Requirements for the Degree of Master of Science
in Environmental Engineering, Environmental Technology Program”

by
Ceren UCAR

June, 2011
IZMIR

M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"ARSENIC REMOVAL FROM DRINKING WATERS BY ELECTROCOGULATION AND FILTRATION"** completed by **CEREN UÇAR** under supervision of **AYŞEGÜL PALA** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

APala

Prof. Dr. Ayşegül PALA

Supervisor

Prof. Dr. Delya SPONZA

(Jury Member)

Assoc. Prof. Dr. Nihal BEKTAŞ

(Jury Member)

Prof.Dr. Mustafa SABUNCU
Director
Graduate School of Natural and Applied Sciences

ACKNOWLEDGEMENTS

I would like to appreciate to my advisor Prof. Dr. Aysegul PALA for her valuable advices, encouragement, motivation, support and guidance during my M.S.c. period. I am also grateful Assist. Prof. Meltem Bilici BASKAN who was guided me in experimental part of this study by giving valuable advices and support.

I would also like to thank Platin P.V.C. Metal Accessory Ltd. Company for their equipment and specially Academist Bahattin AGADAY for their equipment support and guidance. I also thank to IZCEV Environment Laboratory for their laboratorial support.

Special thanks to my friends Sena ALKAN, Ilkem SARIYER, Merdiye MUTLU, Michael TILL for their support and encouragement.

Finally I would like to deeply thanks my dear parents SEVGI and ARSLAN UCAR and especially to my brother ERDEM UCAR for their patience, understanding, encouragement and support during this study and my life.

Ceren UCAR

ARSENIC REMOVAL FROM DRINKING WATERS BY ELECTROCOAGULATION AND FILTRATION

ABSTRACT

Arsenic removal from drinking waters was investigated using Electrocoagulation (EC) process followed by filtration process in this study. Batch electrocoagulation experiments were performed in the laboratory scale using iron electrodes, which were placed horizontal in the electrocoagulation reactor and connected to a power supply in monopolar, parallel arrangement.

Non-toxic and readily available iron plate was used as electrode material because of its strong adsorption affinity for arsenic. Moreover, when iron electrodes are used in EC process, depending on range of pH, it can generate by-products such as iron hydroxides, hematite, maghemite, magnetite, goethite, lepidocrocite, rust, which are widely used in arsenic removal from drinking waters.

The experiments were carried out to investigate the effects of initial arsenic concentration, residence time, current, presence of salt, surface area of electrodes and oxidation states of arsenic (As(V) and As(III)) at pH 6-8.

The sand filter was used to remove flocs, which were generated in EC. During the filtration process air was injected with the aquarium pump through air diffuser (air stone) to remove excessive iron species (ferric, ferrous) occurred in EC depending on pH changing and other factors.

The initial arsenic concentration and the electrode surface area had no significant effect on arsenic removal. It was observed that the changing of current and residence time are significant for optimizing and controlling of EC performance. When natural contaminated groundwater (As(III)) in Sasali-Izmir was investigated and compared with arsenate (As(V)) contaminated solutions, slower removal then arsenate removal was observed due to oxidation As(III) to As(V).

As well, with addition of salt, bigger and dense flocs (green rust) formation was obtained. The residual arsenic and iron concentrations were determined by ICP-OES. The ninety nine percentage of arsenic removal was achieved in the EC experiments.

Keywords: Electrocoagulation, arsenic, drinking water, production of iron coagulant, residence time, current density.

ICME SULARINDAN ELEKTROKOAGULASYON VE FILTRASYONLA ARSENIK GIDERIMI

OZ

Bu calısmada, icme sularindan arsenik giderimi electrokoagulasyon (EK) islemi ardindan, filtrasyon islemi kullanilarak arastirildi. Kesikli elektrokoagulasyon deneyleri, laboratuvar olceginde, guc kaynagina monopolar ve parallel baglanmıs duzenekte, elektrokoagulasyon reaktoru icine yerlestirilmis demir elektrotlari kullanilarak yurutulmustur.

Guclu adsorpsiyon ozelligi nedeniyle toksik olmayan ve kolayca bulunan demir plaka, elektrot materyali olarak kullandi. Ayrica demir elektrodu kullanildiginda, pH araligina bagli olarak, elektokoagulasyon islemi sirasinda demir hidroksit, maghemit, magnetit, götit, lepidokrosit, pas gibi icme sularindan arsenik gideriminde cokca kullanilan yan urunler meydana gelir.

Deneyler, pH 6 - 8 aralığında, baslangic arsenik konsantrasyonu, temas suresi, akim, tuz varligi, elektrot yuzey alani ve arsenik oksidasyon durumlarinin (As(III) ve As(V)) etkilerini belirlemek icin yurutulmustur.

Elektrokoagulasyon sirasinda olusan floklari gidermek icin kum filtresi kullanilmistir ve filtrasyon islemi sirasinda, pH degisime ve diger nedenlere bagli olarak olusan, fazla demir iyonlarini (ferrik, ferrus) gidermek icin akvaryum pompasina bagli difuzor (hava tasi) ile hava enjekte edilmistir.

Başlangic arsenik konsantrasyonu ve elektrot yuzey alaninin, arsenik giderimi icin onemli bir etkisi yoktur. Akim ve temas suresi degisiminin, elektrokoagulasyon performansinin kontrolu ve optimizasyonu icin onemli oldugu gorulmustur. Dogal arsenik kirliligine sahip Izmir-Sasalı yeralti suyu incelendiginde ve arsenatla kirletilmis cozeltilerle kiyaslandiginda; As(III)`nin As(V) oksidasyonu nedeniyle arsenattan daha yavas arsenik giderimi gozlemlenmistir.

Ek olarak, tuz eklenmesiyle daha buyuk ve yogun floklarin (yesil pas) olusumu saglandi. ICP-OES ile kalan arsenik ve demir konsantrasyonlari tespit edilmistir. EK deneylerinde yuzde doksan dokuz arsenik giderimi saglanmistir.

Anahtar sozcukler: Elektrokoagulasyon, arsenik, icme suyu, demir koagulant uretimi, alikonma suresi, akim yogunlugu.

CONTENT

CHAPTER ONE
INTRODUCTION

1.1 Background

Arsenic is the 20th most abundant element in the earth`s crust and 14th in the seawater (Moreno, H., 2007). It can be released into the environment through a wide variety of natural and anthropogenic activities (Rubidge, G. R., 2004). In organic arsenic occurs in two valance states; As(III) and As(V) are the most widespread forms in natural water. (Lakshmanan, D., 2007). Exposure to arsenic can cause various health effects. Due to risk concern, WHO (World Health Organization) and USEPA (United States Environmental Protection Agency) has reduced the MCL (maximum contamination level) from 50µg/L to 10 µg/L (WHO, 1993; USEPA, 2001).

Many technologies have been developed for the removal of arsenic. All technologies depend on a few basic chemical processes that can be applied alone simultaneously or in sequence: oxidation reduction, coagulation-filtration, precipitation, adsorption and ion exchange, solid/liquid separation, physical exclusion, membrane technologies, biological methods, etc. (Litter, M. I. ,et al., 2010).

Electrocoagulation simple, efficient and promising method where the flocculating agent is generated by electro-oxidation of a sacrificial anode generally made up iron or aluminum without adding any chemical coagulant or flocculant (Nouri, J., et al., 2010). It has been applied for treatment of drinking water and urban wastewater.

Until now, several studies have reported arsenic removal from waters by electrocoagulation. (Parga, J. R., et al., 2005; Hansen H. K., et al.2008; Daida, P., 2005; Moreno, H. A. C., 2007; Kumar et al. 2004; ,Lakshmanan, D., 2007; Wan W., 2010; Addy, S. E. A. 2008 etc.).

In EC, with electrical current following between the electrodes, coagulant is produced by electrolytic oxidation at anode (Fe). The generated $Fe^{2+}_{(aq)}$ or $Fe^{3+}_{(aq)}$ to produce $Fe(OH)_n$ (Larue, O., et al., 2003). Several physical and chemical factors can influence removal efficiency of arsenic by electrocoagulation such as design of EC reactor, electrode material, current density, residence time, pH.

1.2 Objectives of the Study

The main objective of this study was maximum efficiency and minimum energy consumption (low-cost) and time for arsenic removal by EC process. Factors studied were initial arsenic concentration, residence time, current density, presence of salt, electrode surface area, arsenic oxidation state. Another objection of this study was large and dense floc formation and minimization of passivation.

CHAPTER TWO
ARSENIC AND ARSENIC REMOVAL METHODS

2.1 Arsenic

Arsenic is the 20th most abundant element in the earth`s crust and 14th in the seawater (Moreno, 2007). It can be released into the environment through a wide variety of activities of natural and anthropogenic origin, for example volcanic action, erosion of rocks, forest fires, burning fossil fuels, paper production, cement manufacturing, mining, pesticide application, spills, and landfills (Rubidge, 2004; SOS-arsenic.net, n.d.). Most countries around the world are exposed to excess of the maximum contaminant level in their drinking water.

Arsenic, with atomic number 33, and situated in Group 15 (or VA) of the periodic table, directly below phosphorus, occurs both organic and inorganic form. In organic arsenic occurs in two valance states; As(III) and As(V) are the most widespread forms in natural water (Dutre et. al., 1999; Escobar et al., 2006).

Exposure arsenic treats the human health. Arsenic also known as the "inheritance powder", "the King poisons", it has been known to humankind for thousands of years (Ravenscroft, et al., 2009). Inorganic arsenic is considered as a human carcinogen and according to epidemiological studies; it has higher risks of skin, bladder, lung, liver cancer and other non-cancerous health effects that cause by consumption of arsenic contaminated drinking water (Guha Mazumder et al., 1998; Lakshmanan, 2007).

Most countries around the world are exposed to excess of the maximum contaminant level in their drinking water such as USA, Mexico, Chile, Peru, some small regions in European countries, Turkey (Kutahya province) several countries of Southeast Asia including Bangladesh, India , Nepal, Myanmar, Pakistan, Vietnam, Cambodia, several regions of China and Taiwan, therefore be regarded as a global issue.

The control of arsenic began in 1975 when the EPA established the first maximum contamination level (MCL) for it at 50µg/L. Due to this risk concern, the World Health Organization (WHO) and the U.S. Environmental Protection Agency (USEPA) revised their regulations and reduced the maximum contamination level (MCL) in drinking water from 50 µg/L to 10 µg/L (WHO, 1993; USEPA, 2001).

As to Turkey, TURKISH STANDARDS INSTITUDE revised the arsenic limit and it reduced from 50 µg/L to 10 µg/L in 2005 when Regulation on Water Indented for Humanitarian Consumption was published and came into force (Turkish Standards 2005).

2.2 Arsenic Removal Methods

Many convectional and emerging technologies have been applied to remove arsenic from drinking waters.

The convectional and emergent arsenic removal technologies are presented below, along with a brief description of how removal efficiency is affected by arsenic concentration.

2.2.1 Convectional Technologies

The conventional treatment processes for removal of arsenic can be classified based on the mechanisms involved: (1) precipitation, (2) adsorption, (3) ion exchange, (4) membrane technology (Shih, 2005). Comparison of convectional technologies for arsenic removal with their advantages and disadvantages is given in Table 2.1.

Table 2.1 Advantages and disadvantages of arsenic removal convectional technologies for arsenic removal (Litter et al., 2010).

Technologies	**Advantages**	**Disadvantages**
Oxidation and Reduction	Simple small installation costs. As(III) can be directly oxidized by a number of chemicals or/and UV lights.	Some oxidants produce toxic and carcinogenic by-products. Needs further removal treatment.
Precipitation	Solid obtained can be removed by sedimentation and filtration.	Solids rather unstable and inadequate for direct disposal as they can produce As-containing liquid residues.
Coagulation/ Filtration	Simple, easily applied to large water volumes. Effective when As(V) is the only contaminant. Low capital and operative costs.	Low removal efficiency. pH needs adjustment. Disposal of the arsenic-contaminated sludge can be concern.
Lime softening	pH>10.5 provides efficient arsenic removal. Efficient to treat water with high hardness.	Low removal efficiency. High coagulant dosage. High pH in the effluent. Secondary treatment may require.
Adsorption (activated carbon, iron oxides/hydroxides, TiO_2, cerium oxide, metals)	Simple. Not other chemicals required. Highly selective towards As(V). effective with water with high TDS.	Moderate efficiency. Replacement/ regeneration required.
Membrane **Reverse osmosis** **Nanofiltration and Electrodialysis**	Useful for small scale treatment. No toxic solid wastes produced. Well defined and high removal efficiency. Efficiency similar to RO, effective treating water with high TDS. Minimize scaling by periodically reversing the flows of dilute and concentrate and polarity of electrons.	Poor As (III) removal. For high water volumes, multiple membrane units required. Very high capital and operation costs. High tech operation and maintenance. Membrane fouling. Much interference. 20-25% water rejection. Other ions can be removed. High electrical consumption.
Ion exchange	Effective removal. In depend of pH and influent concentration.	As(III) not removed. Sulfate, TDS , Se, F^- and NO_3^-. SS and precipitated iron cause clogging. Pretreatment may require.

2.2.2 Emergent Technologies

Alternative technologies have been developed for the removal of arsenic to minimize costs of investment, operation and maintenance especially for small-scale or household treatments. Emergent technologies include:

In situ treatment describes water purification which is conducted “in place.” (Miller, G. P., 2008). For in-situ removal of pollutants, the use of permeable reactive barriers (PRB) and reactive zones are one of the most efficient technologies, especially for arsenic removal from ground water. Gilbert et al., (2009) investigated in-situ removal of removal arsenic form groundwaters by using permeable reactive barriers (PRB) and they achieved 99% arsenic and other metals removal.

Removal with natural geological materials is emerging solution for poor people in rural area at household level. Fe-rich and Al-rich minerals such as goethite(α-FeOOH), lepidocrocite (γ-FeOOH), hematite (α-Fe_2O_3), magnetite (Fe_3O_4), gibbsite (γ-$Al(OH)_3$), indigenous lime stone (Soyatal), iron-coated zeolites, clay minerals are alternative adsorbents for small water volumes (Litter, et al., 2010).

The precipitation/coprecipitation method was used for arsenic removal from drinking water by ferric chloride, ferric sulfate and ferrous sulfate as coagulant. When the Box-Behnken statistical experimental design method was used, ferric chloride was found as an effective coagulant considering required concentrationand residual iron and arsenateconcentration (Bilici-Baskan, M., 2008).

Aeration combined with rapid sand filtration is promising for iron-rich groundwater areas in Bangladesh (Feenstra et al., 2007).

Material based on iron and manganese removal can result in important arsenic removal, such as greensand (Feenstra et al., 2007).

Recently zero-valent iron (ZVI) has became one of the most common adsorbent for fast removal of As (III) and As(V) from subsurface environment. The reactivity of ZVI has recently been improved by the development of smaller sized, i.e. nanoscale zero-valent iron (NZVI) (Rahmani et al., 2010). Nanoparticle zero-valent iron could remove arsenic from aqueous solution at a short time (minute scale) over a wide range of pH (Rahmani et al., 2010).

Biological removal arsenic from water is known less, though these methods show a great potential because of its environmental compatibility and possible cost effectiveness. This method uses living organisms (such as plants, fungi, or bacteria) or biological materials (such as bones, biomass, hair, seeds, leaves, or woods) to sorb or treat contaminants (Henke, 2009).

Photochemical technologies are cheap technologies which can be used arsenic removal by using of solar light or artificial light and dissolved iron (Litter et al., 2010).

The SORAS (Solar Oxidation and Removal of Arsenic) is a simple technique for arsenic removal based on solar oxidation followed by precipitation and filtration (Ahmed, 2001).

TiO_2 immobilization on a PET surface combined with co-precipitation of arsenic on iron (III) hydroxides (oxides) can be an efficient way for total inorganic arsenic removal from waters. Owing to their very strong affinity for arsenic, iron compounds are used by many removal systems (Duarte et al, 2009).

Comparison of emerging arsenic removal technologies with their advantages and disadvantages is given are shown in Table 2.2.

Table 2.2 Advantages and disadvantages of emergent technologies for arsenic removal (Litter, 2010).

Technologies	**Advantages**	**Disadvantages**
In-situ remediation (PRBs)	Low operational costs. Low-cost local materials can be used.	High impact microbiological and geochemical processes at long terms. Corrosion of materials. Permeability diminished by precipitation of sulfides, oxides, hydroxides, and carbonates.
Zerovalent iron	Widely available local iron materials at low-cost. As(III) and As(V) can be treated.	Produces toxic wastes.
Zerovalent iron nano particles	Higher contact surface results in a lower amount of iron. As(III) and As(V) can be treated.	Complicate synthesis of material.
Geological materials as natural adsorbents	Feasible process in developing countries.	Possible growth of microorganisms. Becomes clogged, if excessive iron.
Biological methods: biadsorption, ex-situ bioleaching, biofiltration, phytofiltration, phytoremediation.	Environmental compatibility and possible cost- effectiveness.	Much research still needed.
Photochemical oxidative technologies: Fe salts/solar light, SORAS, TiO_2 Heterogeneous Photocatalysis, ZVI, NVI	Friendly and non-expensive technologies poor and isolated populations. Based on use of solar light and low-cost materials. Simultaneous oxidation of As and removal of organic pollutants, toxic metals and microbiological contamination can be achieved in most of the cases.	External addition of iron to waters before or after treatment is needed.
Reactive TiO_2 Heterogeneous Photocatalysis	Provides immobilized As on TiO_2	Addition of organic donors and acid pH is required. Much research is still needed.

CHAPTER THREE
ELECTROCOAGULATION

3.1 Introduction

Arsenic occurs naturally in groundwater and arsenic can also occur because of industrial waste discharges, pesticides, herbicides and mining. Exposure to arsenic can cause various health effects. Therefore WHO (World Health Organization) and USEPA (United States Environmental Protection Agency) has reduced the MCL (maximum contamination level) from 50µg/L to 10 µg/L (WHO, 1993; USEPA, 2001).

There are several methods such as oxidation, coagulation, adsorption precipitation, and filtration which have been using for removal arsenic from drinking waters. Electrocoagulation simple, efficient and promising method where the flocculating agent is generated by electro-oxidation of a sacrificial anode generally made up iron or aluminum without adding any chemical coagulant or flocculant (Nouri, et al., 2010). It has been applied for treatment of drinking water and urban wastewater.

In the late nineteenth century, it was seen as a promising technology - in fact, several water treatment plants were successfully operated in London at this time. A plant was built in Salford, England, in 1889 (for the treatment of sewage by mixing with seawater and electrolyzing) using iron electrodes with seawater as the source for chlorine disinfection. In 1909, in the United States J. T. Harries received a patent for wastewater treatment by electrolysis with sacrificial (consumable) aluminum and iron anodes, electrolytic sludge treatment plants were operating as early as 1911 in some parts of the United States of America, and in the following decades, plants were also operated there to treat municipal wastewater. By the 1930’s, however, all such plants had been abandoned owing to perceived higher operating costs, and the ready availability of mass-produced alternatives for chemical coagulant dosing (Holt, et al., 2002).

Electrocoagulation resurfaced periodically during the last century. Matteson et al. (1995) describe a device of the 1940`s, the “Electronic Coagulator” which electrochemically dissolved aluminum (from the anode) into solution, reacting this with hydroxyl ion (from cathode) to produce aluminum hydroxide (Holt, P. K., et al., 2006). Through the 1940’s Stuart (1946) and Bonilla (1947) reported on an electrochemical water treatment process, but this was received with little interest. During the 1970’s and 1980’s significant interest was generated by Russian scientists researching the application of electrocoagulation for a sort of water treatment processes (Holt, et al., 2002).

Presently electrocoagulation is marketed by a small number of companies around the world. It is clear that electrocoagulation has the capability to remove large range of pollutants such as suspended solids, heavy metals, petroleum products, dye containing solutions etc. (Holt, et al., 2006).

Recent studies have shown that arsenic can be treat from the natural water and industrial effluents by electrocoagulation. Arienzo et al. (2002) investigated the retention on hydrous ferric oxides generated by electrochemical using two steel electrodes. They reported more than 99% removal of As(III) using EC process. Kumar et al. (2004) reported that electrocoagulation had a better As(III) efficiency and attributed the reason to removal mechanism of simultaneous oxidation of As(III) to As(V) and removal by adsorption with the metal hydroxides generated in the process. The literature on electrochemical oxidation of As(III) indicates that traces of free chlorine generated at the anode rapidly oxidize As(III) (Lakshmanan, 2007).

3.2 Electrocoagulation

3.2.1 Electrochemical cell

To understand electrochemical cell mechanism in the EC systems, a summary that based on mostly Addy (2008) is given below.

The cell potential is the sum of many potential differences across the cell, including each interface between phases and the ohmic drop across the electrolyte. To measure or control the potential at the working electrode alone, the non-working electrode is often reference electrode, made up of components with essentially constant composition capable of maintaining a constant interface potential over a wide range of currents. The ohmic drop can be minimized by reducing the bulk solution resistance. The internationally accepted primary reference is standard hydrogen electrode (SHE) in which H_2 gas is bubbled. Standard potentials of a half reaction are measured in simple electrochemical cell in which one electrode is a SHE…. Control over the potential of the working electrode is thus achieved only with respect to the constant of reference….

The critical potentials at which these processes occur are related to the standard potentials…. (standard state; 1M at 25^0C and 1 bar total pressure), E^0, for the specific chemical substances in the system….

Frequently, the concentrations of the reduced or oxidized species are different from 1M.

Consider the reaction:

$O + n_e e^- \leftrightarrow R$

O= Oxidized species
R=Reduced species

In this case the critical potential is given by the Nernst equation:

$$E = E^{0`} + \frac{R \times T}{ne \times F} \times ln\frac{[Co]}{[CR]} \tag{3.1}$$

R= Universal gas constant [kJ/mol-K]
T= Temperature [K]

n_e= number of electrons in redox reaction
F=Faraday`s constant [96,485.4 C/ mol e^-]
C_O= Concentration of oxidized species [M]
C_R= Concentration of reduced species [M].

