Arsenic Removal from Drinking Water by Electrocoagulation

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IN
CHEMICAL ENGINEERING

Submitted by

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DECLARATION

I hereby declare that thesis entitled **“Arsenic Removal from Drinking Water by Electro-coagulation”** is an authentic record of my work carried out as per the requirements for the award of degree of **M.Tech. (Chemical Enigineering)** at **Thapar University, Patiala**, under the guidance of **Dr. R.K Gupta**, (Assistant Professor) and **Mr. V.K Sangal**, (Assistant Professor) **Department of Chemical Engineering**, Thapar University, Patiala during **July 2009 to July 2010**. The matter embodied in this thesis has not been submitted in part or full to any other university or institute for the award of any degree.

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This is to certify that above declaration made by the student concerned is correct to the best of our knowledge and belief.

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ABSTRACT

Arsenic is a toxic element which occurs in water due to mineral dissolution. Arsenic occurs in water mainly in the form of arsenite [As(III)] and arsenate [As(V)]. Maximum allowable limit for arsenic in drinking water is 0.01 mg/I as per WHO guidelines. In India the most severe outbreak of arsenic poisoning have been associated with ground water in the Bengal Delta including Bangladesh and West Bengal (Eastern India) where an estimated total of 120 million people (80 million in Bangladesh, 40 million in India) are at risk.

The purpose of this study was to investigate the effects of the operating parameters, such as pH, treatment time, current density, and inter-electrode spacing on arsenic removal from drinking water in the batch electro-coagulation (EC) process. pH 7 was found to be appropriate for treating the drinking water for arsenic removal by EC. Also, the effect of pH on arsenic removal was not significant and remained in the permissible limit for initial pH range of 6 to7.

The removal of arsenic increased with decreasing inter-electrode spacing. However, for inter-electrode spacing less than 1 cm, there was no further improvement in the arsenic removal.

Better removal of arsenic was observed with increasing current density. It was found that for current density equal to 6.57 mA/cm^2 (with 2.5 A current) with four electrodes gave better result as compared to 3.94 and 5.25 mA/cm^2. It was possible to bring the residual arsenic content in the treated water within the permissible limit (10 ppb) in 40 minutes of electrolysis time.

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CHAPTER-1

INTRODUCTION

Arsenic (atomic number 33) is ubiquitous and ranks 20th in natural abundance, comprising about 0.00005% of the earth's crust, 14th in the sea water, and 12th in the human body. It's concentration in most rocks ranges from 0.5 to 2.5 mg/kg. It is a silver-grey brittle crystalline solid with atomic weight 74.9, specific gravity 5.73, melting point 817 °C (at 28 atm) and sublimation point at 613°C (Pendias et al., 2000 and Mandal et al., 2004). Existence of arsenic in chemistry and nature is shown in Figure 1.

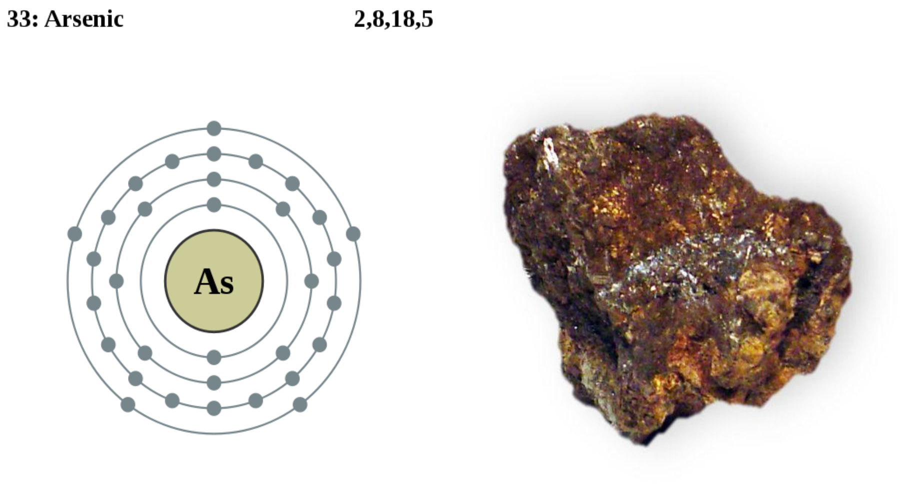


Figure 1. Existence of arsenic in chemistry and nature

Arsenic is mobilized by natural weathering reactions, biological activity, geochemical reactions volcanic emissions and other anthropogenic activities (Mackenzie et al., 1979). Most environmental arsenic problems are the result of mobilization under natural conditions. However, mining activities, combustion of fossil fuels, use of arsenic pesticides, herbicides, and crop desiccants and use of arsenic additives to livestock feed create additional impacts. Arsenic exists in the −3, 0, +3 and +5 oxidation states (Smedley et al., 2002). Arsenic (III) is a hard acid and preferentially complexes with oxides and nitrogen. Conversely, arsenic (V) behaves like a soft acid, forming complexes with sulfides. Inorganic forms of arsenic most often exist in water supplies (Bodek et al.,1998).

1.1 Occurrence of arsenic in water

Arsenic is widely distributed throughout the earth's crust. Arsenic is introduced into water through the dissolution of minerals and ores, and concentrations in groundwater in some areas are elevated as a result of erosion from local rocks. Industrial effluents also contribute arsenic to water in some areas. Arsenic is also used commercially e.g. in alloying agents and wood preservatives.

Background arsenic concentrations in natural water are low, but elevated arsenic concentrations are common in groundwater as a result of natural conditions or anthropogenic impacts. Natural oxidation and/or reduction reactions involving arsenic bearing rocks under favorable temperature and pH conditions may mobilize the arsenic and increase arsenic concentrations in groundwater. Human activities that could increase arsenic concentrations in ground waters and surface waters include: oil and coal burning power plants, waste incineration, cement works, disinfectants, household waste disposal, glassware production, electronics industries, ore production and processing, metal treatment, galvanizing, ammunition factories, dyes and colours, wood preservatives, pesticides, pyrotechnics, drying agents for cotton, oil and solvent recycling and pharmaceutical works.

Inorganic arsenic can occur in the environment in several forms but in natural waters, and thus in drinking water. It is mostly found as trivalent arsenite [As (III)] or pentavalent arsenate [As (V)]. Organic arsenic species, abundant in seafood, are very much less harmful to health, and are readily eliminated by the body. Arsenic contaminated drinking water poses the greatest threat to public health (Lee et al., 2002).

1.2 Environmental levels and standards

Concentrations in water are usually < 10 µg/l, although higher concentrations can occur near natural mineral deposits or anthropogenic sources. Arsenic levels in groundwater average about 1–2 µg/l, except in areas with volcanic rock and sulfide mineral deposits where arsenic levels can range up to 3400 µg/l. In India the most severe outbreak of arsenic poisoning have been associated with ground water in the Bengal Delta including Bangladesh and West Bengal (Eastern India) where an estimated total of 120 million people (80 million in Bangladesh, 40 million in India) are at risk. Also, more than 16 districts of Bihar have reported arsenic contamination of groundwater sources, out of these Bhojpur emerged on top, with 1,861 parts per billion (ppb) against the World Health Organization's limit of 10 ppb. Arsenic contamination in the affected districts of the Bengal Delta is the greatest environmental calamity ever reported.

The International Standards for drinking water was established 0.20 mg/L as an allowable concentration for arsenic by WHO in 1958. In 1963 the standard was re-evaluated and reduced to 0.05 mg/L. In 1984, this was maintained as WHO's "Guideline Value"; and many countries have kept this as the national standard or as an interim target. According to the WHO guidelines for drinking water quality:

- Inorganic arsenic is a documented human carcinogen.
- 0.01 mg/L was established as a provisional guideline value for arsenic.
- Based on health criteria, the guideline value for arsenic in drinking water would be less than 0.01mg/L.
- The guideline value is restricted by measurement limitations, and 0.01 mg/L is the realistic limit to measurement, this is termed a provisional guideline value.

The WHO guidelines for drinking water quality is intended for use as a basis for the development of national standards in the context of local or national environmental, social, economic, and cultural conditions.

Indian Standard specifications for drinking water IS: 10500 the limit is 0.05 mg/L.

1.3 Effect of arsenic on humans

Arsenic has effects on widely different organ systems in the body. It has produced serious effects in humans after both oral and inhalation exposure. A peculiarity of arsenic carcinogenicity is that the information mainly comes from experience with exposed humans.

Ingestion of high doses of arsenic may lead to acute symptoms within 30–60 min, but the effects may be delayed when the arsenic is taken with food. Acute gastrointestinal syndrome is the most common presentation of acute arsenic poisoning. This syndrome starts with a metallic or garlic-like taste associated with dry mouth, burning lips and dysphagia. Violent vomiting may ensue and may eventually lead to haematemesis. Gastrointestinal symptoms, which are caused by paralysis of the capillary control in the intestinal tract, may lead to a decrease in blood volume, lowered blood pressure and electrolyte imbalance. Thus, after the initial gastrointestinal problems, multi-organ failure may occur, including renal failure, respiratory failure, failure of vital cardiovascular and brain functions, and death. Survivors of the acute toxicity often develop bone marrow suppression (anaemia and leukopenia), haemolysis, hepatomegaly, melanosis and polyneuropathy resulting from damage to the peripheral nervous system. Polyneuropathy is usually more severe in the sensory nerves, but may also affect the motor neurons (NRC, 1999).

Fatal arsenic poisonings have been described after oral exposure to estimated doses of 2 g, 8 g and 21 g, and cases with non-fatal outcome (usually after treatment) have been reported after oral doses of 1–4 g up to 8–16 g arsenic. Serious, non-fatal intoxications in infants have been observed after doses of 0.7 mg of arsenic trioxide (As_2O_3) (0.05 mg/kg), 9–14 mg and 2400 mg (4 mg/kg). Incidents of continuous or repeated oral exposure to arsenic over a short period of time have been described. When they drank water containing 108 mg As/liter for 1 week, 2 out of 9 exposed persons died, 4 developed encephalopathy and 8 gastrointestinal symptoms. No deaths, but symptoms mainly from the gastrointestinal tract and skin, were observed among 220 patients studied among 447 who had been exposed to arsenic in soy sauce at a level of 100 mg/litre for 2–3 weeks; the estimated daily dose of arsenic was 3 mg.

A case of lung cancer associated with exposure to arsenical dust was brought to the notice of the British Factory Department, and some further cases were detected in the early 1940's. These reports were followed by an investigation of the matter, and a remarkably elevated relative cancer mortality rate from lung and skin cancer was observed in a sheep-dip factory manufacturing sodium arsenite.

Chronic skin effects of arsenic, including pigmentation changes, hyperkeratosis and skin cancer, from medicinal use but also from drinking water, were reported as early as the 19th century. A large number of case series on arsenical skin cancer after exposure via drinking water were published from Argentina, Chile, Mexico and Taiwan in the early 1900s. An endemic peripheral vascular disease (PVD), known as black foot disease (BFD), leading to progressive gangrene of the legs, has been known in Taiwan since 1920 (Acharyya et al.,1999). Figure 2 shows the several harmful effects of drinking arsenic contaminated water (Zhuo, 2004).

