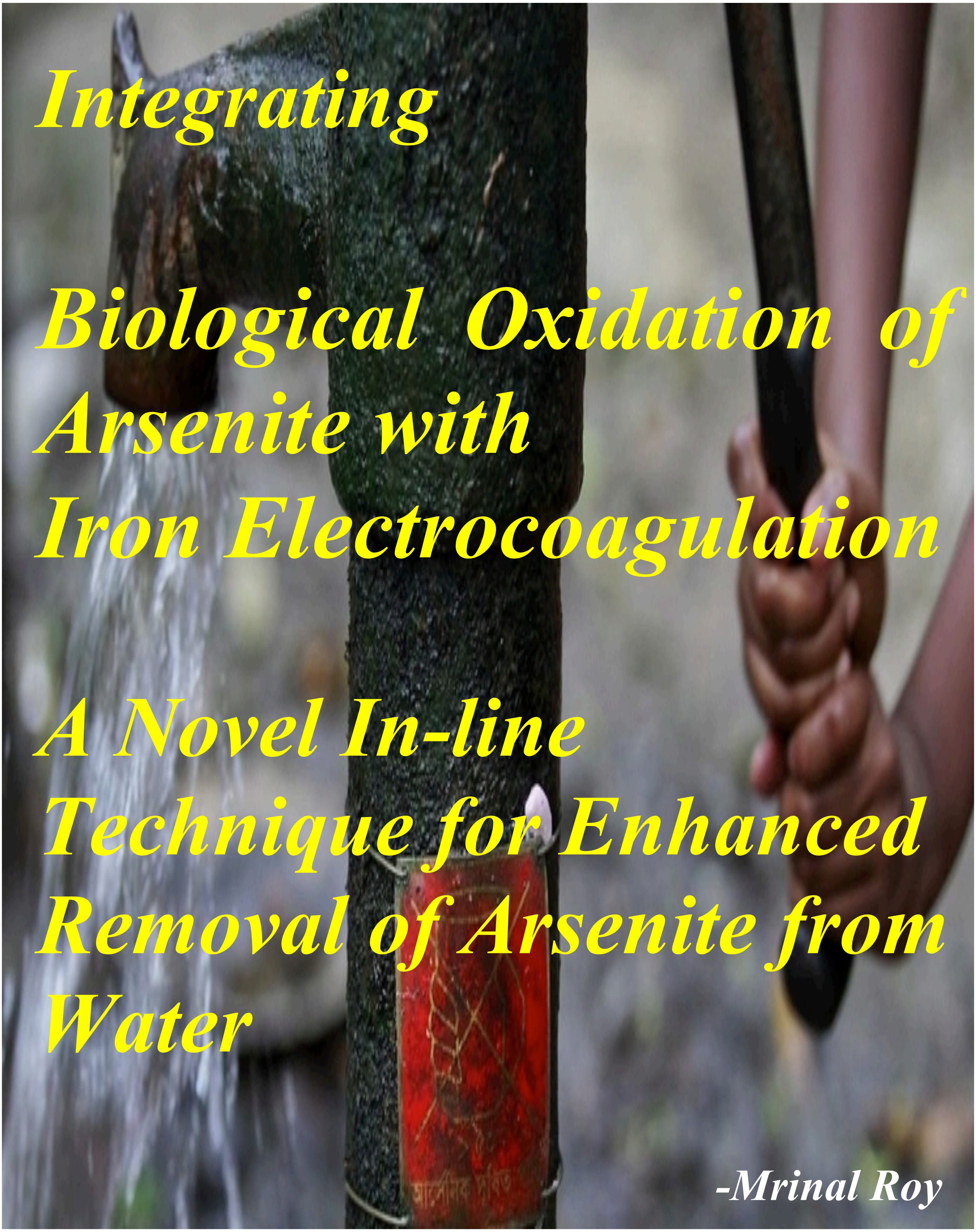

Integrating

Biological Oxidation of Arsenite with Iron Electrocoagulation

A Novel In-line Technique for Enhanced Removal of Arsenite from Water

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Integrating Biological Oxidation of Arsenite with Iron Electrocoagulation - A Novel In-line Technique for Enhanced Removal of Arsenite from Water

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Abstract

Human exposure to the toxic element arsenic due to consumption of arsenic contaminated water is still a global issue worldwide. Conventional treatment techniques are not very efficient at removing arsenite, which is the predominant species of arsenic in raw groundwater. Biological oxidation of arsenite by arsenic oxidizing bacteria (AsOB) has shown potential to effectively oxidize arsenite to arsenate without use of any chemicals. Arsenite is then effectively removed by adsorption or separation technologies. Iron Electrocoagulation (Fe-EC) is also emerging as an influential technique for arsenic removal that involves in-situ generation of iron coagulants using iron electrodes by electrolytic oxidation of anode. The main advantage of Fe-EC is that it does not require dosage of chemical coagulants so can be beneficial to communities with better access to electricity than chemicals.

This research work is done to combine the two techniques: biological oxidation of arsenite and Fe-EC, for better removal of arsenite from water. Batch studies on Fe-EC were performed in the laboratory to investigate the effects of charge dosage, charge dosage rate, initial arsenic concentration, arsenic oxidation state and different water matrices on the rate and extent of arsenic removal. Also, growth of AsOB on suitable bio-carrier was performed by continuous dosing of 150 µg/L arsenite-spiked water over a period of 49 days. The AsOB grown on the bio-carriers performed 90 % oxidation of 150 µg/L arsenite after a period of 35 days. Finally, two continuous flow system were developed one containing arsenite oxidation step by AsOB followed by Fe-EC and rapid sand filtration whereas the other contained only Fe-EC and rapid sand filtration. The system containing biological oxidation followed by Fe-EC removed arsenite below the WHO standard (10 µg/L) from an initial arsenite concentration of 150 µg/L at a low iron dosage compared to the system where only Fe-EC was applied.

Nomenclature

List of Acronyms

SBGW	Synthetic Bangladesh Groundwater
Fe-EC	Iron Electrocoagulation
TAs	Total Arsenic
As (III)	Arsenite
As (V)	Arsenate
Fe	Iron
Al	Aluminium
Ca	Calcium
Mg	Magnesium
Si	Silicon
Cl	Chlorine
DC	Direct Current
AsOB	Arsenic/Arsenite Oxidizing Bacteria
ARE	Arsenic Removal Efficiency
WHO	World Health Organization
CD	Charge Dosage
CDR	Charge Dosage Rate
MP-P	Monopolar Parallel
MP-S	Monopolar Serial
BP-S	Bipolar Serial
HFOs	Hydrous Ferric Oxides
DO	Dissolved Oxygen
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
rpm	Revolutions per minute

List of Symbols

mm/cm/m	millimeter/ centimeter/ meter
g/kg/ng/ µg	gram/ kilogram/ nanogram/ microgram
mM/M	millimoles/ moles
Eh	Redox potential
mA/A	milliampere/ Ampere
sec/min/hr	seconds/ minutes/ hours
L	Litre
w	Amount of electrode material dissolved (mg/L)
kWh	kilowatt hour
C	Coulomb
q	Charge dosage (C/L)
i	Current (A or mA)
t	Electrolysis time (sec)
M	Molecular weight of metal ion (mg/mol)
F	Faraday’s Constant (C/mol)
n_e	Number of electrons
V	Volume of solution (L)
J	Current density (mA/cm^2)
A_e	Active electrode area (cm^2)
dq/dt	Charge dosage rate (C/L/min)
C_{energy}	Consumption of energy per m^3 (kWH/m^3)
U	Potential of the EC reactor (V)
C_i	Initial arsenic concentration before EC, (µg/L)
C_f	Final arsenic concentration after EC, (µg/L)

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1. Introduction

1.1. Background

Arsenic (As) is a metalloid element belonging to Group VA in the periodic table. Its atomic number, atomic mass and density are 33, 74.92 amu and 5.72 g/m^3 respectively (Song et al., 2017; Nidheesh and Singh, 2017. Presence of arsenic has been reported throughout the environment specifically in air, soil, sediments, earth's crust, surface and groundwater's, etc. The presence of arsenic in the earth's crust is in the form of metals such as arsenides, arsenates and arsenic sulfides having concentrations of about 1.5 mg/L whereas in air, freshwater, soil and sea-water the concentrations are typically 3 ng/m^3, 10 µg/L, 100 mg/kg and 1.5 µg/L respectively (Mandal and Suzuki, 2002; WHO, 2011; Rieuwerts, 2015). In the environment arsenic is present in both organic and inorganic forms. Organic arsenic compounds include cacodylic acid ($C_2H_7AsO_2$), adamsite ($C_{12}H_9AsCIN$), mathylarsonic acid (CH_5AsO_3), etc (Nidheesh and Singh, 2017). The presence of these organic compounds are not very significant in groundwater but they are mainly present in surface water affected by industrial pollution (Smedley, 2008). In the environment, inorganic forms of arsenic are available in four oxidation states: +5 (arsenate), +3 (arsenite), 0 (metallic arsenic) and -3 (arsenide). Out of these four oxidation states, arsenite (As (III)) and arsenate (As (V)) are mainly found in water and wastewaters (Song et al., 2017). Both As (III) and As (V) are frequently found in sediments and water bodies under anaerobic and aerobic conditions (Panagiotaras and Nikolopoulos, 2015). However, under anaerobic condition As (III) is thermodynamically stable and is more prevalent whereas under aerobic condition As (V) is more stable and prevalent (Jiang, 2001). The oxidation state of the arsenic in a solution mainly depends on the redox potential and pH of the solution (Figure 1). From Figure 1 it can be seen that under reducing conditions arsenic is present mainly as As (III) and at pH 3-9 the main As (III) species is H_3AsO_3, which is neutral whereas at pH 9-11 it is in the form of $H_2AsO_3^-$, which is negatively charged. However, under oxidizing conditions the main arsenic species is As (V), which is present as negatively charged $H_2AsO_4^-$ at pH 3-7 and $HAsO_4^{2-}$ at pH 7-11 (Song et al., 2017).

The usage of arsenic and its compounds have been seen in industries, medicine, agriculture, etc. In industries it is mainly used for semiconductors, glass, transistors, dyes and pigments production whereas in agriculture it is used e.g. as insecticides and pesticides

(WHO, 2011; Singh et al., 2015). In spite of various applications of arsenic and its compounds, the use of various arsenic compounds have been banned because arsenic is very poisonous and have harmful effects on human health (van Halem, 2011). It is one of the 'big four' toxic non-essential elements (mercury, arsenic, lead and cadmium) and is considered as potential carcinogen for humans (Roy and Saha, 2002).

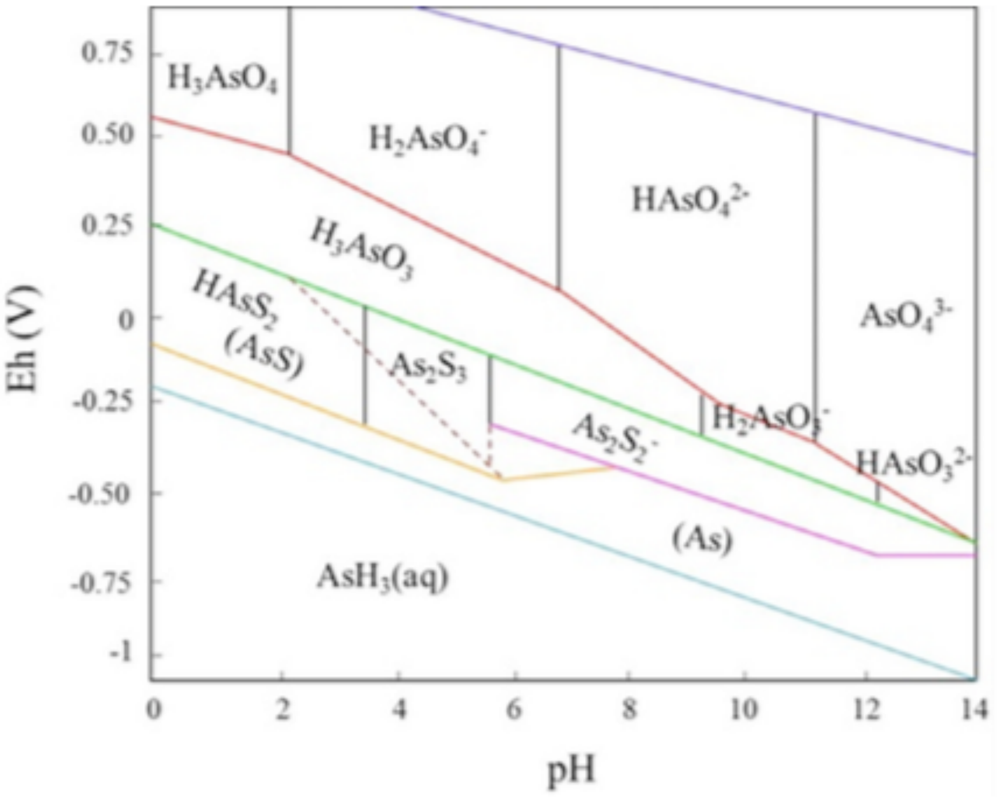


Figure 1: Eh-pH diagram for aqueous arsenic species (Song et al., 2017)

Humans are exposed to arsenic mainly by the consumption of water or food contaminated with arsenic or through use of cigarettes and cosmetics containing arsenic (Chung et al., 2014). However, the main exposure pathway is consumption of arsenic contaminated water, as arsenic compounds are readily dissolved in water (Wang and Mulligan, 2006). Arsenic contamination of water bodies are caused by natural and anthropogenic sources. Natural sources mainly cause contamination of groundwater whereas anthropogenic sources contaminate surface waters (Shankar et al., 2014). Arsenic contamination of groundwater by natural sources include: geothermally influenced groundwater, desorption in the oxidizing environment, mineral dissolution and reductive desorption and dissolution (van Halem, 2011). Anthropogenic sources include release of wastes or effluents (containing arsenic compounds) from industries involved in manufacturing of glass, cotton, wool, semiconductors, pesticides, etc., as well as from petroleum refineries, rare earth industries and chemical industries (Nidheesh and Singh, 2017). Also mining operations, hazardous waste sites and processing of ores can cause arsenic contamination of water sources (Duarte et al., 2009).

Arsenic pollution in groundwater has been a serious health issue for humans in USA, China, Taiwan, Mexico, Argentina, West Bengal (India) and Bangladesh. Of the various regions, India and Bangladesh were badly affected by arsenic, as majority of the population in these regions are dependent on groundwater (contaminated by arsenic due natural causes) from tube wells as primary source of water supply. Also, World Health Organization (WHO) has considered arsenic presence in Bangladesh groundwater as “the largest mass poisoning of a population in history” (Singh et al., 2015). To all life forms, arsenic is very toxic and World Health Organization (WHO) has classified it as a Group 1 carcinogenic substance (Singh et al., 2015). Of the various arsenic species, the inorganic ones are more toxic than the organic ones. Comparing for toxicity, As (III) is 25-60 times more toxic than As (V) and it is much more harmful to human health owing to its high genotoxic, cytotoxic, soluble and mobile nature (Nicomel et al., 2016). For human beings, long term exposure to arsenic through ingestion of arsenic-contaminated food or water as well as through contact with arsenic contaminated air, having concentration above 50 μg/L, leads to various diseases such as skin lesions and cancers, collectively termed as arsenicosis (Singh et al., 2015). Based on such harmful affects on human health, WHO restricted the concentration of arsenic in drinking water to 50 μg/L initially. However, owing to high carcinogenic threat at 50 μg/L, the level was reduced to 10 μg/L in 1993 (Nidheesh and Singh, 2017).

Arsenic removal from arsenic contaminated water is dependent on the water composition (Singh et al., 2015). Most of the methods normally used for arsenic removal from water are based on adsorption or separation techniques. As it is impossible to degrade arsenic, the best way to remove it is by conversion from the aqueous phase to another phase (mainly solid phase) and then remove it by a separation technique (Nidheesh and Singh, 2017). The available arsenic treatment technologies are coagulation and flocculation, ion exchange, adsorption on iron oxides, lime softening and reverse osmosis (Katsoyiannis and Zouboulis, 2004). Of the various removal technologies, adsorption of arsenic on metal oxides and then its removal by filtration is advantageous due to strong attraction between arsenic and metal oxides, mainly iron oxides (Johnston, 2008). However, most of these technologies are not very effective for As (III) removal, which is primarily present in raw groundwater (Katsoyiannis and Zouboulis, 2004; Nicomel et al., 2016). In reducing groundwater having a pH value at circumneutral, arsenic is mainly present in the form of As (III) as undissociated arsenious acid, which is non-charged and thus making it less suitable for ion exchange, adsorption or precipitation (Katsoyiannis, Zikoudi and Hug, 2008; Nicomel et al., 2016). However, under circumneutral pH, As (V) species are negatively charged and due to electrostatic attraction these As (V) species are then more susceptible to get adsorbed on positively charged metal hydroxide surfaces (commonly used as adsorbents) and so can be more easily removed compared to As (III) (Wan et al., 2011). So, an effective arsenic removal technique for raw groundwater (containing mainly As (III)) will be a two-step process: first oxidation of As (III) to As (V) and then removal by adsorption or using a separation technique. As (III) oxidation can be carried out by air oxidation or chemical oxidation using ozone, hydrogen peroxide, potassium permanganate, manganese oxides, etc. (Nidheesh and Singh, 2017). Though the air oxidation of As (III) is thermodynamically possible, the process is very slow and it may take days to happen while the usage of chemical reagents causes secondary problems such as formation of residuals and by-products, while increasing the operational costs (Nidheesh and Singh, 2017; Katsoyiannis and Zouboulis, 2004). Also, the conventional separation techniques are subjected to various drawbacks like lower removal of As (III), consumption of chemicals, high operating cost, handling of secondary pollutants, etc (Song et al., 2017). Hence, there is still a need to develop a low cost, environmental friendly and effective arsenic removal technology from water that can be easily implemented in the regions where arsenic pollution of drinking water sources is still a major issue and where arsenic removal treatment systems are still not available or the available techniques are not very efficient.

On the above context, biological oxidation of arsenite to arsenate by arsenic oxidizing bacteria (AsOB) has been reported to meet the demands. Presence of AsOB has been observed in raw sewage, arsenic contaminated water, sediments, etc., and their application to oxidize As (III) has been effective (Ike et al., 2008; Gude et al., 2018; Ito et al., 2012). Also, these bacteria were found to be grown easily on sand by just dosing As (III) spiked water for a period of time (Gude et al., 2018).

Electrocoagulation (EC) is another technique, which is emerging as a water and wastewater treatment technology, has shown benefits for arsenic removal over the conventional methods. In this method, in-situ generation of metal coagulants takes place by passing direct current through metal electrodes (iron, aluminum etc.). For arsenic removal, iron oxides are commonly used as sorbents and in electrocoagulation using iron electrodes these iron oxides are formed in the solution due to electrolytic oxidation of the anode. So, addition of chemicals as coagulant is not required in electrocoagulation. Several studies have shown the effective removal of arsenic from groundwater, surface water and wastewater from industries using electrocoagulation having efficiency as high as 99% (Wan et al., 2011; Kobya et al., 2006; Lakshmanan et al., 2010; Chen, 2004).

1.2. Research Framework

1.2.1. Problem Statement and Research Objective

As mentioned above that As (III) is difficult to remove and use of conventional techniques creates secondary problems. So, comparing with the common techniques used for As (III) oxidation and then its removal, combining biological oxidation of As (III) with iron electrocoagulation (Fe-EC) has theoretical advantages. Though, Fe-EC has shown potential to remove both As (III) and As (V), but comparing with removal efficiency under a given iron dosage, As (V) showed better results than As (III) (Kumar et al., 2004; Wan, 2010). So, for removing arsenic from water (containing mainly As (III)) using Fe-EC, a prior oxidation will be an advantageous move and this can be achieved by biological oxidation. In biological oxidation, As (III) is oxidized by arsenic oxidizing bacteria, so there is no use of any chemicals. Also these bacteria have been reported to be grown on rapid sand materials (like sand) easily without any isolation from a source and can oxidize As (III) in a continuous flow system (Gude et al., 2018). Considering Fe-EC, where in-situ generation of iron coagulants take place to remove arsenic by adsorption has shown advantages like less use of coagulants, less sludge generation, small space requirement and low capital costs compared to chemical coagulation (Lakshmanan et al., 2010). In many studies where Fe-EC was used for arsenic removal, were performed in batch mode and few were done in a continuous flow system. Also, prior oxidation of As (III) using AsOB followed by Fe-EC has not been performed before. So, this study is an attempt to develop a continuous flow system that removes arsenic from water through biological oxidation, Fe-EC and rapid sand filtration.

Based on the above discussions, the main objective of this research is to develop vertical down-flow filtration columns, to remove arsenite from water below the WHO limit (10 µg/L) through biological oxidation followed by electrocoagulation in a continuous flow mode, that can be used as a centralized and de-centralized system for arsenic removal in various parts of the world.

1.2.2. Research Questions

Before developing the filtration columns, batch studies on arsenic removal by Fe-EC and growth of arsenic oxidizing bacteria on suitable bio-carriers were performed in order to address the following research questions:

1) What is the optimum operational parameter such as charge dosage and charge dosage rate required for Fe-EC to remove arsenic from water below WHO Limit? Charge dosage and charge dosage rate in Fe-EC defines the amount of iron dosed in a particular volume of solution and the rate at which it is dosed.

2) What is the effect of initial arsenic concentration on arsenic removal by Fe-EC?

3) What is the effect of initial arsenic oxidation state on arsenic removal by Fe-EC?

4) What is the affect of water matrix on arsenic removal by Fe-EC?

5) What is the arsenic oxidation efficiency by arsenic oxidizing bacteria grown on different bio-carriers?

6) What is the minimum iron dosage and iron dosage rate required to remove certain concentration of arsenic from water containing As (V) due to biological oxidation of As (III) below the WHO limit?

2. Theoretical Background

2.1. Electrocoagulation

2.1.2. Theory

Electrocoagulation (EC) is an electrochemical technique used for treating polluted water and wastewater containing various contaminants including arsenic (Holt et al., 2005; Mollah et al., 2004; Chen, 2004; Amrose, 2013; Kumar et al., 2004; van Genuchten et al., 2012). It is a separation process that involves various physical and chemical mechanisms to remove the contaminants present in a solution (Mollah et al., 2004). In this method electric current is passed through metal electrodes (iron, aluminum, etc.,) resulting in generation of coagulant species due to electrolytic oxidation of sacrificial anode. Depending on solution pH, the metal ions produced from the anode through electrochemical dissolution undergo hydrolysis. This hydrolysis results in formation of hydroxide precipitates (having capability to remove pollutants by adsorption/settling) and other ions metal species that acts as coagulants. Also, the reactions happening at cathode allows pollutant removal by means of deposition on cathode electrode or through flotation due to evolution of H_2 gas at the cathode. So, basically EC process comprises of in-situ production of coagulating ions and consists of the following three successive stages: (i) coagulant formation through electrolytic oxidation of the sacrificial electrode (anode), (ii) destabilization of contaminant, suspension of particulate, and breaking of emulsions and (iii) flocs formation by aggregation of the destabilized phases. The hydroxides, oxyhydroxides and solid oxides produced by EC have active surfaces that allow the pollutants to get adsorbed (Mollah et al., 2004). The commonly used electrodes for EC are made of aluminum (Al) or iron (Fe) materials owing to their easy availability at low price and also the precipitates formed of these metals are non-toxic in nature. Generally, direct current (DC) is used for release of metal ions, hence the anode and cathode are made of same materials (Hakizimana et al., 2017; Mollah et al., 2004).

In an EC process, when a current is applied to the electrodes (Fe or Al) the following two reactions take place:

- From the anode, Fe or Al ions get released into the solution that hydrolyzes to form polymeric iron or aluminum hydroxide. These polymeric hydroxides act as very good coagulating agents. The metal ions produced at anode coagulate with the negative particles produced near the cathode. Electrophoretic motion carries the negative particles towards the anode. The contaminants present in a water source are then treated in the EC reactor by chemical reactions and precipitation or by physical and chemical attachment to colloidal materials being generated by the electrode erosion. The coagulants containing the contaminants can then be removed either by sedimentation and filtration or by electroflotation. Hence, in this process no chemical coagulants are added externally as coagulating species are generated in-situ.

- Electrolysis of water also takes place simultaneously in the EC reactor generating H_2 gas at the cathode that helps in attracting and floating the flocculated particles through natural buoyancy (Deniel et al., 2008; Mollah et al., 2004; UÇAR, 2011).

Other than the above two reaction, the following physiochemical reactions can also take place in the EC reactor:

- Impurity reduction at the cathode.
- Colloidal particles can get discharged and coagulate.
- Ion migration in the solution due to electrophoretic motion.
- H_2 bubbles produced at the electrodes can cause electroflotation of the coagulated particles.
- Metal ions reduction at the cathode.

When a constant DC current is applied to the electrode or electrode assembly in an EC reactor, the amount of metal ions released from the electrodes into the solution depends on the current (i) passed through electrolytic solution or the total charge loading (q) (total charge passed through solution by the current), and can be measured using Faraday's law as shown in Eq. 2.1. The charge loading (q) can be measured based on the electrode area (A_e), active solution volume (V), current density (J) and electrolysis time (t) as shown in Eq. 2.2 The charge dosage rate (dq/dt) is proportional to the rate of metal dissolution into a unit volume of solution during electrolysis and can be depicted as in Eq. 2.3 (Amrose et al., 2013; Kobya et al., 2016).

$$w = \frac{qM}{nF} = \frac{itM}{n_e FV} \qquad \text{Eq. 2.1}$$

where,
w = Amount of electrode material dissolved (mg/L)
q = Total charge loading (C/L)
i = Current (mA)
t = Electrolysis time (sec)
M = Molecular weight of the metal ion (mg/mol)
F = Faraday's constant (96485 C/mol)
n_e = Number of electrons in oxidation/reduction reaction (2 for iron)
V= Volume of solution (L)

$$q = \frac{JtA_e}{V} = \frac{it}{V} \qquad \text{Eq. 2.2}$$

where,
q = Total charge loading (C/L)
J = Current Density (mA/cm^2)
t = Electrolysis time (sec)
V = Volume of solution (L)
A_e = Active electrode area (cm^2)
i = Current (mA)

$$\frac{dq}{dt} = \frac{i}{V} = \frac{JA}{V} \qquad \text{Eq. 2.3}$$

2.1.3. Mechanism of Electrocoagulation

A bench scale diagram of electrocoagulation reactor is shown in Figure 2.1 consisting of 2 electrodes, one acting as anode and the other as cathode. When a current is applied from an external power source, at anode oxidation reaction takes place where as at cathode reduction reaction takes place. The electrochemical reactions happening at anode and cathode having electrodes of metal M are shown below:

At anode:

$M (s) \rightarrow M^{n+} (aq) + ne^-$ Eq. 2.4

$2H_2O \rightarrow 4H^+ (aq) + O_2 (g) + 4e^- (E^0 = 1.23 V)$ Eq. 2.5

$2Cl^- \rightarrow Cl_2 + 2 e^- (E^0 = 1.36 V)$ Eq. 2.6

At cathode:

$nH_2O + ne^- \rightarrow (n/2) H_2 (g) + nOH^- (aq)$ Eq. 2.7

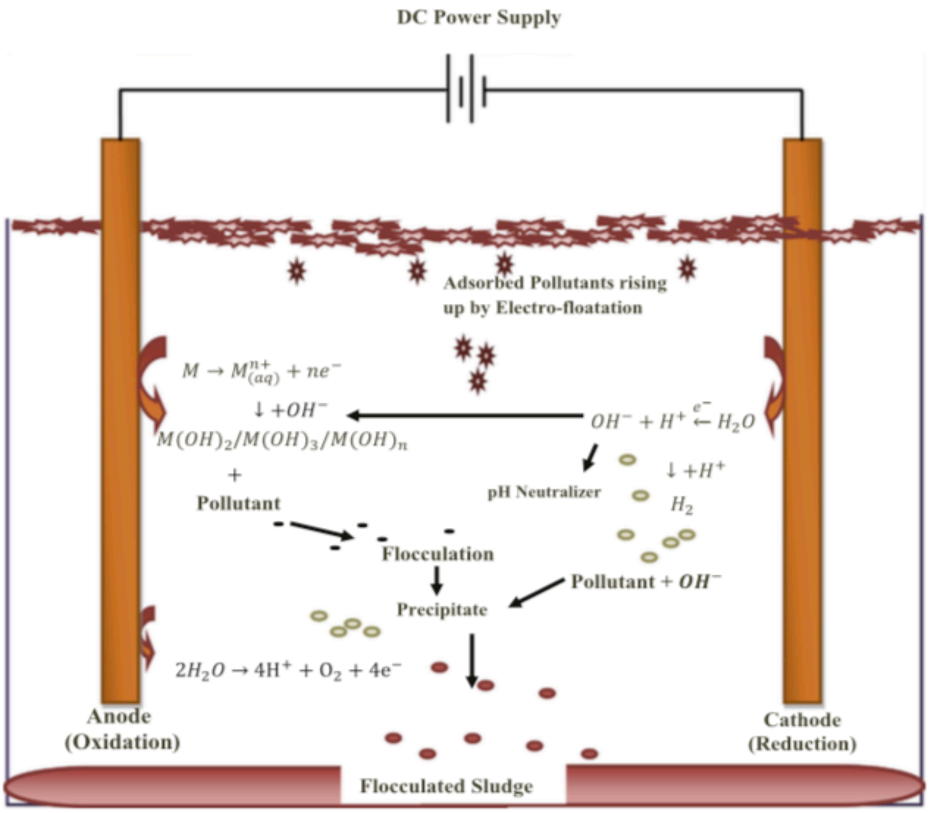


Figure 2.1: A bench scale Electrocoagulation Reactor (Nidheesh and Singh, 2017)

At the anode, divalent or trivalent metallic ions get released due to oxidation along with equal number of electrons in the solution as shown in Eq. 2.4. In presence of high anode potential, oxidation of water may take place at anode creating O_2 gas and hydronium cation (Eq. 2.5). Also, if the water solution contains chloride ions, oxidation of chloride ions to chlorine gas can also take place at anode under high anode potential (Eq. 2.6). At the cathode, reduction of water takes place generating H_2 gas and OH^- ions as shown in Eq. 2.7. The OH^- ions generated at the cathode then combines with metallic ions at the anode to form metallic hydroxides. These metallic hydroxides are very good adsorbents for the pollutants present in a solution and their characteristics such as monomeric or polymeric and soluble or insoluble (amorphous) are dependent on the pH of the aqueous solution. These amorphous metallic hydroxides $M(OH)_n$ posses large surface area and high adsorption capacity and they make bonds with the pollutants to form flocs. These metallic flocs attain a self-settling size by enlarging their size from micro to macro and can be removed by gravitational settling. Those micro flocs that can never settle are removed by use of hydrogen gas produced at cathode. The gas takes the micro flocs to the top of the aqueous solution through a process called electroflotation resulting in formation of foam like phase at the top of the solution that can be removed by skimming (Hakizimana et al., 2017; Singh and Ramesh, 2014; Kobya et al., 2006; Calvo et al., 2003; Mollah et al., 2004; Nidheesh and Singh, 2017).

When Fe is used as electrode, Fe^{2+} ions get released into the solution due to oxidation, which then gets oxidized to insoluble Fe^{3+} ions by the dissolved oxygen present in the solution. The Fe^{3+} ions formed by electrolytic oxidation then combine with OH^- ions to form monomeric species such as $Fe(OH)_3$ and polymeric hydroxy complexes such as $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_6^{3+}$, $Fe_2(H_2O)_8(OH)_2^{4+}$, $Fe(H_2O)_4(OH)_2^+$ and $Fe_2(H_2O)_6(OH)_4^{4+}$ depending on pH. On the other hand, in case of Al electrodes, the Al^{3+} ions get released into the solution from Al electrode directly by oxidation which then hydrolyzes to form $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, etc., over a wide range of pH (Mollah et al., 2004).

For removal of arsenic (As (III) and As (V)), Fe electrodes are commonly used, where Fe^{3+} ions are normally formed by electrolytic oxidation. During the oxidation of Fe^{2+} to Fe^{3+} by dissolved oxygen, reactive intermediates or Fenton-type products are also produced as by-products. These Fenton-type products effectively oxidize non-ionic As (III) to As (V) oxyanion, which can be sorbed easily. The Fe^{3+} then produce insoluble Fe^{3+} hydroxides, oxyhydroxides, etc., or in other words hydrous ferric oxides (HFOs) solids that have strong adsorption for both As (III) and As (V) ions (Kobya et al., 2016). The arsenic-laden precipitates then can be removed from the electrolyte by gravitational settling or by filtration (van Genuchten et al., 2012; van Genuchten et al., 2016).

2.1.4. Factors affecting Arsenic Removal by Electrocoagulation

Several operational parameters affect the efficiency of arsenic removal by electrocoagulation. For instance the solution pH influences the arsenic species distribution as well as the surface charge of the coagulants and complexes formed during electrocoagulation process (Song et al., 2017). Also, the oxidation state of arsenic and the presence of competitive anions affect the arsenic removal. A brief explanation of the primary operational parameters affecting the effectiveness of EC for arsenic removal are discussed below:

2.1.4.1. Electrode Material

Using a proper electrode material is an important parameter in electrocoagulation as it controls the various reactions taking place in EC thereby influencing the performance of EC (Garcia-Segura et al., 2017). Various electrode materials used for arsenic removal by EC includes iron, aluminum, zinc, copper, brass and titanium. Maldonado et al. (2007) has reported the efficiency of various materials for arsenic removal when used as anode as iron ≈ zinc > brass > copper. This difference in removal efficiency was due to electrochemical reactions and electrochemical intrinsic properties of the metal electrodes (Maldonado et al., 2007). Out of all the electrode materials, iron and aluminum are most widely used due to their easily availability, low cost and high removal efficiency for arsenic (Nidheesh and Singh, 2017). However, comparing between iron and aluminum electrodes for removing arsenic by EC, iron proved to be more efficient than aluminum owing to the high solubility of aluminum salts and lower adsorption capacity of aluminum complexes generated in-situ during the EC process (Kumar et al., 2004; Lacasa et al., 2011). Also, the iron precipitates formed during Fe-EC have large reactive area and high affinity for adsorbing contaminants (van Genuchten et al., 2014). Another advantage of Fe electrodes over Al electrodes is usage of Al electrodes doesn't cause oxidation of As (III) to easily adsorbed As (V) during EC as no Fenton type products are produced like reported for Fe electrodes. Studies were also done using combined electrode system such as iron anode-aluminum cathode (Fe-Al) and aluminum anode-iron cathode (Al-Fe) in order to improve the EC efficiency. A study by Gomes et al., (2007) has reported the arsenic removal efficiency of EC process using Al-Al, Fe-Fe and Al-Fe electrode system, where Fe-Fe and Al-Fe systems showed more efficient removal than Al-Al system. Electrodes made up of stainless steel and aluminum alloy (containing iron, zinc, silicon) has also proved efficient to remove arsenic from water solution through EC (Vasudevan et al., 2010a; Moussa et al., 2017).