Here $E^{0`}$ is the formal potential, related to E^0 by:

$$E^{0`} = E^0 + \frac{R \times T}{\mathrm{ne} \times \mathrm{F}} \times ln \frac{\gamma \mathrm{O}}{\gamma \mathrm{R}} \tag{3.2}$$

γO=activity coefficient of oxidized species
γR=activity coefficient of reduced species.

The take-away from the Equations (4.1 and 4.2) is that the critical potential depends on environmental conditions, such as temperature, as well as the relative concentrations of the reactants near the electrode surface and the activity of those reactants.

For faradic processes, the number of electrons that cross an interface is related stoichiometrically to extent of chemical reaction (i.e. the amount of reactant consumed and product generated). Current is the total is the total charge passed per unit time, thus the current is a measure of rate of chemical reactions occurring in the cell….

If well-defined redox couple exists at each electrode, then equilibrium can be established and the cell will have a well defined equilibrium potential, or open circuit potential, E_{eq}. This is the potential; one would measure across the electrodes if no net current was flowing. In many cases, there is no well-defined equilibrium state for the cell, and the open circuit potential can only be placed within a potential range. The departure of the electrode potential from the equilibrium value upon the passage of faradic current is termed polarization. The extent of polarization is measured by the overpotential, η:

$$\eta = E - E_{eq} \qquad (3.3)$$

η = overpotential

E= current potential

E_{eq}= a well defined equilibrium potential, or open circuit potential

The overpotential (η) can be considered a sum of terms associated with different reaction steps:

$$\eta = \eta_{Mt} + \eta_{Ct} + \eta_{rxn} \qquad (3.4)$$

η_{Mt}= mass-transfer overpotential [V]

η_{Ct}= charge-transfer overpotential [V]

η_{rxn}= the overpotential associated with a preceding reactions [V]

η_{Mt} is the overpotential necessary to drive mass-transfer, the physical movement of ions from the bulk solution to the electrode surface where reactions take place….

Both η_K (kinetic overpotential; the sum of η_{Mt} and η_{Ct}) and η_{Mt} increase as current density, j= i/A, increases. An exact relationship can be derived in the simple case of a one step, one electron process, following to the Butler-Volmer formulation. For the case of interface equilibrium and a solution in which the bulk oxidized species concentration is equal to the bulk reduced species concentration, the Butler-Volmer formulation:

$$j = Fk^0[C_O\,(0,t)e^{-\alpha f\eta} - C_R(0,t)e^{(l-\alpha)f\,\eta}] \qquad (3.5)$$

j= Current density

F= Faraday`s constant

k^0=standard rate constant for the reaction (s^{-1}) [when η =0]

$C_O(0,t)$= concentration of oxidized species at the electrode surface as a function of time

$C_R(0,t)$= concentration of reduced species at the electrode surface as a function of time

α= transfer coefficient, ranging from zero to unity

f= F/RT

η = overpotential at the electrode….

The applied cell potential necessary to get the desired current take into account the potential across the working electrode, E (which includes the overpotential), as well as the voltage drop across the solution due to the bulk solution resistance, R_s. Using the convection of positive current, I, for oxidation resistance, (or anodic) current, the applied cell potential, E_{appl} is:

$$E_{appl} = E_{eq} + \eta + iR_s \tag{3.6}$$

The solution resistance, Rs(Ω), is determined by:

$$Rs = \frac{d}{A \times K} \tag{3.7}$$

d= distance between electrodes [m]

A= active surface area of anode [m^2]

K= specific conductivity of bulk solution [10^3 mS/m]

The bulk resistance Rs, and hence the iRs-drop (uncompensated resistance), can be reduced by decreasing the distance between electrodes, increasing the submerged surface area of anode, or increasing the specific conductivity of the bulk solution …. (Addy, 2008, chap.2.).

3.2.2 Mechanism of Electrocoagulation

The EC process operates on the principle that cations produced electrolytically from iron and/ or aluminum anodes enhance the coagulation of contaminants from an aqueous medium. The sacrificial (consumable) metal anodes are used to produce hydroxides/polyhydroxides/polyoxyhydroxides such as iron or aluminum hydroxides in vicinity of anode. Coagulation occurs when these metal cations combine with negative particles carried toward the anode by electrophoretic motion (Deniel et al, 2008). The negative ions neutralize ionic species in the solution, reducing electrostatic interparticle repulsion until van der Waals attraction predominates, helping coagulation and aggregation into flocs. The flocs formed due to coagulation generate a sludge blanket that entraps and bridges colloidal particles remaining in the water. Contaminants are removed by either chemical reactions or precipitation or physical and chemical attachment to colloidal materials being generated by the electrode corrosion. Then they are removed by electroflotation, or sedimentation and filtration. Thus, rather than adding coagulating chemicals as in usual coagulation processes, these coagulating agents are generated in the EC.

During the EC process, water is also electrolyzed in parallel reaction, producing small bubbles of oxygen at anode and hydrogen at cathode. These bubbles attract the flocculated particles and, because of the natural buoyancy, float the flocculated contaminants to the surface.

Additionally, the following reactions can also occur in the electrocoagulation cell:

- Cathodic reduction impurities.
- Discharge and coagulation of colloidal particles.
- Electrophoretic migration of ions in the solution
- Electroflotation of coagulated particles by O_2 and H_2 bubbles produced at the electrodes.
- Reduction of metal ions at the cathode.
- Other electrochemical and chemical processes (Mollah et al., 2004).

The removal mechanisms in EC involve oxidation, reduction, decomposition, deposition, coagulation, absorption, adsorption precipitation, and flotation.

In EC, with electrical current following between two electrodes, coagulant is produced by electrolytic oxidation at anode (Fe). The generated $Fe^{2+}_{(aq)}$ or $Fe^{3+}_{(aq)}$

ions directly undergo further spontaneous reactions to produce $Fe(OH)_n$. Two mechanisms for the production of the iron hydroxides have been suggested (Larue et al., 2003):

(a) Mechanism 1

Anode:

$$4Fe_{(s)} \rightarrow 4Fe^{2+}_{(aq)} + 8e^- \quad (3.8)$$

$$4Fe^{2+}_{(aq)} + 10H_2O + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H^+_{(aq)} \quad (3.9)$$

Cathode:

$$8H^+_{(aq)} + 8e^- \rightarrow 4H_{2(g)} \quad (3.10)$$

Overall:

$$4Fe_{(s)} + 10H_2O + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)} \quad (3.11)$$

(b) Mechanism 2

Anode:

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \quad (3.12)$$

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)} \quad (3.13)$$

Cathode:

$$2H_2O + 2e^- \rightarrow 2OH^-_{(aq)} + H_{2(g} \quad (3.14)$$

Overall :

$Fe_{(s)} + 2H_2O \rightarrow Fe(OH)_{2(s)} + H_{2(g)}$ (3.15)

For the arsenic removal process, the generation of metallic cations takes place at the anode, whereas at the cathode, generally a H_2 production occurs together with OH^-release. When applying iron electrodes the process produces iron hydroxides, which would co-precipitate with arsenic anions. The major electrode reactions are at neutral pH (Hansen et al., 2008):

Anodic Reactions

$Fe \rightarrow Fe^{2+} + 2e^-$ (3.16)

$2H_2O \rightarrow O_2 + 4H^+ + 2e^-$ (3.17)

If anode potential is sufficiently high, secondary reaction can occur at anode, such as direct oxidation of organic compounds and of OH^- or Cl^- present in water (Deniel, et al., 2008).

$2Cl^-(aq) \rightarrow C1_2(g) + 2e-$ (3.18)

$2H_2O \rightarrow 4H^+ + O_2 (g) + 4e-$ (3.19)

Cathodic Reaction

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (3.20)

When introducing air (or oxygen) to the process, Fe^{2+} is oxidized rapidly:

$O_{2(g)} + 4Fe^{2+} + 2H_2O \rightarrow 4Fe^{3+} + 4OH^-$ (3.21)

The rate of the oxidation depends on the availability of dissolved oxygen.

In general at the cathode the solution becomes alkaline with time. The applied current force OH^- ion migration towards the anode (and Fe^{3+} to the cathode), hence supporting ferric hydroxide formation:

$$Fe^{+3} + 3OH^- \rightarrow Fe(OH)_3 \tag{3.22}$$

Arsenate co-precipitates with or adsorbs to $Fe(OH)_3$:

$$\alpha Fe(OH)_3(s) + \beta AsO_4^{3-}(aq) \rightarrow [\alpha Fe(OH)_3{}^{*}\beta AsO_4^{3-}] \tag{3.23}$$

For effective arsenate removal because of precipitation, the ratio α/β should be higher than. In electrocoagulation, iron hydroxide particles are formed in the presence of As(V). This can be more efficient for arsenic removal than adsorption to pre-formed Fe(III) particles.

The As(V) can be removed more efficiently than As(III), since As(V) anions (AsO_4^{3-}, $HAsO_4^{2-}$, or $H_2AsO_4^-$) are adsorbed stronger by iron oxides than As(III). If present, it would be necessary to oxidize As(III) to As(V). However, oxidised conditions in general favour arsenic removal in waters (Hansen, et al. 2008). It can be seen from Figure 3.1, schematic representation of removal of arsenate ions from the arsenic contaminated water by EC.

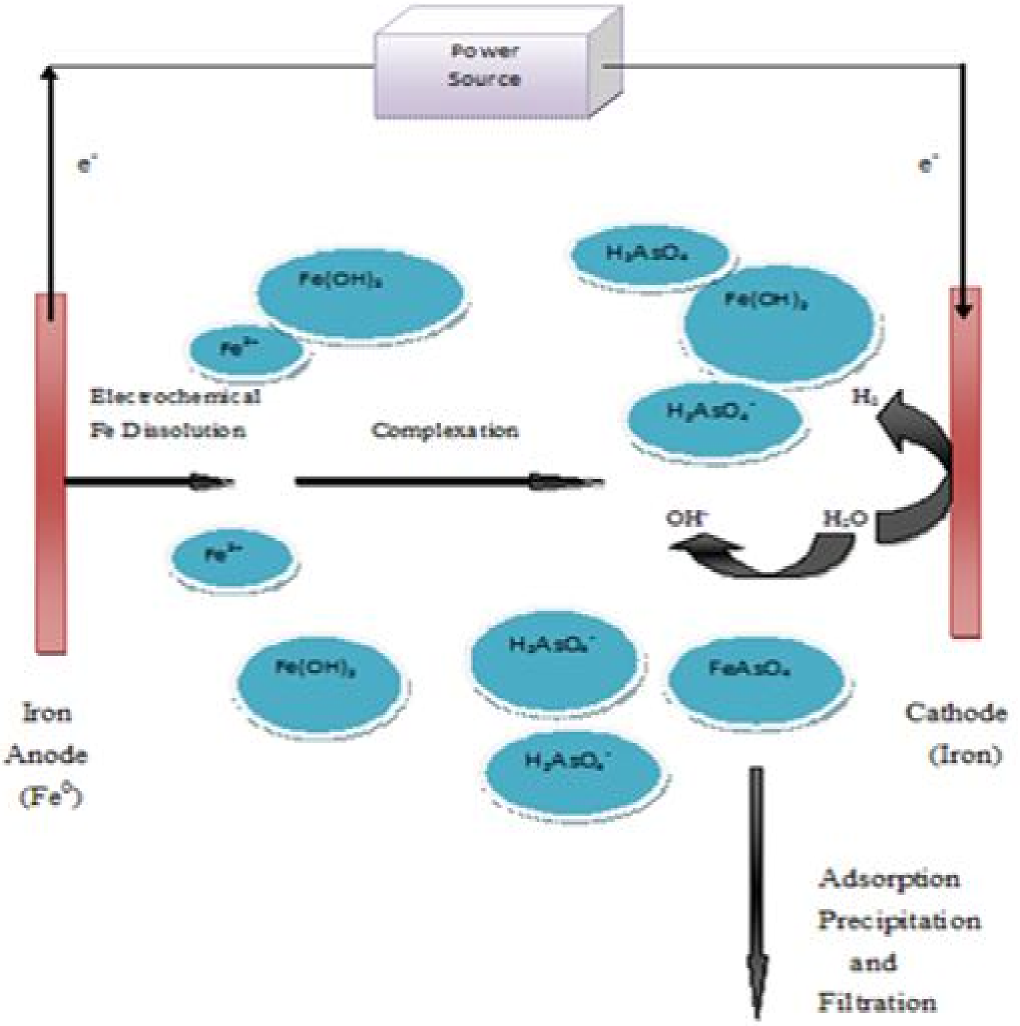


Figure 3.1 Schematic representation of removal of arsenate ions from solution by EC with iron electrodes. For this schematic, Fe^{3+} ions are dissolving from, the electrode though Fe^{2+} ions can dissolve as well. Moreover, $Fe(OH)_3$ is used to represent the precipitation iron (hydr)oxides (Addy, 2008).

3.3 Factors Affecting Electrocoagulation

3.3.1 Design

It is important to design the EC cell so that maximum efficiency can be achieved (Mollah et al., 2004). In addition to this, the lack of mechanistic understanding of electrocoagulation is reflected in the design of reactors.

The electrocoagulation process can be combined with many units including microfiltration, dissolved air flotation (DAF), sand filtration and electroflotation. Clearly, pre- and post- water treatment impacts significantly on the performance of the electrocoagulation reactor. The design phase should consider the following physical factors:

- Reactor geometry
- Reactor scale-up
- Continuous versus batch operation
- Current density

The control, operation and chemical interactions of the system influence performance and reliability. The chemical interactions of the pollutants (type and concentration) with the electrode material, electrode passivation and methods used for passivation control should be considered for the variety of reactor designs and operational region (Holt et al., 2006).

3.3.1.1 Geometry

Geometry of the reactor affects operational parameters including bubble path, flotation effectiveness, floc formation, fluid regime and mixing/settling characteristics (Hansen et al., 2007).

3.3.1.2 Scale-up Issues

One of the bases of chemical engineering is to establish key scale-up parameters to define the relationships between laboratory and full-scale equipment.

The surface area to volume ratio (S/V) is a significant scale-up parameter. Electrode area influences current density, position and rate of cation dosing, in addition to bubble production and bubble path length. Holt. et al. (2006) reported that when the S/V ratio increases the optimal current density decreases.

To scale up an electrocoagulation-flotation system from laboratory to industrial scale, the following dimensionless scale-up parameters were chosen by Zolotukhin (1989) to ensure correct sizing and proportioning of the reactors:

- Reynolds number (provides measure of the fluid flow regime)
- Froude number (provides measure of the importance of gravitational forces in the system)
- Weber criteria (provides measure of the importance of surface tension related forces in the system)
- Gas saturation similarity (related with the volumetric bubble density in the system)
- Geometric similarity (Holt et al., 2002).

3.3.1.3 Electrode Arrangement

Electrode design determines coagulant release and bubble type, thereby influencing flotation, mixing, mass transfer and pollutant removal. In flotation mode, electrolytic bubble production is required. Therefore, an electrochemically inert electrode is needed. And also current density is determined by operating current and electrode surface area. For consistent and predictable anodic dissolution and hydrogen production rates, constant current density is important.

An electrode with a known flat surface area, such as a plate electrode, and constant spacing from other electrodes ensures constant current density.

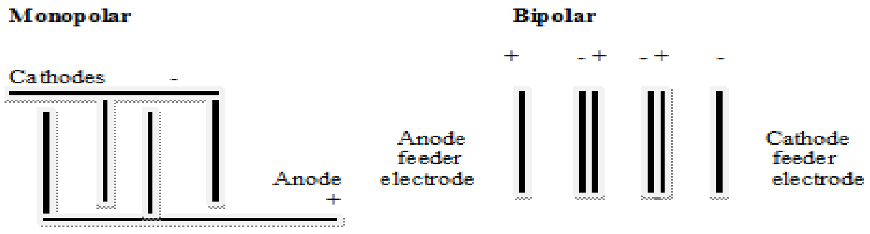
The electrode connections in an electrocoagulation reactor can be monopolar or bipolar. In monopolar arrangement, each pair of sacrificial electrodes is internally connected with each other, and has no interconnection with outer electrodes. This arrangement of monopolar electrodes with cells in series is electrically similar to single cell with many electrodes and interconnections. The conductive metal plates or rods are used in EC fabrication or commonly known as “sacrificial electrodes.”

The sacrificial electrode and cathode may be made up the same or different materials.

In a bipolar arrangement, the sacrificial electrodes are placed between the two parallel electrodes without any electrical connection (Comninellis and Chen, 2010). Just two monopolar electrodes are connected to electric power source with no interconnection between the sacrificial electrodes. This cell arrangement provides simple setup, which facilities easy maintenance. When an electric passed through the two electrodes, the neutral sides of the conductive plate will be transformed to charged sides, which contain opposite charge compared to the parallel side it. The consumable electrodes in this situation can be known as bipolar (Mollah et al., 2004).

A simple arrangement of the electrode connections is shown in Fig. 3.2, where the electrodes are monopolar and bipolar connections in the electrocoagulation reactor.

With monopolar connections an electric potential is connected between n pairs of anodes and cathodes. Parallel connections to each electrode cause current (I_0) to pass across each electrode and solution but if an electrical potential (U_0) is applied between two feeder electrodes, a series connections to bipolar electrodes cause the same current to pass through ‘‘n’’ electrode pairs (Emamjomeh et al., 2009).



Cell voltage, $U_0 = U_T$
Cell current, $I_T = I_0$
Parallel connections

Cell voltage, $U_T = U_{01} + U_{02} + ... + U_{0n}$
Cell current, $I_T = I_{01} + I_{02} + ... + I_{0n}$
Series connections

Figure 3.2 Monopolar and bipolar electrode connections in the EC reactor (Emamjomeh, et al., 2009).

3.3.1.4 Reactors

Both batch and continuous reactors have been used for EC. Batch reactors are commonly used for laboratory tests and continuous reactors used larger scale water and wastewater treatment. Electrochemical reactors may be classified according to the electrodes are placed as horizontal, vertical and concentric configurations; how electrodes are connected whether in monopolar (series or parallel) or bipolar varying the number of plates between poles. Each design has its own set of advantages and disadvantages. It is not easy to design an EC reactor that can have good performance with all of the possible waters and wastewaters because of the great variability in composition of those waters. Some important factors to consider are flow, pressure drop, suspended and settable solids, and distance between electrodes, gas evolution, polarity switching to avoid the undesirable effect of passive film formation, electrode materials, etc. (Moreno, 2007). Characteristics of batch and continuous systems can be seen in Table 3.1.

Table 3.1 Comparison between batch and continuous systems (Holt et al., 2002).

Batch	Continuous
No feed flowrate-constant volume	Constant flowrate
Internal concentrations change with time	Internal concentrations constant
Performance related to reaction time (i.e. time in reactor)	Performance related to residence time (space-time) in reactor
Naturally dynamic operation	Steady-state operation
Reactor contents are well-mixed (uniform composition)	Mixing varies between extremes of well-mixed and plug-flow

3.3.2 Current Density and Charge loading

Current density (i) is the current distributed to the electrode divided by the active area of the electrode. The current density not only determines the coagulant dosage rate, but also bubble production rate and size. Thus, this parameter has a significant impact on pollutants removal efficiencies (Deniel et al., 2008).

A large current means a small electrocoagulation unit. However, when too large current is used, there is a high chance of wasting electrical energy in heating up water (Al Anbari et al., 2008). More importantly, a too large current density would result in a significantly decrease in CE.

In fact, the amounts of iron and hydroxide ions produced at a given time, within the electrocoagulation cell are related to the current flow, using Faraday's law:

$$m = \frac{I \times t \times MW}{Z \times F} \tag{3.24}$$

where I: operating current(A),
t : processing time,
MW: molecular weight (of iron, 55.85g/mol)
Z: number of electrons transferred in the reaction (n= 2or 3 for Fe^{2+} or Fe^{3+})
F: Faraday's constant (96500 C/mol e^-) (Lakshmanan, 2007).

When the current decreased, the time needed to achieve similar efficiencies increased. This expected behavior is explained by the fact that the treatment efficiency was principally affected by charge loading ($Q = I * t$), as reported by X. Chen et al. (2000). As the time progresses, the amount of oxidized iron and the needed charge loading increase.

However, these parameters should be kept at low level to obtain a low-cost treatment. At high current density, the bubble density and upwards flux increased and resulted in a faster removal of the coagulant by floatation. Thus, there is a reduction in the probability of collision between the coagulant and pollutants. The lowest current should be selected to obtain the best removal rate without increasing of cost (Al Anbari et al., 2008).

Oxidation at anode can produce Fe^{2+} or Fe^{3+}:

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \qquad (3.25)$$

$$Fe_{(s)} \rightarrow Fe^{3+}_{(aq)} + 3e^- \qquad (3.26)$$

According to Faradays law, the theoretical concentration of Fe^{2+} or Fe^{3+} ions released from anodes can be calculated by:

$$[Fe^{2+} \text{or } Fe^{3+}] = \frac{Qe}{Z \times F} \qquad (3.27)$$

(Z = 2 for Fe^{2+} and for Fe^{3+} 3, Qe: charge loading)
And as charge loading increased, removal efficiencies increase.

Different current densities are preferred in different situations. High current densities are desirable for separation processes involving flotation cells or large settling tanks, when small current densities are appropriate for electrocoagulators that are integrated with typical sand and coal filters. A systematic analysis is required to define the relationship between current density and desired separation effects (Holt et al., 2006).

3.3.3 Effect of Overpotential

Concentration overpotential, also known as mass transfer or diffusion overpotential is caused by the differences in electroactive species concentration between the bulk solution and electrode surface. This can be overcome by increasing the masses of metal ions can be transported from anode surface to bulk of the solution. (The increased transport of metal can be achieved by mechanical stirring of the solution).

Kinetic overpotential (also called activation potential) has its origin in the activation energy barrier to electron transfer reactions. The activation overpotential is particularly high evolution of gases on certain electrodes. Both kinetic and concentration overpotentials will increases in current (Daida, 2005).

