# MODIFICATION OF AN ANION EXCHANGE RESIN WITH ZERO VALENT IRON FOR THE REMOVAL OF Sb(III) AND Sb(V) FROM WATERS

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**Begüm AKARSU**

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We approve the thesis of **Begüm AKARSU**

**Examining Committee Members:**

**Prof.Dr. Ahmet E. EROĞLU**
Department of Chemistry, İzmir Institute of Technology

**Prof.Dr. Aysun SOFUOĞLU**
Department of Chemical Engineering, İzmir Institute of Technology

**Assoc.Prof.Dr. Sait C. SOFUOĞLU**
Department of Chemical Engineering, İzmir Institute of Technology

**Prof.Dr. F. Nil ERTAŞ**
Department of Chemistry, Ege University

**Assoc.Prof.Dr. Mustafa M. DEMİR**
Department of Chemistry, İzmir Institute of Technology

**11 July 2013**

**Prof.Dr. Ahmet E. EROĞLU**
Supervisor, Department of Chemistry
İzmir Institute of Technology

**Prof.Dr. Ahmet E. EROĞLU**
Head of the Department of Chemistry

**Prof.Dr. R. Tuğrul SENGER**
Dean of the Graduate School of
Engineering and Sciences

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# ABSTRACT

## MODIFICATION OF AN ANION EXCHANGE RESIN WITH ZERO VALENT IRON FOR THE REMOVAL OF Sb(III) AND Sb(V) FROM WATERS

Antimony is non-essential for life, a cumulative toxic element and accepted as a significant contaminant by the European Union which established a maximum admissible concentration of 5.0 $\mu gL^{-1}$ total antimony in drinking water. There are usually two oxidation states of antimony in surface waters; namely, Sb(III) and Sb(V) where Sb(V) is generally the most commonly found form due to oxidative properties of these types of water.

In this study, a new sorbent was developed for removal of inorganic antimony species from contaminated waters. For this purpose, Amberlite IRA 458 resin was treated with ferric ion and then the ferric ions were reduced by sodium borohydride in order to modifiy the resin surface with zero valent iron (ZVI). Both unmodified and nZVI modified IRA 458 resin were investigated for their sorption towards antimony species.

Batch type sorption experiments were verified with ultrapure water spiked with 100.0 $\mu gL^{-1}$ antimony species. Antimony content was determined by hydride generation atomic absorption spectrometry (HGAAS). The optimized sorption parameters for the new sorbent were determined to be 7.0 for pH, 50.0 mg for sorbent amount, 25 ˚C for sorption temperature, 60 min for shaking time for 20.0 mL of 100.0 $\mu gL^{-1}$ of antimony species. With this methodology, an effective antimony removal was obtained to range between 94.5% and 97.7% for Sb(III), and 83.2% and 97.1% for Sb(V).

# ÖZET

## SULARDAN Sb(III) VE Sb(V)'İN GİDERİLMESİ İÇİN ANYON DEĞİŞTİRİCİ BİR REÇİNENİN SIFIR DEĞERLİKLİ DEMİR İLE MODİFİKASYONU

Antimon, hayati gerekliliği olmayan, kümülatif etkiye sahip toksik bir element olup mühim bir atık olarak tarafından kabul edilmiş Avrupa Birliği'ne göre içme sularında maksimum konsantrasyonu 5.0 µgL$^{-1}$ olarak belirlenmiştir. Yüzey sularında, antimon iki oksidasyon formunda bulunur, şöyle ki, Sb (III) ve Sb (V) ve Sb (V) genel olarak bu tür sular arasında oksidatif özellikleri sebebiyle en yaygın bulunan formdur.

Bu çalışmada, kontamine sulardaki inorganik antimon türlerinin giderilmesi için yeni bir sorbent geliştirilmiştir. Bu amaç için, Amberlite IRA 458 reçinesi demir iyonları yüklenmiş ve reçine yüzeyinin sıfır değerlikli demir ile modifikasyonu için demir iyonları sodium borhidrür ile indirgenmiştir. Her iki modifiye edilmemiş ve sıfır değerlikli demir ile modifiye edilmiş IRA 458 reçinenin antimon türlerine karşı olan sorpsiyonu araştırılmıştır.

Sorpsiyon çalışmaları 100.0 µgL$^{-1}$ antimon türlerinden katılmış ultra saf su ile doğrulanmıştır. Antimon içeriği hidrür oluşturmalı atomik absorpsiyon spektrometri ile tayin edilmiştir. Modifiye edilen sorbent için optimize edilmiş sorpsiyon parametreleri; pH 7.0, sorbent miktarı 50.0 mg, sorpsiyon sıcaklığı 25 ˚C, çalkalama süresi 60 dakika, antimon çözeltisi 20,0 mL 100,0 µgL$^{-1}$ olarak belirlenmiştir. Bu yöntem ile verimli bir antimony giderimi elde edilmiş olup Sb(III) için % 94.5 ile % 97.7, Sb(V) için ise % 83.2 ile % 97.1 arasında değiştiği bulunmuştur.

*Dedicated to my lovely mother;*

*"Hayal Akarsu"*

*who has always believed in me more than I did.*

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# CHAPTER 1

# INTRODUCTION

## 1.1. General Description of Antimony

Antimony is a chemical element with symbol as Sb and atomic number as 51 (Bhakhar 2006). Antimony is a silvery gray metalloid which has the characteristics of both metals and nonmetals (Bhakhar 2006). Antimony has been known since ancient times. The element was probably first named by Roman scholar Pliny (A.D. 23-79), who called it stibium. Muslim alchemist Abu Musa Jabir Ibn Hayyan (c.721-c.815) probably first called it antimony — anti ("not") and monos ("alone"). The name comes from the fact that antimony does not occur alone in nature. and is usually obtained from the ores stibnite ($Sb_2S_3$) and valentinite ($Sb_2O_3$). The first detailed reports about antimony were published in 1707 when French chemist Nicolas Lemery published his famous book, Treatise on Antimony (Mellor 1964).

## 1.2. Antimony Species in the Environment

Antimony can exist in a variety of oxidation states (-III, 0, III, V) but it is mainly found in two oxidation states (III and V) in environmental, biological and geochemical samples (Bhakhar 2006). Antimony and its compounds are considered as pollutants of priority interest by the Environmental Protection Agency of the United States (USEPA 1979) and the European Union (EU 1976). According to the USEPA, the maximum contaminant level goal (MCLG) and maximum contaminant level (MCL) are both 6 $\mu gL^{-1}$ for antimony in drinking water (USEPA 1999). Whereas EU established the maximum admissible concentration of antimony in drinking water as 5 $\mu gL^{-1}$ (EU 1998). Dissolved antimony concentration in unpolluted waters are less than 1 $\mu gL^{-1}$. The mean antimony concentration in surface marine waters is 184 ± 45 $\mu gL^{-1}$ (Fiella 2002). In addition, higher concentrations of antimony can be found near the anthropogenic sources (Fiella 2002).

According to thermodynamic equilibrium, antimony exists in the form of Sb(V) in oxic systems and Sb(III) in anoxic systems (Fiella 2002). The redox behavior of antimony demonstrated in Eh-pH diagram in Figure 1.1. According to this diagram, antimony exists in the form as soluble antimonite ($Sb(OH)_6^-$) in oxic systems and as soluble antimonous acid ($Sb(OH)_3$) in anoxic ones around natural pH values. Under reducing conditions, and in the presence of sulfur, stibnite, $Sb_2S_3$(s) occurs between low to intermediate pH values. Again in the presence of sulfur, at higher pH values, the $Sb_2S_4^{2-}$ species are formed instead of stibnite.

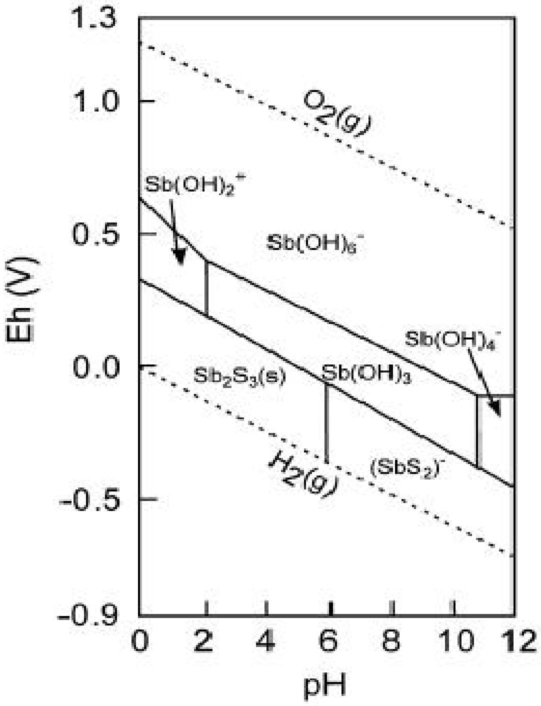


Figure 1.1. Eh-pH diagram of antimony in the Sb-S-$H_2O$ system at a dissolved antimony concentration of $10^{-8}$ mol/L and a dissolved sulfur concentration of $10^{-3}$ mol/L (Source: Fiella 2002)

## 1.3. Antimony in History

Antimony exists in the environment as a result of natural processes and human activities (Filella 2002). Antimony was known to the ancients by the fact that it can dissolve many other metals including gold. Thus, this property of antimony was used for purifying gold from copper and silver up to the 18th century (Shotyk 1996). Antimony is a poor conductor of heat and electricity. Pure antimony is used for certain types of semiconductor devices, such as diodes and infrared detectors. Furthermore, antimony is alloyed with lead to increase lead's durability (Holmyard 2008). Antimony alloys are also used in batteries, low friction metals, type metal and cable sheathing among other products (Holmyard 2008). Antimony compounds are used to make flame-proofing materials, paints, ceramic enamels, glass and pottery (Grund 2006). It is known that antimony trioxide has a bright yellow color which leds antimony to be also used for pigments in plastics, paints, rubber and in addition antimony has a wide variety of minor uses, including medicines and fireworks (Grund 2006).

The largest producers of antimony are China, Russia, Bolivia, South Africa, and Kyrgyzstan, in that order. Antimony occurs in the earth's crust at a concentration of 0.2-0.3 ppm (Carlin 2011). It is found in more than 100 minerals, but is mined mainly from stibnite ($Sb_2S_3$), kermesite ($2Sb_2S_3$ $Sb_2O_3$), alentinite ($Sb_2O_3$), cervantite ($Sb_2O_4$), stibiconite ($Sb_2O_4$ $2H_2O$, tetrahedride $[Cu\ Fe]_{12}$ $Sb_4S_{13}$), jamesonite ($Pb_4Fe$ $Sb_6S_{14}$), and pyrargyrite ($Ag_3SbS_3$) (Léonard & Gerber, 1996).

Large amount of antimony is found in sediment, soil, and rocks which is strongly attached to dust and dirt or found to be buried in minerals. Thus, it can not easily interact with living. However, some amount of antimony in the environment is less tightly attached to particles and can be taken up by plants and animals. The concentration of antimony in air ranges from 1 ng/m$^3$ to about 170 ng/m$^3$ (ATSDR 1992). However, near companies which change antimony ores into metal or produce antimony oxide, concentration of antimony rises up to 1000 ng/m$^3$. Soil usually contains very low concentrations of antimony, less than 1 mg/kg (Sundar 2010). However, concentrations close to 9 mg/kg have been found (ATSDR 1992). The highest soil concentrations found at hazardous waste sites on the National Priorities List (NPL) and at antimony-processing sites range from 109 to 2550 mg/kg (ATSDR 1992). Concentrations of antimony in groundwater and surface water normally range from 0.1 to 0.2 µgL$^{-1}$ (WHO 2011). Marine antimony concentrations are approximately 0.15 µgL$^{-1}$ (Andreae 1981). Antimony is not likely to exist as high concentrations in natural waters, except in those areas affected by acid mine drainage. Domestic wastewater contains almost no antimony, in despite of wastewater from glass or metal processing foundations (WHO 2011).

In a recent study of antimony in bottled waters produced in Canada and Europe, it was pointed out that the waters become contaminated during storage because of antimony leaching from polyethylene terephthalate (PET), especially under high temperatures (Shotyk 2006). Elevated concentrations of Sb in bottled waters are due mainly to the $Sb_2O_3$ used as the catalyst in the manufacture of PET. In 14 brands of bottled water from Canada, Sb concentrations increased on average 19% during 6 months storage at room temperature, but 48 brands of water from 11 European countries increased on average 90% under identical conditions. A mineral water in PET from France, purchased in Germany, yielded 725 $ngL^{-1}$ when first tested, but 1510 $ngL^{-1}$ when it was stored for 6 months at room temperature; the same brand of water, purchased in Hong Kong, yielded 1990 $ngL^{-1}$ Sb (Shotyk 2007).

## 1.4. Effect of Antimony Species on the Environment and Health

Antimony has no known biological function and like arsenic, it is toxic. Trivalent species are reported to be more toxic than pentavalent forms (Bencze 1994). The toxicity of antimony is a function of the water solubility and the oxidation state of the antimony species under consideration (Fowler and Goering 1991). In general, antimony (III) is more toxic than antimony (V), and the inorganic compounds are more toxic than the organic compounds with stibine ($SbH_3$), a lipophilic gas, being most toxic (by inhalation) (Stemmer 1976). Trivalent and pentavalent forms of antimony exhibit distinct differences in their analytical behavior, and toxicity. Due to the pentavalent antimony being the predominant species in most environmental waters, in order to estimate the physiological or environmental risks, it is inadequate to determine only the total amount of antimony in a given sample. There are more than 3000 organic compounds of antimony stated in literature, only two of them are present in natural waters (methylstibonic acid and di-methyl-stibinic acid), which are known to be less toxic than inorganic forms (Ariza 2000).

Oral uptake of soluble antimony salts causes a strong irritating effect on the gastrointestinal mucosa and leads to continual vomiting. In addition to these effects, abdominal cramps, diarrhoea and cardiac toxicity also can be observed (Elinder and Friberg 1986). Also, chronic respiratory uptake of antimony containing dusts results as irritation on the respiratory tract and causes liver damage (Winship 1987). The greatest concern of the carcinogenicity effect of antimony compounds relates to the inhalation route. In inhalation studies, it is observed that antimony trioxide has a carcinogenic effect on the experimental animals (IARC 1989) and caused lung damage followed by chronic inhalation as an outcome of excess amount of insoluble particulates (Newton 1994).