2.1.4.2. Electrode Connection Mode

Based on the electrode connection modes, EC reactors can be classified as monopolar parallel (MP-P), monopolar serial (MP-S), and bipolar-serial (BP-S) as shown in Figure 2.2. In the MP-P connection mode there is parallel connection between cathodes and anodes causing division of current. In this configuration, the voltage of each unit is same and the sum of the sub-current divided in each unit represent the total current. In MP-S mode, there is an internal connection in each pair of anodes. Here the current in each unit is same whereas the cell voltage is distributed among the units. Comparing between MP-P and MP-S mode, the MP-P system requires a lower potential difference whereas a MP-S system require a high potential difference to provide a given current. In BP-S connection mode, only the outermost electrodes are connected to the power supply and there is no connection between the inner electrodes. The outer electrodes act as monopolar plates whereas the inner electrodes as bipolar plates and the cell voltage is divided among the various units in BP-S. Comparing between the three connection modes, MP-S mode is considered as the most efficient in terms of arsenic removal efficiency as well as operating cost (Song et al., 2017; Nidheesh and Singh, 2017).

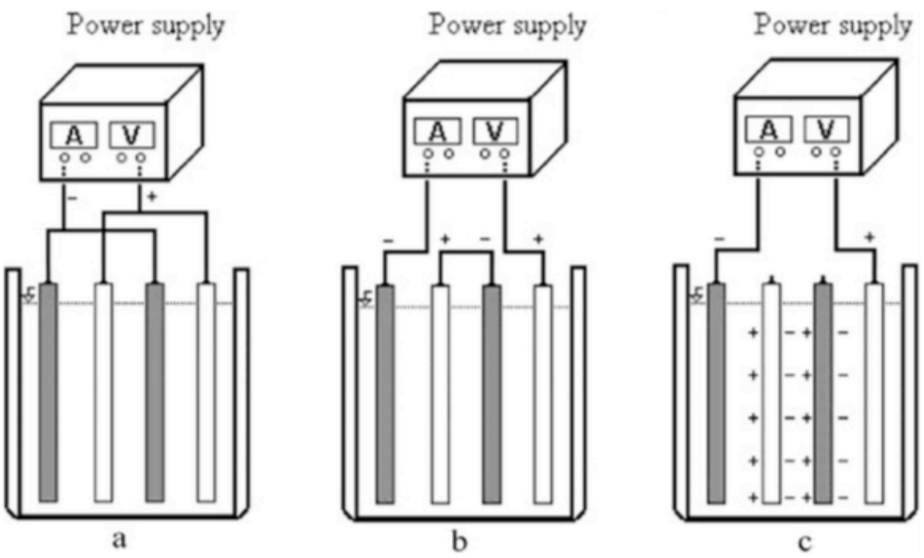


Figure 2.2: Connection modes of electrodes in an EC system: (a) MP-P (b) MP-S (c) BP-S (Song et al., 2017)

2.1.4.3. Initial pH of the solution

During EC the solution pH is observed to change making it difficult to develop a good relation between the pH of the solution and the efficiency of EC to remove arsenic, so while talking about the effect of solution pH on EC efficiency it is referred as initial pH of the solution (Moussa et al., 2017). The solution pH affects the electrochemical and chemical coagulation processes taking place during EC (Song et al., 2017). Studies have shown that optimal initial pH required in a solution for optimal arsenic removal in EC varies with the type of electrode material. An initial pH of 6.5 and 7.0 was found to be optimum to remove arsenic while using Fe and Al electrodes respectively (Kobya et al., 2011a). Whereas while using combine Fe-Al electrode system an initial pH range of 5.0-7.0 was found optimum with lower arsenic removal with increase in pH (Song et al., 2014). pH of the solution also determines the form of Fe, As and Al in the solution thereby influencing the arsenic removal efficiency (Song et al., 2014). It was reported that positively charged colloid particles of ferric hydroxide and ferrous hydroxide starts generating from pH around 3.0 and 7.0

respectively. However, the amount of ferric hydroxide decreased when the pH is above 12 i.e., highly alkaline (Song et al., 2014). On the other hand, aluminum hydroxide starts forming at pH around 4.0 and gradually starts dissolving at around 10.0 (Song et al., 2014). Also, Al_{13} polymer that allows good removal of arsenic forms at pH range 5.0-7.0 (Hu et al., 2016). Considering As (III), when solution pH is below 9.0, As (III) exists as H_3AsO_3 which is a neutral molecule and difficult to adsorb, whereas when the pH increases from around 7.0, the concentration of H_3AsO_3 form decreases and the negatively charged form $H_2AsO_3^-$ increases (Song et al., 2017). This phenomenon validates why As (III) removal by EC is high at higher pH as the negatively charged form can be easily adsorbed. On the other hand, for As (V), at pH below 3.0 it exist as a neutral molecule H_3AsO_4, but at pH between 3.0-7.0 and 7.0-11.0, it exists as negatively charged form: $H_2AsO_4^-$ and $HAsO_4^{2-}$ respectively. However at pH above 10.0, As (V) mainly exist in the form of AsO_4^{3-}. So, at pH around and greater circumneutral, arsenic removal by adsorption can be expected to be higher owing to their presence in negatively charged form.

The pH not only affects the speciation of arsenic and iron, but also the oxidation rate of Fe^{2+}. When the pH is high, the oxidation of Fe^{2+} to Fe^{3+} is also high that results in higher generation rate for Fe (IV), which is a highly reactive oxidizing species and can cause oxidation of As (III) to As (V) (Banerji and Chaudhari, 2016). Study by Banerji and Chaudhari (2016), reported highest As (III) oxidation during Fe-EC at pH 7.0 that resulted in highest arsenic removal compared to 6.0 and 8.0 for same amount of Fe added. The oxidation of As (III) at pH 8.0 was found to be poor compared to pH 7.0 because of relative quick oxidation of Fe^{2+} resulting in less utilization of Fe (IV) for As (III) oxidation. Also, at pH 6.0, though the Fe^{2+} oxidation is less compared to pH 7.0 and 8.0, but the Fe (IV) was very unstable resulting less oxidation of As (III).

When the EC process starts and the initial pH is ranging from 3.0-7.0, an increase in the final pH was observed, which is obvious due to the generation of OH^- ions and H_2 gas at the cathode (Song et al., 2014). But when the pH is above 9.0, decrease in the final pH was observed due to hydrolysis reactions and consumption of OH^- ions while formation of metal hydroxides or oxyhydroxides as shown in Eqs. 2.8-2.14 (Kumar et al., 2004; Wan et al., 2011).

$$Fe^{2+}\,(aq) + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ \qquad \text{Eq. 2.8}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^{+} \quad \text{Eq. 2.9}$$

$$Fe^{2+} + 3OH^{-} - e^{-} \rightarrow FeOOH + H_2O \quad \text{Eq. 2.10}$$

$$Fe(OH)_3 + OH^{-} \rightarrow [Fe(OH)_4]^{-} \quad \text{Eq. 2.11}$$

$$[Fe(OH)_4]^{-} + 2OH^{-} \rightarrow [Fe(OH)_6]^{3-} \quad \text{Eq. 2.12}$$

$$Al^{3+}(aq) + 3H_2O \rightarrow Al(OH)_3 + 3H^{+} \quad \text{Eq. 2.13}$$

$$Al(s) + 4OH^{-} \rightarrow [Al(OH)_4] + 3e^{-} \quad \text{Eq. 2.14}$$

2.1.4.4. Current Density

Current density (J) is defined as the amount of current (i) applied into an electrolytic cell per unit active surface area of the electrodes (Can et al., 2014). It is an important parameter in the EC process as it controls the coagulant and gas bubbles generation rate as well as the size and distribution of the flocs formed during EC process (Song et al., 2017). Hence, this parameter affects the pollutant removal efficiency during EC (Kobya et al., 2011b).

Almost all the studies done on arsenic removal by EC have considered current density as an important operational parameter for EC and all concluded that arsenic removal by EC got improved with increase in current density for a constant electrolysis time. This is due to the fact that with increase in current density by increasing the current (i) applied to the electrodes the amount of metal ions released from the electrodes into the solution also increases as per Faradays' law (Eq. 2.1). This results in formation of more hydroxide cationic complexes that can strongly adsorb the pollutants or co-precipitate with them (Song et al., 2017). Also, high current density increases H_2 gas production rate and smaller sized bubbles that results in enhanced flocculation performance and mass transfer in EC process, thereby causing high removal efficiency for pollutants (Song et al., 2017). However, for arsenic removal when the current density is higher than a particular value a stage of stagnation occurs due to formation of enough metal hydroxides or oxyhydroxides through anodic oxidation and hydrolysis (Wan et al., 2011). Though an increase in current density improves the arsenic removal but it was reported that the final total arsenic removal doesn't depend on current density. Instead an increase in current density just makes the removal rapid or decreases the electrolysis time required to remove a certain amount of arsenic (Kumar et al., 2004)

Though the increase in current density increases the removal of arsenic for a constant electrolysis time (Kobya et al., 2011b; Kumar et al., 2004; Can et al., 2014) but the operating cost also increases due to high consumption of electrical energy as shown in Eq. 2.15.

$$C_{energy} = \frac{Uit}{V} \quad \text{Eq. 2.15}$$

where,
C_{energy} = Consumption of electricity per m^3 (kWh/m^3)
U = Potential of the EC reactor (V)
i = current applied
t = electrolysis time

So, an optimum condition has to be maintained regarding the operating time and current density for high arsenic removal with low operating cost. Kobya et al., (2011a) has reported a longer operating time with a constant current density helps in achieving higher arsenic removal efficiency with low electric energy consumption using Fe electrodes. However, for Al electrodes, the energy consumption was high compared to Fe electrodes owing to higher potential required for Al electrode to reach a particular current density. But for Al electrodes, a high current density with lower operating time is beneficial as it helps is high generation of medium polymer species such as Al_{13} during EC that allows good removal of arsenic (Hu et al., 2016).

2.1.4.5. Charge Density or Charge Loading or Charge Dosage

Charge density or charge loading or charge dosage (CD) (q) is defined as the total charge passed through a defined volume solution by the applied current. In almost all the studies done on arsenic removal by Fe-EC, current density (J) is always taken as an important parameter that determines the removal efficiency. But in those studies, the current density is increased by increasing the current applied instead of changing the active surface area of electrodes. On the contrary, some studies showed that it’s the charge density not the current density that plays the important role (Chen et al., 2000; Kumar et al., 2004). Chen et al., (2000) and Kumar et al., (2004) have reported that increasing the current density by keeping the charge loading constant doesn’t have any affect on the removal efficiency of arsenic rather it just decreases the time required to dose a certain amount of iron. The reason is in EC, the pollutants are mainly removed by formation of metal hydroxides or oxyhydroxides. So, higher the amount of metal ions released into the solution higher will be the formation of metal hydroxides or oxyhydroxides and as per Eq. 2.1, which is directly proportional to the charge loading (q). So, charge loading instead of current density can serve as a better parameter for EC processes.

2.1.4.6. Charge Loading Rate or Charge Dosage Rate

Charge loading rate or charge dosage rate (CDR) (dq/dt) in EC can be defined as the amount of charge applied to a solution per unit time. In other words it can be defined as the rate at which the metal ions are released into the solution from the electrodes. CDR can be increased by increasing the applied current and thereby decreasing the electrolysis time required to dose a certain amount of metal ions. This results in decreasing the operating cost in EC (Delaire et al., 2017). In an Fe-EC system, the CDR affects the oxidation of As (III) due to competition between Fe^{2+} and As (III) for Fenton type products, which is an important factor in EC as As (V) has higher affinity to get sorbed on iron precipitates than As (III). Also, CDR defines the As (III)/Fe^{2+} ratio and average contact time of arsenic with iron precipitates during EC and these factors has been reported to affect arsenic removal (Amrose et al., 2013). In almost all the studies on arsenic treatment by EC, current density is taken as important parameter that controls the treatment time. This factor is true when the active electrode area and the volume of the solution to be treated are held constant because then an increase in current density will be equal to increase in charge dosage rate as per Eq. 2.3. However, in EC reactors when its difficult to keep the active electrode area and the volume of solution constant, charge dosage rate over current density is the more accurate and applicable scaling parameter (Amrose et al., 2013).

2.1.4.7. Oxidation state of Arsenic

In Fe-EC system removing arsenic, the removal of As (V) is observed more efficient compared to As (III). As (V) has much more affinity to get adsorbed on Fe^{3+} precipitates than As (III), so As (V) removal by adsorption on iron precipitates are more favored over As (III) in Fe-EC (Kumar et al., 2004; Wan, 2010). So in arsenic removal by Fe-EC containing mainly As (III), its better to oxidize As (III) to As (V) for better removal. Reports have shown that during Fe-EC, oxidation of As (III) to As (V) takes place (Kumar et al., 2004; van Genuchten et al., 2012; Banerji and Chaudhari, 2016). The reason suggested was during oxidation of Fe^{2+} to Fe^{3+}, an oxidizing intermediate Fe (IV) is produced, which causes oxidation of As (III) to As (V) via As (IV) (Li et al., 2012; van Genuchten et al., 2012; Hug and Leupin, 2003). Wan (2010) has reported 25 % oxidation of As (III) to As (V) when treating As (III) solutions by Fe-EC, validating the oxidation of As (III) to As (V) during Fe-EC. Other reports also suggested the oxidation of As (III) to As (V) by addition of chemical oxidants then treating by EC. Flores et al., (2013), used hypochlorite to oxidize As (III) that helped in improving the efficiency of EC process. Likewise, Zhang et al., (2014) combined EC process with anodic oxidation process for As (III) oxidation. In anodic oxidation process, oxygen over-voltage anodes or dimensionally stable electrodes are used to generate hydroxyl radicals that have high oxidation potential. These hydroxyl radicals can then easily oxidize all As (III) to As (V) (Zhang et al., 2014).

2.1.4.8. Initial Arsenic Concentration

If the operational parameters of EC such as current density, charge loading rate, and initial pH are kept constant in a Fe-EC system, then an increase in initial arsenic concentration will cause an increase in iron dosage required to remove arsenic below a certain value. This is due to when initial arsenic concentration is high, more HFOs were required to decrease the dissolved arsenic concentration to a desired amount by adsorption or co-precipitation.

2.1.4.9. Presence of coexisting ions

In real groundwater and surface water, along with arsenic there exists various anions like nitrate, phosphate, sulfate, silicate, chloride, fluoride, carbonate and bicarbonate; cations like calcium, magnesium, sodium that may affect the removal efficiency of arsenic by electrocoagulation. A brief explanation on the influence of various ions on arsenic removal by EC are given below:

Phosphate:

It has been reported that presence of phosphate ions act as an inhibitor for arsenic removal by EC with Fe-electrodes. This is due to the fact that both phosphorous and arsenic belong to the same group in the periodic table (indicating they have same charge) and also they have same tetrahedral structure and chemical behavior, so both of them can be adsorbed on the same adsorption site of iron hydroxide and hence there is a competition (Wan et al., 2011; Lakshmanan et al., 2010). Wan et al., (2011) has reported that the inhibitory effect of phosphate ions become more significant at higher phosphate concentration and there was considerable amount of phosphate removal along with arsenic due to adsorption on iron precipitates formed during Fe-EC, indicating competition between arsenic and phosphate ions for adsorption on iron precipitates. Other explanations of the inhibitory affect of phosphate on arsenic removal were given as decrease in the sorbent formation rate due to slower oxidation of Fe^{2+} to Fe^{3+} in the presence of phosphate and also formation of Fe^{3+}-phosphate solids during Fe^{2+} oxidation in phosphate-rich solutions (Wan et al., 2011; Voegelin et al., 2010). Quick removal of phosphate ions compared to arsenic in EC was also reported due to faster reaction of phosphate with iron than arsenic making arsenic removal more difficult (You and Han, 2016).

Sulfate:

Presence of sulfate ions (low as well as high concentration) along with arsenic species didn't show any affect on the arsenic removal efficiency by EC with iron electrodes (Wan et al., 2011; You and Han 2016; Song et al., 2017). The reasons explained are sulfate ions don't influence the formation of iron hydroxides/oxyhydroxides and also sulfate doesn't get adsorb on the iron precipitates as strong as arsenic and phosphate (Wan et al., 2011; Song et al., 2014).

Silica:

The influence of silica on the removal efficiency of arsenic by EC is quite debatable. Some studies have shown no inhibitory effect of silica on the arsenic removal efficiency (Wan et al., 2011; Song et al., 2014). Study by Wan et al., (2011) reported no considerable effect on arsenic removal in solutions containing 5 and 20 mg/L dissolved silica. However there was considerable amount of silica removal during Fe-EC and also prevention of formation of iron oxides. The reason explained was low affinity of silica for metal hydroxides/oxyhydroxides. On the contrary, other studies showed inhibitory effect of dissolved silica on arsenic removal when present at a concentration of 20 mg/L and the inhibitory effect become more intense with increase in pH (Vasudevan et al., 2010a,b). This inhibition effect may be due to polymerization of silica causing blockage of the adsorption sites present in the internal pores of the metal hydroxides/oxyhydroxides (Zeng et al., 2008).

Chloride:

Chloride slightly improves the arsenic removal efficiency in EC by penetrating the passivation layer formed on anode surface and thus decreasing the obstruction in the release of metal ions from anode (Song et al., 2014). Also, when chloride is present in higher concentration, pitting corrosion phenomenon takes place that catalyzes the metal dissolution. Hence, chloride ions help in dissolution of more metal ions into the solution and thereby formation of more metal hydroxides/oxyhydroxides as coagulants that improves the arsenic removal efficiency (Hu et al., 2003). Besides, increase in the concentration of chloride ions increases the conductivity of solution and thereby reducing the voltage or power required to run the EC process. This decrease in required voltage and power results in lower energy consumption (Song et al., 2017).

Calcium:

Presence of calcium ions has shown to improve the arsenic removal efficiency by EC. This is due to the fact that calcium helps in removing competing anions from the solution such as phosphate through precipitation. In wastewater treatment, phosphate is commonly remove by adding lime and ferric chloride so that it can precipitate as $Ca_5(PO_4)_3$ and $FePO_4$ (Majumder and Gupta, 2010). Another reason for increased arsenic removal efficiency during Fe-EC in presence of calcium is reduction of zeta potential of the iron oxide surface that helps in arsenic adsorption (Smith and Edwards, 2005). Also, it has been reported that presence of calcium ions increases the As (V) uptake rate per mass of Fe due to electrostatic interactions and direct bonding of calcium ions with As (V) ions (van Genuchten et al., 2014)

Magnesium:

Presence of magnesium ions has also showed improvement of arsenic removal by Fe-EC and the reason is same as that of calcium ions, which is due to increase in As (V) uptake rate per mass of Fe owing to electrostatic interactions and direct bonding of magnesium ions with As (V) ions (van Genuchten et al., 2014). However, the affect of magnesium ions is not as pronounced as for calcium ions (van Genuchten et al., 2014).

2.1.5. Merits and Demerits of Electrocoagulation

The EC process has been reported to have a lot of advantages over the traditional coagulation process. For instance, the various equipment's used for EC are very simple and easy to operate resulting its application in compact and small treatment facilities at relatively low cost. Also, the EC equipment's doesn't have any moving parts and the most of them are controlled using electricity so it requires low maintenance. In addition, the EC can be performed by using solar energy, so it is beneficial for areas which doesn't have access to electricity. Moreover, it is a suitable choice in places where decentralized treatment technique is preferred over centralized one (Mollah et al., 2001; Holt et al., 2005).

The major advantage of EC process is it doesn't require addition of any chemicals thereby lowering the secondary pollution. Also, the amount of sludge produced is low in EC compared to chemical coagulation that are easy to settle and dewater. The flocs formed during EC are bigger in size, have high stability, resistant to acid and contain less bound water resulting in easy removal by filtration. During EC the bubbles formed at cathode also helps in carrying the flocs to the top of the EC reactors resulting in easy collection and removal of the flocs (Dura, 2013).

Though EC process has many advantages but it also got some drawbacks and limitations. The main limitation of EC is the use of electricity owing to high energy costs. Also there is a decrease in EC process efficiency over time due to formation of surface layer on the electrodes due to deposition of metal ions on the electrodes that grows over time and causes less discharge of metal ions in the solution for a given applied current (Müller et al., 2019). Moreover, the conductivity of the solutions need to be high sometimes to allow the required current to pass and in some cases (Islam, 2019).

2.2. Biological Oxidation of As (III) to As (V)

Microorganisms play a significant role in the arsenic geochemical cycle and bacteria as well as phytoplankton can oxidize, reduce and methylate arsenic (Garcia-Dominguez et al., 2008). So, biological oxidation of As (III) to As (V) by microorganisms can be an important way in the treatment of water containing As (III), as As (V) is easily removed by conventional treatments compared to As (III). Oxidation of arsenic by bacteria was first reported back in 1918 when oxidation of arsenite was observed in cattle-dipping tanks (Green, 1918). After that isolation of many arsenic oxidizing microorganisms have been reported (Weeger et al., 1999; Mokashi and Paknikar, 2002). Existence of arsenic/As (III) oxidizing bacteria (AsOB) have been reported in raw sewage (Philips and Taylor, 1976,), mines (Santini et al., 2000), arsenic contaminated water (Weeger et al., 1999), geothermal waters (Salmassi et al., 2002), sediments and soil (Garcia-Dominguez et al., 2008), groundwater aquifers and groundwater treatment filters (Liao et al., 2011; Cavalca et al., 2013a).

AsOB have an enzyme, named arsenic oxidase, in their protoplasm that helps them to oxidize As (III) to As (V) (Dey, Chatterjee and Mondal, 2016). AsOB can be both heterotrophic as well as chemolithoautotrophic and both of them have been characterized to have enzyme arsenic oxidase (Cavalca et al., 2013b). Heterotrophic AsOB follows detoxification mechanism to oxidize As (III) and for that they require organic matter. However, chemolithoautotrophic AsOB use As (III) as their primary electron donor in catabolism and for carbon source they use inorganic carbon. Classification of most AsOB by phylogenetic study has put them in the Proteobacteria phylum (Gude et al., 2018). In this phylum the AsOB are again subdivided as α-Proteobacteria, β- Proteobacteria and γ-Proteobacteria. Most of the AsOB in α-Proteobacteria are chemolithoautotrophic whereas in β- Proteobacteria most of them are heterotrophic, but all AsOB in γ- Proteobacteria are heterotrophic (Gude et al., 2018).

Application of arsenic oxidizing bacteria for oxidation of As (III) to As (V) has been reported in many studies where these bacteria were either isolated from a particular source (activated sludge, soil, etc) or grown in a suitable bio-carrier (sand) (Ito et al., 2012; Gude et al., 2018; Zouboulis and Katsoyiannis, 2005). Zouboulis and Katsoyiannis (2005) showed that biological removal of dissolved iron from groundwater through biological oxidation is also an efficient technique to simultaneously oxidize As (III) to As (V) and subsequent removal. In the study they used polystyrene beads as bio-carrier in an upflow fixed bed filtration column. On the bio-carriers, the bacteria causing oxidation of iron and arsenic were grown by just allowing groundwater spiked with Fe^{2+} and As (III) to flow through the bio-carrier column over a period of time. The results have shown 90 % removal of both iron and arsenic after proper growth of the microorganisms. Similar study was also conducted by Gude et al., (2018), where the growth of AsOB in rapid sand filter containing quartz sand (as bio-carrier) was investigated in the presence and absence of other biological and chemical processes. The results obtained concluded that AsOB can grow in rapid sand filters in the presence of other oxidizing bacteria (Fe and NH_4) as well as naturally formed mineral precipitates such as MnO_2 and hydrous ferric oxides. Also, it was observed that these AsOB can be grown on sand by continuous dosing of As (III) spiked water having concentration 100 μg/L or dosing raw groundwater having As (III) concentration as low as 13 μg/L for a period of time. Ito et al., (2012) also showed the biological oxidation of As (III) by arsenic oxidizing bacteria isolated from activated sludge under various initial nitrogen source concentration, pH and temperature of water. A spherical polyvinyl alcohol gel was used in this study to act as bio-carrier for immobilizing the isolated AsOB in a vertical continuous flow mode reactor. The results from that study showed decrease in the As (III) and increase in the As (V) concentration indicating microbial oxidation. These studies clearly show the potential of bacterial oxidation of arsenite as a cheap and sustainable way to treat water contaminated mainly by As (III).

2.2.1. Effect of Physio-Chemical Parameters on Biological Arsenite Oxidation

2.2.1.1. pH

In most of the studies where As (III) in water has been oxidized to As (V) by biological oxidation, the optimum pH mentioned for oxidation activity and bacterial growth was 5.0-9.0. Battaglia-Brunet et al., (2002) used an autotrophic As (III) oxidizing population selected from the Cheni gold mine site (France), named CASO1 for As (III) oxidation. The experiments for As (III) oxidation was carried out in batch studies and the results showed that the As (III) oxidizing rate and bacterial growth rate increased when the pH increases from 2.0-6.0 and beyond that both the rate decreased. Ito et al., (2012) also reported similar pH value in their study where batch studies on As (III) oxidation was performed by arsenite-resistant bacteria isolated from the activated sludge from aeration tank in a sewage treatment plant in Iwate Prefecture, Japan. The isolated AsOB preferred a pH value between 6.0-8.0 for complete As (III) oxidation.

2.2.1.2. Temperature

Ike et al., (2008) used AsOB obtained from soil samples in Suita Campus of Osaka university, Japan and reported that the oxidation rate of As (III) was higher at 30^0C when 75 mg/L of As (III) was completely oxidized to As (V) in 5 days. However at 20^0C, it took 14 days and no oxidation was observed at 40^0C. Similar study done by Battaglia-Brunet et al., (2002) obtained an increase in the oxidation rate of As (III) when the temperature rises from 10^0C to 25^0C. Also, Ito et al., (2012) achieved full As (III) oxidation by AsOB at temperature greater than 20^0C. These studies indicated that lower water temperatures adversely affect the As (III) oxidation (Ito et al., 2012).

3. Materials and Methods

The laboratory works performed for this research work can be divided into two phases. In phase I, batch studies on Fe-EC were performed under various EC operational parameters in order to understand the efficiency of Fe-EC to remove of As (III) and As (V) from different water composition. Also during Phase I, AsOB were grown on suitable bio-carrier by continuous dosing of As (III) spiked water through different bio-carriers. In phase II, continuous downflow vertical column filters were developed to remove arsenic from water (containing mainly As (III)) by first oxidizing As (III) to As (V) using AsOB (grown on the bio-carrier during phase I) followed by As (V) removal through iron electrocoagulation (Fe-EC) and rapid sand filtration. Based on the batch studies on Fe-EC during phase I, the optimum operation value for Fe-EC in the filter columns developed in Phase II were chosen to have arsenic concentration below the WHO limit in the effluent of the columns.

3.1. Phase I

3.1.1. Iron Electrocoagulation Reactor for the Batch Studies

A schematic diagram and lab setup of the Fe-EC reactor used for the batch studies is shown in Figure 3.1. It consists of a 1 L glass beaker (Borosilicate Glass 3.3 1000 ml) into which 0.8 L of water was poured for all experiments and two iron (Fe) electrodes were immersed into the solution. The electrodes used were Steel S235 with 0.22% Carbon (C), 0.05% Phosphorus (P), 1.6% Manganese (Mn), 0.05% Silicon (Si) and 0.05% Sulphur (S). The electrodes were provided by the Dienst Elektronische en Mechanische Ontwikkeling (DEMO), TU Delft having a size of 50 mm x 20 mm x 0.5 mm. The total submerged area of each electrode was 12 cm^2 and the gap between the two electrodes into the solution was kept at 1 cm. Before running the experiments, the electrodes were immersed in 0.01 M H_2SO_4 (Merck Millipore) for 2 min and then abraded with sand paper to remove any scales and finally cleaned by demi-water. The electrodes were connected to a direct current supplier (TENMA® 72-10500 DC Power Supply, 0-30 V) in MP-P connection mode. During each experimental run, the solution was stirred using a magnetic stirrer (LABINCO L23) at 150 rpm. The initial pH of the water solution in all the experimental runs were maintained between 7.0-8.0 by adjusting the pH using 0.01 M H_2SO_4 and 0.1 M NaOH. In order to get the required conductivity to allow the desired current to apply, NaCl was used in the aqueous solutions. The initial dissolved oxygen (DO) concentration in all the aqueous solutions used for each experimental run was kept around 8.0-9.0 mg O_2/L.

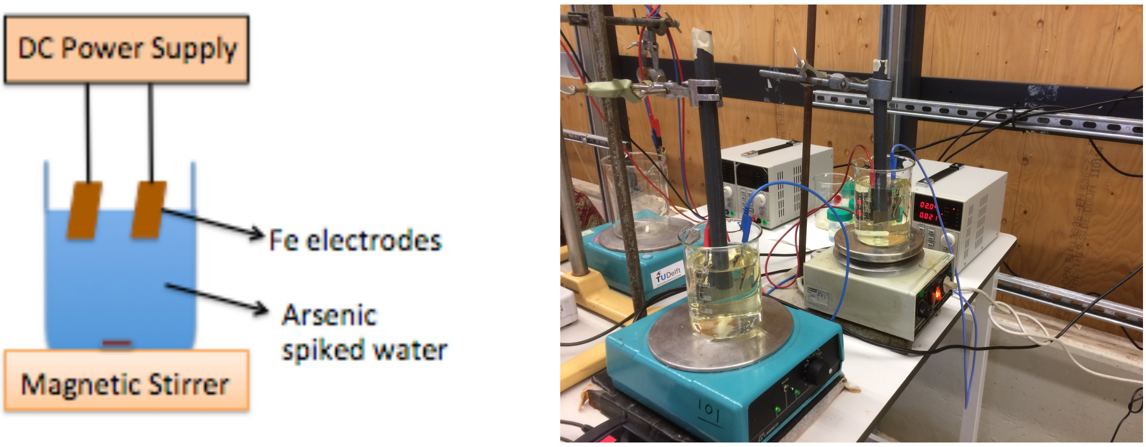


Figure 3.1: Schematic diagram (left) and lab setup (right) of the electrocoagulation reactor used in the batch studies

3.1.2. Operational Parameters for EC Batch Studies

In the batch studies 3 types of water were used: Ultrapure water, Tap water and Synthetic Bangladesh Groundwater (SBGW). For the 3 types of water NaCl was added to get the required conductivity. The initial pH and initial DO value in all the batch experiments were maintained at 7.0-8.0 and 8.0-9.0 mg O_2/L respectively. Ultrapure water was obtained from PURELAB Ultra water purification system having resistivity 18.2 MΩ.cm. Before using the tap water an initial characterization was done and the chemical composition is shown in Table 3.1. The chemical composition of SBGW was taken from van Genuchten et al., (2012), which was derived by the analysis done over 3500 tubewells from 61 districts of Bangladesh by British Geological Survey (Table 3.2). During the batch studies of EC, various operational parameters, arsenic species and arsenic concentrations were taken into consideration and a brief explanations of all the variations are given below.

Table 3.1: Characterization of Tap water

Compound	Concentration (mg/L)
PO_4^{3-}	0
SO_4^{2-}	52.1 ± 0.98
NO_2^-N	0
NO_3^-N	2.39 ± 0.31
NH_4^+-N	0

As	0
Fe	0
Ca	49.76 ± 0.3
Na	41.50 ± 0.42
Si	2.15 ± 0.04
Mg	6.95 ± 0.09

Table 3.2: Chemical composition of SBGW

Ion	**Concentration**
HCO_3^- (mg/L)	275
PO_4^{3-} (mg/L)	4
SO_4^{2-} (mg/L)	8
SiO_3^{2-} (mg/L)	53
Mg^{2+} (mg/L)	8
Ca^{2+} (mg/L)	61
As (III) (µg/L)	50/150/500
Na^{2+} (mg/L)	Varied depending on the conductivity required
Cl^- (mg/L)	Varied depending on the conductivity required

3.1.2.1. Charge Dosage (q) and Charge Dosage Rate (dq/dt)

In all the batch experiments of EC, six charge dosages: 10, 25, 50, 100, 150 and 200 C/L under three charge dosage rates: 5, 15 and 60 C/L/min were used. For applying the required charge dosage (q) under a constant charge dosage rate (dq/dt) the electrolysis time was changed keeping the applied current constant, which is calculated by dividing charge dosage from charge dosage rate (shown in Table 3.3). Also, in order to get the required charge dosage rate the current to be applied was changed in the DC supplier based on the calculation shown in Table 3.3.

3.1.2.2. Applied Current (i) and Current Density (J)

The current (i) to be applied mainly dependent on the charge dosage rate (dq/dt) and volume (V) of the water solution to be treated and was calculated using Eq. 2.2. So, for a charge dosage rate of 5, 15 and 60 C/L/min and 0.8 L solution volume, the current to be applied was calculated to be 0.07, 0.20 and 0.80 A respectively (Table 3.3). Therefore, the current density (J) applied for submersible electrode area of 12 cm^2 was 6, 17 and 67 mA/cm^2 respectively, which corresponds to the charge dosage rate of 5, 15 and 60 C/L/min. So, by increasing the current density (J) (by increasing the applied current (i)) the charge dosage rate (dq/dt) can be increased. At a given current density (J) or charge dosage rate (dq/dt) an increase in charge dosage (q) will cause an increase in EC time, which can be seen in Table 3.3.

3.1.2.3. Initial Arsenic Concentration

To study the effect of initial arsenic concentration on EC efficiency, three As (III) concentrations were used: 50 µg/L, 150 µg/L and 500 µg/L for the three types of water (ultrapure water, tap water and SBGW).

3.1.2.4. Arsenic Species

The efficiency of EC to remove As (III) and As (V) from water were studied separately. Tap water containing As (III) and As (V) separately at two concentrations (150 and 500 µg/L) were studied under different charge dosages (q) and charge dosage rates (dq/dt) and the results were compared.

Table 3.3 gives an overview of the operational parameters used during the batch studies. All the batch experiments for EC were performed twice and for each experiment the samples were analyzed in triplicates. So, the results shown are average of 6 values (3 from each experiment).

Table 3.3: Various Operational Parameters used in EC

Initial As Conc.	Charge Loading	Charge Loading Rate	EC Time	Volume	Current	Electrode Area	Current Density
(µg/L)	(C/L)	(C/L/min)	(min)	(L)	(A)	(cm^2)	(mA/cm^2)
	A	B	C=A/B	D	E =(A*D)/C	F	G =E/F
50/150/500	10	5	2	0.8	0.07	12	6
50/150/500	25	5	5	0.8	0.07	12	6
50/150/500	50	5	10	0.8	0.07	12	6
50/150/500	100	5	20	0.8	0.07	12	6
50/150/500	150	5	30	0.8	0.07	12	6
50/150/500	200	5	40	0.8	0.07	12	6
50/150/500	10	15	0.67	0.8	0.2	12	17
50/150/500	25	15	1.67	0.8	0.2	12	17
50/150/500	50	15	3.33	0.8	0.2	12	17
50/150/500	100	15	6.67	0.8	0.2	12	17
50/150/500	150	15	10.00	0.8	0.2	12	17
50/150/500	200	15	13.33	0.8	0.2	12	17
50/150/500	10	60	0.17	0.8	0.8	12	67
50/150/500	25	60	0.42	0.8	0.8	12	67
50/150/500	50	60	0.83	0.8	0.8	12	67

50/150/500	100	60	1.67	0.8	0.8	12	67
50/150/500	150	60	2.50	0.8	0.8	12	67
50/150/500	200	60	3.33	0.8	0.8	12	67

3.1.2. Growth of Arsenic Oxidizing Bacteria

3.1.2.1. Experimental Set-up and Procedure

The setup used for the growth and accumulation of arsenic oxidizing bacteria (AsOB) consists of two identical downflow vertical-cylindrical columns having height 2 m and diameter 9 cm (Figure 3.2) (image of the lab setup is in Appendix: Figure A3). At the bottom of the columns, 30 cm of garnet (0.3 - 0.6 mm size), coarse sand (1.4 – 2.0 mm size) and anthracite (2.0 - 4.0 mm size) layers (obtained from Aqua Techniek) were put one above another. The 3 layers together acted as rapid sand filters and were used as bio-carriers for growth of AsOB. The supernatant water level above the anthracite layer was around 1 m. Before starting the columns, backwashing was performed to remove any dirt present in the materials.