3.3.4 Time

Time is important for the removal ways such as flotation and settling. To facilitate this discussion, two description of time, removal and contact time, are significant. Removal time is the time for the contaminant aggregate to the surface or the base. Contact time is the time for the contact between a particular coagulant and contaminant particles. Adequate contact time is required for aggregation and the formation of larger particles, which are easier to remove particularly by settling.

Separation by flotation is expected to occur faster than by separation by gravitational sedimentation. Faster removal decreases the contact time between coagulant and contaminant particles decreasing the coagulant efficiency (Holt et al., 2002).

3.3.5 Electrode Materials

A vital aspect of an electrochemical process is the selection of the appropriate materials for the electrodes. Working electrode and counter electrode materials cannot always be selected independently as there will be significant interactions of the cell chemistry to consider. The choice of materials for electrodes is determined by their corrosion resistance, high conductivity and material strength together with considerations concerning the price of the material and methods applied for shaping and processing the metals and their respective costs. (Alaton, 2005).

- Criteria for electrode material selection
- Suitable electrochemical properties
- Chemical and electrochemical stability
- Physical and thermal stability
- Suitable physical form and fabrication

- Good electrical conductivity
- Low over-voltage
- Environmentally suitable (non-polluting/non-contaminating)
- Low cost

The electrode material for drinking water treatment should be non-toxic to human health. Hence iron, aluminum and titanium can be chosen as electrode material since these are non toxic and readily available.

The electrode material impacts obviously on the performance of the electrocoagulation reactor. The anode material determines the cation introduced into solution. Several researchers have studied the choice of electrode material with a variety of theories as to the preference of a particular material (Holt et al., 2006). Conventionally, iron and aluminum are found to be effective electrode materials because of their abundance, cost and efficiency of their oxyhydroxides as coagulating agents (Daida et al., 2005).

Efficiencies with different electrode materials followed the sequence: iron>titanium>aluminum. The process was able to remove more than 99% of arsenic from an As contaminated water and met drinking water standard of 10 $\mu g^{-1}$with iron electrode. As(III) was more efficiently removed in electrocoagulation than chemical coagulation, whereas, As(V) removal performance of both electrocoagulation and chemical coagulation nearly same (Farooqui, 2004).

Iron oxides have been generally used as sorbents for arsenic removal. They usually have strong adsorption affinities for arsenic and they can have large specific surface areas (Dixit and Hering, 2003). Arsenic is present in water and wastewater mostly in the forms of arsenate (As(V)) and arsenite (As(III)). In the environmentally relevant pH range of 4-10, the dominant As(V) species are negatively charged ($H_2AsO_4^-$ and $HAsO_4^{2-)}$, when the dominant As(III) species is neutrally charged (H_3AsO_3). The negatively charged As(V) species are more likely to be adsorbed and are usually more easily removed than As(III) in treatment systems (Balasubramanian and Madhavan, 2001; Kumar et al., 2004; Parga et al., 2005; Wan, 2010).

The distance between electrodes is also an important factor because it reduces the IR drop, thereby reducing solotion resistance. The IR-drop is related to the distance (d in cm) between the electrodes, surface area (A in m^2) of the cathode and specific conductivity of solution (k in mSm^{-1}) and current (I in A) by the equation below:

$$ŋIR = \frac{I \times d}{A \times k} \tag{3.28}$$

The IR-drop can be easily minimized by decreasing distance between the electrodes and increasing the area of cross-section of the electrodes and the specific conductivity of the solution (Daida, 2005).

3.3.6 Presence of NaCl

Addition of salt to the arsenic contaminated aqueous medium in an electrocoagulation cell increases conductivity of aqueous medium thereby decreasing the IR drop somewhat. The IR reduction leads to less power consumption (Daida, 2005). Besides NaCl`s ionic contribution in carrying the electric charge, it was found that chlorine ions can significantly reduce adverse effect of ions such as HCO_3^-, SO_4^{2-}. The existence of the carbonate or sulfate ions can cause to precipitation of Ca^{2+} and Mg^{2+} ions that forms an insulating layer on the surface of the electrodes. This insulating layer can sharply increase potential between electrodes and result in significant decrease in the current efficiency. Therefore it’s recommended that among the anions present, there should be 20% Cl^- to ensure a normal operation in electrocoagulation in water treatment (G. Chen, 2004).

In case of NaCl, the electrochemically generated chlorine is also effective for water disinfection in large scale process (Daida, 2005).

3.3.7 Passivation

One of the significant operational issues with electrocoagulation is electrode passivation. The passivation of electrodes is concern for the long life of the process.

The major problem of the iron electrode is its passivation, which is caused by iron hydroxide produced during the discharge process and prevents further anodic utilization. Passivation of the anode surface is possible in these systems because of high current densities and high concentrations of Fe^{2+}, Fe^{3+}, and OH^- ions at the anode surface. (Hansen et. al, 2008).

Electrode passivation has been widely observed and recognized as harmful to reactor performance. This formation of an inhibiting layer, generally an oxide on the electrode surface, will prevent metal dissolution and electron transfer, thus limiting coagulant addition to the solution. After a while, the thickness of this layer increases, reducing the effectiveness of the electrocoagulation process. The use of new materials different electrode types and arrangements, more sophisticated reactors operational strategies (such as periodic polarity reversal of the electrodes) have definitely let to significant reductions of impact passivation.

Besides, addition of anions will also slow down the electrode passivation. The positive effect was follows: $Cl^- > Br^- > I^- > F^- > ClO_4^- > OH^-$ and SO_4^{2-}. Specially, addition of certain amount of Cl^- into the aqueous solution will inhibit the electrode passivation process largely. It is also necessary to clean regularly the surface of the electrode and the surface of the electrode plates (Comninellis et al., 2010).

Nikolaev et al (1982) investigated various methods of preventing and / or controlling electrode passivation including:

- Changing polarity of the electrode;
- Hydromechanical cleaning;
- Introducting inhibiting agents;

- Mechanical cleaning of the electrodes.

According to these researchers, the most efficient and reliable method of electrode maintenance was to periodically mechanically clean the electrodes which for large-scale, continuous processes is a non-trivial issue (Holt et al., 2006).

3.3.8 Solution pH

Solution pH determines the speciation of metal ions. The pH affects the state of other species in solution and the solubility of products formed. Therefore, solution pH influences the overall efficiency and effectiveness of electrocoagulation.

The pH of the solution can easily be altered. An optimal pH seems to exist for a given pollutant, with optimal pH values ranging from 6.5 to 7.5 (for arsenic and iron) (Holt et al., 2006).

3.3.8.1 Production of Iron Oxide Coagulants and Effects of pH on Arsenic Removal with Iron Coagulants

Arsenic is present in water and wastewater mostly in the forms of arsenate (As(V)) and arsenite (As(III)). In the environmentally relevant pH range of 4-10, the dominant As(V) species are negatively charged ($H_2AsO_4^-$ and $HAsO_4^{2-}$), when the dominant As(III) species are neutrally charged (H_3AsO_3) (Figure 4.3). The negatively charged As(V) species are more likely to be adsorbed and are usually more easily removed. As(V) is removed more efficiently than As(III) (Balasubramanian and Madhavan, 2001; Kumar et al., 2004; Parga et al., 2005).

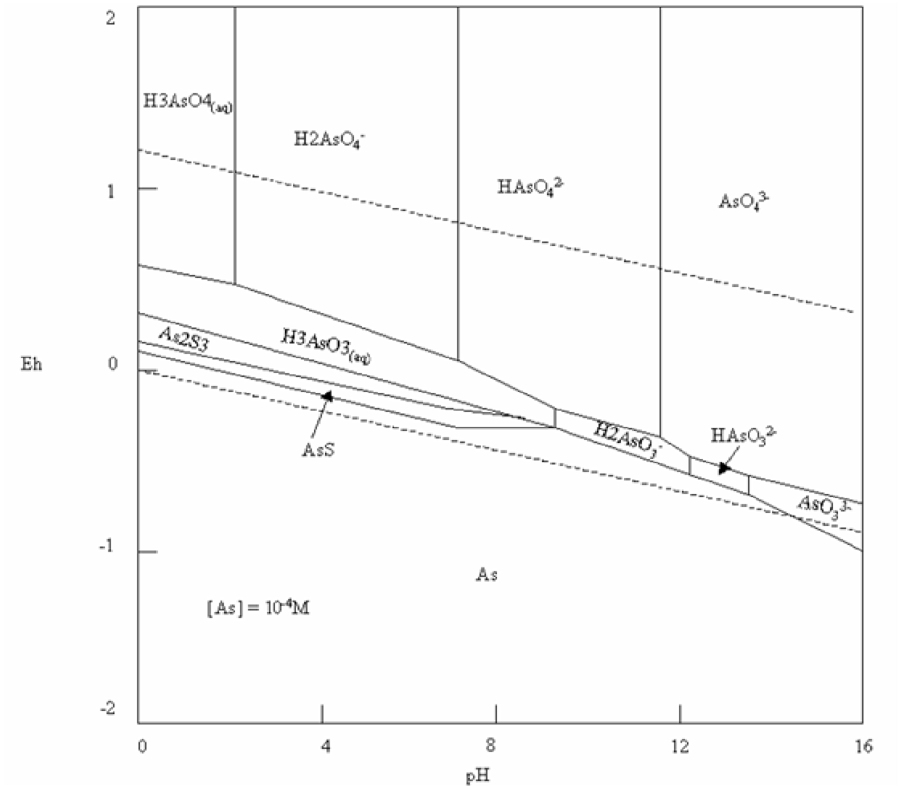


Figure 3.3 Distribution of dissolved arsenical species as a function of pH (Rubidge, 2004).

Iron oxides have been generally used as sorbents for arsenic removal. They mostly have strong adsorption affinities for arsenic and they can have large specific surface areas. Iron oxides have been used in different forms for arsenic removal. It has been reported for arsenic removal either in the form of iron oxide suspensions, packed beds of iron oxides, usual chemical coagulation or electrocoagulation using iron electrodes.

Several water chemistry factors can affect arsenic removal by electrocoagulation. The amount of Fe^{2+}or Fe^{3+} produced in the reaction depends primarily on the solution pH (Jehangir, 2006). The pH of the water influences arsenic removal by electrocoagulation by affecting arsenic species distribution, the surface charge of the metal oxides produced during electrocoagulation, and the rate of Fe(III) production from the Fe(II) released from the iron anode (Wan, 2010).

Ferric ions generated by electrochemical oxidation of iron electrode can form monomeric ions, $Fe(OH)_3$ and polymeric hydroxyl complexes namely $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5(OH)_2^{+}$, $Fe(H_2O)_4(OH)_2^{+1}$, $Fe_2(H_2O)_8(OH)_2^{4+}$, $Fe_2(H_2O)_6(OH)_4^{4+}$depending on the pH of aqueous medium. These hydroxides/polyhydroxides/polyoxyhydroxide metallic compounds have as strong affinity for dispersed particles and counter ions to cause coagulation. Moreover both the As(V) and As(III) can be strongly sorbed by iron(III) oxides such as amorphous $Fe(OH)_3$, Hydrous Ferrous oxide (HFO) and Goethite . Arsenate anion bound to HFO can form common naturally occurring arsenate minerals $FeAsO_4.2H_2O$ (Scorodite) and $FeHAsO_4.8H_2O$ (Symplesite) as dominant solid phase. Thus, arsenic is removed by iron species by either or both compound formation and adsorption. The gases evolved at the electrodes can impinge on and cause flotation of coagulated materials (Daida, 2005). The production of by-products of EC depending on pH values are shown in Table 3.2.

Table 3.2 The reactions in the Electrocoagulation cell (Moreno-Casillas, et al., 2007)

pH	**Anode**	**Cathode**
water& **pH<5**	$Fe \rightarrow Fe^{2+} + 2e^{-}$ $2\ Fe^{2+} \rightarrow 2Fe^{3+}$ In fact Iron also undergoes hydrolysis $Fe + 6H_2O \rightarrow Fe(H_2O)_4(OH)_{2(aq)} + 2H^{+1} + 2e^{-1}$ $Fe + 6H_2O \rightarrow Fe(H_2O)_3(OH)_{3(aq)} + 3H^{+1} + 3e^{-1}$	$2H^{+} + 2e^{-} \rightarrow H_{2(g)}\uparrow$

Electrochemistry depends on thermodynamics and kinetics. The rate of reaction will depend on the removal of [H^{+}] via H$_2$ evolution; this reaction will proceed fast for low pH values for a strong acid. For a weak acid the rate will depend on pKa of the acid. Electro neutrality principle has to be kept in any step.

pH	**Anode**	**Cathode**
5<pH<7	$Fe(H_2O)_3(OH)_{3(aq)} \rightarrow Fe(H_2O)_3(OH)_{3(s)}$ More hydrogen evolution and Fe(III) hydroxide begin to precipitate floc with yellowish color. Formation of rust: $2Fe(H_2O)_3(OH)_3 \leftrightarrow Fe_2O_3(H_2O)_6$	$2H^{+} + 2e^{-} \rightarrow H_{2(g)}\uparrow$
6<pH<8	$Fe(H_2O)_3(OH)_{3(aq)} \rightarrow Fe(H_2O)_3(OH)_{3(s)}$ $Fe(H_2O)_4(OH)_{2(aq)} \rightarrow Fe(H_2O)_4(OH)_{2s)}$ Hydrogen evolution continues and precipitation of Fe(II) hydroxide also occurs presenting a dark green floc. The pH for minimum solubility of Fe(OH)n is between 7-8 Formation of rust. Oxides are dehydrated hydroxides. $2Fe(OH)_3 \leftrightarrow Fe_2O_3 + 3H_2O$ $Fe(OH)_2 \leftrightarrow FeO + H_2O$ $2Fe(OH)_3 + Fe(OH)_2 \leftrightarrow Fe3O_4 + 4H_2O$ Polymerization of iron oxyhydroxides to form the floc.	$2H^{+} + 2e^{-} \rightarrow H_{2(g)}\uparrow$

This mechanism follows the Pourbaix diagram, Figure for hydroxides, and also the characterization of EC products made by Parga et al. Conditions during the cell are not constant. Potential, concentrations, species and pH are changing. It can be said that in the iron Pourbaix diagram we are moving to the right in parallel to hydrogen evolution as highlighted in Figure

pH>8	$Fe + 6H_2O \rightarrow Fe(H_2O)_4(OH)_{2(aq)} + H_{2(g)}\uparrow$ $Fe + 6H_2O \rightarrow Fe(H_2O)_3(OH)_{3(aq)} + 1\ 1/2H_{2(g)}\uparrow$ Sludge and rust generation continues. In fact iron oxides are dehydrated iron hydroxides, and some of this oxidation occurs on the surface of the floated sludge. It can also occur during filtration and preparation of the sample.	

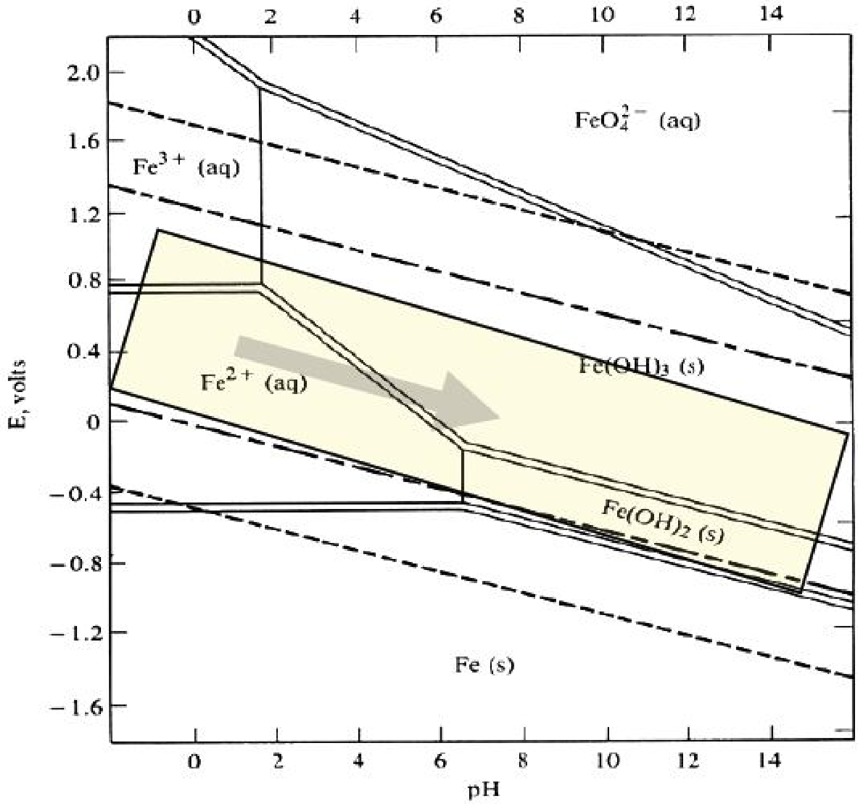


Figure 3.4 Iron Pourbaix Diagram, showing the region and direction where the EC process proceeds (Moreno et al., 2007).

3.4 Corrosion

Generally, “Rusting” is well known, but not the only form of corrosion. Contrary to mechanical damage, metal corrosion is a reaction of the metal with its environment, starting from the surface of the metal. The real corrosion reactions occur in a few nanometers thick metal/electrolyte interface, which does not correspond to the bulk phases on either the metallic or the electrolyte side. Moreover, “corrosion products” can be present as a thin, well-adhering oxidic surface film, which protects the underlying metal from excessive corrosion (passive film) (Elsener, n.d.).

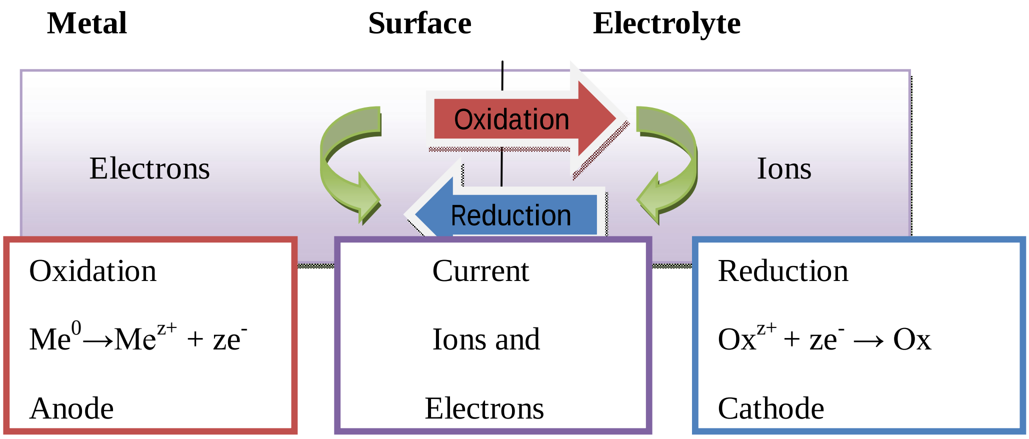


Figure 3.5 Schematic of a corroding metal electrode. Formal breakdown into two half-cells of a galvanic element (oxidation at anode, reduction at cathode (Elsener, n.d.).

Corrosion processes on metallic materials are generally electrochemical processes (Redox processes) as in Figure 3.5. The total reaction can be separate into two partial reactions:

a) Oxidation reaction: This is the real corrosion process, i.e. the **metal dissolution (**conversion of iron atoms from the metallic into the ionic state) the oxidation reaction occurs at the anode:

$$Fe \rightarrow Fe^{2+} + 2\ e- \qquad (3.29)$$

b) Reduction reaction: Because of the electro-neutrality principle, the electrons released during the anodic reaction must be taken up by a part of the environment close to the metal, which is then reduced. This process occurs at the cathode. If the corrosive agent is an acidic solution, protons are reduced generating hydrogen gas:

$$2\ H^+ + 2\ e^- \rightarrow H_{2\ (g)} \qquad (3.30)$$

On the contrary, if **oxygen**, dissolved in (neutral or alkaline) electrolytes, interacts with the metal, oxygen is the oxidizing agent, i.e. it will be reduced:

$$O_2 + 2\ H_2O + 4\ e^- \rightarrow 4OH \qquad (3.31)$$

Because of the electro-neutrality (the electrons released from the iron atom need to be taken up by the oxidizing agent), the total corrosion process is composed of at least one oxidation and one reduction process, which must take place at the same time.

An anodic (positive) current signifies the iron dissolution; a cathodic (negative) current signifies to the reduction reaction. Because metals (iron) are electrical conductors and the electrolyte is generally well electrolytically conductive, both the anodic and cathodic reaction constitutes a short-circuited galvanic element – a current I (corrosion current) is flowing:

$$I = \Delta U / (R_a + R_c + R_e) \qquad (3.32)$$

The intensity of the corrosion current is adjusted by the voltage difference ΔU of the galvanic element and the resistance of the anode R_a, the cathode R_c and the electrolyte R_e. Thermodynamic and kinetic basic principles of the corrosion reaction allow the prediction of if a corrosion reaction is possible or not (thermodynamics) and how fast it proceeds (kinetics). Both thermodynamic and kinetic considerations have to take both the metal and its environment into account (Elsener, n.d.).

3.4.1 Thermodynamics

Whether corrosion reaction can occur or not can be derived from the thermodynamic laws.

$\Delta G<0$: the reaction occurs

$\Delta G>0$: the reaction does not occur.

For electrochemical reactions, ΔG is replaced by the cell potential U ($\Delta G=nF\Delta U$), which can be calculated from the equilibrium potentials E_a and E_c of anodic and cathodic partial reactions, respectively:

$$\Delta U= E_a-E_c \qquad (3.33)$$

The equilibrium potentials can be calculated with the help of standart potentials and Nernst`s law:

$E_a = E^0 + 2.3\ RT/nF \times \ln(c_{Mez+})$ (3.34)

E_a: normal potential
E^0: standart potential
c_{Mez+}: concentration of metal ions in solution
n: number of transmitted electrons

Using the general logarithm, the equation can be formulated as:

$E_a = E^0 + 0.059/n \times \log(c_{Mez+})$ (3.35)

(For $Fe \rightarrow Fe^{2+} + 2e^-$ $E^0_{Me/Me+}$ (V) = - 0.44, $E^`_{Me/Me+}$ (V) = - 0.61 with $c_{Mez+} = 10^{-6}$ mol/l) (Elsener, n.d.).

