USE OF ION EXCHANGE RESINS MODIFIED WITH ZERO-VALENT IRON FOR THE SORPTION/SPECIATION OF INORGANIC As(III) AND As(V) IN WATERS

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ABSTRACT

USE OF ION EXCHANGE RESINS MODIFIED WITH ZERO-VALENT IRON FOR THE SORPTION/SPECIATION OF INORGANIC As(III) AND As(V) IN WATERS

Arsenic is a cumulative toxic element and according to Environmental Protection Agency its maximum admissible concentration is established as 10.0 μgL^{-1} in drinking water. The consumption of arsenic via drinking contaminated water causes chronic and acute poisoning which result in different cancer types. Therefore, determination, speciation and removal of arsenic compounds from waters are important. This study aims to develop a novel sorbent for removal of inorganic arsenic species from contaminated waters. For this purpose a strong anion exchange resin (Amberlite IRA 458) was modified with zero valent iron (ZVI).

In the first part of the study, various commercial anion exchange resins and novel resins prepared in the study were used for sorption and speciation of inorganic arsenic. For all the sorbents, the optimized sorption parameters were determined to be 25 °C for sorption temperature, 50.0 mg for sorbent amount, 60 min for shaking time for 20.0 mL of 100.0 μgL^{-1} of arsenic species. The release of As(III) and As(V) from the sorbents was realized using two eluents, 2% (m/v) NaOH + 3% (m/v) NaCl and 5% (m/v) NaOH + 3% (m/v) NaCl, respectively. The accuracy of the proposed methodology was verified with sorption studies for various water types spiked with 100.0 μgL^{-1} As(III) and As(V). Sorption values of ZVI-IRA 458 were determined to range between 59.1% and 100% for As(III) and between 61.5% and 100% for As(V). Moreover, the sorption efficiencies of the novel sorbents were compared with those of the commercial sorbents.

In the final part of the study, the sorption results demonstrated that the most effective immobilization method was $NaBH_4$ reduction and the most efficient resin to be modified was Amberlite IRA 458. Also, the sorption characteristic of ZVI-modified resins showed that the removal efficiency depended on the type of resins and arsenic species in water.

ÖZET

SULARDAKİ ANORGANİK As(III) VE As(V)'İN SORPSİYONU/TÜRLEMESİ İÇİN SIFIR DEĞERLİKLİ DEMİR İLE MODİFİYE EDİLMİŞ İYON DEĞİŞTİRİCİ REÇİNELERİN KULLANILMASI

Arsenik, kümülatif etkiye sahip toksik bir elementtir ve Çevre Koruma Ajansı'na göre içme sularında maksimum kabul edilebilir derişimi 10,0 μgL^{-1} olarak belirlenmiştir. Kontamine içme suyu yoluyla arsenik tüketimi farklı kanser türlerine neden olabilecek kronik ve akut zehirlenmelere yol açar. Arsenik tayini, türlemesi ve giderilmesi bu nedenle önemlidir. Bu çalışmada, kontamine sulardaki inorganik arsenik türlerinin giderilmesi için yeni bir sorbent geliştirilmesi amaçlanmış ve bu amaçla kuvvetli anyon değiştirici reçine olan IRA 458 sıfır değerlikli demir ile modifiye edilmiştir.

Çalışmanın birinci bölümünde, çeşitli mevcut (anyon ve katyon değiştirici) ticari reçineler ve bu çalışmada hazırlanan/modifiye edilen reçineler inorganik arsenik sorpsiyonu ve türlendirilmesinde kullanılmıştır. Tüm sorbentler için optimize edilmiş sorpsiyon parametreleri; sorpsiyon sıcaklığı 25 °C, sorbent miktarı 50,0 mg, çalkalama süresi 60 dakika, arsenik çözeltisi 20,0 mL 100,0 μgL^{-1} olarak belirlenmiştir. As(III) ve As(V), kullanılan sorbentlerden sırasıyla, 2% (m/v) NaOH + 3% (m/v) NaCl ve 5% (m/v) NaOH + 3% (m/v) NaCl ile desorbe edilmiştir. Önerilen metodun kesinliği çeşitli sulara 100,0 μgL^{-1} seviyelerinde As(III) ve As(V) standart katma/sorpsiyon testleriyle gösterilmiştir. Sıfır değerlikli demir ile modifiye edilmiş IRA 458 sorbenti için elde edilen değerlerin, As(III) için % 59,1 ile % 100,0, As(V) için ise % 61,5 ile % 100,0 arasında değiştiği bulunmuştur. Ayrıca, yeni sentezlenen sorbentlerin sorpsiyon verimleri ticari sorbentlerin sorpsiyon verimleriyle karşılaştırılmıştır.

Çalışmanın son bölümünde ise sorpsiyon sonuçları, en etkili immobilizasyon yönteminin $NaBH_4$ indirgemesi ve modifiye edilen en verimli reçinenin Amberlite IRA 458 olduğunu göstermiştir. Ayrıca, sıfır değerlikli demir ile modifiye edilmiş reçinelerin sorpsiyon davranışları, giderme verimliliğinin reçinelerin çeşidine (tipine) ve sudaki arsenik türlerine bağlı olduğunu göstermiştir.

Dedicated to;

"my grandmother"

for her endless support through all my life

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CHAPTER 1

INTRODUCTION

1.1. General Description of Arsenic

Arsenic (As, atomic number 33) is a chemical element classified as a metalloid because it has characteristics of both metals and nonmetals. It is a silver-grey brittle crystalline solid with an atomic weight of 74.9, specific gravity 5.73, melting point 817 ºC (at 28 atm), boiling point 613 ºC, vapor pressure 1 mm Hg at 372 ºC and is an element of Group V in the periodic table (Mohan and Pittman 2007). Elemental arsenic was first reported by the Greek historian Zosimus in the 5th century A.D. although it is claimed that Albertus Magnus, the 13th century German scholastic philosopher, was the first to isolate and identify it as an element. Since its isolation in 1250 A.D. by Albertus Magnus, this element has been a center of controversy in human history (Mandal and Suzuki 2002).

1.2. Arsenic Species in the Environment

Arsenic occurs both organic and inorganic forms in nature (EPA 2000), and exists in the (-3), (0), (+3) and (+5) oxidation states (Smedley et al. 2002). Organic species of arsenic are monomethyl arsenic acid (MMAA), dimethyl arsenic acid (DMAA) and arseno-sugars found in foodstuffs such as shellfish (EPA 2000). Inorganic species of arsenic occur in both arsenite (AsIII) which consist predominantly of arsenious acid (H_3AsO_3) in natural waters, and arsenate (AsV) which consist predominantly of $H_2AsO_4^-$ and $HAsO_4^{2-}$ in natural waters (EPA 2000). Pentavalent (+5), also called arsenate species, predominate and is stable in oxygen rich aerobic environments whereas trivalent (+3), also called arsenite, predominate in moderately reducing anaerobic environments (Mohan and Pittman 2007). According to the environmental conditions such as redox potential (Eh), the presence of complexing ions like ions of sulfur, iron, and calcium, pH and microbial activity, arsenic valence and

speciation may change (EPA 2000). Figure 1.1 displays the distribution of arsenic species.
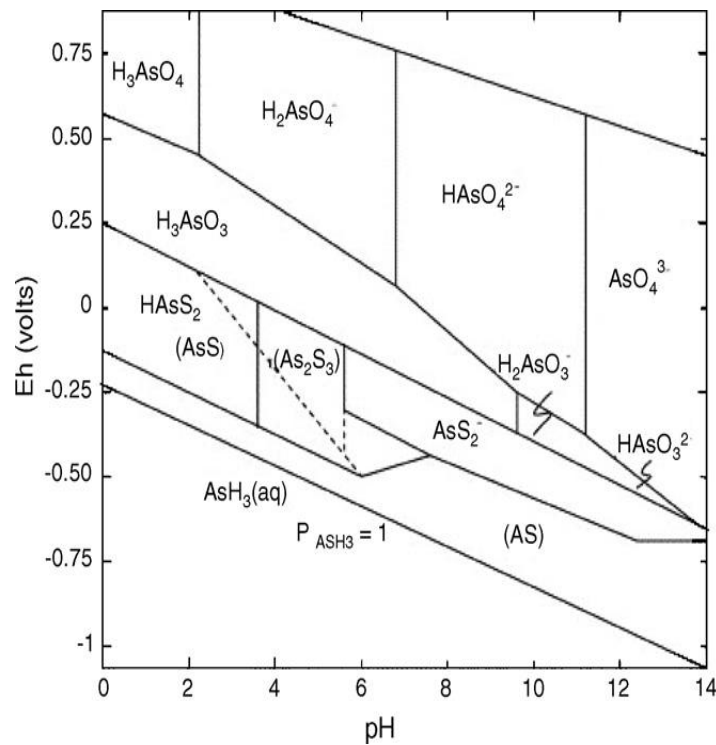
Figure 1.1 The Eh-pH diagram for arsenic at 25 °C and 101.3 kPa
(Source: Mohan and Pittman 2007)

1.3. Effect of Arsenic Species on the Environment and Health

Arsenic occurs naturally in rocks, soil, water, air, plants, and animals (EPA 2000) and is found in a large variety of samples such as in fresh and sea waters, sediments, soils, marine organisms and body fluids. It is a ubiquitous element that ranks 20th in abundance in the earth crust, 14th in the sea water and 12th in the human body (Mandal and Suzuki 2002).

Arsenic is widely distributed in nature, even though it is one of the least plentiful elements in the earth's crust. The percentage of arsenic in the crust is comparable to that of tin and molybdenum. Natural activities such as volcanic action, erosion of rocks, and forest fires, can release arsenic into the environment (EPA 2000). Virgin soils usually contain a few parts of arsenic per million, but the concentration often increases several hundredfold after several years of application of pesticides that contain arsenic. Arsenic is also found in concentrations of several tenths per million parts in seawater. Arsenic

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exists in minerals such as arsenide, arsenite and arsenate, all of which are more frequently found in nature when compared with the deposits of elemental arsenic. For example; arsenopyrite ($FeS_2.FeAs_2$) is the most abundant mineral.

By means of both geological and anthropogenic activities, arsenic contamination is introduced into the environment. For example as a geological activity, weathering of rocks, followed by leaching of metals, leads to the introduction of arsenic into soil and water (Butcher 2007). Another significant source for the introduction of arsenic into the environment are the anthropogenic activities, some of which are stated below:

i.   Commercial arsenic (enriched arsenic concentrations) is recovered as by-products of processing mining activities (gold, silver, lead, copper, nickel and cobalt ores).

ii. Coal combustion may produce ash with high arsenic levels.

iii. A number of manufacturing processes employ arsenic trioxide including ceramics, glass, electronics, fireworks, antifouling agents and cosmetics.

iv. Chromated copper arsenate has been employed to minimize biological degradation of wood (Nico et al. 2006).

v.   Many pesticides and herbicides also contain arsenic as a major component. For example, lead arsenate and calcium arsenate have been employed in orchards as horticultural pesticides (Mahimairaja 2005).

The two inorganic oxyanions, arsenous acid (arsenite or As(III)) and arsenic acid (arsenate or As(V)) are the most common forms of arsenic. According to environmental conditions, these compounds may change their oxidation state. Generally, their toxicity is decreased with the methylation of these inorganic compounds (Butcher 2007). Furthermore, arsenates closely resemble the corresponding phosphates in solubility and crystal form, but they hydrolyze more than the phosphates. Sodium arsenate ($Na_3AsO_4.12H_2O$) is used in printing inks, in dyeing textiles, and in preparing arsenates such as lead and calcium arsenates used in insecticides. Potassium dihydrogen arsenate, also known as Macquer's salt, is used in the manufacture of flypaper and insecticides, the dyeing of textiles and the preservation of hides. Sodium meta-arsenite ($NaAsO_2$) is used in the manufacture of soaps and insecticides, and in dyeing and preserving hides. Arsenites of copper are used in Paris green (copper(II) acetoarsenite) as an insecticide and Scheele's green (copper arsenite) as a pigment.

Food and water are the most important sources of human exposure to arsenic (Terlecka 2005). However, contaminated water is the most considerable risk for human

health because most arsenic in food is organic arsenic (Butcher 2007). Hence, the major pathway to human exposure to arsenic is drinking polluted groundwater (Konstantina et al. 2006) and it is considered as one of the most significant environmental causes of cancer in the world (Kapaj et al. 2006). Long-term exposure to the consumption of arsenic in drinking water causes skin, lung, kidney, bladder and liver cancers as well as pigmentation changes and skin thickening (hyperkeratosis) (Mohan and Pittman 2007). A negative effect of arsenic to vascular system is gangrene, also known as a Blackfoot Disease, is a peripheral vascular disease (EPA 1999). These effects differ from acute poisoning, which typically causes vomiting, oesophageal and abdominal pain, and "rice water" diarrhea (Mohan and Pittman 2007). Other potential effects include neurologic impairment (Lomaquahu and Smith 1998). For example, long-term accumulated arsenic may cause neurobehavioral effects in adolescence, and may affect memory and intellectual functions (Kapaj et al. 2006).

In order to minimize the health effects of arsenic, in 2001 the United States Environmental Protection Agency (USEPA) adopted a maximum contaminant level (MCL) for arsenic in drinking water at 10 parts per billion (ppb), replacing the old standard of 50 ppb (0.05 mg/L) (DeMarco et al. 2003; USEPA 2001). Also, the World Health Organization (WHO) designated the guideline value of 0.01 mg/L (10 ppb-µg/L) as a provisional on the basis of treatment performance and analytical achievability.

The toxicity of arsenic is dependent upon its chemical forms and oxidation states (Mandal and Suzuki 2002). The decreasing of the toxicity of arsenicals occurs in the following order, arsines > As(III) > arsenoxides > As(V) > arsonium compounds > As (Mandal and Suzuki 2002). Table 1.1 displays the structures and acidity dissociation constants of arsenic species used throughout this study.

Table 1.1. Arsenic species used throughout the study

As species	Structure	pKa
Arsenite As(III)		9.2 12.1 13.4
Arsenate As(V)		2.3 6.8 11.6
Monomethylarsonic acid MMA(V)		3.6 8.2
Dimethylarsinic acid DMA(V)		6.3
Arsenobetaine AsB		2.2

1.4. Arsenic Determination Methods

There are various instrumental techniques to determine arsenic concentration in various matrices. In theory, all atomic spectrometry systems may be used as a detector (Butcher 2007). However, inductively coupled plasma-mass spectrometry (ICP-MS) is the most widely used system because samples are continuously introduced into the plasma and ICP-MS is relatively easy to interface with most chromatographic systems for the speciation of arsenic (Kinoshita et al. 2005; Butcher 2007). Also, it offers

excellent sensitivity and long linear dynamic ranges (Butcher 2007). On the other hand, a major disadvantage of it is that it is affected from spectral interference of $^{40}Ar^{35}Cl$ on the monoisotopic ^{75}As signal in the chloride-containing matrixes. This interference effect can be eliminated by matrix separation provided by hydride generation (Menegario and Gine 2000; Sabarudin et al. 2005), or can be corrected with the use of interference-correction equations.

Another useful technique is Hydride generation atomic absorption spectrometry (HGAAS), which is applied after a suitable pre-treatment step or directly (Menegario and Gine 2000; Bundaleska et al. 2005; Yersel et al. 2005). Hydride generation has an advantage for the determination of the different forms of arsenic (different oxidation states and forms a bound to organic matter) on the basis of different kinetics of hydride generation by each species (Niedzielski et al. 2002).

In addition, Inductively coupled plasma-atomic emission spectrometry (ICP-AES) and HG-ICP-AES are the other instrumental techniques used for the determination of arsenic (Dambies 2004; Faria et al. 2002). High-pressure liquid chromatography (HPLC) in combination with ICP-MS can be used to determine various arsenic species (WHO 2011; Afton et al. 2008; Ammann 2010). Also, Atomic fluorescence spectroscopy (Simon et al. 2004; Schaeffer et al. 2005) and ICP or ICP-MS (Gomez-Ariza et al. 2000; Nakazato and Tao 2006) have been used for the detection of arsenohydrides in the recent studies (Sharma and Sohn 2009).

1.5. Arsenic Removal Methods

Drinking water is generally treated to remove color, turbidity and fecal microorganisms, and these are performed with a suitable combination of coagulation-flocculation-sedimentation-filtration and disinfection processes. However, if the removal of chemicals like arsenic from water is expected, more complex methods are required (Esparza 2006). To remove arsenic from drinking water precipitative processes, adsorption processes, ion exchange processes, separation (membrane) processes and other alternative methods are used (EPA 2000). Owing to the uncharged state of the arsenite species under pH 9, all processes are limited with lower efficiency for the removal of arsenite. For this reason, if arsenite is the predominant species

present, oxidation to arsenate may be required to achieve the desired removal (EPA 1999).

1.5.1. Precipitative Processes

Precipitative processes including coagulation/filtration (C/F), direct filtration, coagulation assisted microfiltration, enhanced coagulation, lime softening (LS) and enhanced lime softening are the methods used most frequently to treat arsenic contaminated water.

Coagulation/filtration is one of the precipitative processes which uses ferric salts, (e.g. ferric chloride), ferric sulfate, ferric hydroxide, aluminum sulfate and alum (aluminum hydroxide) as a coagulant. 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 (typically aluminum sulfate, ferric chloride, or ferric sulfate) (EPA 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/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 arsenic concentration and the valence of the arsenic species (As(III) or As(V)) (EPA 2000). The model of a precipitation/coprecipitation system is shown in Figure 1.2.

Figure 1.2. The Model of a Precipitation/Coprecipitation System
(Source: Arsenic Treatment Technologies for Soil, Waste, and Water – EPA 2002)

1.5.2. Adsorptive Processes

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).