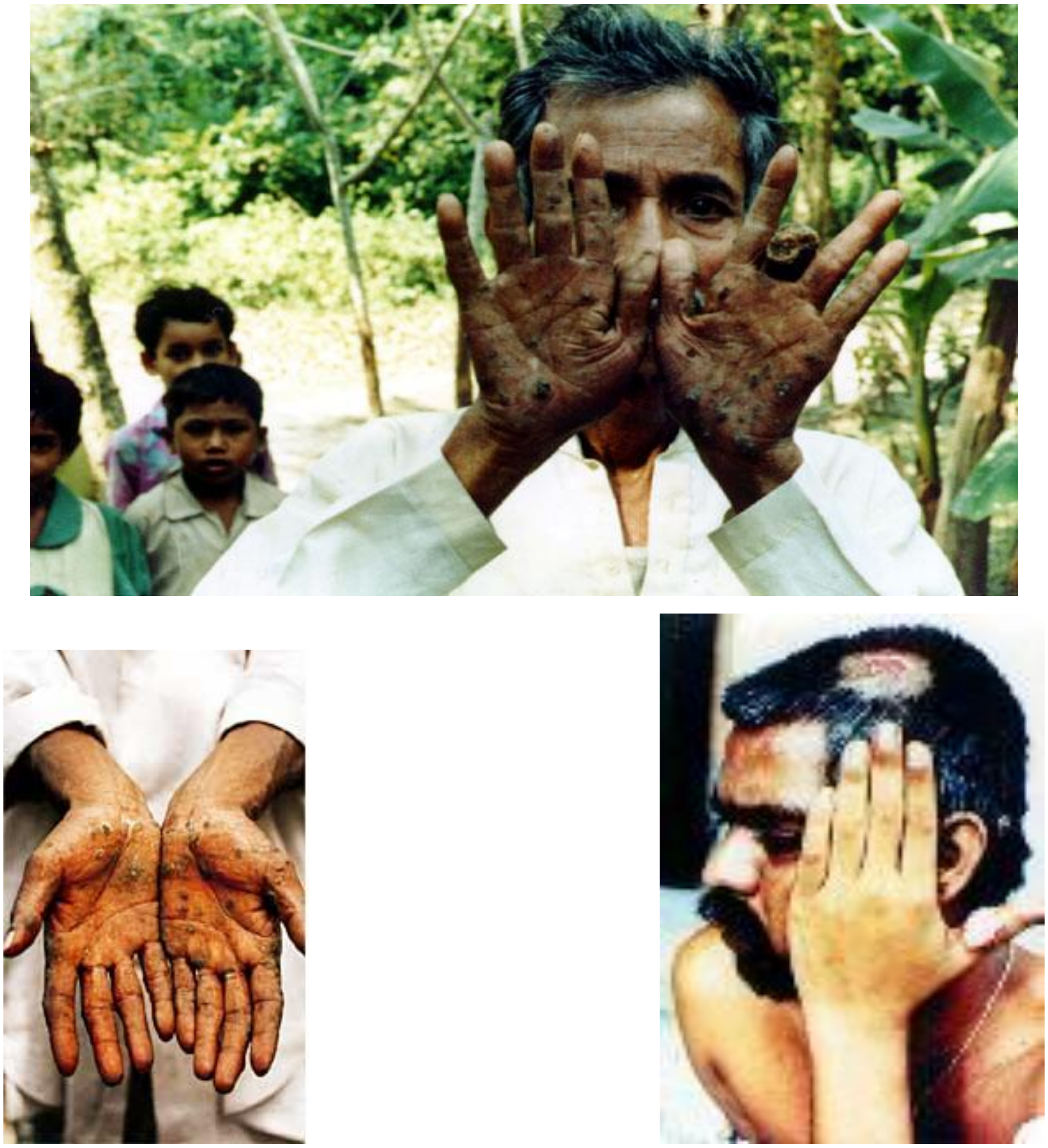


Figure 2. Harmful effects of arsenic

(Arsenic lesions on hands, missing finger, Spotted. Kertosis on Palm, Arsenic lesions on head)

Unfortunately, there is no known cure for arsenic poisoning and therefore providing arsenic free drinking water is the only way to diminish the adverse health effects of arsenic. Consequently, several methods are proposed to provide arsenic-free water. These methods suggest either the treatment of arsenic contaminated groundwater, or looking for the alternative options (e.g. surface water treatment, rain-water harvesting, etc).

The use of alternative water sources, however, can only be possible after a major and costly technological shift and thus, the treatment of arsenic contaminated water to the guideline values is the preferred option. Apart from India, high concentrations of arsenic in water and soil have been documented in Taiwan, Argentina, the USA, Chile and many other countries but of these, the most severe outbreaks of arsenic poisoning have been associated with ground waters in the Bengal Delta including Bangladesh and West Bengal (Eastern India).

CHAPTER-2

ARSENIC REMEDIATION TECHNOLOGIES

2.1 Processes for arsenic removal

The general categories of remediation processes for arsenic removal are discussed below.

2.1.1 Oxidation

Of the two predominant forms of arsenic in water, arsenate and arsenite, most treatment processes are effective at removing arsenate, but not arsenite, since arsenite is typically non-charged below pH 9.2. Therefore, treatment for the removal of arsenic often includes an oxidation step to convert arsenite to arsenate.

Oxidation can be simply the addition of oxygen to a compound, or more generally, any reaction involving the loss of electrons from an atom. Aeration, the supplying of air, oxidizes arsenic, converting arsenite to arsenate, and the iron that co-occurs. This is precipitated as $FeAsO_4$. Arsenic can also be oxidized by a number of other chemicals including chlorine, hypochlorite, ozone, permanganate, hydrogen peroxide and Fenton's reagent (H_2O_2/Fe^{2+}). Photochemical oxidization proceeds from the reaction of radiant energy and a chemical system. Oxidation alone does not remove arsenic from solution but must be combined with an arsenic removal process (Borho et al., 1996).

2.1.2 Filtration

Conventional filtration is the separation of solid particles from water by passing the solution through a medium. Particles are removed during filtration as a result of any one or combination of mechanisms: mechanical straining, sedimentation, flocculation, adsorption and/or biological metabolism. The filter medium may be of various materials, for example, sand, anthracite coal, activated carbon, cloth, paper, that retains the solid on its surface and allows the water to pass through. Common particulates removed by filtration include silt, clay, colloidal and precipitated natural organic matter, naturally-occurring iron and manganese precipitates, precipitates from metal salt or polymer coagulation, microorganisms. Filters may be classified in various ways, according to the type of granular medium used, by the hydraulic system (e.g.

gravity, up-flow, etc.), rate of filtration, and/or by the location of particle accumulation (Clifford et al., 1999).

2.1.3 Adsorption

Adsorption is the accumulation of materials at an interface, the liquid/solid boundary layer. It is a mass transfer process where a substance is transferred from the liquid phase to the surface of a solid and becomes bound by chemical or physical forces. Adsorption can take place on suspended particles, as part of the process of coagulation/co-precipitation, or on fixed media. Since adsorption is a surface phenomenon, the greater the surface area of the medium, the greater it's capacity to accumulate material. Each adsorbent medium has different associated properties, performances and costs. Arsenic is adsorbed onto the surface of various granular, activated, clay and celluosic adsorbents, including the following:

- Oxides (e.g. hydrated ferric oxide, titanium oxide, silicium oxide).
- Iron oxide-coated or MnO_2-coated sand.
- Bauxite, hematite, feldspar.
- Clay minerals (e.g. kaolinite, bentonite, Bijoypur clay).
- Synthetic anion exchange resins.
- Chitin and chitosan.
- Bone char.
- Cellulose materials (sawdust, newspaper pulp) (Nenov et al., 1986).

2.1.4 Ion Exchange

Ion exchange is the reversible interchange of ions between the solid and the liquid phase where there is no permanent change in the structure of the solid. Developed for large-scale applications, ion exchange is probably not appropriate for small hand-pumped wells, but could potentially be used on a small scale.

Synthetic ion exchange resins are based on a cross-linked polymer matrix, typically composed of polystyrene cross-linked with vinyl benzene. Charged functional groups are attached to the matrix through covalent bonding and fall into the following four groups:

- Strongly acidic
- Weakly acidic
- Strongly basic
- Weakly basic

Various strong base anion exchange resins are commercially available that can effectively remove arsenic from water, producing effluents with less than 1 µg/L arsenic. Arsenic, being uncharged, is not removed, unless an oxidation step to convert arsenite to arsenate is included in the process.

Conventional sulfate-selective resins are particularly suited for arsenate removal. Nitrate-selective resins also remove arsenic, but arsenic breakthrough occurs earlier. Ion exchangers are typically down-flow, packed bed columns with ion exchange resin beads pre-saturated with an exchangeable ion. Source water is passed through the packed bed until the appearance of the unwanted contaminant in the effluent. At this stage, the ion exchange media is reactivated with a regenerant solution and rinsed with water in preparation for another treatment cycle. Both the redox potential and pH are important factors with regard to arsenic removal by ion exchange (Benefield et al., 1990).

2.1.5 Coagulation/Co-precipitation

Coagulation encompasses all reactions, mechanisms and results in the overall process of particle growth (floc formation) and particle aggregation within water being treated, including in situ coagulant formation, chemical particle destabilization and physical inter-particle contacts. Coagulation involves the removal of colloidal (0.001 - 100 microns) and settleable (> 100 microns) particles. However the term also commonly refers to the removal of dissolved ions (< 0.001 microns), which is actually precipitation. Chemical precipitation is the process by which dissolved ions in solution form an insoluble solid via a chemical reaction. For example, naturally occurring dissolved iron in groundwater, when exposed to oxygen, forms a precipitate. Co-precipitation occurs when an inorganic contaminant forms an insoluble complex with the coagulant. Both the valence of the inorganic contaminant and the pH of the solution are important removal by co-precipitation.

Coagulation converts soluble arsenic into insoluble reaction products, allowing separation by sedimentation and/or filtration. Factors affecting arsenic removal by coagulation/precipitation include coagulant type and dose, mixing time and speed, pH, arsenic oxidation state and concentration, presence of inorganic solutes.

Three mechanisms are mainly involved in arsenic removal:

- Precipitation: The formation of insoluble compounds Al (AsO_4) or Fe (AsO_4).
- Co-precipitation: Incorporation of soluble arsenic species into the metal hydroxide floc.
- Adsorption: The electrostatic binding of soluble arsenic to the external surfaces of the insoluble metal hydroxides.

Direct precipitation plays the least important role in arsenic removal however; co-precipitation and adsorption are both active arsenic removal mechanisms (Novikova et al., 1982).