## 1.5. Methods for Antimony Determination

There are several methods for the determination of antimony in various samples. Conventional methods such as gravimetry and volumetry can be used in the cases where the concentration of antimony is relatively high. For instance, Sb(III) can be titrated with standard triiodide solution in iodimetric method (Skoog 1998). Also, with using a thin-film gold electrode potentiometric stripping analysis was used for the determination of Sb(III) (Wang 1984).

Atomic fluorescence spectrometry is considered to be an another practical process for antimony determination (Cava-Montesinos 2003). Neutron activation analysis (NAA) coupled with hydride generation is a very sensitive technique for the determination of antimony (Sun 1999). Spectrophotometric determination of Sb(III) can be carried out after complexing it with some complexing agents such as mandelic acid, malachite green (Sato 1985) and chromium (VI) solution (Yonehara 1985).

Among all these techniques, inductively coupled plasma mass spectrometry (ICP-MS) (Ponce de León 2002) and atomic absorption spectrophotometry (AAS) are the most useful and the most sensitive techniques for antimony determination and with some modifications, a more accurate analysis is achieved (Kubota 2001).

By the use of AAS, antimony can be determined in the air-acetylene flame practically free of interferences. However, little is available about the determination of this element by FAAS since antimony is mostly present in very low concentrations and so the analysis must be carried out using a more sensitive technique. Furthermore, antimony can be determined by GFAAS under stabilized temperature platform furnace (STPF) conditions and using the Pd-Mg modifier (Welz 2008). Concentrations of NaCl of up to 30 $gL^{-1}$ is reported to have no influence on the Sb signal under these conditions. Sulfate contents more than 20 $mgL^{-1}$ cause a slight gas-phase interference that can not be completely eliminated by creating a thermal pretreatment condition (Welz 2008). In HGAAS determination of antimony, the atomization signal is dependent on the oxidation state and the hydride form of antimony. In batch systems Sb(III) generates a signal that is nearly twice as high as it is for the same mass of Sb(V). In flow systems this difference can be more than one order of magnitude, depending on the reaction zone. These differences are also pH dependent; this suggests the possibility, for instance, of selectively determining Sb(III) at pH 8.0 in the presence of a large amount of Sb(V) (Welz 2008).

For the determination of total antimony content it is necessary to apply a prereduction step to guarantee that all of the antimony in the given sample is present in the form as Sb(III). For this purpose, a solution of potassium iodide in hydrochloric acid is frequently used. However it must be considered that the high acid concentration and also the potassium iodide pose a substantial disposal problem. Furthermore, potassium iodide solutions only have limited stability. Thus, L-cysteine is highly recommended as the reductant and has major advantages compared to other reagents that are known as being practically non-toxic and keeping the solutions stable for several weeks (Welz 2008).

## 1.6. Antimony Removal Technologies

Water purification is the removal of contaminants from untreated water to produce drinking water that is pure enough for the most critical of its intended uses, usually for human consumption.

Some of the most common treatment systems performed are chlorination, solar disinfection, combined filtration with chlorination and combined flocculation with chlorination (USEPA 2004). However, in a case which the water is rich in antimony that causes a highly toxic and hazardous medium for human health, it is necessary to approach to a more complex method because of the fact that antimony changes its form according to pH range. Thus, it is important to develop a method that can be effective in the removal of both antimony forms. For this purpose, there are some technologies that are developed and considered for the removal of antimony species from drinking waters; separation (membrane) methods, precipitative methods, ion exchange methods and adsorption methods.

### 1.6.1. Membrane Methods

In membrane filtration, a solvent is passed through a semi-permeable membrane. The membrane's permeability is determined by the size of the pores in the membrane, and it will act as a barrier to particles which are larger than the pores, while the rest of the solvent can pass freely through the membrane. The result is a cleaned and filtered fluid on one side of the membrane, with the removed solute on the other side.

Membrane methods are classified into four categories: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) among which reverse osmosis is the most frequently used for the removal of antimony.

Reverse osmosis is highly effective in removing several impurities from water such as total dissolved solids (TDS), turbidity, asbestos, lead, other toxic heavy metals and many dissolved organics. The pore structure of RO membranes is much tighter than UF membranes. Natural osmosis occurs when solutions with two different concentrations are separated by a semi-permeable membrane. Osmotic pressure drives water through the membrane; the water dilutes the more concentrated solution; and the end result is an equilibrium. RO also involves an ionic exclusion process. Only, solvent is allowed to pass through the semi-permeable RO membrane, while virtually all ions and dissolved molecules are retained (including salts and sugars). The semi-permeable membrane rejects salts (ions) by a charge phenomena action that is explained as the greater the charge, the greater the rejection. Therefore, the membrane rejects nearly all (>99%) strongly ionized polyvalent ions but only 95% of the weakly ionized monovalent ions like sodium.

Reverse osmosis can be used to remove antimony from water sources. RO can reject compounds by either size exclusion or charge. Approximately 80% removal of Sb(V) can be achieved over the pH range 3 to 10. It is stated that Sb(III) removal decreases with increasing pH. Removal efficiency of Sb(III) with RO is apprimately 30% to 60% which is considered to be low (Kang 2000). The model of the reverse osmosis system is shown in Figure 1.2.

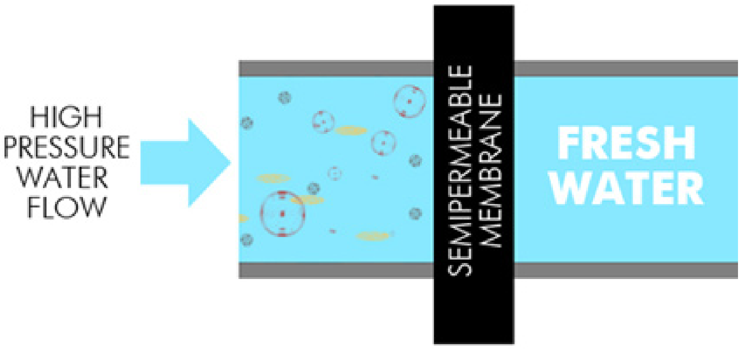


Figure 1.2. The model of a Reverse Osmosis System
(Source: http://www.freedrinkingwater.com, Water Filtration Methods 2013)

### 1.6.2. Precipitative Methods

Coagulation/filtration (C/F), direct filtration, coagulation assisted microfiltration and lime softening (LS) are the examples of precipitative methods used to treat antimony in drinking water.

Coagulation/filtration is the most common precipitative methods which uses coagulants such as; ferric salts, (e.g. ferric chloride), ferric sulfate, ferric hydroxide, aluminum sulfate and alum (aluminum hydroxide). This process is used not only to remove solids from drinking water supplies but also to change some dissolved species (e.g., natural organic matter (NOM), inorganics, and hydrophobic synthetic organic compounds (SOCs) to insoluble by means of the metal salt coagulants (generally aluminum sulfate, ferric chloride, or ferric sulfate) (USEPA 2000).

Coagulation is a two-stage process used to remove the suspended or dissolved compounds. In the first stage, the compound in water is destabilized by altering its physical and chemical properties and in the second stage the destabilized compound is removed by filtration. Removal extremely relies on the coagulant type, dosage of coagulant, coagulation pH, initial antimony concentration and the valence of the antimony species; Sb(III) or Sb(V).

Coagulation and filtration uses the conventional treatment processes such as chemical addition, coagulation, and dual media filtration. Ferric chloride ($FeCl_3$) was observed to be most effective at pH range from 4.5 to 5.5 with some Sb removal observed over the range of pH from 4.0 to 10.0. Aluminum sulfate $Al_2(SO_4)_3$ is much less effective and may not be practicle for Sb removal (Guo 2009). Sb(III) is more easily removed with coagulation than Sb(V), however, Sb(V) removal effiencies can reach to as high as 98% with sufficient concentration of coagulant at optimal pH (Guo 2009). The model of a precipitation/coprecipitation system is shown in Figure 1.3.

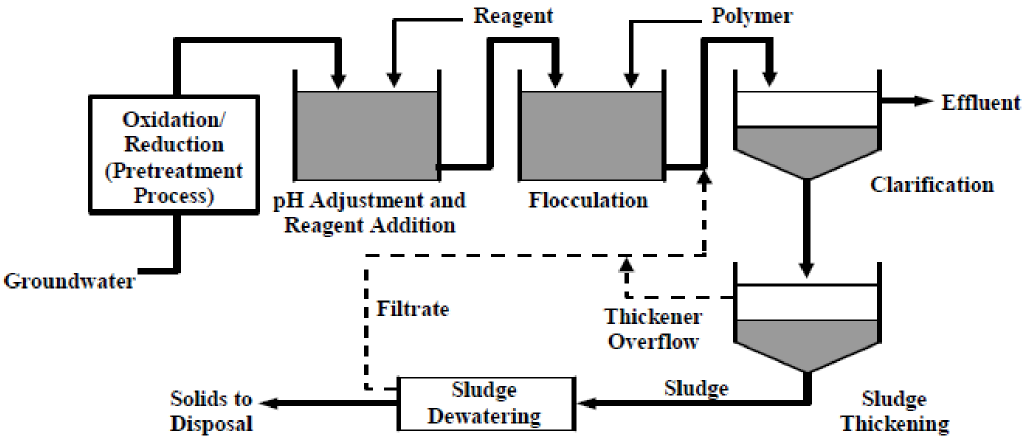


Figure 1.3. The model of a Precipitation/Coprecipitation System
(Source: Arsenic Treatment Technologies for Soil, Waste and Water – USEPA 2002)

## 1.6.3. Ion Exchange Methods

The ion exchange process percolates water through bead-like spherical resin materials (ion-exchange resins). Ions in the water are exchanged for other ions fixed to the beads. The two most common ion-exchange methods are softening and deionization.

Softening; is used primarily as a pretreatment method to reduce water hardness prior to reverse osmosis processing. The softeners contain beads that exchange two sodium ions for every calcium or magnesium ion removed from the softened water. Deionization (DI) beads exchange either hydrogen ions for cations or hydroxyl ions for anions. The cation exchange resins, made of styrene and divinylbenzene containing sulfonic acid groups, will exchange a hydrogen ion for any cations they encounter (e.g., $Na^+$, $Ca^{++}$, $Al^{+++}$). Similarly, the anion exchange resins, made of styrene and containing quaternary ammonium groups, will exchange a hydroxyl ion for any anions (e.g., $Cl^-$). The hydrogen ion from the cation exchanger unites with the hydroxyl ion of the anion exchanger to form pure water. These resins may be packaged in separate bed exchangers with separate units for the cation and anion exchange beds. Or, they may be packed in mixed bed exchangers containing a mixture of both types of resins. In either case, the resin must be regenerated after it has exchanged its hydrogen or hydroxyl ions for charged contaminants in the water. This regeneration reverses the purification process, replacing the contaminants bound to the DI resins with hydrogen and hydroxyl ions. The model and a simple mechanism of the ion exchange system is shown in Figure 1.4. and Figure 1.5., respectively.

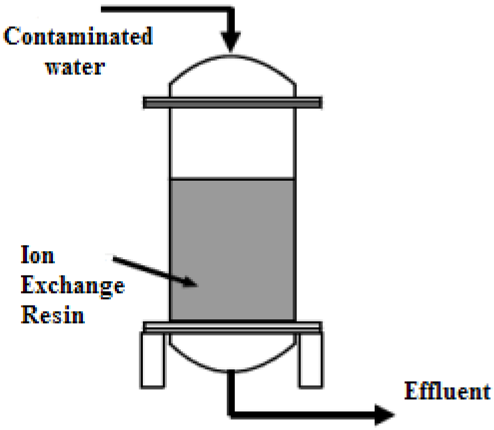


Figure 1.4. The model of an Ion Exchange System
(Source: Arsenic Treatment Technologies for Soil, Waste and Water – USEPA 2002)

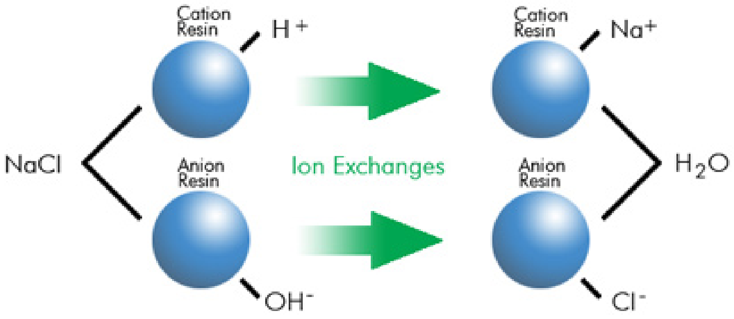


Figure 1.5. A simple mechanism of an Ion Exchange System
(Source: http://www.freedrinkingwater.com, Water Filtration Methods 2013)

## 1.6.4. Adsorptive Methods

In this process, the adsorption media is usually packed into a column. While the contaminated water is passed through the column, contaminants are adsorbed by media. When adsorption sites become filled, the column must be regenerated or replaced with new media (EPA 2002). Activated carbon (AC), activated alumina (AA), copper-zinc granules, granular ferric hydroxide, iron oxide coated sand, greensand filtration ($KMnO_4$ coated glauconite), and surfactant-modified zeolite are types of sorbents which are used in adsorptive methods. Very little information is available about the adsorption/desorption behaviour of Sb(V) or Sb(III). However, the concentrations of antimony in soils and sediments are likely to be controlled by adsorption reactions (Crecelius 1975).

Among the adsorptive sorbent studies for antimony removal from water, granulated ferric hydroxide is found to be one of the most effective sorbents with the adsorption capacity of 85.04 µg/g (Ilavsý 2008). In addition, iron oxide coated olivine (IOCO) is possible to use for the removal of antimony (V), especially at high pH. (Bhakhar 2006).

## 1.7. Nanoscaled Zero-Valent Iron (nZVI)

Over the past few years, various methods have been developed for antimony removal; namely, ion-exchange, chelating sorption and co-precipitation. Beside these methods, nanoscience and nanotechnology have been widely used for remediation of environmental problems. Nanosorbents have many advantages such as low cost, high adsorption capacities and fast adsorption rates for heavy metal ions. Especially, zero valent iron nanoparticles are considered to be very promising for Sb removal with the advantages of providing a high surface area and high sorption capacity. In spite of these advantages, lack of knowledge about the behavior of nanoparticles in living systems requires close control of their concentrations in many applications.