The columns were fed with a mixture of tap water and demiwater containing As (III), at the top. The tap water was introduced from a main flow pipe through a connection using gravity and pressure developed in the connecting pipe whereas the As (III) spiked demiwater was dosed using peristaltic dosing pumps (Watson-Marlow 120 U/DV). The flow rate at which the tap water was introduced into the columns was maintained at 6 (±1) L/hr per column by adjusting valves whereas, As (III) spiked demiwater was introduced from two 25 L jerrycans into the two columns separately at a flow rate of 0.3 (±0.1) L/hr per column. This combined flow rate resulted in maintaining a downward flow velocity of 1 (±0.5) m/hr inside each column.

Both the columns were dosed with water having As (III) concentration of 150 (±50) µg/L. The concentration of As (III) in the 25 L jerrycans was calculated based on the flow rate of tap water and demiwater, so that there mixture results in an arsenic concentration of 150 µg/L. The As (III) spiked demiwater was freshly prepared every 2 days and 5 ml of 2.5 M H_2SO_4 was also added in each 25 L demiwater jerrycans so that the pH of water in the jerrycans stay between 3.0-4.0, preventing oxidation of As (III) in the jerrycans.

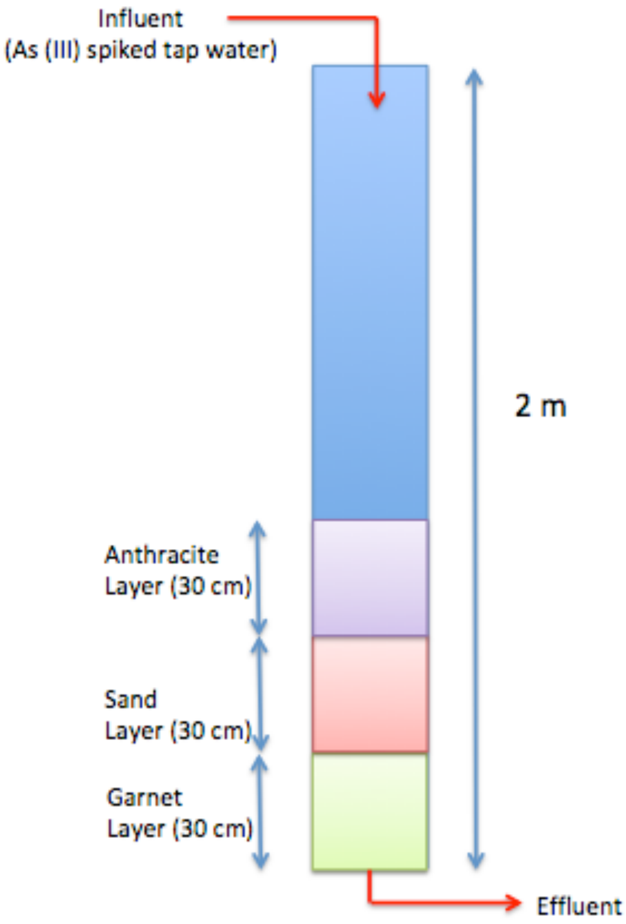


Figure 3.2: Schematic diagram of the vertical columns used for the growth of arsenic oxidizing bacteria

The columns were continuously fed with arsenic spiked tap water for the entire batch study period (approximately 2 months) and during that period no backwashing was performed. Also, it was taken proper care that the columns did not come in contact with sunlight that may influence the results by placing the columns in a location where the sunrays did not fall in directly.

3.1.3. Performing Fe-EC after Biological Oxidation

After the end of 2 months used for the growth of AsOB in the columns, 5 L of the effluent from both the columns were collected and Fe-EC was performed. The EC was performed like the batch studies using 0.8 L of effluent each at 10, 25, 50, 100, 150, 200 C/L charge dosage under 5 C/L/min charge dosage rate using a stirring speed of 150 rpm. No NaCl was added in the water solutions as the current applied was small (0.07A) and the conductivity of the effluent water was good enough to pass the current. Based on charge dosage required to remove arsenic below the WHO standard in the effluent of the two columns, the operational parameters of EC in the final filtration columns were decided.

3.2. Phase II

3.2.1. Development of the Filtration Columns

At the end of 2 months, the biological oxidation capacity of the AsOB grown on various bio-carriers (anthracite, coarse sand and garnet) was analyzed and it was observed that the water after passing through the anthracite layer contains arsenic mostly in the form of As (V). So, the anthracite was taken as the main oxidation layer for As (III) and the two columns used for growth of AsOB were modified to develop the final filtration columns.

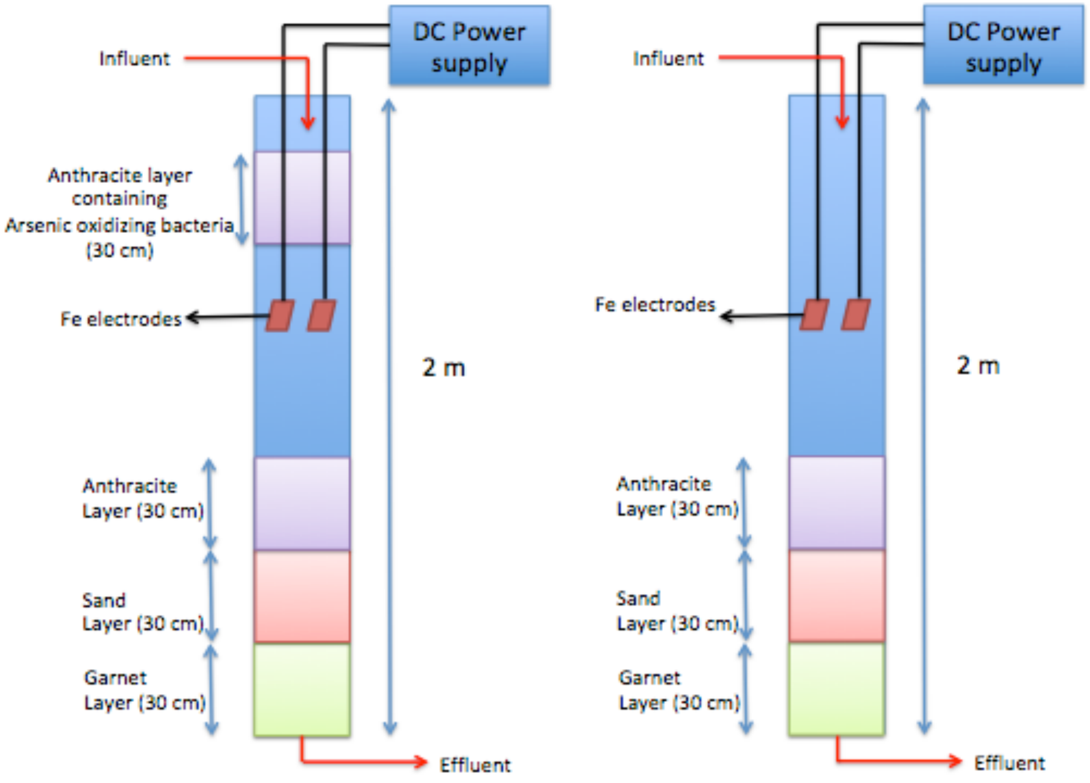


Figure 3.3: Schematic diagram of the final filtration columns. Column 1 (left) containing biological oxidation layer, EC unit and rapid sand filtration and Column 2 (right) containing only EC unit and rapid sand filtration unit

Figure 3.3 shows the schematic diagram of the final filtration columns (Column 1 (left) and Column 2 (right)) developed as the main objective of this research project (image of the lab setup is in Appendix: Figure A4). Column 1 contains the biological oxidation layer (anthracite layer for prior oxidation of As (III) before EC), Fe-EC unit and rapid sand filtration while column 2 contains only the Fe-EC unit and rapid sand filtration (no prior As (III) oxidation before EC). In column 1, the anthracite layer (30 cm) on which the AsOB were grown was taken up from the bottom and placed on the top location in the column. A new anthracite layer was also put at the bottom over the already existing coarse sand and garnet layer for rapid sand filtration. A supernatant water level of 10 cm was maintained in column 1 above the biological layer. The Fe electrodes for EC were placed between the biological layer and the rapid sand filter in column 1. In column 2 only the Fe electrodes were put above the rapid sand filter and the anthracite, coarse sand and garnet layer (containing AsOB) were kept same as before at the bottom used for growth of AsOB. No biological oxidation of As (III) prior to Fe-EC was applied in column 2. Both the columns contain effluent pipes of 2mm diameter over the height connected at right angles to the columns.

The electrodes used for Fe-EC in both the columns were the same as used in the batch studies having a size of 6 cm x 3 cm. The electrodes were connected to a DC current supplier (same as used in batch studies) placed at the top of the columns. The influent of the two columns was the same as used for growth of AsOB i.e., a mixture of tap water and demiwater maintaining an influent As (III) concentration of 150 $\mu g/$L. The procedure for introduction of tap water and As (III) containing demiwater was also the same as used for growth of AsOB and the flow of water inside the two filtration columns was also 1 (± 0.5) m/hr.

The constant current applied for EC in this continuous flow was 0.02 A for both the columns and they were run for 6 continuous hours as experimental run. After, 6 hrs of experimental run, the EC was shut off, but water in the columns was allowed to run as usual. The current was kept at 0.02 A in order to apply a charge dosage of 10 C/L of 5 C/L/min charge dosage rate so that the iron concentration of water becomes 3 mg/L. This charge dosage and charge dosage rate value was chosen for Fe-EC in the two filtration columns because it was observed as the optimum operational parameters to remove 150 μg/L of As (V) (after biological oxidation) below the WHO standard in the batch studies. The current value of 0.02 A was calculated using Eq. 2.1 where the flow rate in the columns was taken as 6 L/hr or 1 m/hr.

The experimental run in the columns were performed 3 times keeping all the parameters same and after 3 runs it was backwashed using tap water.

3.3. Reagents Used

In the batch studies for Fe-EC, three types of water: ultrapure water, tap water and SBGW were used for various experiments. For the experimental runs during EC batch studies, 5 L of arsenic spiked solutions were prepared every day.

For all the types of water used in EC batch studies, the required concentration of As (III) and As (V) was obtained by adding defined volumes of 0.067 mM sodium (meta) arsenite ($NaAsO_2$) and 0.067 mM of sodium arsenate dibasic heptahydrate ($Na_2HAsO_4.7H_2O$) stock solutions respectively. The stock solutions were freshly prepared each day by dissolving the defined amount of reagent grade chemicals- $NaAsO_2$ and $Na_2HAsO_4.7H_2O$ (purchased from Sigma-Aldrich) in 1 L of ultrapure water.

For preparing 5 L of SBGW (Table 3.2) every day, 3 L of ultrapure water was first taken and in that defined amounts of reagent grade chemicals-$NaHCO_3$, $Na_2HPO_4.7H_2O$, $CaCl_2$, $MgCl_2$ and $CaSO_4.2H_2O$ (purchased from Sigma-Aldrich) were added and then mixed properly for total dissolution. After that, the pH of the solution was taken below at around 6.5 by bubbling CO_2 gas and then a defined volume of 0.07 M $Na_2SiO_3.5H_2O$ (purchased from Sigma-Aldrich) stock solution was added and mixed properly. The stock solution for $Na_2SiO_3.5H_2O$ was prepared freshly every 3 days and was kept in the refrigerator at 4^0C. Due to addition of $Na_2SiO_3.5H_2O$ the pH of the solution rises and was found to be between 7.0-8.0. Finally, the required volume of 0.067 mM $NaAsO_2$ stock solution and ultrapure water was added to make 5 L of SBGW.

For dosing As (III) spiked demiwater in the columns for growth of AsOB as well as for influent in final filtration columns required amount of sodium (meta) arsenite ($NaAsO_2$) were mixed in 25 L demiwater jerrycans and in that 2.5 M H_2SO_4 (Merck Millipore) was added.

3.4. Sampling and Analysis

3.4.1. Fe-EC Batch Studies

In all the EC batch studies, two types of samples were collected: filtered and unfiltered. The filtered samples were analyzed for concentration of arsenic, sodium, magnesium, silicon, calcium, phosphate, sulfate, and chloride whereas unfiltered samples were analyzed for iron concentration, before and after electrolysis run. For arsenic speciation, the Clifford method was used. In this method 80 ml of anionic exchange resin (Amberlite* IRA-400 chlorite form resin) was taken in a syringe (100 ml) and 150 ml of solution sample was passed through that 80 ml resin layer. As (V) species were retained in the resin layer and the filtrate coming out was assumed containing only As (III). The difference between total arsenic and As (III) concentration then gave the As (V) concentration in the solution. Out of that 150 ml solution sample the first 50 ml was discarded and the remaining 100 ml was taken for analysis. This speciation method is robust, but it was also found that the resin retains some As (III) (around 14 %) (Gude et al., 2018).

For ultrapure water and tap water, the samples (filtered and unfiltered) collected before and after EC were analyzed for concentration of total arsenic, As (III) and Fe. The filtered samples were collected using 0.45 µm polysthersulfone filters (Macherey-Nagel GmbH & Co. KG). All the samples collected for analysis were acidified using ultrapure nitric acid (Nitric acid Ultra quality, ROTIPURAN® Ultra 69 %) to dissolve any particles present in the sample and to preserve it. The samples were kept in the refrigerator at 4^0C before being analyzed. The analysis of the samples for total arsenic, As (III) and Fe were carried out using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Alanlytik Jena model PlasmaQuant MS).

For SBGW, the concentration of arsenic, iron, chloride, phosphate, sulfate, silicon, calcium, magnesium and sodium were analyzed before and after EC. ICP-MS was used to analyze water samples for arsenic, iron, silicon, calcium, magnesium and sodium, however test kits were used for chloride (LCK 311, HACH chloride cuvette test), phosphate (LCK 349, HACH phosphate (Ortho/Total cuvette test)) and sulfate (Spectroquant® Sulfate cell test, 5-250 mg/L SO_4^{2-}, Merck Millipore).

For EC performed after biological oxidation using the effluent of the two columns, samples were collected before and after EC and analyzed for total arsenic, As (III) and Fe using ICP-MS.

The pH and DO of the water samples before, during and after EC were monitored using a multimeter (WTW^{TM} MultiLine^{TM} Multi 3630 IDS). The conductivity of the water samples were measured before EC using a conductivity meter (WTW^{TM} inoLab^{TM} Multi 9420 IDS^{TM} Digital Benchtop Multiparameter)

3.4.2. Biological Oxidation of Arsenite

In order to check whether biological oxidation of As (III) was occurring in the columns by AsOB or not, water samples were collected and analyzed for total arsenic and As (III) concentration at various positions in the two columns at an interval of 1 week for 49 days. For the entire run period, samples were collected from 2 locations: the supernatant of the columns (acting as influent) and the effluent coming out at the bottom of the columns. The collected samples were filtered using 0.45 µm filters and analyzed for total arsenic and As (III) concentration using ICP-MS. However, at the end of 49 days, water samples were collected from the supernatant, after anthracite layer, after coarse sand layer and after garnet layer (which is the effluent) to determine where the activity of AsOB was maximum to completely oxidize As (III) to As (V). The pH, DO, temperature and conductivity of the water samples were measured using the same instruments as mentioned before.

3.4.3. Filtration Columns

The experimental run for the filtration columns was 6 hours and sampling was done before the run and every 1-hour during the run. Before the experimental run, the samples were collected from the supernatant and after the biological layer of column 1 to check whether oxidation of As (III) was happening by AsOB or not whereas for column 2 only the influent sample was taken. During, the experimental runs in column 1 and 2, the water samples were taken from two locations, one before the rapid sand filter and one after rapid sand filter or effluent of the two columns. The samples taken were analyzed for total arsenic, As (III), As (V) and Fe concentration using ICP-MS and the sampling procedure was same as mentioned before. In order to measure the head loss in the columns due to removal of iron precipitates in the rapid sand filter, the effluent pipes connected at various positions in the columns were connected to piezometers and the head loss was measured by the difference in water levels in the piezometers.

The pH, DO, conductivity and temperature of the water samples were also measured using the same instruments as mentioned before.

4. Results and Discussions for Phase I: Fe-EC Batch Studies and AsOB Growth

4.1. Fe-EC Batch Studies

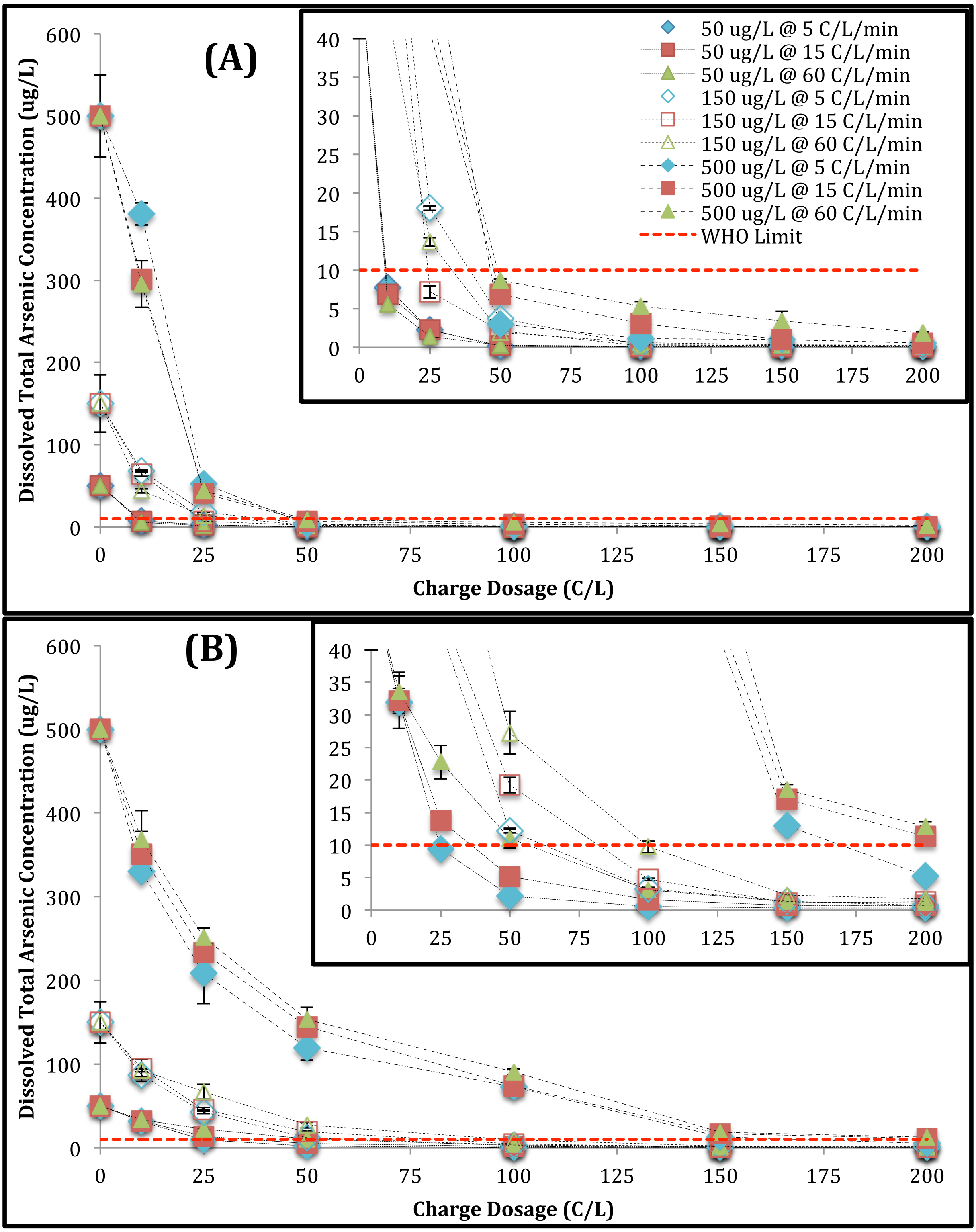
During the EC process, the color of the different water solutions changed from colorless to orangish/reddish brown (typical of Fe (III) (oxyhydr) oxides) with increase in charge dosage (images are shown in Appendix: Figure A17). The precipitates that are formed during Fe-EC were also orangish/reddish brown in color but while using ultrapure water, sometimes at high charge dosage value formation of black precipitates were also observed. Also, it was observed that with increase in charge dosage value the iron concentration in the solution also increased (explained in section 4.1.6). The initial pH of all the solutions in which Fe-EC was applied was maintained at 7.0-8.0, which is the pH range of groundwater and also the optimum pH range reported in studies for efficient removal of arsenic by Fe-EC (Banerji and Chaudhari, 2016; Thakur and Mondal, 2017). During the experimental run, the pH of the solution was observed to increase slightly with electrolysis time. This increase was due to formation of H_2 gas and OH^- ions at the cathode in the solution (Thakur and Mondal, 2017). However, in all the experimental runs the final pH of the solution after EC never exceeded 8.5. Considering the value of dissolved oxygen (DO), for all the solution the DO was around 8 mg/L and during experimental run the DO was observed to decrease with increase in electrolysis time. This decrease in DO was due to the usage of the DO for Fe^{2+} oxidation to Fe^{3+} (Wan et al., 2011). The removal of arsenic during Fe-EC under different operational parameters as well as arsenic species and arsenic concentration are explained below:

4.1.1. Effect of Charge dosage (q) and Charge dosage rate (dq/dt) on Arsenic Removal

The effect of charge dosage and charge dosage rate on removing arsenic (mainly As (III)) for different types of water matrix and initial arsenic concentrations are shown in Figures 4.1 (A), (B) and (C). The figures show that an arsenic concentration below the WHO standard (10 µg/L) is achievable by Fe-EC for all the 3 types of water (containing mainly As (III)) and having different initial arsenic concentrations over a range of (10-200 C/L) charge dosage and (5-60) C/L/min charge dosage rate. However, for SBGW containing initial As (III) concentration of 500 μg/L, the arsenic concentration after EC did not go below the WHO limit (even at 200 C/L charge dosage), but based on the trend shown in the graph a concentration below the WHO limit can be reached at a higher charge dosage. From the results it can be concluded that an increase in charge dosage (q) decreased the concentration of dissolved arsenic in the solution, indicating arsenic ions have been adsorbed and co-precipitated with the HFOs formed (Kobya et al., 2016). In removal of arsenic by using $FeCl_3$ as chemical coagulant it has been reported that increase in $FeCl_3$ dosages increases the arsenic removal (Hering et al., 1996). Similarly, in Fe-EC an increase in charge dosage (q) by increasing the EC time in a defined volume of water and at constant charge dosage rate (dq/dt) will cause a linear increase in iron concentration in the solution as per Faraday's law (Eq. 2.1). So, at high charge dosage (q) more iron is released from the electrode that will lead to formation of more HFOs resulting in more arsenic removal by arsenic-HFO complexes formation (Kumar et al., 2004).

For ultrapure water a minimum charge dosage of around 10, 25 and 50 C/L under all charge dosage rates (dq/dt) was required to have dissolved arsenic concentration below the WHO limit for initial dissolved arsenic concentration (mainly As (III)) of 50, 150 and 500 μg/L respectively. For tap water and SBGW it was 50, 100, 200 C/L and 100, 150 and more than 200 C/L (not shown in the graph but at 200 C/L the dissolved arsenic concentration was above WHO limit for initial arsenic concentration of 500 μg/L) respectively. These results confirm that arsenic removal by Fe-EC is dependent on the amount of coagulant generated as the applied charge loading (q) required to remove arsenic below WHO standard increases with increase in initial arsenic concentration.

Another important thing observed, that for ultrapure water at high charge dosage value, arsenic removal below 1 μg/L was also achieved, which is the new guideline of arsenic concentration in many drinking water companies in the Netherlands (Gude et al., 2018). For instance, in ultrapure water a charge dosage of 50, 100 and 200 C/L under all charge dosage rates caused arsenic removal below 1 μg/L for an initial As (III) concentration of 50, 150 and 500 μg/L respectively. Considering tap water and SBGW, though arsenic removal below 1 μg/L was not achieved under all experiments but with the decreasing trend of dissolved arsenic concentration, a charge dosage higher than 200 C/L could achieve the new drinking water limits of the Netherlands.


(A)
Dissolved Total Arsenic Concentration (ug/L)
Charge Dosage (C/L)
0
100
200
300
400
500
600
0
25
50
75
100
125
150
175
200
0
5
10
15
20
25
30
35
40
50 ug/L @ 5 C/L/min
50 ug/L @ 15 C/L/min
50 ug/L @ 60 C/L/min
150 ug/L @ 5 C/L/min
150 ug/L @ 15 C/L/min
150 ug/L @ 60 C/L/min
500 ug/L @ 5 C/L/min
500 ug/L @ 15 C/L/min
500 ug/L @ 60 C/L/min
WHO Limit
(B)
Dissolved Total Arsenic Concentration (ug/L)
Charge Dosage (C/L)

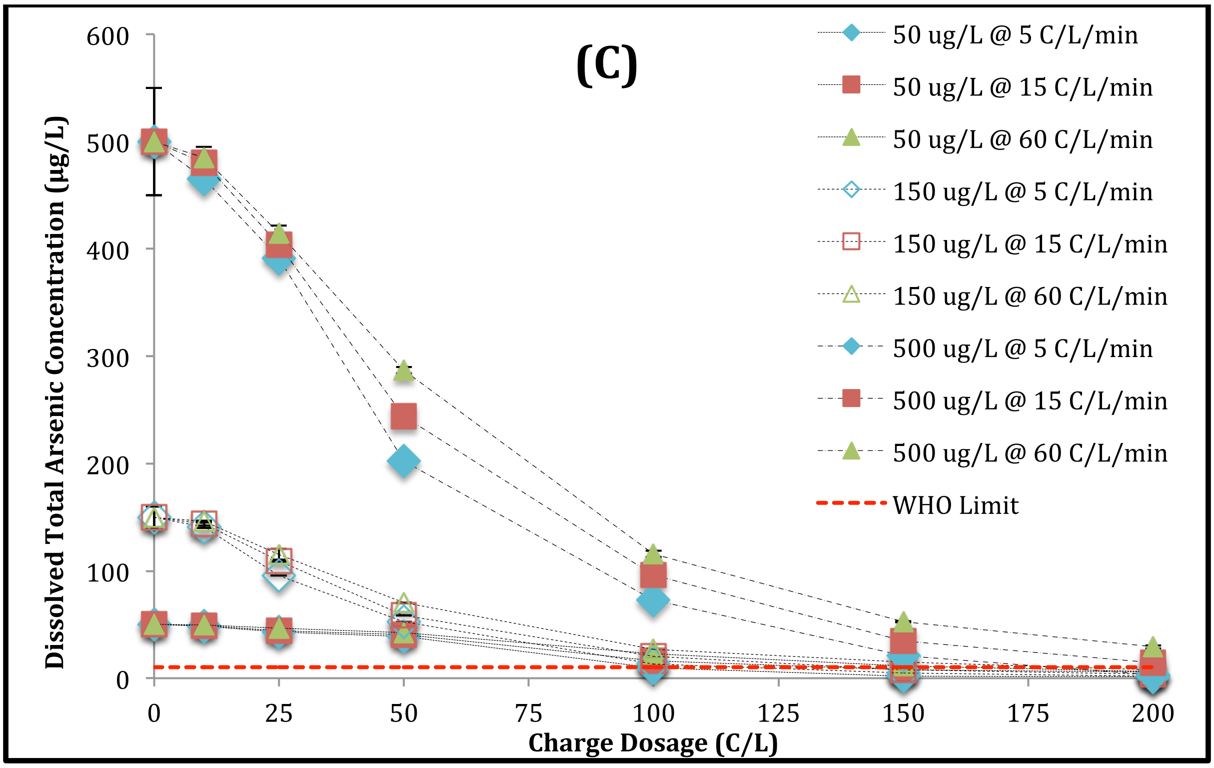


Figure 4.1: Change in dissolved arsenic concentration post-treatment w.r.t 10-200 C/L charge dosage at 5,15 and 60 C/L charge dosage rate for initial As (III) concentrations of 50, 150 and 500 µg/L using ultrapure water (A), tap water (B) and SBGW (C)

Three charge dosage rates 5, 15 and 60 C/L/min used in this study were applied by increasing the current in the DC supplier. This increase in charge dosage rate (dq/dt) helped in decreasing the EC time required to apply a certain charge dosage value (q). For instance, considering ultrapure water having initial As (III) concentration of 500 µg/L, a charge dosage of 50 C/L was required to have dissolved arsenic concentration below WHO limit (Figure 4.1 (A)), but this removal was achieved at an EC time of 0.83 min at 60 C/L/min charge dosage rate compared to 3.33 min and 10 min at 15 C/L/min and 5 C/L/min respectively. Also, from the Figures 4.1 (A), (B) and (C) it can be seen that the dissolved arsenic concentration at different charge dosage rate (dq/dt) but under same charge dosage value (q) for a given initial arsenic concentration was almost the same. However for ultrapure water it was observed that at a constant charge dosage (q) value, a higher charge dosage rate (dq/dt) showed a little more arsenic removal than a lower one. On the other hand, for tap water and SBGW it got reversed, where low charge dosage rate (dq/dt) showed a little more removal compared to the higher value. Similar results were also observed in the study by Amrose et al. (2013) and Kobya et al. (2016), where higher charge dosage rate (dq/dt) showed lower arsenic removal.

Amrose et al. (2013) reported that the contact time between the HFOs formed during Fe-EC with the arsenic remained in the solution is dependent on the charge dosage rate (dq/dt). For a high charge dosage (q) and low charge dosage rate (dq/dt) value, the EC time increases which results in higher average As/HFO ratio and a longer contact time of HFOs with arsenic. This effect causes an increase in arsenic removal efficiency (ARE) (defined as amount of arsenic removed per unit of iron dosage) thereby decreasing the minimum charge dosage (q) required to remove a certain amount of arsenic ions. Furthermore, the ratio of As (III)/Fe^{2+} during EC is also controlled by the charge dosage rate (dq/dt). Study by Roberts et al., (2004) reported that adsorption capacity of Fe^{2+} salts were high due to high As (III)/Fe^{2+} ratio when the salt was added in a multiple number of small dosages compared to a single high dosage. This high As (III)/Fe^{2+} value increased the competitive advantage of As (III) over Fe^{2+} for reactive oxidants or Fenton-type products to undergo oxidation in the system designed by Roberts et al., (2004). Similar to the phenomenon, in Fe-EC where oxidation of As (III) takes place by the Fenton type products generated during Fe^{2+} oxidation to Fe^{3+}, a high As (III)/Fe^{2+} value due to low charge dosage rate will result in more As (III) oxidation. This improvement of As (III) oxidation to As (V) at low charge dosage rate will have caused better removal of arsenic for tap water and SBGW as HFOs have higher affinity for As (V) to get adsorbed (Wan et al., 2011). However, though the arsenic removal efficiency is slightly improved for tap water and SBGW when charge dosage rate (dq/dt) was decreased but the EC time also got increased.

4.1.2. Effect of Initial Arsenic concentration on Arsenic Removal

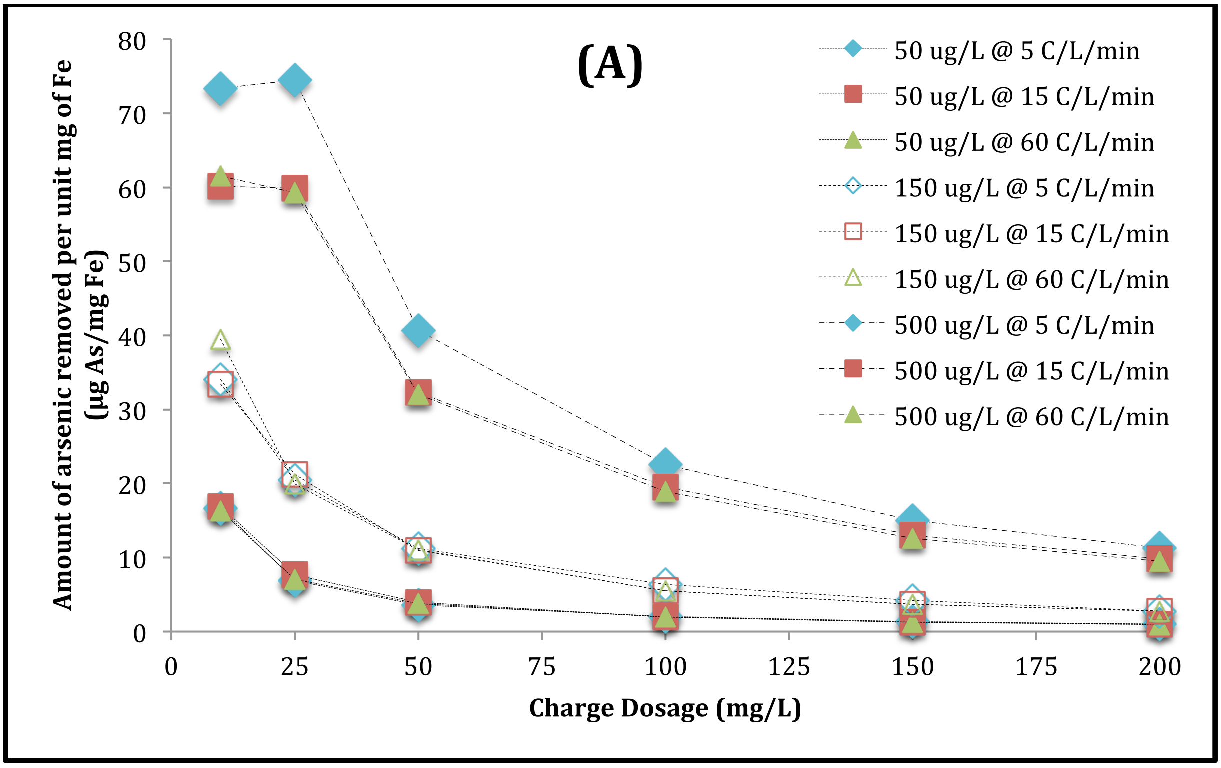
The effect of initial arsenic concentration on arsenic removal by EC for all the 3 types of water can be observed in Figures 4.1 (A), (B) and (C). The experimental data showed that as the initial As (III) concentration increased the charge dosage or iron dosage required to have dissolved arsenic concentration below the WHO limit also increased for all the types of water. For ultrapure water, having an initial arsenic concentration of 50, 150 and 500 µg/L required a charge dosage of 10, 25 and 50 C/L respectively to have dissolved arsenic concentration below WHO limit (10 µg/L) under all charge dosage rate (dq/dt). Similarly for tap water and SBGW, it required a charge dosage of 50, 100, 200 C/L and 100, 150, more than 200 C/L to have final dissolved arsenic concentration below 10 µg/L for initial arsenic concentration of 50, 150 and 500 µg/L respectively under all charge dosage rate. These results show that when initial arsenic concentration is high, more amount of iron is required to be released from the anode to get the dissolved concentration post treatment below a required limit by adsorption or co-precipitation with iron precipitates. Similar results were also reported in other studies and the reason given was as the amount of Fe released was the same at a given charge dosage for all initial arsenic concentration, the iron was not sufficient for solutions containing high initial arsenic concentration to remove arsenic by adsorption. Hence solutions containing high initial arsenic concentration required a high charge dosage or iron dosage compared to solutions containing low initial arsenic concentration, to remove arsenic below a certain standard (Can et al., 2014; Wan et al., 2011, Amrose et al., 2013).