Out of various types of sorbents such as 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, AA is the most commonly used one to remove arsenic from drinking water (EPA 2002).

AA is an effective treatment technique for arsenic removal because arsenic ions in feed water can be sorbed by the oxidized activated alumina surface (EPA 2000). Although the chemical reactions involve exchange of contaminant ions (such as fluoride, arsenic, selenium and silica) with the surface hydroxides on the alumina, activated alumina is considered to be an adsorption process (EPA 2000). Also, iron oxide coated sand was used for the removal of arsenic where the ions are exchanged with the surface hydroxides (EPA 2000).

1.5.3. Ion Exchange Processes

Ion exchange is a physical and chemical process in which ions are held electrostatically on the surface of a solid phase are exchanged for ions in the feed water (EPA 2002). This solid phase is typically a resin made from synthetic organic materials, inorganic materials, or natural polymeric materials containing specific ionic functional groups to which exchangeable contaminant ions are attached (EPA 2002). The resin is usually packed into a column and while contaminated water is passing through the column, contaminant ions are exchanged for other ions. Also, ion exchange resins must be periodically regenerated to remove the adsorbed contaminants (EPA 2002). The model of ion exchange system is illustrated in Figure 1.3.

Strong acid, weak acid, strong base and weak base types of media have been used for ion exchange. Strong and weak acid resins exchange cations while strong and weak base resins exchange anions. Weak base resins tend to be effective over a smaller pH range and strong base resins are typically used for arsenic treatment because

dissolved arsenic is usually in an anionic form. Furthermore, cation exchange can be used for both water softening and removal of heavy metals. Also, anionic resins are generally used in the removal of nitrate, arsenic and selenium species (EPA 2002).

As cation exchange resins, Ce(IV)-loaded resins, Cu(II)-loaded resins, Fe(III)-loaded resins, La(III)-loaded resins, Y(III)-loaded resins and Zr(IV)-loaded resins were used to remove of As(V) in some research, and macroreticular chelating resins and anion exchange resins were used for the same purpose (Mohan and Pittman 2007). In another study for arsenic removal by ion exchangers, Dominguez et al. (2003) synthesized fiber like ion exchange resin from vinylbenzyl chloride and found that the fiber ion exchange resin showed preferable kinetic performance than commercial resins.
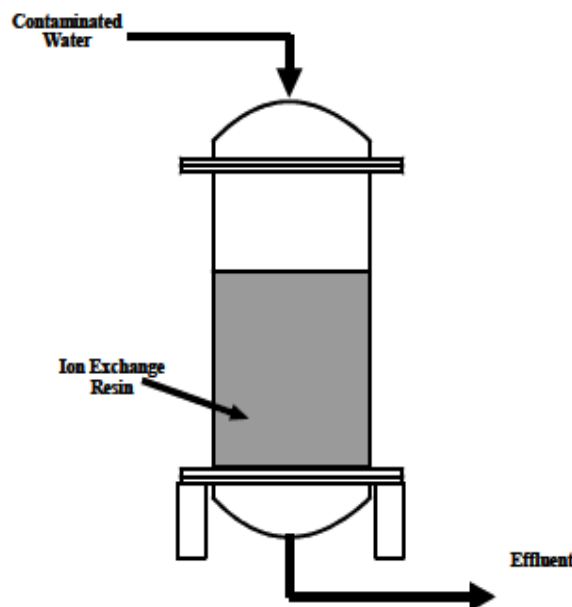
Figure 1.3. The Model of an Ion Exchange System
(Source: Arsenic Treatment Technologies for Soil, Waste, and Water – EPA 2002)

1.5.4. Membrane Processes

Membrane filtration separates contaminants from water passing through a semi-permeable barrier or membrane. The membrane allows some constituents to pass through while blocking the passage of others (EPA 2002). Figure 1.4 is displayed the model of a membrane filtration system.

A driving force (i.e. a potential difference between the two sides of the membrane) is required for the movement of constituents across a membrane and according to the type of driving force (e.g., pressure, concentration, electrical potential, and temperature), membrane processes are classified. Among all these methods, pressure-driven membrane processes which are classified into four categories: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) are the most frequently used for the removal of arsenate. Also, these methods are categorized by the size of the particles which can pass through the membranes or by the molecular weight cut off (i.e., pore size) of the membrane (EPA 2002).

The pore size of the membrane is strongly dependent on the applied pressure. If two solutions are separated by a semipermeable membrane, the solvent will naturally pass from the lower-concentration solution to the higher-concentration solution. This process is known as osmosis (WHO 2011). It is also possible to change the flow of solvent in the opposite direction, from the higher to the lower concentration, by increasing the pressure on the higher-concentration solution (WHO 2011). Reverse osmosis and nanofiltration, which remove constituents primarily through chemical diffusion, have relatively small pore sizes and a high pressure application. Therefore, these two processes are capable of removing significant portions of the dissolved arsenic compounds in natural waters due to their small pore size. NF is a reliable arsenic removal process for groundwater which contains up to 90% dissolved arsenic (AWWARF, 1998). Also, in another study RO was combined with NF and the results showed that the removal of arsenic is independent of the pH, and arsenic removal efficiency reaches 90% (Johnston et al. 2001; Esparza 2006).

On the other hand, relatively lower pressure is applied in ultrafiltration and microfiltration removal is achieved through physical sieving. A main drawback of the membrane filtration is reported to be the high cost among the other methods (Choong et al. 2007).
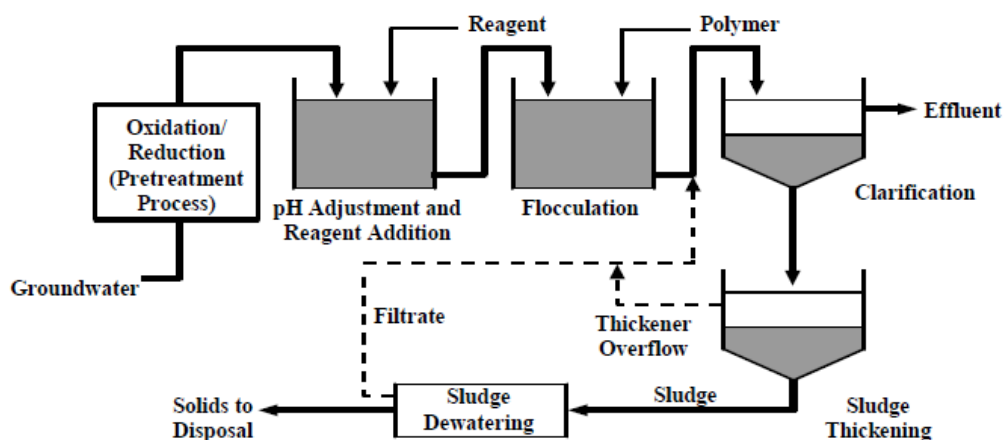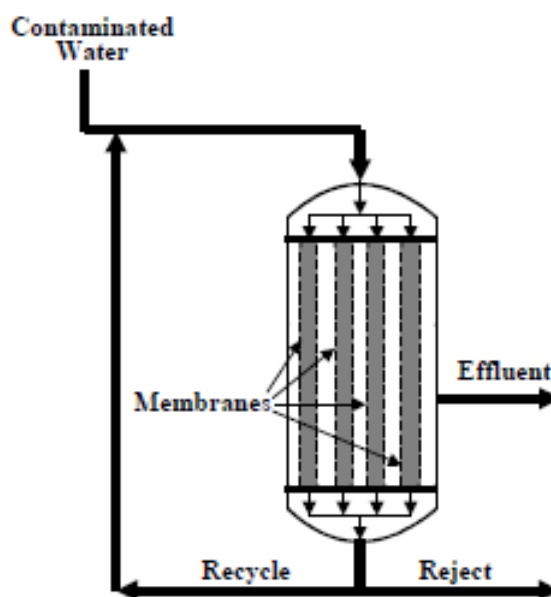
Figure 1.4. The Model of a Membrane Filtration System
(Source: Arsenic Treatment Technologies for Soil, Waste, and Water – EPA 2002)

1.5.5. Alternative Technologies

All the methods for arsenic removal mentioned in the previous sections, have limitations due to their cost or health hazard effects which direct scientist to search for environmentally safe alternative methods. In various processes, bacterial activity may play a significant role as a catalyst for arsenic removal, but little is known about the viability of biological processes in eliminating arsenic from water (Johnston et al. 2001; Esparza 2006). Moreover, another small-scale studies show that optimum conditions of pH, temperature and oxygen enable biological filtration and the simultaneous elimination of As^{3+} and iron (Lehimas et al. 1992). In order to remove arsenic, a filtration methods in which spores are used, are developed successfully (Bencheikh-Latmani and Rizlan 2004; Katsoyiannis et al. 2004).

A variety of biomasses such as chitosan and its modified form is used commonly in other sorption studies since they are low cost and environmentally friendly in nature. For example, in column studies, chitosan is used as a resin for the sorption of arsenic with improved resistance to shrinkage which was obtained by 3,4-diamino benzoic acid fuctionalized cross linked chitosan (Sabarudin et al. 2005). Also, Boddu et al. (2008)

used chitosan dip coated ceramic alumina for As(III) and As(V) removal in column with improved sorption capacity for As(III).

In addition to these technologies, biological treatment is an emerging remediation technology designed to remove arsenic from soil, waste, and water (EPA 2002). According to the theory of biological treatment of arsenic, microorganisms (e.g., sulfate-reducing bacteria and arsenic-reducing bacteria) act directly on arsenic species or create ambient conditions and they cause arsenic to precipitate/ coprecipitate from water and leach from soil and waste (EPA 2002).

1.6. Solid Sorbents

Over the past few years, various methods have been developed for As removal namely, ion-exchange, chelating sorption and co-precipitation. Beside these methods, nanoscience and nanotechnology have 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. For instance, zero valent iron nanoparticles are more promising for As removal with its high surface area and high sorption capacity. In spite of these advantages, lack of knowledge about nanoparticles behavior in living systems requires the immobilization of ZVI on to supporting surface.

In this study, firstly various anion and cation exchange resins were loaded with Fe^{3+} ions by different methods and were then treated with sodium borohydride ($NaBH_4$) or sodium hydroxide (NaOH). Secondly, batch type sorption experiments were carried out and the selectivity of the new sorbents were investigated towards As(III) and As(V). Finally, according to the sorption results, the most effective immobilization method and resin were chosen as $NaBH_4$ reduction and IRA 458, respectively. All in all further experiments were performed with Amberlite IRA 458 acrylic gel type strongly basic anion exchange resin.

1.6.1. Nanoscaled Zero-Valent Iron (nZVI)

Iron (Fe) is a transition metal with atomic number 26. It is placed in group VIII and period IV of periodic table. The oxidation states and reduction potentials of iron species are shown in Figure 1.5. 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. Several studies have demonstrated that zero-valent iron is effective at stabilization or destruction of a host of pollutants by its highly reducing character.
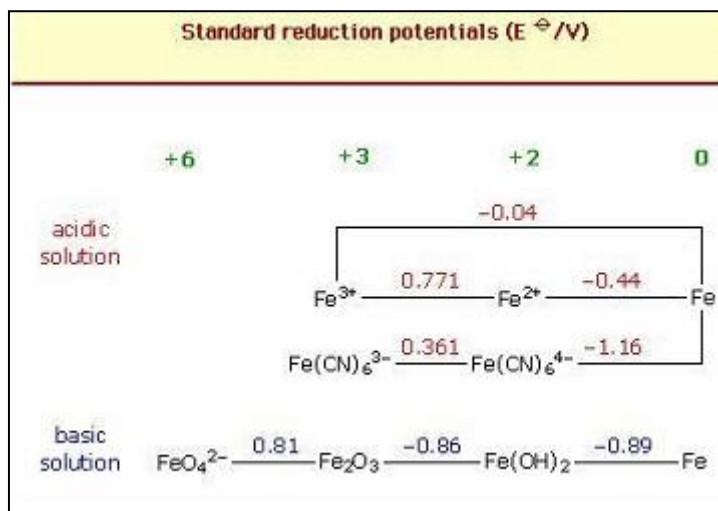
Figure 1.5. Standart reduction potentials of iron species
(Source: Web of Element 2008)

There are several physical and chemical synthesis techniques for the synthesis of nanoscaled zero-valent iron (Sun et al. 2006; Nurmi et al. 2005; Li 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(II) or Fe(III) ions took place in aqueous media. The method presented by Wang and Zhang consists of dropwise addition of sodium borohydride ($NaBH_4$) to a solution of Fe(II) or 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:

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 \downarrow + 3H_2BO_3^- + 12H^+ + 6H_2 \uparrow \quad \text{(Li et al. 2006)} \quad (1.1)$$
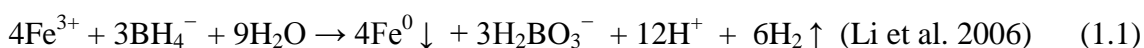
Figure 1.6 displays the model for core-shell structure of nZVI and uptake mechansims of metals suggested by Li and Zhang (2007). The synthesized nZVI particles are usually in spherical shape and have a coreshell structure, are also unstable in atmospheric conditions and it tends to form oxides/hydroxides in the forms Fe_2O_3,

Fe$_3$O$_4$ and FeOOH. As depicted in Figure 1.6, the shell consist of oxides and hydroxides and the core consist of Fe^0 (Martin et al. 2008). Li and Zhang (2007) studied nZVI structure before and after contacting with various metals and 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, that 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 and (iii) only chemical reduction occurs for metal cations with E^0 higher than E^0 (Fe).
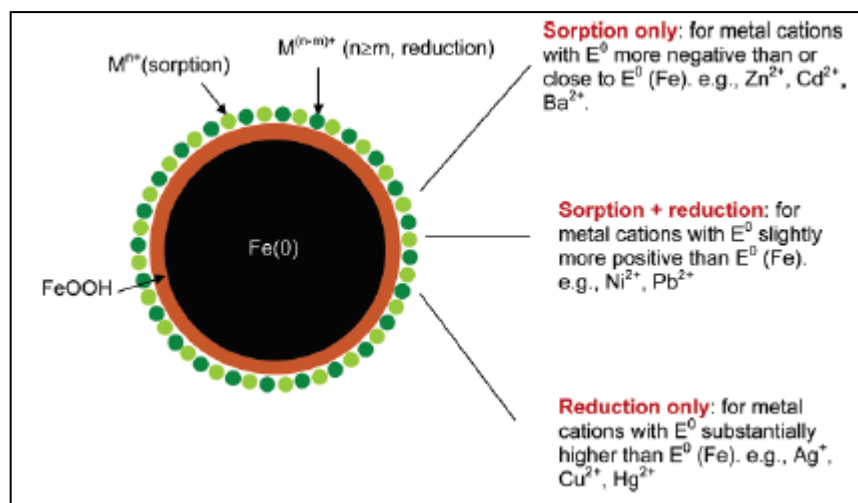
Figure 1.6. The core-shell structure of nZVI and uptake mechansims of metals
(Source: Li and Zhang 2007)

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 (As(V)) from water. In their study, Sasaki et al. (2008) tried to understand the immobilization mechanism of arsenite by ZVI and to determine the capacity of the material to retain arsenic in a PRB. Also, Tyrovola et al. (2006) aimed to show the efficiency of ZVI in removing arsenic from geothermal waters which located in agricultural regions with the high concentrations of nitrate and phosphate.

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 cannot be driven for more than a few meters by the migration of water and probably cannot reach the contaminated zone. The other problem is about the storage of iron nanoparticles for along time without oxidizing; since thermodynamically zero-valent iron tends to react with oxygen. In order to overcome these problems iron nanoparticles can be modified, supported or mixed with a filling material.

1.6.2. Polymeric/Inorganic Hybrid Ion-Exchange Sorbents

A number of arsenic removal technologies mentioned in the previous sections have been tried in the laboratory and/or field-scale testing. Among them, ion exchange processes are attractive for arsenic removal because repeated use of ion exchangers is possible, also many removal technologies focus on metal (hydr)oxides as adsorbent media (Hristovski et al. 2008).

In several studies, ion exchange sorbents were prepared by loading metal ions or metal oxides onto different ion exchangers (Zhu and Jyo 2001; An et al. 2005; Cumbal and SenGupta 2005). For example, Shao et al. (2008) studied the feasibility of using La(III)-, Ce(III)-, Y(III)-, Fe(III)-, and Al(III)-loaded resin as adsorbents to As(III) and As(V) removal from the wastewater. In order to explain the adsorption mechanism some parameters such as the effect of the contact time, pH of solution were investigated in a batch system.

Furthermore, hybrid sorbent produced by dispersing hydrated ferric oxide (HFO) nanoparticles inside a polymeric anion exchanger host material to arsenic removal. For example, DeMarco et al. (2003) reported the results of an extensive investigation about the properties of a polymeric/inorganic hybrid sorbent. They synthesized new hybrid sorbent, referred as hybrid ion exchanger or HIX. It combined mechanical and hydraulic properties of spherical polymeric beads with selective As(III) and As(V) sorption properties of HFO nanoparticles at neutral pH.

In another study, Cumbal and SenGupta (2005) studied the role of Donnan membrane effect in arsenic removal by using polymer-supported hydrated iron(III) oxide nanoparticles. Also, this paper gave more information about the effect of positively and negatively charged groups on the arsenic adsorption, how the anion or

cation exchanger adsorbed arsenic, which one was the efficient resin and what the Donnan membrane effect was. During their studies, As(III) and As(V) concentrations were 100.0 µg/L in the presence of various ions (SO_4^{2-}, Cl^-, HCO_3^-). Their work demonstrated that hybrid ion-exchange media capable of simultaneous removal of arsenate and perchlorate.