Iron is a transition metal with atomic number 26 and symbol Fe. Iron is placed in group VIII and period IV of periodic table. Iron is a very reactive element and is oxidized very rapidly in atmospheric conditions. As a result, it usually exists in nature in the form of magnetite ($Fe_3O_4$), hematite (natural ore) ($Fe_2O_3$) and limonite. In Figure

1.6. the oxidation states and reduction potentials of iron species are represented. Also, several studies demonstrated, with its high capability of reduction characteristics, zero-valent iron is effective at stabilization and destruction of a host of pollutants.

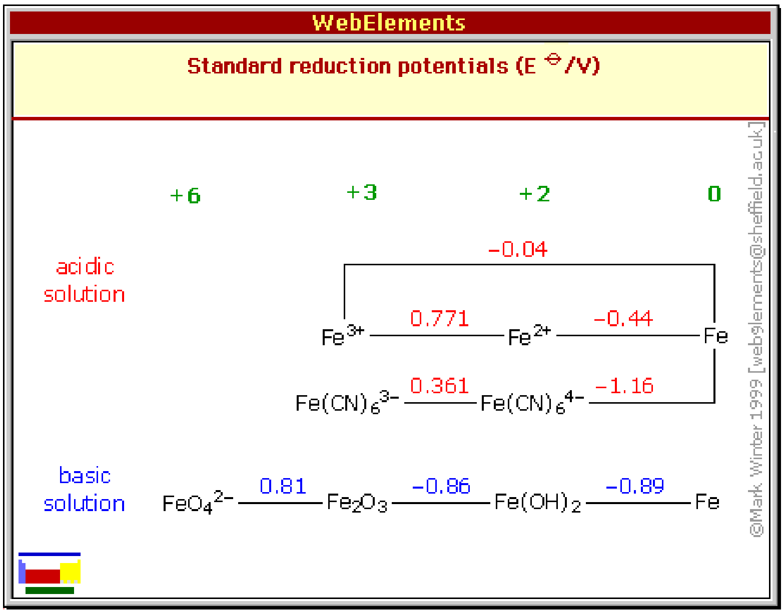


Figure 1.6. Standart reduction potentials of iron species
(Source: Web of Element 2008)

There are several physical and chemical synthesis techniques for the synthesis of nanoscaled zero-valent iron (Li et al. 2006; Nurmi et al. 2005; Sun et al. 2006). A summary of these techniques was outlined in a review paper by Li et al. (2006). The most widely used method for environmental purposes is the liquid phase reduction method. In this method, the borohydrate reduction of Fe(III) ions took place in aqueous media. The method presented by Wang and Zhang consists of dropwise addition of sodium borohydride ($NaBH_4$) into a solution of Fe(III) (Wang and Zhang 1997). Hence, the liquid phase reduction method is also called borohydride reduction. One of the proposed mechanisms for the reaction 1.1 is:

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 \downarrow + 3H_2BO_3^- + 12H^+ + 6H_2 \uparrow \text{ (Li et al. 2006)} \qquad (1.1)$$

In Figure 1.7, the model for core-shell structure of nZVI and uptake mechansims of metals suggested by Li and Zhang (2007). The synthesized nZVI particles are generally occurs in spherical shape and have a coreshell structure, are also unstable in atmospheric conditions and tends to form oxides/hydroxides in the forms $Fe_2O_3$, $Fe_3O_4$ and FeOOH. As demonstrated in Figure 1.7, the shell consist of oxides whereas the core consist of $Fe^0$ (Li and Zhang 2007). The study of Li and Zhang (2007) investigated nZVI structure before and after contacting with various metals and as a result; proposed three possible types of metal uptake on nZVI surface. These mechanisms are:

(i) Only physical sorption that takes place for cations with standart reduction potential, $E^0$ is more negative than or closer to that of Fe.

(ii) Both sorption and chemical reduction arises for metal cations having $E^0$ sligthly more positive than that of Fe.

(iii) Only chemical reduction occurs for metal cations with $E^0$ higher than $E^0$ (Fe).

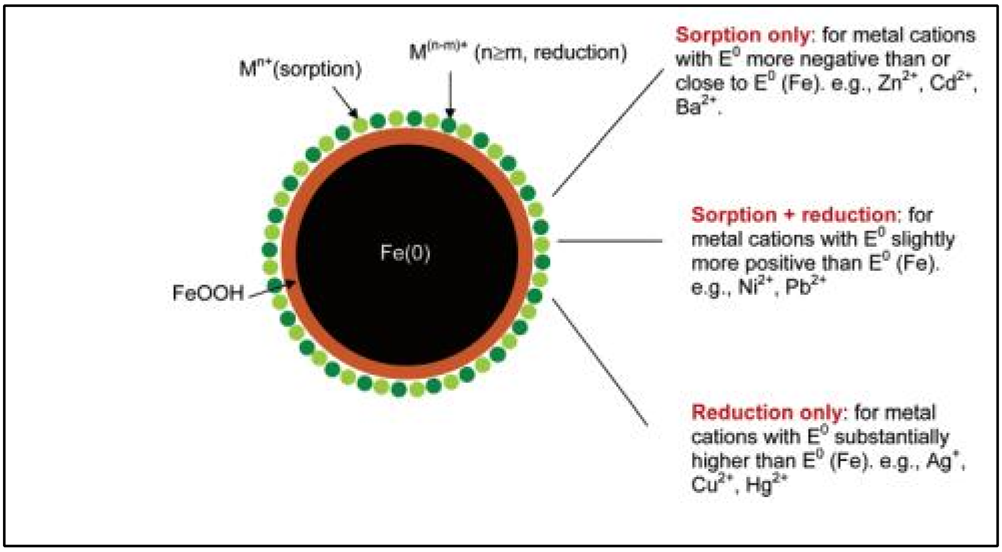


Figure 1.7. The core-shell structure of nZVI and uptake mechanisms of metals (Source: Li and Zhang 2007)

In several studies, ZVI has been used to remove organic and inorganic contaminants from aqueous solutions and these studies reported that ZVI has high arsenic removal capacity and that it can be used as a permeable reactive barrier (PRB) for remediation of polluted groundwater. For this purpose, Biterna et al. (2007) investigated the efficiency of zero valent iron (ZVI) under various conditions to remove arsenate from water. Sasaki et al. (2008) investigated the immobilization mechanism of arsenite by ZVI and attempted to determine the capacity of the material to retain arsenic in a PRB. Dependent on these studies and the chemical similarity of antimony and arsenic elements, a comparative approach on the removal of these elements with ZVI can be considered.

During the real remediation applications, there are some restrictions on the usage of nZVI. For example, iron nanoparticles have positive surface charges within the natural pH range and they tend to repel each other strongly and to keep them stable is very difficult. Another problem is about the colloidal properties of nZVI; particles tend to precipitate and they can not be driven for more than a few meters by the migration of water and probably can not reach the contaminated zone. The other problem arises as an oxidation of iron during the storage of iron nanoparticles for a long time period; since thermodynamically zero-valent iron tends to react with oxygen. In order to prevent and deal with these problems iron nanoparticles are considered to be modified, supported or mixed with a filling material.

## 1.8. The Aim of the Study

The aim of this study is to develop a new zero-valent iron modified sorbent for the removal of inorganic antimony species (antimonous acid and antimonate) from contaminated water samples prior to determination by atomic spectroscopy techniques. For this purpose, a strong anion exchange resin (Amberlite IRA 458) was modified with ferric ion and then reduced by sodium borohydride in order to immobilize zero valent iron (ZVI) onto resin surface. Both unmodified and nanoscale zero valent iron (nZVI) modified IRA 458 resin was investigated for their sorption behavior towards antimony species. Throughout the study, the characterization of the sorbents was investigated prior to sorption studies. In addition, the sorption performance of the sorbents in terms of solution pH, reaction temperature, shaking time, sorbent amount and initial concentration of antimony species were experimented by batch type sorption studies.

# CHAPTER 2

# MATERIALS AND METHODS

## 2.1. Instrumentation and Apparatus

Throughout the analysis of antimony, a Thermo Elemental Solaar M6 Series atomic absorption spectrometer (Cambridge, UK) with an air-acetylene burner was used utilizing the Hydride Generation (HGAAS) unit, shown in Figure 2.2. A Thermo Elemental Antimony hollow cathode lamp operated with a maximum current of 10 mA at 217.6 nm and deuterium (D2) background correction was used in all measurements. In HGAAS, the quartz tube atomizer was 10 cm long, 8 mm in internal diameter and 10 mm in external diameter with a 4 mm a bore inlet tube fused in the middle used for sample introduction. The external heating of the quartz tube was adjusted by air-acetylene flame and as the carrier gas, nitrogen was used . In addition, an Agilent 7500ce Series (Tokyo, Japan) inductively coupled plasma mass spectrometer (ICP-MS) (shown in Figure 2.1.) equipped with a high solid nebulizer, a Peltier-cooled spray chamber (2°C), and an octopole collision/reaction cell with helium gas pressurization was used for some experiments in which simultaneous element analysis were required. There are two naturally occurring isotopes of antimony, $^{121}$Sb with a natural abundance of 57.36% and $^{123}$Sb with a natural abundance of 42.64%. Signal of $^{121}$Sb was choosen to be checked by ICP-MS for the analysis of antimony and nitric acid ($HNO_3$) was used for acidification during the sorption experiments that were analyzed by ICP-MS. Operating parameters for the ICP-MS and HGAAS system are given in Table 2.1 and Table 2.2, respectively.

In HGAAS, antimony in solution reacted with trace metal grade acid ($HNO_3$) along with sodium borohydride ($NaBH_4$, a reducing reagent) leading the formation of volatile metal-hydride compounds. This results as an interference which affects the degree of ultratrace determination of antimony. In order to eliminate this interference, hydrochloric acid (HCl) was used for acidification during the sorption experiments prior to HGAAS determination.

For batch sorption experiments, GFL 1083 water bath shaker (Burgwedel, Germany) equipped with a microprocessor thermostate was used in order to control the temperature of the reaction media and to provide efficient mixing. The pH values adjustments were performed with WTW Series InoLab pH 720 precision pH meter (Weilheim, Germany). Molecular weight determinations were performed in Petrotest capillary viscosimeter (Dahlewitz, Germany).

Images of the synthesized sorbents were taken with Philips XL-30S FEG scanning electron microscopy (Eindhoven, The Netherland) that was employed for SEM characterization to obtain information about the size and the morphology of the crystals. In addition, the elemental composition of the synthsized sorbents was determined by LECO-CHNS-932 elemental analyzer (Mönchengladbach, Germany).

Lastly, information about the crystallographic properties of the synthesized sorbent were obtained by using Philips X'Pert Pro X-Ray Diffractometer (Eindhoven, The Netherland).

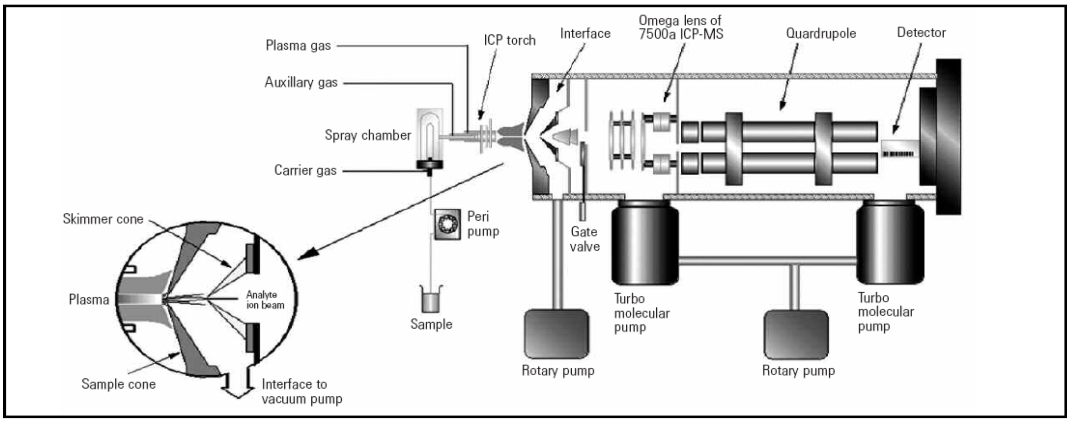


Figure 2.1. Inductively Coupled Plasma Mass Spectrometer (ICP-MS) system (Source: Boumans 1987)

Table 2.1. ICP-MS operating parameters.

| **Operating Parameters** | |
|---|---|
| Forward power | 1500 W |
| Reflected power | 1 W |
| Coolant gas flow rate | 15 mL min$^{-1}$ |
| Sample uptake time | 25 sec |

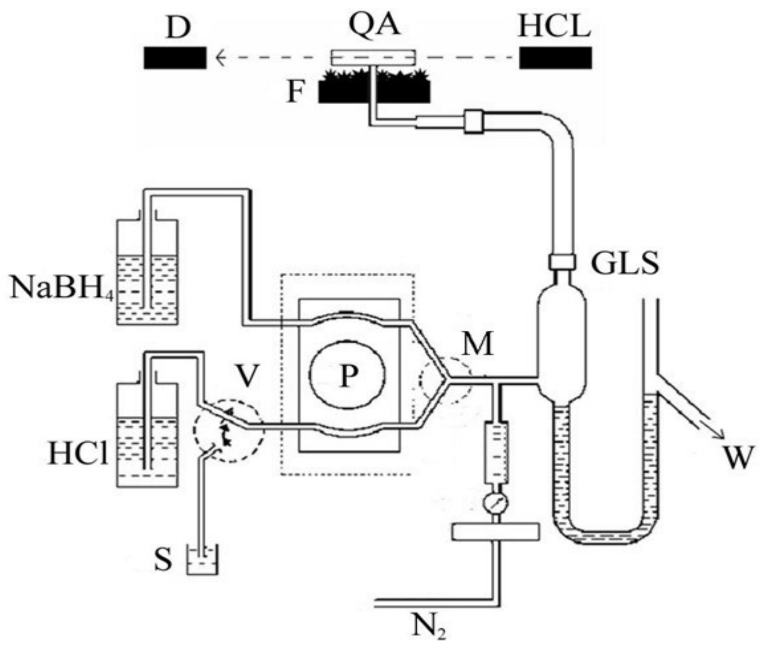


Figure 2.2. Segmented Flow Injection HGAAS system D: deuterium lamp, QA: quartz atomizer, HCL: hollow cathode lamp, F: flame, GLS: gas-liquid separator, W: waste, P: peristaltic pump,V: threeway valve and S: sample (Source: Yersel et al. 2005)

Table 2.2. HGAAS operating parameters.

| **Operating Parameters** | |
|---|---|
| Carrier gas ($N_2$) flow rate | 200.0 mL $min^{-1}$ |
| HCl concentration | 2.0% (v/v) |
| HCl flow rate | 6.1 mL $min^{-1}$ |
| $NaBH_4$ concentration | 1.0 % (w/v) stabilized with 0.10 % (w/v) NaOH |
| $NaBH_4$ flow rate | 3.0 mL $min^{-1}$ |
| Sample flow rate | 7.0-8.0 mL $min^{-1}$ |

## 2.2. Chemicals and Reagents

During the study, all chemicals were of analytical reagent grade and ultrapure water (18.2 MΩ, Millipore, and Billerica, MA, USA) was used throughout the preparation of all standard solutions. Glassware and plastic containers were cleaned by soaking in 10% (v/v) nitric acid overnight and washed with ultrapure water before being used. Standard Sb(III) stock solution (1000.0 $mgL^{-1}$):prepared by dissolving 0.685 g of $C_8H_4K_2O_{12}Sb_2.3H_2O$ in ultrapure water and diluted to 250.0 mL with ultrapure water. Standard Sb(V) stock solution (100.0 $mgL^{-1}$):prepared by dissolving 0.054 g of $KSb(OH)_6$, in ultrapure water and diluted to 250.0 mL with ultrapure water.