2.1.6 Membrane/Reverse osmosis

Membrane separation uses semi-permeable membranes that are selectively permeable to water and certain solutes to separate impurities from water. Membranes are able to remove many different kinds of dissolved solids, including arsenic, from water. However, they are usually expensive and therefore are typically considered in applications such as desalination, brackish water conversion and for removal of specific ions, such as arsenic, that are difficult to remove by other means. There are many different membrane alternatives including microfiltration, reverse osmosis, electrodialysis, ultra filtration and nanofiltration. Membrane process treatment performance is dependent on the quality of the feed water and the desired quality of the product water. Generally the more contaminated the feed water and the higher the desired product water quality, the greater the likelihood of membrane fouling caused by particulate matter, scaling and bio fouling (Kang et al., 2000).

2.1.7 Biological

Biological treatment transforms, stabilizes and/or removes arsenic by means of microorganisms. Microorganisms, primarily certain specific bacteria, accomplish this by oxidation/reduction, mineralization, detoxification or methylation. Critical factors include energy and carbon source, aerobic-anoxic or anaerobic conditions, temperature, and pH (Mohan et al., 2007).

2.1.8 Electro-coagulation

The EC technology offers an alternative to the use of metal salts or polymers and polyelectrolyte addition for breaking stable emulsions and suspensions. The technology removes metals, colloidal solids and particles, and soluble inorganic pollutants from aqueous media by introducing highly charged polymeric metal hydroxide species. These species neutralize the electrostatic charges on suspended solids and oil droplets to facilitate agglomeration or coagulation and resultant separation from the aqueous phase. The treatment prompts the precipitation of certain metals and salts.

In its simplest form, an electro-coagulating reactor may be made up of an electrolytic cell with one anode and one cathode. When connected to an external power source, the anode material will electrochemically corrode due to oxidation, while the cathode will be subjected to passivation. But, this arrangement is not suitable for wastewater treatment, because for a workable rate of metal dissolution, the use of electrodes with large surface area is required. This has been achieved by using cells with monopolar electrodes either in parallel or series connections (Mollah et al., 2001).

2.1.9 Other

- *Dug Wells*
- *Deeper Tube Wells*
- *Ponds*
- *Solar Distillation*

Solar distillation uses the sun's energy to evaporate water, which then recondences. The process of evaporation and recondensation separates all chemicals, including arsenic, from the water. In Bangladesh, where solar energy is plentiful, this approach may be especially suited for application in crisis areas, and, if cost-effective approaches can be developed, in rural areas (Nojiri et al., 1998).

Comparison of arsenic removal technologies (Mohan et al., 2007)

Technique		**Advantage**	**Disadvantage**
Oxidation/precipitation	Air oxidation	Relatively simple, low-cost but slow process; arsenic removal; also oxidizes other inorganic and organic constituents in water.	Mainly removes arsenic(V) and accelerate the oxidation process.
	Chemical oxidation	Oxidizes other impurities and kills microbes; relatively simple and rapid process; minimum residual mass	Efficient control of the pH
Sorption and ion-exchange	Activated alumina	Relatively well known and commercially available	Needs replacement after four to five regeneration
	Iron coated sand	Cheap; no regeneration is required; remove both As(III) and As(V)	Not standardized; produces toxic solid waste
	Ion-exchange resin	Well-defined medium and capacity; pH independent; exclusive ion specific resin to remove arsenic	High cost medium; high-tech operation and maintenance; regeneration creates a sludge disposal problem; As(III) is difficult to remove; life of resins

Reverse osmosis		No toxic solid waste is produced	High tech. operation and maintenance
Electrodialysis		Capable of removal of other contaminants	Toxic wastewater produced
Coagulation/electrocoagulation /coprecipitation	Alum coagulation	Durable powder chemicals are available; relatively low capital cost and simple in operation; effective over a wider range of pH	Produces toxic sludges; low removal of arsenic; pre-oxidation may be required
	Iron coagulation	Common chemicals are available; more efficient than alum coagulation on weigh basis	Medium removal of As(III); sedimentation and filtration needed
	Lime softening	Chemicals are available commercially	Readjustment of pH is required
	Electro-coagulation	High removal efficiency, Low cost process, can handle high range of pollutant	Replacement of Iron and Aluminium electrodes

CHAPTER-3

ELECTRO-COAGULATION

Electrocoagulation (EC) is an electrochemical method of treating polluted water whereby sacrificial anodes corrode to release active coagulant precursors (usually aluminum or iron cations) into solution. Accompanying electrolytic reactions evolve gas (usually as hydrogen bubbles) at the cathode. Electrocoagulation has a long history as a water treatment technology having been employed to remove a wide range of pollutants (Mameri et al., (1998).

3.1 Description of the technology

In its simplest form, an electrocoagulating reactor may be made up of an electrolytic cell with one anode and one cathode. When connected to an external power source, the anode material will electrochemically corrode due to oxidation, while the cathode will be subjected to passivation. But, this arrangement is not suitable for wastewater treatment, because for a workable rate of metal dissolution, the use of electrodes with large surface area is required. This has been achieved by using cells with monopolar electrodes either in parallel or series connections.

Different types of arrangement of electrodes in EC are:

(i) A simple arrangement of an EC cell with a pair of anodes and a pair of cathodes in parallel arrangement is shown in Figure 3. It essentially consists of pairs of conductive metal plates placed between two parallel electrodes and a direct current power source. The experimental set up also requires a resistance box to regulate the current density and a multimeter to read the current values. The conductive metal plates are commonly known as ‘sacrificial electrodes’. The sacrificial electrodes may be made up of the same or of different materials (Pretorius et al., 1991).

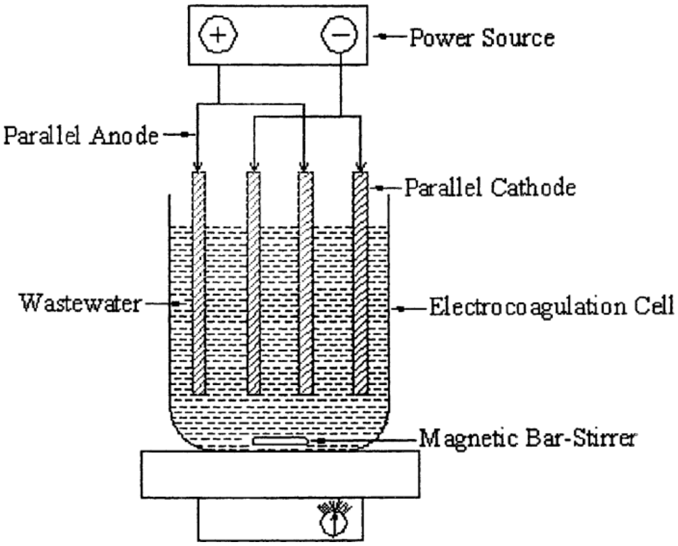


Figure 3. Bench-scale EC reactor with monopolar electrodes in parallel connection

(ii) An arrangement of an EC cell with monopolar electrodes in series is shown in Figure 4. As can be seen from Figure 4, each pair of 'sacrificial electrodes' is internally connected with each other, and has no inter connections with the outer electrodes. This arrangement of monopolar electrodes with cells in series is electrically similar to a single cell with many electrodes and interconnections (Pretorius et al., 1991).

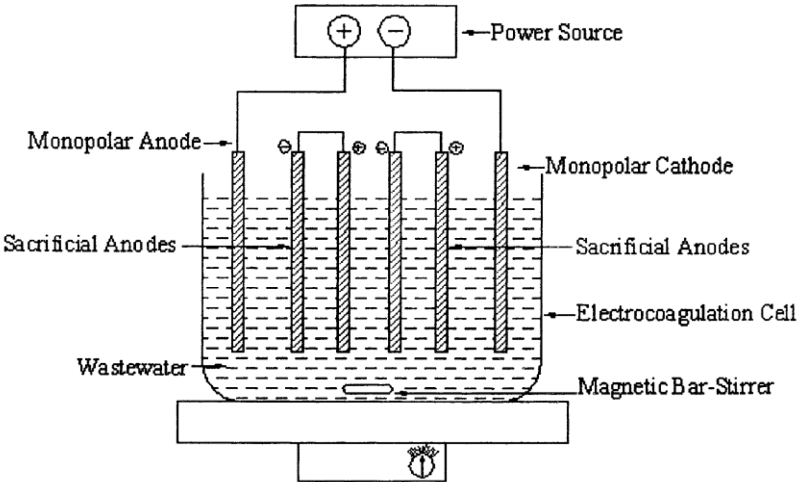


Figure 4. Bench-scale EC reactor with monopolar electrodes in series connection

In series cell arrangement, a higher potential difference is required for a given current to flow because the cells connected in series have higher resistance. The same current would, however, flow through all the electrodes. On the other hand, in parallel arrangement the electric current is divided between all the electrodes in relation to the resistance of the individual cells.

(iii) An arrangement of an EC cell with bipolar electrodes in parallel is shown in Figure 5. The sacrificial electrodes are placed between the two parallel electrodes without any electrical connection. Only the two mono polar electrodes are connected to the electric power source with no interconnections between the sacrificial electrodes. This cell arrangement provides a simple set-up, which facilitates easy maintenance during use. When an electric current is passed through the two electrodes, the neutral sides of the conductive plate will be transformed to charged sides, which have opposite charge compared to the parallel side beside it. The sacrificial electrodes in this case are also known as bipolar electrodes (Pouet et al., 1995, and Mameri et al., 1998).

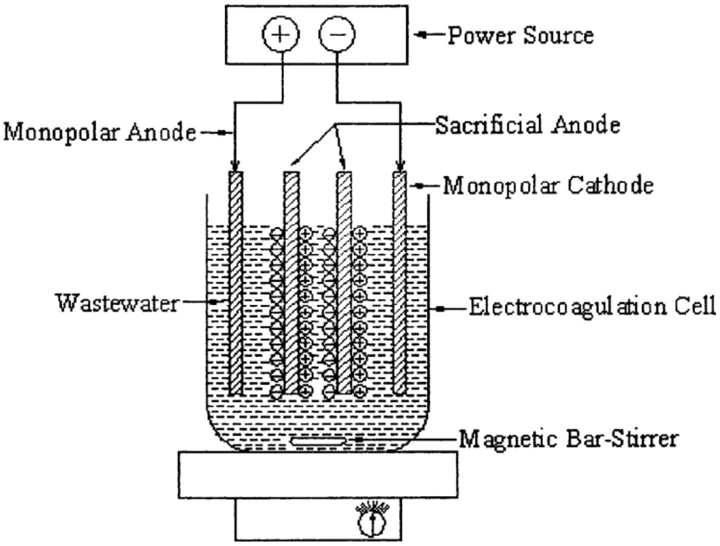


Figure 5. Bench-scale EC reactor with bipolar electrodes in parallel connection

3.2 Theory of EC

It is generally accepted that the EC process involves three successive stages: (a) formation of coagulants by electrolytic oxidation of the ‘sacrificial electrode’; (b) destabilization of the contaminants, particulate suspension; (c) aggregation of the destabilized phases to form flocs.