In another study publised by Sarkar et al. (2007) a hybrid anion exchanger (HAIX) was used for arsenic removal units in remote villages of India. HAIX which offered a very high selectivity for sorption of oxyanions of arsenic due to the Donnan membrane effect were spherical anion exchange resin beads containing dispersed nanoparticles of hydrated ferric oxide. They investigated first polymer-based commercially available arsenic-selective sorbent. The sorption columns used in field experiment were single or split-column design. Also, every unit run for more than 20.000 bed volumes in order to reach maximum contaminant level. However, during their experiments the maximum arsenic concentration applied in sorption was 1.000 µg/L.

In other study, Vatutsina et al. (2007) investigated the possibility of synthesis of hybrid inorganic/polymeric fibrous sorbents with high selectivity toward arsenic. They also developed and evaluated the performance of a new chemosorbent for the selective arsenic removal from drinking water. Their study showed the loading of largest amount of Fe(III) into a weak base anion exchanger(up to 1.4 mmol Fe/gram of dry fiber). Even if this sorbent provided a high selectivity toward both As(III) and As(V), the arsenic concentration 50-100 ppb in column experiments. In the field experiment of natural water containing 60 ppb As allowed purification of 10.000 bed volumes of water to 10 ppb of As. Also, Hristovski et al. (2008) studied for simultaneous removal of arsenate (As(V)) and perchlorate by means of hybrid ion-exchange (HIX) media.

In addition to these studies, Awual et al. (2008) prepared a novel fibrous weak-base anion exchanger (FVA) of non-ligand exchange type for rapid and selective As(V) removal from water based on electron irradiation induced graft polymerization technique. During the study, two types of FVA were synthesized. FVA-c sorbent was a non-woven cloth type to perform batch type study used for the investigation of uptake of arsenate in different pH and the presence of chloride and sulfate ions as interference. The other FVA-f sorbent was a filamentary type to perform column type study elucidated that the removal of arsenate from neutral pH samples containing 1.0-99 mg/L As(V) can be achieved. Besides, Korngold et al. (2001) performed experiments for the

selective removal of As(V) from drinking water by strong base anion exchange resins. They investigated the effect of various types of anion exchange resin and water composition on sorption. Kim and Benjamin (2004) studied for modeling a novel ion exchange process to removal of arsenate, sulfate and nitrate.

1.7. The Aim of This Work

The aim of this study is to develop synthesis of a new zero-valent iron modified sorbents for the removal of inorganic (arsenite and arsenate) arsenic species from contaminated waters prior to determination by atomic spectrometric techniques. For this purpose, different commercial ion exchange resins were treated with ferric ion and by reducing sodium borohydride (to immobilize zero valent iron(ZVI) onto resin surface) zero-valent iron containing sorbents were prepared. Various materials such as different commercial ion exchange resins and nanoscale zero valent iron (nZVI)-modified resins were investigated for their sorption behavior towards arsenic species. Before the sorption studies, the characterization of the sorbents was realized. The sorption performance of the sorbents in terms of solution pH, reaction temperature, shaking time, sorbent amount, and initial concentration of arsenic species were carried out through batch type sorption studies. Column type sorption was also performed for nZVI-modified sorbents.

CHAPTER 2

MATERIALS AND METHODS

2.1. Instrumentation and Apparatus

In the determination of arsenic (As), an Agilent 7500ce Series (Tokyo, Japan) inductively coupled plasma mass spectrometer (ICP-MS) 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 in all measurements. Because ICP-MS is one of the most sensitive techniques for As determination. Naturally occurring arsenic is composed of one stable isotope, ^{75}As (74.92160). Therefore any signal occurred by other isotopes is not required to be checked. However, there is one commonly occurring interference that affects the degree of ultratrace determination difficulty of arsenic and the results are affected by the spectral interference of ^{40}Ar^{35}Cl = 74.93123 on the monoisotopic ^{75}As = 74.9216 signal in the chloride-containing matrices. In order to eliminate this interference, the nitric acid (HNO$_3$) was used for acidification during the sorption experiments. Also, it can be eliminated by matrix separation provided by hydride generation or corrected with the use of interference-correction equations. Operating parameters for ICP-MS system are given in Table 2.1.

For heavy matrix solutions such as the eluates after desorption studies, a Thermo Elemental Solaar M6 Series atomic absorption spectrometer (Cambridge, UK) with an air-acetylene burner was used in arsenic determinations utilizing the Segmented Flow Injection Hydride Generation (SFI-HGAAS) unit (Figure 2.1). An arsenic hollow cathode lamp at the wavelength of 193.7 nm was used as the source line and a deuterium lamp was employed for background correction. In HGAAS, the quartz tube atomizer was 10.0 cm long, 8.0 mm in internal diameter and 10.0 mm in external diameter with a 4.0 mm a bore inlet tube fused in the middle for sample introduction. Air-acetylene flame was used for heating the quartz tube externally and nitrogen was used as the carrier gas. Operating parameters for the HGAAS system are given in Table 2.2.
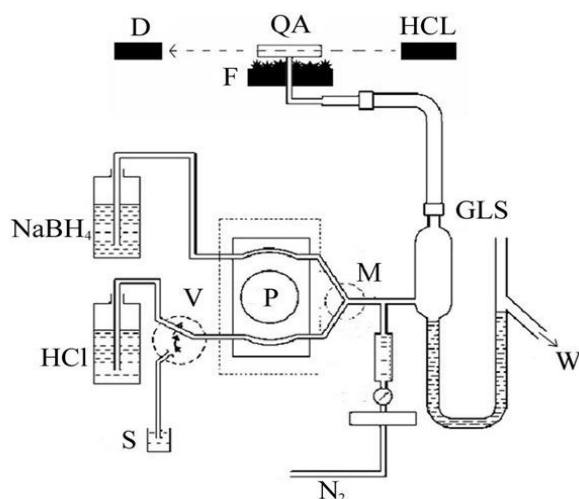
Figure 2.1. Segmented Flow Injection HGAAS system used in arsenic determinations. D: deuterium lamp, QA: quartz atomizer, HCL: hollow cathode lamp, F: flame, GLS: gas-liquid separator, W: waste, P: peristaltic pump, V: threeway valve and S: sample (Source: Yersel et al. 2005)

Table 2.1. ICP-MS operating parameters.

Operating Parameters	
Forward power	1500 W
Reflected power	1 W
Coolant gas flow rate	15 mL/min
Auxilary flow rate	0.90 mL/min
Sample uptake time	25 sec
Integration time	100 msec

Table 2.2. HGAAS operating parameters.

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

In batch sorption experiments, GFL 1083 water bath shaker (Burgwedel, Germany) equipped with a microprocessor thermostate was used to control the temperature and also to provide efficient mixing. The pH values adjustments and measurements were measured with WTW Series InoLab pH 720 precision pH meter (Weilheim, Germany). Hettich EBA 12 centrifuge (Tuttlingen, Germany) was used to separate the sorbent for reuse throughout the repetitive loading studies.

To characterize the synthesized sorbents, different techniques were applied. Firtstly, crystallographic properties were obtained with Philips X'Pert Pro X-Ray Diffractometer(Eindhoven, TheNetherland). Secondly, images of the synthesized sorbents were taken with Philips XL-30S FEG scanning electron microscopy (Eindhoven, The Netherlands). This instrument was employed for SEM characterization to obtain information about the morphology and the size of the crystals. Another technique, Perkin Elmer Pyris Diamond TG/DTA (Boston, MA, USA), was used for the investigation of the thermal properties of the sorbents. Finally, the elemental composition of the synthsized sorbents was determined by LECO-CHNS-932 elemental analyzer (Mönchengladbach, Germany).

2.2. Aqueous Calibration Plot

In this section, information related to the standart solutions prepared for the instruments used in the present study was explained in detail. The standard solutions from 0.0005 mgL^{-1} to 100.0 mgL^{-1} were prepared from 2000.0 mgL^{-1} As(III), 1000.0 mgL^{-1} As(V), 1000.0 mgL^{-1} DMA (Dimethylarsinic acid), 553.0 mgL^{-1} MMA(Monomethylarsonic acid) and 1031.0 mgL^{-1} AsB (Arsenobetaine) respectively with simple dilution. All the standards contained 1.0% (v/v) HNO_3 and were measured with ICP-MS. The HGAAS was used to detect the results of the desorption study of As(III) and As(V). Standard solutions from 0.0010 mgL^{-1} to 0.050 mgL^{-1} were prepared from 2000.0 mg L^{-1} As(III). For the desorption of As(III) and As(V), 0.5 M NaOH and 0.5 M KH_2PO_4 solutions were used. Furthermore, a reduction step was required to observe the arsenic signal for As(V). Therefore, L-cysteine at the concentration of 0.50% (w/v) was added to all samples and standards after which As(V) reduced As(III) and finally arsenic signal was obtained for As(V). Additionally, the limit of detection (LOD) based on 3S (3 times of the standard deviation of blank value) and the limit of

quantification (LOQ) based on 10S (10 times of the standard deviation of blank value) were also evaluated for the both detection methods.

2.3. Chemicals and Reagents

During the study, all chemicals were of analytical reagent grade and all standard solutions were prepared in ultrapure water (18.2 MΩ, Millipore, and Billerica, MA, USA). Glassware and plastic containers were cleaned by soaking in 10% (v/v) nitric acid overnight and washed with distilled water before being used. Table 2.3 shows these reagents with their concentrations.

Standard As(III) stock solution (2000.0 mg/L) was prepared by dissolving 0.659 g of As_2O_3 in 5.0 mL NaOH and 2.5 mL H_2SO_4 and diluted to 250.0 mL with ultrapure water.

Standard As(V) stock solution (1000.0 mg/L) was prepared by dissolving 0.1534 g of As_2O_5 in 1.0% (v/v) HCl and diluted to 500.0 mL with ultrapure water.

Standard DMA stock solution (1000.0 mg/L) was prepared by dissolving 0.7135 g of $(CH_3)_2As(O)ONa.3H_2O$ in ultrapurewater and diluted to 250.0 mL.

Standard MMA stock solution (553.0 mg/L) was prepared by dissolving 0.5385 g of $CH_3AsNa_2O_3.6H_2O$ in ultrapurewater and diluted to 250.0 mL.

Standard AsB stock solution (1031.0 mg/L) in water (BCR 626) was obtained from BCR (Brussels, Belgium).

Sodium borohydrate ($NaBH_4$) 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 0.50% (w/v) was added into the all samples and standard solutions to reduce As(V) to As(III) prior to the determinations.

Calibration standards were prepared daily by preparing buffer stock solution 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 NaOH - HCl solutions for HGAAS determinations.

Table 2.3. Reagents used through the study.

Reagent	Concentration used	Company	Cas no.	Purpose of use
As_2O_3		Fischer	[1327-53-3]	Preparation of As(III) stock solution for sorption study
As_2O_5		Merck	[1303-28-2]	Preparation of As(V) stock solution for sorption study
DMA		Merck	[6131-99-3]	Preparation of DMA stock solution for sorption study
MMA		Supelco	[144-21-8]	Preparation of MMA stock solution for sorption study
AsB			[BCR 626]	Preparation of AsB stock solution for sorption study
Amberlite IRA-458,chloride form		Supelco	[1-0330]	Synthesis of nZVI-modified IRA 458
Amberlite IRA-400,chloride form		Fluka	[9002-24-8]	Synthesis of nZVI-modified IRA 400
Amberlite IRA-67,free base		Sigma	[80747-90-6]	Synthesis of nZVI-modified IRA 67
Amberlite IRA-743- free base		Aldrich	[81133-21-3]	Removal of boron species from solution or water
$FeCl_3.6H_2O$	1.0 M	Merck	[10025-77-1]	Synthesis of nZVI-modified resins
$FeCl_2.4H_2O$	1.0 M	Sigma	[13478-10-9]	Synthesis of nZVI-modified resins

Table 2.3. (cont.)

Reagent	Concentration used	Company	Cas no.	Purpose of use
L-cysteine	0.50% (w/v)	Merck	[52-90-4]	Reduction of As(V) to As(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]	AsH$_3$ generation in HGAAS
HNO$_3$	0.1 M	Merck	[7697-37-2]	Desorption of As(III) and As(V) from nZVI-modified IRA 458
HNO$_3$	1.0 M	Merck	[7697-37-2]	Dissolvation of iron into nZVI-modified resins
HNO$_3$		Merck	[7697-37-2]	Acidification
NaCl	5% (w/v)	Riedel-de Haen	[7647-14-5]	Synthesis of different type of modified resins
HCl	8.0 M	Merck	[7647-01-0]	Synthesis of nZVI-modified resins
HCl		Merck	[7647-01-0]	Acidification
(NH$_4$)(NO$_3$)	0.1 M	Sigma	[6484-52-2]	Desorption of As(III) and As(V) from nZVI-modified IRA 458
KH$_2$PO$_4$	0.1 M	Fluka	[7778-77-0]	Desorption of As(III) and As(V) from nZVI-modified IRA 458

Table 2.3. (cont.)

Reagent	Concentration used	Company	Cas no.	Purpose of use
KH$_2$PO$_4$	0.5 M	Fluka	[7778-77-0]	Desorption of As(III) and As(V) from nZVI-modified IRA 458
KH$_2$PO$_4$	1.0 M	Fluka	[7778-77-0]	Desorption of As(III) and As(V) from nZVI-modified IRA 458
NH$_3$	0.5 M	Merck	[7664-41-7]	Desorption of As(III) and As(V) from nZVI-modified IRA 458
NaOH (pellets)	0.1 M	Sigma-Aldrich	[1310-73-2]	Desorption of As(III) and As(V) from nZVI-modified IRA 458
NaOH (pellets)	5% (w/v)	Sigma-Aldrich	[1310-73-2]	Synthesis of different type of modified resins
NaOH (pellets)	0.5 M	Sigma-Aldrich	[1310-73-2]	Desorption of As(III) and As(V) from nZVI-modified IRA 458
NaOH (pellets)	0.10% (w/v)	Sigma-Aldrich	[1310-73-2]	Stabilization of NaBH$_4$ solution
Absolute Ethanol		Sigma	[64-17-5]	Synthesis of nZVI-modified resins
Absolute Ethanol		Sigma	[64-17-5]	Washing of nZVI-modified resins

2.4. Synthesis of Zero-Valent Iron Modified Sorbents

To synthesize nZVI-modified resins, iron(III) chloride hexahydrate ($FeCl_3$. $6H_2O$) and sodium borohydride ($NaBH_4$) were used for iron(III) and borohydride sources respectively. During the synthesis of these sorbents, iron was immobilized through two different types, namely anionic and cationic forms.

2.4.1. Synthesis of ZVI-Modified Sorbents with Cationic Form of Iron

The immobilization of iron as a cationic form (Fe(III)) to resin was performed with both batch and column types.

2.4.1.1. 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 resin (Amberlite IRA-458, Amberlite IRA-400, Amberlite IRA-67) was added to this solution and the mixture was kept waiting on a magnetic stirrer to be mixed for 24 hours. After that process, the vacuum filtration was applied and the mixed slurry was washed with water-ethanol in order 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, black solid sorbents were formed. Soon after all the $NaBH_4$ was added to the solution, reduction of Fe(III) to Fe(0) was occured. After adding all the borohydride solution to the mixture, it was left for another 10 minutes of stirring.

The reaction can be represented by the following redox reaction 2.1:

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

After the reduction, the vacuum filtration was applied to separate the synthesized ZVI-modified sorbents from liquid phase. Two sheets of blue band Whatman filter papers were used in the filtration process during which the solid particles were washed with the absolute ethanol to remove all of the water and this washing process is

probably the keystep of the synthesis because it prevents the rapid oxidation of the zero-valent iron nanoparticles. Finally, it was 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 2.2.
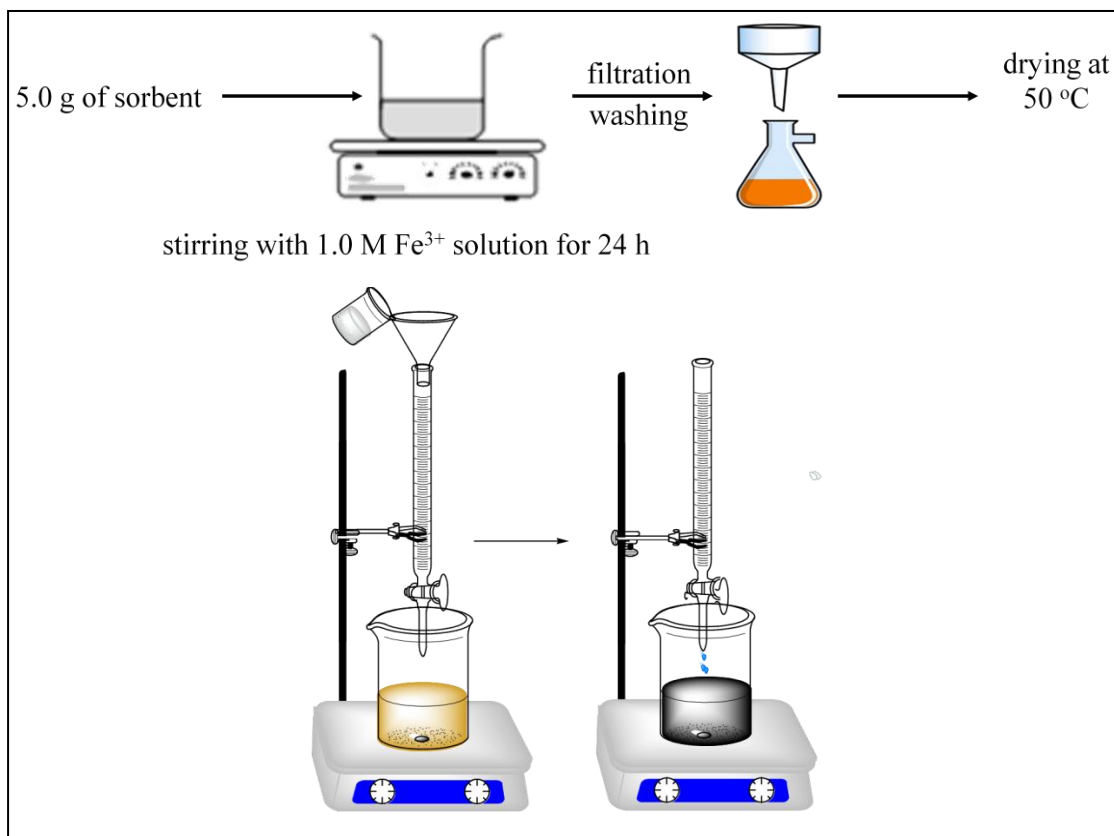
Figure 2.2. The pathway of the synthesis of ZVI-modified resin.