Sodium borohydride ($NaBH_4$) solution of 1.0% (w/v) was prepared for a daily usage from fine granular product and stabilized by 0.10% (w/v) NaOH in water also 2.0% (v/v) HCl solution was prepared for HGAAS determination.

L-cysteine at a concentration of 0.10% (w/v) was added into the all samples and standard solutions to reduce Sb(V) to Sb(III) prior to the HGAAS determination.

Calibration standards were prepared just before the analysis by making buffer stock solution out of the stock standards.

The pH adjustments were done by using different concentration (0.01 M, 0.1 M, 1.0 M) of $NH_3$ - $HNO_3$ solutions for ICP-MS and (0.01 M, 0.1 M, 1.0 M) NaOH - HCl solutions for HGAAS determinations. Table 2.3 shows these reagents with their concentrations.

## 2.3. Synthesis of Zero-Valent Iron Modified Sorbents

Iron(III) chloride hexahydrate ($FeCl_3$. $6H_2O$) and sodium borohydride ($NaBH_4$) were used in the synthesis of nZVI-modified resins, respectively. During the synthesis of these sorbents, iron was immobilized through two different types, namely; anionic ($FeCl_4^-$) and cationic ($Fe^{3+}$) forms.

Table 2.3. Reagents used through the study

| Reagent | Concentration used | Company | Cas no. | Purpose of use |
|---|---|---|---|---|
| Potassium antimonyl tartrate trihydrate | | Sigma-Aldrich | [28300-74-5] | Preparation of Sb(III) stock solution for sorption study |
| Potassium antimonate | | Riedel-de Haen | [12208-13-8] | Preparation of Sb(V) stock solution for sorption study |
| Amberlite IRA-458,chloride form | | Supelco | [1-0330] | Synthesis of nZVI modified IRA 458 |
| $FeCl_3.6H_2O$ | 1.0 M | Merck | [10025-77-1] | Synthesis of nZVI modified resins |
| L-cysteine | 0.10 % (w/v) | Merck | [52-90-4] | Reduction of Sb(V) to Sb(III) |
| $NaBH_4$ (granular) | 3.5 %(w/v) | Aldrich | [16940-66-2] | Synthesis of nZVI modified resins |
| $NaBH_4$ (granular) | 1.0 % (m/v) | Aldrich | [16940-66-2] | $SbH_3$ generation in HGAAS |
| $HNO_3$ | | Merck | [7697-37-2] | Acidification |
| HCl | 8.0 M | Merck | [7647-01-0] | Synthesis of nZVI modified resins |
| HCl | | Merck | [7647-01-0] | Acidification |
| NaOH (pellets) | 0.10 % (w/v) | Sigma-Aldrich | [1310-73-2] | Stabilization of $NaBH_4$ solution |
| Absolute Ethanol | | Sigma | [64-17-5] | Washing of nZVI modified resins |

## 2.3.1. Synthesis of ZVI-Modified Sorbents with Cationic Form of Iron

The immobilization of iron as a cationic form ($Fe^{3+}$) onto IRA 458 resin was performed with both batch and column types. Fort the preperation of the cationic form of iron, iron(III) chloride hexahydrate ($FeCl_3$. $6H_2O$) is dissolved only in ultra pure water.

### 2.3.1.1. Batch Type Immobilization

In the batch type immobilization, first 13.52 g $FeCl_3.6H_2O$ was dissolved in the 50.0 mL water. Then, 5.0 g of Amberlite IRA-458 resin was added to the solution and the mixture was placed on a magnetic stirrer in order to be mixed for 24 hours. Afterwards, the vacuum filtration was applied and during this process, the mixed slurry was washed with first water, then ethanol to remove the excess $Fe^{3+}$ ions. Then, 100 mL 3.5% (m/v) $NaBH_4$ solution was poured into a burette and added gradually to Fe (III)-treated resin. After the addition of the first drop of sodium borohydride solution, the formation of black solid sorbents begun After adding all the borohydride solution to the mixture, reduction of Fe(III) to Fe(0) occured supported by visible color change and the solution left on magnetic stirrer to be stirred homogenously for 10 minutes. The reaction can be represented by the following redox reaction, Equation 2.1:

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0\downarrow + 3H_2BO_3^- + 12H^+ + 6H_2\uparrow \text{ (Sun et al. 2006) (2.1)}$$

After the reduction step, vacuum filtration was applied to separate the synthesized ZVI modified sorbent from liquid phase. The solid particles were washed with the absolute ethanol to remove all the water particles and this washing process is probably the keystep of the synthesis because it prevents the rapid oxidation of the zero-valent iron nanoparticles. Finally, the synthesized sorbent was collected on a blueband Waltman filter paper and dried in the oven at 50 °C for 24 hours. The pathway of the synthesis of ZVI modified resin with batch type immobilization is illustrated in Figure 2.3.

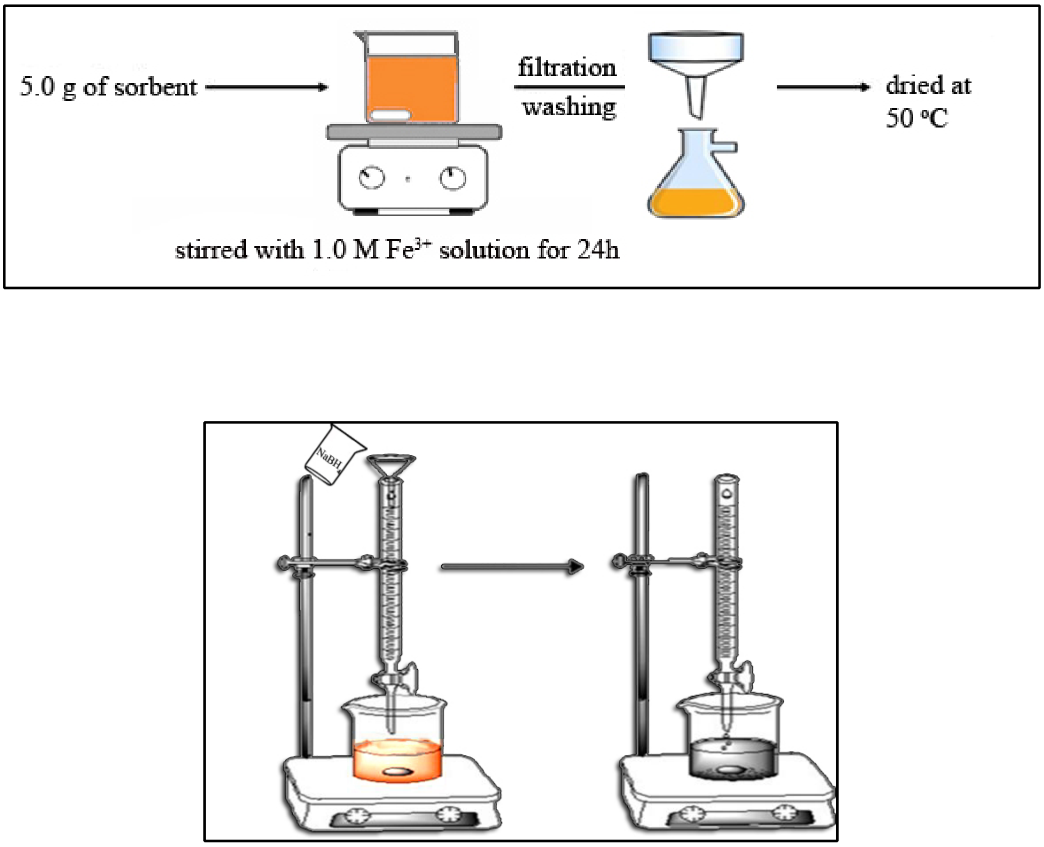


Figure 2.3. The synthesis of ZVI-modified IRA 458 resin (batch type).

#### 2.3.1.2. Column Type Immobilization

First 13.52 g $FeCl_3.6H_2O$ was dissolved in the 50.0 mL water for the preparation of $Fe^{3+}$ solution. Then, a column was filled with 5.0 g of Amberlite IRA 458 resin that was inflated in water and $Fe^{3+}$ solution was loaded three times onto resin. Later, resin collected from the column, was washed with first water, then ethanol by using vacuum filtration. After vacuum filtration, resin on the blue band Waltman filter paper was placed in a beaker, carefully. Then treated with 100 mL 3.5% (m/v) sodium borohydride drop by drop for the reduction of the loaded $Fe^{3+}$ ions to $Fe^0$. After the addition of all the sodium borohydride solution, the vacuum filtration was applied again to separate the synthesized ZVI modified IRA 458 sorbent from the liquid phase. The two sheets of blue band Whatman filter papers were used in the filtration. Solid particles were washed with absolute ethanol to remove all the water particles. Finally, the synthesized sorbent was dried in the oven at 50 °C overnight. The phases of ZVI modified resin synthesis via column type immobilization is shown in Figure 2.3. In this type of immobilization, due to the high pressure of $H_2$ gas that released during the $NaBH_4$ reduction step, the reduction process was considered to be challenging.

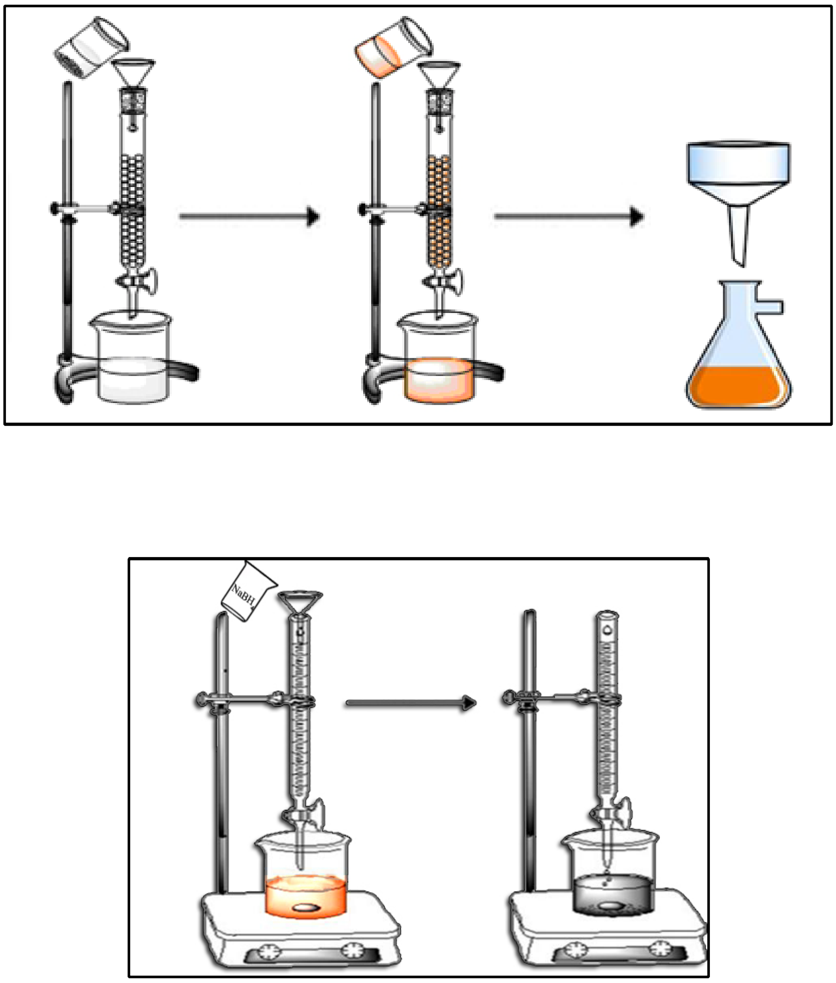


Figure 2.4. The synthesis of ZVI-modified IRA 458 resin (column type)

## 2.3.2. Synthesis of ZVI-Modified Sorbents with Anionic Form of Iron

The immobilization of iron as an anionic form ($FeCl_4^-$) to resin was performed with column type immolization as explained earlier. For the synthesis of the modified resin, 13.52 g $FeCl_3.6H_2O$ was dissolved in the 50.0 mL 8 M hydrochloric acid (HCl) solution. Later, a column was filled with 5.0 g of Amberlite IRA-458 resin that inflated in water and $FeCl_4^-$ solution was loaded through the column for three times. Then, $FeCl_4^-$ treated resin was drained from the column into a beaker. After that, the vacuum filtration was applied and mixed slurry was washed with water, ethanol, respectively.

Once again the treated resin was put in a beaker after vacuum filtration and 100 mL 3.5% (w/v) $NaBH_4$ solution was poured into a burette for the addition into resin to reduce the loaded $FeCl_4^-$ ions to $Fe^0$. After the addition of the first drop of sodium borohydride solution, black solid sorbents were formed. The addition of the borohydride solution was completed and the mixture was left on magnetic stirrer to be stirred for another 10 minutes to guarantee a homogenous reduction. The pathway of the synthesis of ZVI modified resin is the same as shown in Figure 2.4. in column type immobilization.

In order to separate the synthesized ZVI modified IRA 458 resin from the liquid phase, the vacuum filtration was used. In this filtration, two sheets of blue band Whatman filter papers were used. At this stage, to remove all the water solid particles were washed with absolute ethanol. In the final stage, the synthesized resin was dried in the oven at 50 °C overnight.