The destabilization mechanism of the contaminants, particulate suspension, has been described in broad steps and may be summarized as follows:

1. Compression of the diffuse double-layer around the charged species, which is achieved by the interactions of ions generated by dissolution of the sacrificial electrode, due to passage of current through the solution.
2. Charge neutralization of the ionic species present in wastewater, which is caused by the counter ions, produced by the electrochemical dissolution of the sacrificial electrode. These counter ions reduce the electrostatic inter particle repulsion sufficiently so that the vander Waals attraction predominates, thus causing coagulation. A zero net charge results in the process.
3. Floc formation, and the floc formed as a result of coagulation creates a sludge blanket that entraps and bridges colloidal particles that have not been complexed (Mollah et al., 2001).

Reaction types involved in the EC process as described by Hansen et al. (2007) are:

For iron electrode:

Mechanism 1

At anode:

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

$4Fe^{2+}{}_{(aq)} + 10\ H_2O_{\ (l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H+_{\ (aq)}$

At cathode:

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

Overall:

$4\ Fe_{(s)} + 10\ H_2O_{\ (l)} + O_{2\ (g)} \rightarrow 4\ Fe\ (OH)_{\ 3(s)} + 4\ H_{2\ (g)}$

Mechanism 2

At anode:

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

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

At cathode:

$2\ H_2O_{\ (l)} + 2e- \rightarrow H_{2\ (g)} + 2OH^{-}{}_{(aq)}$

Overall:

$Fe_{(s)} + 2\ H_2O_{(l)} \rightarrow Fe(OH)_{2\,(s)} + H_{2\,(g)}$

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

$Fe(OH)_{3\,(s)} + AsO_4^{3-}\,(aq) \rightarrow [Fe(OH)_{3} * AsO_4^{3-}]_{(s)}$

3.3 Advantages of EC

EC requires simple equipment and is easy to operate with sufficient operational latitude to handle most problems encountered on running. It is a low sludge producing technique and the sludge formed by EC tends to be readily settable and easy to de-water, because it is composed of mainly metallic oxides/hydroxides. Flocs formed by EC are similar to chemical floc, except that EC floc tends to be much larger, contains less bound water, is acid-resistant and more stable, and therefore, can be separated faster by filtration. The EC process has the advantage of removing the smallest colloidal particles, because the applied electric field sets them in faster motion, thereby facilitating the coagulation. The EC process avoids uses of chemicals, and so there is no problem of neutralizing excess chemicals and no possibility of secondary pollution caused by chemical substances added at high concentration as when chemical coagulation of wastewater is used. The gas bubbles produced during electrolysis can carry the pollutant to the top of the solution where it can be more easily concentrated, collected and removed. The electrolytic processes in the EC cell are controlled electrically with no moving parts, thus requiring less maintenance. The EC technique can be conveniently used in rural areas where electricity is not available, since a solar panel attached to the unit may be sufficient to carry out the process.

3.4 Disadvantages of EC

The ‘sacrificial electrodes’ are dissolved into wastewater streams as a result of oxidation, and need to be regularly replaced. The use of electricity may be expensive in many places. An impermeable oxide film may be formed on the cathode leading to loss of efficiency of the EC unit. High conductivity of the wastewater suspension is required. Gelatinous hydroxide may tend to solubilize in some cases (Mollah et al., 2001).

CHAPTER-4

LITERATURE REVIEW

Several investigations have been worked on the removal of arsenic by electro-coagulation. These are reported below.

Eilen et al. (1984) studied the electro-coagulation of potable water. They gave the following correlation between the current density and aluminum dosing and provided results showing the necessary over potential to effect electro coagulation. Their correlations are:

Aluminum dosing: $W = itM / ZF$ (4.1)

where

W = Aluminum dissolving (g Al/cm^2)

i = Current density (A cm $^{-2}$)

M =Molecular weight of Al (M=27)

Z = Number of electrons involved in reaction.

F = Faraday's constant

Applied over potential: $\eta_{AP} = \eta_K + \eta_{Mt} + \eta_{IR}$ (4.2)

where

η_{AP} = Applied over potential (V)

η_K = Kinetic over voltage (V)

η_{Mt} = Mass transfer over voltage (V)

η_{IR} = Potential caused by solution resistance (V), IR drop.

The amount of chemical, which has been to be transported, was lower than the conventional treatment (approx 1/10 of the amount) and a lesser amount of sludge was formed, because of the higher dry solids content.

Mameri et al. (1998) studied the electro coagulation process with aluminum bipolar electrodes. The influence of such parameters as inter-electrode distances, fluoride concentration, temperature and pH of solution, were investigated and optimized with synthetic water in batch mode. The optimization process was continued with Oued Souf (South Algeria) water where the influence of current density and area/volume ratio on the defluorination process was evaluated. With the use of bi-polar electrodes several advantages were observed such as more efficient current distribution. The use of bi-polar electrodes induces a reduction of the necessary time of the treatment and an increase of the anode area. They used a magnetic stirring (40 rpm) to have a homogeneous solution in the electrochemical reactor in batch mode and aluminum electrode purity was about 99.5 %.

The current efficiency (C_E) is calculated by using the equation:

$$C_E \% = (1 - m_c)/m_t * 100 \qquad (4.3)$$

Where $m_t =$ Theoretical mass obtained by using the Faraday equation.

$m_c =$ Electrode mass difference before and after electro-coagulation process.

Current efficiency is superior to 100 % for the batch mode. The process efficiency decreases with increase in temperature, and deflourination process was found to be more efficient for a pH ranging from 5 to 7.6. The increase in anode area i.e. increases of the A/V parameter induces a decrease of necessary time for a given current density. The inter-electrode distance is chosen in the range of 5 to 30 mm. With small inter-electrode distance, the gas, which was blown in the cathode compartment, induces the floating of the flouro aluminium complex formed on the anode electrode. However, for short inter-electrode distances the current density becomes too high and can cause short-circuiting. Therefore, the experiment had been conducted with an inter-electrode distance of 20 mm, with larger ohmic resistance.

Mollah et al. (2000) studied electro-coagulation is an evolving technology that is being effectively applied today for wastewater treatment, the paucity of scientific understanding of the complex chemical and physical processes involved is limiting future design and hindering progress. Chemistry and physical processes involved into perspective are fully explained.EC process involves three successive stages: (a) formation of coagulants by electrolytic oxidation of the ‘sacrificial electrode’; (b) destabilization of the contaminants, particulate suspension, and breaking of emulsions; (c) aggregation of the destabilized phases to form flocs.

Gregor (2001) studied the effect of forms and concentrations of arsenic on its removal through aluminium-based coagulation treatment processes were tracked for three drinking water treatment plants. This has provided direct evidence of where and how arsenic is removed. In general, soluble As (V) is converted to particulate As (V) by adsorption during rapid mixing, and is removed along with naturally occurring particulate arsenic predominantly by clarification. Soluble As (III) tracks through the treatment processes and is converted to soluble As (V) during final chlorination. The ability of a water treatment process to achieve the maximum acceptable concentration for arsenic in drinking water is dependent on the concentration of As (III) in the source water.

Kumar et al. (2004) studied (EC) as a treatment technology for arsenite [As (III)] and arsenate [As(V)] removal from water. Laboratory scale experiments were conducted with three electrode materials namely, iron, aluminum and titanium to assess their efficiency. Arsenic removal obtained was highest with iron electrodes. EC was able to bring down aqueous phase arsenic concentration to less than 10 µg $l^{-}1$ with iron electrodes. Current density was varied from 0.65 to1.53 mAcm^{-2} and it was observed that higher current density achieved rapid arsenic removal. Effect of pH on arsenic removal was not significant in the pH range 6–8. Comparative evaluation of As (III) and As (V) removal by chemical coagulation (with ferric chloride) and electro-coagulation has been done. The comparison revealed that EC has better removal efficiency for As (III), whereas As (V) removal by both processes was nearly same. The removal mechanism of As (III) by EC seems to be oxidation of As (III) to As (V) and subsequent removal by adsorption / complexation with metal hydroxides generated in the process.

Hansen et al. (2005) had studied the continuous flow treatment consisted of an electro-coagulation reactor with two parallel iron plates and a sedimentation basin. The results showed that the electro-coagulation process of a 100 mg/L As (V) solution could decrease the arsenic concentration to less than 2 mg/L in the effluent with a current density of 1.2 A/dm^{2} and a residence time of around 9 min. Liquid flow was 3 L/h, and the DC current was reversed each 2 min. Increasing the current density from 0.8 to 1.2 A/dm2, the Fe^{3+} and OH^{-} dosages increase too, and thereby favoring the As removal. On the other hand, it seems that increasing the current density beyond a maximum value, the electro-coagulation process would not improve further. This is due to explained by passivation of the anode.

Cockea et al., (2005) had performed a study of introduction to the fundamental concepts of the EC method. In this study, powder X-ray diffraction, scanning electron microscopy, transmission Mossbauer spectroscopy and Fourier transform infrared spectroscopy were used to characterize the solid products formed at iron electrodes during the EC process. The results showed that magnetite particles and amorphous iron oxyhydroxides present in the EC products removed arsenic (III) and arsenic (V) with an efficiency of more than 99% from groundwater in a field pilot scale study.

Parga et al. (2006) studied combination of electrodes, such as aluminum and iron in a single electrochemical cell provide an alternative method for removal of arsenic from water by electro-coagulation. The removal process has been studied with a wide range of arsenic concentration (1–1000 ppm) at different pH (4–10). Analysis of the electrochemically generated by-products by XRD, XPS, SEM/EDAX, FT-IR, and Mossbauer Spectroscopy revealed the expected crystalline iron oxides (magnetite (Fe_3O_4), lepidocrocite (FeO(OH)), iron oxide (FeO)) and aluminum oxides (bayerite ($Al(OH)_{3)}$, diaspore (AlO(OH)), mansfieldite ($AlAsO_4{\cdot}2(H_2O)$)), as well as some interaction between the two phases. The amorphous or very fine particular phase was also found in the floc. The substitution of Fe^{3+} ions by Al^{3+} ions in the solid surface has been observed, indicating an alternative removal mechanism of arsenic in these metal hydroxides and oxy hydroxides by providing larger surface area for arsenic adsorption via retarding the crystalline formation of iron oxides.

Grandon et al. (2007) studied arsenic removal from wastewater is a key problem for copper smelters. This work shows results of electro-coagulation of aqueous solutions containing arsenic with three different process designs and operating parameters. Three types of electro-coagulation reactors were tested and compared: (a) a modified flow continuous reactor, (b) a turbulent flow reactor and (c) an airlift reactor. All used iron as sacrificial anodes. The results showed that the electro-coagulation process of a 100 mg/L As (V) solution could decrease the arsenic concentration to less than 2 mg/L in the effluent with a current density of 1.2 A/dm2 with both the modified flow and the airlift reactor. The removal of arsenic with the turbulent flow reactor did not reach the same level but the Fe-to-As ratio (mol/mol) achieved in the coagulation process was in this case lower (approximately 7) than with the other two reactors.

In addition, it seems that increasing the current density beyond a maximum value, the electro-coagulation process would not improve any further. This could probably be explained by passivation of the anode.