3.4.2 Pourbaix diagram of iron

These generally used diagrams show how corrosion behaviour depends on electrical potential (E) and pH. A simplified Pourbaix diagram for iron is shown here.

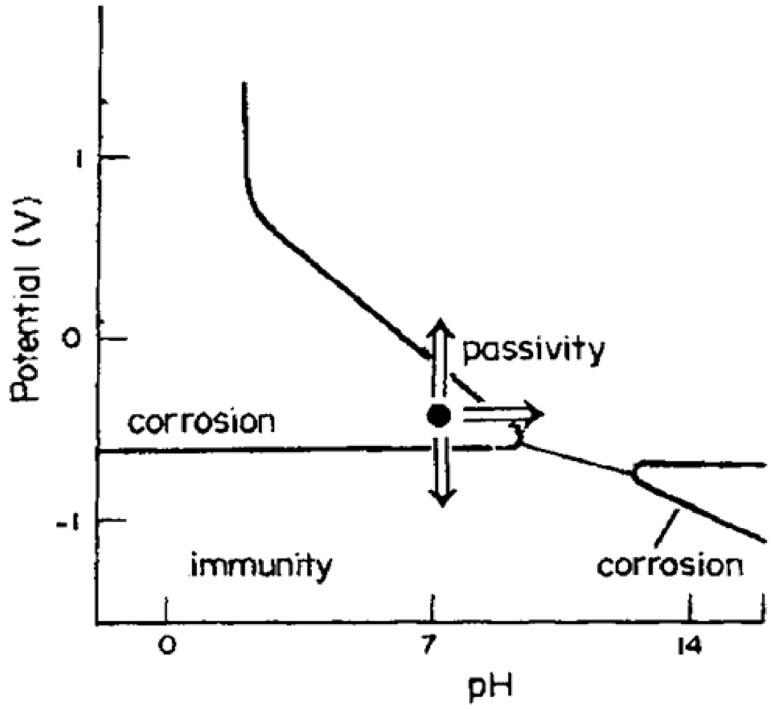


Figure 3.6 Pourbaix diagram for iron, showing regions of active corrosion, passivity and immunity (Kruger, J., 2001).

Immunity; refers to metal as a thermodynamically stable phase. Corrosion is thermodynamically impossible.

Corrosion; occurs if compound of metal is thermodynamically stable state unless below applies. The most stable form is the metal cation. Corrosion will occur until the metal consumed.

Passivity; occurs when a sparingly soluble metal compound forms a thin, protective film (usually an oxide or hydroxide) on the surface rate. The protective properties of a surface film of corrosion products are best established by practical experience, guided by knowledge of corrosion kinetics. The passive region an insoluble protective layer (hydroxide or oxide layer) is the most stable form; corrosion will occur until a protective layer is formed (Moreno-Casillas., 2007).

3.4.3 Corrosion of Iron

All major iron (hydr)oxides have been identified in the corrosion products of iron and steel. In some cases, the physical placement of corrosion products is more or less random, while in others, the different oxides are arranged in layers. Layer-type rust results from potential or chemical gradients across the oxide film. Such gradients often change with film thickness, leading to rust composition changes with distance from metal. Arsenic adsorption onto ZVI is thought to primarily occur on the oxide film forming around iron fillings. In EC, it is obvious whether arsenic removal is due to adsorption to an iron (hydr)oxides formed in solution (Addy, 2008).

The rust (Figure 3.7) of iron in natural conditions is known to require oxygen. Iron does not rust in water unless O_2 is present. Other factors such as the pH of the solution, the presence of ionized salts, contact with the metals more difficult to oxidize than iron, electric current and stress on the iron can accelerate rusting (Moreno, 2007).

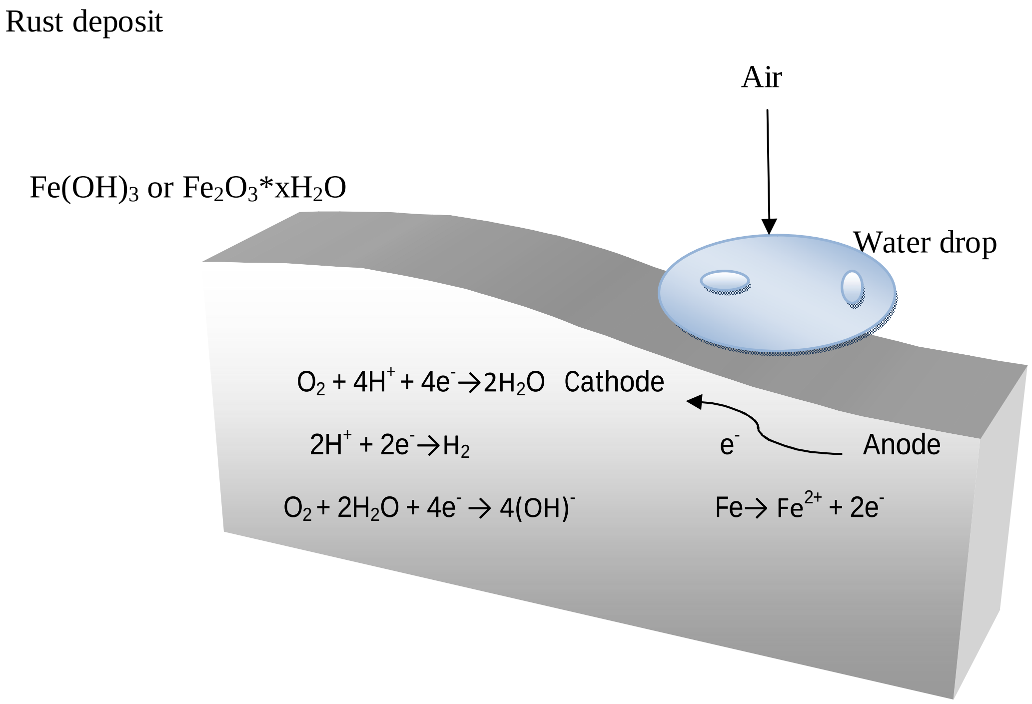


Figure 3.7 Corrosion of iron in contact with water (Moreno, 2007).

The overall corrosion process may be subdivided into a number of simplified steps:

1) Mass transport of reactants, O_2, to the surface via convection and diffusion
2) Adsorption of reactants, O_2, H_2O and H^+
3) Electrochemical reactions:

Anode $2Fe - 4e^- \rightarrow 2Fe^{+2}$ (3.36)

Cathode $O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^-$ (3.37)

Cell $2Fe + O_2 + 2H_2O \rightarrow 2Fe^{+2} + 4(OH)^-$ (3.38)

4) Desorption of products (Fe^{2+} and $(OH)^-$) or reaction between products: e.g.

$2Fe^{+2} + 4(OH)^- \rightarrow 4Fe(OH)_2$ (3.39)

then $2Fe(OH)_2 + O_2 + (n-2)H_2O \rightarrow Fe_2O_3{*}nH_2O$ (3.40)

5) Mass transport of products (Fe^{+2} and $(OH)^-$) away from the surface by migration and convective diffusion (Moreno, 2007).

3.5 Adsorption mechanisms and materials

3.5.1 Arsenic sorption onto iron (hydr)oxides

Adsorption, which is shown in Figure 3.8, is generally defined as the concentration of a substance at an interface or surface. The process can occur at an interface between any two phases, like liquid-liquid, gas-liquid, gas-solid, or liquid-solid interfaces.

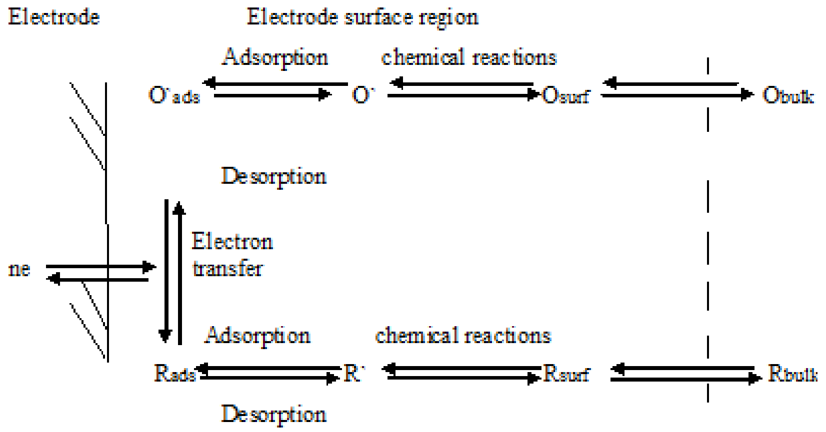


Figure 3.8 Pathway of general electrode reaction (Holt, 2002).

Arsenite (As(III)) and arsenate (As(V)) show strong affinity to iron surfaces and form surface complexes. Arsenic can associate with iron surfaces either by forming inner-sphere or outer-sphere complexes. Inner-sphere complexes are formed between arsenic anions and electron donating oxygen ions of the iron surface. Outer-sphere complexes are formed when arsenic anions are within a critical distance of the surface functional group of the iron surfaces, usually arsenic anions are separated from iron surface by one (or more) water molecules in outer-sphere complexes (Badruzzaman, 2005).

The mechanism of adsorption is generally chemical interactions between the adsorbate and surface rather than electrostatic interactions. In this case, the adsorbate is said to be chemically or specically adsorbed (often called chemisorbed). If the adsorbate is attracted to the surface only through electrostatic interactions, then it is said to be physically or non-specically adsorbed. The interaction between dissolved arsenic oxyanions and iron (hydr)oxides occurs at the surface.

In the presence of water, the surface of an oxide is presumed to be hydrated and covered with a layer of OH_x groups (either from the oxide structure or bound water molecules). Functional hydroxyl groups on a surface have the same donor atoms as functional groups insoluble ligands, as so behave in the same way. The groups have ionizable atoms and so can protonate (positive) and deprotonate (negative) as a function of pH (i.e. acid/base reactions). In the case of arsenic oxyanions, the major mechanism of adsorption is ligand exchange; the surface hydroxyl group is exchanged for another ligand. Ligand exchange can occur at one or two surface hydroxyl groups on the oxide, designated by S-OH, according to following:

$$\text{S-OH} + \text{L} \leftrightarrow \text{S-L}^{+} + \text{OH}^{-} \qquad (3.41)$$

$$2\ \text{S-OH} + \text{L} \leftrightarrow \text{S}_2\text{L}^{2+} + 2\text{OH}^{-} \qquad (3.42)$$

These bonds are strong and are known as inner-sphere complexes. If the bond occurs at one hydroxyl group (Eq. 3.39), it is known a monodentate complex. If it occurs at two hydroxyl groups (Eq. 3.40), it is a bidentate complex. Because adsorption is coupled with the release of OH^- in both cases, complexation tends to be favored by lower pH values. A complex where the adsorbate retains its waters of hydration (when still engaging in a chemical bond) is known as an outer-sphere complex.

The capacity of a suspended solid surface adsorbent to adsorb a species of ion from solution depends on many factors, including the number of available sites on its surface, the affinity of adsorbate for each site, in addition to on the amount of adsorbate available near the surface. The availability of sites on the adsorbent depends on the adsorbent surface area, the protonation (positive) state of the surface hydroxyl groups (which depends on pH), and the concentration of competing ions for the same sites. The affinity of the adsorbate for a site depends on local electrostatic conditions (partially created by the protonation state of the surface hydroxyl groups) and the thermodynamic favorability of a chemical reaction. Each of these factors can limit and/or control the quantity of adsorbate removed from the solution via adsorption (Addy, 2008).

The amount of material adsorbed per unit amount of adsorbent is called the adsorption density. Any model that relates the amount of adsorbate at the surface to that in the solution in equilibrium systems at constant temperature is called an adsorption isotherm. Adsorption of As[III] and As[V] to iron oxides and iron hydroxides can be described by Langmuir isotherm. The form of the Langmuir isotherm for a simple system with a single adsorbate is:

$$qA = \frac{\mathrm{Kads} \times \{A\}}{1 + \mathrm{Kads} \times \{A\}} \times qmax \qquad (3.43)$$

qA = adsorption density (moles adsorbed per gram of adsorbent)
K_{ads} = constant defining affinity of adsorbent for adsorbate
{A} = activity × aqueous concentration of adsorbate A
qmax = maximum adsorption density.

As $K_{ads}\{A\} << 1$, the isotherm becomes linear: $qA \approx Kads\{A\}qmax$. Over this limited range of adsorbate concentrations, one can expect the percentage of adsorbate removed from solution to be almost constant. When $K_{ads}\{A\} >> 1$, $qA \approx qmax$, and the percentage of adsorbate removed will decrease will increasing adsorbate concentration. If multiple adsorbates are in solution, they can compete for adsorption sites on a single adsorbent. In the event of j adsorbates, the Langmuir adsorption isotherm for any species i become:

$$qi = \frac{\mathrm{Kads{,}iai}}{1 + \sum_j \mathrm{Kads{,}jaj}} \times qmax \qquad (3.44)$$

Kads;i = constant defining affinity of adsorbent for adsorbate i
ai = {A} for adsorbate i

The surface of the adsorbent can acquire electric charge though chemical reactions via ionizable functional groups (i.e. acid/base reactions, dependant on pH), isomorphic replacements of atoms in the surface lattice, and adsorption. The charge can influence the affinity of the adsorbent for the adsorbate. To take this into consideration, the constant Kads can be modified by an exponential term that is a function of the surface potential. Generally, a more charged surface will have an increased affinity for opposite-charge adsorbates and a decreased affinity for same-charge adsorbates. The stable forms of arsenate between pH 6-9 are negatively charged (H_2AsO^{2-} and $HAsO_4{}^{2-}$) while the stable form of arsenite is neutral ($H3AsO_3{}^0$).

If the adsorption density becomes high enough, it is possible for the adsorbate to form precipitate. In theory, this would eliminate the limiting capacity of the solid for adsorbate, because ions from the bulk could always (subject to solubility equilibrium) be incorporated into a new precipitate layer as opposed to competing for adsorption sites. This appears to provide a method for distinguishing adsorption from surface precipitation by measuring the isotherm behavior (a surface precipitate should have no qmax). Nevertheless, in practice it almost impossible to distinguish the two states from isotherms alone. Surface precipitation is likely to be accompanied by adsorption to other parts of the surface with the sum of both behaviors appearing in the isotherm. Besides, if the affinity of the adsorbent for the adsorbate varies across the surface (as it often does), the isotherm may appear to increase indefinitely as strong binding sites become saturated but weaker binding sites continue to come into play at higher adsorbate concentrations - the isotherms become almost impossible to distinguish from the expected isotherm of surface precipitation. Sensitive spectroscopic techniques are generally used to clarify the uncertainty instead (Addy, 2008).

3.6 Characterization Techniques

It is hard to differentiate between iron oxide and oxyhydroxide species by only a single analytic technique. Powder X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission Mossbauer spectroscopy (TMS) are used to characterize the solid products formed from iron electrodes during EC (Parga, et al., 2005).

Parga et al. (2005) used X-ray diffraction (XRD), scanning electron microscopy(SEM) and transmission Mossbauer spectroscopy (TEM) Fourier transform infrared spectroscopy (FT-IR) to characterize magnetite, goethite, lepidocrocite, iron hydroxide (non-stoichiometric magnetite) or iron hydroxides in the solid products formed carbon steel electrodes during EC.

Moreno (2007) used X-ray diffraction (XRD). XRD of the sludge the combined Fe and Al electrodes demonstrated armorphous poorly-crystalline phases for aluminum hydroxide/ oxyhydroxyides (bayerite Al(OH) and diaspore AlO(OH)); while aluminum arsenate (mansfieldite $AlAsO_4.2(H_2O)$), and iron oxyhydoxides (lepidocrocite FeO(OH), magnetite Fe_3O_4, and iron oxide (FeO) were identified.

3.6.1 Scanning Electron Microscopy and Energy Dispersive X-Ray spectroscopy

Scanning electron microscopy (SEM) is a method for high-resolution imaging of surfaces. The SEM uses electrons for imaging, much as a light microscope uses visible light. The advantages of SEM over light microscopy contain much higher magnification (>100,000X) and greater depth of field up to 100 times that of light microscopy. Qualitative and quantitative chemical analysis information is also obtained using an energy dispersive x-ray spectrometer (EDS) with the SEM.

The SEM produces a beam of incident electrons in an electron column above the sample chamber. The electrons are produced by a thermal emission source. The energy of the incident electrons can be as low as 100 eV or as high as 30 keV depending upon the evaluation objectives. The beam can also be focused at a single point or scanned along a line for x-ray analysis. The beam can be focused to a last probe diameter as small as about 10 Å.

The SEM column and sample chamber are at a moderate vacuum to let the electrons to travel freely from the electron beam source to the sample and then to the detectors. High-resolution imaging is done with the chamber at higher vacuum, generally from 10^{-5} to 10^{-7} Torr.

Energy Dispersive X-ray Spectroscopy (EDS or EDX) is a chemical microanalysis technique applied in conjunction with scanning electron microscopy (SEM). The EDS technique detects x-rays emitted from the sample during bombardment by an electron beam to characterize the elemental composition of the analyzed volume. Features or phases as small as 1µm or smaller can be analyzed (Larry and Hanke, 2001).

3.6.2 Fourier Transform-Infrared Spectroscopy

Fourier Transform-Infrared Spectroscopy (FTIR) is an analytical method used to identify organic (and in some cases inorganic) materials. This method measures the absorption of infrared radiation by the sample material versus wavelength. The infrared absorption bands identify molecular components and structures.

When a material is irradiated with infrared radiation, absorbed IR radiation generally excites molecules into a higher vibrational state. The wavelength of light absorbed by a specific molecule is a function of the energy difference between the at-rest and excited vibrational states. The wavelengths which are absorbed by the sample are characteristic of its molecular structure.

The FTIR spectrometer uses an interferometer to modulate the wavelength from a broad band infrared source. A detector measures the strength of transmitted or reflected light as a function of its wavelength. The signal obtained from the detector is an interferogram, which must be analyzed with a computer using Fourier transforms to achieve a single-beam infrared spectrum. The FTIR spectra are generally presented as plots of strength versus wave number (in cm^{-1}). Wave number is the reciprocal of the wavelength. The strength can be plotted as the percentage of light transmittance or absorbance at each wave number.

To detect the material being analyzed, the unknown IR absorption spectrum is compared with standard spectra in computer databases or with a spectrum obtained from a known material. Spectrum matches detect the polymer or other constituent(s) in the sample. Absorption bands in the range of 4000 - 1500 wave numbers are typically because of functional groups (e.g., -OH, C=O, N-H, CH_3, etc.). The region from 1500-400 wave numbers is referred to as the fingerprint region. Absorption bands in this region are usually due to intramolecular phenomena and are highly specific to each material. The specificity of these bands allows computerized data searches within reference libraries to detect a material (Larry and Hanke, 2001).

3.6.3 X-ray Diffraction

X-ray diffraction depends on the dual wave/particle nature of X-rays to get information about the structure of crystalline materials. A most important use of the technique is the identification and characterization of compounds based on their diffraction model.

The main effect that occurs when an incident beam of monochromatic X-rays interacts with a target material is scattering of those X-rays from atoms within the target material. In materials with usual structure (i.e. crystalline), the scattered X-rays undergo constructive and destructive interference. This is the process of diffraction. The diffraction of X-rays by crystals is explained by Bragg’s Law, $n\lambda=2d \sin\theta$. The directions of possible diffractions depend on the size and shape of the unit cell of material. The intensities of the diffracted waves depend on kind and arrangement of atoms in the crystal structure. Nevertheless, most materials are not single crystals, but are composed of many tiny crystallites in all possible orientations called a polycrystalline aggregate or powder. While a powder with randomly oriented crystallites is placed in an X-ray beam, the beam can see all possible interatomic planes. If the experimental angle is systematically changed, all possible diffraction peaks from the powder can be identified (Orkide, 2009).

Powder diffraction (XRD) is a method used to characterize the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered (Wikipedia, n.d.).

3.7 Comparison between Electrocoagulation and Chemical Coagulation

Chemical coagulation and electrocoagulation have the phenomenon where the charged particles in colloidal suspension are neutralized by mutual collision with metallic hydroxide ions and are agglomerated, followed by sedimentation or flotation. The main difference between electrocoagulation and chemical coagulation is in the way of which aluminum or iron ions delivered.

Electrocoagulation process contains generating metallic hydroxide flocs within the water by electro-dissolution of the soluble anodes, generally made of iron or aluminum. In chemical coagulation, hydrolyzing metal salts, based on aluminum or iron, e.g., aluminum and ferric sulfates and chlorides, are usually used as coagulants in water treatment. There are some advantages of EC, when it is compared with chemical coagulation(Comninellis et al., 2010), thus if EC can replace conventional chemical coagulation, very little modification is required to make the present treatment plants more efficient and resolve the many problems caused by chemical coagulation (Emamjomeh et al., 2009), which are as follows:

1. In the chemical coagulation process, the hydrolysis of the metal salts will cause pH decrease and it is always needed to arrange the effluent pH. The chemical coagulation is highly sensitive to pH change and effective coagulation is achieved at pH 6-7. Whereas in the electrocoagulation, the pH neutralization effect made it effective in a much wide pH range (4-9).

2. Flocs formed by EC are like chemical floc. But, EC floc tends to be much larger, contains less bound water, is acid resistant, is more stable and is easily filterable. In the chemical coagulation process, it is always followed by sedimentation and filtration. Whereas in the electrocoagulation process, it can be followed by sedimentation or flotation. The gas bubbles generated during electrolysis can carry the pollutant to the top of the solution where it can be more easily concentrated, and removed.

3. Sludge formed by EC tends to be readily settable and easy to de-water, since it composed of mainly metallic oxides/hydroxides that

pass the leachability tests. Especially, it is a low-sludge producing technique. EC sludge disposal costs are lower (lower volume, and non-hazardous nature of the sludge) and EC sludge can be used as a soil additive. EC produces an environmentally friendly sludge in the 6 to 7 pH range.