## 2.4. Characterization of the Synthesized Sorbents

Various methods were applied to characterize the synthesized sorbents. Elemental analysis was implemented in order to learn the percentages of nitrogen, sulfur, hydrogen and carbon in the sorbents. Scanning electron microscopy (SEM) was applied in order to analyze the images of the synthesized ZVI-modified sorbents. In addition, X-Ray Diffraction (XRD) was used in order to investigate the material structure of nZVI modified resin.

## 2.5. Sorption Studies

Batch type sorption studies were performed for all the sorbents which were synthesized during the optimization stage, nZVI sorbent, ZVI-IRA 458 modified sorbent and unmodified IRA 458 resin. The effects of the solution pH, amount of sorbent, shaking time, initial concentration of antimony and reaction temperature on sorption behavior were investigated seperately. The preliminary sorption conditions were determined as the following values: antimony concentration was 0.10 $mgL^{-1}$, pH of the solution was 7.0, the volume of the solution shaked was 20.0 mL, the shaking time was 60 min, the amount of sorbent was 50.0 mg, the temperature was 25.0 ºC.

In all these experiments, batch type sorption was followed by the filtration of the mixture through blue-band filter paper and analysis of the filtrate was performed with HGAAS in order to determine the remaining antimony amount. Prior to HGAAS determination, all filtrates were acidified with concentrated HCl in the ratio of 1.0% (v/v). In HGAAS determination, antimony reacted with tetrahydroborate in acidic medium to form volatile hydrides, which are subsequently analyzed. However the formation of hydrides are dependent on the oxidation state of the element and according to the literature Sb(V) does not form hydrides. Thus, for the determination of Sb(V), L-cysteine was added to all Sb(V) sorption solutions and standart solutions in the ratio of 0.1% (w/v) concentration according to the final solution. This addition was aimed to prereduce Sb(V) to Sb(III) before $NaBH_4$ reduction step since efficiency of the HGAAS method depends strongly on the oxidation state of Sb.

Standard solutions of 2.0, 5.0, 10.0, 20.0, 40.0, 50.0, 75.0 and 100.0 $\mu gL^{-1}$ concentrations were prepared by appropriate dilution of 1000 $\mu gL^{-1}$ of stock Sb(III) or 100 $\mu gL^{-1}$ Sb(V) solutions to the required volume. The percentage of antimony sorption was calculated using the Equation 2.2. represented below, where *Ci* is the initial and *Cf* is the final concentration in the solution.

$$Sorption\ \% = \frac{C_i - C_f}{C_i} \times 100\% \text{ (Source: Sorption and Biosorption Ch.6 2003)} \qquad (2.2)$$

The optimization of the sorption for Sb(III) and Sb(V) was carried out with ZVI-IRA 458. The studied parameters and their ranges were summarized in Table 2.4.

Table 2.4. Studied parameters and respective ranges

| Studied parameters | Ranges |
|---|---|
| Solution pH | 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, 12.0, 13.0, 14.0 |
| Amount of sorbent (mg) | 5.0, 10.0, 25.0, 50.0 and 100.0 |
| Shaking Time (min) | 1, 5, 15, 30, 60 and 120 |
| Temperature (°C) | 25, 40, 60 |
| Initial concentration (mg/L) | 0.005, 0.05, 0.1, 0.5, 1.0 and 10.0 |

### 2.5.1. The Effect of Solution pH

Solution pH is one of the most important factors influencing the sorption of Sb species. Initial experiments were performed for each sorbent; namely, ZVI-modified IRA 458 resin and unmodified IRA 458 in order to investigate the interaction between the species of antimony and the functional groups on the sorbents, and to determine the optimum pH for the sorption. 100 $\mu gL^{-1}$ Sb(III) or Sb(V) standard solutions were prepared and the initial pH of these solutions was adjusted to 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, 12.0, 13.0 and 14.0 by using dilute HCl or $NH_3$. From each of these solutions 20.0 mL was taken into 50 mL centrifuge tube before which were filled with 50.0 mg sorbent. The mixture was placed in a thermostated water bath shaker and was shaken for 60 minutes at 25 ºC. Then, the mixture was filtered in order to separate the sorbent. Finally, the filtrate was analyzed for its antimony content with HGAAS as explained previously.

### 2.5.2. The Effect of Sorbent Amount

The effect of the sorbent amount was investigated by using 5.0, 10.0, 25.0, 50.0 and 100.0 mg for unmodified af resin and ZVI-IRA 458 modified resin while the antimony concentration, solution volume, shaking time, solution pH and reaction temperature were fixed at 100.0 $\mu gL^{-1}$, 20.0 mL, 60 min, 7.0, and 25 ºC, respectively.

### 2.5.3. The Effect of Shaking Time

Effect of the shaking time on the sorption of Sb(III) and Sb(V) with ZVI-IRA 458 and unmodified IRA 458 was investigated for time intervals of 1, 5, 15, 30, 60 and 120 minutes. Meanwhile, the antimony concentration, solution volume, sorbent amount, solution pH and reaction temperature were fixed at 100.0 $\mu gL^{-1}$, 20.0 mL, 50.0 mg, 7.0, and 25 ºC, respectively.

### 2.5.4. The Effect of Initial Sb(III) and Sb(V) Concentrations

The sorption capacity of ZVI-IRA 458 and unmodified IRA 458 were investigated for the initial Sb(III) and Sb(V) concentrations of 0.005, 0.05, 0.1, 0.5, 1.0 and 10.0 mgL$^{-1}$. The other parameters were fixed at 50.0 mg sorbent amount, 60 min shaking time, 20.0 mL solution volume, 25.0 °C sorption temperature and pH 7.0.

### 2.5.5. The Effect of Reaction Temperature

The sorption efficiency of a sorbent is dependent on the reaction temperature. Thus, the effect of the temperature on the sorption of antimony was investigated at 25.0 °C, 40.0 °C and 60.0 °C while the other parameters were fixed at 100.0 µgL$^{-1}$ antimony concentration, 20.0 mL solution volume, 50.0 mg sorbent amount and pH 7.0. The sorption results were also used to investigate the thermodynamic parameters (ΔG°, ΔS° and ΔH°) utilizing the well-known Equations 2.3, 2.4, and 2.5 :

$$\Delta G^{\circ} = -RTlnR_d \text{ (Yersel et al. 2005)} \qquad (2.3)$$

$$\Delta H^{\circ} = Rln\frac{R_d(T_2)}{R_d(T_1)}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)^{-1} \text{ (Yersel et al. 2005)} \qquad (2.4)$$

$$\Delta S = \frac{\Delta H^{\circ}-\Delta G^{\circ}}{T} \text{ (Yersel et al. 2005)} \qquad (2.5)$$

$R_d$ (mL g$^{-1}$) is the ratio of antimony ions distributed between solid phase (sorbent) and liquid phase at equilibrium and is defined by the Equation 2.6. $C_{solid}$ is the concentration of antimony in sorbent (mg g$^{-1}$) and $C_{liquid}$ is the concentration of antimony ions in solution after sorption (mgL$^{-1}$).

$$R_d = \frac{C_{solid}}{C_{liquid}} \text{ (Yersel et al. 2005)} \qquad (2.6)$$

## 2.6. Amount of Iron into/onto Modified Sorbents

In order to find out the most efficient modification type and to minimize the use of sodiumborohydride for the reduction of iron by determining the optimum amount of iron needed, the synthesized sorbents were dissolved in nitric acid. Likewise the sorption experiements, 50.0 mg of each synthesized sorbent was placed into the 50 mL centrifuge tube. 20.0 mL of 1.0 M $HNO_3$ solution added to each one. Then, tubes was placed in a thermostated water bath shaker and was shaken for 60 minutes which is followed by a filtration step. After the filtration step, the sorbent on the filter paper collected in an empty centrifuge tube and was shaken again for 60 minutes with the addition of 20.0 mL 1.0 M $HNO_3$ solution inside the tube. Overall, this process was repeated three times. Finally, all the filtrates were analyzed for their iron content by HGAAS.

## 2.7. Optimization Studies of ZVI-IRA 458

According to results from the previous experiments, the commercial Amberlite IRA 458 resin was chosen for the loading of zero valent iron (ZVI) in the anionic form of iron.

### 2.7.1. Effect of NaBH4 Concentration in the Preparation of Modified Resin

Several sorption experiments were performed in order to find out the most adequate concentration of $NaBH_4$ which was used as a reducing agent during the synthesis of modified IRA 458 resin. This process was important to prevent using excess amount of sodium borohydride and also to prevent possible excess boron passing into the solution. Firstly the amount of the iron which was loaded onto resin was determined by HGAAS. Then, according to the reaction which is represented by the following redox reaction shown below, the stoichiometric factor of $NaBH_4$ solution was calculated.

$$4Fe^{3+} + 3BH_4^{-} + 9H_2O \rightarrow 4Fe^{0} \downarrow + 3H_2BO_3^{-} + 12H^{+} + 6H_2 \uparrow$$ (Sun et al. 2006)

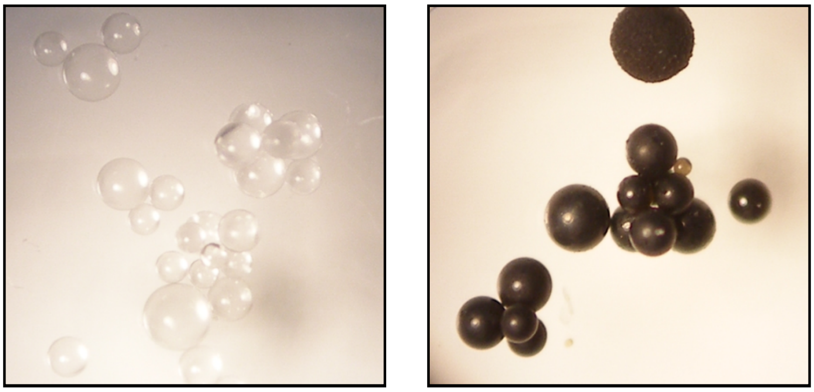
Lastly, the sorption experiments were performed with the synthesized ZVI modified IRA 458 sorbent. Each sorbent was loaded with various concentrations of $NaBH_4$ solution and the analysis of these experiments were done by ICP-MS.

# CHAPTER 3

# RESULTS AND DISCUSSION

## 3.1. Characterization of Ion Exchange Resins

For the illumination of the elemental content, structural features, morphology and particle size of the sorbents, scanning electron microscopy (SEM) along with energy dispersive X-Ray spectroscopy (EDX), optical microscopy (OM) and X-Ray Diffraction (XRD) were used. Throughout this study, Amberlite IRA 458 and ZVI modified Amberlite IRA 458 were used as sorbents. Amberlite IRA 458 is an acrylic gel type strongly basic anion exchange resin. It combines high operating capacity and low silica leakage values. The general properties and its structure are shown in Table 3.1. and Figure 3.2., respectively. Also, the optical images of unmodified IRA 458 and ZVI IRA 458 resin are displayed in Figure 3.1. As shown in the Figure 3.1, the unmodified anion exchange resin (IRA 458) are transparent before modification. However as it can be seen from optical image, its colour turned into black when modified with ZVI.



(a) (b)

Figure 3.1. Optical images of (a) IRA 458, (b) ZVI-IRA 458.

Table 3.1. General properties of Amberlite IRA 458.

| **Properties of Amberlite IRA 458** | |
|---|---|
| **Physical form** | Translucent white spherical beeds |
| **Matrix** | Crosslinked acrylic gel structure |
| **Functional Group** | Quaternary ammonium |
| **Ionic form as shipped** | Chloride |
| **Particle size** | |
| Uniformity Coefficient | ≤ 1.90 |
| Harmonic mean size | 0.600 to 0.900 mm |
| < 0.300 mm | 2.0 % max |
| **Suggested Operating Parameters** | |
| **pH range** | 0 to 14 |
| **Maximum operating temperature** | $35^0$C |

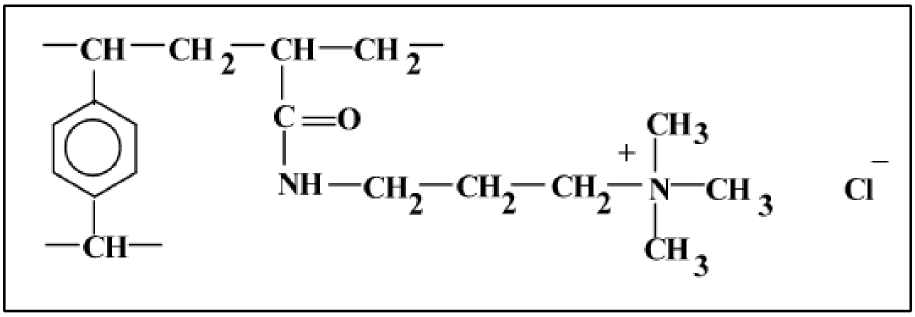


Figure 3.2. The structure of Amberlite IRA 458 resin
(Source: Hubicka 2001)

During modification part of IRA 458 resin, two different forms of iron were studied. As explained earlier in materials and methods section, both anionic and cationic forms of iron were studied in loading the resin. The SEM images of these ZVI-modified and unmodified Amberlite IRA 458 resin are given in Figure 3.3. The bright spots on the SEM images refer to iron particles on the resin surface. Figure 3.4 shows the SEM image of each resin and its corresponding EDX spectra in which the approximate amount of iron on the desired areas of the resin can be seen.

From the Atomic Absorption Spectrometric analysis of the iron concentration that passed into the solution as a result of nitric acid treatment, the amount of loaded iron onto the modified resins was calculated by using the Equation 3.1. The results of this calculation and related sorption experiments are given in Table 3.2.