2.4.1.2. Column Type Immobilization

In the column type immobilization, first 13.52 g $FeCl_3.6H_2O$ was dissolved in the 50.0 mL water. Different from the batch type immobilization in which the resin was put in a baker, in the column type immobilization 5.0 g of resin (Amberlite IRA-458, Amberlite IRA-400 and Amberlite IRA-67) which swelled in water was filled in a column and Fe^{3+} solution was loaded three times onto resin. Later, resin was washed with water-ethanol in a column. After that resin was treated with 100 mL 3.5% (m/v) sodium borohydride to reduce the loaded Fe^{3+} ions to Fe^0. After the addition of all the $NaBH_4$ solution to the resin, the vacuum filtration was applied to separate the synthesized ZVI-modified sorbents from the liquid phase. The two sheets of blue band

Whatman filter papers were used in the filtration. At this stage, solid particles were washed with absolute ethanol so as to remove all the water. At last, 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 immobilization, due to the high pressure of H_2 gas released during the $NaBH_4$ reduction, the reduction process was difficult in the column. Additionally, zero-valent iron nanoparticals (nZVIs) synthesized with this method did not disperse homogeneous onto the resin surface. Owing to all these reasons, this method was not implemented again.
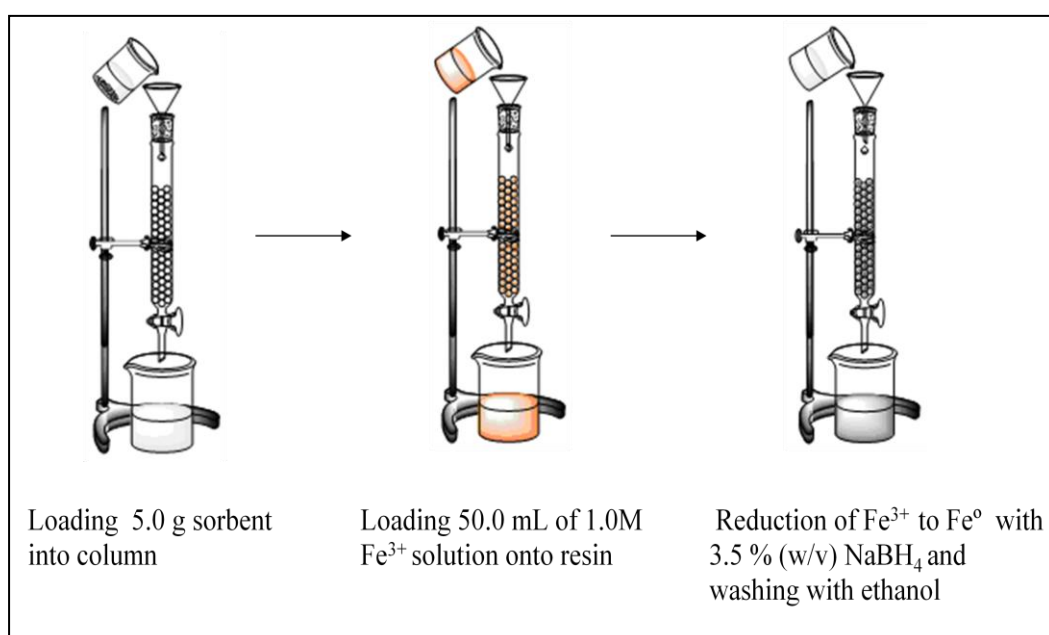
Figure 2.3. Phases of the synthesis of ZVI-modified resin
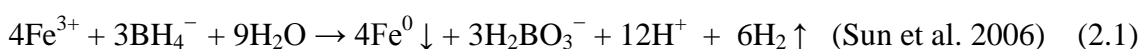
2.4.2. Synthesis of ZVI-Modified Sorbents with Anionic Form of Iron

The immobilization of iron as an anionic form ($FeCl_4^-$) to resin was performed with column type. In order to synthesize the modified resin, 13.52 g $FeCl_3.6H_2O$ was dissolved in the 50.0 mL 8 M hydrochloric acid (HCl) solution. Later, 5.0 g of resin (Amberlite IRA-458, Amberlite IRA-400 and Amberlite IRA-67) which swelled in water was filled in a column and $FeCl_4^-$ solution was loaded three times onto resin. Then, $FeCl_4^-$ treated resin was taken from the column. After that, the vacuum filtration was applied and mixed slurry was washed with water-ethanol. Afterwards, the treated

resin was put in a baker and batch type mixing was used in the reduction process in which 100 mL 3.5% (w/v) $NaBH_4$ solution was poured into a burette and gradually added 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 over to be stirred for another 10 minutes. The pathway of the synthesis of ZVI-modified resin is shown in Figure 2.4. To separate the black synthesized ZVI-modified 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 $^{\circ}$C overnight before being used.
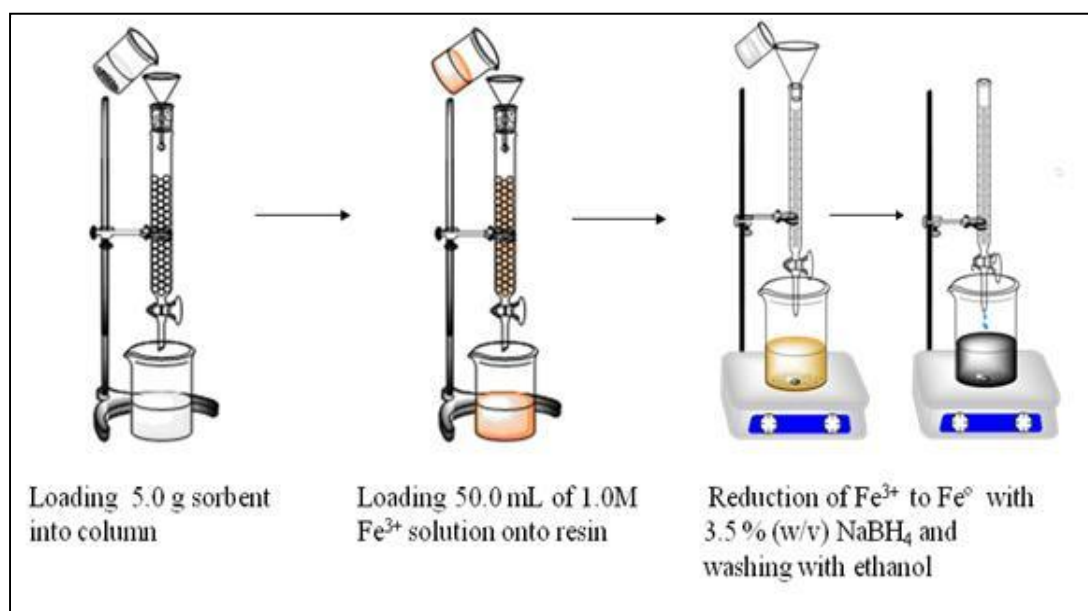
Figure 2.4. Pathway of the synthesis of ZVI-modified resin

2.4.3. Synthesis of Polymeric/Inorganic Hybrid Sorbents

While the ZVI-modified sorbents were being synthesized, the polymeric/inorganic hybrid sorbents (iron oxide based) which became a commercial resin product at literature were also synthesized. Then, these sorbents were tested in sorption studies and compared with the ZVI-modified sorbents.

At this process, first 13.52 g $FeCl_3.6H_2O$ was dissolved in the 50.0 mL 8 M hydrochloric acid (HCl) solution and 5.0 g of resin (Amberlite IRA-458, Amberlite

IRA-400, Amberlite IRA-67) which swelled in the water was filled in a column and $FeCl_4^-$ solution was loaded three times onto resin. The synthesis of polymeric/inorganic hybrid sorbent was also similar to the synthesis of ZVI-modified sorbents with anionic form of iron. Then, the treated resin was loaded 100 mL NaOH/NaCl solution 5% (w/v) - 5% (w/v), respectively. Later, polymeric/inorganic hybrid sorbents which contained hydrated iron oxide were synthesized. Finally, these sorbents were dried at 50 ºC for 24 h before being used.

2.5. Characterization of the Synthesized Sorbents

Characterization is a significant issue especially to explain the structure and properties of the synthesized sorbents, because the structural details may help to understand the possible interaction/sorption mechanisms between the arsenic species and the solid sorbents. For that reason, various methods were applied to characterize the synthesized sorbents. For instance; to learn the percentages of nitrogen, sulfur, hydrogen and carbon in the sorbents, elemental analysis was implemented. The images of the synthesized ZVI-modified sorbents were taken with the scanning electron microscopy (SEM). Additionally, in order to determine the point of zero charge of sorbents the potentiometric mass titration technique was used. Besides, the crystallographic properties together with thermal gravimetric degradation were also investigated by using X-Ray Diffraction (XRD) and TGA, respectively.

2.6. Sorption Studies

Batch type sorption and column type sorption experiments were carried out for all the sorbents which were synthesized during the optimization stage of the synthesis of ZVI-modified sorbents (ZVI-IRA 458, ZVI-IRA 400 and ZVI-IRA 67) and unmodified resins. The effects of the solution pH, amount of sorbent, shaking time, concentration of arsenic, reaction temperature on sorption were investigated seperately. The preliminary sorption conditions were determined as the following values: arsenic concentration was 10.0 mg/L or 0.10 mg/L, pH of the solution was 7.0, the volume of the solution was 20.0 mL, the shaking time was 120 min, the amount of sorbent was 50.0 mg, the temperature was 25.0 ºC. In all experiments, batch sorption was followed by the

filtration of the mixture through blue-band filter paper. Then, analysis of these filtrates were performed in order to determine their arsenic content with ICP-MS. Before ICP-MS determination, all filtrates were acidified with concentrated HNO_3 to form 1.0% (v/v) HNO_3 in the final solutions. The percentage of arsenic sorption was calculated using Equation 2.2, where Ci is the initial and Cf is the final concentration in the solution.

$$Sorption\ \% = \frac{c_i - c_f}{c_i} \times 100\% \qquad (2.2)$$

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

Table 2.4. Studied parameters and 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
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)	0.01, 0.1, 1.0, 10.0 and 100.0

2.6.1. Effect of Solution pH

Solution pH is one of the most important factor influencing the sorption of As species (arsenite As(III) and arsenate As(V)). Initial experiments were carried out with each sorbent; namely, ZVI-modified resin (ZVI-IRA 458) and unmodified resin (IRA 458) in order to investigate the interaction between the species of arsenic and the functional groups on the sorbents, and to find the optimum pH for sorption. 100 µg/L As(III) or As(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, and 10.0 with dilute HNO_3 or NH_3. From each of these solutions 20.0 mL was taken into 50 mL centrifuge tube and 50.0 mg sorbent was added. Then, the mixture was shaken on the thermostated water

bath shaker at 25 ºC for 120 minutes. Finally, the mixture was filtered to separate the sorbent and the filtrate was analyzed for its arsenic content with ICP-MS as explained previously section.

2.6.2. Effect of Sorbent Amount (Solid/Liquid Ratio)

The effect of the sorbent amount was investigated by using 5.0, 10.0, 25.0, 50.0 and 100.0 mg for unmodified resin (strong base anion exchanger IRA 458) and ZVI-modified resin (ZVI-IRA 458) while the other parameters were fixed at 100.0 μgL^{-1} arsenic concentration, 120 min shaking time, 20.0 mL solution volume, 25.0 °C sorption temperature and pH 7.0.

2.6.3. Effect of Shaking Time

Effect of the shaking time on the sorption of As(III) and As(V) by ZVI-IRA 458 and unmodified IRA 458 was investigated for time intervals of 1, 5, 15, 30, 60 and 120 minutes. The arsenic concentration, solution volume, sorbent amount, solution pH and reaction temperature were fixed at 100.0 µg/L, 20.0 mL, 50.0 mg, pH 7.0, and 25 ºC, respectively.

2.6.4. Effect of Initial As(III) and As(V) Concentrations

The sorption capacity of ZVI-IRA 458 and IRA 458 were also investigated for the initial As(III) and As(V) concentrations of 0.010, 0.10, 1.0, 10.0, 30.0, 60.0 and 100 mgL^{-1}. For this purpose, other parameters such as 60 min shaking time, 20.0 mL solution volume, 25.0 °C sorption temperature, pH 7.0 and 50.0 mg sorbent amount were fixed.

2.6.5. Studies Utilizing Synthesized ZVI-IRA 458 with Various Immobilization Types

Sorption studies were performed with commercial strong anion exchanger Amberlite IRA-458 modified through both batch process and column process. During these processes sorbents are named as unmodified IRA-458, ZVI-IRA 458(batch), ZVI-IRA 458(column), IRA 458-NaOH(batch), IRA 458-NaOH (column). In order to compare sorption capacity of these sorbents which were synthesized with various immobilization types, two different arsenic concentrations were studied. The sorption parameters were as follows; 0.10 mgL^{-1} and 10 mgL^{-1} As(III) or As(V) solutions, shaking time of 60 min, solution volume of 20.0 mL, sorbent amount of 50.0 mg, sorption temperature of 25 °C, the solution pH of 7.0. After shaking, the filtrated solutions were analyzed in ICP-MS.

2.6.6. Amount of Iron into/onto Modified Sorbents

In order to find out which synthesis type was the most efficient, synthesized sorbents were dissolved in nitric acid. As indicated in the results of "effects of solution pH", under pH 3 the iron which was immobilizied onto resin surface dissolved in solution. For this purpose, 50.0 mg different synthesized sorbent was added into the 50 mL centrifuge tube containing 20.0 mL of 1.0 M HNO$_3$ solution. The mixture 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 same resin on which the filter paper was used again for shaking by adding 20.0 mL 1.0 M HNO$_3$ solution. This process was repeated three times. Finally, after three filtration steps, all the filtrates were analyzed for their iron content by HGAAS.

2.6.7. Studies Utilizing Synthesized Various ZVI-modified Sorbents and Polymeric/Inorganic Hybrid Sorbents

Sorption experiments were performed with commercial ion exchanger resins (Amberlite IRA-458, Amberlite IRA-400 and Amberlite IRA-67) modified through column type immobilization with NaBH$_4$ (as described in 2.4.2 section) or NaOH/NaCl

(as described in 2.4.3 section). In order to compare the sorption capacities of these sorbents, two different arsenic concentrations were studied. The sorption parameters were as follows; 0.10 mgL^{-1} and 10 mgL^{-1} As(III) or As(V) solutions, shaking time of 60 min, solution volume of 20.0 mL, sorbent amount of 50.0 mg, sorption temperature of 25 °C, the solution pH of 7.0. After shaking, filtrated solutions were analyzed with ICP-MS.

In order to investigate which synthesis type and which resin were the most efficient, synthesized sorbents were dissolved in nitric acid. For this purpose, 50.0 mg different synthesized sorbents was added into the 50 mL centrifuge tube containing 20.0 mL of 1 .0 M HNO$_3$ solution (as descriped in 2.6.6 section). All filtrates were analyzed for the investigation of the amount of their iron content with HGAAS.

2.6.8. 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).

2.6.8.1. Effect of NaBH$_4$ Concentration in the Preparation of Modified Resin

In this section, the sorption experiments were performed for the determination of the most appropriate concentration of NaBH$_4$ which was used as a reducing agent in the synthesis of ZVI on the resin. For this purpose, firstly the amount of the iron which was loaded onto resin was determined by AAS. Then, according to the reaction which is represented by the following redox reaction 2.3, the stoichiometric factor was calculated for the concentration of NaBH$_4$ solution. Lastly, the sorption experiments were carried out with the synthesized ZVI-modified IRA 458 sorbent which was loaded with different concentration of NaBH$_4$ solution in ICP-MS.

$$4Fe^{3+} + 3BH_4^{-} + 9H_2O \rightarrow 4Fe^0 \downarrow + 3H_2BO_3^{-} + 12H^{+} + 6H_2 \uparrow \quad \text{(Sun et al. 2006)} \quad (2.3)$$
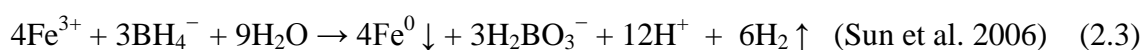
2.6.8.2. Studies for the Removal of Boron

Sorption and sorbent optimization studies pointed out that the control of the boron concentration which passed into the solution was another important issue. During the sorption experiments, a useful sorbent was developed for the removal of arsenic but the amount of boron which passed from ZVI-modified resin to water reached very critical values. The results showed that the values of the boron concentration were greater than the maximum contaminant level. In order to eliminate the high concentration of boron in water, experiments were performed with Amberlite IRA 743 chelating resin which has the selectivity for boric acid and borate ion. At this stage, the optimization of the removal of boron was attempted using three different methods.