4. Use of chemical is not necessary in EC process. Therefore, it does not need to neutralize excess chemicals, and secondary pollution caused by chemical substances that are added can be avoided.

5. The EC has no temperature effect; can operate over a wide range of temperature, EC process has the advantage of treating the water with low temperature and low turbidity. In this case, the chemical coagulation has difficulty in achieving a satisfying result.

6. EC requires simple equipment and easy to be operated. EC has minimal setup; turn on the switch and small space requirement. Maybe most important, electrocoagulation can precipitate out large quantities of different contaminants in one operation.

7. EC requires no chemicals, requires no toxic chemical safety requirements, kills virus and cysts and coliform bacteria, and provides better removal capabilities for the same species which chemical coagulation can remove, removes many species which chemical coagulation cannot remove, produces cleaner water, and has no moving parts.

The disadvantages of EC are follows. (1) The “sacrificial electrodes” are dissolved into water due to oxidation, and require be regularly replaced. (2) The passivation of electrodes over time has limited its implementation. (3) The use of electricity can be expensive in many places (Comninellis et al., 2010).

3.8 Filtration

Filtration is usually the mechanical or physical operation which is used for the separation of solids from fluids (liquids or gases) by interposing a medium through which only the fluid can pass. Oversize solids in the fluid are retained, but the separation is not complete; solids can be contaminated with some fluid and filtrate can contain fine particles (depending on the pore size and filter thickness) (Wikipedia, n.d.).

Generally a filtration process is used to remove the flocs which occurs during the electrocoagulation. Different type of filters can be used for filtration following the EC process. Wan (2010), Parga J. R. & et al. (2005), Kobya M. and et al. (2011), Addy (2008) used respectively candle filter, cellulose filter paper, a 45 µm membrane, vacuum filter following the EC processes processes.

The sand filter can be also used after the EC process. The sand filter process allows the take off the water all suspended solids which cause the turbidity of water, like sludge, mud; this process is used to filter water from well waters or from surfaces sources.

The process simply consists of the flowing of the water through several layer of selected quartz sand (or other inert materials), with different grain-sizes, and a layer of anthracite (dual media or multi-media filter).

Usually the water flows from the top to the bottom of the filter and solids retained by the first layer of sand improves the action of the following ones.

The better results in filtration are obtained when the suspended solids in flocculated form; in many cases addiction of flocculating agent to water is required upstream of the filtration through the bed of sand (NOBEL, n.d.). In electrocoagulation systems, to form large and dense flocs, either salt or polyelectrolyte can be added (NOBEL, (n.d.).

CHAPTER FOUR
MATERIALS AND METHODS

4.1 Arsenic Removal by Electrocoagulation and Filtration

In this study, EC process followed by filtration was investigated as an alternative technology for arsenic removal from drinking waters. EC was carried out in different operating conditions, with iron electrodes in monopolar-parallel (MP-P) connection .

4.1.1 Reagents

In this study, two different types of water; tap and groundwater was used. Physical and chemical composition of waters is shown in the following tables.

The stock solution was prepared by using the sodium arsenate ($Na_2HAsO_4.7H_2O$) as As(V) source (purchased from Sigma) and synthetic contaminated tap water of 2 mg/L concentration was spiked with As(V). This stock arsenic solution was used in the experiments after diluted until desired concentration. The characterization of tap water used for experiments is given in Table 4.1.

Table 4.1 Characterization of tap water used for experiments.

Components	**Concentration**
pH	8.2
Turbidity, NTU	0.1
Chloride, mg/L	46
Nitrate, mg/L	3
Iron, mg/L	0.0343
Aluminum, mg/L	0.012
Manganese, mg/L	0.0141
Sodium, mg/L	23
Conductivity, $\mu S\ cm^{-1}$	463
Sulfate, mg/L	36

To investigate the effect of oxidation state on arsenic removal, a groundwater sample taken from Sasali region in Izmir was used. Characterization of ground water is shown in Table 4.2.

Table 4.2 Characterization of Sasali groundwater used for experiment.

Components	**Concentration**
Arsenic (As(III)), µg/L	951
pH	8.2
Turbidity, NTU	-
Nitrate, mg/L	0.005
Iron, mg/L	0.011
Aluminum, mg/L	0.001
Manganese, mg/L	0.018
Sodium, mg/L	307.1
Conductivity, µS/cm	1219
Sulfate, mg/L	90.34
Phosphate, mg/L	0.284
Vanadium, mg/L	0.023
Calcium, mg/L	4.405
Magnesium, mg/L	6.219
Hardness, mg$CaCO_3$/L	5.29

The pHs of solutions were adjusted by adding aliquots of 1M HCl or 1M NaOH and they were kept nearly constant in the range of 6 - 8, the pH indicator used the control of pH as it given in Figure 4.1.

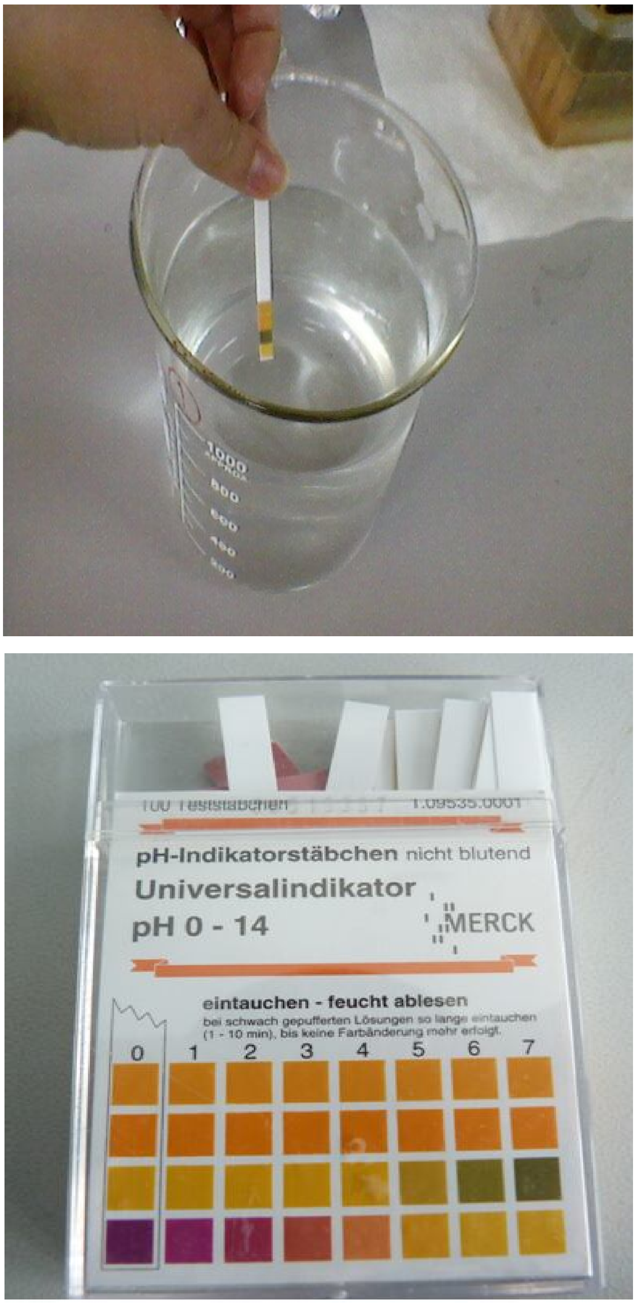


Figure 4.1 pH indicator was used for adjusting the pH of the As-containing solutions.

All experiments were carried out at ambient temperature (25°C). To investigate the effect of salt on arsenic removal, 0.01M NaCl (0.58 g/L and 1400 µmhos) and 0.02M NaCl (1.16 g/L and 2500 µmhos) were added into the solutions below the standard values given as 2500 µmhos/cm in Turkish Standard for drinking waters (Turkish Standards 2005).

4.1.2 Electrocoagulation Reactor

The eletrocoagulation setup which has a volume of 2 L was used in the experiments (Figure 4.2). Inside the EC reactor, six iron plates were placed 1.2 cm apart from each other. The plates have a width of 0.3 cm, a length of 19 cm and a depth of 3.5 cm (Figure 4.3). The total submerged surface area of each electrode was 66.5 cm^2. After each experiment, the electrodes were regularly cleaned with sand paper and then with pure water to remove the fouling scales.

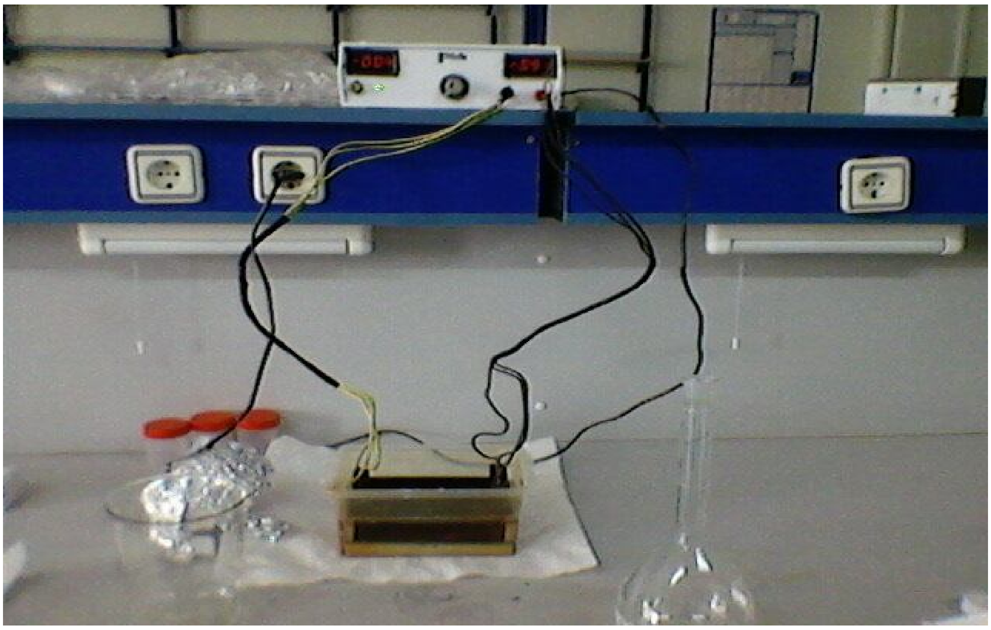


Figure 4.2 The electrocoagulation setup which was used in this study.

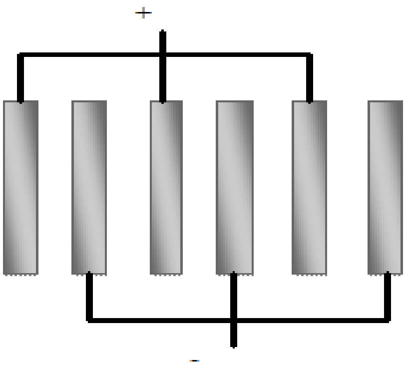


Figure 4.3 Monopolar parallel connections (Moreno, H., 2007).

A direct current (DC) by stabilized with a power supply (0 - 9.2V) was applied to the iron electrodes, which were placed horizontal, in monopolar and parallel connections (Figure 4.4). In monopolar-paralell connection which is shown in Figure 4.3; the electric current is divided between all the electrodes in relation to the resistance of the individual cells (Mollah, 2001). This cell arrangement provides a simple set-up, which facilitates easy maintenance during the use.

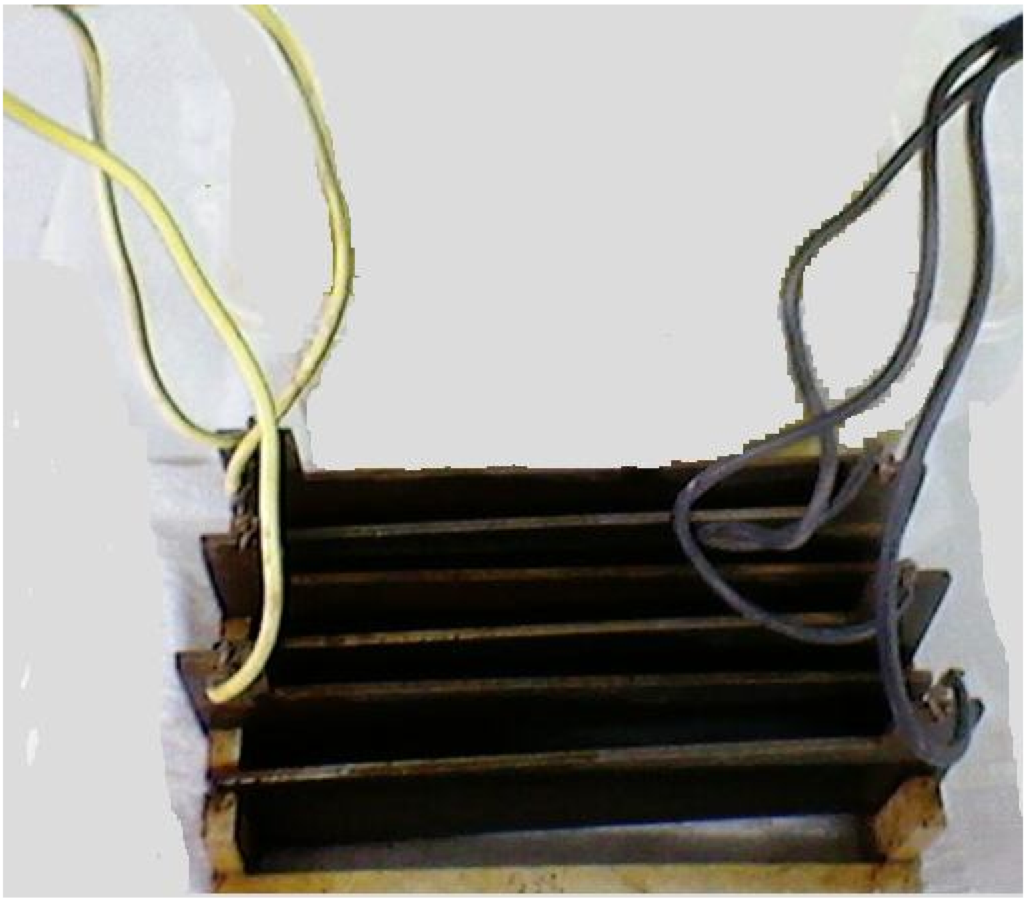


Figure 4.4 The arrangement of the electrodes in monopolar and parallel connections.

4.1.3 Filtration Process

The classical sand filter containing quartz sand particles which has 0.2 mm particle size (Figure 4.5) was used in this study. Thus, the residual particles in the EC effluent water trapped between these sand particles and separated from the water.

Figure 4.5 Quartz sand was used in the filtration process.

In the experiments, after the EC process, 30 min was waited for precipitation of flocs and then filtration process was started. The filtration rate of water in the quartz sand filter was adjusted to a flow rate of 7 ml/min. In addition, an aquarium pump through an air diffuser (air stone) (Figure 4.6)was used during the filtration process as shown in Figure 4.7, to provide oxidation of Fe^{2+} species, which were generated by EC process to Fe^{3+} species and remove by achieving the iron standard value which is given as 300 µg/L by USEPA.

Figure 4.6 The aquarium pump and the air diffuser (air stone).

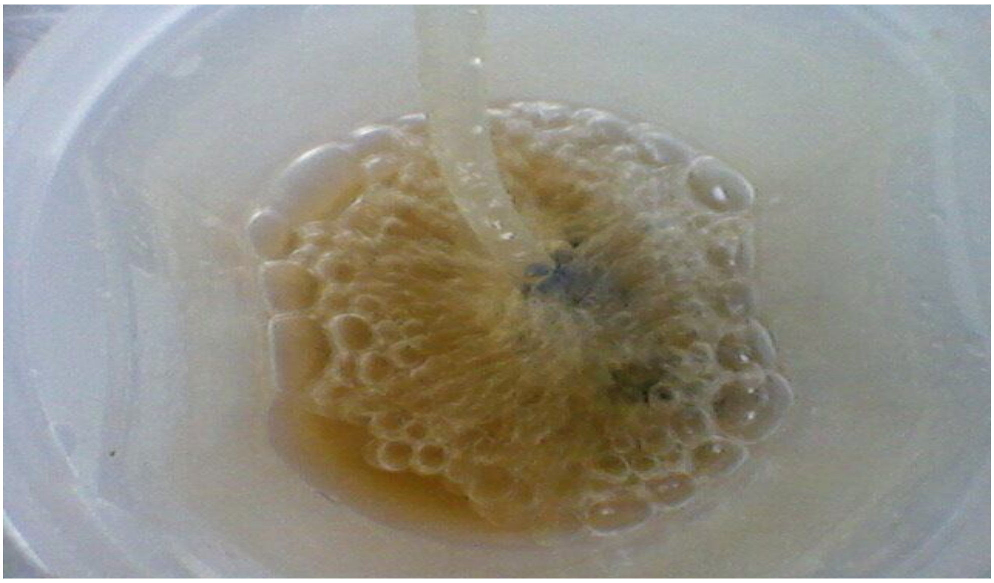


Figure 4.7 The air injection with the aquarium pump through air diffuser (air stone) in the filtration process.

Figure 4.8 Filtration of flocs after EC process.

200 ml solution was taken from the 1L EC beaker for filtration of flocs generated by EC process. The water passed through the sand from top to bottom. The flocs were left behind in the top layers of quartz sand and the clean water which passed

through the filter (Figure 4.8). And then 50 ml sample was taken for analysis. At the end of this process sand filter was washed with pure water of 7 L.

4.1.4 Analytical Methods

Developing highly sensitive methods is necessary for determination of inorganic arsenic species in different matrixes. The most popular method for determination of inorganic arsenic species is hydride generation (HG).

In environmental samples, this hydride generation method has been used with inductively coupled plasma optical emission spectrometry (ICP-OES), since 1978. More recently USEPA has been developing this method and combined it with a continuous flow system.

The continuous flow hydride generator, introduced recently, offers the advantages of simplicity in operation, excellent reproducibility, low detection limits, and high sample volume throughput for inorganic arsenic analysis. This method is applicable to determination of arsenic by conversion to arsine gas by sodium borohydride reduction and transported into plasma of ICP-OES for analysis.

Arsenite, As(III) oxidation state is instantaneously converted by sodium borohydride in acid solution to arsine. The arsine is purged continuously by argon into plasma of ICP-OES and converted to gas-phase atom. Arsenate, As(V) oxidation state of arsenic reduced relatively slowly by sodium borohydride to As(III), which is then immediately converted to arsine. The arsine atoms emission peaks generally are decreased by one-fourth to one-third for As(V) when compared to As(III). Determination of total arsenic requires that all inorganic arsenic compounds be in the As(III) state. Organic and inorganic forms of arsenic are first oxidized to As(V) by acid digestion. The As(V) is quantitatively reduced to As(III) with sodium or potassium iodine before reaction with sodium borohydride.

The hydride generation technique is used for the separation of the analyte arsenic from the matrix by conversion to its volatile hydride called arsine (AsH_3). This technique offers a route to the trace analysis of several important arsenic species that specific problem when analyzed by conventional methods. Conventional methods of ICP-EAS for arsenic determination are poor because of problems associated with concentration by the sample matrix. HG-ICP-OES is an alternative method for arsenic analysis due to its sensivity (Muakthong, 2006).

After the electrocoagulation and filtration process, the filtered and acid-treated samples (50 ml samples were taken and 0.75 ml HCl was added) analyzed for the total concentration of As and Fe by ICP-OES. These analyses were carried out by IZCEV Environment laboratories in Izmir.

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 Arsenic Removal and Production of Iron Coagulants by Electrocoagulation

The main objective of this study was to provide maximum efficiency and minimum energy (low-cost) and shorter time consumption for arsenic removal by EC process. Because of this, the effects of initial arsenic concentration, residence time, current density, presence of salt, electrode surface area and arsenic oxidation state were investigated and compared with the previous studies. The standard values which have to comply is given in Table 5.1.

Table 5.1 Standard values for drinking waters.

Components	**USEPA**	**WHO**	**TSE**
Arsenic (µg/L) (MCL)	10	10	10
Iron (µg/L)	300	-	200
Conductivity (µmhos)	-	-	2500

5.1.1 Effect of Initial Arsenic Concentration

The EC experiments were carried out with different initial arsenic concentrations; 50 µg/L, 200 µg/L, 350 µg/L, 500 µg/L for evaluating the effect of initial arsenic concentration at pH 6 - 8, in 5 min at 0.3 A (4.5 mA/cm^2). At the end of the 5 min, 200 ml solution was taken from the EC reactor for filtration of flocs generated during EC process. It was filtrated using quartz sand filter. This process was repeated for each initial arsenic concentration.

For the first 5 min., the relation between arsenic removal and residual arsenic concentration is given in Figure 5.1.

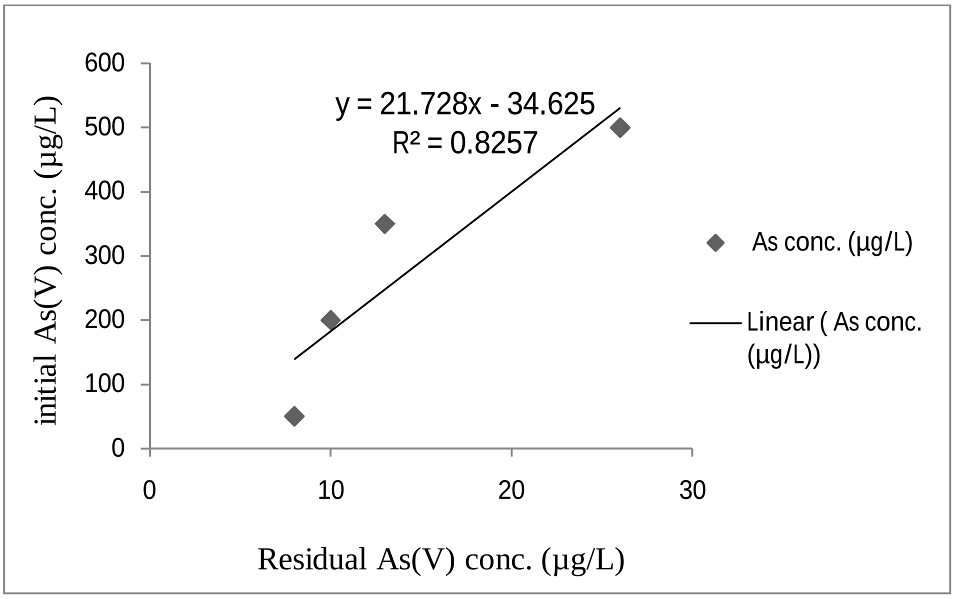


Figure 5.1 The correlation between the residual and initial As(V) concentration.