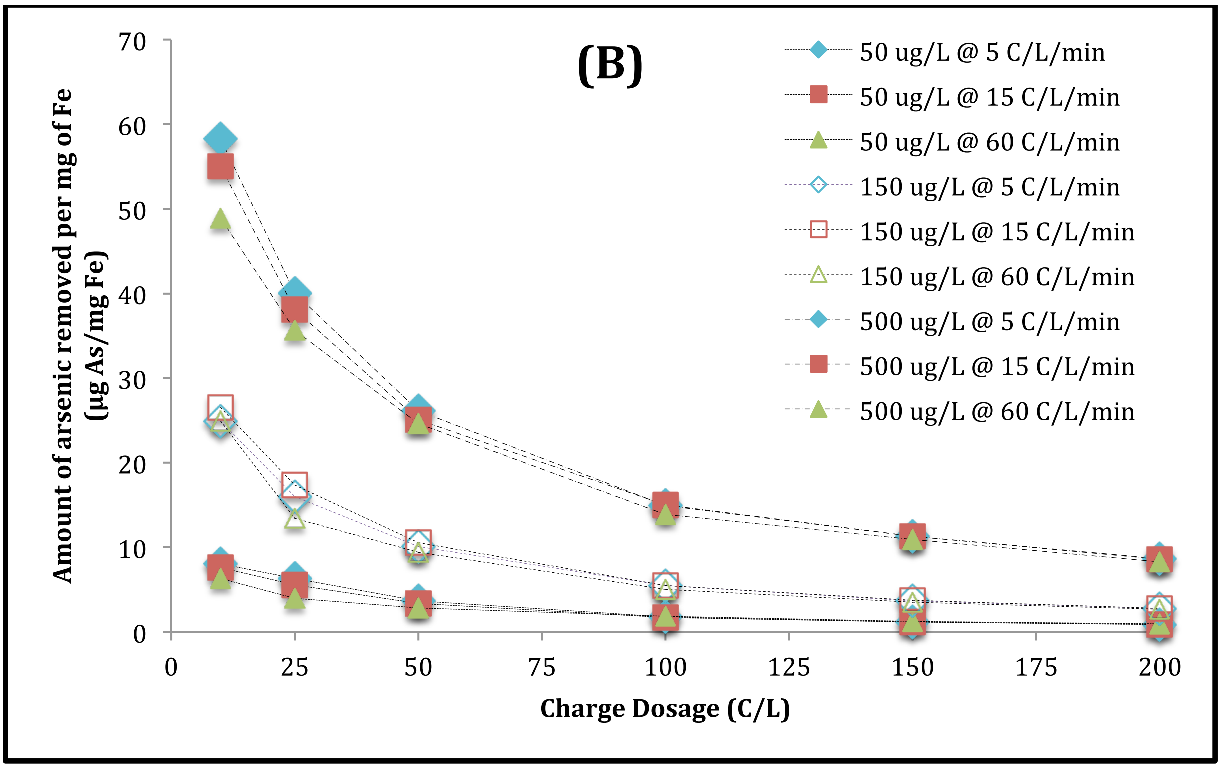
It was also observed that for all initial arsenic concentration, the arsenic removal efficiency value (ARE) (Eq. 4.1) defined as the amount of arsenic removed per unit of charge dosage (Fe dosage) was high initially when charge dosage/iron dosage was low and then decreased gradually with increase in charge dosage/iron dosage and became constant at the end of EC under all charge dosage rate for all the 3 types of water (figures 4.2 (A), (B) and (C)). This is due to the fact that as arsenic was removed by adsorption on HFOs, the release of Fe^{2+} ions from the anode and thereby formation of HFOs was continuous resulting in the decrease of As/HFO ratio. Hence, as the dissolved arsenic concentration decreases with increase in iron dosage, the maximum loading of arsenic on unit amount of HFO in equilibrium also decreases (Amrose et al., 2013). Also, there may be aggregation of the HFOs as it ages in the solution causing reduction in available surface area and adsorption sites. However, this effect was countered due to continuous generation of HFOs causing increase in adsorption sites (Kobya et al., 2016, Amrose et al., 2013).

$$\text{ARE} = \frac{C_i - C_f}{q} \text{ or } \frac{(C_i - C_f)}{w} \qquad \text{Eq. 4.1}$$

where ARE = µg of As removed/C or µg of As removed/ mg Fe, C_i and C_f are the initial and final arsenic concentration in µg/L in the solution and w is the iron concentration in mg/L and q is the charge dosage in C/L.

Also it was observed from Figures 4.2 (A), (B) and (C) that the ARE value for a given type of water at high initial arsenic concentration was higher than that of low initial arsenic concentration. Based on the charge dosage (q)/iron dosage required to have dissolved arsenic concentration below WHO limit, the amount of As (µg) removed per mg of Fe were for ultrapure water was 16.5 (±0.5) for 50 µg/L initial arsenic concentration; 21 (± 1) for 150 µg/L initial arsenic concentration and 40 (± 3) for 500 µg/L initial arsenic concentration under all charge dosage rate. For tap water and SBGW the ratios were 3 (± 0.7), 5.25 (± 0.25), 8.3 (± 0.3) and 1.3 (± 0.5), 3.2 (± 0.2), 8.5 (± 0.6) for initial arsenic concentration of 50 µg/L, 150 µg/L and 500 µg/L respectively under all charge dosage rates (dq/dt). So, for ultrapure water ARE value increased by 2.42 times when the initial arsenic concentration increased by 10 times (50 – 500 µg/L), when minimum Fe dosage was considered to have final dissolved arsenic concentration below 10 µg/L. Similarly for tap water and SBGW it was 2.76 and 6.53 respectively. This phenomenon shows that the arsenic removal efficiency is dependent on the initial arsenic concentration.





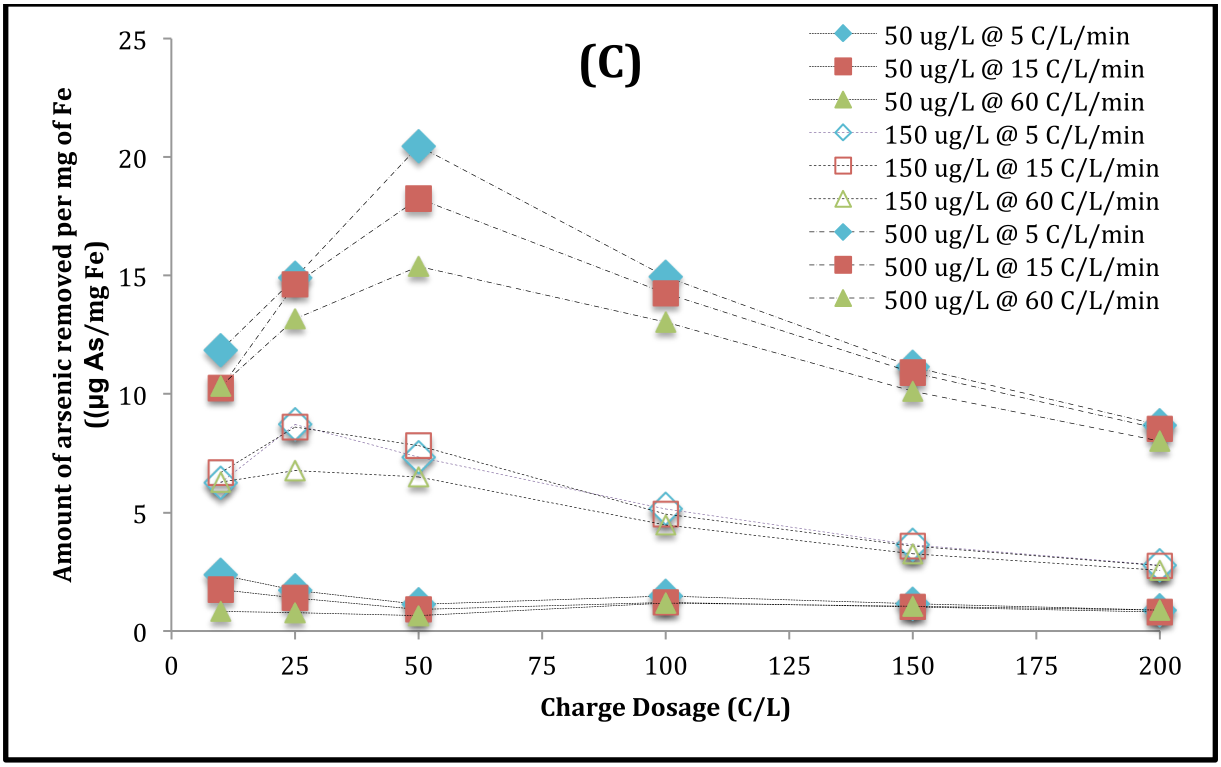


Figure 4.2: Change in arsenic removal efficiency w.r.t (10-200) C/L charge dosage at 5,15 and 60 C/L charge dosage rate for initial As (III) concentrations of 50, 150 and 500 $\mu g/L$ using ultrapure water (A), tap water (B) and SBGW (C)

However, for SBGW it was observed that the arsenic removal efficiency increased as the charge dosage increased from 10 to 25 C/L and 10 to 50 C/L for initial arsenic concentration of 150 and 500 μg/L respectively and then decreased with increase in charge dosage under all charge dosage rates (Figure 4.2 (C)). This initial rise of ARE value could have resulted due to presence of phosphate in SBGW. Phosphate ions have been reported to compete with arsenic ions for adsorption sites on HFOs (Wan et al., 2011; Lakshmanan et al., 2010; You and Han, 2016; Vasudevan et al., 2010a,b). So, when the charge dosage is low (10 C/L) the amount of iron released from the electrode was low resulting in low formation of HFOs. As a result phosphate ions could have adsorbed first on the adsorption sites of the HFOs and causing less availability of adsorption sites for arsenic ions. However when charge dosage increased (25 or 50 C/L), this competitive effect decreased due to increase in HFOs production as the amount of iron released into the solution increased but the concentration of phosphate and arsenic ions remained constant. So, as the charge dosage increased, though there was competitive effect but there was also increase in the adsorption sites onto which the arsenic ions could have adsorbed thereby increasing the ARE value initially.

4.1.3. Effect of Water Matrix on Arsenic Removal

Figure 4.3 shows the effect of water matrices on arsenic removal by Fe-EC. Comparing the effectiveness of Fe-EC to remove As (III) below the WHO limit from the 3 water types, ultrapure water required the lowest charge dosage. So, it can be said that with increase in the water complexity, the amount of arsenic removed for a constant charge dosage value decreased. This decrease in arsenic removal with increase in water complexity could be due to the presence of inhibitory ions like silicate and phosphate (Banerji and Chaudhari, 2016, Wan et al., 2011). Phosphate and silicate has been reported to inhibit the arsenic removal by Fe-EC and so their presence in tap water (no phosphate) and SBGW could have caused less arsenic removal for a given charge dosage compared to ultrapure water, which contains only NaCl. This less removal of arsenic in SBGW water and tap water compared to ultrapure water can also be compared with the ARE values (Figures 4.2 (A), (B) and (C)), where it was observed that ARE value (minimum iron dosage required to remove arsenic below the WHO standard under different As (III) concentration) for ultrapure water (16.5 (±0.5), 21 (± 1), 40 (± 3) for initial As (III) concentration of 50, 150, 500 μg/L respectively) was higher than that of tap water (3 (± 0.7), 5.25 (± 0.25), 8.3 (± 0.3)) and SBGW (1.3 (± 0.5), 3.2 (± 0.2), 8.5 (± 0.6)).

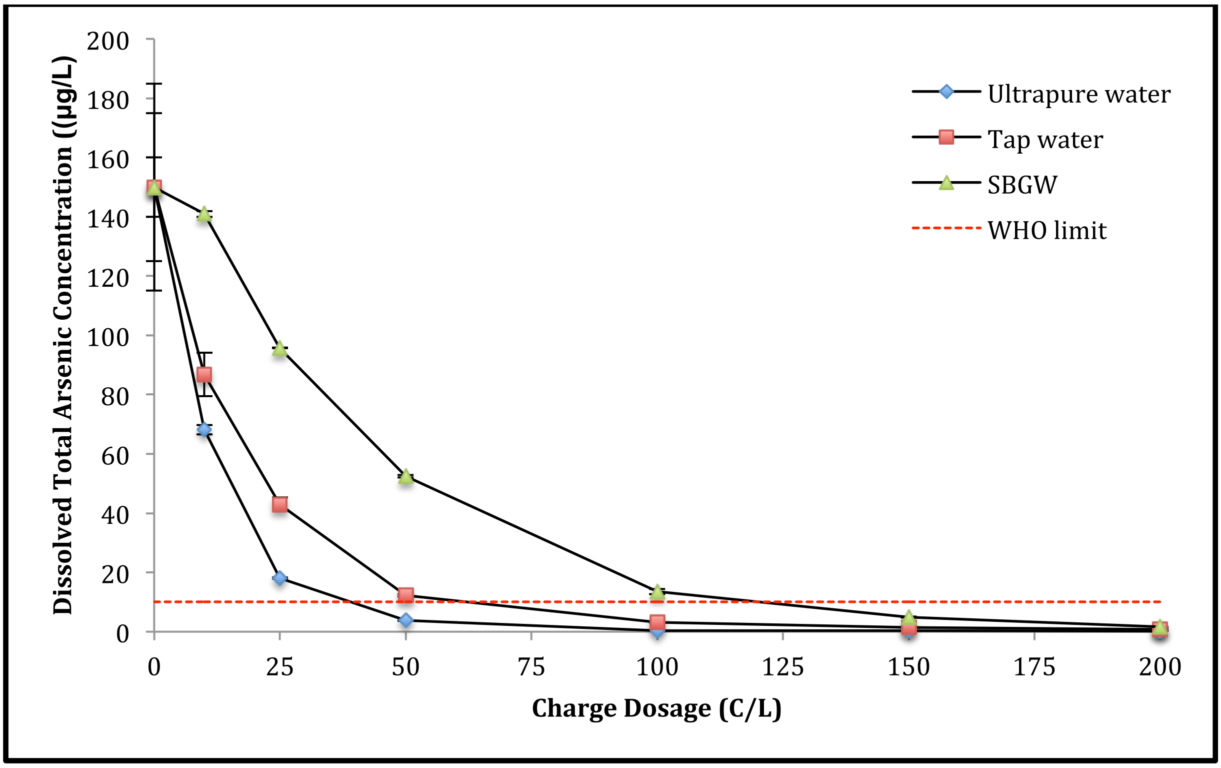
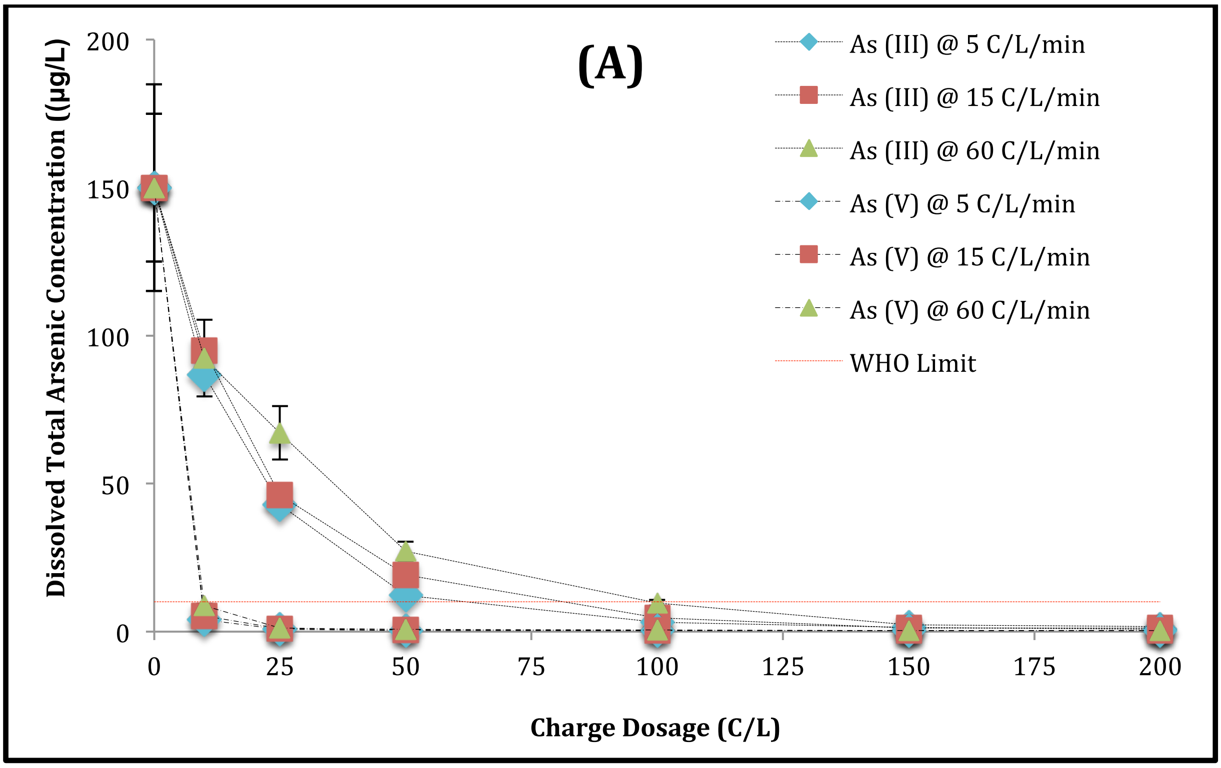


Figure 4.3: Change in dissolved arsenic concentration w.r.t (10-200) C/L charge dosage at 5 C/L/min charge dosage rate for ultrapure water, tap water and SBGW having initial As (III) concentration of 150 µg/L

4.1.4. Comparison of Arsenite (As (III)) and Arsenate (As (V)) Removal

Solutions containing As (V) as the initial arsenic species showed removal of arsenic below the WHO limit at low charge dosage or low EC time (under a constant charge dosage rate) compared to the one containing As (III) indicating that As (V) removal in Fe-EC was faster compared to As (III) (Figures 4.4 (A) and (B)). Similar results were also reported by Wan (2010) for Fe-EC with initial As (III) and As (V) solutions using Fe electrodes where it was observed that at a constant applied current, As (V) removal below 1 µg/L required less EC time or in other words low iron dosage compared to As (III). From Figures 4.4 (A) and (B) it can be reported that using As (V) as initial arsenic species, the residual arsenic concentration goes below WHO limit (10 µg/L) at 10 C/L and 50 C/L charge dosages for initial concentration of 150 µg/L and 500 µg/L respectively. However for As (III), it took 100 C/L and 200 C/L for initial arsenic concentration of 150 µg/L and 500 µg/L to go below WHO limit (10 µg/L). This could be due to the fact that in Fe-EC arsenic is removed by adsorption on HFOs and these HFOs have higher affinity for As (V) to get adsorbed than As (III) (Wan et al., 2010). Also in Fe-EC, it has been proposed that oxidation of As (III) to As (V) happens by Fenton type products produced during Fe-EC and then the arsenic is removed by adsorption on iron precipitates (Kumar et al., 2004; van Genuchten et al., 2016). So, a higher amount of iron dosage will be required to generate sufficient Fenton type products for oxidizing As (III) first and hence a higher charge dosage for beter removal.



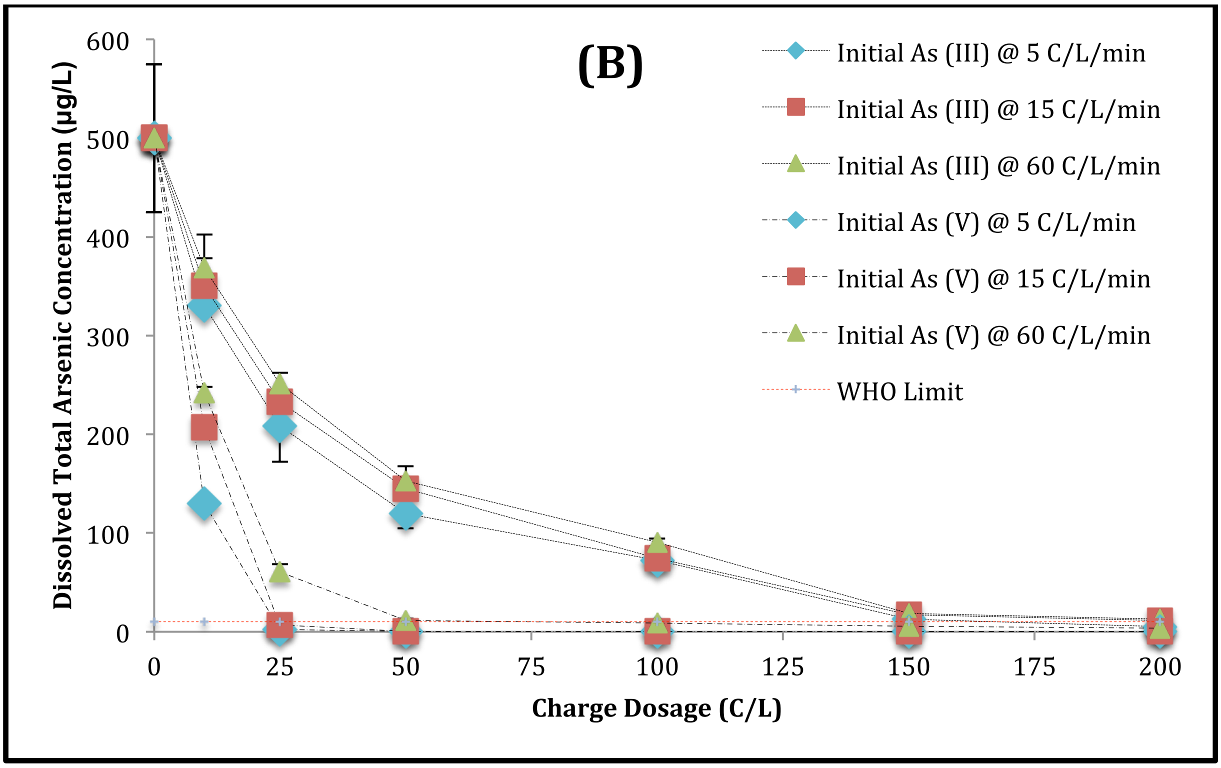
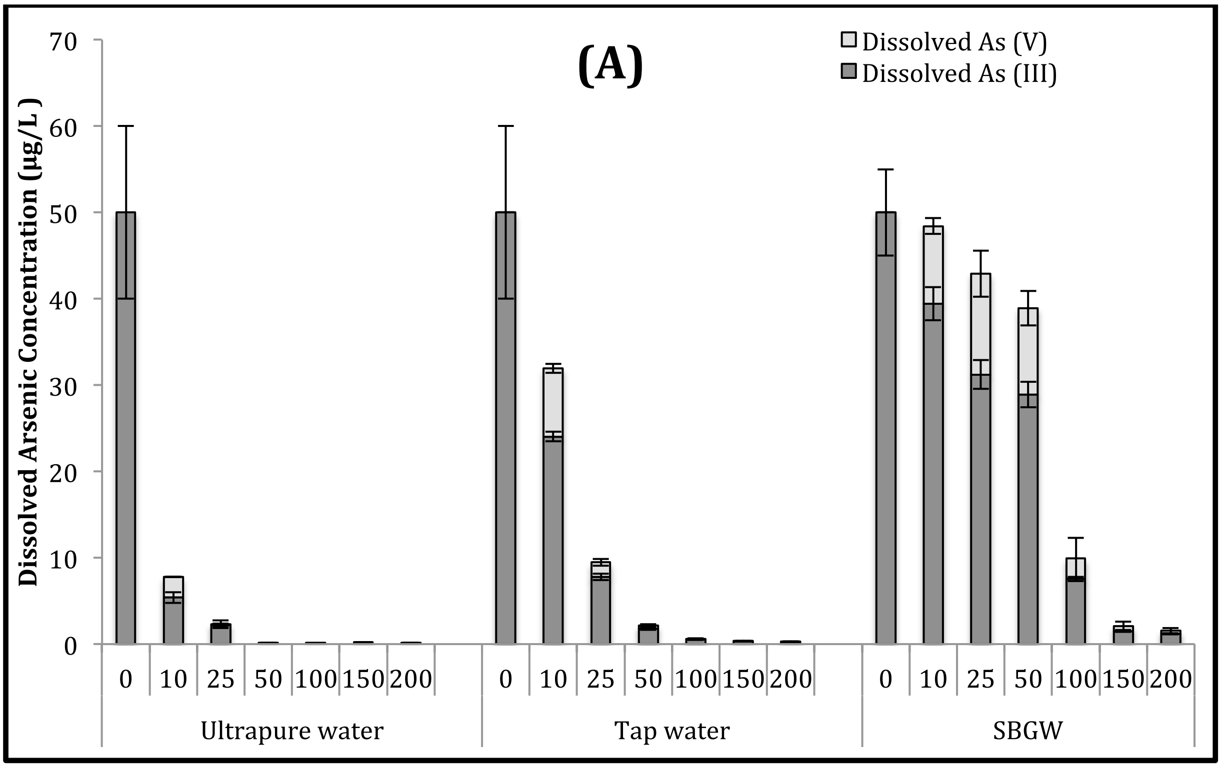


Figure 4.4: Change in dissolved arsenic concentration post-treatment in solutions having initial arsenic species as As (III) and As (V) w.r.t (10-200) C/L charge dosage at 5, 15 and 60 C/L/min charge dosage rate using tap water at initial arsenic concentration of 150 µg/L (A) and 500 µg/L (B)

4.1.5. Change in Arsenite (As (III)) and Arsenate (As (V)) concentration during Fe-EC

In order to check the behavior of As (III) and As (V) during EC, the dissolved As (III) and As (V) concentrations after EC for all 3 types of water containing As (III) as initial arsenic species were measured under various charge dosage (q), charge dosage rates (dq/dt) and initial arsenic concentrations. Figures 4.5 (A), (B) and (C) show the result for change in dissolved As (III) (dark grey columns) and As (V) (light grey columns) post EC w.r.t change in charge dosage (10-200 C/L) at 5 C/L/min charge dosage rate for all the 3 types of water under three initial As (III) concentration (50, 150 and 500 µg/L). The results depicted in the figures show that with increase in charge dosage (or EC time) the dissolved As (III) concentration got decreased. However, the dissolved As (V) concentration increased initially with increase in charge dosage (EC time) under 5 C/L/min charge dosage rate and then subsequently decreased with decrease in total arsenic concentration. Similar behavior was also observed for 15 C/L/min and 60 C/L/min charge dosage rate (data not shown). This decrease in dissolved As (III) and first increase and then decrease of As (V) concentrations indicate some oxidation of As (III) to As (V) during Fe-EC and subsequent removal by adsorption on HFOs mentioned in other studies (Kumar et al., 2004; Banerji and Chaudhari., 2016). Study by Wan (2010) reported 25 % oxidation of As (III) to As (V) during Fe-EC. This oxidation happens as during Fe-EC some reactive intermediate oxidants or Fenton-type products are produced during oxidation of Fe^{2+} to Fe^{3+} that causes oxidation of As (III) to As (V) via As (IV) (van Genuchten et al., 2016; Banerji and Chaudhari, 2016). Also, its been proposed that in the beginning of EC, the rate of As (III) oxidation is higher than the rate of adsorption of As (V) onto HFOs as generation of HFOs will be less initially, that could have resulted in the increase in As (V) concentration initially as shown in Figures 4.5 (A), (B) and (C). However, with increase in EC time or charge dosage the production of HFOs were sufficient to adsorb the generated As (V) and resulted in lowering the As (V) concentration at the end of EC (Zhao et al., 2010).



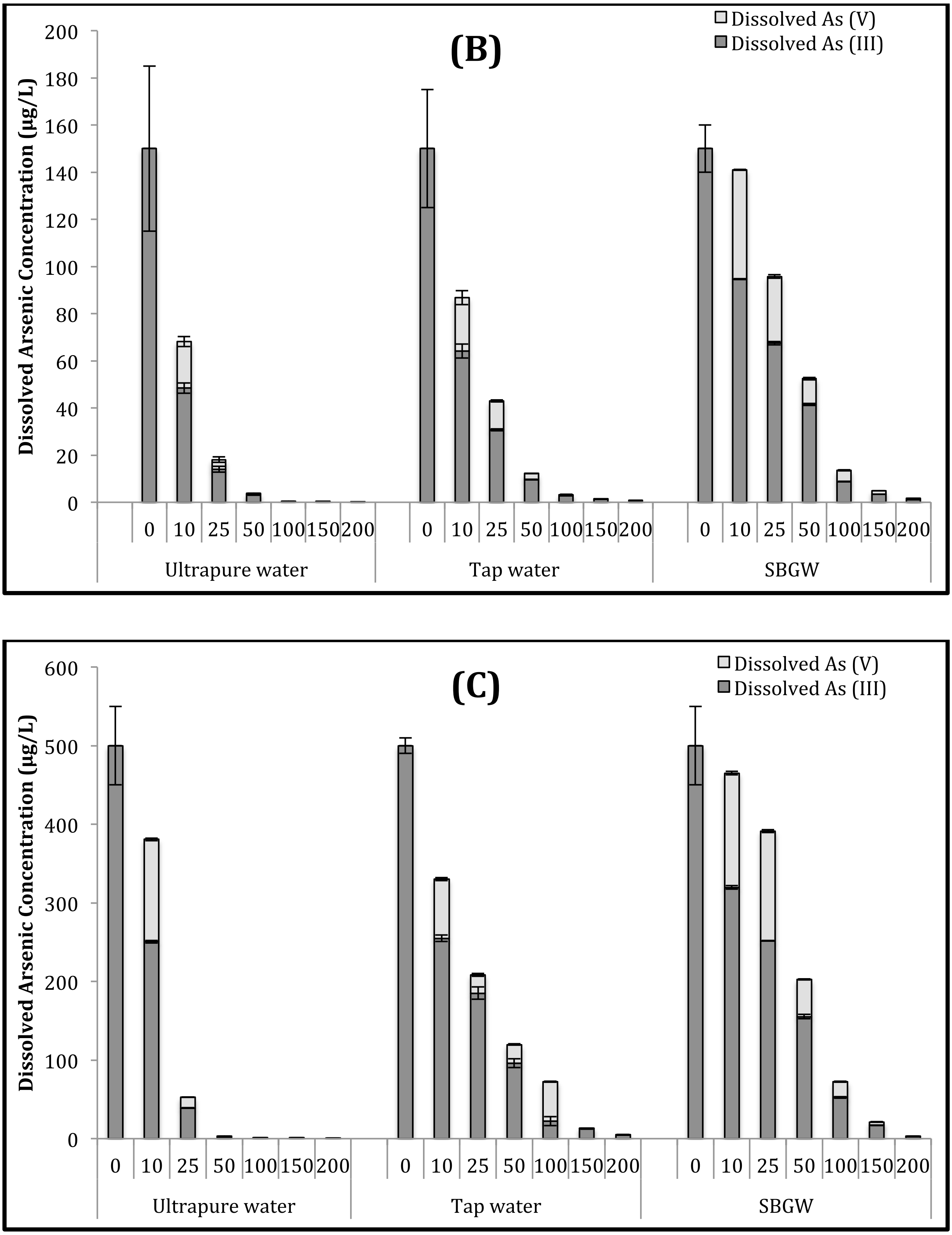


Figure 4.5: Change in dissolved As (III) and As (V) concentration post-treatment in solutions having initial As (III) in ultrapure water, tap water and SBGW w.r.t (10-200) C/L charge dosage at 5 C/L/min charge dosage rate for initial As (III) concentration of 50 µg/L (A), 150 µg/L (B) and 500 µg/L (C)

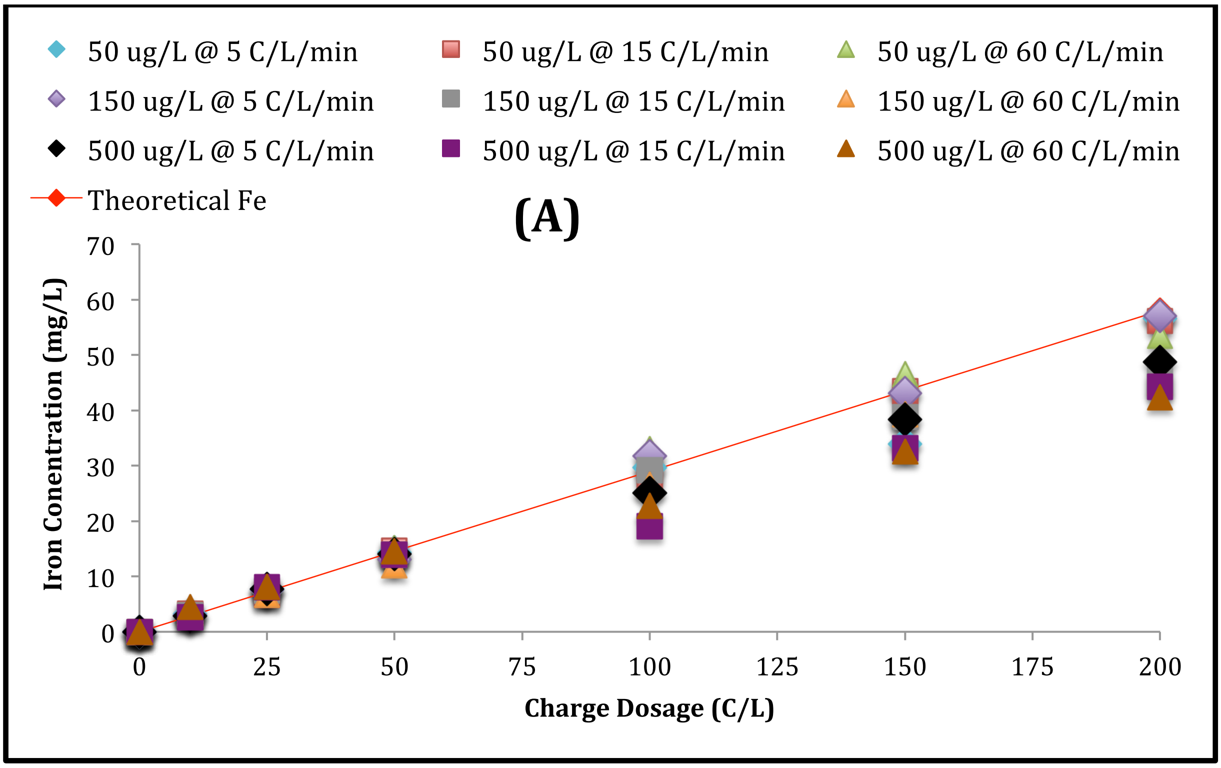
4.1.6. Comparison between the Theoretical and Experimental Iron Elution during EC