Srivastava et al. (2008) investigated the removal of arsenic (As) and chromium (Cr) from aqueous solution by electro coagulation using iron electrodes to evaluate the influence of various experimental parameters on the removal of metal ions. The parameters were initial pH, electrolysis time, initial concentration, electrode gap, stirring rate and current density. Optimum value of initial pH and current density for As and Cr removal were found to be 4.0 and 2.0; and 75 and 50 A/m^2, respectively. Removal efficiency increased with decrease in the initial concentration and electrode gap. The stirring rate of 100 rpm produced sufficient agitation for the proper agglomeration of flocs and optimum removal of ions.

Arslan et al. (2009) studied the treatability of a metal plating wastewater containing complexed metals originating from the nickel and zinc plating process by electro-coagulation using stainless steel electrodes was experimentally investigated. The study focused on the effect of important operation parameters on electro coagulation process performance in terms of organic complex former, nickel and zinc removals as well as sludge production and specific energy consumption. The results indicated that increasing the applied current density from 2.25 to 9.0mA/cm^2 appreciably enhanced TOC removal efficiency from 20% to 66%, but a further increase in the applied current density to 56.25mA/cm^2 did not accelerate TOC removal rates. Electrolyte concentration did not affect the process performance significantly and the highest TOC reduction (66%) accompanied with complete heavy metal removals were achieved at the original chloride content (≈1500mg Cl/L) of the wastewater sample. Nickel removal performance was adversely affected by the decrease of initial pH from its original value of 6. Optimum working conditions for electro-coagulation of metal plating effluent were established as follows: an applied current density of 9mA/cm^2, the effluent’s original electrolyte concentration and pH of the composite sample. TOC removal rates obtained for all electro-coagulation runs fitted pseudo-first-order kinetics very well.

Villafane et al. (2009) studied the effect of design and operation conditions of an electrochemical reactor on the treatment time for arsenic (As) removal from underground water. Experiments were carried out to analyse the energy and electrode consumption. The effects of various factors such as, current density, inter-electrode distance, electrode area–volume ratio, and liquid motion driving mode were evaluated. The response variables were the energy and the electrode consumption and the treatment time to reduce the ground water residual As concentration to $10 \mu g L^{-1}$, which is the maximum contaminant level, established by the World Health Organization (WHO) in drinking water. The results obtained showed that the factor that had the greatest effect on most of the response variables was the liquid motion driving mode. The best residence time was 20 s, which favoured low energy consumption ($58.78 Whm^{-3}$) and low electrode material loss (9.59 g m^{-3}).

Balasubramanian et al. (2009) studied removal of arsenic from aqueous solution. Removal was carried out using electro-coagulation. Experiments were conducted using mild steel sacrificial anode covering wide range in operating conditions to assess the removal efficiency. The maximum arsenic removal efficiency was reported as 94% under optimum conditions. Further the experimental data were tested with different adsorption isotherm model to describe the electrocoagulation process.

Lakshmipathiraj et al. (2010) studied the arsenic removal from aqueous solutions by electro-coagulation using mild steel electrodes. Effect of electrolytes such as NaCl, $NaNO_3$ and Na_2SO_4 on anodic dissolution of iron and in turn the arsenic removal was deliberated. The arsenic removal was observed to be 98% in the presence of NaCl whereas it is around 75% in the presence of Na_2SO_4 and $NaNO_3$. The removal of arsenic by EC process was found to be almost similar irrespective of its oxidation state.

Objectives of the proposed work

The following objectives were set for the present work:

- To investigate the effectiveness of batch electro-coagulation process for arsenic removal.
- To study the effect of following parameters on arsenic removal:
  a) pH
  b) Current density
  c) Inter-electrode spacing

CHAPTER-5

EXPERIMENTAL SETUP AND PROCEDURE

Direct current electro-coagulation technique was used for arsenic removal from drinking water. Electrolysis was conducted in a batch setup to investigate the effect of pH, current density and inter-electrode spacing on electrode spacing.

5.1 Experimental setup

The EC reactor having three liter of capacity was fabricated with acrylic sheet of thickness 5 mm. Iron plates (12.2 cm × 7.8 cm) with a thickness of 1 mm were used as the electrodes for the experiments. EC reactor with mono-polar electrodes connected in parallel was used in the experiments. A regulated direct current supply (0–30 V, 15 A, Make Crown Electronics Delhi, India) was used for the experiments. The experimental setup is shown in Figure 6.

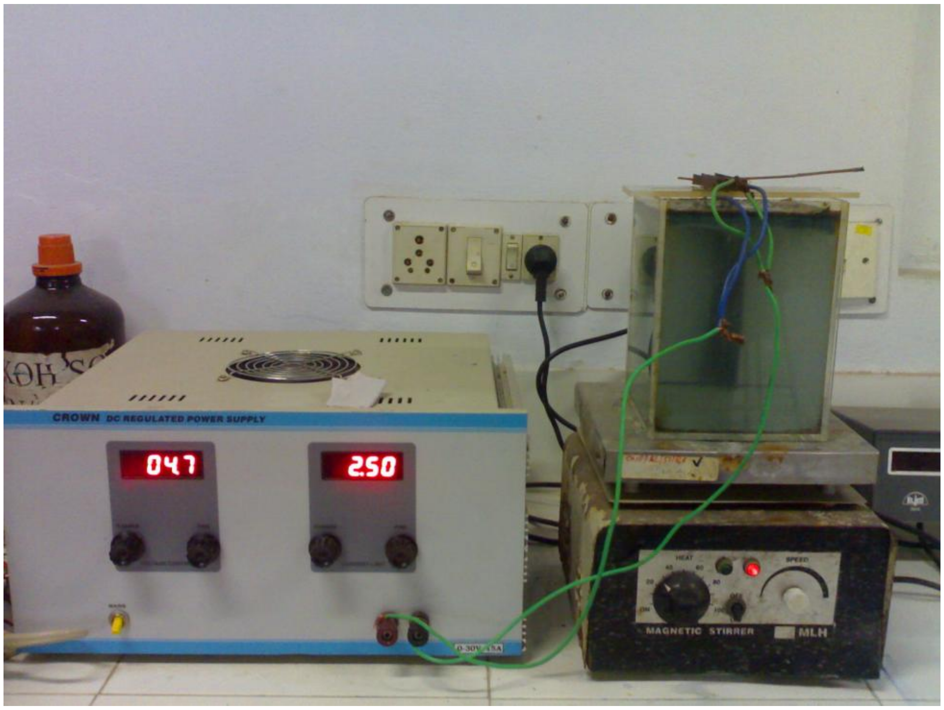


Figure 6. Electro-coagulation set up

5.2 Preparation of sample

The chemicals used were analytical reagent grade. The arsenate solution was prepared from the sodium arsenate, $Na_2HAsO_4 .7H_2O$, procured from (Loba Chemie Private Ltd. Mumbai). The stock solution was prepared by dissolving 0.416 gm of sodium arsenate in 100 ml distilled water [1ml = 1mg As (V)]. The intermediate arsenic solutions were freshly prepared before each experiment. The arsenic sample solution was prepared by dissolving appropriate amount of intermediate solution in tap water. The pH of the sample solution remained in 7.12 to 7.36 range.

5.3 Experimental procedure

The complete experimental procedure is as follows:

1. The sample solution was prepared from the stock solution as required.
2. The pH of the solution was adjusted by adding either dilute HCl or NaOH as per the requirement.
3. Before each experiment, the electrodes were abraded with sand paper to remove scale and then cleaned with successive rinses of water and 1 N H_2SO_4.
4. The electrodes were weighed before and after each run.
5. The inter-electrode spacing was fixed as per the requirement.
6. DC power supply was used to pass 1.5, 2, and 2.5 A current at 4.5 - 5 V.
7. Proper agitation was done by using magnetic stirrer.
8. The samples were taken for residual arsenic analysis.

5.4 Analysis of arsenic in water

Various methods are use for detecting Arsenic in the water. The mainly used methods are as follows:

- Spectrophotometric Methods
- Atomic Absorption Spectrometry (AAS)
- AAS with Hydride Generation Techniques (HG)

In the present work, AAS with Hydride generation technique has been used for arsenic detection. The apparatus is present in Thapar Centre for Industrial Research and Development at Thapar Technology Campus, Patiala.

The hydride technique allows the matrix free determination of the hydride forming elements As, Bi, Sb, Se, Sn and Te. It makes use of the fact that hydrogen, which is liberated when sodium tetrahydridoborate ($NaBH_4$) used as reactant with the weakly to strongly acid sample solutions, forms gaseous metal hydrides with metal ions present. The metal hydrides are conveyed by argon (carrier gas) and by liberated hydrogen to the heated quartz cell where they are decomposed in steps by impact processes with gas particles and the silica glass wall at temperature of 850°C to 1000° C depending on the element until free metal atoms have been generated these adsorb the primary radiation at the resonance line.

The advantage of hydride technique is that spectral interference are virtually ruled out because only the element determined enters the atomizer as gaseous metal hydride. The AAS with Hydride generation technique has been shown in Figure 7.