In the first method, the sample was treated with the synthesized ZVI-modified IRA 458 (batch type) and IRA 743 (column type), respectively. As the first resin provided the removal of arsenic, the removal of boron from solution was aimed with second resin. This method was similar to the previous batch type sorption (as described in 2.6. section). 50.0 mg of ZVI-IRA 458 was shaken with 20.0 mL of 0.10 mgL^{-1} As(III) or As(V) for 60 min. After shaking, filtrate was poured through the column which was filled with 100.0 mg of IRA 743. The two column type sorption parameters were: the solution volume of 20.0 mL and the flow rate of 1.0 mL/min.

In the second method, column was filled with the equal amount of ZVI-IRA 458 and IRA 743 (column type). Firstly, the solution interacted with ZVI-IRA 458 and then interacted with IRA 743 as it flowed through the column. The two different columns were used for the sorption of As(III) and As(V). The column type sorption parameters were: 0.10 mgL^{-1} As(III) or As(V) solutions, solution volume of 20.0 mL, sorbent amount of 100.0 mg and the flow rate of 1.0 mL/min.

In the last method, column was filled with the equal amount of ZVI-IRA 458 and IRA 743 (column type) resins which were mixed homogenously. For the sorption of As(III) and As(V), two different column were used. The column type sorption parameters were: 0.10 mgL^{-1} As(III) or As(V) solutions, solution volume of 20.0 mL, sorbent amount of 100.0 mg and the flow rate of 1.0 mL/min.

All the samples were analyzed with ICP-MS.

2.6.9. Effect of Reaction Temperature

The sorption efficiency of a sorbent may change with the reaction temperature. Thus, the effect of the temperature on the sorption of arsenic was investigated at 25.0 °C, 40.0 °C and 60.0 °C. The other parameters were fixed at 100.0 µgL^{-1} arsenic concentration, 20.0 mL solution volume, 50.0 mg sorbent amount and pH 7.0. The results were also used to investigate the thermodynamic parameters of sorption ($\Delta G°$, $\Delta S°$ and $\Delta H°$) utilizing the well-known Equations 2.4, 2.5, and 2.6 (Atkins and de Paula 2002; Yersel et al. 2005):

$$\Delta G° = -RTlnR_d \qquad (2.4)$$

$$\Delta H° = Rln\frac{R_d(T_2)}{R_d(T_1)}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1} \qquad (2.5)$$

$$\Delta S = \frac{\Delta H° - \Delta G°}{T} \qquad (2.6)$$

R_d (mL/g) is the ratio of arsenic ions distributed between solid (sorbent) and liquid phase at equilibrium and is defined by the Equation 2.7.

$$R_d = \frac{C_{solid}}{C_{liquid}} \qquad (2.7)$$

C_{solid} is the concentration of arsenic in sorbent (mg/g) and C_{liquid} is the concentration of arsenic ions in solution after sorption (mg/L).

2.6.10. Effect of Solution pH on the Organoarsenic Sorption

In order to investigate the effect of pH on the sorption of organoarsenic (DMA, MMA and AsB), 100 µgL^{-1} standard solutions were prepared. Dilute HNO_3 and NH_3 were used to adjust the pH at 4.0, 5.0, 7.0, 8.0 and 10.0. The other parameters and process were similar to previously mentioned in section 2.6.1.

2.7. Desorption Studies

Desorption of As(III) and As(V) species from ZVI-modified commercial strong ion exchanger resin Amberlite IRA-458 (ZVI-IRA 458) were investigated by the means of various eluents. Different desorption matrices have been studied to seek whether the sorbent in desorbing solution dissolved or not. Desorption eluents are given in Table 2.5. The standards for drawing calibration curve were prepared in the same matrix of each desorption solutions. Both the ICP-MS and the HGAAS were used for the analysis. In order to determine the arsenic concentration for heavy matrices, the HGAAS was used. Before HGAAS both samples and standarts were acidified with concentrated HCl to form 1.0% (v/v) of HCl in the final solution. Arsenic signal for As(V) was obtained by reducing As(V) to As(III) by adding 0.50% (w/v) L-cystein into the both sample solutions and standards.

Table 2.5. Desorption Eluents.

Eluents
0.1 M NaOH
0.5 M NaOH
0.5 M NH_3
0.1 M $(NH_4)(NO_3)$
0.1 M HNO_3
0.5 M KH_2PO_4
0.1 M KH_2PO_4
1.0 M KH_2PO_4
2% (m/v) NaOH + 3% (m/v) NaCl
5% (m/v) NaOH + 3% (m/v) NaCl

2.8. Method Validation with Spiked Samples

ZVI-modified commercial strong ion exchanger resin Amberlite IRA 458 (ZVI-IRA 458) was used on the sorption of arsenate and arsenite ions in various types of water samples. In order to investigate the sorption efficieny of sorbents, four types of water samples (tap water from İYTE, tap water from Gülbahçe, river water from İYTE, rain and sea water) were spiked with As(III) or As(V) standard solutions. The spike concentration was 100.0 μgL^{-1} while the other parameters were as follows: solution pH 7.0, shaking time 60 min, solution volume 20.0 mL and reaction temperature 25.0 °C.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Characterization of the Sorbents

In order to elucidate the elemental content, structural features, morphology and particle size of the sorbents, scanning electron microscopy (SEM), thermo gravimetric analysis (TGA), and X-Ray Diffraction (XRD) were used.

3.1.1. Commercial and ZVI-Modified Ion Exchange Resins

The surfaces and structures of synthesized and commercial sorbents were investigated using scanning electron microscopy (SEM) and optical microscopy (OM). The optical images of unmodified and ZVI-modified resins are displayed in Figure 3.1.
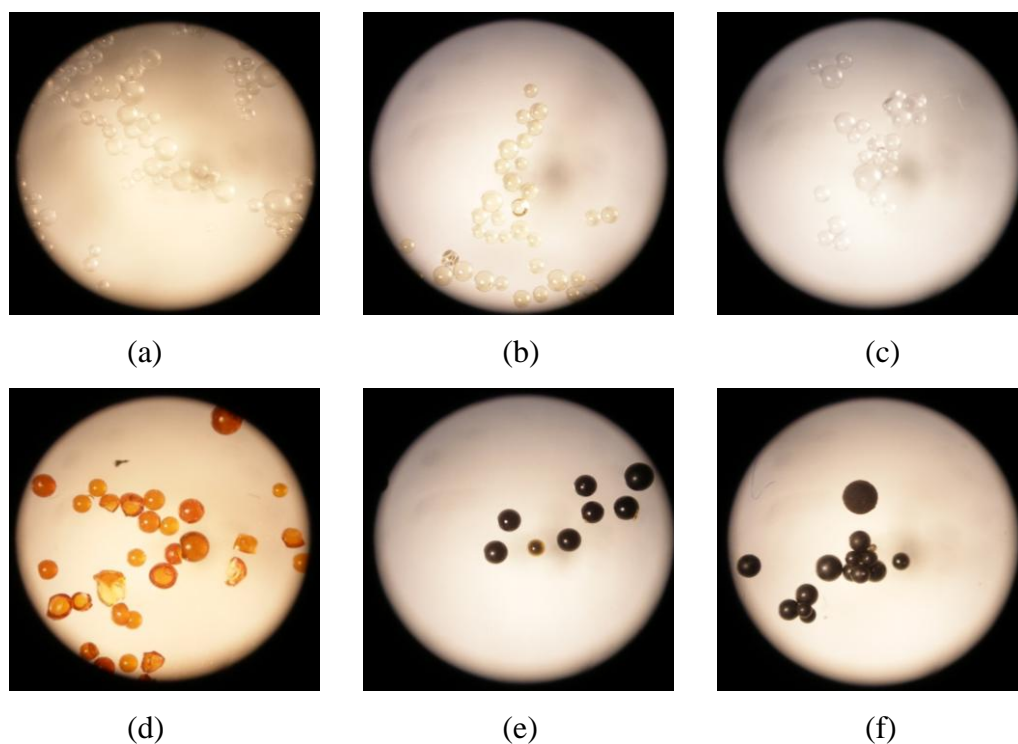

Figure 3.1. Optical images of (a) IRA 67, (b) IRA 400, (c) IRA 458; (d) ZVI-IRA 67, (e) ZVI-IRA 400, (f) ZVI-IRA 458.

As shown in the Figure 3.1, the unmodified anion exchange resins are transparent before modification. When modified with ZVI, their colours changed. Moreover, Table 3.1 lists the properties of the resins used in the study.

Table 3.1. The properties of the anion exchange resins used in this study.

Resins	Amberlite IRA 67	Amberlite IRA 400	Amberlite IRA 458
Type	Weakly basic anion exchanger	Strongly basic anion exchange	Strongly basic anion exchange
Functional Group	Tertiary amine	Quaternary ammonium	Quaternary ammonium
Matrix	Crosslinked acrylic-DVB	Polystyrene-DVB	Crosslinked acrylic-DVB

As explained in the synthesis of these sorbents (Section 2.4), anionic and cationic salts of iron were used in loading the resin. The immobilization of iron in cationic form (Fe(III)) to resin was carried out by both batch and column methods. In the "batch" type immobilization (Section 2.4.1.1), $NaBH_4$ was added drop by drop into the resin which was stirred in Fe^{3+} solution. On the other hand, in the "column" type immobilization (Section 2.4.1.2), the resin which was filled in a glass column was treated first with Fe^{3+} solution and then $NaBH_4$. In the immobilization of iron in anionic form (Fe(III)) to resin, $FeCl_3$ was dissolved in 8.0 M HCl (therefore, converted to $FeCl_4^-{}_{(aq)}$) and the resin which was filled into the column was loaded with $FeCl_4^-$ (Section 2.4.2). The SEM images of these ZVI-modified and unmodified Amberlite IRA 458 resin are given in Figure 3.2. The bright spots on the SEM images belong to iron particles on the resin surface. In the column type synthesized resins (e and f), the annular shapes where the resin spheres contact with each other represent highly intense iron particle formation. Figure 3.3 shows the resins which were loaded with iron in anionic form and later treated with $NaBH_4$ for reduction.
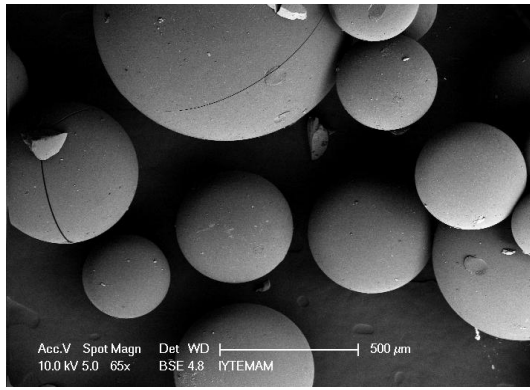
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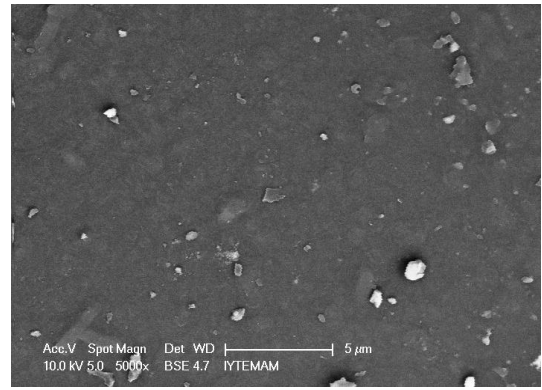
(b)
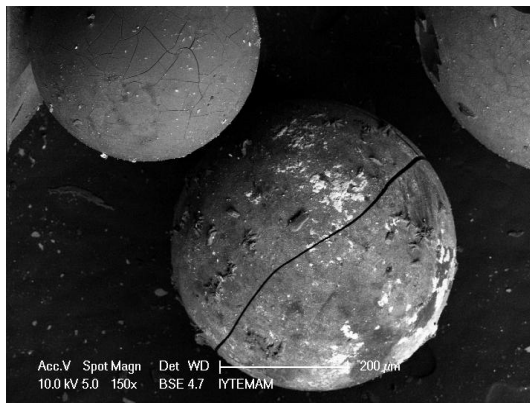
(c)
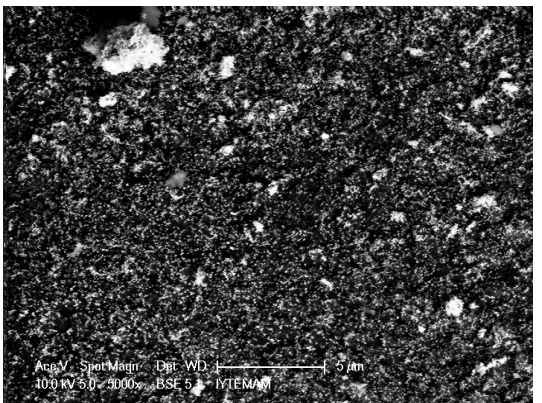
(d)
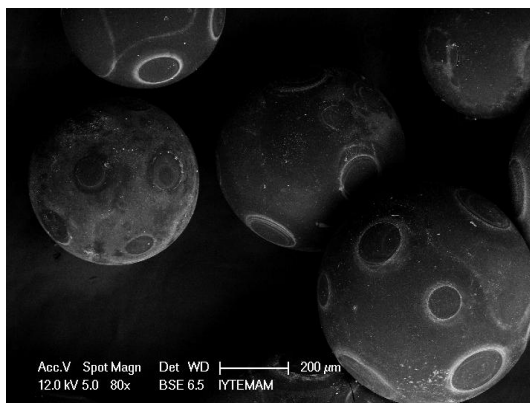
(e)
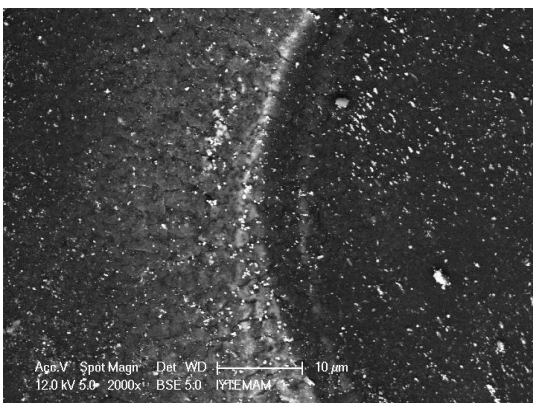
(f)

Figure 3.2. SEM images of (a), (b) IRA 458; (c), (d) ZVI-IRA 458 (batch type modification); (e), (f) ZVI-IRA 458 (column type modification).

(a)   (b)
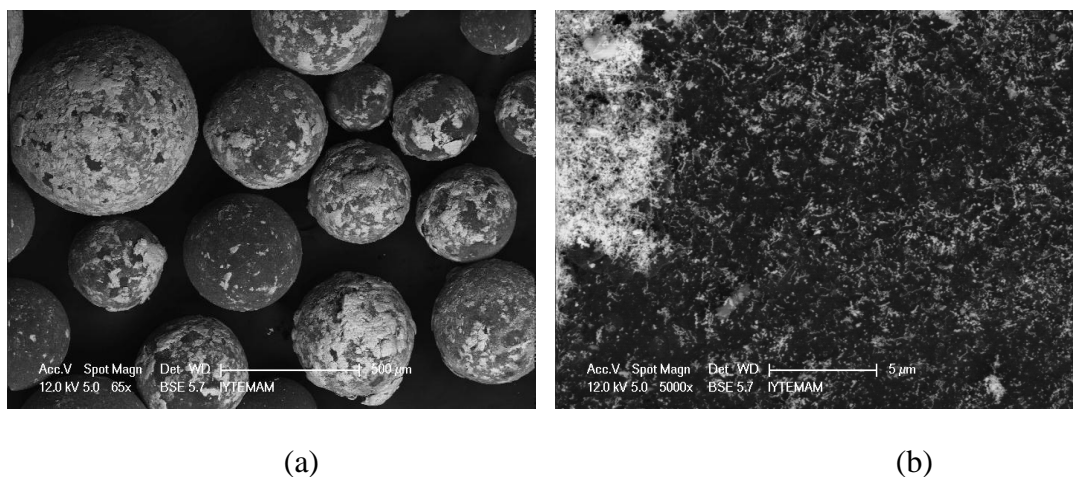
Figure 3.3. SEM images of ZVI-IRA 458 loaded with $FeCl_4^-$ (in 8.0 M HCl)

The amount of loaded iron onto the modified resins was derived from the atomic absorption spectrometric determination of the concentration of iron that passed into the solution as a result of nitric acid treatment. The results are given in Table 3.2. It is expected for strong anion exchanger resin (Amberlite IRA 458) to adsorb the anionic form of iron in a higher amount. Results showed that anionic form of iron ($FeCl_4^-$) was loaded onto resin surface two times higher than cationic form (Fe^{3+}). SEM images also proved this idea. Therefore, further modifications were done using anionic form of iron ($FeCl_4^-$).

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

| Sorbents | mgFe/g sorbent | Sorption (%) | | | |
| | | As(III) | | As(V) | |
		0.1 ppm	10.0 ppm	0.1 ppm	10.0 ppm
ZVI-IRA 458 Batch (Fe^{3+} form)	28.99	96.76	83.97	98.81	99.66
ZVI-IRA 458 Column (Fe^{3+} form)	37.94	95.65	95.56	99.02	99.91
ZVI-IRA 458 ($FeCl_4^-$ form)	69.20	98.27	96.78	99.73	99.45

In addition, the amount of iron loaded onto the surface of ion-exchange resins was compared after two types of modification; the first method was the modification by $NaBH_4$ reduction (our method), and the second method was the formation of ion-oxide species on the surface after NaOH/NaCl treatment (DeMarco et al. 2003; Cumbal and SenGupta 2005). As mentioned in the synthesis of polymeric/inorganic hybrid sorbents (Section 2.4.3), iron that was loaded in anionic form was oxidized to iron oxide particles by NaOH/NaCl solution. These two methods were tested with different commercial resins; Amberlite IRA 458 (strong anion exchanger), Amberlite IRA 67 (weak anion exchanger), and Amberlite IRA 400 (strong anion exchanger). The SEM images of these resins which were treated with iron and reduced by $NaBH_4$ or NaOH/NaCl solution in addition to the unmodified, are given in Figure 3.4. As the figure illustrates, the strong anion exchange resins uptake higher amount of iron than the weak anion exchange resin. The amount of iron loaded onto the modified resins is given in Table 3.3.