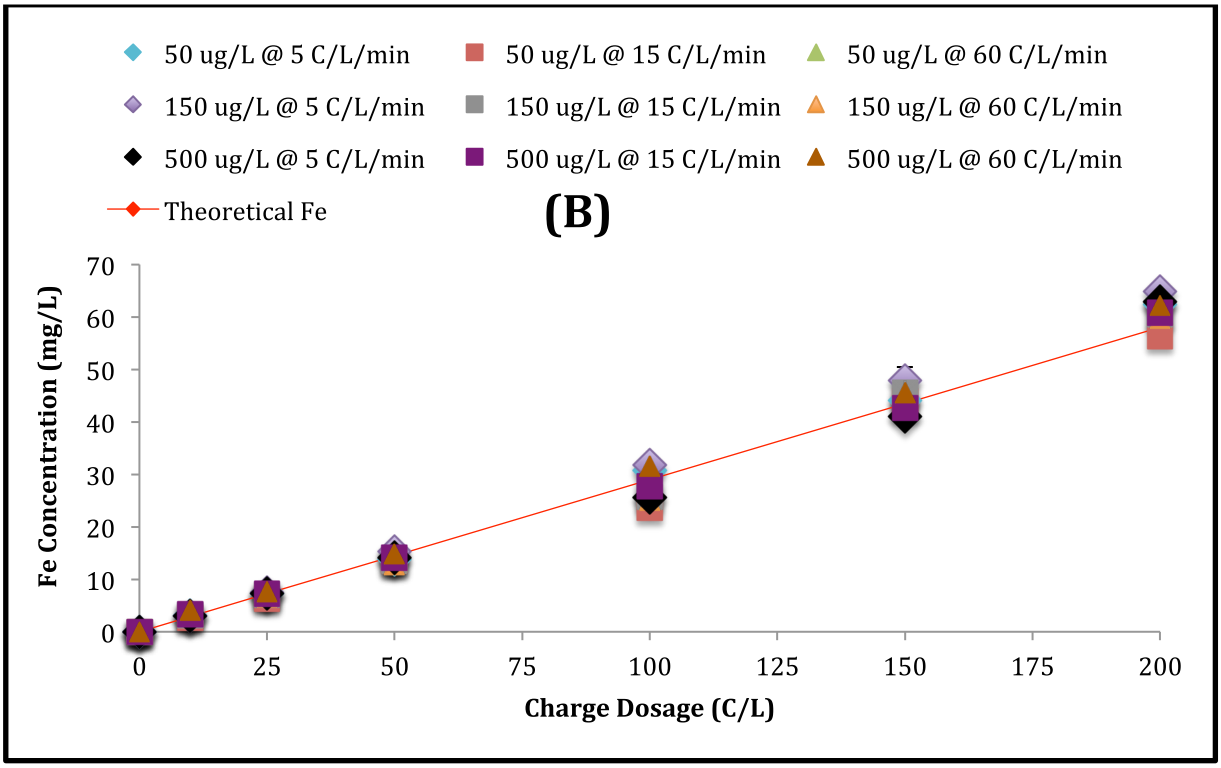
In order to check whether the experimental iron concentration after each batch run in Fe-EC matches with the theoretical iron concentration calculated using Faraday's law (Eq. 2.1), the residual iron concentration for all the three types of water were measured after each EC run for different charge dosage and charge dosage rate and the results are shown in Figures 4.6 (A), (B) and (C). This comparison of experimental and theoretical iron concentration can be referred to as Faradic efficiency, which is defined as the ratio between the experimental concentration and theoretical calculation as shown in Eq. 4.2 (Khaled et al., 2015). From the figures it can be reported that the iron generated during EC for all the types of water at different charge dosage and charge dosage rate closely follows the theoretical value or the Faradic efficiency is around 1. However, at lower charge dosage the theoretical and experimental values were quite similar but at higher charge dosage values there was a little deviation. In some cases the Faradic efficiency was less than 1 whereas in other cases it was greater than 1. A Faradic efficiency greater than 1 could have resulted due to chemical dissolution of the electrodes (Khaled et al., 2015). Also, corrosion and oxidation of the electrode surface under the influence of chloride ions could have resulted in more production of iron oxides or hydroxides (Secula et al., 2012). However a Faradic efficiency lower than 1 could have resulted due to two phenomenon's. One when current is applied to the iron electrodes, the Fe^{2+} ions that been released from the anode got deposited on the electrodes forming a macroscopic electrode surface layer. This generated surface layer then grows by trapping more Fe^{2+} ions generated during EC and decreasing the Faradic efficiency. The other phenomenon can be when the current is applied to the electrodes, instead of oxidizing the iron anode the current oxidizes water or redox active solutes depending on the anodic interface potential (high interface potential favors competing oxidation reactions) and thereby decreasing the Faradic efficiency (Müller et al., 2019).

$$\text{Faradic efficiency} = \frac{c_{\text{experimental}}}{c_{\text{theoretical}}} \qquad \text{Eq. 4.2}$$

where,

$c_{\text{experimental}}$ = Dissolved iron concentration in the solution measured experimentally (mg/L)
$c_{\text{theoretical}}$ = Iron concentration measured using Faraday's law (mg/L)


50 ug/L @ 5 C/L/min
50 ug/L @ 15 C/L/min
50 ug/L @ 60 C/L/min
150 ug/L @ 5 C/L/min
150 ug/L @ 15 C/L/min
150 ug/L @ 60 C/L/min
500 ug/L @ 5 C/L/min
500 ug/L @ 15 C/L/min
500 ug/L @ 60 C/L/min
Theoretical Fe
(A)
Iron Conentration (mg/L)
70
60
50
40
30
20
10
0
0
25
50
75
100
125
150
175
200
Charge Dosage (C/L)


50 ug/L @ 5 C/L/min
50 ug/L @ 15 C/L/min
50 ug/L @ 60 C/L/min
150 ug/L @ 5 C/L/min
150 ug/L @ 15 C/L/min
150 ug/L @ 60 C/L/min
500 ug/L @ 5 C/L/min
500 ug/L @ 15 C/L/min
500 ug/L @ 60 C/L/min
Theoretical Fe
(B)
Fe Concentration (mg/L)
70
60
50
40
30
20
10
0
0
25
50
75
100
125
150
175
200
Charge Dosage (C/L)

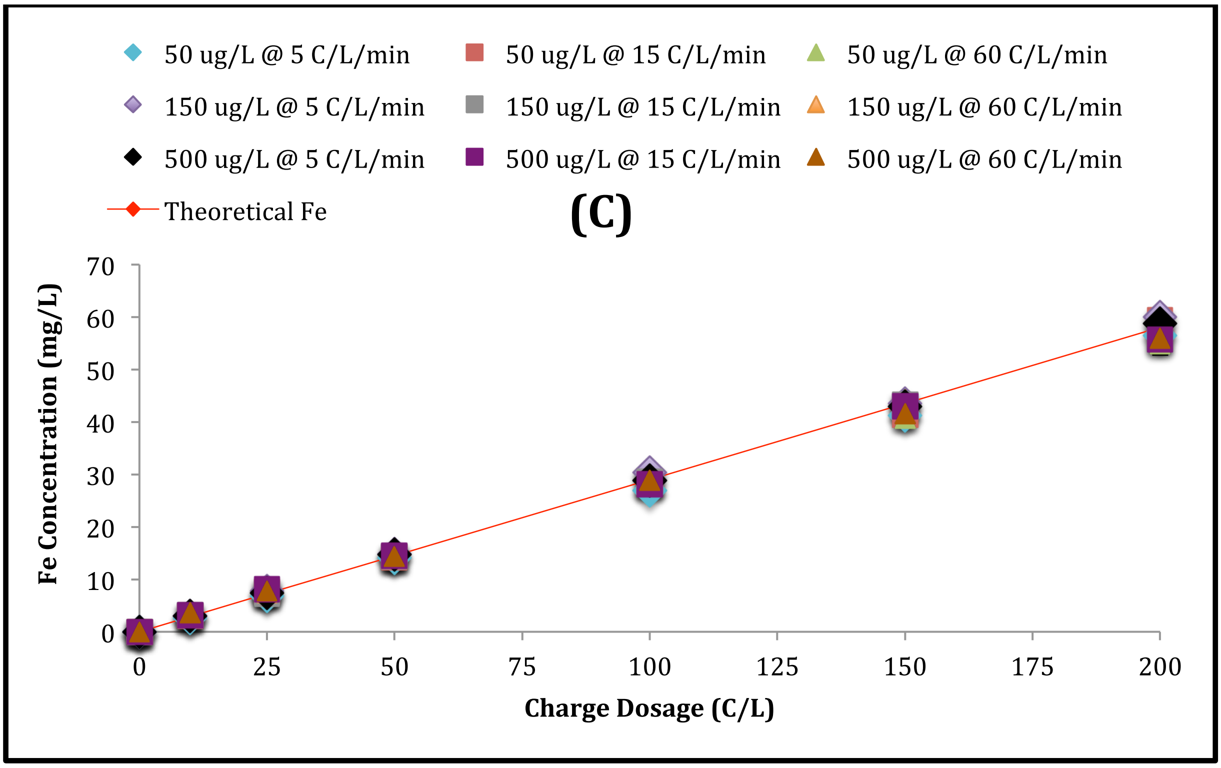


Figure 4.6: Comparison of experimental and theoretical iron concentration post-treatment in solutions having initial As (III) concentration of 50 μg/L, 150 μg/L and 500 μg/L w.r.t (10-200) C/L charge dosage at 5, 15 and 60 C/L/min charge dosage rate using ultrapure water (A), tap water (B) and SBGW (C)

4.1.7. Removal of Other Ions along with Arsenic during Fe-EC

In order to check whether other ions that are present along with arsenic in water gets removed during Fe-EC, the concentration of PO_4^{3-}, SO_4^{2-}, Ca, Si, Mg, Na, Cl^- before and after EC were measured for SBGW. Out of all the ions, PO_4^{3-} and Si showed a significant change in their concentration post-electrolysis (Figures 4.7 (A) and (B)). For PO_4^{3-} and Si, Figure 4.7 (A) and (B) show a decreasing trend in PO_4^{3-} and Si concentration w.r.t (10-200) C/L charge dosage for initial As (III) concentration of 150 µg/L and 500 µg/L under 5, 15 and 60 C/L/min charge dosage rate. From the figures it can be reported that along with arsenic, PO_4^{3-} and Si also got removed due to adsorption on HFO or due to bonding with iron during EC (Wan et al., 2011). Also, the amount of PO_4^{3-} and Si removed for a given charge dosage or for a given amount of Fe was observed to be independent of the initial arsenic concentration.

Considering PO_4^{3-} ions, the removal of PO_4^{3-} ions along with arsenic during Fe-EC has been reported in other studies and PO_4^{3-} has been reported to have inhibition effect on arsenic removal by Fe-EC (You and Hun, 2016; Wan et al., 2011; Banerji and Chaudhari, 2016). Arsenic and phosphorus belongs to the same group in the periodic table and also both of them have same tetrahedral structure and chemical properties. In aqueous environment, both As (V) and phosphorus exist in the form of oxyanions arsenate (AsO_4^{3-}) and phosphate (PO_4^{3-}) resulting in same charge for arsenic and phosphorus and also the structure is tetrahedral surrounded by four oxygen atoms, one oxygen atom linked to arsenic or phosphorus via a double bond whereas the other three oxygen atoms attached via single bonds. Due to this same chemical speciation between arsenate and phosphate they are considered chemical analogues and can substitute for each other in chemical reactions (Strawn, 2018). So, both arsenic (present mainly in the form of As (V)) and phosphate have affinity to get adsorbed on the same adsorption site on HFOs (Kumar et al., 2004; Lakshmanan et al., 2010). Comparing Figures 4.7 (A) and 4.1 (C) for SBGW having initial As (III) concentration of 150 and 500 µg/L, at a charge dosage of 50 C/L almost all the PO_4^{3-} ions got removed however there was still high concentration of arsenic ions that got removed at a higher charge dosage. This shows both PO_4^{3-} and As ions compete each other for adsorption sites on iron precipitates but the removal of PO_4^{3-} was faster. Also, a higher oxidation time for As (III) during Fe-EC has been reported in presence of PO_4^{3-} ions causing the PO_4^{3-} ions to win the competition over arsenic for adsorption sites on iron precipitates as As (III) has less affinity to get adsorbed on iron precipitates (Banerji and Chaudhari, 2016). This inhibitory effect of PO_4^{3-} ions could have resulted in higher charge dosage requirement for removing arsenic below the WHO standard in SBGW compared to ultrapure water and tap water (Figure 4.3) due to competitive adsorption of PO_4^{3-} on the adsorption sites of the iron precipitates thereby leaving less adsorption sites for arsenic (Wan et al., 2011). Also, as the removal of PO_4^{3-} ions by adsorption on HFOs have been observed to be faster than that of arsenic ions, this could have resulted in increasing the ARE value with increase in charge dosage for SBGW (Figure 4.2 (C)). So, when a low charge dosage is applied the amount of iron released into the solution was low and onto which the PO_4^{3-} ions got adsorbed first leaving less available adsorption sites for arsenic to get adsorbed and removed. However, as the iron concentration in the solution increased with increase in charge dosage, though there was adsorption of PO_4^{3-} ions first, but there was also availability of higher adsorption sites for arsenic. This could have resulted in increase in ARE value with initial increase in charge dosage for SBGW as observed in Figure 4.2 (C).

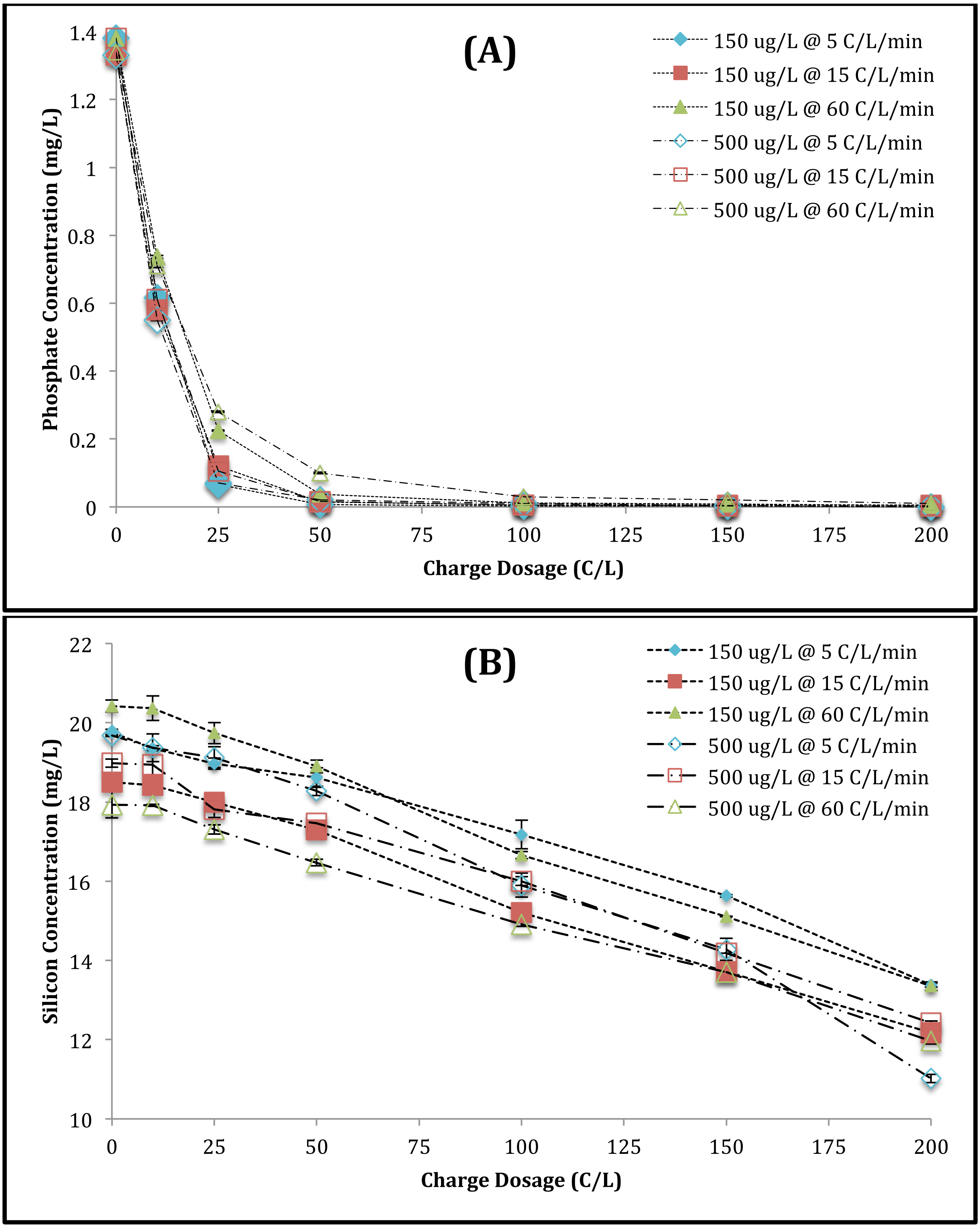


Figure 4.7: Change in dissolved PO_4^{3-} (A) and Si (B) concentration w.r.t (10-200) C/L charge dosage and 5, 15 and 60 C/L/min charge dosage rate for initial As (III) concentration of 150 µg/L and 500 µg/L in SBGW

Though concentration of Si (present in the form of silicate) also got reduced with increase in charge dosage (but not as much as phosphate) (Figure 4.7 (B)) indicating some removal of silicate along with arsenic during Fe-EC, but the inhibitory effect of silicate ions on arsenic removal by Fe-EC is quite unclear. Study by Wan (2010) showed no significant effect of 5 and 20 mg/L silicate on arsenic removal by Fe-EC even though considerable amount of silicate was removed. However, Zeng et al. (2008) observed inhibitory effects of silicate (20 mg/L) on As (V) removal by adsorption on iron-based sorbent. So, in order to check whether silicate ions were affecting the arsenic removal, a study on Fe-EC on solutions containing arsenic and silicate only should have been performed, which was not done in this research work. Banerji and Chaudhari, (2016) did the study on effect of silicate on arsenic removal at three Si concentration of 10, 20 and 30 mg/L for initial As (III) concentration of 1000 µg/L. At Si concentration of 10 and 20 mg/L there was no affect on arsenic removal as the amount of arsenic removed for a given charge dosage in the solution containing As (III) and Si was similar to the one containing only As (III). However, at 30 mg/L Si concentration, the amount of dissolved arsenic in the solution was higher than that without Si and also the amount of As (III) oxidized also got reduced at Si concentration of 30 mg/L. So, comparing to that study where ratio of Si/As was 30, in this study the ratio was 128 and 38 for initial arsenic concentration of 150 and 500 µg/L respectively, it can be said Si could have some inhibitory effect on arsenic removal by Fe-EC. The main reason could be when Si is present in high concentration, silica polymerize and physically block the path to adsorption sites present in the internal pores of the iron precipitates. This phenomenon reduces the adsorption sites for arsenic by physical blocking and not by competitive adsorption (Wan et al., 2011).

For other ions such as SO_4^{2-}, Ca, Mg, Na, Cl^-, the concentration before and after EC was observed to be similar (data shown in appendix). So, it can be reported that these ions did not get removed during Fe-EC.

4.2. As (III) Oxidation Profile by AsOB in the Columns

Figures 4.8 (A) and (B) show the concentration of As (III) and As (V) in the influent and effluent of the two columns (1 and 2) during a period of 49 days. The average total arsenic and As (III) concentration in the influent during the entire run period was 170 µg/L (max 180 µg/L; min 150 µg/L) and 143 µg/L (max 167 µg/L; min 116 µg/L) for column 1 whereas for column 2 it was 169 µg/L (max 196 µg/L; min 130 µg/L) and 140 µg/L (max 156 µg/L; min 115 µg/L). Though the dosing jerrycans contain As (III) but due to homogeneous oxidation in the jerrycans there was some As (V) in the influent of both the columns (Gude et al., 2018). Also, the total arsenic concentration in the effluent was always lower than that of the effluent indicating retention of some dosed arsenic in the bio-carriers.

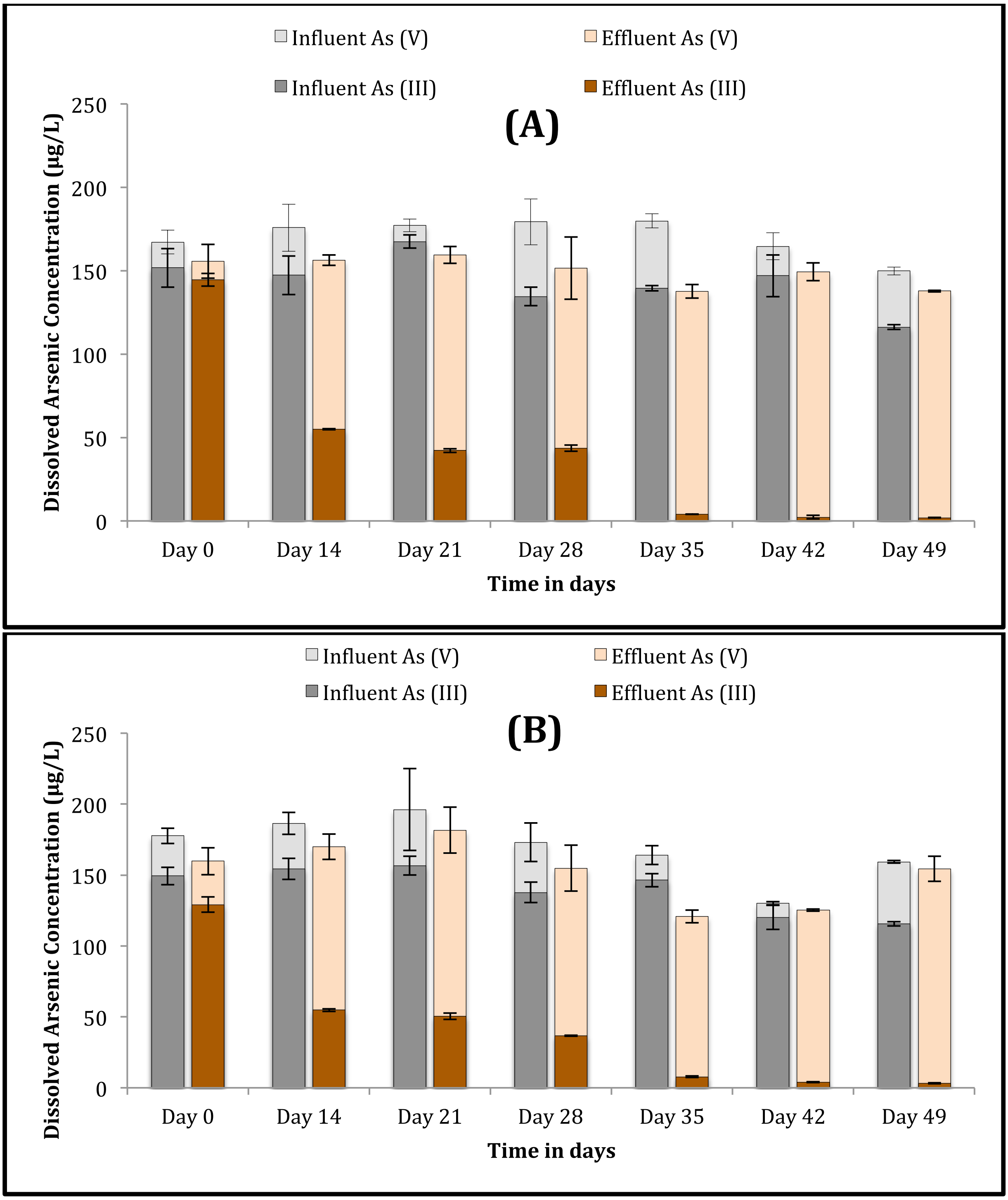


Figure 4.8: Concentration of dissolved As (III) and As (V) in the influent and effluent over time for column 1 (A) and column 2 (B)

From Figures 4.8 (A) and (B) it can be said that after 14 days around 66(±2) % of As (III) oxidation was observed in the effluent for both the columns. However, at 49 days almost 99 % As (III) oxidation was observed in the effluents of column 1 and 2. These results indicate growth of AsOB on the bio-carriers as no other arsenic oxidizing compounds were present in the water. Similar results were also observed by Gude et al., (2018) where 98 % of As (III) oxidized to As (V) at the end of 38 days in the effluent of sand columns dosed with drinking water spiked with 100 µg/L As (III). Though microbial analysis was not performed in this study, but comparing with the similar study done by Gude et al., (2018) where microbial community profiling of the biomass on sand filters showed presence of AsOB, it can be reported that in this study also AsOB was causing the biological oxidation of As (III) to As (V). Also, it can be reported from the results that the AsOB grown on the bio-carriers were quite effective to completely oxidize 150 µg/L As (III) in a continuous flow mode.

Also after 49 days the concentration of As (III) and As (V) at various locations in the two columns were measured to determine where the maximum oxidation of As (III) was happening in the columns. From Figures 4.9 (A) and (B) it can be observed that 95 % of As (III) oxidation occurred in water samples collected after the anthracite layer for columns 1 and 2. So, the AsOB present in the anthracite layer was actually playing the important role in oxidizing As (III). Also, in the study by Gude et al., (2018) on As (III) oxidation using sand layer as bio-carrier, vertical distribution of biomass over the sand layer was observed where highest concentration of AsOB was reported on the top portion of the sand layer and lowest concentration at the bottom. So, comparing with that study it can be said that in this study also the concentration of bacteria was highest in the anthracite layer compared to coarse sand and garnet layer. This higher concentration of bacteria at the top could be due to the fact that in the top location the bacteria were getting As (III) directly compared to lower locations, which is their main source of growth.

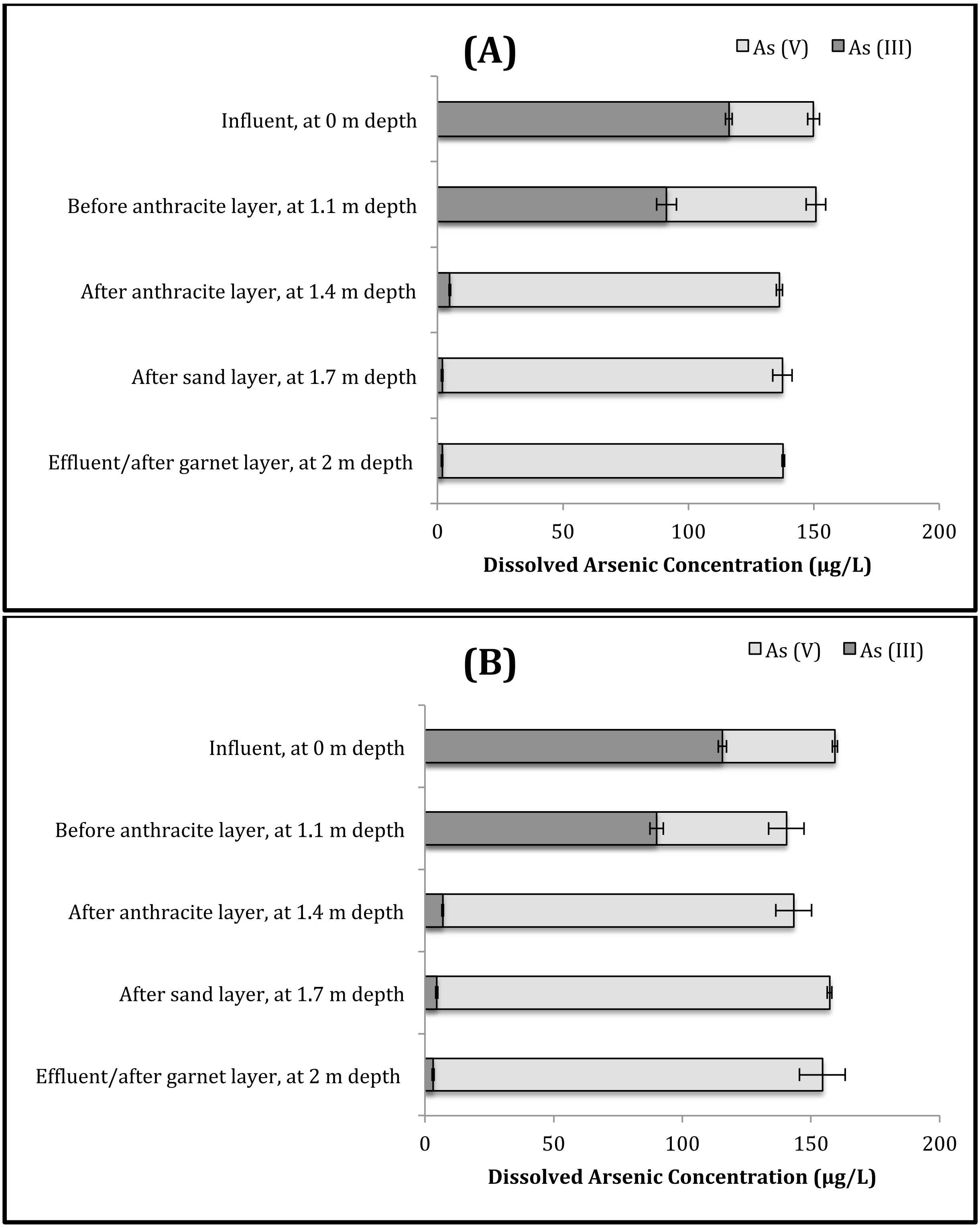


Figure 4.9: Concentration of dissolved As (III) and As (V) w.r.t depth or location after 49 days column run in column 1 (A) and column 2 (B)

The pH, DO, conductivity and temperature of all the water samples taken during this 49 days period was 7.5 (±0.5), 8 (±1) mg/L, 300 (±100) µS/cm and 20 (±2) ^{0}C.

4.3. Application of Fe-EC on the Effluent of the Columns containing AsOB

In order to check the effectiveness of Fe-EC for removing As (III) from water after biological oxidation of As (III) to As (V), effluents from column 1 and 2 were taken after the anthracite layer where more than 90 % oxidation of As (III) was observed after 49 days column run as shown in Figure 4.10 and then on that water Fe-EC was applied. Fe-EC on both the effluents of the two columns were performed under 10, 25, 50, 100, 150 and 200 C/L charge dosage at 5 C/L/min charge dosage rate and the results are shown in Figure 4.11 (blue points with continuous and dashed lines in the figure). Also the results obtained when Fe-EC was applied on tap water containing 150 µg/L As (III) and As (V) as initial arsenic species under same charge dosage and charge dosage rate values, are also shown in Figure 4.11 (green point with continuous and dashed lines in the figure) in order to compare the removal behavior of arsenic in the column water (containing mainly As (V)) and in water containing As (III) and As (V) as initial arsenic species. From the results obtained, the removal behavior of arsenic by Fe-EC from the column effluents is observed to be similar when Fe-EC was performed on tap water containing As (V) as initial arsenic species at 150 µg/L as shown in Figure 4.11 (comparing blue points with continuous and dashed lines with green points with dashed line). The results show that for both the column effluents (containing mainly As (V) at concentration around 150 µg/L) and tap water (containing 150 µg/L As (V) as initial arsenic species) a charge dosage of 10 C/L at 5 C/L/min charge dosage rate removed arsenic below the WHO standard. Also the measured iron concentration in both the water types was around 3 mg/L for a charge dosage of 10 C/L. As biological oxidation converted most of the As (III) to As (V) in the effluents of the two columns, so the column effluents and tap water containing As (V) as initial arsenic species behaved as a similar water type and both the water types showed arsenic removal below WHO standard at 10 C/L charge dosage at 5 C/L/min charge dosage rate. Also comparing with tap water containing 150 µg/L As (III) and As (V) as initial arsenic species, water containing As (III) as initial arsenic species requires a charge dosage of 100 C/L to remove arsenic below the WHO standard compared to 10 C/L for water containing As (V) as initial arsenic species (green points with continuous line in Figure 4.11). These results clearly show the potential advantage of applying Fe-EC after biological oxidation of As (III) for removal of As (III) from water bodies as very small charge or iron dosage was required after As (III) oxidation in order to take the dissolved arsenic concentration below the WHO standard.

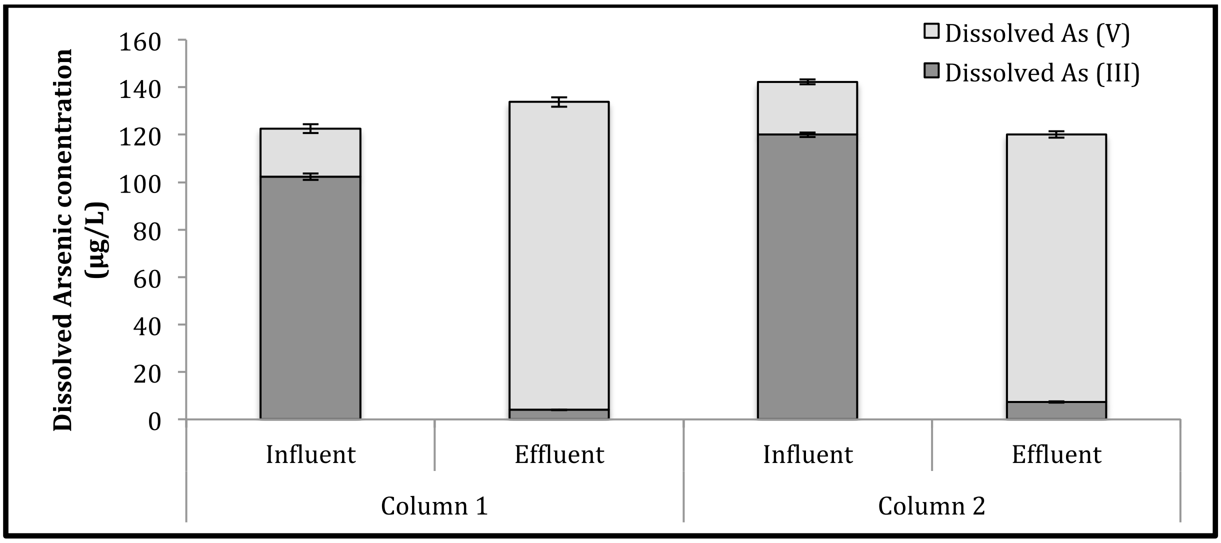


Figure 4.10: Concentration of As (III) and As (V) in the influent and after anthracite layer/effluent of column 1 and column 2 after 49 days column run

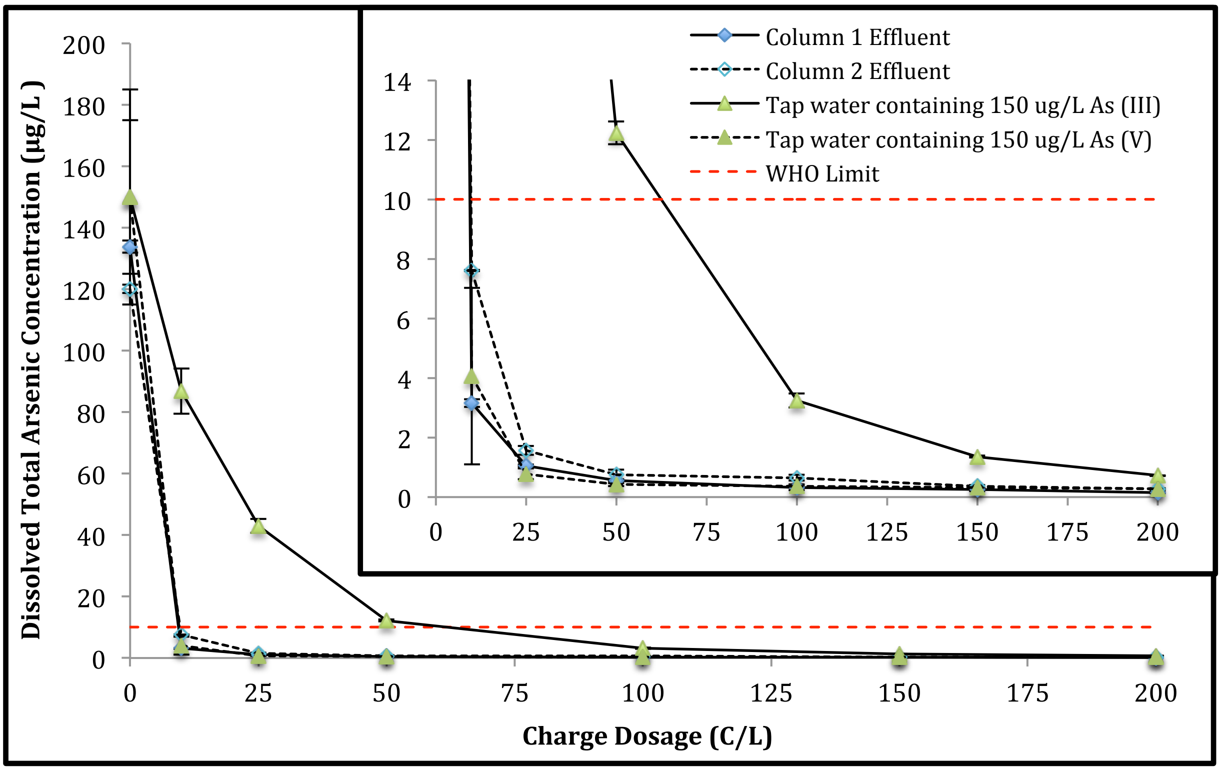


Figure 4.11: Change is dissolved arsenic concentration w.r.t (10-200) C/L charge dosage at 5 C/L/min charge dosage rate for effluents after anthracite layer of column 1 and 2 after 49 days column run and for tap water containing 150 µg/L As (III) and As (V) as initial arsneic species

4.4. Summary of Phase I Studies

Based on the various experiments and analysis performed during Phase I, the following important points can be summarized:

1) Performance of Fe-EC on removal of arsenic from water

    - The main factor that decides the removal of arsenic in Fe-EC is the amount of coagulant generated due to release of iron from the anode. Also, the amount of iron dosed and the rate at which it is dosed into a solution is better defined by charge dosage and charge dosage rate rather than current density (which is considered as the main operational parameter for EC in various studies).