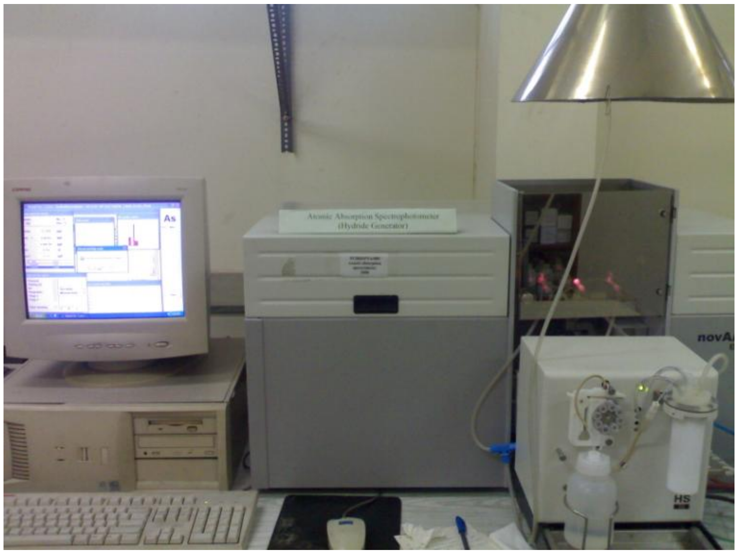
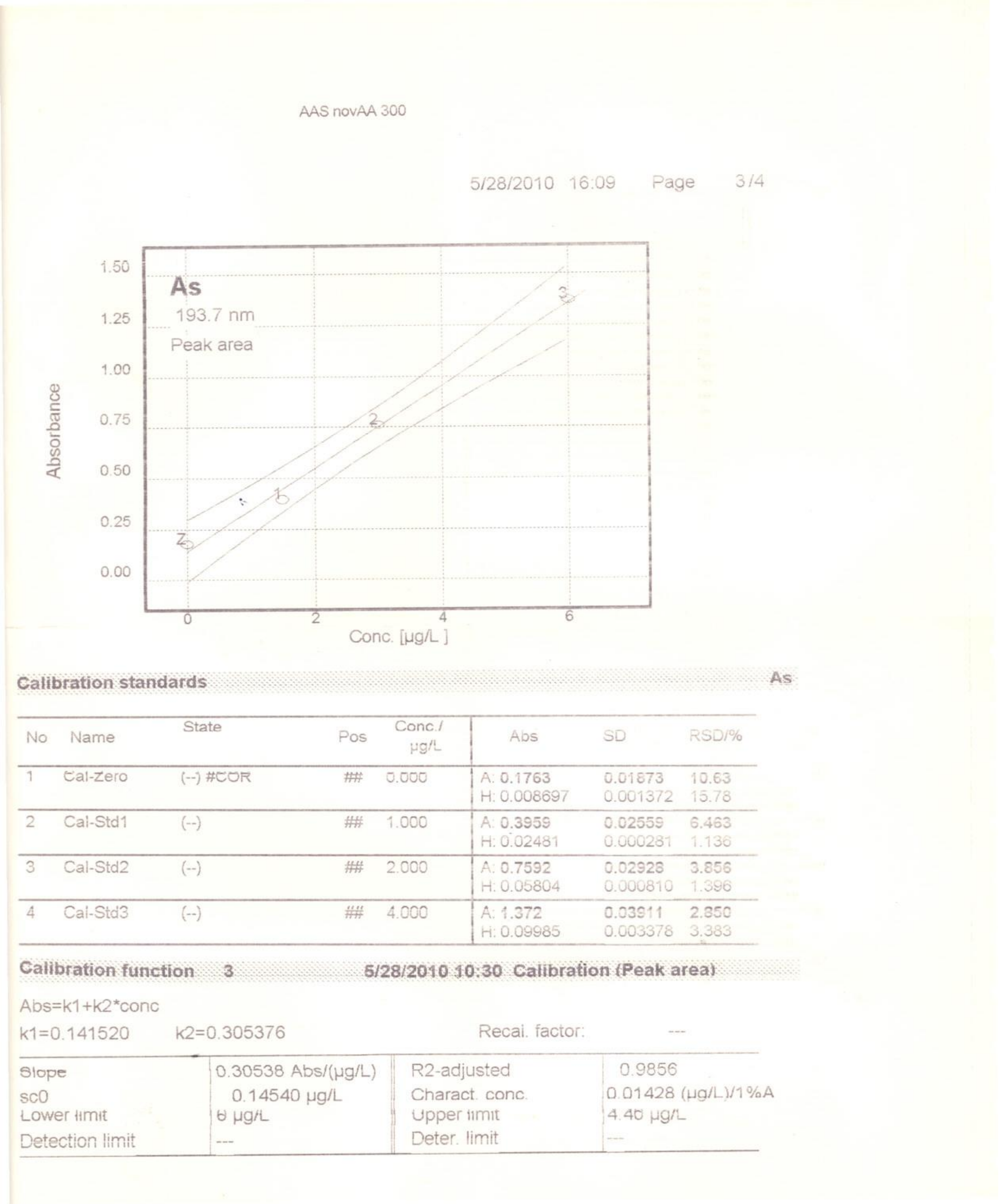


Figure7. Atomic Absorption Spectrometry with Hydride Generation Techniques (HG)

Calibration Curve:

The calibration curve of AAS with hydride generation has been shown below:



AAS novAA 300

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Calibration standards **As**

No	Name	State	Pos	Conc./ μg/L	Abs	SD	RSD/%
1	Cal-Zero	(--) #COR	##	0.000	A: 0.1763 H: 0.008697	0.01873 0.001372	10.63 15.78
2	Cal-Std1	(--)	##	1.000	A: 0.3959 H: 0.02481	0.02559 0.000281	6.463 1.136
3	Cal-Std2	(--)	##	2.000	A: 0.7592 H: 0.05804	0.02928 0.000810	3.856 1.396
4	Cal-Std3	(--)	##	4.000	A: 1.372 H: 0.09985	0.03911 0.003378	2.850 3.383

Calibration function 3 5/28/2010 10:30 Calibration (Peak area)

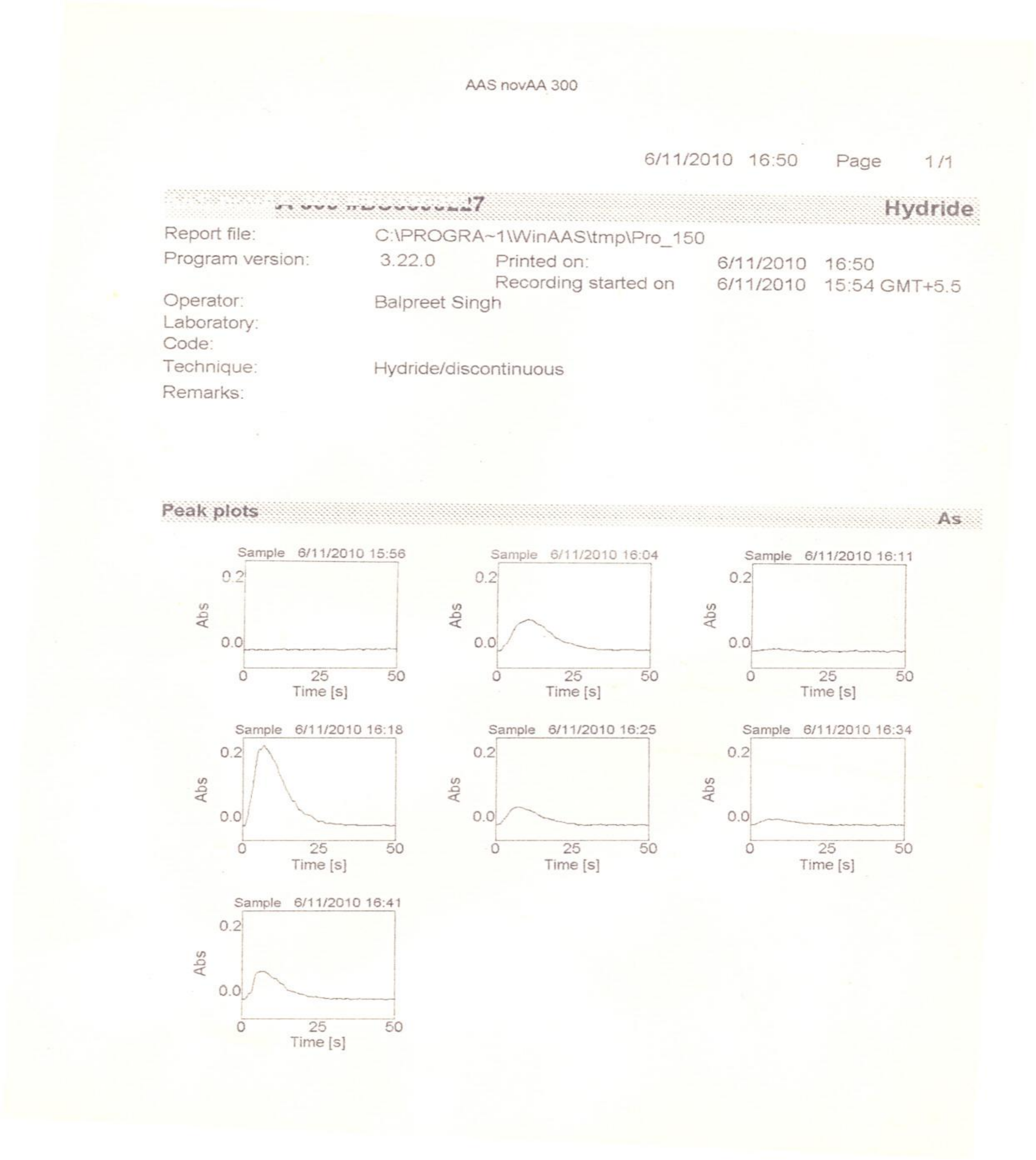
Abs=k1+k2*conc

k1=0.141520 k2=0.305376 Recal. factor: ---

Slope	0.30538 Abs/(μg/L)	R2-adjusted	0.9856
sc0	0.14540 μg/L	Charact. conc.	0.01428 (μg/L)/1%A
Lower limit	0 μg/L	Upper limit	4.40 μg/L
Detection limit	---	Deter. limit	---

Absorption curve:

Depending on the element free metal atoms generates, these adsorb the primary radiation at the resonance line. This is represented in the form chart given below.



AAS novAA 300

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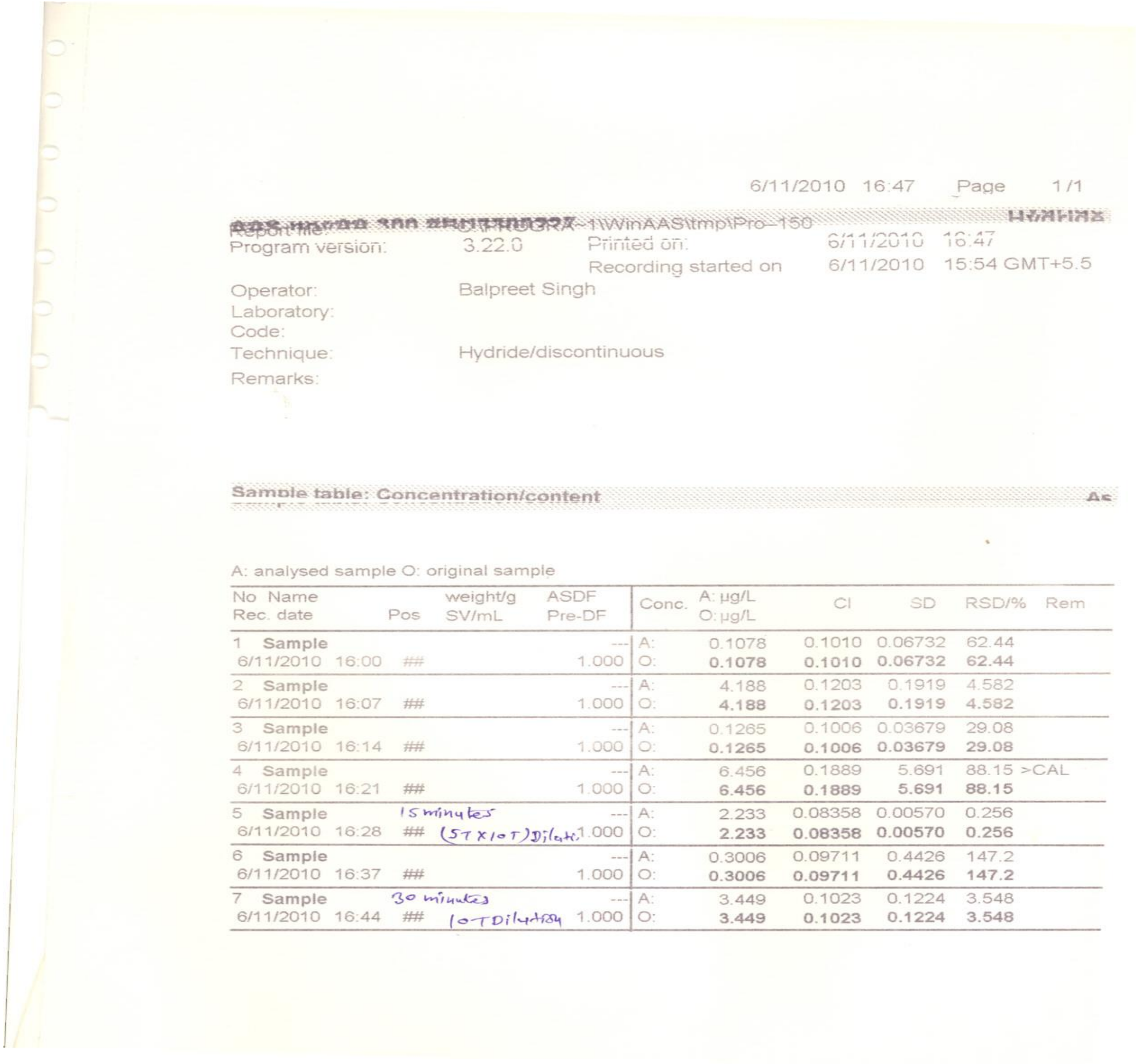
[illegible]7 **Hydride**

Report file: C:\PROGRA~1\WinAAS\tmp\Pro_150
Program version: 3.22.0
Printed on: 6/11/2010 16:50
Recording started on 6/11/2010 15:54 GMT+5.5
Operator: Balpreet Singh
Laboratory:
Code:
Technique: Hydride/discontinuous
Remarks:

Peak plots **As**

Results' report:

The result is given in the form of following table.