Table 3.3. The amount of iron immobilized with different modifications onto resin surface

Sorbents	mg Fe / g sorbent	mg Fe / 50mg sorbent
ZVI-IRA 67/BH_4	58.4	2.9
ZVI-IRA 67/OH	55.2	2.8
ZVI-IRA 400/BH_4	31.0	1.6
ZVI-IRA 400/OH	35.8	1.8
ZVI-IRA 458/BH_4	69.2	3.5
ZVI-IRA 458/OH	83.0	4.2
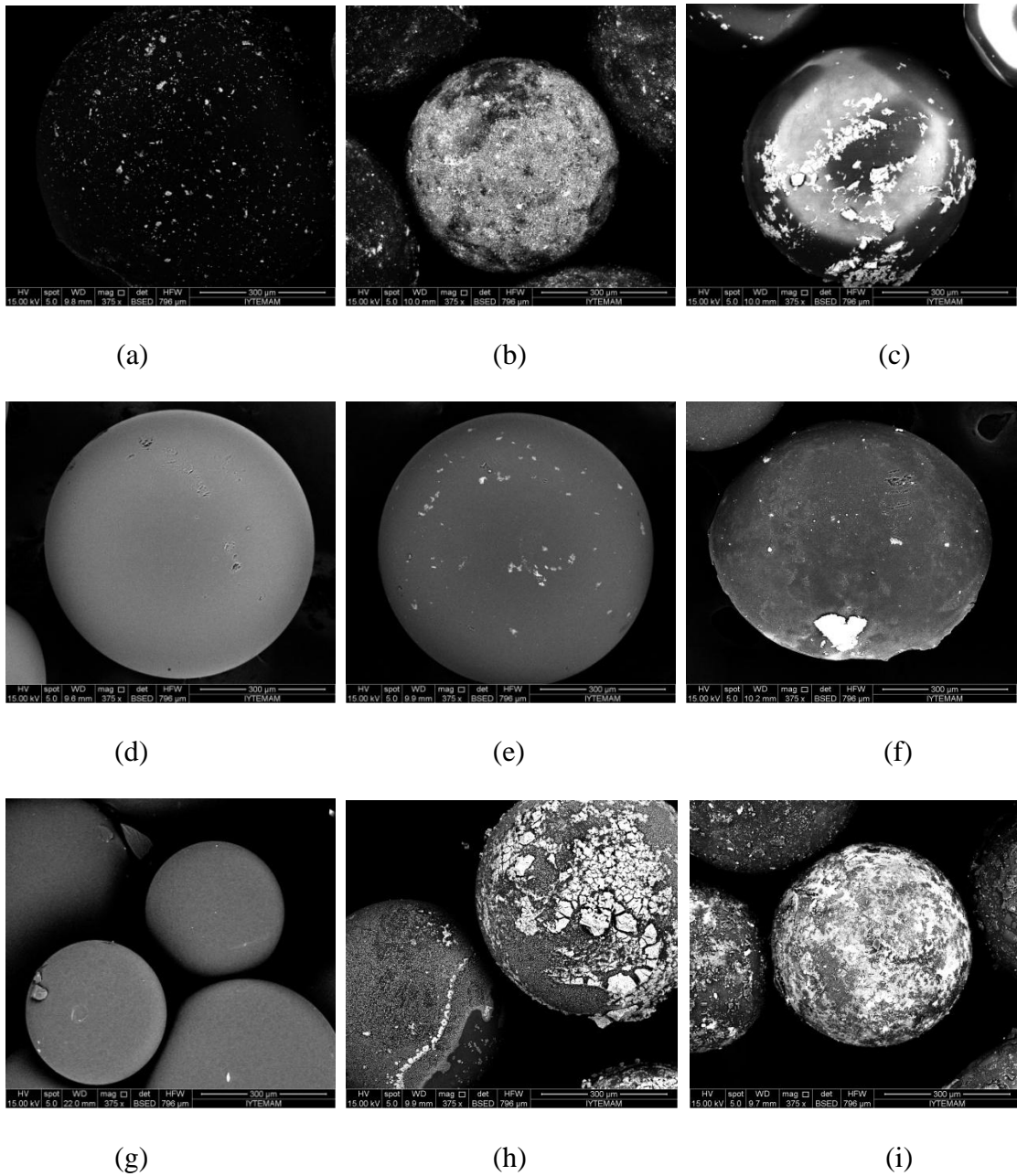
Figure 3.4. SEM images of (a) IRA 67, (b) ZVI-IRA 67/OH, (c) ZVI-IRA 67/BH$_4$; (d) IRA 400, (e) ZVI-IRA 400/OH, (f) ZVI-IRA 400/BH$_4$; (g) IRA 458, (h) ZVI-IRA 458/OH (i) ZVI-IRA 458/BH$_4$.

The modified resins were tried to be crushed and examined under SEM; also, their EDX spectra were taken. The images and EDX spectra (Figure 3.5) demonstrate that the zero valent iron not only occurs on the surface of the resins but also inside them.
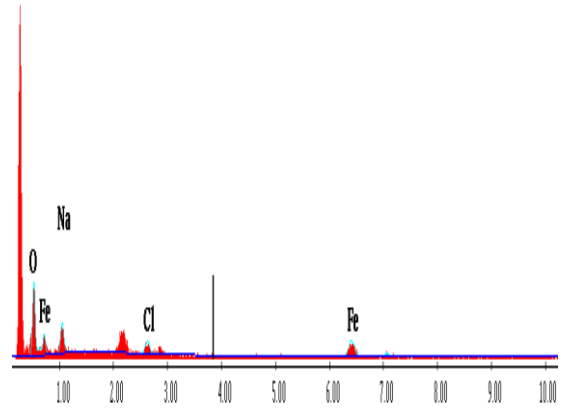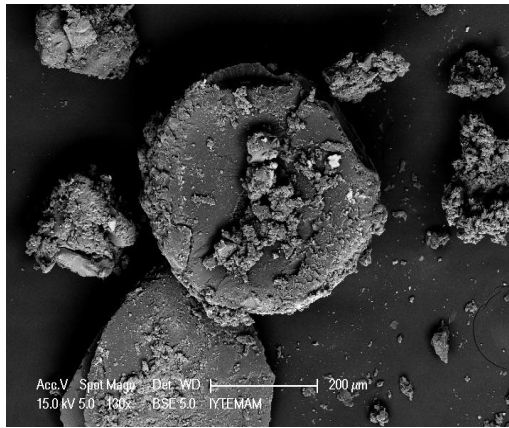
(a)
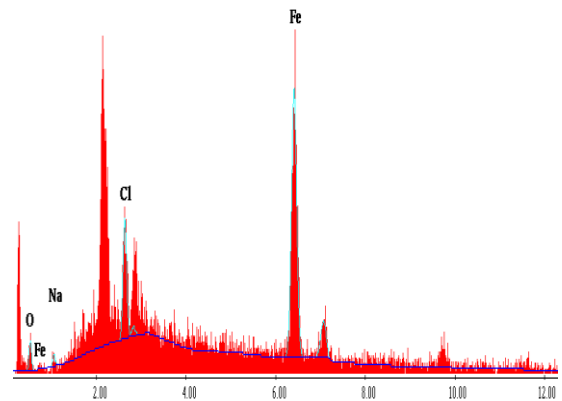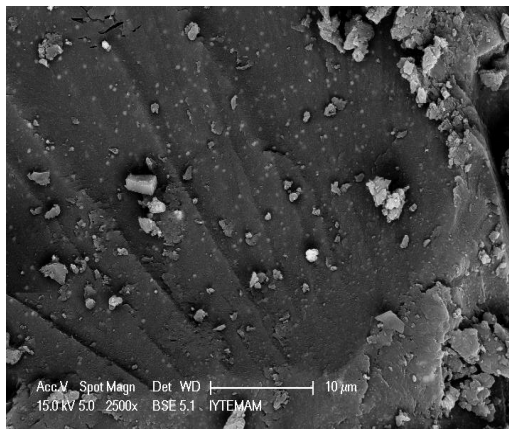
(b)
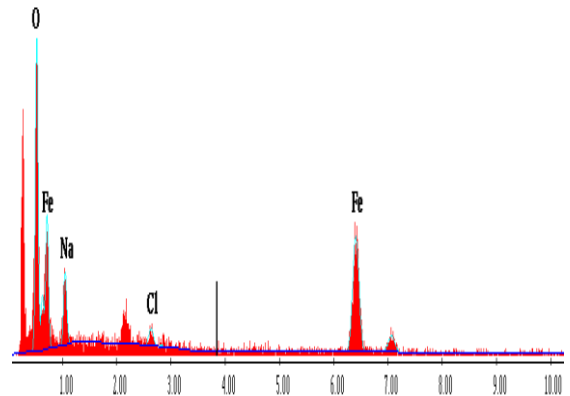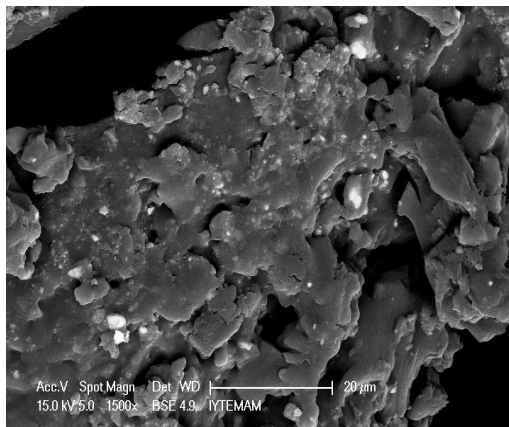
(c)

Figure 3.5. SEM images and corresponding EDX spectra of (a) ZVI-IRA 67, (b) ZVI-IRA 400, and (c) ZVI-IRA 458.

Thermo gravimetric analysis (TGA) was applied to the unmodified IRA 458 resin and to the modified sorbents to investigate the degree of modification by observing the change in percent weight of the samples with temperature change. As shown in Figure 3.6, unmodified and ZVI-modified IRA 458 resins reveal approximately 12% weight loss between 0-200°C due to the vaporization of water adsorbed on the surface of resin. Also, thermal behavior of the unmodified and modified sorbents show similar weight losses between 280-800°C because of the thermal decomposition of the functional groups.
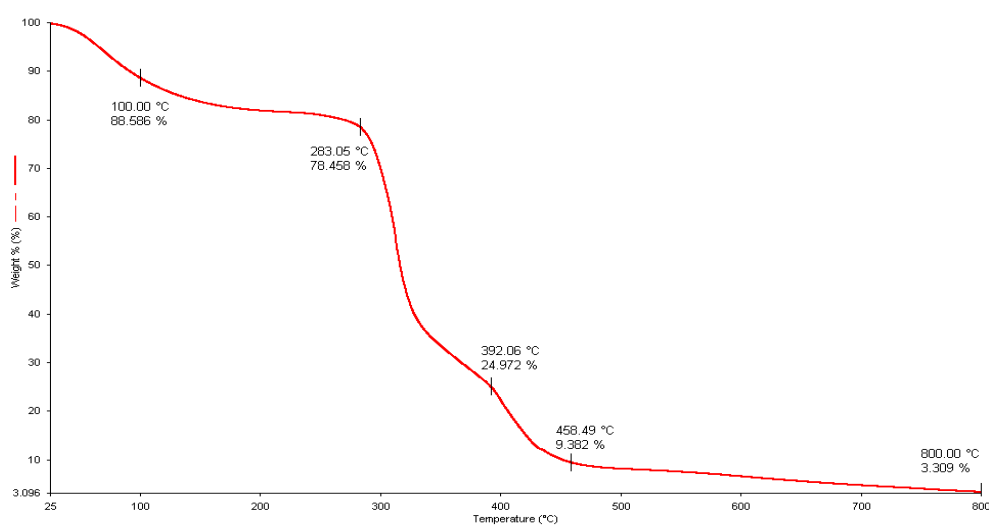
(a)
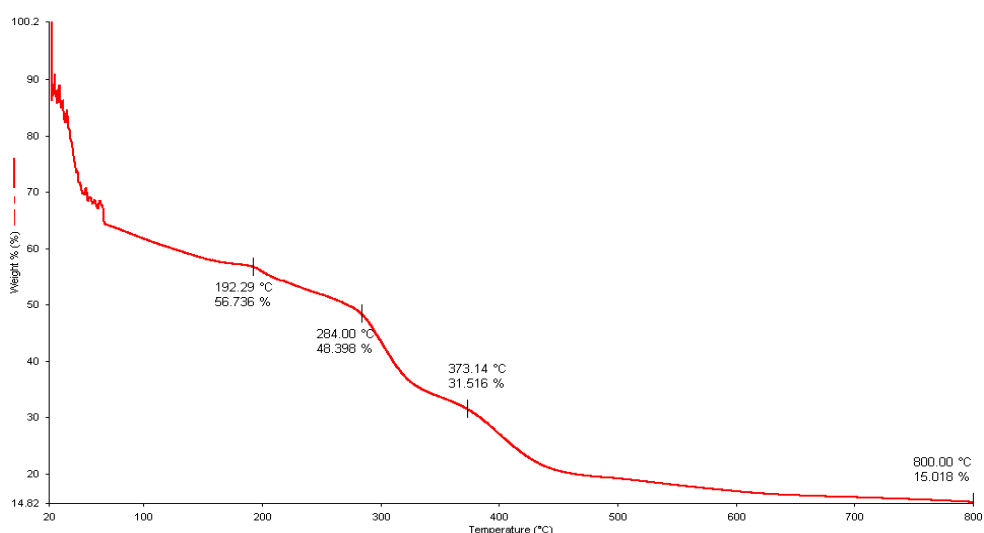
(b)

Figure 3.6. TGA curves of (a) unmodified IRA 458, (b) ZVI-IRA 458

Various iron species such as Fe(0), Fe_2O_3, Fe_3O_4 and FeOOH, are expected to occur on the surface of the resins upon treatment. In order to enlighten the surface, the XRD patterns were obtained. One of these, the XRD pattern of ZVI-IRA 458, shown in Figure 3.7 indicates the presence of Fe(0) ($2\theta \sim 45°$) in addition to the other peaks.
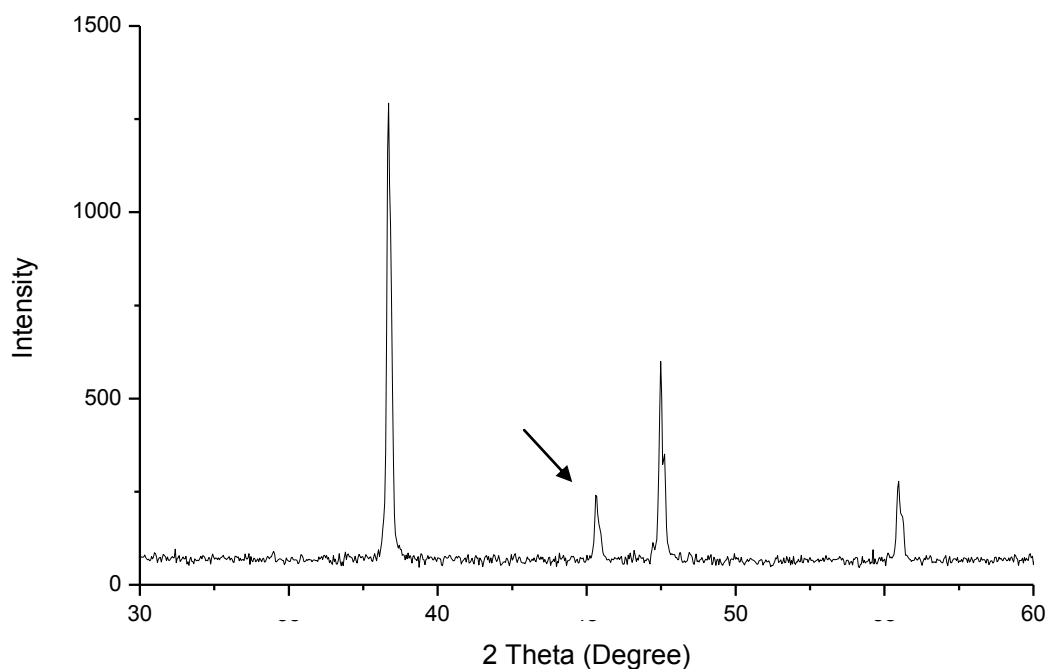
Figure 3.7. XRD pattern of ZVI-IRA 458.