    - Fe-EC has shown potential to remove both As (III) and As (V) from different water solutions at different initial concentrations below the WHO standard (10 µg/L) by increasing the charge dosage or iron dosage in the solutions. Also, Fe-EC has shown potential to remove arsenic below 1 µg/L, which is the new guideline for drinking water in the Netherlands.

    - Comparing between the arsenic species, solution containing As (V) as initial arsenic species required less charge dosage or iron dosage compared to solution containing As (III) to remove arsenic below the WHO standard by Fe-EC. This phenomenon validates that As (V) has higher affinity to get adsorbed on the HFOs formed during Fe-EC than As (III).

    - Increasing the charge dosage rate by increasing the current applied helped to reduce the electrolysis time required to dose a defined amount of iron with a little loss in the amount of arsenic removed for tap water and SBGW.

    - Increasing the initial arsenic concentration increases the charge dosage or iron dosage required to remove arsenic below the WHO standard (10 µg/L).

    - ARE was high initially at the start of the EC but gradually decreases as the electrolysis time increases and becomes constant at the end of EC due to decrease in As/Fe ratio with electrolysis time.

- ARE value for a given solution having high initial arsenic concentration was higher than that of low initial arsenic concentration.

- Oxidation of As (III) to As (V) during Fe-EC was observed, which could be due to the formation of Fenton type products that can oxidize As (III) in Fe-EC.

- Along with arsenic, phosphate and silica also gets removed in Fe-EC.

2) Growth and Performance of AsOB

- Continuous dosing of tap water containing 150 µg/L As (III) in vertical columns containing rapid sand filter materials as bio-carriers over a period of 7 weeks resulted in growth of AsOB on the bio-carriers.

- More than 90 % oxidation of 150 µg/L As (III) in the filtrate of the columns was observed at 35 days (5 weeks) indicating the potential of AsOB to oxidize As (III) in a continuous flow mode.

- The majority of the As (III) oxidation was happening at the top layer of rapid sand filter (anthracite layer) indicating that the population of bacteria was highest at the top layer.

- As no other arsenic oxidizing compounds were present in the tap water dosed into the bio-carriers, so the main oxidation mechanism of As (III) was by growth of AsOB on the bio-carriers.

3) Performance of applying Fe-EC after biological oxidation of As (III)

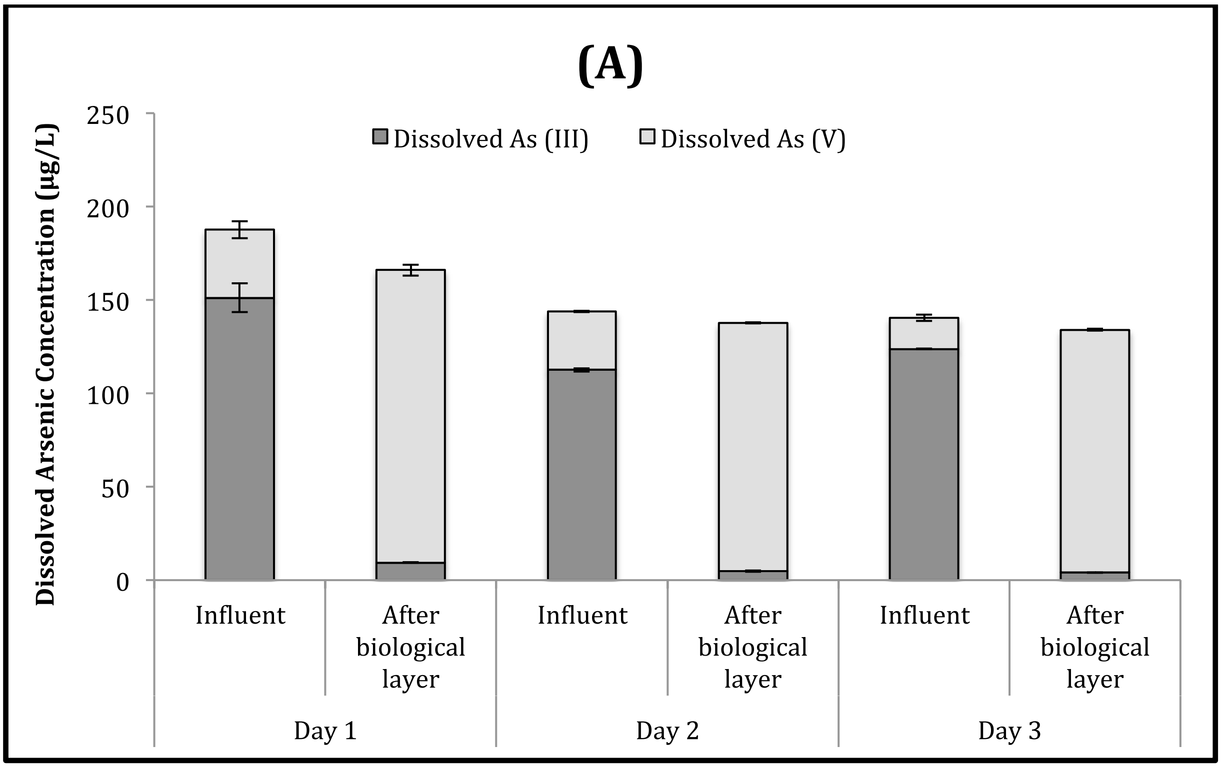
- Performing biological oxidation of As (III) to As (V) and then applying Fe-EC in a batch system helped in removing 150 µg/L of arsenic from water below the WHO standard (10 µg/L) at a low charge dosage or iron dosage (10 C/L) compared to water containing arsenic initially in the form of As (III) (100 C/L).

5. Results and Discussions for Phase II: Filtration Columns

5.1. Column 1: Containing Biological Oxidation Layer followed by EC unit

Figure 5.1 (A) shows the concentration of dissolved As (III) and As (V) in water at the influent and after passing through the biological layer in column 1 for all the 3 days. In all the 3 days, the influent arsenic concentration was around 150 (±35) µg/L and most of the arsenic was in the form of As (III) (shown as dark grey columns in Figure 5.1 (A)). However, after passing through the anthracite layer having the AsOB, more than 90 % oxidation of As (III) to As (V) was observed (shown as light grey columns in Figure 5.1 (A)) and the total arsenic concentration was little less than the influent, which could be due to retention of some arsenic in the biological layer. So, the arsenic contaminated water going for EC contain mainly As (V). Though during EC batch studies, the solution was constantly stirred for proper mixing of iron precipitates but in the columns the iron released was allowed to mix by the flow itself. Regarding EC in the column, a 10 C/L charge dosage at 5 C/L/min charge dosage rate was applied (by applying 0.02 A current) and this operational parameter was based on the results obtained for batch studies when EC applied on the column effluents (used as growth of AsOB) as shown in Figure 4.11. The batch study results showed that a charge dosage of 10 C/L at 5 C/L/min charge dosage rate resulting in an iron dosage of 3 mg/L was sufficient to have dissolved arsenic concentration below 10 µg/L when 150 µg/L of As (III) was oxidized to As (V) by AsOB (Figure 4.11), so similar operational parameter was also maintained in the final filtration columns.

After Fe-EC, for day 1, the dissolved arsenic concentration in water before rapid sand filtration decreased with increase in run time and at 5th and 6th hour the concentration goes below the WHO standard (blue points in Figure 5.1 (B)). These results for day 1 indicate that the system took time to get stable initially and once got stabled the oxidized As (V) was able to get adsorbed on the iron that was being released continuously from the electrodes during the 6 hours run time. Also, improper mixing of iron in the flowing water could have resulted in less iron removal in the initial hours of day 1. However for day 2 and 3, the dissolved arsenic concentration in water after EC and before rapid sand filtration goes below the WHO standard for all the hours even though the operation parameters were kept constant as in day 1. Though the EC operational parameters in day 2 and day 3 were same as that of day 1 but it was observed that the iron concentration in water after EC for day 2 and 3 (around 8 mg/L) was higher than that of day 1 (around 3 mg/L) (shown in Appendix: Figures A6, A7 and A8). This high concentration of iron in day 2 and day 3 could be due to fluctuations in water flow inside the columns or due to accumulation of iron precipitates over the rapid sand filter from day 1 as no backwashing was performed. The presence of higher iron concentration in water could have resulted in better arsenic removal for the entire experimental run in day 2 and day 3 compared to day 1 (Figure 5.1 (B)).



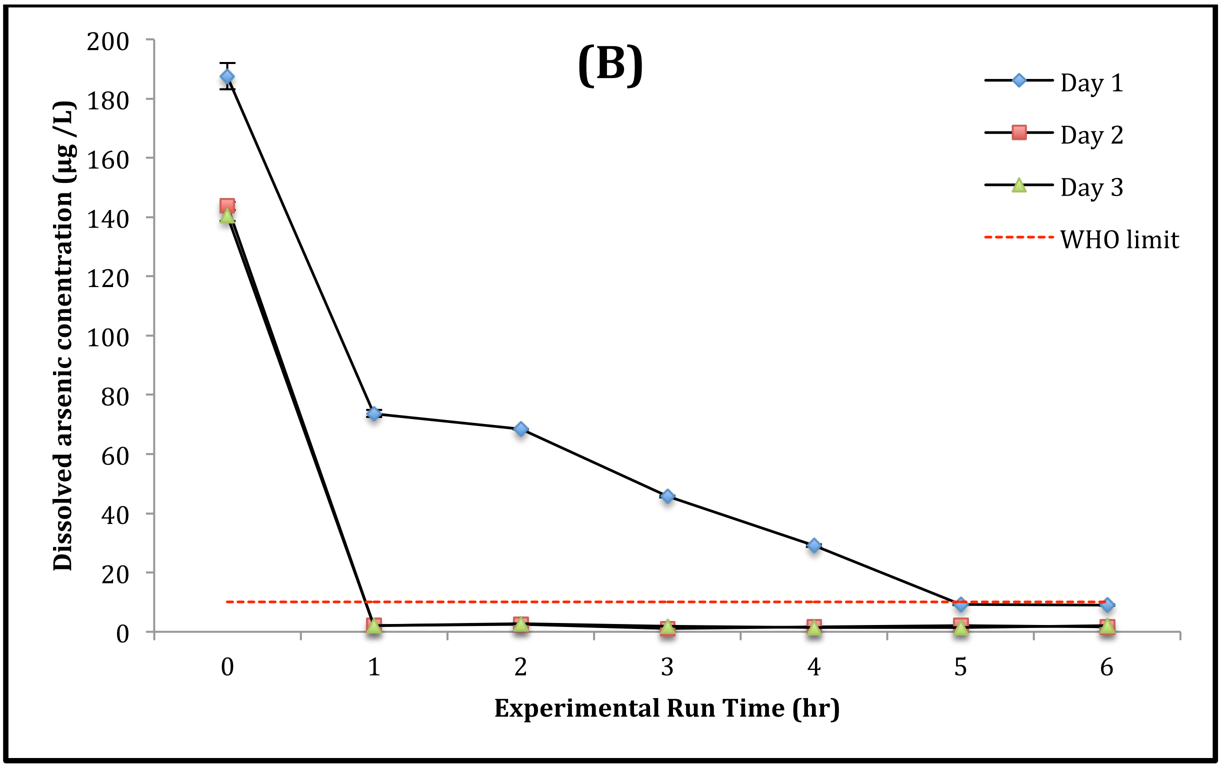


Figure 5.1: (A): Concentration of As (III) and As (V) in the influent and after biological layer in column 1 for Day 1, 2 and 3 in column 1 just before starting of the experimental run. (B) Concentration of dissolved arsenic w.r.t 6 hours experimental run in column 1 for Day 1, 2 and 3 before rapid sand filtration

By performing biological oxidation followed by Fe-EC helped to reduce 150 µg/L of dissolved arsenic concentration in water below the WHO standard by adsorption of arsenic on iron precipitates. But after rapid sand filtration or in the effluent of the column 1 there was increase in dissolved total arsenic concentration in the water (containing mainly As (V)) compared to before rapid sand filtration for all the 3 days (data shown in Appendix: Figures. A9 (i), A10 (i) and A11 (i)). Also, it was observed that the iron concentration in the effluent was below detection limit (data shown in Appendix: Figures. A6, A7 and A8), indicating that the iron precipitates that formed by EC and onto which the arsenic got adsorbed was totally removed in the rapid sand filter. For the initial experimental hours this high concentration of arsenic in the effluent was acceptable due to retention time of water in the column resulting in the EC treated water to reach the effluent at longer time but for later experimental hours this presence of high concentration of arsenic was not reasonable. This presence of As (V) in the effluent could be due to desorption of As (V) from the rapid sand filter materials. During the growth of AsOB it was observed that there was some retention of arsenic in the rapid sand filter materials, and the arsenic that got retained were in equilibrium at 150 µg/L arsenic concentration. But due to EC, the water entering into the rapid sand filter had arsenic concentration way less than 150 µg/L and that could have disturbed the equilibrium resulting in release of As (V) from the rapid sand filter materials (Gude et al., 2018).

5.2. Column 2: Containing only EC unit

For column 2 also the dissolved arsenic concentration after EC and before rapid sand filtration decreases with increase in run time in day 1, whereas in day 2 and day 3 there was no effect of time as shown in Figure 5.2. The average arsenic concentration after EC and before rapid sand filtration for the entire experimental run was 65 µg/L (maximum = 85 µg/L; minimum = 50. 74 µg/L) in day 1 and for day 2 and day 3 it was 43 µg/L (maximum = 48 µg/L; minimum = 33 µg/L) and 35 µg/L (maximum = 37 µg/L; minimum 33 µg/L). The dissolved arsenic concentration in day 2 and day 3 in column 2 after EC was also observed to be low compared to day 1 even though the operational parameters were constant. The reason for higher arsenic removal in day 2 and day 3 for column 2 was also the same as that of column 1 due to higher iron concentration in water for day 2 and 3 (around 7 mg/L) compared to day 1 (around 3 mg/L) (data for iron concentration is shown in Appendix: A6, A7 and A8). However, for column 2 though the dissolved arsenic concentration after EC and before rapid sand filtration decreases compared to the influent for all the 3 days but it doesn't go below the WHO standard as observed in column 1 even though the operational parameters were same (Figures 5.1 (B) and 5.2). Also it was observed that the dissolved arsenic concentration in the effluent of column 2 showed higher concentration compared to before rapid sand filtration (data shown in Appendix: Figures. A9 (ii), A10 (ii) and A11 (ii)) and it was mainly As (V), as observed in column 1. This high concentration of As (V) in the effluent was also due to desorption of As (V) from the rapid sand filter materials as explained for column 1.

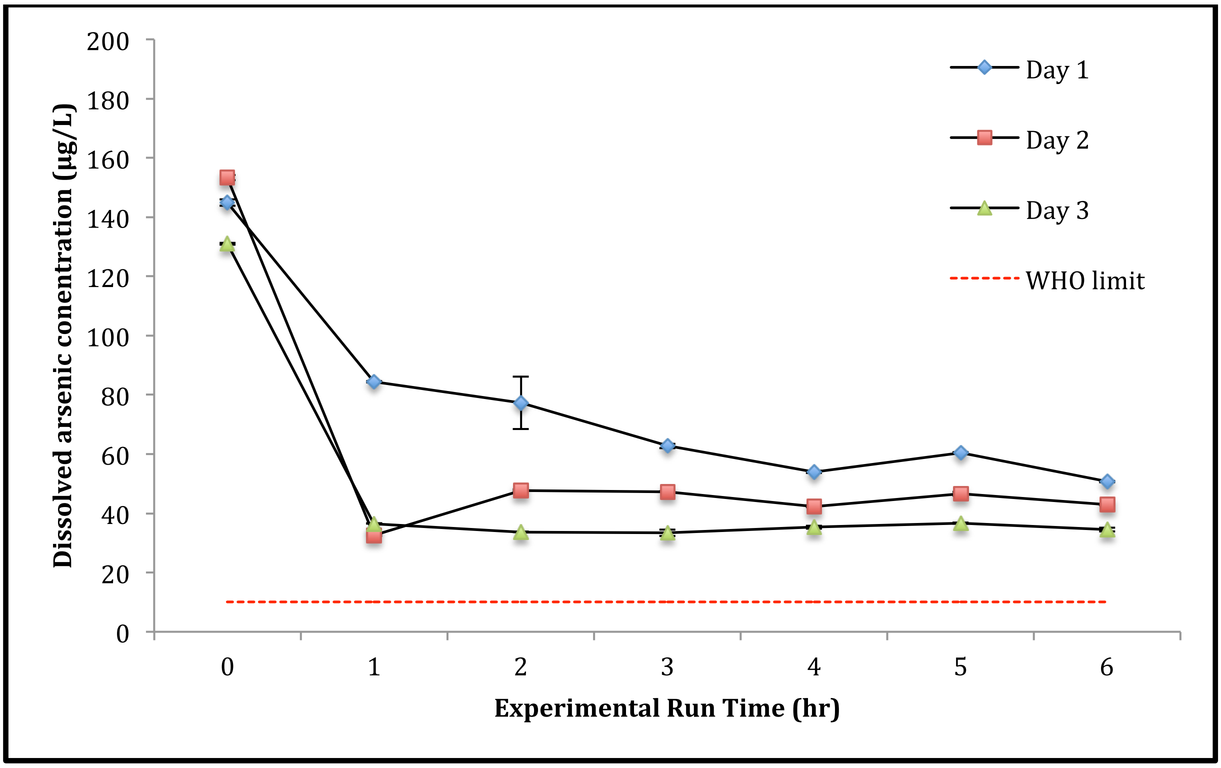


Figure 5.2: Concentration of dissolved arsenic w.r.t 6 hours experimental run time in column 2 for Day 1, 2 and 3 before rapid sand filtration

5.3. Comparison of Arsenic Removal between Column 1 and Column 2 along with Fe-EC Batch Studies

The main difference between column 1 and column 2 was that in column 2 no pre-oxidation of As (III) by AsOB was performed before applying Fe-EC and the major effect it had can be seen in Figure 5.3 (right). Figure 5.3 (right) shows the dissolved arsenic concentration after EC and before rapid sand filtration for 6 hours experimental run in both the columns for day 2 and 3. Though both the columns showed removal of arsenic due to adsorption on iron precipitates but the removal was better in column 1 even though the EC operational parameters were the same for the columns. In column 1, arsenic removal below the WHO standard (10 µg/L) from initial As (III) concentration of around 150 µg/L was achieved during the entire experimental run for day 2 and 3 compared to column 2, where it was above the WHO limit. These column results clearly show the advantage of applying biological oxidation of As (III) pre-EC. As observed in batch studies of Fe-EC that for an initial arsenic concentration of 150 µg/L, when the initial arsenic species was As (V) a charge dosage of 10 C/L at 5 C/L/min charge dosage rate (resulting in an iron dosage of 3 mg/L) was enough to take the dissolved arsenic concentration below WHO standard compared to As (III) species which required a charge dosage of 100 C/L (iron dosage around 30 mg/L)(Figure 5.3 (left)). Similarly, for column 1 where most of the arsenic present in the water in which EC was applied was in the form of As (V) due to biological oxidation compared to column 2 where majority of arsenic was As (III) (as no biological oxidation was applied prior EC), resulted in better removal of arsenic for a similar charge dosage. This is due to the fact that iron precipitates formed during EC have higher affinity for As (V) over As (III) to get adsorbed (Wan et al., 2011).

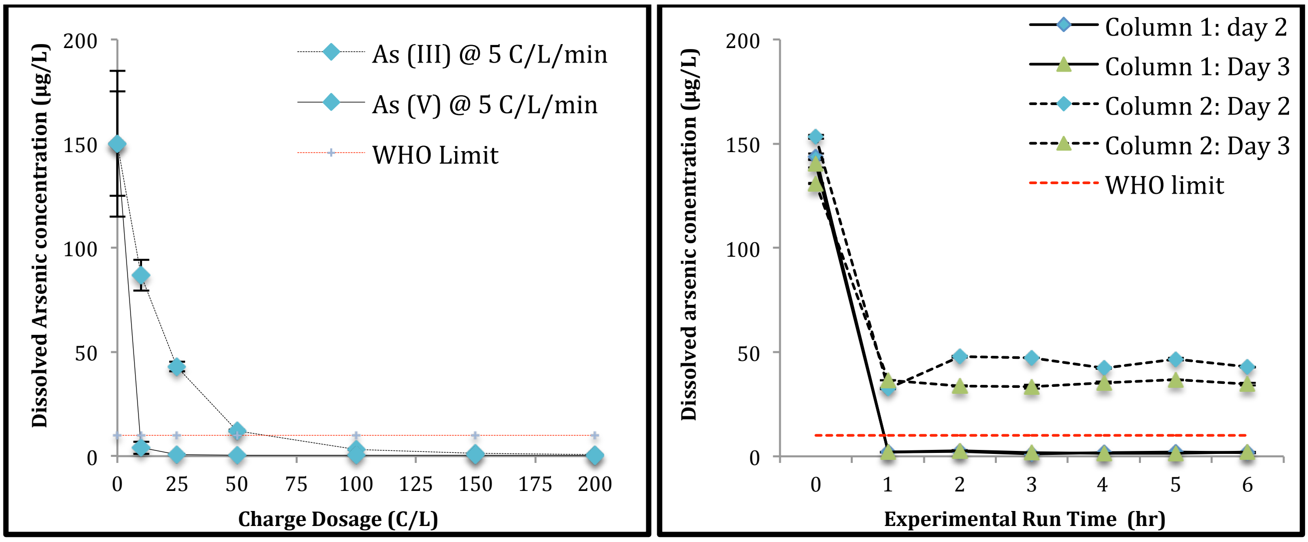


Figure 5.3: Left: Comparison of As (III) and As (V) removal by Fe-EC in batch studies; Right: Comparison of arsenic removal in the filtration columns 1 and 2

Also, comparing the in-line system with the batch system, where the water type, initial arsenic concentration and operational parameters of EC in both the systems were kept same (charge dosage of 10 C/L at 5 C/L/min charge dosage rate), the arsenic removal behavior was also observed to be same. For instance, comparing column 1 (where the water on which EC was applied contain mainly As (V)) with the batch system (where EC was applied on tap water containing As (V) as initial arsenic species), a charge dosage of 10 C/L in both the systems resulted in the dissolved arsenic concentration after EC below 10 µg/L from initial arsenic concentration of 150 µg/L (Figures 5.3 (left) and (right)). Likewise, for column 2 which contains mainly As (III) an EC of 10 C/L charge dosage at 5 C/L/min charge dosage rate resulted in a dissolved arsenic concentration of around 40 µg/L for both day 2 and 3 from initial arsenic concentration of around 150 µg/L (Figure 5.3 (right)). However, comparing column 2 with batch studies of As (III) removal, a charge dosage of 25 C/L at 5 C/L/min charge dosage rate showed a dissolved arsenic concentration of 43 µg/L post EC (Figure 5.3 (left)) when the dissolved iron concentration was 6.73 mg/L. As mentioned before that in day 2 and day 3 of column 2 the iron concentration in the water was around 7 mg/L (though charge dosage was 10 C/L at 5 C/L/min charge dosage rate resulting in an iron concentration of 3 mg/L theoretically), so it can be said that the arsenic removal for both the systems were similar based on the amount of iron available for arsenic.

5.4. Measured pH, DO, Conductivity, Temperature, Applied Voltage and Head Loss during the Filter Run

The pH, DO, conductivity and water temperature of the various water samples collected from the two columns at various positions during the 6 hours experimental run were measured instantly and the values observed for all the samples were are shown in Table 5.1. Considering DO, the concentration was high in the influent (around 8.5 mgO_2/L) compared to after EC (around 7.7 mgO_2/L) indicating consumption of DO for Fe^{2+} oxidation.

Table 5.1: Measured values of pH, DO, Conductivity and Temperature of water samples collected in the two columns during 6 hours experimental runs for 3 days (The values shown are average of 6 hours runs for 3 days with standard deviation)

	Column 1			**Column 2**		
	Influent	**After Fe-EC**	**Effluent**	**Influent**	**After Fe-EC**	**Effluent**
pH	7.5 ± 0.5	7.6 ± 0.2	7.5 ± 0.5	7.8 ± 0.8	7.7 ± 0.3	7.7 ± 0.2
DO (mgO_2/L)	8.5 ± 0.3	7.7 ± 0.3	8 ± 0.3	8.5 ± 0.2	7.8 ± 0.2	7.9 ± 0.3
Conductivity (µS/cm)	435 ± 15	425 ± 25	425 ± 25	430 ± 15	430 ± 20	425 ± 25
Temperature (^0C)	22.1 ± 0.1	22 ± 0.3	22 ± 0.3	22.4 ± 0.3	22 ± 1	22 ± 0.5

The average voltage applied for applying a current of 0.02 A for 6 hours experimental run was 2.1 V in day 1 and 1.93 V in day 2 and day 3 indicating that there was no significant increase in power requirement after 3 days column run. Also, it was observed that the voltage decreases with the experimental run time. For instance in day 1, the initial voltage applied was 2.18 V but by 6 hours the voltage dropped to 1.88 V for applying a constant current of 0.02 A in column 1.

Furthermore, the total head loss observed in the columns after 3 days column runs was 10 (±2) cm in each column. But after backwash, the head loss got reduced.

5.5. Summary of Phase II Studies

The following important points can be summarized from phase II studies:

- In a continuous flow mode, filter column containing biological oxidation of As (III) by AsOB followed by Fe-EC has shown potential to remove arsenic below the WHO standard from an initial concentration of 150 μg/L As (III), compared to the column containing only Fe-EC under a constant charge or iron dosage by Fe-EC in both the columns.

- Both the batch and continuous flow system behaved similarly based on the amount of arsenic removed by Fe-EC for an optimum charge or iron dosage applied in both the system having arsenic in the form of As (III) or As (V). For both the system a charge dosage of 10 C/L at 5 C/L/min charge dosage rate was observed to be optimum to remove 150 μg/L of As (V) from tap water below the WHO standard.

- Desorption of arsenic (mainly As (V)) from rapid sand filter materials were observed due to saturation of rapid sand filter materials to arsenic concentration of 150 μg/L. As the water entering into the rapid sand filter got arsenic concentration below 150 μg/L due to Fe-EC, the state of equilibrium for filter materials with arsenic got disturbed and resulted in desorption of arsenic.

6. Cost of Operation for Arsenic Removal in the Filtration Columns

In order to apply a new technique or technology for water and wastewater treatment, the operating cost is the most influential parameter that defines its implementation. Not only a technique should be efficient but also economically feasible. The operation cost mainly includes cost of the material, utility cost, cost of maintenance, labor cost and some fixed costs. In this study only the material and utility cost are taken into consideration. For the filtration columns the operating cost was focused mainly on the EC unit, as it requires application of electricity. So, the electricity cost for EC during the 6 hours experimental run, cost of iron released from the electrodes and costs of any chemicals used during the experimental runs for the filters are considered as the important cost items and taken for calculation of the operating cost (€/m^3) and calculated using Eq. 6.1 (Kobya et al., 2011b).

$$\text{Operating Cost } (€/m^3) = xC_{energy} + yC_{electrode} + zC_{chemicals} \qquad \text{Eq. 6.1}$$

where,

C_{energy} = Electric energy consumed per m^3 of water (Eq. 2.15), kWh/m^3
$C_{electrode}$ = Consumption of electrode, kg/m^3
$C_{chemicals}$ = Chemical used per m^3 of water, kg/m^3
x = Electricity price in Netherlands, 0.23 €/kWh (DutchNews.nl)
y = Price of steel in Europe, 0.602 €/kg (World steel prices)
z = Price of chemical used, €/kg

Considering Eq. 2.15, C_{energy} = Uit/v is dependent on the voltage applied (U), time of treatment (t), current applied (i) and volume of water treated (v). For column 1, in day 1 for a flow rate of 1 m/hr the volume of water treated in 6 hours was 0.04 m^3 and the average voltage applied was 2.08 V. So, using Eq. 2.15, C_{energy} for column 1 in day 1 was 0.006 kWh/m^3. Similarly for day 2 and day 3 the C_{energy} was also around 0.006 kWh/m^3 for an average voltage of 1.93 V in each day. The current applied to the electrodes was 0.02 A so that an iron concentration of 3 mg/L was achieved in the water after EC. So, $C_{electrode}$ for column 1 in each day was 3 mg/L. As, no extra chemicals were used in the filtration columns, so $C_{chemicals}$ was taken as zero. Finally, with all the values the operating cost calculated using Eq. 6.1 in column 1 for day 1, 2 and 3 was 0.003 €/m^3.

Similarly for column 2, all the values were same accept the average voltage, which were 2.83 V, 2.38 V and 2.21 V for day 1, 2 and 3 respectively. Accordingly, using Eq. 6.1

the operating cost for column 2 was 0.004, 0.004 and 0.003 €/m^3 for day 1, 2 and 3 respectively.

During the calculations of operating cost it was assumed that the flow rate in both the columns was 1 m/hr during the experimental runs resulting in a volume of 0.04 m^3 of water treated in 6 hours. Also, it was assumed that the iron concentration in the water after electrocoagulation was 3 mg/L for both the columns.

The operational cost of column 2 was observed to be more than that of column 1 even though the operational parameters were same in both the columns. This difference of operational cost was due to different voltage required to apply a current of 0.02 A in both the columns. Though same current was applied in both the columns but a difference a voltage could have resulted due to difference in water conductivity. Also, it should be taken into consideration that for column 2 the dissolved arsenic concentration after Fe-EC did not go below the WHO standard. Comparing with the batch studies where 150 µg/L As (III) in tap water required a charge dosage of 100 C/L to remove arsenic below WHO standard, the operational cost of column 2 would be much higher compared to column 1 to have removal efficiency same as column 1 because a higher current need to be applied to apply the high charge dosage and also the amount of iron used will also be high. This high requirement of operational cost of column 2 also shows the advantage of having a pre-oxidation step of As (III) before Fe-EC for As (III) removal by Fe-EC.

Comparing the operating costs of other arsenic oxidation or removal techniques, Chen et al., (2015) reported operating cost for removing 82% arsenic from initial concentration of 117 µg/L by coagulation, precipipitation and filtration using $FeCl_3$ was 0.01 USD/m^3 (0.01 €/m^3) of water treated. Also, Bordoloi et al., (2013), performed field studies on removing 196-238 µg/L arsenite below the WHO standard from ground water by first oxidizing it with $KMnO_4$ and then its removal by coagulation using $FeCl_3$ and the operating cost was found to be 0.17 USD/m^3 (0.15 €/m^3) water treated. So, comparing with these techniques the operating cost of the integrated system developed in this research work can be reported to be less. However, in cases where arsenic concentration is high the operating cost will increase based on the amount of iron required to be generated during Fe-EC.

Apart from the operational cost, the investment cost for developing such a system should also be taken into consideration. However, in this research study the main investment cost includes the development of the columns, the use of rapid sand filter materials and EC setup. Considering the construction of the columns and use of rapid sand filter materials, these were already available in the laboratory from other research studies so they are not included in the investment cost. However, for EC setup the main investment cost was the DC supplier which cost around 130 €. Also, the backwashing was performed using the same tap water that was used as influent under pressure, so there was no major cost associated with backwashing. Another thing to be considered while developing such system in large scale is the operational cost for mixing after EC. For large systems a proper mixing need to be provided for homogeneous distribution of the iron precipitates in the arsenic contaminated water and this will increase the operational cost.

7. Conclusion

This research work was the first attempt where biological oxidation of As (III) technique was combined with Fe-EC in a continuous flow mode and also a successful implementation of Fe-EC in a continuous flow vertical column system for removal of arsenic. Applying biological oxidation of As (III) and then its removal by Fe-EC through adsorption or co-precipitation with iron precipitates has shown potential for enhanced removal of 150 μg/L As (III) at low iron dosage in Fe-EC. One of the major advantages of this type of integrated system is that it doesn't require use of additional chemicals, generally required for chemical oxidation and chemical coagulation of arsenic. From this study it has also been proved that AsOB, that have capability to completely oxidize As (III), can be easily grown on suitable bio-carriers by simply dosing As (III) spiked water over a period of time. So, in situations where drinking water sources contain As (III) and chemical oxidation of As (III) is not feasible, biological oxidation can be the suitable pathway as these bacteria has been reported to grow on bio-carrier by dosing raw groundwater having As (III) concentration as low as 13 μg/L (Gude et al., 2018). This type of integrated system can be easily used as a de-centralized way to remove arsenic from drinking water sources in the rural areas of India and Bangladesh, where human exposure to arsenic contaminated drinking water is still a major problem. Also, considering the situation in the Netherlands where the new aim is to have arsenic concentration below 1 μg/L in drinking water, this type of integrated system can be linked to the already existing treatment systems utilized currently in the water treatment plants for removing arsenic as arsenic removal below 1 μg/L was also observed during Fe-EC.

8. Recommendations for Future Study

From the research the following recommendations and suggestions for future study are extracted:

- As it was observed that there was desorption of arsenic (mainly As (V)) from the rapid sand filters due to disturbance in the equilibrium of rapid sand filter materials with low arsenic concentration, in future works such type of integrated filtration columns should be run for a longer period so that a new equilibrium state with lower arsenic concentration in achieved in the rapid sand filter and a better removal of arsenic is achieved in the effluent of the columns.

- A better design of the filtration columns should me made so that the biological layer during backwashing remains intact as in this research while backwashing the columns the biological layer has to be taken out otherwise the entire layer was overflowing out of the column.