6/11/2010 16:47 Page 1 /1

Report file: C:\PROGRA~1\WinAAS\tmp\Pro–150

Program version: 3.22.0 Printed on: 6/11/2010 16:47

Recording started on 6/11/2010 15:54 GMT+5.5

Operator: Balpreet Singh

Laboratory:

Code:

Technique: Hydride/discontinuous

Remarks:

Sample table: Concentration/content As

A: analysed sample O: original sample

No Name Rec. date	Pos	weight/g SV/mL	ASDF Pre-DF	Conc.	A: µg/L O: µg/L	CI	SD	RSD/%	Rem
1 **Sample**			---	A:	0.1078	0.1010	0.06732	62.44	
6/11/2010 16:00	##		1.000	O:	**0.1078**	**0.1010**	**0.06732**	**62.44**	
2 **Sample**			---	A:	4.188	0.1203	0.1919	4.582	
6/11/2010 16:07	##		1.000	O:	**4.188**	**0.1203**	**0.1919**	**4.582**	
3 **Sample**			---	A:	0.1265	0.1006	0.03679	29.08	
6/11/2010 16:14	##		1.000	O:	**0.1265**	**0.1006**	**0.03679**	**29.08**	
4 **Sample**			---	A:	6.456	0.1889	5.691	88.15	>CAL
6/11/2010 16:21	##		1.000	O:	**6.456**	**0.1889**	**5.691**	**88.15**	
5 **Sample**		15 minutes	---	A:	2.233	0.08358	0.00570	0.256	
6/11/2010 16:28	##	(5T x 10T) Dilati	1.000	O:	**2.233**	**0.08358**	**0.00570**	**0.256**	
6 **Sample**			---	A:	0.3006	0.09711	0.4426	147.2	
6/11/2010 16:37	##		1.000	O:	**0.3006**	**0.09711**	**0.4426**	**147.2**	
7 **Sample**		30 minutes	---	A:	3.449	0.1023	0.1224	3.548	
6/11/2010 16:44	##	10T Dilution	1.000	O:	**3.449**	**0.1023**	**0.1224**	**3.548**	

CHAPTER-6

RESULTS AND DISCUSSION

The experiment results of arsenic removal from drinking water by electro coagulation are presented in this chapter. The treatment process has to ensure that arsenic concentration in the supernatant is within the permissible limit of 10 ppb as prescribed by WHO. Therefore the concentration of arsenic in treated water is more important than the percentage of arsenic removed.

6.1 Effect of pH on arsenic removal

The result has been discussed at current density of 6.57 mA/cm^2, 5V and at an inter-electrode spacing of 1cm. The pretreated sample was found to have arsenic content of 1194 ppb. The treated water sample was analyzed after the experimental run. The results are given in Table 1 and Figure 8.

Table 1. Effect of pH on arsenic removal

Sr. No	Initial pH of the sample	Residual Arsenic content (ppb)
1.	**5**	**17.36**
2.	**6**	**6.558**
3.	**7**	**4.523**
4.	**8**	**1.244**

The results show that with increasing pH the residual arsenic content in the water decreases. At low pH the solution protons were reduced at the cathode to H_2 and the same proportion of hydroxide ions cannot be produced. Effect of pH on arsenic removal was not significant in the pH range 6–8. Kumar et al. (2004) in their work have also made the similar observation. The further experimentations were performed at pH of 7 as the drinking water is near to this range.

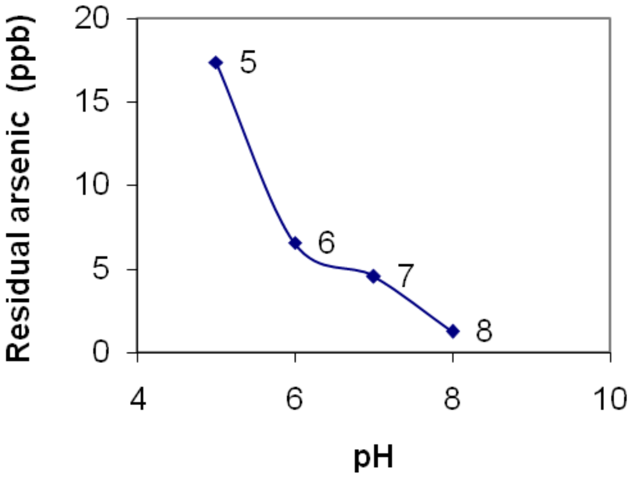


Figure 8. Effect of pH on arsenic removal

Variation in pH with time:

The pH of the water increased with time of electro-coagulation as shown in Table 2 and Figure9. The initial pH for this run was 7.12. The current density was kept at 6.57 mA/cm^2.

Table 2. Variation of pH with time

Sr. No.	**Time (min)**	**pH**
1	0	7.12
2	10	7.18
3	20	8.05
4	30	8.38
5	40	8.56

The pH increase in electro-coagulation is attributed to formation of hydrogen gas at the cathode, also a slight increase in pH may be caused by the sorption reaction of As (V) which release OH^- groups from sorbents as a result of ligand exchange (Kumar et al., 2004).

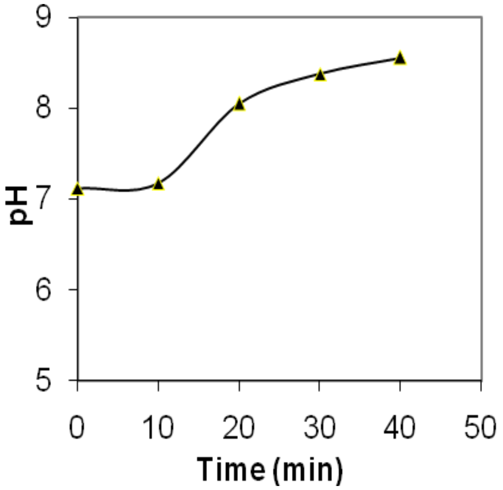


Figure 9. Variation of pH with time

6.2 Effect of current density on arsenic removal

The arsenic removal by electro-coagulation process is affected by applied current density. Different set of experiments was performed at current density varying from 3.94 to 6.54 mA/cm^2. The inter-electrode spacing was kept at 1cm. it was found that electro-coagulation gave the best result when current density was near 6.54 mA/cm^2 with current at 2.50 A for a four electrode system. At this current density the residual arsenic content is 10 ppb in 40 minute of electrolysis time as shown in Table 3 and Figure 10.

Table 3. Effect of current density on arsenic removal

Sr. No.	**Time (min)**	**Residual arsenic (6.54 mA/cm^2)**	**Residual arsenic (5.25 mA/cm^2)**	**Residual arsenic (3.943mA/cm^2)**
1	0	1192.2	1192	1192
2	10	129.2	192.7	200
3	20	123.6	101.2	66.69
4	30	22.5	38.3	32.75
5	40	10	17.88	19.59

The higher the current, the shorter the treatment required. This is ascribed to the fact that at high current density, the extent of anodic dissolution of iron increases, resulting in a greater amount of precipitate for the removal of pollutants. Moreover, bubble generation rate increases, bubble size decreases, greater upward flux and hence faster removal of arsenic can be seen with increasing current density. These effects are both beneficial for high pollutant/ arsenic removal by H_2 flotation. Several other researchers have made this observation.

The most of the arsenic removal occurred within 10 minute of the electrolysis time as shown in Figure 10. After the initial time period, the removal rate decreased gradually for rest of the processing time. Arsenic ions are more abundant at the beginning of the EC process, and the generated iron hydroxides due to corrosion of the anode at that time will form complexes with arsenic and therefore rapid removal of arsenic was observed. However, as the experiment proceeds the aqueous phase arsenic concentration goes on decreasing and simultaneously hydrous ferric oxides concentration increases, thereby abundance of hydrous ferric oxides occur at the end of the process.

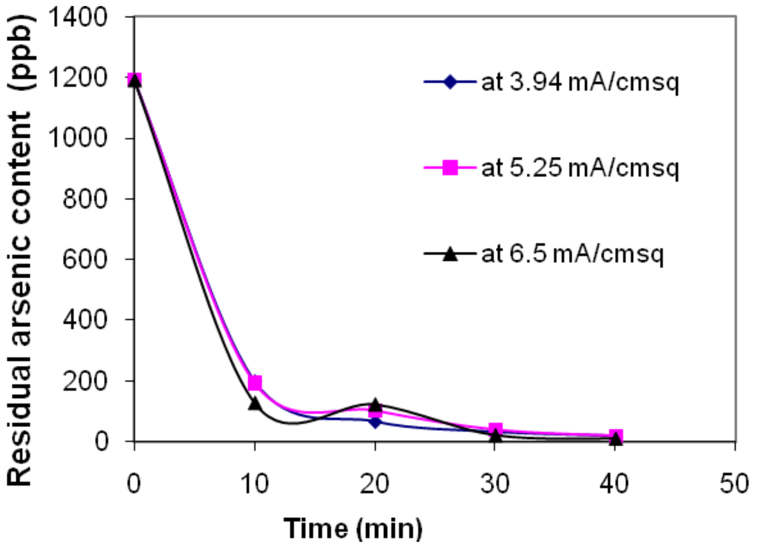


Figure 10. Effect of Current density on arsenic removal

A comparison was made between Theoretical and Experimental electrode dissolve in EC are shown in Figure 11. The experimental value has been calculated by weighing the iron electrodes (anodes) before and after EC whereas, theoretical values has been calculated using correlation given below:

$$W = itM\ /\ ZF$$

where,

W = Iron dissolving (g Fe/cm^2)

i = Current density (A cm^{-2})

M =Molecular weight of Fe (M=55.84)

Z = Number of electrons involved in reaction.