3.2. Calibration Plots

3.2.1. Calibration Curves for As(III), As(V), DMA, MMA and AsB Using ICP-MS

Figure 3.8 shows signal intensity versus concentration for As(III), As(V), DMA, MMA and AsB standards obtained with ICP-MS. The limit of detection (LOD) based on 3s was calculated as 0.0178 μgL^{-1} and limit of quantification (LOQ) based on 10s was 0.0595 μgL^{-1}.
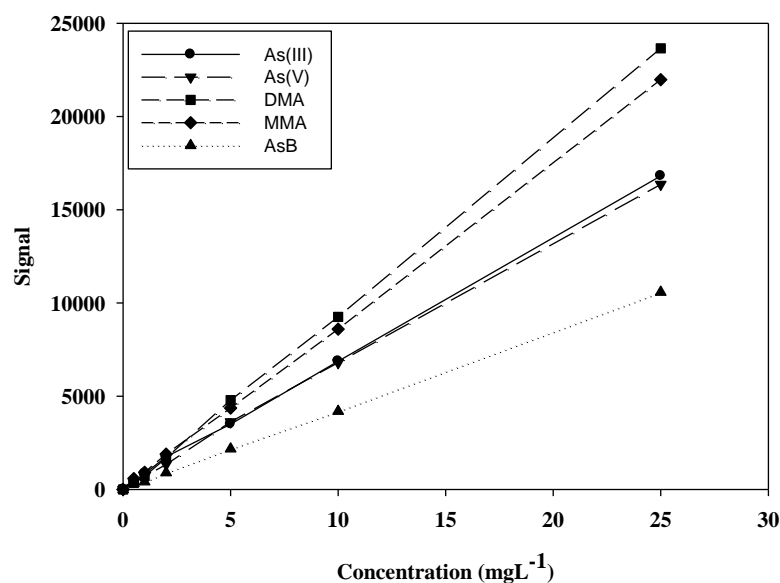
Figure 3.8. Calibration plots of As(III), As(V), DMA, MMA and AsB. (●) As(III) (y=667.4x+164.35,R^2=0.9995),(▼)As(V) (y=653.06x+124.35,R^2=0.9995), (■) DMA (y=950.25x−125.52, R^2=0.9998), (♦) MMA (y=874.17x+43.183, R^2=0.9998), (▲) AsB (y=421.04x+39.222, R^2=0.9998)

3.2.2. Calibration Curves for As(III) Using HGAAS

Figure 3.9 illustrates the plot of absorbance versus As(III) concentration using HGAAS. The limit of detection (LOD) based on 3s was calculated as 0.1249 μgL^{-1} and limit of quantification (LOQ) based on 10s was 0.4164 $\mu g\ L^{-1}$.
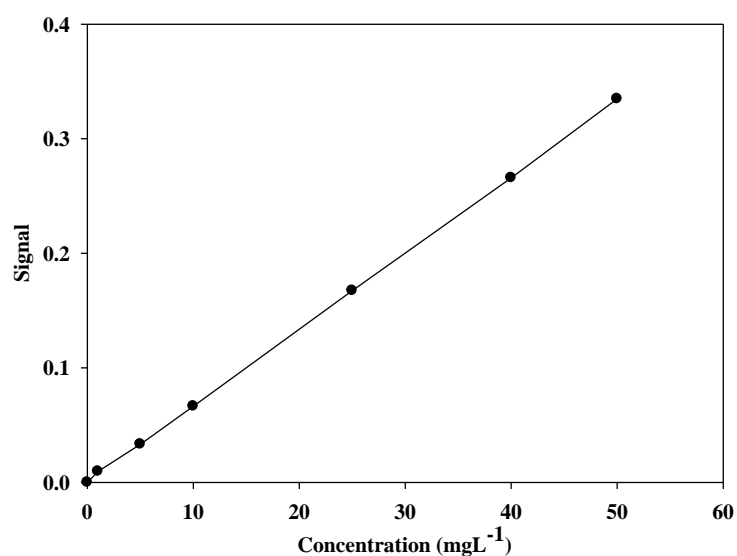
Figure 3.9. Calibration plot of As(III) with HGAAS. (y=0.0067x + 0.0007, R^2=0.9999)

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3.3. Sorption Studies

For all ZVI-modified sorbents (ZVI-IRA 458, ZVI-IRA 400 and ZVI-IRA 67) and unmodified resins, both batch type and column type sorption experiments were performed. Effects of solution pH, amount of sorbent, shaking time, arsenic concentration and reaction temperature on sorption were investigated separately.

3.3.1. The Sorption Studies Utilizing Various Iron-Based Resins

Anion exchange resins (IRA 458, IRA 400 and IRA 67) loaded with nano zero-valent iron were tested and compared with the polymeric/inorganic hybrid sorbents (iron oxide based) which have been commercialized as described in literature (DeMarco et al. 2003; Cumbal and SenGupta 2005). The synthesis method and the sorption properties of these resins were also compared as described in section 2.6.7. For the investigation of the sorption capacity, IRA 458, IRA 400 and IRA 67 resins were used in sorption of arsenite and arsenate.

The sorption studies for As(III) and As(V) were performed with unmodified resins (IRA 458, IRA 400 and IRA 67), zero-valent iron modified resins (ZVI-IRA 458, ZVI-IRA 400 and ZVI-IRA 67) and iron oxide modified resins (IRA 458-OH, IRA 400-OH and IRA 67-OH) at two different concentrations (0.10 mgL^{-1} and 10.0 mgL^{-1}). In addition, the sorption performances of the resins were compared.

The sorption results of the investigated sorbents are given in Table 3.4 and Table 3.5 for As(III) and As(V), respectively.

As illustrated in Table 3.4, the three unmodified resins (IRA 458, IRA 400 and IRA 67) showed no sorption for As(III) at 0.10 mgL^{-1} level whereas a very small sorption (< 8.3 (±2.7)%) at 10.0 mgL^{-1} level. The resins prepared by both modification methods showed similar As(III) sorption features at 0.10 mgL^{-1} concentration and the sorption capacity reached 90.0% values. Modified IRA 67 and IRA 400 resins obtained by modifying the resins with zero-valent iron and iron oxide showed 61% - 75% for modified IRA 67 and 61% - 54% for modified IRA 400 at 10.0 mgL^{-1} arsenite concentration. As mentioned previously in Section 3.1.1, the strong anion exchange resin IRA 458 was loaded with the highest amount of iron. As(III) sorption results showed that the zero-valent iron-modified IRA 458 reached a very high sorption value

even at the concentration of 10.0 mgL^{-1}. The results also provided with information about the highest amount of the iron immobilization. For ZVI-IRA 458 and IRA 458-OH sorbents, these sorption values were 92% and 94%, respectively.

Although both IRA 400 and IRA 458 strong base anion exchange resins have "quaternary ammonium" groups, it is thought that the reason of displaying differences in loaded iron amount together with sorption of arsenic is due to the presence of different polymer matrices. IRA 458 has a hydrophilic acrylic polymer matrix which enables the interaction between functional groups and iron solution more easily. On the other hand, IRA 400 has styrene/divinylbenzene matrix which is more hydrophobic than IRA 458 matrix and therefore, it has less interaction between functional groups with iron solution.

Table 3.4. Effect of initial As(III) concentration on the sorption efficiency for various sorbents. (50.0 mg sorbent amount, at pH 7.0 in 20.0 mL As(III) solution, 60 min shaking time, 25.0 °C reaction temperature)

	Sorption (%)	
Sorbents	**0.10 mg/L As(III)**	**10.0 mg/L As(III)**
IRA 67	~ 0	5.8 (±1.6)
ZVI-IRA 67/OH	88.8 (±0.6)	61.1 (±3.8)
ZVI-IRA 67/BH$_4$	92.8 (±1.1)	75.1 (±1.8)
IRA 400	~ 0	8.3 (±2.7)
ZVI-IRA 400/OH	89.5 (±1.3)	61.2 (±1.8)
ZVI-IRA 400/BH$_4$	92.3 (±0.2)	53.8 (±0.3)
IRA 458	~ 0	0.4 (±0.6)
ZVI-IRA 458/OH	94.5 (±0.6)	91.9 (±1.3)
ZVI-IRA 458/BH$_4$	92.8 (±1.3)	93.6 (±0.2)
nZVI	95.6 (±0.2)	99.1 (±0.2)

As mentioned in the previous paragraphs, the concentration experiments were repeated for As(V). Table 3.5 shows the effect of initial As(V) concentration on the sorption efficiency for the same sorbents described above. Unmodified IRA-458 and IRA-400 strong anion exchange resins showed a very high sorption (> 95%) at both

concentrations. Despite this fact, the results indicated that IRA 67 weak anion exchange resin showed no sorption. The strong anion exchange resins (ZVI-IRA 400/IRA 400-OH and ZVI-IRA 458/IRA 458-OH) modified by both methods showed similar sorption capacities compared to unmodified resins (IRA 400 and IRA 458). At this stage, the iron modification appears not to be necessary for As(V) sorption, since the unmodified resins have high sorption for this oxidation state already. However, for As(III) sorption/removal, modification of the resin with nZVI is required due to the irresponsive nature of the commercial resins to the lower oxidation state. If anaerobic (unoxygenated) conditions are taken into consideration, the importance of modification arises in the case of arsenic removal from contaminated underground water. While the modification of weak anion exchange resin with zero-valent iron or iron oxide showed no significant differences at 0.10 mgL^{-1} arsenate concentration, the results indicated that the zero-valent iron modified resin was observed to have a higher sorption at 10.0 mgL^{-1} concentration. These results which show quite different sorption behavior for As(III) illustrated that "quaternary ammonium" functional groups of strong anion exchange resin were active in the sorption of As(V). In the absence of "quaternary ammonium" groups (as IRA 67 resin), zero-valent iron or iron oxide particles were effective in the sorption.

Table 3.5. Effect of initial As(V) concentration on the sorption efficiency for various sorbents. (50.0 mg sorbent amount, at pH 7.0 in 20.0 mL As(V) solution, 60 min shaking time, 25.0 °C reaction temperature)

	Sorption (%)	
Sorbents	**0.10 mg/L As(V)**	**10.0 mg/L As(V)**
IRA 67	5.1 (±2.6)	12.3 (±2.4)
ZVI-IRA 67/OH	93.8 (±1.4)	62.7 (±3.4)
ZVI-IRA 67/BH$_4$	96.2 (±0.7)	98.6 (±0.1)
IRA 400	95.7 (±0.1)	99.2 (±0.1)
ZVI-IRA 400/OH	96.8 (±0.2)	99.4 (±0.1)
ZVI-IRA 400/BH$_4$	96.1 (±0.5)	99.3 (±0.2)
IRA 458	95.9 (±0.3)	99.2 (±0.1)
ZVI-IRA 458/OH	94.6 (±1.8)	99.2 (±0.1)
ZVI-IRA 458/BH$_4$	93.7 (±1.4)	99.1 (±0.1)
nZVI	96.8 (±0.2)	99.8 (±0.1)

3.3.2. Optimization Studies of ZVI-IRA 458

According to the sorption results explained in the previous paragraphs, Amberlite IRA 458 resin was considered to be the most suitable immobilization matrix, since it has shown the best sorption performance upon modification with nZVI.

3.3.2.1. Effect of NaBH$_4$ Concentration in the Preparation of Modified Resin

The sorption experiments were performed with zero-valent iron modified-IRA 458 resin in order to investigate the optimization of the Fe(0) reduction step by determining the concentration of NaBH$_4$. In this study, firstly the amount of iron loading was determined by AAS. Then, according to the redox reaction 3.1 formulated below, the required concentration of NaBH$_4$ solution was calculated from the stoichiometric factor. At the specified experimental conditions, the stoichiometric concentration was found to be 0.050 M NaBH$_4$. Different concentrations of NaBH$_4$ solution were also tested. The results are given in Table 3.6.

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0\downarrow \ + 3H_2BO_3^- \ + 12H^+ \ + \ 6H_2\uparrow \quad \text{(Sun et al. 2006)} \quad \text{(3.1)}$$
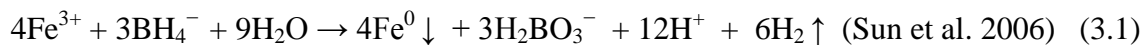
Table 3.6. Effect of NaBH$_4$ concentration on the amount of iron loading on IRA 458.

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

Figure 3.10 displays the results of the As(III) sorption performed with resins which were modified with the use of different concentrations of NaBH$_4$. The results illustrated that increasing NaBH$_4$ concentration also increased the sorption of arsenite. At the first point, unmodified resin was used and the sorption was 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 As(III) was about 60%. Here, it must be reminded that the experiments were performed with 50.0 mgL^{-1} As(III) solution which was very well above the legal limit of 0.010 mgL^{-1}. As verified by these experiments, 0.15 M NaBH$_4$ concentration which was 3 times the stoichiometric factor was chosen for further studies and in this concentration BH$_4^-$/Fe^{3+} ratio was approximately 2.5.

Figure 3.11 shows the results of the As(V) sorption performed with resins modified with different concentrations of NaBH$_4$ solution. The concentration of As(V) was 100.0 mgL^{-1}. As depicted in Figure 3.11, unmodified IRA 458 resin showed approximately 60% sorption. Then, the sorption decreased at 0.05 M NaBH$_4$ and stayed almost constant from 0.15 to 0.50 M NaBH$_4$. Excess amount of reducing agent should be used so that the reaction can take place and zero-valent iron on the resin surface can be formed.
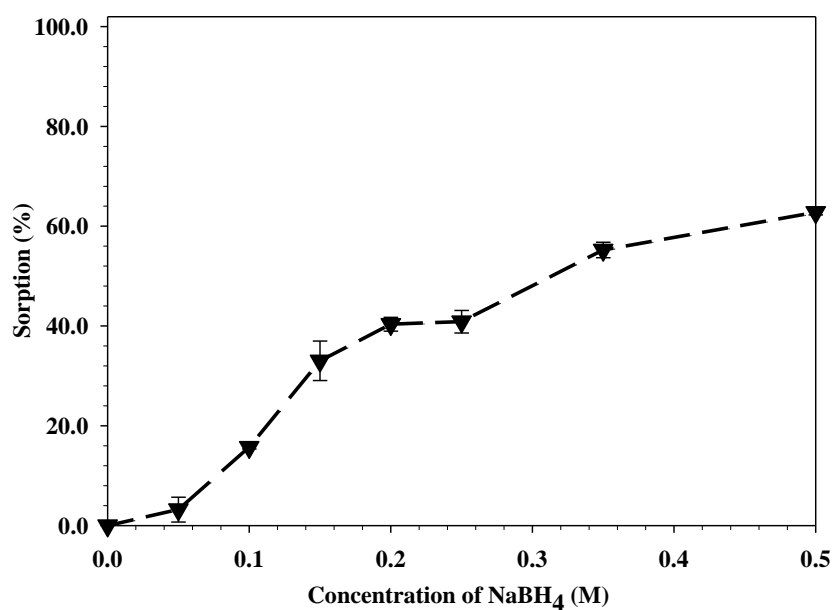
Figure 3.10. Effect of the concentration of NaBH$_4$ on the sorption of As(III) for (▼) ZVI-IRA 458. (20.0 mL and 50.0 mgL^{-1} As(III) solution, pH 7.0, 60 min shaking time, 50.0 mg sorbent, 25.0 °C reaction temperature)
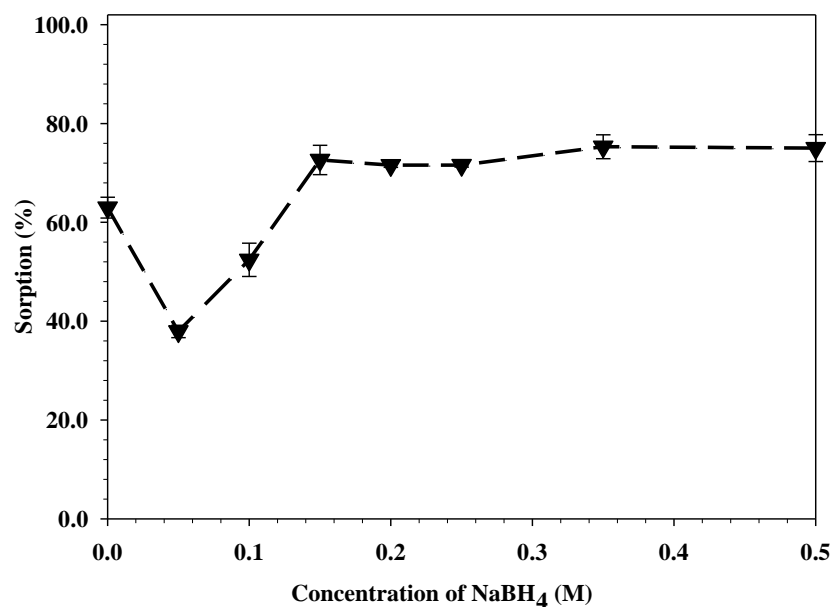
Figure 3.11. Effect of the concentration of NaBH$_4$ on the sorption of As(V) for (▼) ZVI-IRA 458. (20.0 mL and 100.0 mgL^{-1} As(V) solution, pH 7.0, 60 min shaking time, 50.0 mg sorbent, 25.0 °C reaction temperature)

3.3.3. Effect of Solution pH

The pH-dependent sorption/speciation performance of the unmodified IRA 458 and ZVI-IRA 458 resins are given in Figure 3.12 and Figure 3.13, respectively. Moreover, the distribution of As(III) and As(V) species as a function of pH is given additionally in Figure 3.14, in order to realize the sorption mechanism better. For arsenite, at lower pHs H_3AsO_3 and at high pHs $H_2AsO_3^-$ predominates. For arsenate, the percentage of the species (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}) changes in accordance with pH.

From pH 2.0 to 10.0, both the unmodified IRA 458 and ZVI-IRA 458 resins had > 99% sorption for arsenate, As(V), species. On the other hand, unmodified IRA 458 showed no affinity for the arsenite, As(III), species, whereas ZVI-IRA 458 showed > 95% sorption for this species at pH 2.0 to 10.0.

At pH 2.0, the observed sorption (if any) was due to the presence of the original functional groups of the resin (quaternary ammonium groups) since this pH was inconvenient for nZVI. nZVI formed on the surface and the interstices of the ion exchange resins is dissolved at pHs lower than 3.0.