As it seen from Figure 5.1, there is high positive correlation (R^2=0.8257) between initial As(V) concentrations and the residual As(V) concentrations for the first 5 min. in the EC process with a current density of 4.5 mA/cm^2.

On the other hand, Wan, W., 2010 reported that the final arsenic removal efficiencies to achieve the standard limit values were independent from initial arsenic concentration when he studied with air injected EC setup, which is followed by candle filter, a long period of 120 min., at 2A air injected EC system.

The MCL (Maximum contamination level for arsenic; USEPA 2001) was not achieved for the solutions which contain high initial As concentration and iron concentrations in the solutions increased over than the standard values (USEPA = 300 µg/L and TS266= 200µg/L) for drinking waters occurred in the effluent water (Figure 5.2).

Bazrafshan et al (2006) , who studied with 5 - 500 mg/L initial conc. and in the range of pH (3 – 10) reported at lower concentrations, the removal efficiency was almost complete at all pH values whereas, at high concentration, however, the complete removal might require longer time.

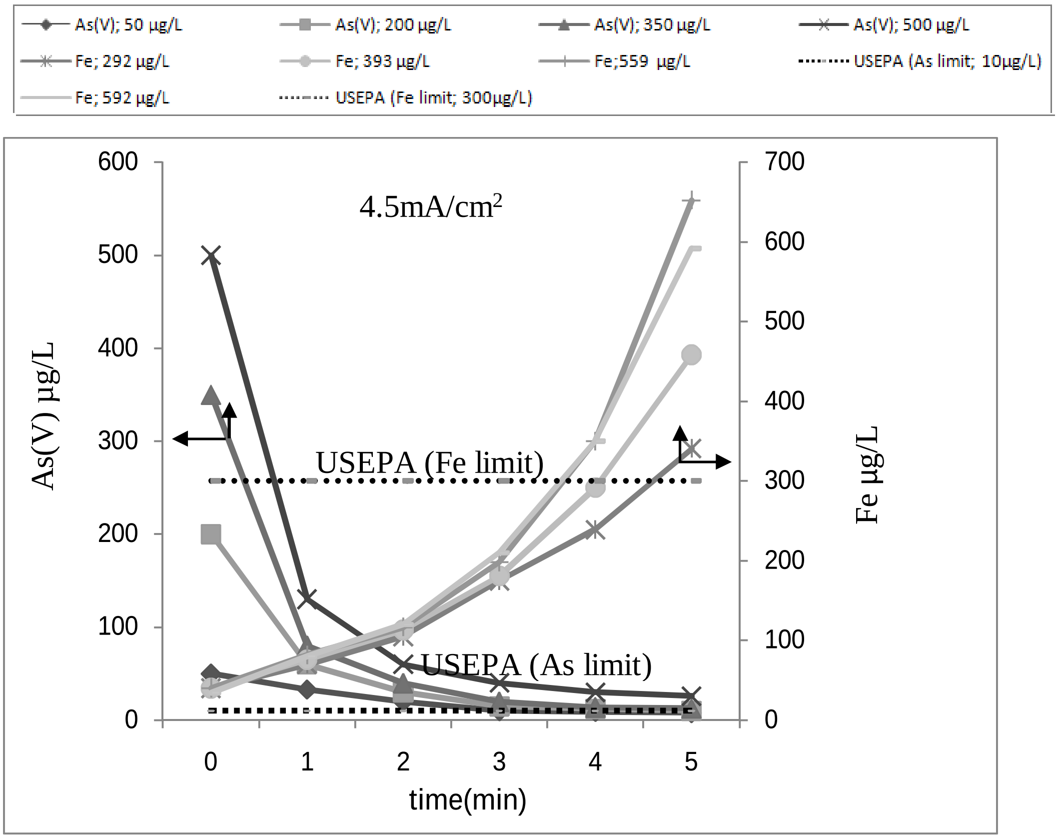


Figure.5.2 Effect of initial arsenic concentration on the arsenic removal and total iron conc. (t_{EC}: 5 min, I: 0.3 A (4.5 mA/cm^2), pH: 6 - 8**).**

As Bazrafshan et al (2006) metioned the high initial arsenic concentration is required more time to obtain enough iron coagulant formation. Since As (V) co-precipitate with or adsorps to $Fe(OH)_n$ and removed. Otherwise, the ferrous ions (Fe^{2+}) passing through filter can remain in the effluent water, resulting in secondary contamination as seen in these experiments (Figure 5.2). Therefore, the amount of iron coagulant formed; in addition other factors such as presence of silica and changing in the pH values of water can be affect arsenic removal efficiencies in the EC as predicted by the literature.

Similarly Lakshmanan et al. (2011) reported that the electrolytic oxidation of iron rod (Fe^0) at the anode resulted in the generation of ferrous ions (Fe^{2+}), while the electrolytic reduction of water resulted in the production of hydrogen gas at the cathode and the electrolytic reduction of water at the cathode also resulted in the formation of hydroxides, which were consumed by the protons resulting from hydrolysis of Fe^{2+} and Fe^{3+} ions (produced by subsequent oxidation of Fe^{2+} by DO depending on pH) to form Fe hydroxide complexes. And also he reported the ferrous ions/hydroxides (Fe^{2+}) remaining decreased with increasing pH. He observed,. during electrolysis, a significant increase in pH from the initial pH which was due to the continuous production of hydroxide ions and the slow formation of Fe hydroxide complexes.

Figure 5.3 The EC effluent water in yellowish color.

At the end of the EC part of the experiments, yellowish effluent water was observed shown as Figure 5.3 Depending on pH changing, this situation was explained by Moreno (2007) with these possible reactions ($5<pH<7$);

Anode:

$$Fe(H_2O)_3(OH)_{3(aq)} \rightarrow Fe(H_2O)_3(OH)_{3(s)} \qquad (5.1)$$

Cathode:

$$2H^+ + 2e^- \rightarrow H_{2(g)}\uparrow \qquad (5.2)$$

More hydrogen evolution and Fe(III) hydroxide begin to precipitate floc with yellowish color. Formation of rust (Moreno-Casillas, H. A., et al., 2007):

$$2Fe(H_2O)_3(OH)_3 \leftrightarrow Fe_2O_3(H_2O)_6 \quad (5.3)$$

Consequently, agreed with Moreno (2007) and Lakshmanan et al. (2011), because of the pH change during the EC and as a result of this slow iron hydroxides/oxyhydroxides formed to adsorb and co-precipitate As(V), yellowish color of rust formation was observed in this study for 5min of residence time.

5.2.2 Effect of Residence time

Residence time is a significant parameter for EC process which is operated at a constant current. Because reported that faster removal decreased the contact time between coagulant and contaminant particles decreasing the coagulant efficiency (Holt, 2006).

When studied with high initial arsenic concentration, more residence time was required revising standard value was given as 10 µg/L. Therefore, the effect of residence time on arsenic removal and residual iron concentration was investigated in this study.

To investigate the effect of residence time, the EC process was conducted in 0-15min time range and with 100 µg/L initial arsenic concentration (As(V)) , at pH 6-8, and at 0.3A. At the end of the EC process, 200 ml solution was taken from the EC beaker for the filtration of flocs generated during EC process. 30 min. was waited before the filtration. An aquarium pump added into filtration; try to avoid soluble Fe^{2+} species passing through filter, causing secondary contamination. This process was repeated at the end of every 2min.

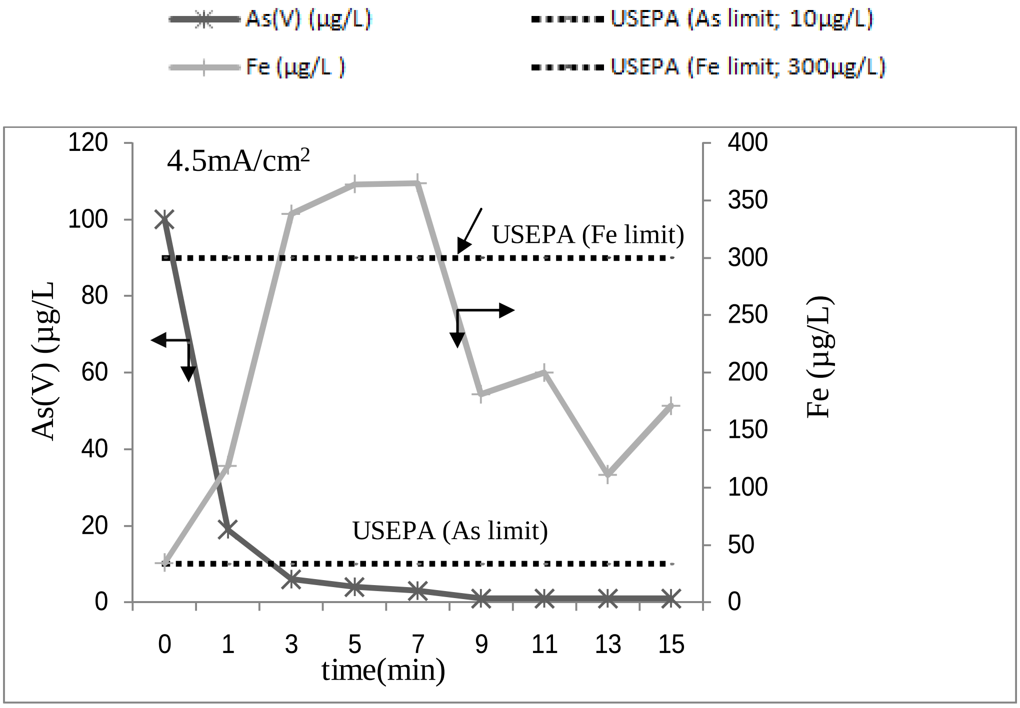


Figure 5.4 Effect of residence time on arsenic removal and total iron conc. (Ci: 100 µg/L, I: 3 A (4.5 mA/ cm^2), pH 6 - 8, air pump used in filtration part).

As Holt, (2006) mentioned, when the residence time increased, formation of the iron hydroxide increased and more As (V) removal occurred (Figure 5. 4). The arsenic removal completed at the end of the 9 min and MCL (WHO and USEPA; 10µg/L) in drinking waters was achieved with 99% arsenic removal. As to final iron concentration, with increase of the residence time more floc formation was obtained and therefore, total iron concentration started to decrease after a while (in 7 min). Moreover during the filtration process with the injection of air, residual Fe^{2+} was oxidized to Fe^{3+} and removed. In this way, the standard iron values for drinking water (TS 266= 200µg/L and USEPA =300µg/L) was achieved.

5.2.3 Effect of Current

Current determines coagulant dosage, bubble production rate, which has important effect of pollutant removal and mass transfer at the electrodes. Generation and production of coagulant and bubbles is determined by the electrochemical behavior of anode and cathode. Iron generation capacity based on Fe^{2+} production at the anodes.

To determine the current efficiency, the amount of iron generation was calculated using Faraday`s law:

$$m = \frac{I \times t \times MW}{Z \times F} \tag{5.4}$$

In the Equation 5.4; m is the mass in the grams of Fe generated at a specific current (I, amperes) over a time interval (t, sec), Z number of electrons transferred per Fe atom (eq/mol), MW is the molecular weight (55.85g/mol), and F is Faraday`s constant (96.485 C/eq).

To investigate effect of current on arsenic removal during the EC process, experiments were conducted with 100µg/L As(V) concentration at pH 6-8, in 5min, EC process was operated at different current values (0.1-0.6A; 1.5-9 mA/cm^2). After the EC process 200ml solution was taken for aeration and filtration process.

Kumar et al. (2004) and Parga et al. (2005) (3.7-4.6mA/ cm^2) reported there was no significant effect of current density in the range of 0.65-1.53 mA/cm^2 and 3.7-4.6mA/ cm^2 respectively. On the other hand, Addy (2008) reported that in the range of 0.07-1.1 mA/cm^2 current density had some effect on arsenic removal capacity due to a change in iron hydroxides composition in EC. Kobya et. al (2011) reported that rapid arsenic removal was achieved at higher current densities (≤1,75 A/m^2) with the coprecipitation and adsorption on the metal hydroxide particles of arsenic ions in short residence times.

In this study, the standard value for arsenic for arsenic is given by USEPA was obtained in applied current of 0.3A and current density of 4.5 mA/cm^2.. Furthermore, arsenic removal of 99% efficiency was achieved at 0.6A current and 9 mA/cm^2 current density. Also the residual iron concentration was less then the standard 300 µg/L given by USEPA (Figure 5.5). As Kobya (2006) mentioned rapid arsenic removal was occured The reason of high arsenic removal efficiency could be explained with the increasing of the coagulant and bubble generation rate by the increasing current effect.

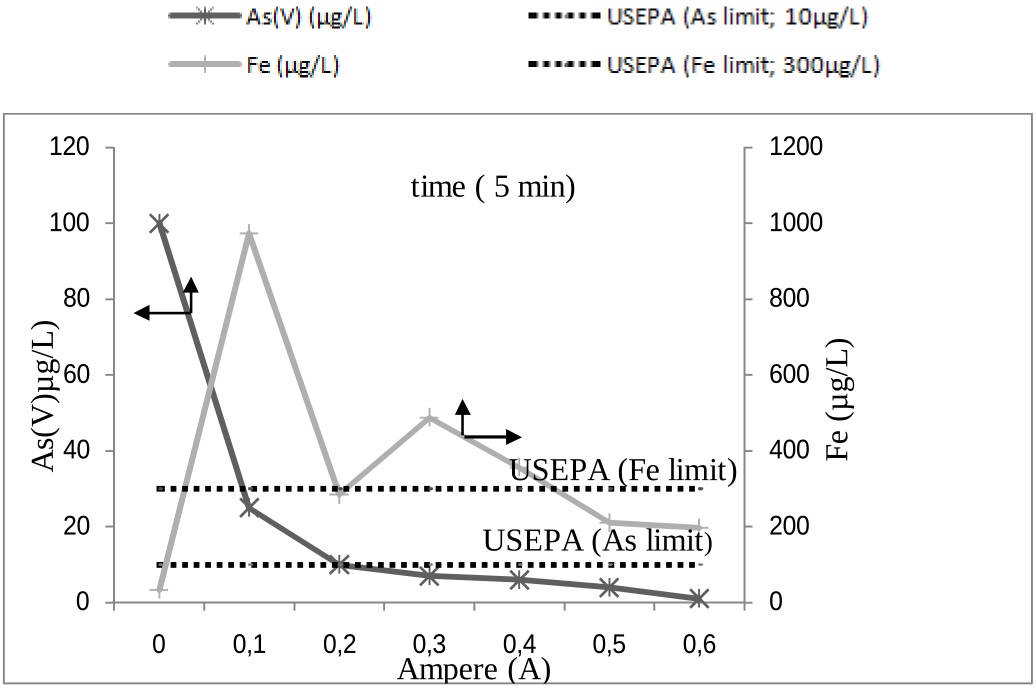


Figure 5.5 Effect of ampere on arsenic removal and total iron conc. (CD=1.5 - 9 mA/ cm^2, Ci=100µg/L, t_{EC}: 5 min, pH 6 - 8 and an aquarium pump used in the filtration part.

Hansen et al. (2007) reported that the passivation of in the EC systems due to high current densities and high concentrations of Fe^{2+}, Fe^{3+} and OH- ions at anode. On the other hand, Lakshmanan et al. (2011) reported that during electrolysis under open atmospheric conditions, the percentage Fe^{2+} remaining decreased with increase in current as shown Figure 5.5 and the significance increased with increase in pH.

Therefore, by calculating theoretical iron amount, optimum currents can be estimated. In Figure 5.14, theoretical iron generations versus to current in the range of 0.1 - 0.6 A is given Figure 5.6.

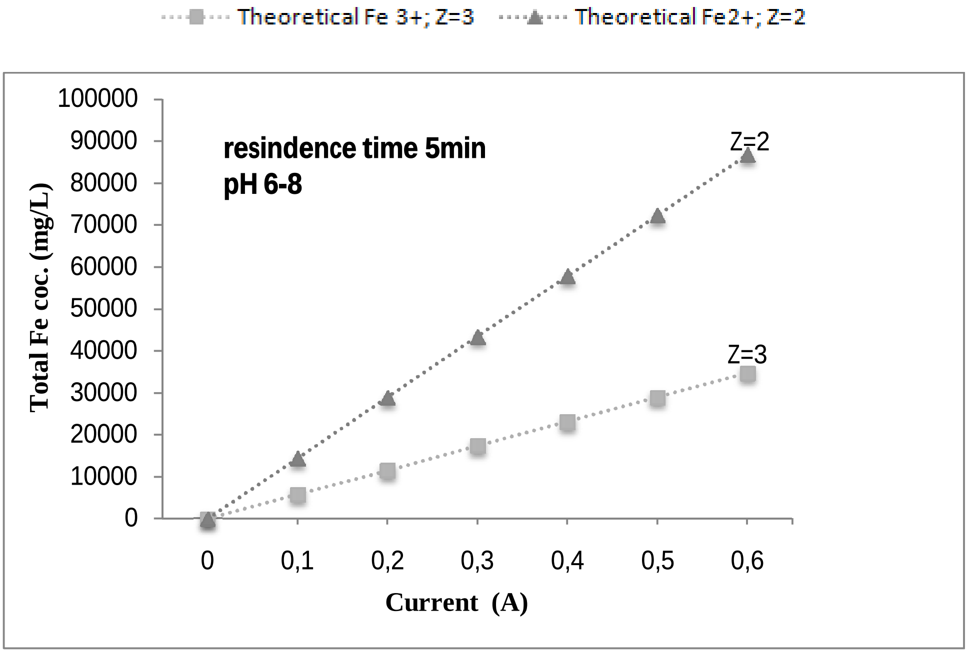


Figure 5.6 Theoretical iron generation for number of electrons transferred per atom of two and three (Z= 2 and Z= 3) based on Faraday`s law for applied currents of 0.1 - 0.6 A at pH6 - 8 in 5 min.

According to Faraday`s law (Equation 5.4), the mass of iron generated while ferrous ion generation; Z= 2 and ferric ion generation; Z= 3 at the anode is proportional to the current applied during electrocoagulation. It can be seen from the Figure 5.6 that the total iron generation would be 1.5 times higher if ferrous (Fe^{2+}) is generated at anode in comparison to ferric (Fe^{3+}) as Lakshmanan et al. (2011) reported for any particular residence time and current .

Lakshmanan (2007) also reported that the total mass of iron generated experimentally at pH 6.5 correlated with theoretical iron generation based on Fe^{2+}, Z=2 in Faraday`s law in the current range of 0.05 to 0.8 A.

The feasibility of treatment depends strongly on its energy requirement. Apart from the residence time, energy consumption is controlled by the applied ampere and voltage. The electrical energy required for the removal of arsenic is given in Equation 5.5.

$$E=\frac{U\times I\times\times t_{EC}}{V} \tag{5.5}$$

E= energy consumption kWh/m^3,

U= Volt (V),

I= ampere (A),

t_{EC}= resindence time (h),

V =volume of water in EC reactor (m^3) (Laue, O., et al., 2003).

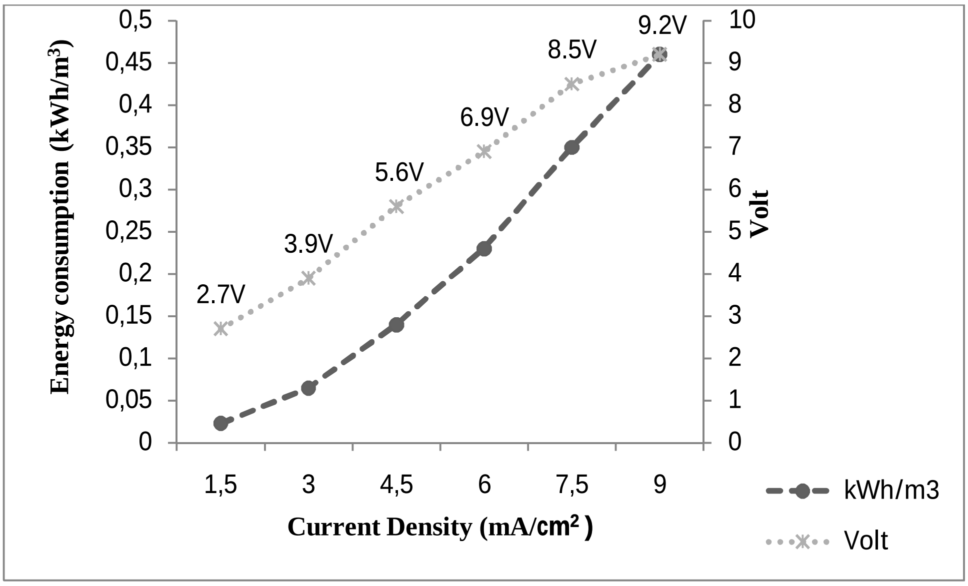


Figure 5.7 The energy consumption at various current densities for EC.

The energy consumptions versus increasing current density at different volt values for 5 min was shown in the Figure 5.7. Although arsenic removal efficiency increased with the increasing of applied ampere to the EC process (Figure 5.6), agreed with Bayramoglu et al. (2007), who reported by increasing either current density or voltage the energy consumption of EC process increased.

In addition, Kobya et al. (2011) reported that the major operating cost of EC was associated with electrical energy consumption during the process. And also he mentioned that the efficieny of EC enhanced by increasing current density and operating time, the cell voltage, energy consumption and operating costs increased.