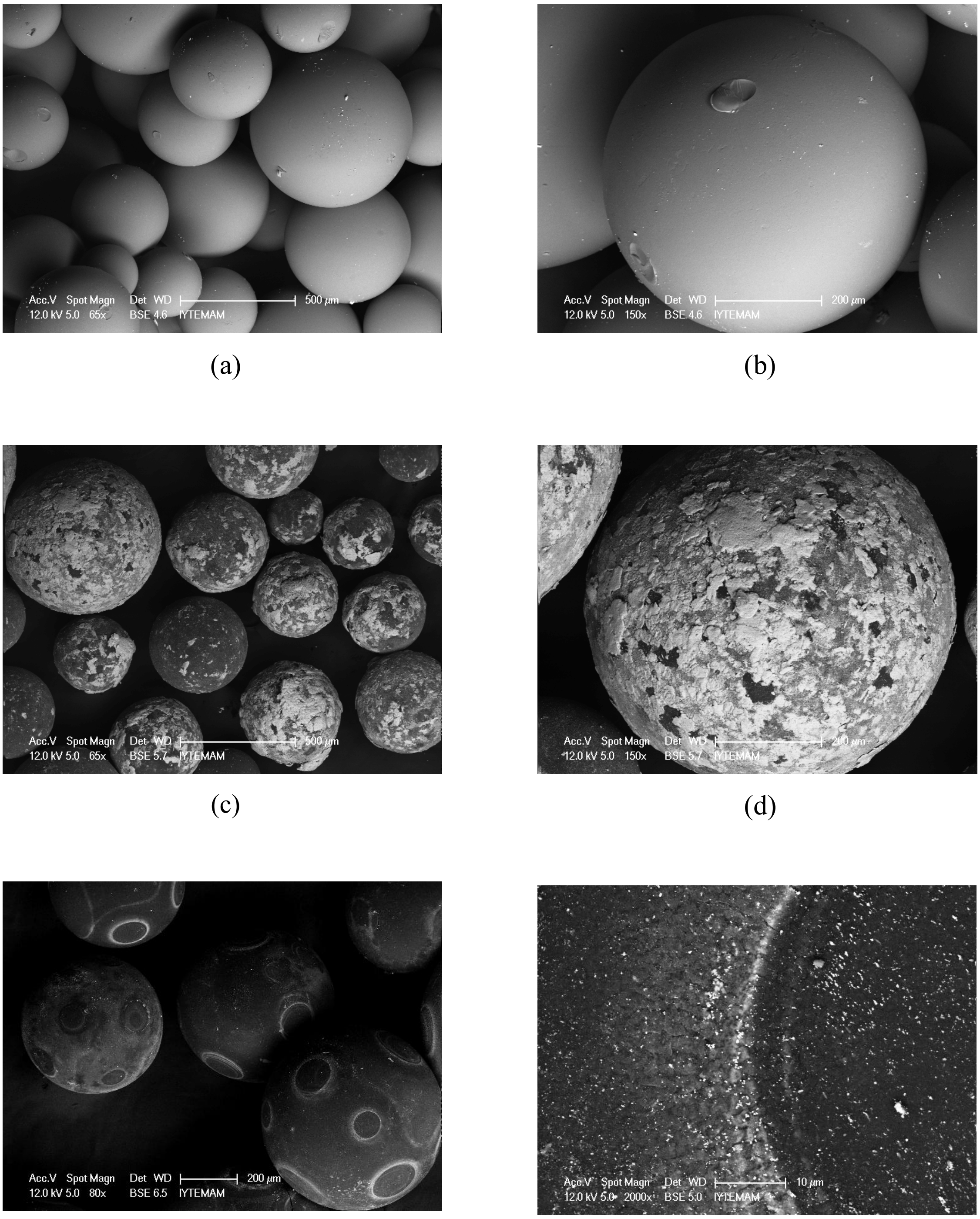
$$Q = [(C_i - C_f)/m]\ v \quad \text{(Yazdani 2010)} \qquad (3.1.)$$

In Equation 3.1., Q represents Fe uptake (mg metal/mg sorbentmass), $C_i$ represents initial Fe concentration ($mgL^{-1}$), $C_f$ represents final Fe concentration ($mgL^{-1}$), m represents the quantity of dry sorbent (mg) and v is the volume (mL).

Table 3.2. ZVI-IRA 458 synthesized by different modification methods

| | | **Sorption %** | |
|---|---|---|---|
| | | **Sb(III)** | **Sb(V)** |
| **Type of Sorbent** | **mgFe/g Sorbent** | **0.1 $mgL^{-1}$** | **0.1 $mgL^{-1}$** |
| ZVI-IRA 458 Batch ($Fe^{3+}$ form) | 25.96 | 87.70 | 89.60 |
| ZVI-IRA 458 Column ($Fe^{3+}$ form) | 33.89 | 81.50 | 83.20 |
| ZVI-IRA 458 Column ($FeCl_4^-$ form) | 70.59 | 93.20 | 98.60 |

Amberlite IRA 458 (strongly basic anion exchanger) resin is expected to adsorb the anionic form of iron in a higher amount compared to cationic form of modification. Results supported this expectation and as shown in Table 3.2, the anionic form of iron ($FeCl_4^-$) was loaded onto resin surface two times higher than cationic form ($Fe^{3+}$). SEM images also supported this result. Along with the high sorption results, the modification of anionic form of iron ($FeCl_4^-$) of IRA 458 was choosen for further experiments.

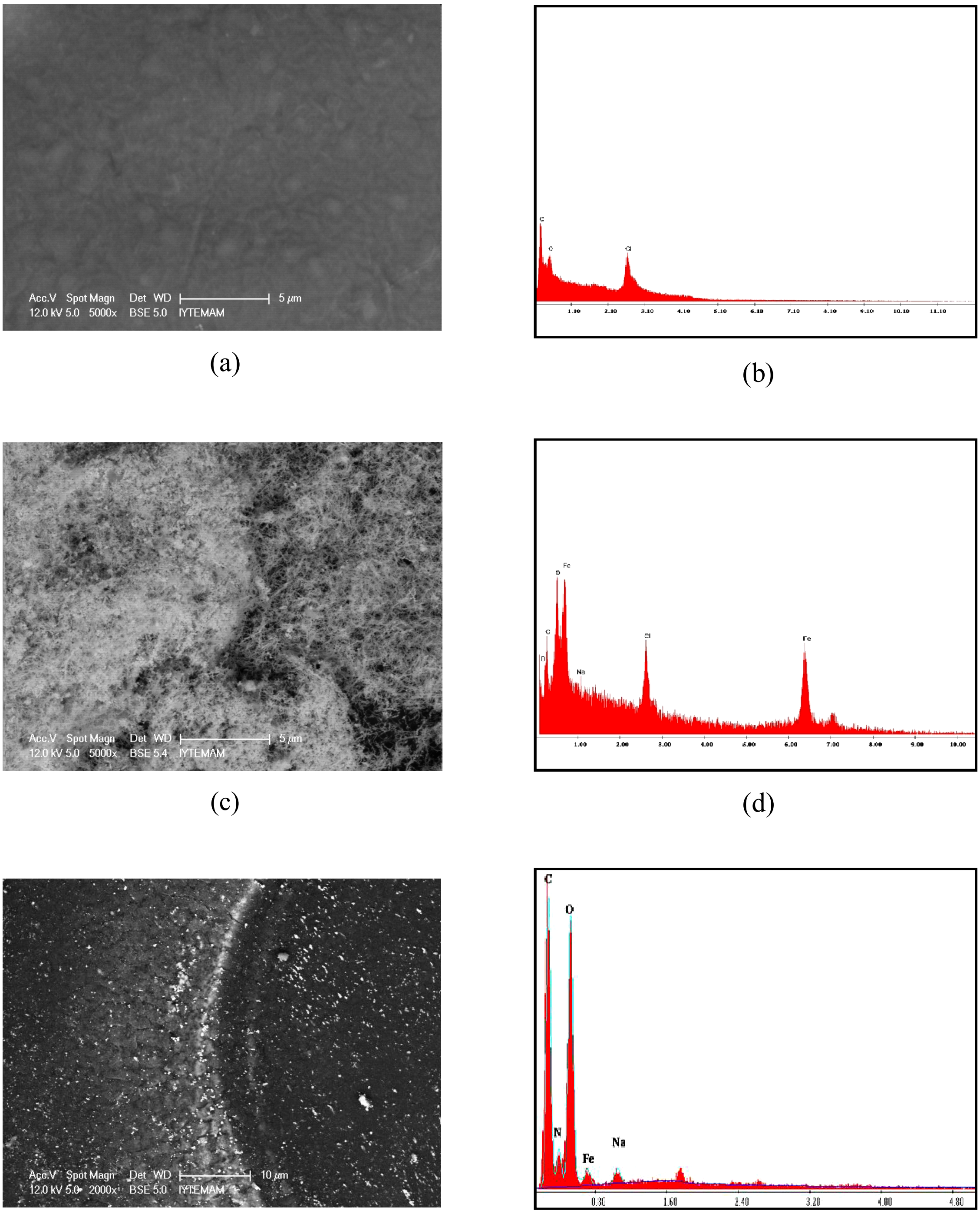


(a) (b)

(c) (d)

(e) (f)

Figure 3.3. SEM Images of (a),(b) IRA 458, (c),(d) ZVI-IRA 458 loaded as $FeCl_4^-$, (e),(f) ZVI-IRA 458 loaded as $Fe^{3+}$



(a)

(b)

(c)

(d)

(e)

(f)

Figure 3.4. SEM Images and Corresponding EDX Spectra of (a),(b) IRA 458, (c),(d) ZVI-IRA 458 loaded as $FeCl_4^-$, (e),(f) ZVI-IRA 458 loaded as $Fe^{3+}$

On the surface of the modified resin, different species of iron such as Fe(0), $Fe_2O_3$, $Fe_3O_4$ and FeOOH were expected to occur. To enlighten this expectation, XRD patterns were obtained. However, due to the physical form of iron loaded resins, it was difficult to form a pellet of the resins. The XRD pattern of ZVI-IRA 458, shown in Figure 3.5. indicates the presence of Fe(0) ($2\theta \sim 45^{o}$) in addition to the other forms of iron. Also in the pattern, presence of hematite ($Fe_2O_3$) was seen at $2\theta \sim 38^{o}$ and $2\theta \sim 56^{o}$ and presence of goethite (FeOOH) was seen at $2\theta \sim 47^{o}$. Thus, as expected the surface of the resin was not completely zero valent iron, a thin layer of iron oxide species was found and detected by the use of XRD.

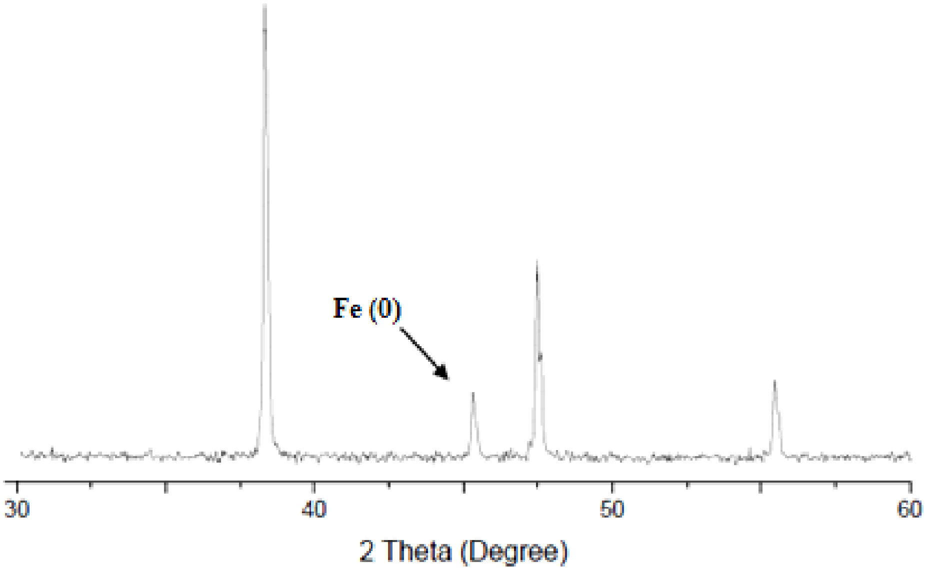


Figure 3.5. XRD pattern of ZVI-IRA 458.

## 3.2. Optimization and Sorption Studies

For both ZVI modified IRA 458 resin and unmodified resin, batch type sorption experiments were performed. Effects of solution pH, amount of sorbent, shaking time, antimony concentration and reaction temperature on sorption were investigated separately. Dependent on the sorption results indicated earlier in Table 3.2., due to highest sorption performance, nZVI modified Amberlite IRA 458 resin in the anionic form of iron was choosen for further optimization experiments.

### 3.2.1. Effect of $NaBH_4$ Concentration in the Preparation of Modified Resin

Sorption experiments were carried out with zero-valent iron modified-IRA 458 in order to determine the optimum concentration of $NaBH_4$ that was used for the reduction of Fe(III) to Fe(0). Various concentrations of $NaBH_4$ were applied to the resin during reduction step of the modification. Firstly the amount of iron loading of the dry resin was determined by AAS. Then, dependent on the redox reaction 3.1. indicated below, the required concentration of $NaBH_4$ solution was calculated by using the stoichiometric factor.

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 \downarrow + 3H_2BO_3^- + 12H^+ + 6H_2 \uparrow \text{ (Sun et al. 2006)} \quad (3.1)$$

The stoichiometric concentration was found to be 0.050 M $NaBH_4$ under the terms of specified experimental conditions. The results of each concentration are given in Table 3.3.

Table 3.3. Effect of $NaBH_4$ concentration on the amount of iron loading on IRA 458.

| Conc. of $NaBH_4$ (M) | mg Fe/g sorbent | mg Fe/50 mg sorbent |
|---|---|---|
| 0.05 | 15.7 | 0.8 |
| 0.10 | 25.0 | 1.2 |
| 0.15 | 16.6 | 0.8 |
| 0.20 | 30.1 | 1.5 |
| 0.25 | 29.0 | 1.5 |
| 0.35 | 31.7 | 1.6 |
| 0.50 | 38.9 | 1.9 |

The results of the Sb(III) and Sb(V) sorption experiments that performed with resins which were modified at different concentrations of $NaBH_4$ are displayed in Figure 3.6. and Figure 3.7., respectively. Figure 3.6. displays the results of the Sb(III) sorption performed with zero valent iron modified IRA 458 resin that were modified with different concentrations of $NaBH_4$. The results showed that as the $NaBH_4$ concentration increased, the sorption of antimonous acid increased as well. At the beginning point of the graph, unmodified resin was used and thus the sorption was resulted as 0%. Even if the resin was modified by using 0.50 M $NaBH_4$ solution which was the highest concentration used the percent sorption for Sb(III) was about 60%. It must be pointed out that the effect of sodium borohydride on sorption experiments were studied with 100.0 mgL$^{-1}$ Sb(III) solution which was very well above the legal limit of 0.005 mgL$^{-1}$.

Figure 3.7. illustrates the results of the Sb(V) sorption performed with ZVI IRA 458 modified with different concentrations of $NaBH_4$ solution. The concentration of Sb(V) was 100.0 mgL$^{-1}$. As seen in Figure 3.7., unmodified IRA 458 resin showed approximately 60% sorption proving the fact that the quaternary ammonium functional groups of strong anion exchange resin was active in the sorption of Sb(V). Then, the sorption increased slightly from 0.05 M $NaBH_4$ to 0.25 M $NaBH_4$ and almost remained constant between the points of 0.25 M $NaBH_4$ and 0.50 M $NaBH_4$.