- Though in the batch studies with Fe-EC the solution was constantly stirred for proper mixing, the mixing step was not performed in the filtration columns during EC. With proper mixing, better arsenic removal may be achieved. In order to achieve mixing of water after EC in the columns, the electrodes can be arranged in the manner shown in Figure 8.1 so that the flow through the electrodes creates mixing. Other methods can be placing a submersible pump or an aerator after EC electrodes that can create a turbulent zone causing mixing.

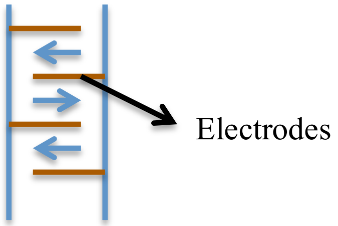


Figure 8.1: Electrode arrangement in the vertical column allowing a mixing zone

- As during Fe-EC oxidation of As (III) to As (V) was observed, a further study on the percentage of oxidation under different charge dosage and charge dosage rate could help to understand the Fe-EC system better.

- The integrated system was studied using arsenic spiked tap water and so the next step could be to scale up the system and to check its efficiency for raw arsenic contaminated groundwater.

- A detailed study of the characterization of the iron precipitates formed during EC under different charge dosage and charge dosage rate should be performed. During Fe-EC, formation of various iron precipitates such as magnetite, maghemite, lepidocrocite, etc., have been reported and these precipitates have shown different adsorption capacity for arsenic (van Genuchten, 2012; Hao et al., 2018). So, a study on the type of iron precipitates formed during EC will help to understand the arsenic removal by Fe-EC better.
- A chemical dynamic kinetic model for As (III) oxidation and As (III), As (V) adsorption as developed in Li et al. (2012) and Delaire et al. (2017) for arsenic removal during Fe-EC under different charge dosage and charge dosage rate can be generated. Though simple pseudo second order kinetic model are used in many reports to model the arsenic removal during Fe-EC (Kobya et al., 2011; Vasudevan et al., 2010a,b), but during EC too many co-occurring reactions take place simultaneously making the application of this simple model invalid during Fe-EC. The dynamic model generated by Li et al. (2012) and Delaire et al. (2017) takes into account a lot of reactions happening during Fe-EC such as As (III) and Fe^{2+} redox reactions, the As (III) and Fe^{2+} oxidation rates, effect of phosphate and silicate, etc. So, in order to apply such dynamic models in this study, additional experimental values will be required which was not performed in this study. Hence, a dynamic model study for arsenic removal based on the different reactions happening during Fe-EC as reported in Li et al. (2012) and Delaire et al. (2017) is recommend as future study for arsenic removal by Fe-EC.

Appendix:

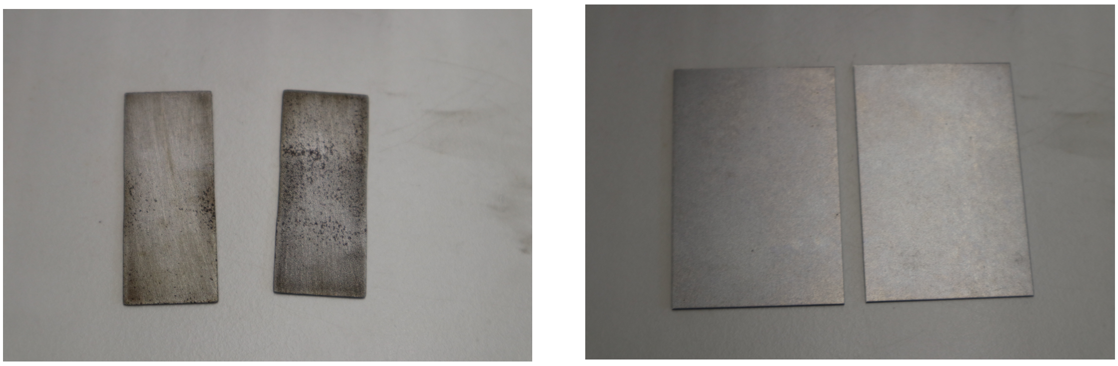


Figure A1: Fe-electrodes used for EC in batch studies (left) and in the filtration columns (right)

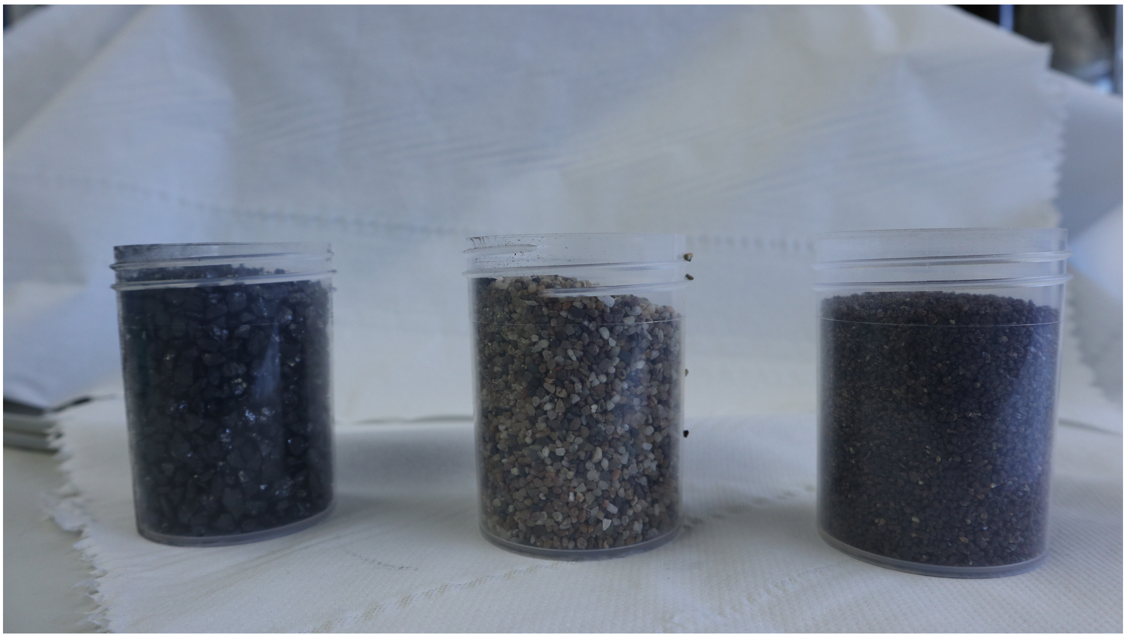


Figure A2: Rapid Sand Filter materials used as bio-carriers: Anthracite (left), Coarse sand (middle), Garnet (right)

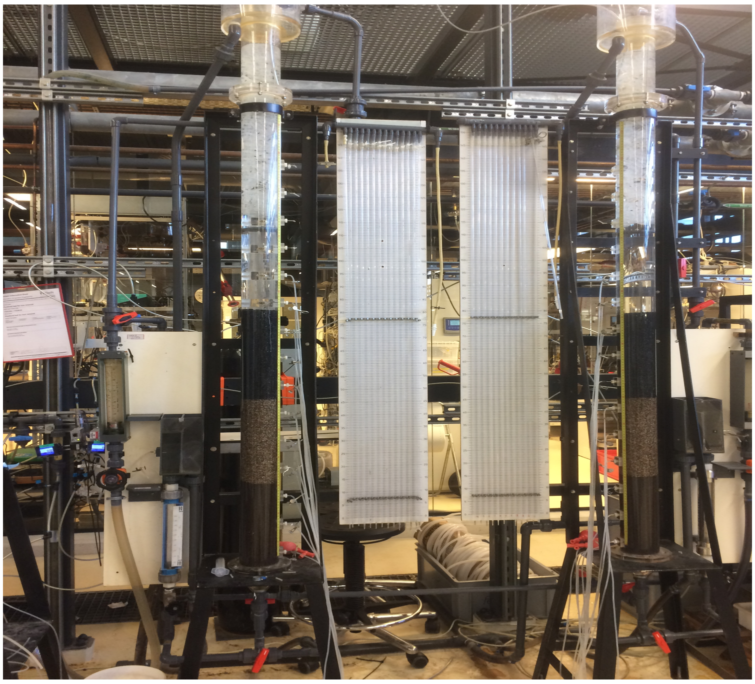


Figure A3: Image of the columns used for growth of AsOB

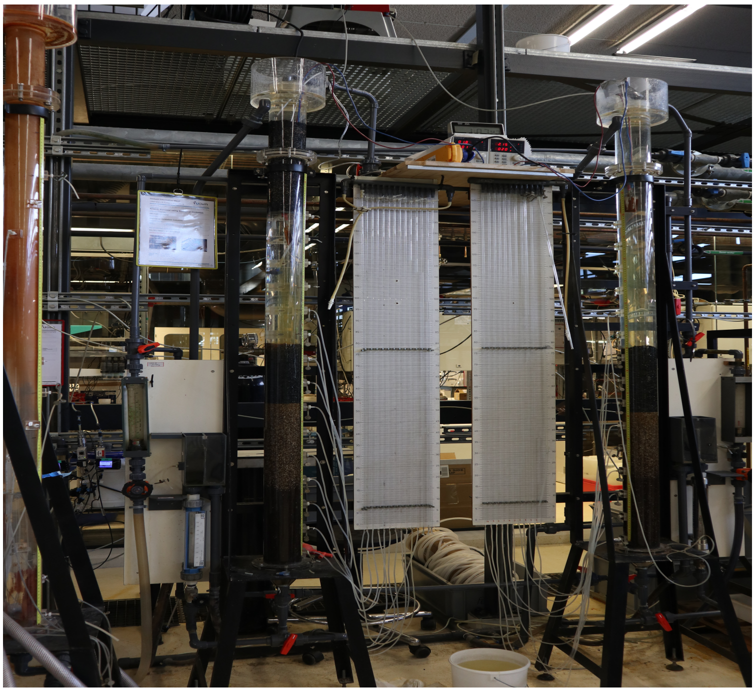
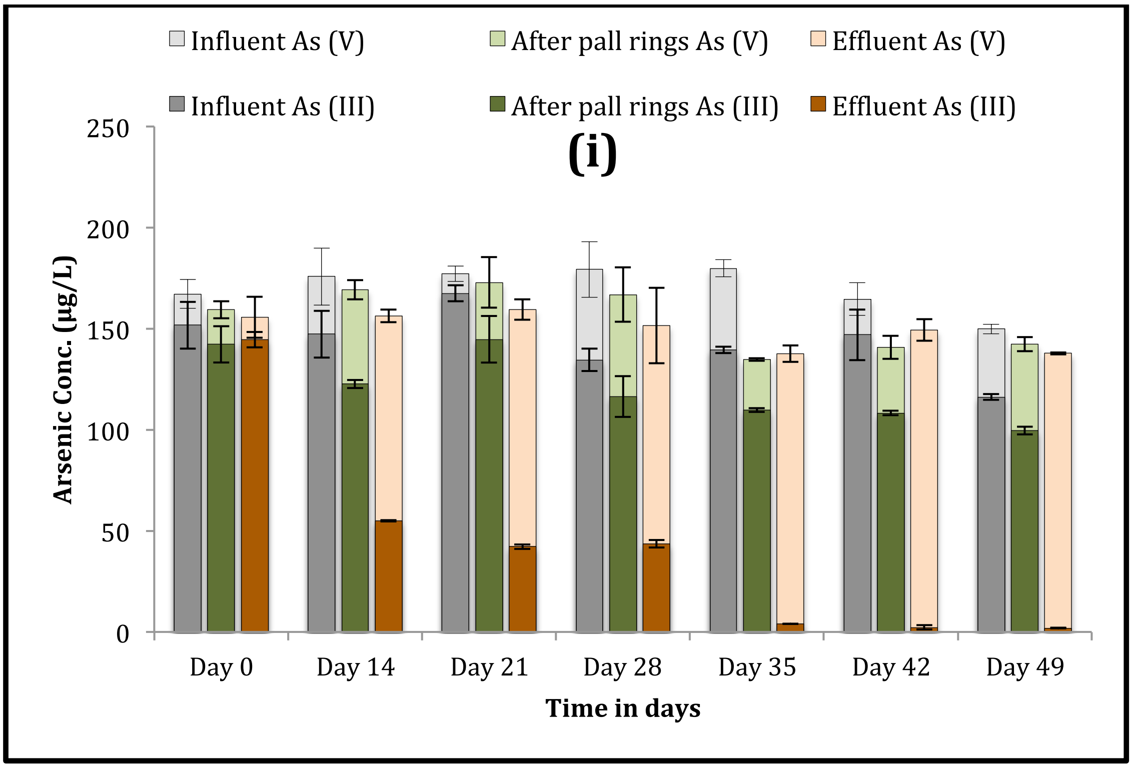


Figure A4: Image of the filtration columns developed in the lab. Left one containing biological layer at the top followed by Fe-electrodes for EC and rapid sand filter at the bottom. Right one contains only Fe-electrodes for EC and rapid sand filter at the bottom

A. Use of pall rings as bio-carriers

Initially, pall rings were used as bio-carriers for growth of AsOB by placing a 30 cm pall rings layer at the top of the two columns. The pall rings used were Raflux ring 25-8, purchased from RVT Process Equipment GmbH, having nominal size 25 mm, specific surface area 220 m^2/m^3, density 79 kg/m^3, void ratio 91% and made up of polypropylene. But after 49 days column run used for the growth of AsOB, it was observed that the water after passing through the pall rings layer showed only 32 (±2) % As (III) oxidation (shown as dark and light green color in Figures A5 (i) and (ii)) as shown in Figures A5 (i) and (ii). The results indicate that AsOB grown on the pall rings was not able to oxidize the entire As (III) compared to the rapid sand filter materials at the bottom of the columns. This could be due to the lower surface area of the pall rings. However, if the columns were run for longer period there would have been sufficient growth of AsOB on the pall rings for performing complete oxidation of 150 µg/L As (III).



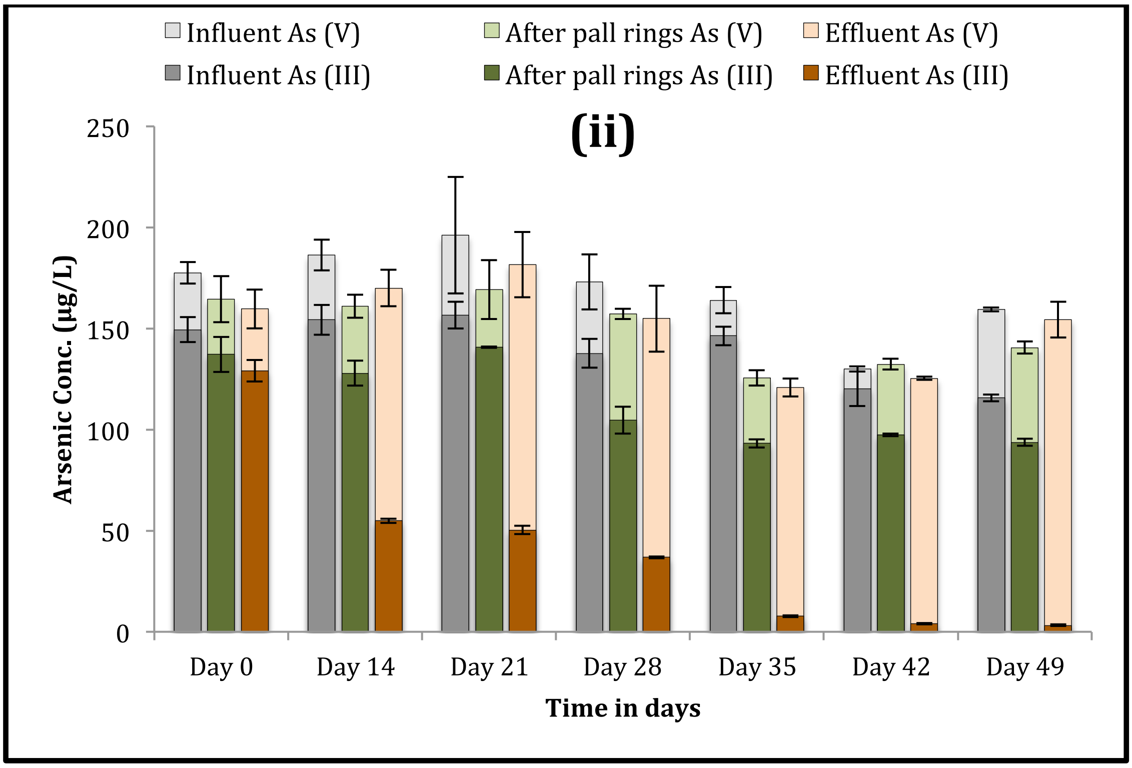


Figure A5: Concentration of dissolved As (III) and As (V) in the influent, after pall rings layer and effluent over time for column 1 (i) and column 2 (ii)

B. Concentration of iron before and after rapid sand filtration in the filtration columns

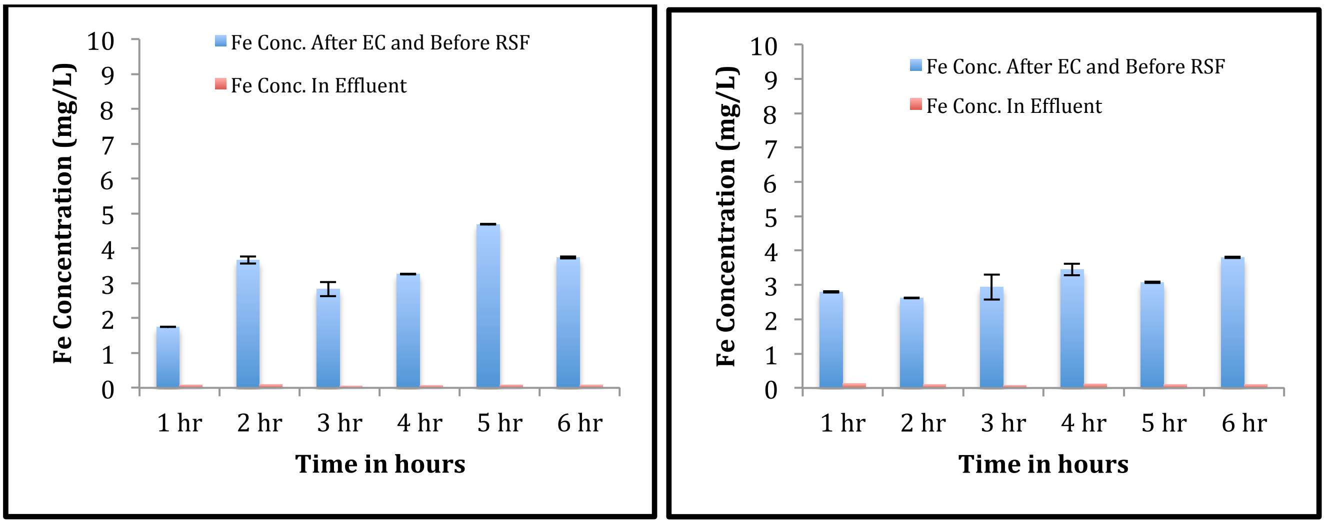


Figure A6: Concentration of iron before and after rapid sand filtration (effluent) in column 1 (left) and column 2 (right) for day 1

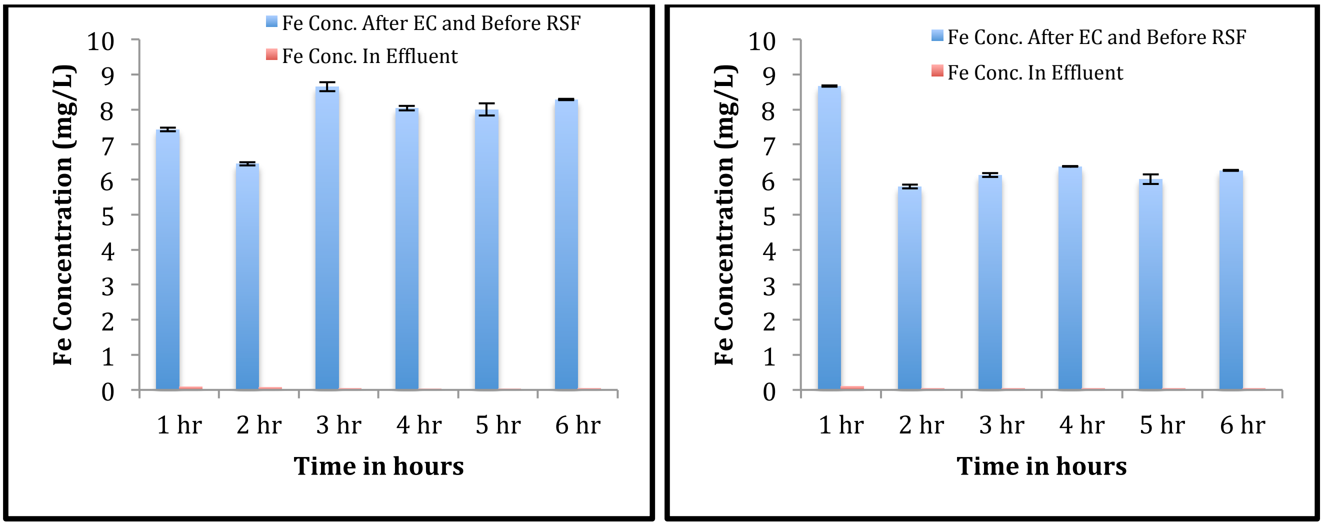


Figure A7: Concentration of iron before and after rapid sand filtration (effluent) in column 1 (left) and column 2 (right) for day 2

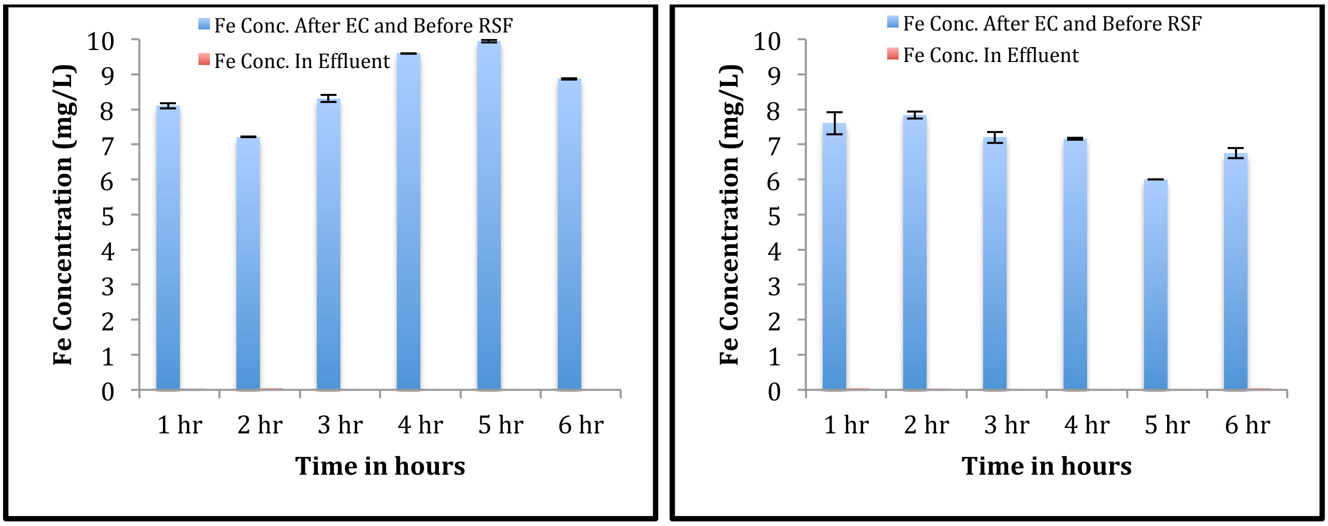
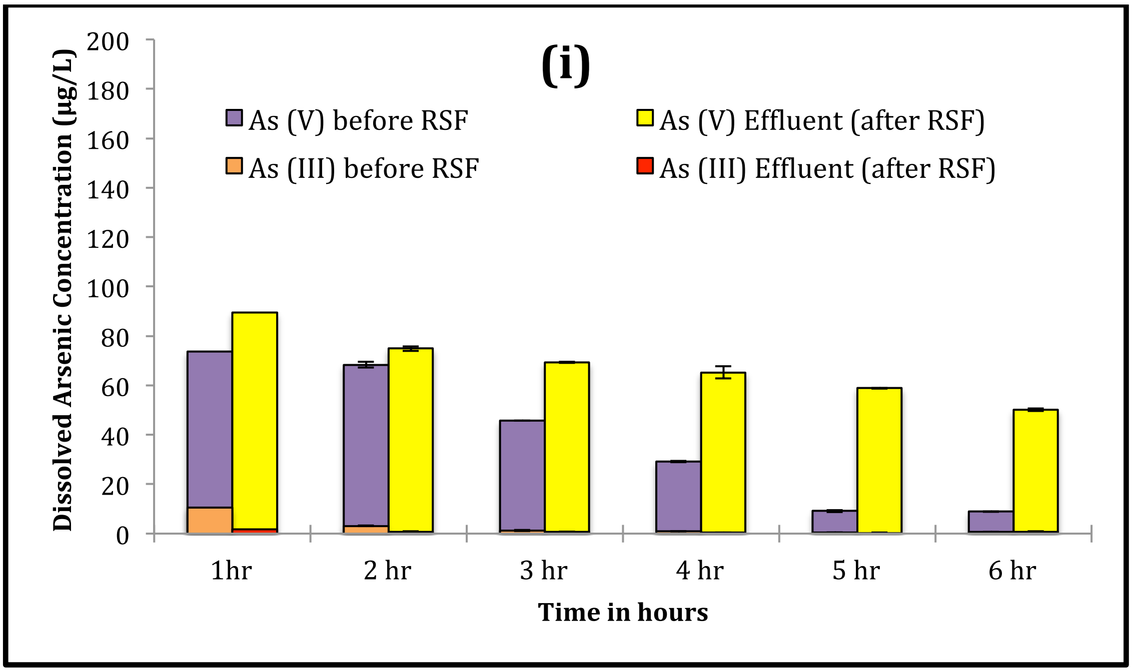


Figure A8: Concentration of iron before and after rapid sand filtration (effluent) in column 1 (left) and column 2 (right) for day 3

C. Dissolved arsenic concentration before and after rapid sand filtration (effluent) in the filtration columns



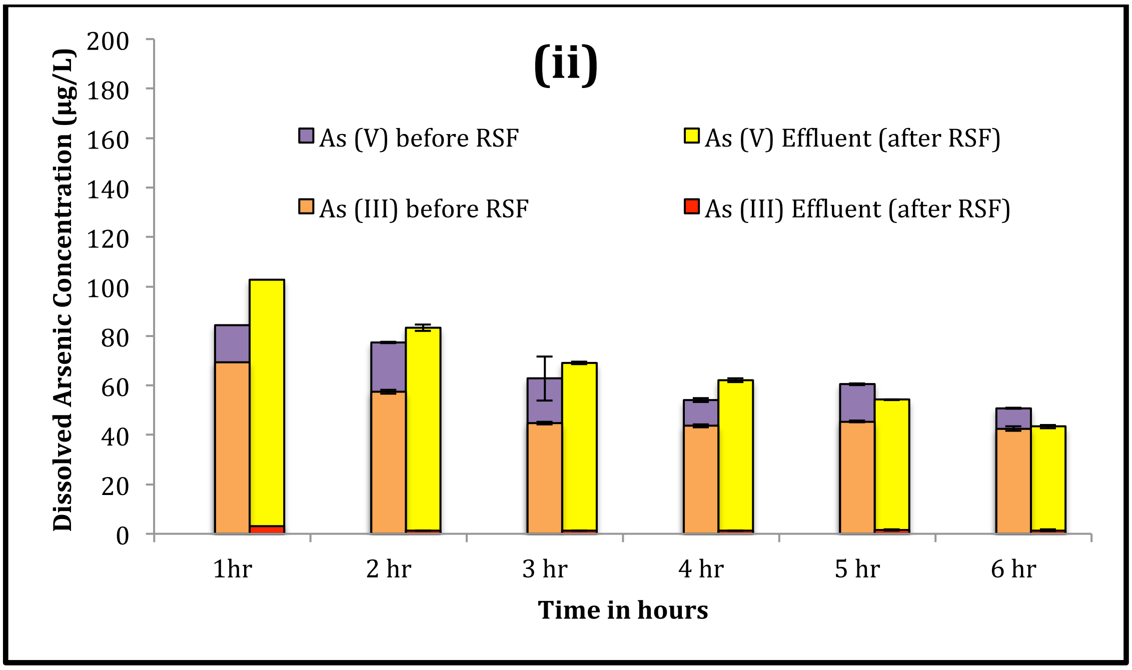
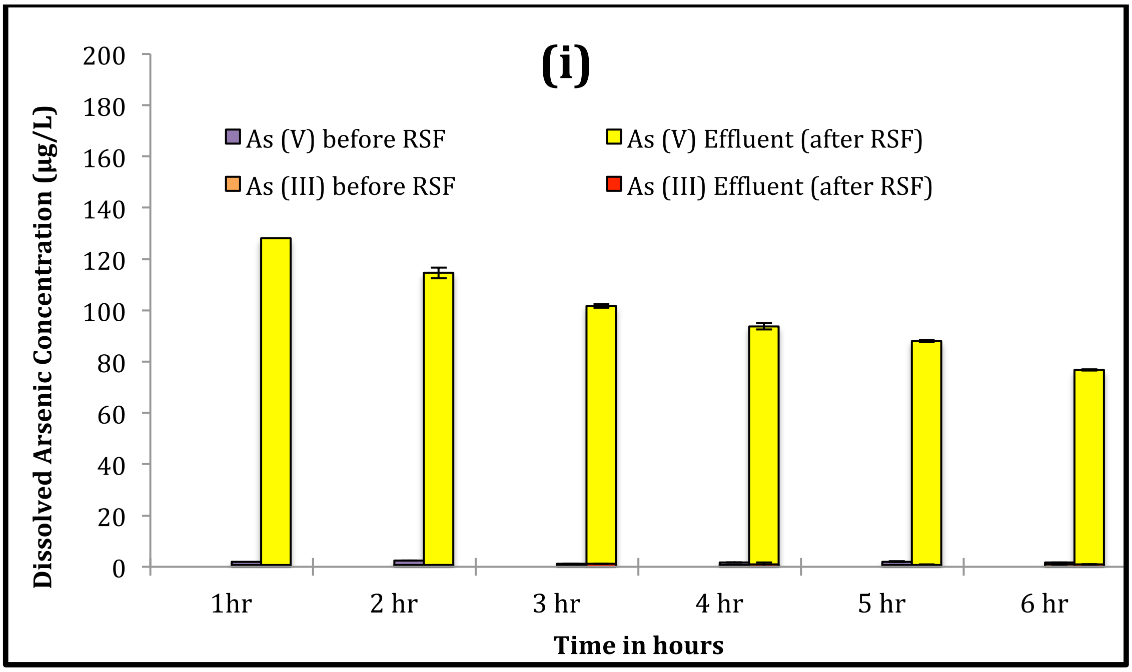


Figure A9: Dissolved arsenic connetration before and after rapid sand filtration (RSF) in column 1 (i) and column 2 (ii) for day 1



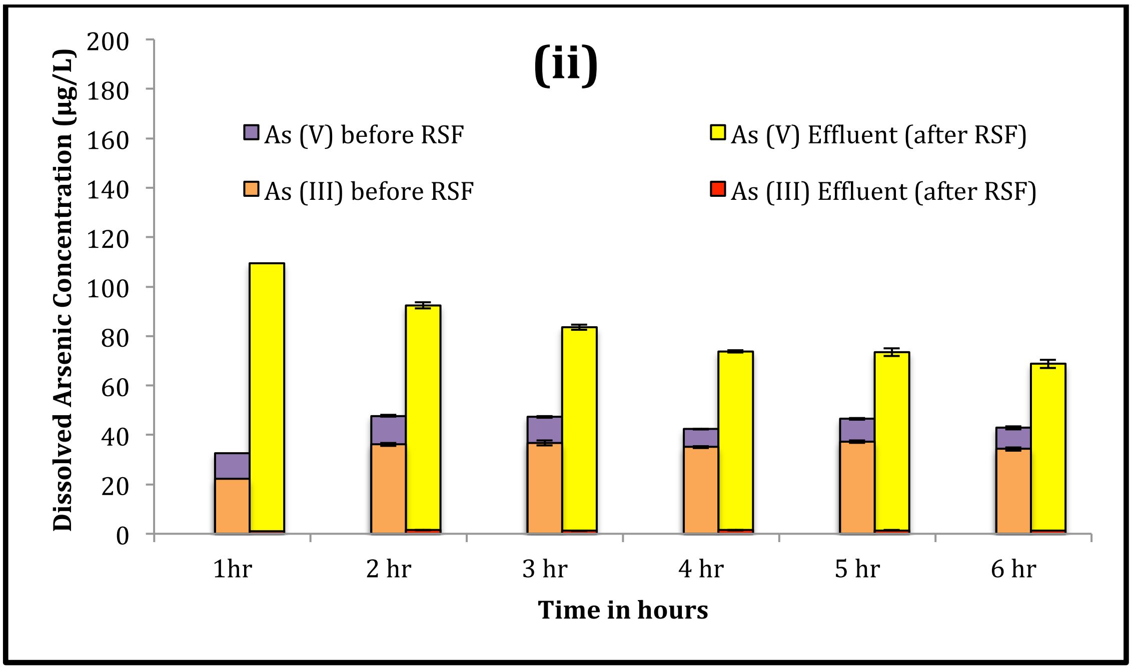
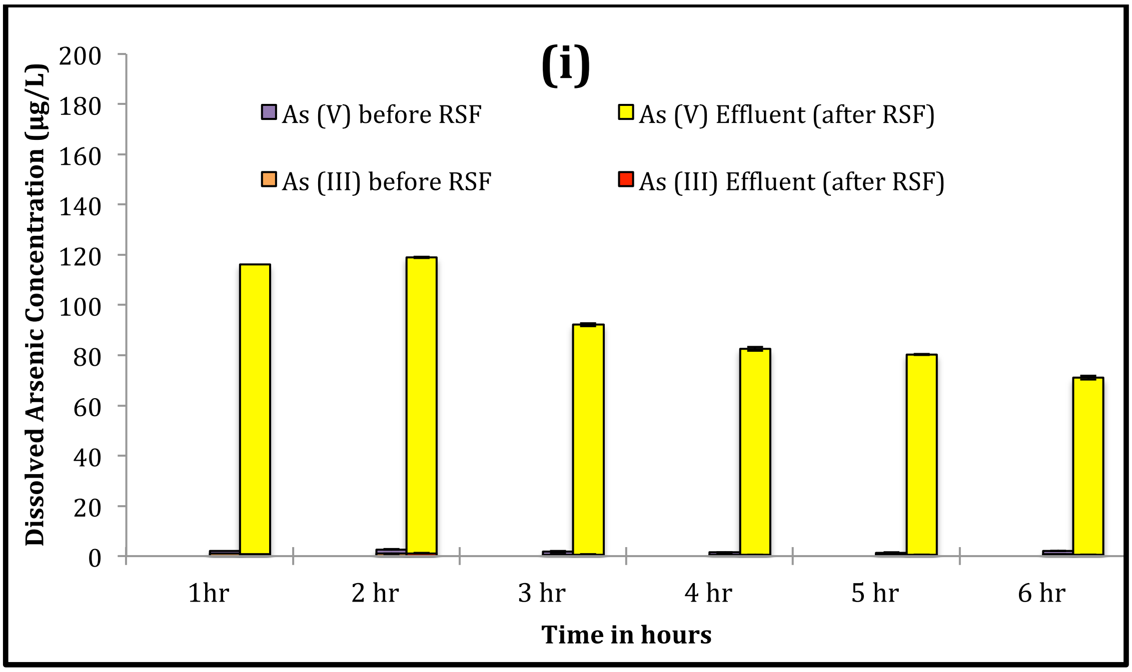