5.2.4 Effect of Electrode Surface Area

Design of EC cell is important to achieve maximum arsenic removal efficiency. The surface area to volume ratio (S/V) is a significant scale-up parameter. The electrode area influences current density, position and rate of cation dosing, in addition to bubble production and bubble path length (Holt. et al., 2006).

In this study, different electrode surface areas were obtained by changing the electrode numbers. To investigate effect of the electrode surface area on arsenic removal, the EC process was operated with 100 µg/L initial As(V) concentration, in the range of pH 6-8, for 5 min, at a constant volt of 9.1 V, by different electrode numbers (n) as shown in Figure 5.8, Figure 5.9 and Figure 5.10. After the EC process 200 ml solution was taken for the filtration process. 30 min was waited before the filtration and during this process air was injected with the aquarium pump. This process was repeated for every electrode surface area which was obtained changing the electrode number (n= 6, n= 4, n= 2)

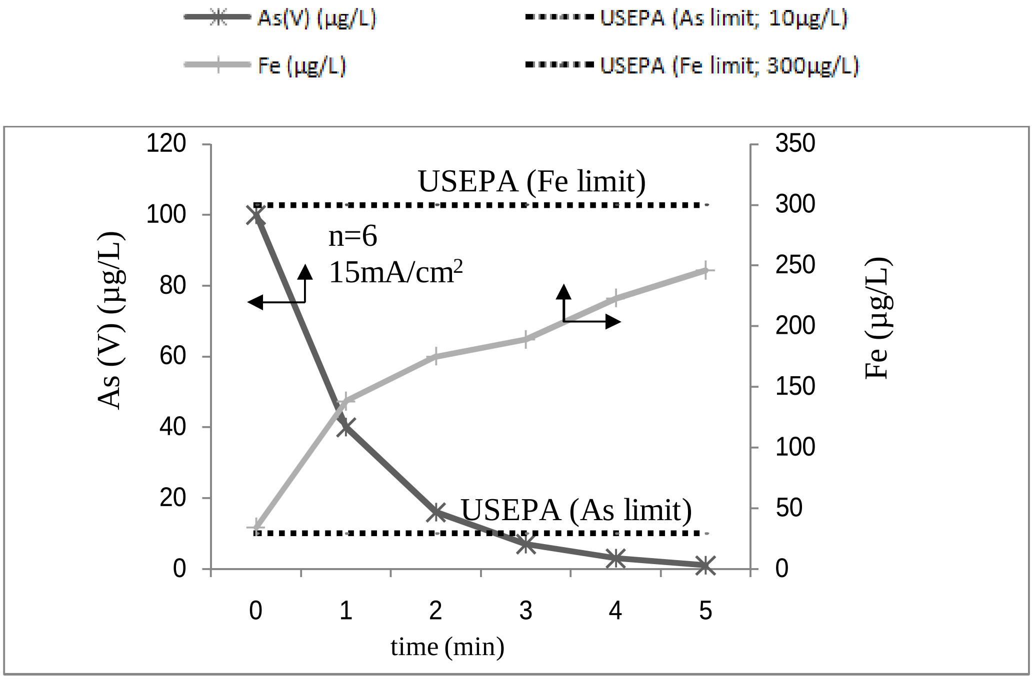


Figure 5.8 Effect of electrode numbers on arsenic removal and total iron concentration (n: electrode number = 6, Ci=100 µg/L, Volt: 9.1 V, t_{EC}: 5 min, pH:6 - 8 and an aquarium pomp used in the filtration part).

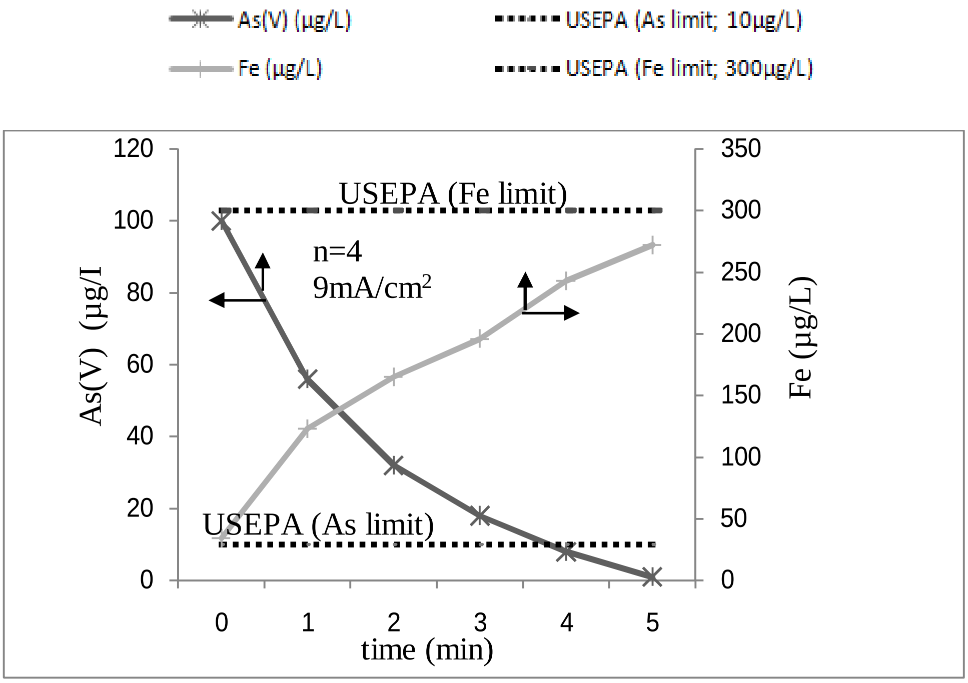


Figure 5.9 Effect of electrode numbers on arsenic removal and total iron concentration (n:electrode number; n= 4, Ci= 100 µg/L, Volt: 9.1 V, t_{EC}: 5 min, pH:6 - 8 and an aquarium pomp used in the filtration part).

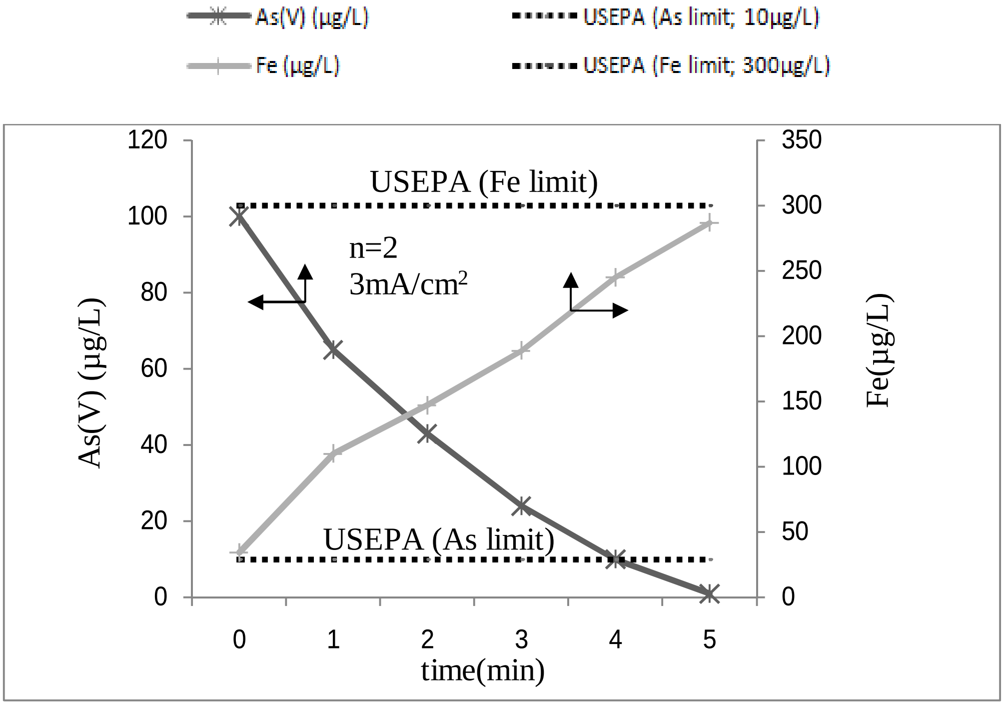


Figure 5.10 Effect of electrode numbers on arsenic removal and total iron concentration (n:electrode number; n= 2, Ci= 100 µg/L, Volt: 9.1 V, t_{EC}: 5 min, pH:6 - 8 and an aquarium pomp used in the filtration part).

It is obviously that faster removal occurred at the beginning of EC process by the effect of increasing current density for constant voltage (9.1V), which has greater electrode surface area(n= 6) **(**Figure 5.8) than the others (n= 4 > n= 2) (Figure 9 and Figure 10). Because the electrode surface area influenced the current density. The increase of the current density (15 mA/cm^2) provided faster removal at beginning. On the other hand, there was no significant effect observed on arsenic removal and for the every electrode surface area maximum arsenic removal efficiency as 99% and standard value for the arsenic given by USEPA was achieved.

Similarly, Charoenlarp and Choyphan (2009) also reported that the greater electrode area, the less effective was the water treatment. And this was explained that the increase of electrode area caused increase of coagulants. Due to the entire effectiveness of the coagulation process depended on the appropriate amount of coagulant, if there was too much or too little coagulant, it could render the coagulation process ineffective. Therefore, if the electrode area was increased, electrical potential and electrolysis time would be decreased (Charoenlarp and Choyphan , 2009). In addition, Mameri et al. (1998) and Holt (2006) reported that when S/V (surface area to volume) ratio increased the optimal current density decreased.

5.2.5 Effect of Presence of Salt on Arsenic Removal

Usually, NaCl is added in order to increase the electrolytic conductivity. The conductivity of the water is adjusted to the desired levels by adding an appropriate amount of NaCl. The presence of chloride ions can limit the formation and/or growth of the passivation layer. This was probably because the Cl^- anions can destroy the passivation layer and increases the anodic dissolution rate of metal, either by the incorporation of Cl^- into the oxide film or by the participation of Cl^- in the metal dissolution reaction. In addition, the increase of the chloride ion concentration in the solution can reduce the overpotential in the anodic oxidation of chloride ions, resulting in a higher current efficiency. The problem of electrode passivation is a serious drawback in the current application of EC process. Destroying the passivation layer and hence enhancing the dissolution rate of Fe is thus crucial. The de-passivation effect was more significant when more Cl^-anions were added to the solution. Therefore, the problem of electrode passivation was partially solved and the performance of the electrocoagulation process was increased when NaCl was used as the electrolyte (Chou et al, n.d.).

In this study, sodium chloride (NaCl) was used as the supporting electrolyte for increasing the conductivity. When investigating the supporting electrolyte’s influence on arsenic removal efficiency, series of experiments were carried out with different initial arsenic concentration and residence time as shown in Table 5.3. The pHs of solutions were adjusted in the range of 6-8, at 9V. 0.01M 0.58 g/L NaCl (1400 µmhos) and 0.02M 1.16 g/L NaCl 1.16 g/L (2500 µmhos) were added into the solutions. Because of Turkish Standard for conductivity of drinking water is given as 2500 µmhos/cm for drinking waters, the addition of NaCl was adjusted either less or equal than this limit value.

Ihos et al., (2005) added 0.01M NaCl as supporting electrolyte, Hansen. et al. (2007) added 10g of NaCl into As solution to increase electrical conductivity in the solution and to minimize the passivation of the anode and Gomes et al., (2007) added 0.8g NaCl into arsenic solution to avoid excessive ohmic drop and prevent the formation of the passivation layer on electrodes and Larue, (2003) and Chou et al (n.d.) reported the addition of chloride salts decreased the energy consumption due to solution conductivity affects the cell voltage and current efficiency. Furthermore, more energy is required for overcoming a high ohmic resistance between an anode and a cathode when electrical conductivity of the solution is low.

In addition, Bayramoglu et al. reported that increasing electrical conductivity caused an increase in the current density at constant cell voltage, or a decreased in the voltage at constant current density.

It is obviously that by adding NaCl, increasing of conductivity obtained. Therefore, an increase in current density was observed which was mentioned by Bayramoglu et al. (Table 5.2).

Table 5.2 The effect of salt on arsenic removal; 0.01M NaCl (1400µmhos, 0.58g/L), 0.02M (2500µmhos, 1.16g/L) was added into solutions which have different initial As(V) conc., Volt=9V, pH 6-8).

Salinity (µmhos)	**Time (min)**	**Initial As Conc. (µg/L)**	**Final As Conc. (µg/L)**	**Current Density (mA/cm^2)**	**Volt**	**Efficiency (%)**
1400 (0.58 g/L salt was added)	15	10	<1	4.8	9	90
1400 (0.58 g/L salt was added)	15	500	<1	4.5	9	99.8
463 (no salt addition;)	15	255	<1	3.3	9	99.6
463 (no salt addition)	9	10	2	1.35	9	80
1400 (0.58 g/L salt was added)	9	255	<1	6.3	9	99.6
463 (no salt addition)	9	500	<1	3.3	9	99.8
2500 (1.16g/L salt was added)	9	500	<1	8.4	9	99.8
1400 (0.58 g/L salt was added)	3	500	<1	6.9	9	99.8
2500 (1.16g/L salt was added)	3	255	<1	4.5	9	99.6
1400 (0.58 g/L salt was added)	3	10	<1	4.5	9	90

It can be seen from the Table 5.3, the addition of salt (NaCl) had no significant effect on residual arsenic concentration. The standard value for the arsenic in drinking water given by WHO and USEPA was achieved at the end of in every experiment.

One of the factors often used to visually determine the success of metals removal with EC is the formation of a dark green floc. Hydrogen formation continues and precipitation of iron hydroxide occurs presenting a dark green floc (6<pH<8) (Moreno, 2007) as shown in Figure 5.11 and Figure 5.12.

Figure 5.11 With the addition of NaCl into the As(V) solution formation of dark green flocs were observed in the EC.

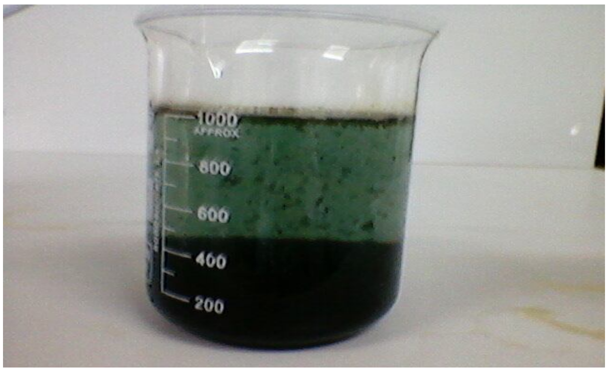


Figure 5.12 30 min. was waited for precipitation of flocs before the filtration.

In the solution by the addition of salt, dark green flocs (Figure 5.11), which show success of EC process according to Moreno (2007), was observed.

5.2.6 The Removal Efficiency of Arsenic from Groundwater by EC process

In this study, real groundwater was used, which was taken from Sasali region in Izmir. Physical and chemical composition of the groundwater was shown in the Table 5.2.

The pH of the solution was adjusted in the range of 6-8. Experiment was carried out at 0.3A, in 5min. After the EC process 200 ml solution was taken for filtration process. During the filtration process air was injected with the aquarium pump and 30 min was waited before filtration process to provide precipitation of them.

As theoretical Moreno-Casillas (2007) explained that As(III) (arsenite) removal by EC process like following:

As(III) is first oxidized to As(V) in the EC process. While using iron electrodes Fe(III) reduces to Fe(II) and As(III) oxidizes to As(V). If As(III) is present, the species H_3AsO_3 and to minor degree $H_2AsO_3^-$ (pK1=9.20) are dominant. Since H_3AsO_3 is neutral, it is not attracted by anode or the cathode. It is carried by electrophoretic current established within the reactor, while $H_2AsO_3^-$ is attracted to the anode. In both cases, arsenic species will close to $Fe(OH)_2^{+1}$. In EC process, As(III) is oxidized to As(V), precipitated and removed as iron arsenate. The following reactions can occur during the EC process:

$$3Fe(OH)_2^{+1} + H_3AsO_3 \rightarrow FeAsO_4 + 2Fe(OH)_{2(aq)} + H_2O + 3H^+ \qquad (5.6)$$

$$3Fe(OH)_2^{+1} + H_2AsO_3^{-1} \rightarrow FeAsO_4 + 2Fe(OH)_{2(aq)} + H_2O + 2H^+ \qquad (5.7)$$

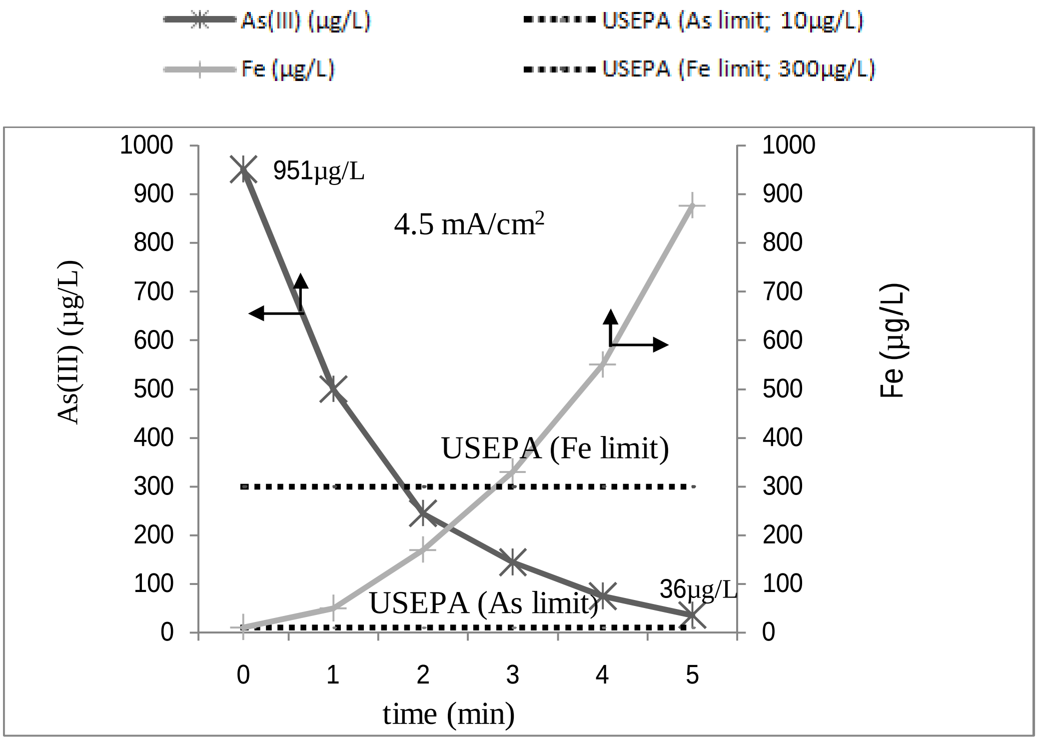


Figure 5.13 As(III) removal from Sasali groundwater and total iron conc at the end of EC - Filtration (t_{EC}: 5 min, I: 0.3A (4.5mA/ cm^2), pH6-8, an aquarium pomp used in the filtration part).

As seen in Figure 5.13, 96% arsenic removal efficiency was obtained but the standard value given by USEPA for arsenic in the residence time of 5 min. was not achieved. Because, more residence time was required to complete oxidation As(III) to As(V) and to achieve standard value. Also Wan W. (2010) reported that As(V) removal was faster than As(III) removal due to the oxidation of As(III) to As(V) increased with the residence time.

In the same way, Lakshmanan, (2011) who compared the As(III) and As(V) adsorption capacities for EC–F and C–F for an equilibrium concentration of 10 μg/L as a function of pH, also found that the As(V) adsorption capacities were much higher than the As(III) adsorption capacities for both processes, which reinforced idea that As(III) must be oxidized to As(V) prior to treatment using iron oxides/hydroxides for sorption regardless of the source of these iron oxides hydroxides.

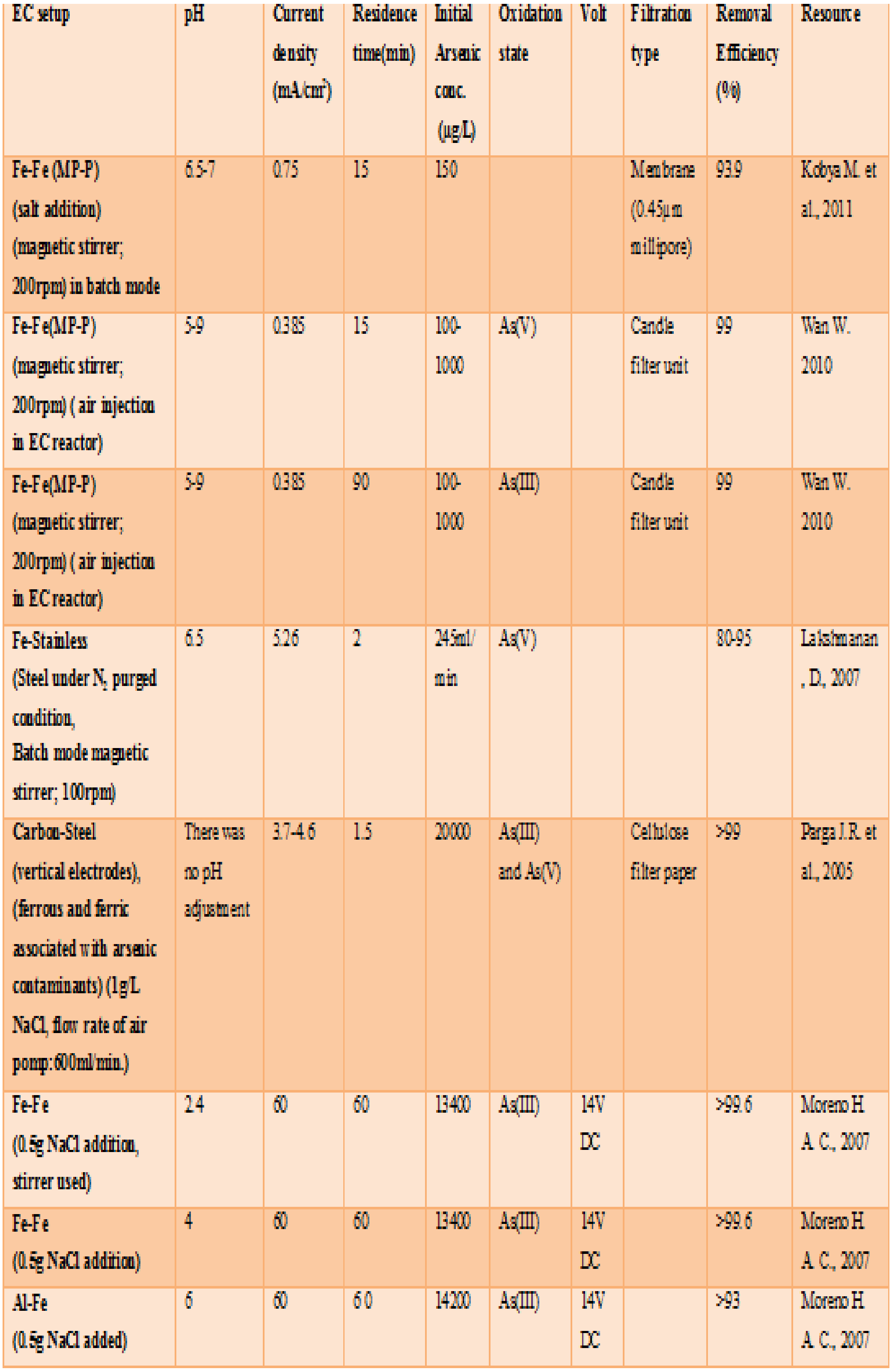
As to iron concentration, Fe^{2+} species was not completely oxidize which result in the desired $Fe(OH)_n(s)$ in EC process and passing through the filter, they caused high iron concentration in effluent water despite injection of air during the filtration.