As a result, verified by these experiments, 0.15 M NaBH4 concentration that was 3 times of the stoichiometric factor was chosen for further experiments.

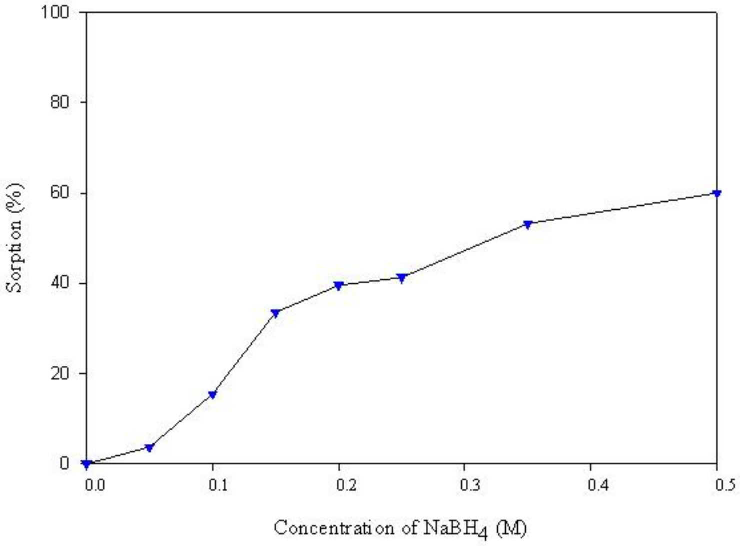


Figure 3.6. Effect of the concentration of $NaBH_4$ on the sorption of Sb(III) (▼) ZVI-IRA 458 (20.0 mL of 100.0 mgL$^{-1}$ Sb(III) solution, pH 7.0, 60 min shaking time, 50.0 mg sorbent, 25.0 °C reaction temperature)

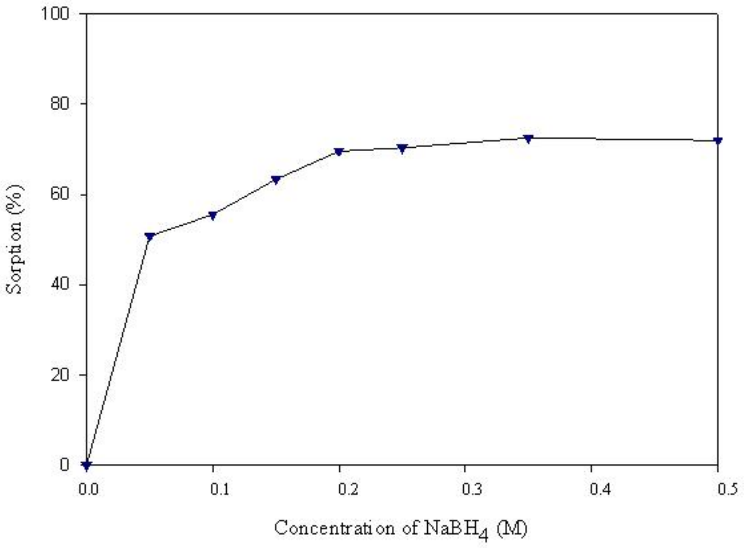


Figure 3.7. Effect of the concentration of $NaBH_4$ on the sorption of Sb(V) (▼) ZVI-IRA 458. (20.0 mL of 100.0 $mgL^{-1}$ Sb(V) solution, pH 7.0, 60 min shaking time, 50.0 mg sorbent, 25.0 °C reaction temperature)

### 3.2.2. The Effect of Solution pH

The pH-dependent sorption performance of the unmodified IRA 458 and ZVI-IRA 458 resins are shown in Figure 3.8 and Figure 3.9., respectively. In addition, the distribution of Sb(III) and Sb(V) species as a function of pH is given in Figure 3.10. for a better comprehension on the sorption characteristics.

From pH 1.0 to 3.0, the observed sorption was due to the presence of the original functional groups of the IRA 458 resin (quaternary ammonium groups) due to inconvenience for nZVI. nZVI formed on the surface and the interstices of the ion exchange resins tends to dissolve at pHs lower than 3.0.

For antimonous acid, from pH 1.0 to 10.0, zero valent iron modified IRA 458 provides a considerably high sorption range between 69% and 100% whereas unmodified IRA 458 (stongly basic anion exchanger) shows a low sorption performance because between this pH range only cation and neutral species ( $Sb(OH)_2^+$ , $Sb(OH)_3$) of antimony dominates to whom IRA 458 has no affinity.

For antimonate, from pH 3.0 to 10.0, only anionic species ($Sb(OH)_6^-$) of antimony dominates. Thus, a high sorption performance is observed by both modified and unmodified resins between pH 3.0 and 8.0.

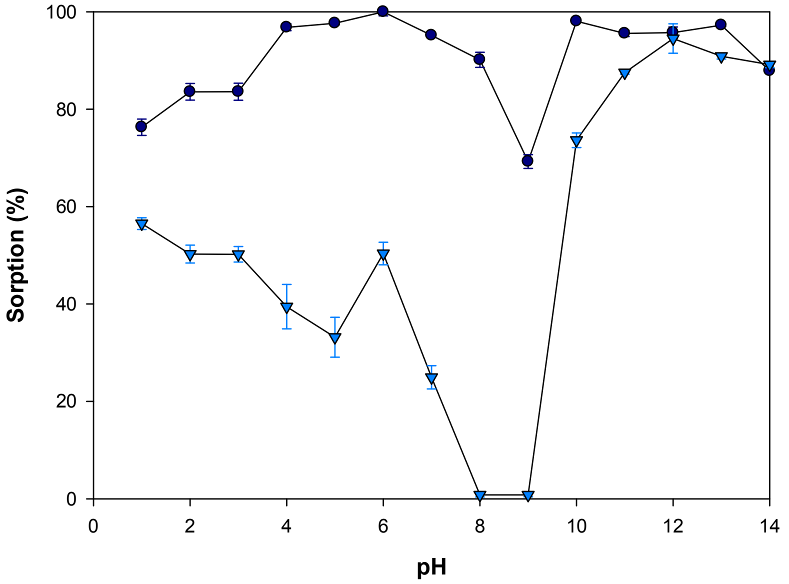


Figure 3.8. Effect of solution pH on the sorption of Sb(III). (▼) IRA 458, (●) ZVI-IRA 458.(20.0 mL of 100.0 µgL$^{-1}$ Sb(III) solution, 60 min shaking time, 50.0 mg sorbent, 25.0 °C reaction temperature)

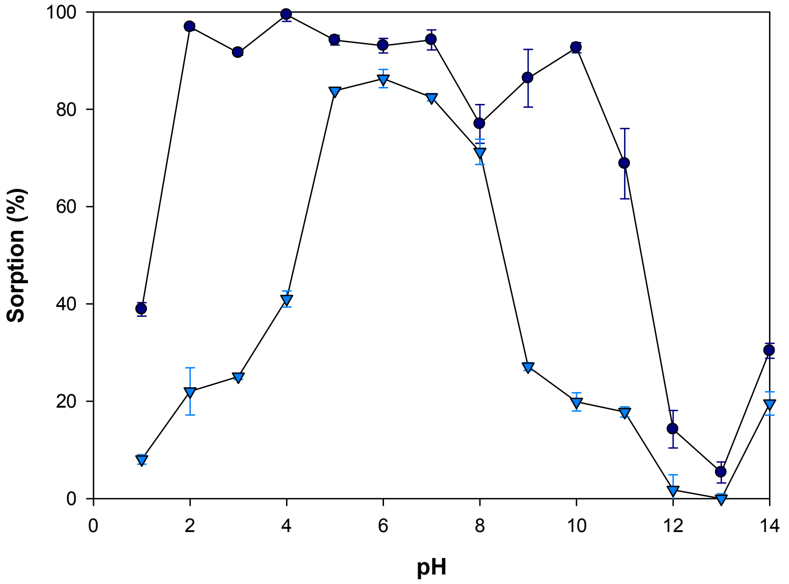
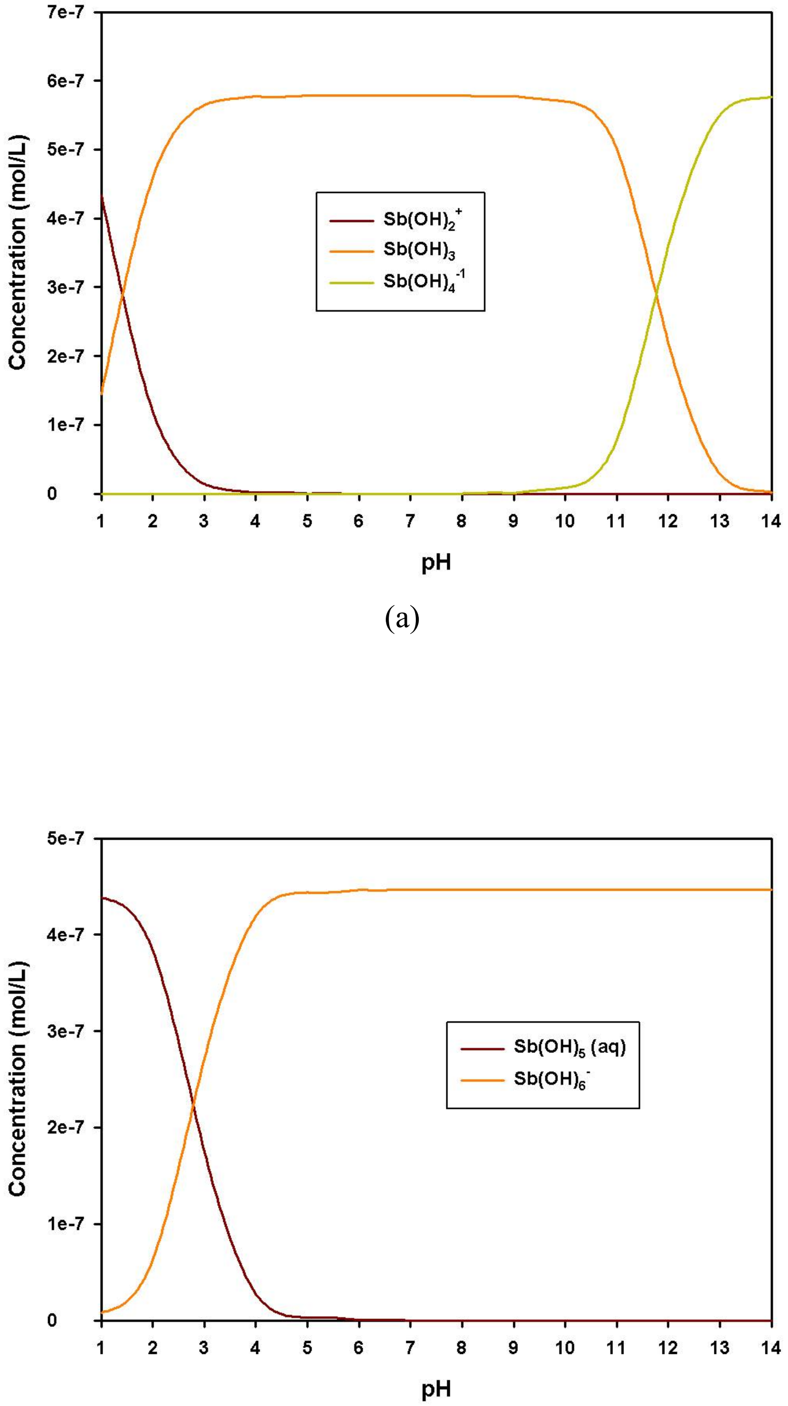


Figure 3.9. Effect of solution pH on the sorption of Sb(V). (▼) IRA 458, (●) ZVI-IRA 458. (20.0 mL of 100.0 µgL$^{-1}$ Sb(V) solution, 60 min shaking time, 50.0 mg sorbent, 25.0 °C reaction temperature)



(a)

(b)

Figure 3.10. Distribution diagram of (a) Sb(III) and (b) Sb(V) in aqueous solutions.
(Source: Visual MINTEQ program)

### 3.2.3. The Effect of Sorbent Amount

For the determination of the optimum amount of sorbent required for the maximum sorption of antimony species, the sorption experiments were carried out with 5.0, 10.0, 25.0, 50.0, and 100.0 mg of the unmodified and zero valent iron modified IRA 458 resins. Sorption behaviour of the antimonous acid, Sb (III), and antimonate, Sb(V) as a function of various amounts of both sorbents are given in Figure 3.11. and Figure 3.12., respectively. The results indicated that 25.0 mg of each sorbent (IRA 458 and ZVI-IRA 458) was enough to provide maximum sorption under the sorption conditions kept as 20.0 mL of 100.0 μgL$^{-1}$ Sb(III) solution, 60 min shaking time, pH 7.0, 25.0 °C reaction temperature. Zero valent iron modified IRA 458 showed very high sorption capacity but in order to guarantee a quantitative sorption, 50.0 mg of ZVI-IRA 458 resin was chosen to be used for further optimization studies. Although 5.0 mg of the ZVI-IRA 458 contains only 0.145 mg Fe, a very high sorption performance (93.8% for Sb(III) and 86.1% for Sb(V)) was reached for both antimony species. This observation supports the idea of the homogeneous distribution of iron particles immobilized on the resin surface. And also, as seen from the comparison of Figure 3.11. and Figure 3.12., unmodified IRA 458 provided higher sorption for Sb(V) due to the presence of anionic species at pH 7.0 that was explained earlier in effect of pH section.