Figure A10: Dissolved arsenic connetration before and after rapid sand filtration (RSF) in column 1 (i) and column 2 (ii) for day 2



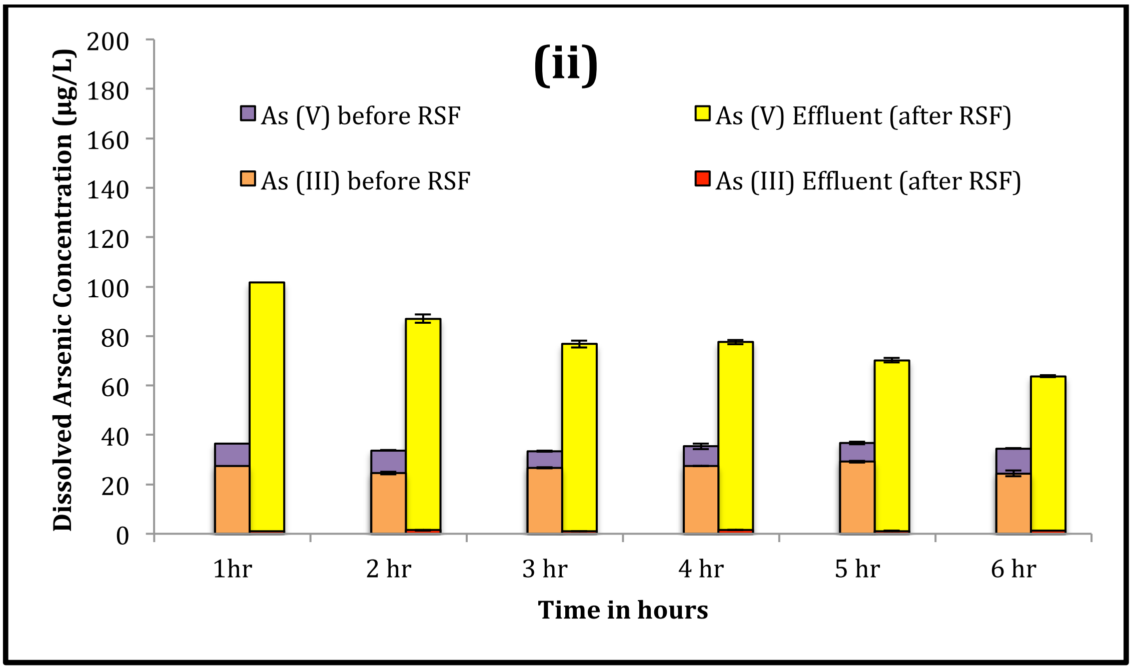


Figure A11: Dissolved arsenic connetration before and after rapid sand filtration (RSF) in column 1 (i) and column 2 (ii) for day 3

D. Change in concentration of SO_4^{2-}, Ca, Mg, Na and Cl^- in SBGW during Fe-EC

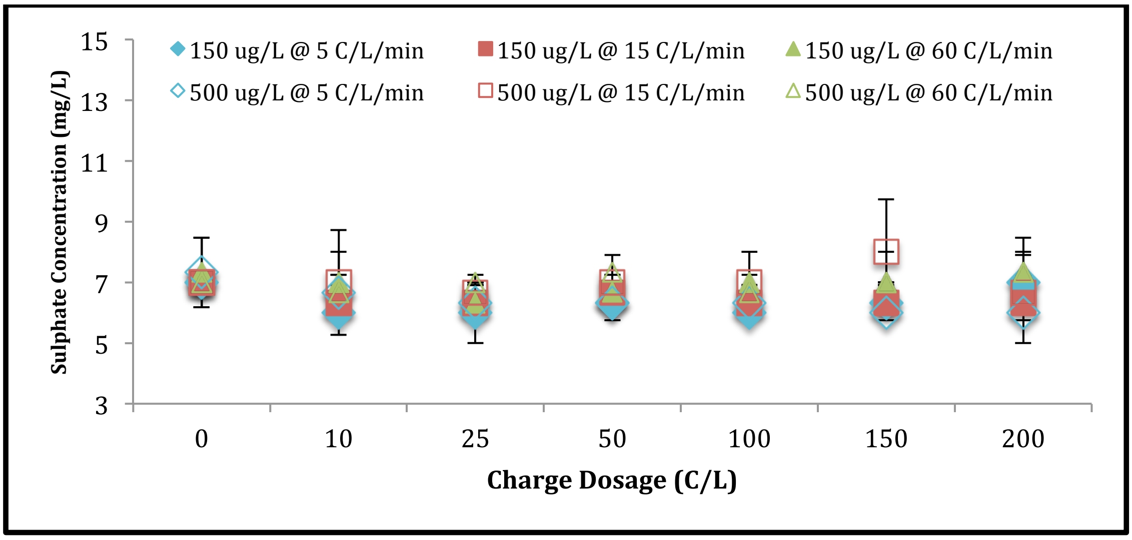


Figure A12: Change in dissolved SO_4^{2-} concentration w.r.t (10-200) C/L charge dosage and 5, 15 and 60 C/L/min charge dosage rate for initial As (III) concentration of 150 µg/L and 500 µg/L in SBGW

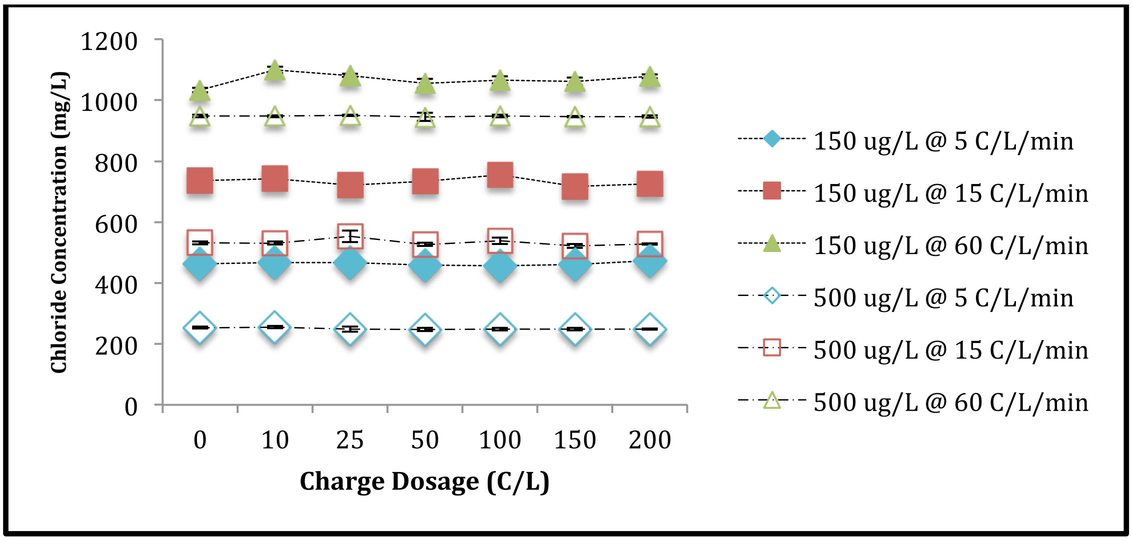


Figure A13: Change in dissolved Cl^- concentration w.r.t (10-200) C/L charge dosage and 5, 15 and 60 C/L/min charge dosage rate for initial As (III) concentration of 150 µg/L and 500 µg/L in SBGW

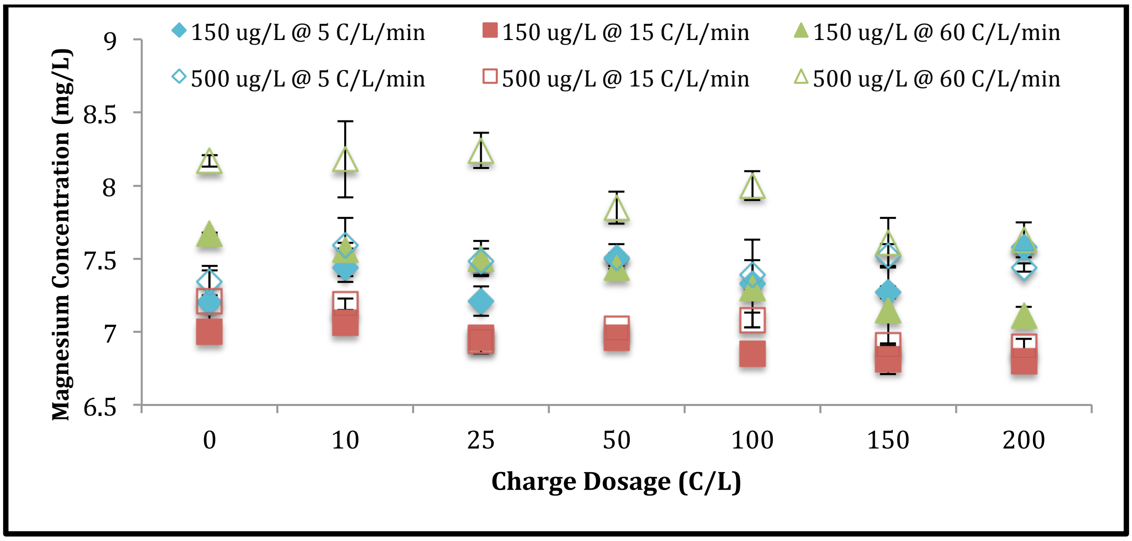


Figure A14: Change in dissolved Mg concentration w.r.t (10-200) C/L charge dosage and 5, 15 and 60 C/L/min charge dosage rate for initial As (III) concentration of 150 µg/L and 500 µg/L in SBGW

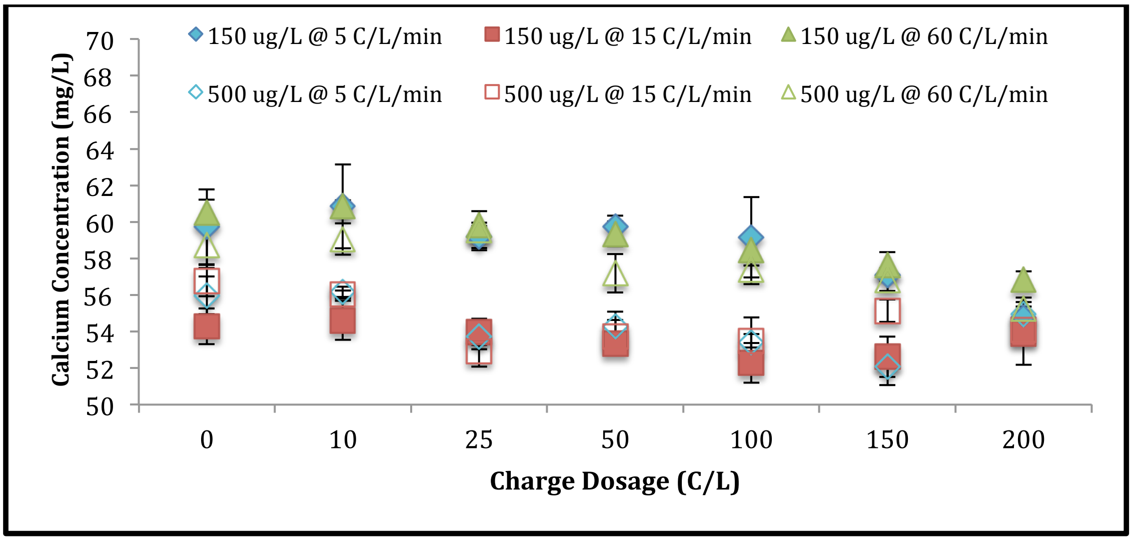


Figure A15: Change in dissolved Ca concentration w.r.t (10-200) C/L charge dosage and 5, 15 and 60 C/L/min charge dosage rate for initial As (III) concentration of 150 µg/L and 500 µg/L in SBGW

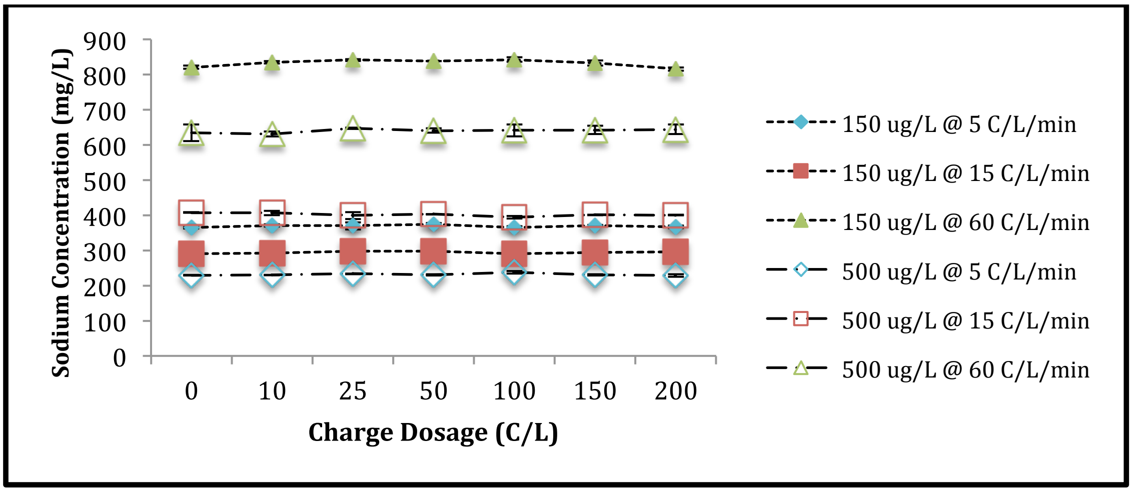


Figure A16: Change in dissolved Na concentration w.r.t (10-200) C/L charge dosage and 5, 15 and 60 C/L/min charge dosage rate for initial As (III) concentration of 150 µg/L and 500 µg/L in SBGW

Figure A17: Images of water solutions after Fe-EC

References:

1) Amrose, S., Gadgil, A., Srinivasan, V., Kowolik, K., Muller, M., Huang, J., & Kostecki, R. (2013). Arsenic removal from groundwater using iron electrocoagulation: effect of charge dosage rate. Journal of Environmental Science and Health, Part A, 48(9), 1019-1030.

2) Arienzo, M., Adamo, P., Chiarenzelli, J., Bianco, M. R., & De Martino, A. (2002). Retention of arsenic on hydrous ferric oxides generated by electrochemical peroxidation. Chemosphere, 48(10), 1009-1018.

3) Banerji, T., & Chaudhari, S. (2016). Arsenic removal from drinking water by electrocoagulation using iron electrodes-an understanding of the process parameters. Journal of Environmental Chemical Engineering, 4(4), 3990-4000.

4) Battaglia‐Brunet, F., Dictor, M. C., Garrido, F., Crouzet, C., Morin, D., Dekeyser, K., ... & Baranger, P. (2002). An arsenic (III)‐oxidizing bacterial population: selection, characterization, and performance in reactors. Journal of applied microbiology, 93(4), 656-667.

5) Bordoloi, S., Nath, S. K., Gogoi, S., & Dutta, R. K. (2013). Arsenic and iron removal from groundwater by oxidation–coagulation at optimized pH: laboratory and field studies. Journal of hazardous materials, 260, 618-626.

6) Calvo, L. S., Leclerc, J. P., Tanguy, G., Cames, M. C., Paternotte, G., Valentin, G., ... & Lapicque, F. (2003). An electrocoagulation unit for the purification of soluble oil wastes of high COD. Environmental Progress, 22(1), 57-65.

7) Can, B. Z., Boncukcuoglu, R., Yilmaz, A. E., & Fil, B. A. (2014). Effect of some operational parameters on the arsenic removal by electrocoagulation using iron electrodes. Journal of Environmental Health Science and Engineering, 12(1), 95.

8) Cavalca, L., Corsini, A., Zaccheo, P., Andreoni, V., & Muyzer, G. (2013a). Microbial transformations of arsenic: perspectives for biological removal of arsenic from water. Future microbiology, 8(6), 753-768.

9) Cavalca, L., Corsini, A., Andreoni, V., & Muyzer, G. (2013b). Draft genome sequence of the arsenite-oxidizing strain Aliihoeflea sp. 2WW, isolated from arsenic-contaminated groundwater. Genome Announc., 1(6), e01072-13.

10) Chen, G. (2004). Electrochemical technologies in wastewater treatment. Separation and purification Technology, 38(1), 11-41.

11) Chen, J., Wang, S., Zhang, S., Yang, X., Huang, Z., Wang, C., ... & Chang, J. (2015). Arsenic pollution and its treatment in Yangzonghai lake in China: In situ remediation. Ecotoxicology and environmental safety, 122, 178-185.

12) Chen, X., Chen, G., & Yue, P. L. (2000). Separation of pollutants from restaurant wastewater by electrocoagulation. Separation and purification technology, 19(1-2), 65-76.

13) Chung, J. Y., Yu, S. D., & Hong, Y. S. (2014). Environmental source of arsenic exposure. Journal of preventive medicine and public health, 47(5), 253.

14) Delaire, C., Amrose, S., Zhang, M., Hake, J., & Gadgil, A. (2017). How do operating conditions affect As (III) removal by iron electrocoagulation?. Water research, 112, 185-194.

15) Deniel, R., Bindu, V. H., Rao, A. V., & Anjaneyulu, Y. (2008). Removal of arsenic from wastewaters using electrocoagulation. J. Environ. Sci. Eng, 50(4), 283-288.

16) Dey, U., Chatterjee, S., & Mondal, N. K. (2016). Isolation and characterization of arsenic-resistant bacteria and possible application in bioremediation. Biotechnology reports, 10, 1-7.

17) Duarte, A. A., Cardoso, S. J., & Alçada, A. (2009). Emerging and innovative techniques for arsenic removal applied to a small water supply system. Sustainability, 1(4), 1288-1304.

18) Dura, A. (2013). Electrocoagulation for Water Treatment: the Removal of Pollutants using Aluminium Alloys, Stainless Steels and Iron Anodes (Doctoral dissertation, National University of Ireland Maynooth).

19) DutchNews.nl (2019, May 7). After a €30 rise in January, Dutch energy prices among highest in EU. Retrieved from:

https://www.dutchnews.nl/features/2019/05/after-a-e30-rise-in-january-dutch-energy-prices-among-highest-in-eu/

20) Flores, O. J., Nava, J. L., Carreño, G., Elorza, E., & Martínez, F. (2013). Arsenic removal from groundwater by electrocoagulation in a pre-pilot-scale continuous filter press reactor. Chemical Engineering Science, 97, 1-6.

21) Garcia-Dominguez, E., Mumford, A., Rhine, E. D., Paschal, A., & Young, L. Y. (2008). Novel autotrophic arsenite-oxidizing bacteria isolated from soil and sediments. FEMS microbiology ecology, 66(2), 401-410.

22) Garcia-Segura, S., Eiband, M. M. S., de Melo, J. V., & Martínez-Huitle, C. A. (2017). Electrocoagulation and advanced electrocoagulation processes: A general review about the fundamentals, emerging applications and its association with other technologies. Journal of Electroanalytical Chemistry, 801, 267-299.

23) Gomes, J. A., Daida, P., Kesmez, M., Weir, M., Moreno, H., Parga, J. R., ... & Cocke, D. L. (2007). Arsenic removal by electrocoagulation using combined Al–Fe electrode system and characterization of products. Journal of hazardous materials, 139(2), 220-231.

24) Green, H.H. (1918). Description of a bacterium which oxidizes arsenite to arsenate, and of one which reduces arsenate to arsenite, isolated from a cattle-dipping tank. South African Journal of Science 14, 465– 467.

25) Gude, J. C. J., Rietveld, L. C., & Van Halem, D. (2018). Biological As (III) oxidation in rapid sand filters. Journal of Water Process Engineering, 21, 107-115.

26) Hakizimana, J. N., Gourich, B., Chafi, M., Stiriba, Y., Vial, C., Drogui, P., & Naja, J. (2017). Electrocoagulation process in water treatment: A review of electrocoagulation modeling approaches. Desalination, 404, 1-21.

27) Hao, L., Liu, M., Wang, N., & Li, G. (2018). A critical review on arsenic removal from water using iron-based adsorbents. RSC advances, 8(69), 39545-39560.

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

29) Holt, P. K., Barton, G. W., & Mitchell, C. A. (2005). The future for electrocoagulation as a localised water treatment technology. Chemosphere, 59(3), 355-367.

30) Hu, C. Y., Lo, S. L., & Kuan, W. H. (2003). Effects of co-existing anions on fluoride removal in electrocoagulation (EC) process using aluminum electrodes. Water research, 37(18), 4513-4523.

31) Hu, C., Wang, S., Sun, J., Liu, H., & Qu, J. (2016). An effective method for improving electrocoagulation process: Optimization of Al13 polymer formation. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 489, 234-240.

32) Hug, S. J., & Leupin, O. (2003). Iron-catalyzed oxidation of arsenic (III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction. Environmental science & technology, 37(12), 2734-2742.

33) Ike, M., Miyazaki, T., Yamamoto, N., Sei, K., & Soda, S. (2008). Removal of arsenic from groundwater by arsenite-oxidizing bacteria. Water Science and Technology, 58(5), 1095-1100.

34) Ito, A., Miura, J. I., Ishikawa, N., & Umita, T. (2012). Biological oxidation of arsenite in synthetic groundwater using immobilised bacteria. Water research, 46(15), 4825-4831.

35) Islam, S. D. U. (2019). Electrocoagulation (EC) technology for wastewater treatment and pollutants removal. Sustainable Water Resources Management, 5(1), 359-380.

36) Jessen, S., Larsen, F., Koch, C. B., & Arvin, E. (2005). Sorption and desorption of arsenic to ferrihydrite in a sand filter. Environmental Science & Technology, 39(20), 8045-8051.

37) Jiang, J. Q. (2001). Removing arsenic from groundwater for the developing world-a review. Water Science and Technology, 44(6), 89-98.

38) Johnston, R. (2008). Chemical interactions between iron and arsenic in water (Doctoral dissertation, The University of North Carolina at Chapel Hill).

39) Katsoyiannis, I. A., & Zouboulis, A. I. (2004). Application of biological processes for the removal of arsenic from groundwaters. Water research, 38(1), 17-26.

40) Katsoyiannis, I. A., Zikoudi, A., & Hug, S. J. (2008). Arsenic removal from groundwaters containing iron, ammonium, manganese and phosphate: A case study from a treatment unit in northern Greece. Desalination, 224(1-3), 330-339.

41) Khaled, B., Wided, B., Béchir, H., Elimame, E., Mouna, L., & Zied, T. (2015). Investigation of electrocoagulation reactor design parameters effect on the removal of cadmium from synthetic and phosphate industrial wastewater. Arabian Journal of Chemistry.

42) Kobya, M., Demirbas, E., Can, O. T., & Bayramoglu, M. (2006). Treatment of levafix orange textile dye solution by electrocoagulation. Journal of hazardous materials, 132(2-3), 183-188.

43) Kobya, M., Ulu, F., Gebologlu, U., Demirbas, E., & Oncel, M. S. (2011a). Treatment of potable water containing low concentration of arsenic with electrocoagulation: Different connection modes and Fe–Al electrodes. Separation and Purification Technology, 77(3), 283-293.

44) Kobya, M., Gebologlu, U., Ulu, F., Oncel, S., & Demirbas, E. (2011b). Removal of arsenic from drinking water by the electrocoagulation using Fe and Al electrodes. Electrochimica Acta, 56(14), 5060-5070.

45) Kobya, M., Demirbas, E., & Ulu, F. (2016). Evaluation of operating parameters with respect to charge loading on the removal efficiency of arsenic from potable water by electrocoagulation. Journal of environmental chemical engineering, 4(2), 1484-1494.

46) Kumar, P. R., Chaudhari, S., Khilar, K. C., & Mahajan, S. P. (2004). Removal of arsenic from water by electrocoagulation. Chemosphere, 55(9), 1245-1252.

47) Lacasa, E., Canizares, P., Sáez, C., Fernández, F. J., & Rodrigo, M. A. (2011). Removal of arsenic by iron and aluminium electrochemically assisted coagulation. Separation and Purification Technology, 79(1), 15-19.

48) Lakshmanan, D., Clifford, D. A., & Samanta, G. (2010). Comparative study of arsenic removal by iron using electrocoagulation and chemical coagulation. Water research, 44(19), 5641-5652.

49) Li, L., van Genuchten, C. M., Addy, S. E., Yao, J., Gao, N., & Gadgil, A. J. (2012). Modeling As (III) oxidation and removal with iron electrocoagulation in groundwater. Environmental science & technology, 46(21), 12038-12045.

50) Liao, V. H. C., Chu, Y. J., Su, Y. C., Hsiao, S. Y., Wei, C. C., Liu, C. W., ... & Chang, F. J. (2011). Arsenite-oxidizing and arsenate-reducing bacteria associated with arsenic-rich groundwater in Taiwan. Journal of contaminant hydrology, 123(1-2), 20-29.

51) Majumder, C., & Gupta, A. (2010). Factorial design approach to investigate the effects of groundwater cooccurring solutes on arsenic removal by electrocoagulation. Journal of Hazardous, Toxic, and Radioactive Waste, 15(1), 55-61.

52) Maldonado-Reyes, A., Montero-Ocampo, C., & Solorza-Feria, O. (2007). Remediation of drinking water contaminated with arsenic by the electro-removal process using different metal electrodes. Journal of Environmental Monitoring, 9(11), 1241-1247.

53) Mandal, B. K., & Suzuki, K. T. (2002). Arsenic round the world: a review. Talanta, 58(1), 201-235.

54) Matteson, M. J., Dobson, R. L., Glenn Jr, R. W., Kukunoor, N. S., Waits III, W. H., & Clayfield, E. J. (1995). Electrocoagulation and separation of aqueous suspensions of ultrafine particles. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 104(1), 101-109.

55) Mollah, M. Y. A., Schennach, R., Parga, J. R., & Cocke, D. L. (2001). Electrocoagulation (EC)—science and applications. Journal of hazardous materials, 84(1), 29-41.

56) Mollah, M. Y., Morkovsky, P., Gomes, J. A., Kesmez, M., Parga, J., & Cocke, D. L. (2004). Fundamentals, present and future perspectives of electrocoagulation. Journal of hazardous materials, 114(1-3), 199-210.

57) Mokashi, S. A., & Paknikar, K. M. (2002). Arsenic (III) oxidizing Microbacterium lacticum and its use in the treatment of arsenic contaminated groundwater. Letters in Applied Microbiology, 34(4), 258-262.

58) Moussa, D. T., El-Naas, M. H., Nasser, M., & Al-Marri, M. J. (2017). A comprehensive review of electrocoagulation for water treatment: Potentials and challenges. Journal of environmental management, 186, 24-41.

59) Müller, S., Behrends, T., & van Genuchten, C. M. (2019). Sustaining efficient production of aqueous iron during repeated operation of Fe (0)-electrocoagulation. Water research, 155, 455-464.

60) Nagy, G., & Korom, I. (1983). Spale hautsymptome der arsenvergifturg aut grund der arsenendemic in bugac-alsomonostor. Z. Hautkr, 58, 961-964.

61) Nicomel, N., Leus, K., Folens, K., Van Der Voort, P., & Du Laing, G. (2016). Technologies for arsenic removal from water: current status and future perspectives. International journal of environmental research and public health, 13(1), 62.

62) Nidheesh, P. V., & Singh, T. A. (2017). Arsenic removal by electrocoagulation process: recent trends and removal mechanism. Chemosphere, 181, 418-432.

63) Panagiotaras, D., & Nikolopoulos, D. (2015). Arsenic occurrence and fate in the environment; a geochemical perspective. Journal of Earth Science & Climatic Change, 6(4), 1.

64) Philips, S. E., & Taylor, M. L. (1976). Oxidation of arsenite to arsenate by Alcaligenes faecalis. Appl. Environ. Microbiol., 32(3), 392-399.

65) Rieuwerts, J. (2017). The elements of environmental pollution. Routledge.

66) Roberts, L. C., Hug, S. J., Ruettimann, T., Billah, M. M., Khan, A. W., & Rahman, M. T. (2004). Arsenic removal with iron (II) and iron (III) in waters with high silicate and phosphate concentrations. Environmental Science & Technology, 38(1), 307-315.

67) Roy, P., & Saha, A. (2002). Metabolism and toxicity of arsenic: A human carcinogen. Current science, 38-45.

68) Salmassi, T. M., Venkateswaren, K., Satomi, M., Newman, D. K., & Hering, J. G. (2002). Oxidation of arsenite by Agrobacterium albertimagni, AOL15, sp. nov., isolated from Hot Creek, California. Geomicrobiology Journal, 19(1), 53-66.

69) Santini, J. M., Sly, L. I., Schnagl, R. D., & Macy, J. M. (2000). A new chemolithoautotrophic arsenite-oxidizing bacterium isolated from a gold mine: phylogenetic, physiological, and preliminary biochemical studies. Appl. Environ. Microbiol., 66(1), 92-97.

70) Shankar, R., Singh, L., Mondal, P., & Chand, S. (2014). Removal of COD, TOC, and color from pulp and paper industry wastewater through electrocoagulation. Desalination and Water Treatment, 52(40-42), 7711-7722.

71) Singh, R., Singh, S., Parihar, P., Singh, V. P., & Prasad, S. M. (2015). Arsenic contamination, consequences and remediation techniques: a review. Ecotoxicology and environmental safety, 112, 247-270.

72) Singh, T. S. A., & Ramesh, S. T. (2014). An experimental study of CI Reactive Blue 25 removal from aqueous solution by electrocoagulation using aluminum sacrificial electrode: kinetics and influence of parameters on electrocoagulation performance. Desalination and Water Treatment, 52(13-15), 2634-2642.

73) Smedley, P. L. (2008). Sources and distribution of arsenic in groundwater and aquifers.

74) Smith, S. D., & Edwards, M. (2005). The influence of silica and calcium on arsenate sorption to oxide surfaces. Journal of Water Supply: Research and Technology-AQUA, 54(4), 201-211.

75) Song, P., Yang, Z., Xu, H., Huang, J., Yang, X., & Wang, L. (2014). Investigation of influencing factors and mechanism of antimony and arsenic removal by electrocoagulation using Fe–Al electrodes. Industrial & Engineering Chemistry Research, 53(33), 12911-12919.

76) Song, P., Yang, Z., Zeng, G., Yang, X., Xu, H., Wang, L., ... & Ahmad, K. (2017). Electrocoagulation treatment of arsenic in wastewaters: a comprehensive review. Chemical Engineering Journal, 317, 707-725.

77) Strawn, D. G. (2018). Review of interactions between phosphorus and arsenic in soils from four case studies. Geochemical transactions, 19(1), 10.

78) UÇAR, C. (2011). Arsenic removal from drinking waters by electrocoagulation and filtration (Doctoral dissertation, DEÜ Fen Bilimleri Enstitüsü).

79) van Genuchten, C. M., Addy, S. E., Peña, J., & Gadgil, A. J. (2012). Removing arsenic from synthetic groundwater with iron electrocoagulation: an Fe and As K-edge EXAFS study. Environmental science & technology, 46(2), 986-994.

80) van Genuchten, C. M., Bandaru, S. R., Surorova, E., Amrose, S. E., Gadgil, A. J., & Pena, J. (2016). Formation of macroscopic surface layers on Fe (0) electrocoagulation electrodes during an extended field trial of arsenic treatment. Chemosphere, 153, 270-279.

81) van Genuchten, C. M., Dalby, K. N., Ceccato, M., Stipp, S. L. S., & Dideriksen, K. (2017). Factors affecting the Faradaic efficiency of Fe (0) electrocoagulation. Journal of environmental chemical engineering, 5(5), 4958-4968.

82) van Genuchten, C. M., Peña, J., Amrose, S. E., & Gadgil, A. J. (2014). Structure of Fe (III) precipitates generated by the electrolytic dissolution of Fe (0) in the presence of groundwater ions. Geochimica et Cosmochimica Acta, 127, 285-304.

83) van Halem, D. (2011). Subsurface iron and arsenic removal for drinking water treatment in Bangladesh.

84) Vasudevan, S., Lakshmi, J., & Sozhan, G. (2010a). Studies relating to removal of arsenate by electrochemical coagulation: Optimization, kinetics, coagulant characterization. Separation Science and Technology, 45(9), 1313-1325.

85) Vasudevan, S., Lakshmi, J., & Sozhan, G. (2010b). Studies on the removal of arsenate by electrochemical coagulation using aluminum alloy anode. CLEAN–Soil, Air, Water, 38(5‐6), 506-515.

86) Vasudevan, S., Lakshmi, J., & Sozhan, G. (2012). Optimization of electrocoagulation process for the simultaneous removal of mercury, lead, and nickel from contaminated water. Environmental Science and Pollution Research, 19(7), 2734-2744.

87) Voegelin, A., Kaegi, R., Frommer, J., Vantelon, D., & Hug, S. J. (2010). Effect of phosphate, silicate, and Ca on Fe (III)-precipitates formed in aerated Fe (II)-and As (III)-containing water studied by X-ray absorption spectroscopy. Geochimica et Cosmochimica Acta, 74(1), 164-186.

88) Wan, W. (2010). Arsenic removal from drinking water by electrocoagulation.

89) Wan, W., Pepping, T. J., Banerji, T., Chaudhari, S., & Giammar, D. E. (2011). Effects of water chemistry on arsenic removal from drinking water by electrocoagulation. Water research, 45(1), 384-392.

90) Wang, S., & Mulligan, C. N. (2006). Occurrence of arsenic contamination in Canada: sources, behavior and distribution. Science of the total Environment, 366(2-3), 701-721.

91) Weeger, W., Lievremont, D., Perret, M., Lagarde, F., Hubert, J. C., Leroy, M., & Lett, M. C. (1999). Oxidation of arsenite to arsenate by a bacterium isolated from an aquatic environment. Biometals, 12(2), 141-149.

92) World Health Organization. (2011). Arsenic in drinking-water: background document for development of WHO guidelines for drinking-water quality, World Health Organization.

93) World Health Organization (2001). Arsenic and arsenic compounds, Environmental Health Criteria 224, Second edition, Geneva.

94) World Steel Prices (2019). European Steel Prices. Retrieved from:

https://worldsteelprices.com/european-steel-prices/

95) You, H. J., & Han, I. S. (2016). Effects of dissolved ions and natural organic matter on electrocoagulation of As (III) in groundwater. Journal of environmental chemical engineering, 4(1), 1008-1016.

96) Zeng, H., Arashiro, M., & Giammar, D. E. (2008). Effects of water chemistry and flow rate on arsenate removal by adsorption to an iron oxide-based sorbent. Water research, 42(18), 4629-4636.

97) Zhang, P., Tong, M., Yuan, S., & Liao, P. (2014). Transformation and removal of arsenic in groundwater by sequential anodic oxidation and electrocoagulation. Journal of contaminant hydrology, 164, 299-307.

98) Zhao, X., Zhang, B., Liu, H., & Qu, J. (2010). Removal of arsenite by simultaneous electro-oxidation and electro-coagulation process. Journal of Hazardous materials, 184(1-3), 472-476.

99) Zouboulis, A. I., & Katsoyiannis, I. A. (2005). Recent advances in the bioremediation of arsenic-contaminated groundwaters. Environment international, 31(2), 213-219.