F = Faraday's constant

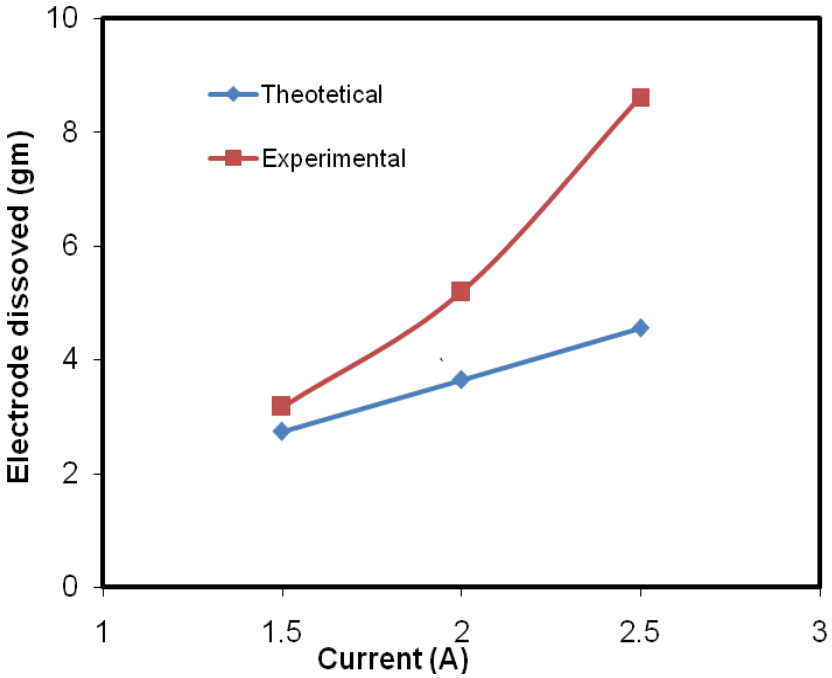


Figure 11. Theoretical and experimental electrode dissolved

6.3 Effect of inter-electrode spacing on arsenic removal

The experiments were carried out at 6.57 mA/cm^2 and 5 V. The experiment was performed at pH of 7. The inter electrode spacing was varied to see the effect on arsenic content in the treated sample. The comparison was made after 30 minutes of experiment run. The results obtained are reported in Table 4 and Figure 12.

Table 4. Effect of inter-electrode spacing on arsenic removal

Sr. No	**Inter-electrode spacing (cm)**	**Concentration (ppb)**
1.	**0.5**	**22.62**
2.	**1**	**22.51**
3.	**1.5**	**34.49**

With short inter-electrode distances the current density becomes too high and can cause short-circuiting. There is not much difference in the results for lowering the electrode spacing beyond 1 cm inter-electrode spacing, due to hydrogen gas evolved at the cathode increases the electrolytic resistance for very small inter-electrode spacing. Paul (1996) has also made this observation.

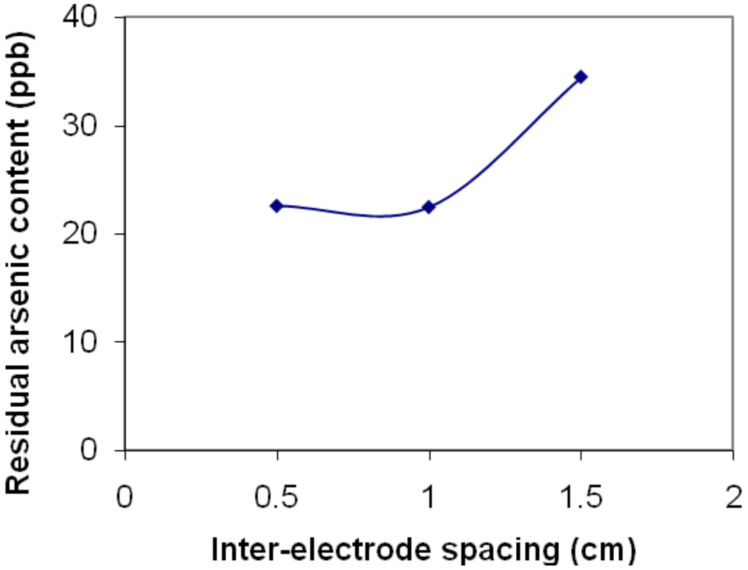


Figure 12. Effect of inter-electrode spacing on arsenic removal

6.4 Sludge formation during electro-coagulation

During electro-coagulation, oxide sludge produced instantaneously floats due to the electrolytically generated hydrogen bubbles. The sludge produced at the top surface has been shown in the Figure 13.

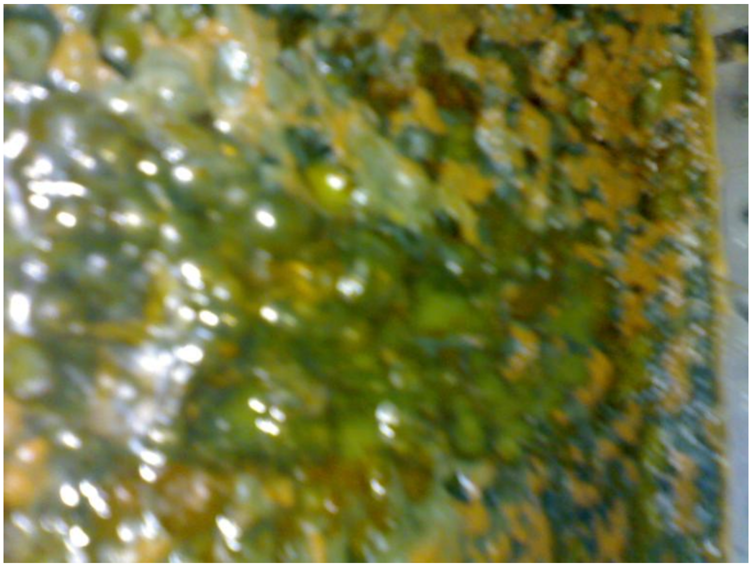


Figure 13. Sludge produced during electro-coagulation at the surface

The sludge produced during electro-coagulation was analyzed using X-ray diffraction (XRD) spectrum. Figure 14 and 15, shows the XRD pattern of the top and bottom sludge taken in the powder form, respectively. Diffractogram was obtained by PAN analyticals X'Perto Pro X-ray diffractometer with CuKα (λ=1.542 Å) as a radiation source filtered with a Nickel filter. The XRD scans were recorded from 0 to 80 degrees with 10 seconds counting time for every step-width. Experiments were run at 45 kV and 40 mA.

The identified species were As-Fe and iron arsenate in crystalline form the top sludge. Parga et al., 2009, also observed the same phenomena. The bottom sludge was observed to be free from arsenate.

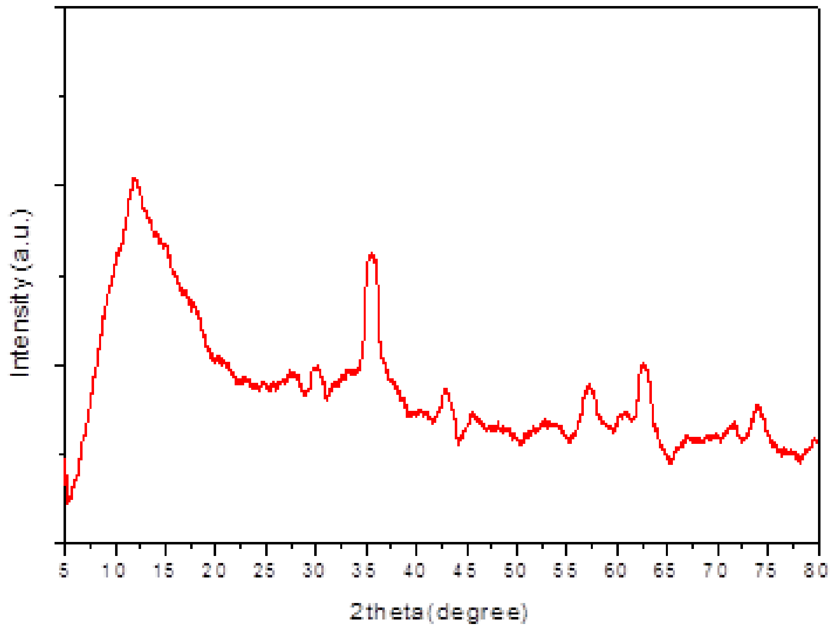


Figure 14. XRD pattern of the top sludge

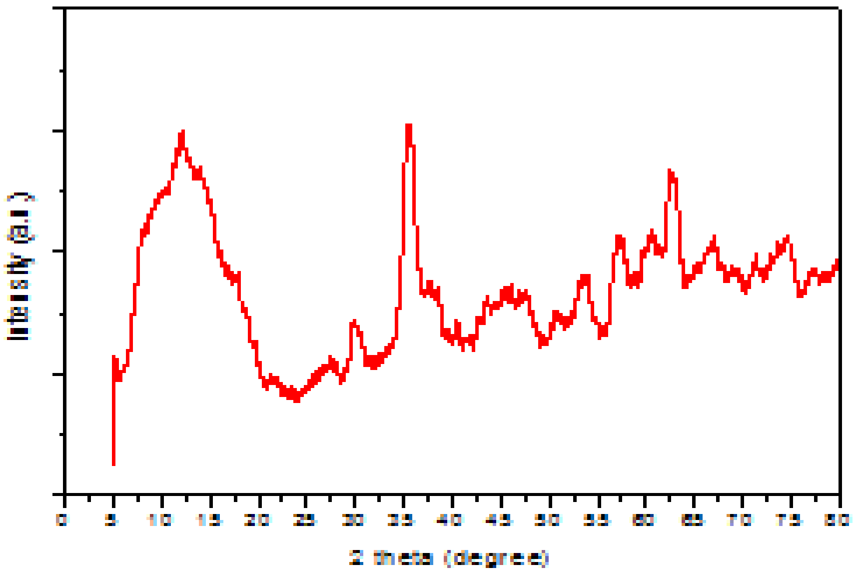


Figure15. XRD pattern of the bottom sludge

CHAPTER-7

CONCLUSIONS

Based on the present work the following conclusions can be drawn:

- pH of 7 was found to be most appropriate for treating the drinking water for arsenic removal by EC.
- With time pH increases but the increase is with in safety limit prescribed by WHO (as per the limit it is safe to drink water upto pH of 8.5).
- Arsenic removal improves with decreasing inter-electrode spacing. However, for inter-electrode spacing less than 1 cm further improvement in the arsenic removal was not observed.
- Better removal of arsenic was observed with increasing current density. It was found that for current density equal to 6.57 mA/cm^2 (with 2.5 A current) with four electrodes gave better result as compared to 3.94 and 5.25 mA/cm^2.
- It was possible to bring the residual arsenic content in the treated water within the permissible limit (10 ppb) in 40 minutes of electrolysis time.

Recommendations for future work

- The arsenic removal from drinking water by electro-coagulation may be studied in continuous mode for determining optimum process parameters using the arsenic contaminated water sample taken from the field.

- Feasibility studies of EC pilot plants for treating arsenic contaminated water may be carried out.

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