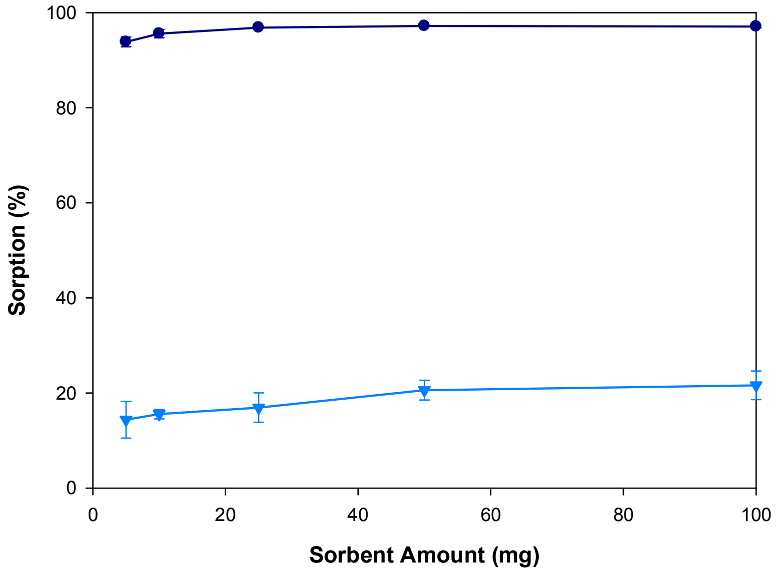


Figure 3.11. Effect of sorbent amount on the sorption of Sb(III). (▼) IRA 458, (●) ZVI-IRA 458. (20.0 mL of 100.0 μgL$^{-1}$ Sb(III) solution, 60 min shaking time, pH 7.0, 25.0 °C reaction temperature)

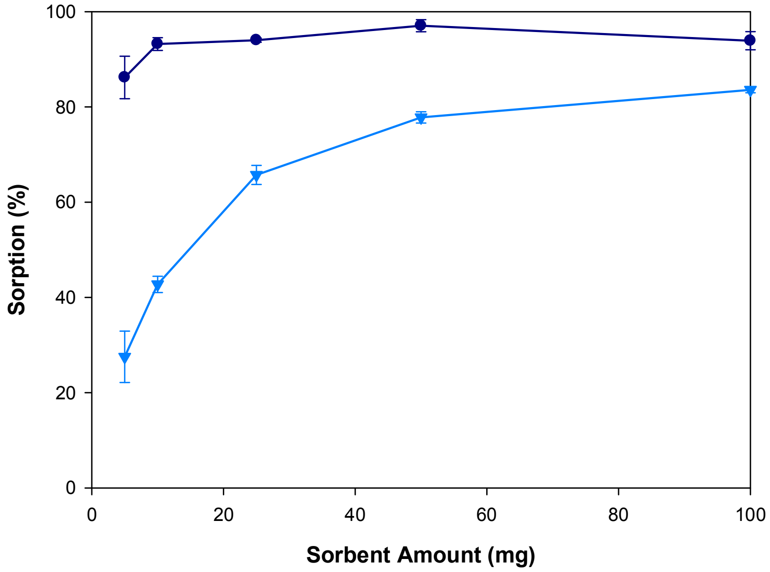


Figure 3.12. Effect of sorbent amount on the sorption of Sb(V). (▼) IRA 458, (●) ZVI-IRA 458. (20.0 mL of 100.0 µg$L^{-1}$ Sb(V) solution, 60 min shaking time, pH 7.0, 25.0 °C reaction temperature)

### 3.2.4. The Effect of Shaking Time

To determine the required reaction time for the maximum sorption of antimony species, batch type sorption was studied by varying the shaking time as 1, 5, 15, 30, 60, and 120 minutes at pH 7.0 for ZVI-IRA 458 resin. As explained in section 2.1, GFL 1083 water bath shaker equipped with a microprocessor thermostate was used in order to control the temperature of the reaction media and to provide efficient mixing The graphics of the results are illustrated in Figure 3.13.. The results indicated that the sorption kinetics was very fast for antimonous acid ($Sb(OH)_3$) and for antimonate ($Sb(OH)_6^-$) sorption begun to increase from 20min to 60min. For both antimony species a very high sorption reached at 60 min and almost stayed constant at 120 min. Thus, for a safe period of time, 60 minutes, was decided to be applied in further studies.

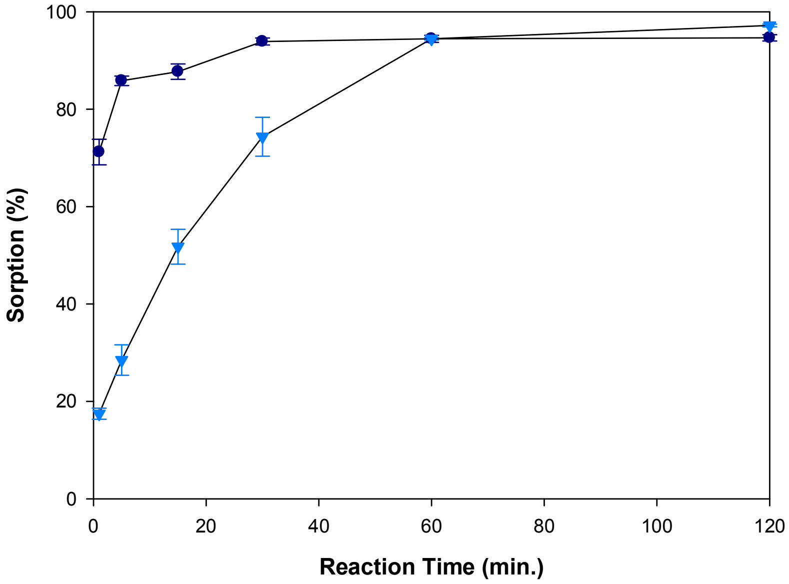


Figure 3.13. Effect of shaking time on the sorption of antimony species. (▼) Sb(V), (●) Sb(III) (20.0 mL of 100.0 μgL$^{-1}$ Sb solution, pH 7.0, 50.0 mg sorbent, 25.0 °C reaction temperature)

### 3.2.5. The Effect of Initial Sb(III) and Sb(V) Concentrations

The sorption efficieny ZVI-IRA 458 as a function of initial Sb(III) and Sb(V) concentrations was tested as the other variables were held at 50.0 mg sorbent amount, at pH 7.0 in 20.0 mL Sb solution, 60 min shaking time, 25.0 °C reaction temperature. The results for different concentrations of Sb (III) and Sb(V) solutions are given in Table 3.4.. As seen from the table, ZVI-IRA 458 shown a very high sorption affinity for both Sb(III) and Sb(V) . The results indicate considerably high sorption, even at a 10.0 mgL$^{-1}$ concentration. It is noteworthy that the iron amount of the zero valent iron modified IRA 458 resin (50.0 mg) we used throughout these experiments was only 1.45 mg.

### 3.2.6. The Effect of Reaction Temperature

The effect of the temperature on the sorption behaviour of antimony was studied at 25, 40 and 60 °C while the other parameters were kept at selected values written in Figure 3.1

Table 3.4. Effect of initial Sb(III) and Sb(V) concentration on the sorption efficiency for ZVI-IRA 458

| **ZVI IRA 458** | **Sorption (%)** | |
|---|---|---|
| **Concentration ($mgL^{-1}$)** | **Sb(III)** | **Sb(V)** |
| 0.005 | 86.59 (±1.4) | 100.00 (±0.0) |
| 0.05 | 96.56 (±0.5) | 94.82 (±1.4) |
| 0.1 | 98.42 (±0.8) | 95.69 (±0.2) |
| 0.5 | 99.81 (±0.1) | 99.06 (±0.2) |
| 1.00 | 99.69 (±0.1) | 99.03 (±1.3) |
| 10.00 | 86.63 (±1.3) | 91.06 (±0.3) |

Antimonous acid ($Sb(OH)_3$) and antimonate ($Sb(OH)_6^-$) sorption performances of ZVI-IRA 458 as a function of temperature are given in Figure 3.13. As seen from the figure, as the temperature increased, ZVI-IRA 458 showed almost no change on the sorption for both antimonous acid ($Sb(OH)_3$) and antimonate ($Sb(OH)_6^-$) which are the dominant forms of Sb(III) and Sb(V) at pH 7.0. Therefore, 25 °C was chosen as a suitable temperature for further experiments.

In addition, the thermodynamic parameters such as standard Gibbs free energy change, $\Delta G^o$, standard enthalpy change $\Delta H^o$, and standard entropy change, $\Delta S^o$ has an important role on the acknowledgement of the effect of temperature on the adsorption. Furthermore, the magnitude of the change in free energy can be used to determine the type of adsorption. The results of thermodynamic calculations are given in Table 3.5.

Table 3.5. Thermodynamic parameters of Sb(III) and Sb(V)

| **Sb(III)** | **ΔH (kJ/mol)** | **ΔG (kJ/mol)** | | **ΔS(J/molK)** | |
|---|---|---|---|---|---|
| | | **298 K** | **313 K** | **298 K** | **313 K** |
| **ZVI IRA 458** | 25.85 | -23.02 | -25.49 | 163 | 164 |

| **Sb(V)** | **ΔH (kJ/mol)** | **ΔG (kJ/mol)** | | **ΔS(J/molK)** | |
|---|---|---|---|---|---|
| | | 298 K | 313 K | 298 K | 313 K |
| **ZVI IRA 458** | 18.74 | 21.65 | 21.8 | 9.76 | 9.77 |

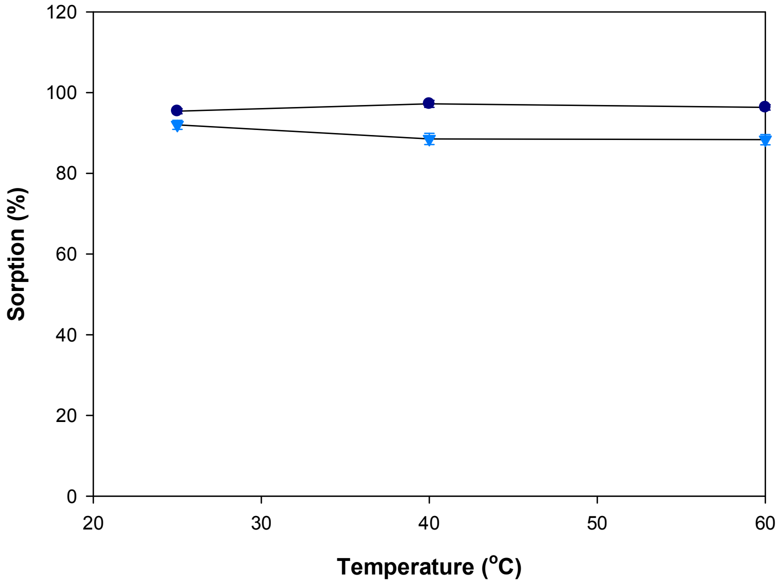


Figure 3.14. Effect of sorption temperature on the sorption of antimony. (▼) Sb(V), (●) Sb(III) (20.0 mL of 100.0 μgL$^{-1}$ Sb solution, pH 7.0, 60 min shaking time, 50.0 mg sorbent)

### 3.2.7. The Amount of Iron Released into the Solution

During the sorption experiments, the possible release of iron was investigated in order to keep the level of contaminant in water in a controlled amount. As seen in the SEM images of the zero valent iron modified IRA 458 resin, some amount of the surface coating in the form of iron oxide tended to fall apart from the resin due to overload of iron. Thus, it was important to analyze the iron content of the solution after sorption experiments.

For this purpose, after sorption, iron concentration in the solution was analyzed by ICP-MS with using $^{56}$Fe signal that has the abundance of 91.72 % in nature. This study is applied for all optimization experiments; the effect of pH, effect of reaction time, effect of reaction temperature and effect of initial antimony concentration. The results of these experiments are shown in Table 3.6., Table 3.7., Table 3.8. and Table 3.9., respectively. According to these results, it can be said that the amount of iron passed into the solution from the modified sorbent was considerably low and under the legal limit which is set as 0.3 mgL$^{-1}$ in well-water by EPA.

Table 3.6. Amount of iron released in the effect of pH study

| Fe Release (mg/L) | | |
|---|---|---|
| **pH** | **Sb(III) Sorption** | **Sb(V) Sorption** |
| 3.0 | 0.120 | 0.040 |
| 5.0 | 0.074 | 0.066 |
| 7.0 | 0.042 | 0.064 |
| 8.0 | 0.045 | 0.067 |
| 10.0 | 0.037 | 0.061 |

Table 3.7. Amount of iron released in the effect of reaction time study

| Fe Release (mg/L) | | |
|---|---|---|
| **Reaction Time (min)** | **Sb(III) Sorption** | **Sb(V) Sorption** |
| 1 | 0.001 | 0.001 |
| 5 | 0.020 | 0.060 |
| 15 | 0.040 | 0.078 |
| 30 | 0.046 | 0.086 |
| 60 | 0.028 | 0.025 |
| 120 | 0.035 | 0.060 |

Table 3.8. Amount of iron released in the effect of reaction temperature study

| Fe Release (mg/L) | | |
|---|---|---|
| **Reaction Temperature ($^0$C)** | **Sb(III) Sorption** | **Sb(V) Sorption** |
| 25 | 0.003 | 0.025 |
| 40 | 0.005 | 0.002 |
| 60 | 0.001 | 0.010 |

Table 3.9. Amount of iron released in the effect of initial concentration study

| Fe Release ($mgL^{-1}$) | | |
|---|---|---|
| **initial concentration ($mgL^{-1}$)** | **Sb(III) Sorption** | **Sb(V) Sorption** |
| 0.1 | 0.040 | 0.028 |
| 0.5 | 0.020 | 0.015 |
| 1.0 | 0.020 | 0.018 |
| 10.0 | 0.018 | 0.025 |

# CHAPTER 4

# CONCLUSION

A newly modified sorbent was used for the sorption and removal of antimony species; Sb(III) and Sb(V) prior to determination by atomic absorption spectrometry. SEM, EDX and XRD was applied for the characterization and the elemental content of both unmodified and modified resin. Thus the characterization results provided a beter reflectance on the success of the modification procedure. Afterwards, the sorption efficiency of the unmodified and the modified sorbents towards antimony species were investigated under specifically selected sorption conditions.

Throughout this study, IRA 458 anion exchange resin was used satisfactorily as immobilization matrix for zero valent iron. Zero-valent iron modified IRA 458 can effectively be employed in the sorption of Sb(III) and Sb(V) in waters. The results of the sorption studies demonstrated that Amberlite IRA 458 resin can be used only for the removal of Sb(V). However, zero-valent iron modified IRA 458 provided more effective sorption results for both antimony species.

ZVI modified-IRA 458 showed considerably high sorption for both Sb species; namely, Sb(III) for all studied pH and Sb(V) for neutral and slightly basic pH while IRA 458 itself did not display significant sorption around neutral pH for Sb(III) since $Sb(OH)_3$ is the dominant form of Sb(III) around the neutral pH range. Slightly faster sorption kinetics was observed for Sb(III) than for Sb(V). Despite the lower amount of the Fe loaded (37.9 mg Fe/g resin), sorption capacity did not change significantly even at 10.0 $mgL^{-1}$ antimony concentration. The most important advantage of this sorbent is that it does not require a pre-adjustment step or a preliminary work which makes it a desirable antimony removal method for contaminated waters, especially for waters containing unknown antimony species.

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