When the EC process is used for arsenic removal from water, high removal efficiencies can be achieved. At the following, the comparison of this EC study with the previous studies was shown in Table 5.3 and Table 5.4.

Table 5.3. The comparison of this study with literature studies (MP-P: monopolar-parallel connections, n: electrode number.).

EC setup	pH	Current density (mA/cm^2)	Residence time(min)	Initial Arsenic conc. (µg/L)	Oxidation state	Volt	Filtration type	Removal Efficiency (%)	Resource
Fe-Fe (MP-P)	6-8	3.9/15	5	100	As(V)	9.1	Sand filter +air injection	99	Electrode Surface area
Fe-Fe (MP-P)	6-8	4.5	9	100	As(V)		Sand filter +air injection	99	Effect of time
Fe-Fe (MP-P)	6-8	9	5	100	As(V)		Sand filter +air injection	99	Effect of current
Fe-Fe (MP-P)	6-8	4.5	5	951	As(III)		Sand filter +air injection	96	Oxidation state
Fe-Fe (MP-P) 1.16 g/L NaCl addition	6-8	6.9	3	500	As(V)	9	Sand filter	99	Salt add.
SBGW-1 (Counter lead, Copper Cathode-Iron Anode, porous glass, Stir bar).	7.04±0.42	1.1	tcp+tm= 8.99+60	570	As(III)/ As total		Pyrex fask vacuum filter (>1µm), (4-5min)	98.6	Addy S.E. A., 2008
SBGW-2 (Counter lead, Copper Cathode-Iron Anode, Insulting membrane, Stir bar).	7.06±0.16	1.1	tcp+tm= 832.5+ 60	560	As(III)/ As total		Pyrex fask vacuum filter (>1µm), (4-5min)	98	Addy S.E. A., 2008
Fe-Fe n=2 (0.8g NaCl)(magnetic stirrer)	2.4	3.0	60	13400	As(III)			>99.6	Gomes J.A.G et al., 2007
Fe-Fe n=2 (0.8g NaCl) (magnetic stirrer)	2.4	3	120	13400	As(III)			>99.6	Gomes J.A.G et al., 2007
Fe-Fe (MP-P) (salt addition) (magnetic stirrer; 200rpm) in batch mode	6.5-7	0.175	15	150			Membrane (0.45µm millipore)	94.3	Kobya M. et al., 2011

Table 5.4 The comparison of this study with literature studies (MP-P: monopolar-parallel connections, n: electrode number.).



EC setup	pH	Current density (mA/cm^2)	Residence time(min)	Initial Arsenic conc. (μg/L)	Oxidation state	Volt	Filtration type	Removal Efficiency (%)	Resource
Fe-Fe (MP-P) (salt addition) (magnetic stirrer; 200rpm) in batch mode	6.5-7	0.75	15	150			Membrane (0.45μm millipore)	93.9	Kobya M. et al., 2011
Fe-Fe(MP-P) (magnetic stirrer; 200rpm) (air injection in EC reactor)	5-9	0.385	15	100-1000	As(V)		Candle filter unit	99	Wan W. 2010
Fe-Fe(MP-P) (magnetic stirrer; 200rpm) (air injection in EC reactor)	5-9	0.385	90	100-1000	As(III)		Candle filter unit	99	Wan W. 2010
Fe-Stainless (Steel under N_2 purged condition, Batch mode magnetic stirrer; 100rpm)	6.5	5.26	2	24.5ml/min	As(V)			80-95	Lakshmanan, D., 2007
Carbon-Steel (vertical electrodes), (ferrous and ferric associated with arsenic contaminants) (1g/L NaCl, flow rate of air pomp:600ml/min.)	There was no pH adjustment	3.7-4.6	1.5	20000	As(III) and As(V)		Cellulose filter paper	>99	Parga J.R. et al., 2005
Fe-Fe (0.5g NaCl addition, stirrer used)	2.4	60	60	13400	As(III)	14V DC		>99.6	Moreno H A. C., 2007
Fe-Fe (0.5g NaCl addition)	4	60	60	13400	As(III)	14V DC		>99.6	Moreno H A. C., 2007
Al-Fe (0.5g NaCl added)	6	60	60	14200	As(III)	14V DC		>93	Moreno H A. C., 2007

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

In this study, maximum arsenic removal efficiency in a short residence time and minimum energy consumption (low-cost) was purposed by EC process. Therefore, the effect of initial arsenic concentration, residence time, current, presence of salt and electrode surface area was investigated on arsenic removal. The EC experiments were performed using iron electrodes in monopolar and parallel connection at pH 6 - 8.

In the EC process, there is high positive correlation between initial As(V) concentrations and the final As concentrations for the first 5 min. at a current density of 4.5 mA/cm^2 (3 A). However, increase of initial As concentration was independent from the final As concentration for longer residence time than short residence time of 5 min.

In the current experiments, at the end of 5 min 93% arsenic removal was obtained at 0.3 A (4.5 mA/cm^2) when current increased up to 0.6 A, 99% arsenic removal was achieved. On the other hand, 99% arsenic removal was achieved when time increased up to 9 min, at 0.3A. This result showed that the residence time is important for arsenic removal efficiency. Since the residence time influences the amount of iron coagulant released. Because of the increasing of coagulant and bubble generation rate, more efficient and faster removal was observed when the current was increased. As a result, when the current decreases, the more time needs to achieve similar efficiencies. Therefore, it can be said that in this study, the maximum efficiencies were achieved in 9 min at 0.3 A (4.5 mA/cm^2).

At the beginning of EC process, which has greater electrode, faster removal occurred due to the electrode surface area influenced the current density. On the other hand, there was no significant effect observed on arsenic removal and for the every electrode surface area maximum arsenic removal efficiency as 99% and standard value for the arsenic given by USEPA was achieved.

When removal of arsenic by EC process from groundwater in Sasali-Izmir was investigated, in 5 min the initial As(III); 951 µg/L decreased to 36 µg/L and 96% arsenic removal efficiency was achieved. The oxidation ratio of As(III) to As(V) increases with residence time, therefore, the long residence time is required to achieve the complete removal of arsenic which is desired standard limit value as 10 µg/L.

To increase conductivity and avoid passivation, NaCl added, an increase in current density and also large and dense, dark green flocs was observed. There was no significant effect on residual arsenic concentration. Moreover, better filtration can be obtain by adding either little amount of salt below the standard value or polyelectrolyte can be added due to large and dense floc formation.

In addition to this, avoiding passivation vicinity of the anode is important for arsenic removal efficiency. This can also be done by adding NaCl and periodically mechanical cleaning of electrodes. And also excessive dissolved iron was removed with the air injection during the filtration process.

The pH affects the state of other species in the solution and the solubility of products formed. Therefore, operation in optimal pH range (6 - 8) is recommended to achieve efficiency and effectiveness of electrocoagulation.

To increase efficiency of the EC process and to reduction of impact passivation, studies on improvement EC reactor design; using different electrode arrangements and changing polarity of the electrodes (such as periodic polarity reversal of the electrodes) is recommended.

References

Addy, S. E. A. (2008). *Electrochemical arsenic remediation for rural Bangladesh.* A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Physics in the Graduate Division of the University of California, Berkeley.

Ahmed, M. F. (2001). An overview of arsenic removal technologies in Bangladesh and India, BUET-UNU International Workshop: *Technologies for Arsenic Removal from Drinking Water*, Dhaka, Bangladesh.

Al Anbari, R. H., Albaidani, J., Alfatlawi, S. M., & Al-Hamdani, T. A. (2008). Removal of heavy metals from industrial water using electrocoagulation technique. *Twelfth International Water Technology Conference*, IWTC12, Alexandria, Egyp.

Alaton, G. I. (2005). *Electrocoagulation and advanced oxidation as intermediate effluent treatment for water reuse in a textile dyeing plant.* Graduate Program in Environmental Technology, Bogazici University.

Badruzzaman, M. (2005). *Mass transport scaling and the role of silica on arsenic adsorption onto porous iron oxide (hydroxide).* The Degree of Doctor of Philosophy, Arizona State University.

Balasubramanian, N., & Madhavan, K. (2001). Arsenic Removal from Industrial Effluent through Electrocoagulation. *Chemical Engineering & Technology, 24,* 519–521.

Bayramoglu, M., Eyvaz, M., & Kobya, M. (2007). Treatment of the textile wastewater by electrocoagulation economical evaluation. *Chemical Engineering Journal*, *128,* 155-161.

Bazrafshan, E., Mahvi, A. H., Naseri, S., & Mesdaghinia, A. R. (2008). Performance evaluation of electrocoagulation process for removal of chromium (vi) from synthetic chromium solutions using iron and aluminum electrodes. *Turkish J. Eng. Env. Sci., 32*, 59 – 66.

Bilici-Baskan, M., Pala, A. (2009). Determination of arsenic removal efficiency by ferric ions using response surface methodology. *Journal of Hazardous Materials, 166*,796–801.

Charoenlarp, K., & Choyphan, W. (2009). Reuse of dye wastewater through colour removal with electrocoagulation process. *Asian Journal Energy and Environment 10* (04), 250-260.

Chen, G. (2004). Electrochemical technologies in wastewater treatment. *Separation and Purification Technology*, *38,* 11-40.

Chen, X. M., Chen, G., & Yue, P. L. (2000). Separation of pollutants from restaurant wastewater by electrocoagulation. *Separation and Purification Tech., 19* (1), 65-76.

Chou,W.-L., Chang, W.-C., & Liu, T.-C. (n.d.). *Electrocoagulation study for cod removal from chemical mechanical polishing wastewater.* Retrieved May 10, 2011 from http://archivos.labcontrol.cl/wcce8/offline/techsched/manuscripts%5Cm3elfn.pdf

Comninellis, C., Chen, G. (2010). *Electrochemistry for the environment.* Springer Science+Business Media.

Daida, P. (2005). *Removal of arsenic from water by electrocoagulation using Al-Al, Fe-Fe, Al-Fe electrode pairs systems and characterization of products.* Degree Master of Science, Lamar University, UMI Microform 1433879.

Deniel, R., Himabindu, V., Prabhakararao, A. V. S., & Anjaneyulu, Y. (2008). Removal of arsenic from wastewaters using electrocoagulation. *Journal of Environ. Science & Engg. 50* (4), 283-288.

Dixit, S., Hering, J. G. (2003). Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. *Environmental Science & Technology, 37,* 4182-4189.

Duarte, A.L.S., Cardoso, S. J.A. & Alçada, A. J. (2009). Emerging and innovative techniques for arsenic removal applied to a small water supply system. *Sustainability ,1,* 1288-1304.

Dutre, V.; Vandecasteele, C.; & Opdenakker, S. (1999). Oxidation of arsenic bearing fly ash as pretreatment before solidification. *Hazard J. Mater., 10;* 68 (3): 205-215.

Elsener, B. (n.d.). *Corrosion and durability of metals Institute for Building Materials, ETH* Zürich. Retrieved April 6, 2011 from http://www.surface.mat.ethz.ch/education/courses/surfaces_and_interfaces/chapter11.

Emamjomeh M. M., & Sivakumar M. (2009). Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes. *Journal of Environmental Management, 90,* 1663–1679.

Escobar, M. E. O., Hue, N.V. & Cutler, W. G. (2006). *Recent developments on arsenic: contamination and remediation.* Retrieved November 10, 2010, from http://www.ctahr.hawaii.edu/huen/Arsenic2006.pdf.

Farooqui, M. S. (2004). *Combined electrooxidation and electrocoagulation process for the treatment of municipal wastewater*. The Degree of Master of Science in

Civil Engineering, King Fahd University of petroleum & Minerals.UMI Microform 1427898.

Feenstra, L., Erkel, J., & Vasak, L. (2007). Arsenic in groundwater: overview and evaluation of removal methods. *International Groundwater Resources Assessment Centre (igrac)*, Report nr. SP 2007-2.

Filtration (n.d.). Retrieved May 20, 2011, from http://en.wikipedia.org/wiki/Filtration.

Gilbert, O., Pablo, J., Cortina, J-L, & Ayora, C. (2009). In-situ of removal arsenic form groundwaters by using permeable reactive barriers of organic matter/limestone/zerovalent Fe mixtures. *International congress on production of safe water*, Izmir, Turkey.

Gomes, A. G. J., Daida P., Kesmez, M., Weir M., Moreno, H., & Parga, J.R., (2007). Arsenic removal by electrocoagulation using combined electrode system and characterization of products. *Journal of Hazordous Materials B 139*, 220-231.

Guha Mazumder, D.N., Hauque, R., Ghosh N., Santra, A., Chaktraborty, D., Smith, A.H., et al., (1998). Arsenic levels in drinking waters and the prevalence of skin, lesions in West Bengal, India. *International Jour. of Epidemiology, 27* (5), 871-877.

Handbook of analytical methods for materials. Materials Evaluation and Engineering, Inc. Retrieved May 3, 2011, from http://www.cientificosaficionados.com/microscopio/MICROSCOPIO%20ELECTRONICO_archivos/hamm72d.pdf.

Hansen H. K., Nunez P., & Jil C., (2008). Removal of arsenic from wastewaters by airlift electrocoagulation. Part 1: Batch reactor experiments. *Separation Science and Technology, 43,* 212-224.

Hansen H. K., Nunez P., Raboy, D., Schippacasse, I., & Grandon, R. (2007). Electrocoagulation in wastewater containing arsenic: comparing different process designs. *Electrochimica Acta,52*, 3464-3470.

Henke, K. (2009). *Arsenic: Environmental chemistry, health threats and waste treatment.* John Wiley & Sons Ltd.

Holt, P. K., Barton, G. W., Wark, M., & Mitchell, C. A. (2002). A quantitative comparison between chemical dosing and electrocoagulation. *Colloids and Surfaces A: Physiochemical and Engineering Aspects , 211* (2-3), 233-248.

Holt, P., Barton, G., M. & Mitchell, C. (2006). Electrocoagulation as a wastewater treatment. Department Of chemical Engineering, The university of Sydney, New South Wales. *The Third Annual Australian Environmental Engineering Research Event*. 23-26 November Castlemanie, Victoria 1999.

Ihos, M., Negrea, A., Lupa, L., Ciopec, M., & Negrea, P. (2005). Comparative study of As(III) removal efficiency and Conventional Coagulation. *Chem. Bull, “PoLITEHICA” Univ. (Timisoara), 50* (64), 1-2.

Jehangir, M. (2006). *Treatment of simulated dairy wastewater by electrocoagulation*. The degree of Master of Science in Civil Engineering, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia.

Kobya, M., Ulu, F., Gebeoglu, U., Demirbas, E., & Oncel, M. S. (2011). Treatment of potable water containing low concentration of arsenic with electrocoagulation: different connection modes and Fe-Al electrodes. *Separation and Purification Technology 77*, 283-293.

Kumar, P. R., Chaudhari, S., Khilar, K.C., & Mahajan, S.P. (2004). Removal of arsenic from water by electrocoagulation. *Chemosphere 55*, 1245–1252

Lakshmanan, D. (2007). *A systematic study of arsenic removal from drinking water using coagulation-filtration and electrocoagulation*. UMI Microform 3273790.

Lakshmanan, D., Cliffford, D. A. & Samanta, G. (2011). Simultaneous oxidation and removal of As(III) and As(V) by electrocoagulation-filtration. *Water Research Foundation and Arsenic Water Technology Partnership.*

Larry D., Hanke, P.E. (2001). *Handbook of analytical methods for materials.* Materials Evaluation and Engineering, Inc.

Larue, O., Vorobiev, E., Vu, C., & Durand, B. (2003). Electrocoagulation and coagulation by iron of latex particles in aqueous suspensions. *Separation and Purification Technology 31,* 177-192.

Litter, M. I. , Morgada, M. E.,& Bundschuh, J. (2010). Possible treatments for arsenic removal in Latin American waters for human consumption. *Environmental Pollution 158*, 1105-1118.

Mollah, M.Y.A., Schennach, R., Parga, J.R., & Cocke, D.L. (2001). Electrocoagulation (EC) – science and applications. *Journal of Hazardous Materials B84,* 29 –41.

Mollah, M.Y. A., Morkovsky P., Gomes, J. A.G., Kesmez, M., Parga, J., & Cocke, D. L., (2004). Fundamentals, present and future perspectives of electrocoagulation. *Journal of Hazardous Materials B114*, 199–210.

Moreno-Casillas, H. A., (2007). *Mechanisms, chemical pathways, and optimization of electrochemical water treatment by electrocoagulation for sustainable water utilization.* The Degree of Doctor of Engineering, Lamar University. UMI Microform 3343910.

Moreno-Casillas, H. A., Cocke D. L., Gomes J. J. A., Parga, J.R. & Morkovsky, P. (2007). Electrocoagulation : COD removal mechanism. *Separation and Putrification Technology 56,* 2, 204-211.

Muakthong, D. (2006). *Chapter 1 Introduction*. Retrieved April 20, 2011, from http://kb.psu.ac.th/psukb/bitstream/2553/1440/6/275682_ch1.pdf.

NOBEL, (n.d.). *Filtration.* Retrieved May 20, 2011, from http://www.nobelitaly.it/ING/Bullettin/RI_25_I-r0.pdf.

Nouri, J., Mahvi, A. H., & Bazrafshan, E., (2010). Application of Electrocoagulation Process in Removal of Zinc and Copper From Aqueous Solutions by Aluminum Electrodes. *Int. J. Environ. Res*., *4* (2), 201-208.

Oruc, N. 2005. Arsenic Levels in Drinking Waters of Emet-Kütahya – Turkey and its Relation to Arsenic Bearing Minerals in Borate Deposits. *Medical Geology Short Courses and Panels with International Participation.*Ankara Uni. Turkey, EPA.

Parga, J. R., Cocke, D. L., Valenzuela J. L., Gomes, J. W., Kesmez M., Irwin, G., et al. (2005). Arsenic removal via electrocoagulation from heavy metal contaminated groundwater in La Comarca Lagunera Mexico. *Journal of Hazordous Materials B124,* 247-254.

Petrusevski, B., Sharma, S., Schippers, J. C., & Shordt, K. (2007). Arsenic in drinking water. *Thematic overview paper 17.* IRC International Water and Sanitation Centre.

Rahmani, A. R., Ghaffari, H. R., & Samadi, M.T. (2010). Removal of arsenic(III) from contaminated water by synthetic nano size zerovalent iron. *World Academy of Science, Engineering and Technology. 62,* 1116-1119.

Ravenscroft, P., Brammer, H., & Richards, K. (2009). Arsenic Pollution: *A Global Synthesis.* Willey-Blackwell.

Rubidge, G. R. (2004). *Evaluation and optimization of selected methods of arsenic removal from industrial effulent.* Doctors Degree in Technology: Chemistry, in the faculty of Applied Science at the Port Elizabeth Technikon.

Shih M. (2005) An overview of arsenic removal by pressure-driven membrane processes, *Desalination*, *172*, 85-97.

SOS-arsenic.net. *Arsenic standard.* Retrieved November 10, 2010, from http://www.sos-arsenic.net/english/contamin/1.html.

The Ministry of Health of Turkey (2005). Turkish Standards Institute 266- Water intended for human consumption.

U.S. Environmental Protection Agency (USEPA) (2001). *Quick reference guide to arsenic and clarifications to compliance and source monitoring rule.* Retrieved November 15, 2010, from www.epa.gov/OGWDW/arsenic/pdfs/quickguide.pdfs.

U.S. Environmental Protection Agency (USEPA). *Secondary drinking water regulations: guidance for nuisance chemicals.* Retrieved May 10, 2010 from http://water.epa.gov/drink/contaminants/secondarystandards.cfm.

Wan, W. (2010). *A thesis on the arsenic removal from drinking water by electrocoagulation.* The degree of Master of Science, Washington University in ST. Louis.

WHO (World Health Organization) (1993). *Guidelines For Drinking-Water.* Retrieved 20 May, 2011, from http://www.who.int/water_sanitation_health/dwq/chemicals/antimonysum.pdf

X-ray scattering techniques (n.d.). Retrieved April 5, 2011, from http://en.wikipedia.org/wiki/X-ray_scattering_techniques.

X-ray Diffraction (XRD), (2009). Retrieved April 5, 2011, from http://orkide33.blogcu.com/x-ray-diffraction-xrd/5058333.