Figure 3.12. Effect of solution pH on the sorption of As(III). ($\bullet$) IRA 458, ($\blacktriangledown$) ZVI-IRA 458. (20.0 mL and 100.0 μgL^{-1} As(III) solution, 120 min shaking time, 50.0 mg sorbent, 25.0 °C reaction temperature)

Figure 3.13. Effect of solution pH on the sorption of As(V). ($\bullet$) IRA 458, ($\blacktriangledown$) ZVI-IRA 458. (20.0 mL and 100.0 μgL^{-1} As(V) solution, 120 min shaking time, 50.0 mg sorbent, 25.0 °C reaction temperature)
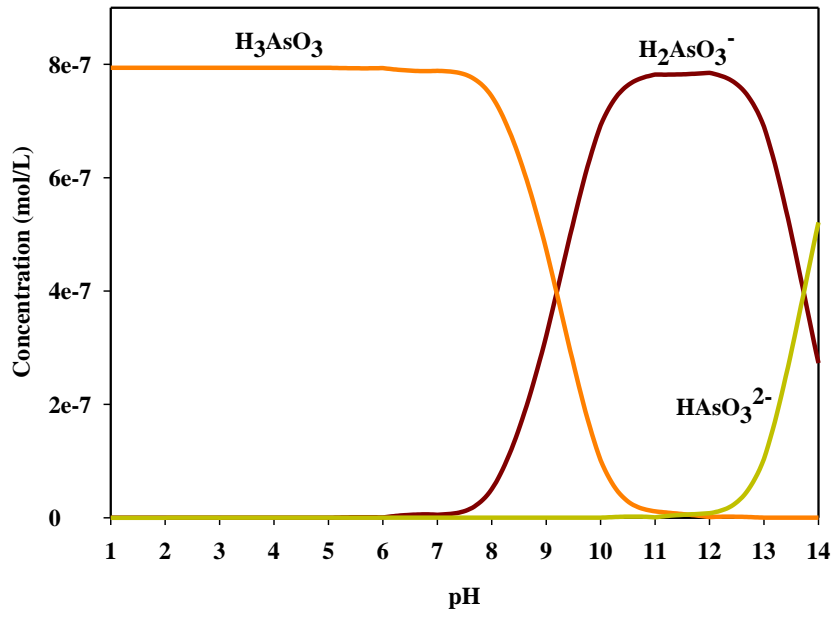
(a)
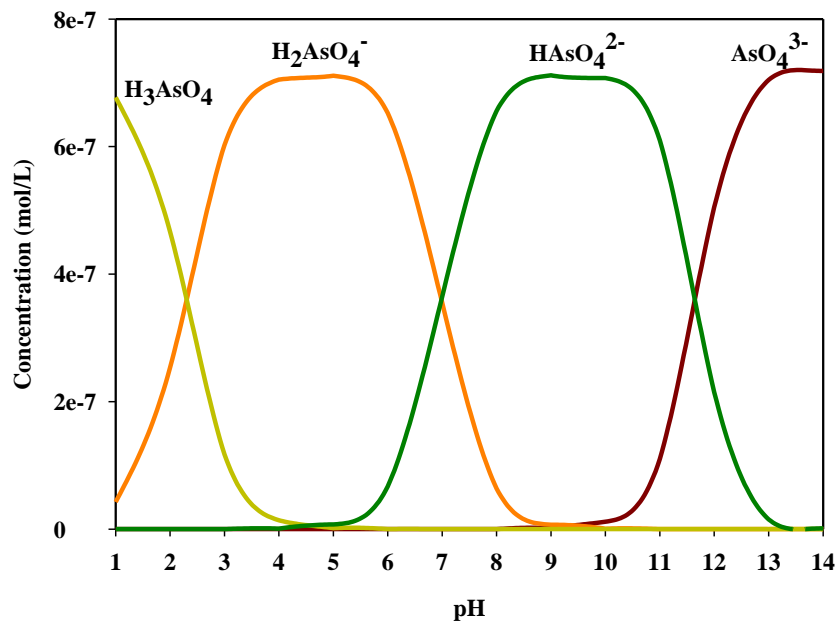
(b)

Figure 3.14. Distribution diagram of (a) As(III) and (b) As(V) in aqueous solutions.
(Source: Visual MINTEQ program)

3.3.4. Effect of Sorbent Amount

To determine the required amount of sorbents for the maximum sorption of arsenic species, the sorption studies were conducted with 5.0, 10.0, 25.0, 50.0, and 100.0 mg of the sorbents. The arsenite, As(III), and arsenate, As(V), sorption behavior as a function of amounts of unmodified IRA 458 and modified ZVI-IRA 458 are given in Figure 3.15 and Figure 3.16, respectively. In the applied sorption conditions, it was observed that 25.0 mg of each sorbent (IRA 458 and ZVI-IRA 458) was enough to provide maximum sorption, but in order to guarantee the quantitative sorption, 50.0 mg sorbents of IRA 458 and ZVI-IRA 458 were used for both arsenic species in further studies. The results demonstrated that these sorbents have very high sorption capacity and, even with 5.0 mg sorbent, a very high sorption (80.0%) was reached for As(V). Also, Figure 3.15 shows that unmodified resin (IRA 458) did not adsorb As(III) although the amount of sorbent increased.

It is noteworthy that 5.0 mg of the modified resin (ZVI-IRA 458) contains only 0.145 mg Fe. This observation is also the indication of the homogeneous distribution of iron particles formed on the resin surface. Whereby the effective surface area and the percentage of sorption increased.

Figure 3.15. Effect of sorbent amount on the sorption of As(III). (●) IRA 458, (▼) ZVI-IRA 458. (20.0 mL and 100.0 μgL^{-1} As(III) solution, 120 min shaking time, pH 7.0, 25.0 °C reaction temperature)
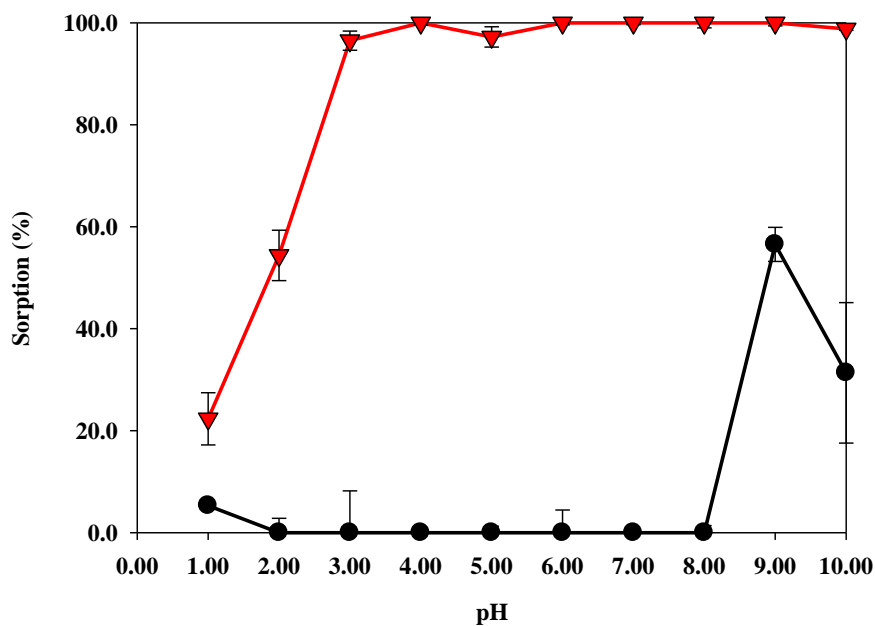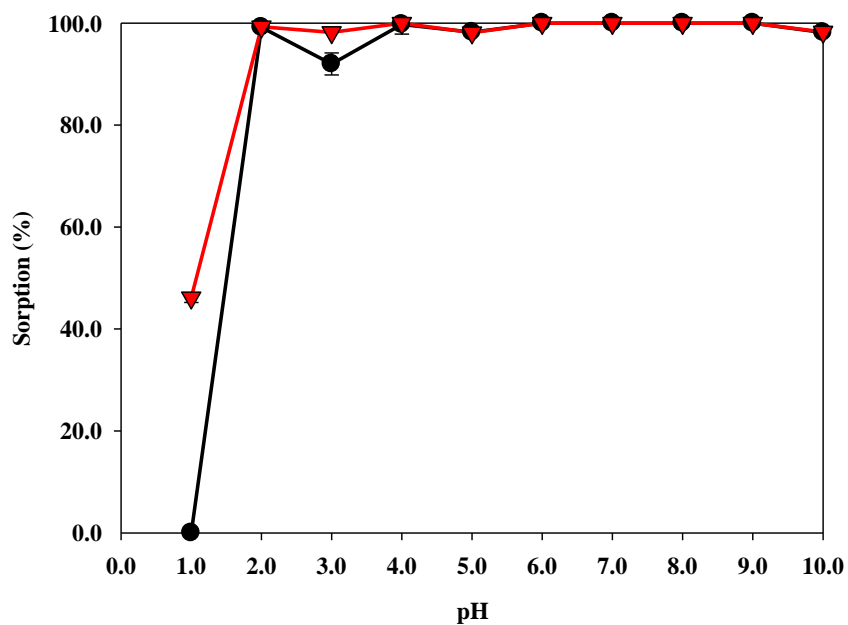

Figure 3.16. Effect of sorbent amount on the sorption of As(V). (●) IRA 458, (▼) ZVI-IRA 458. (20.0 mL and 100.0 μgL^{-1} As(V) solution, 120 min shaking time, pH 7.0, 25.0 °C reaction temperature)

3.3.5. Effect of Shaking Time

Batch sorption time was investigated for 1, 5, 15, 30, 60, and 120 minutes at pH 7.0 for both unmodified IRA 458 and ZVI-IRA 458, as illustrated in Figure 3.17 and Figure 3.18, respectively. The results indicated that the sorption kinetics was very fast for both sorbents.

According to Figure 3.17, the As(III) sorption with modified sorbent reached approximately 80% in 5 min and > 99.0% in 30 min. On the contrary, there was no improvement in the sorption of As(III) with unmodified sorbent with increasing shaking time.

Even if the sorption reached > 99.0% at 30 minutes, a safe period of time, 60 minutes, was decided to be applied in further studies.
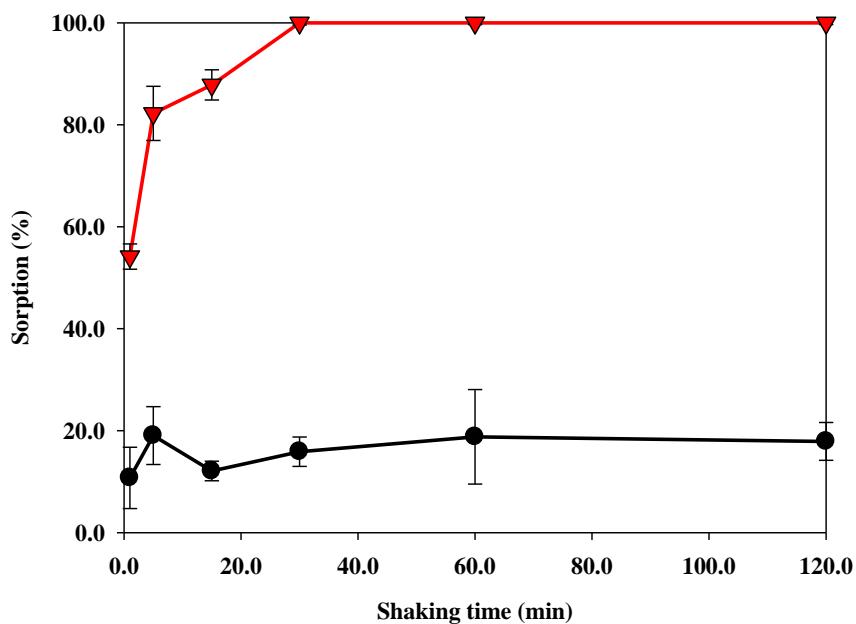
Figure 3.17. Effect of shaking time on the sorption of As(III). (●) IRA 458, (▼) ZVI-IRA 458. (20.0 mL and 100.0 µgL^{-1} As(III) solution, pH 7.0, 50.0 mg sorbent, 25.0 °C reaction temperature)

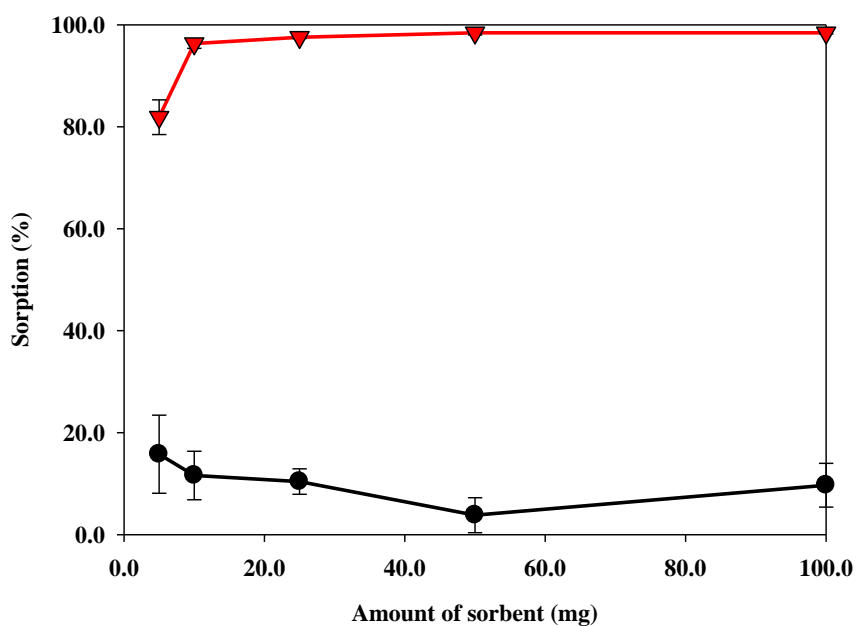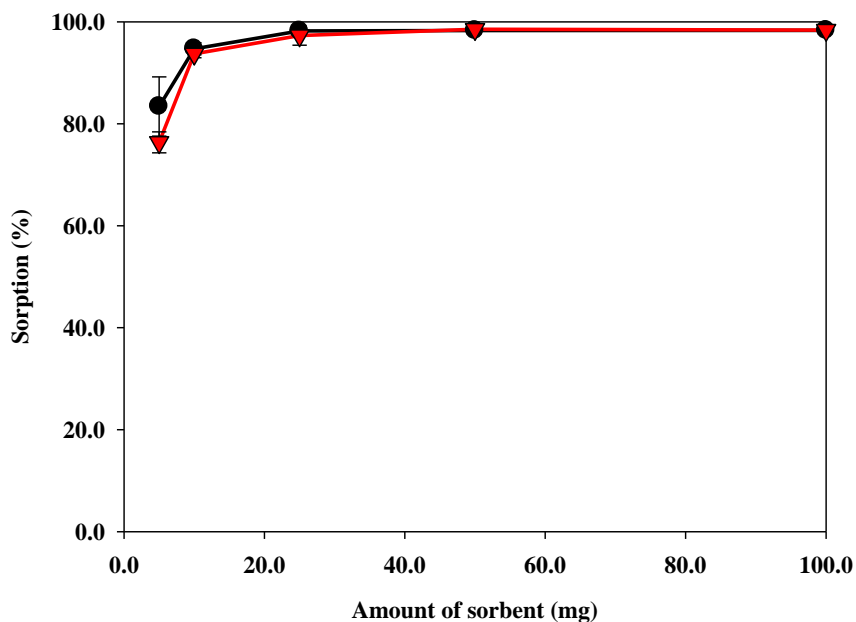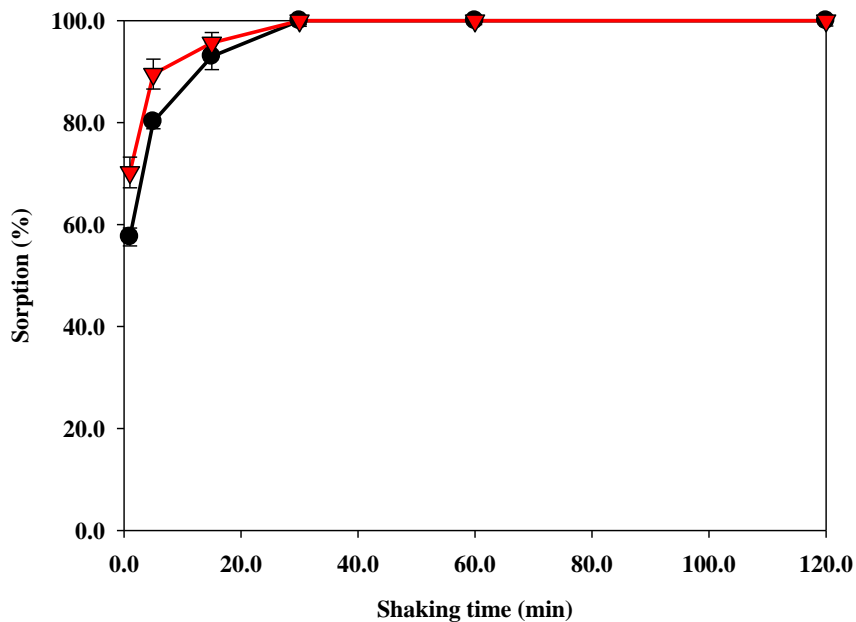

Figure 3.18. Effect of shaking time on the sorption of As(V). (●) IRA 458, (▼) ZVI-IRA 458. (20.0 mL and 100.0 µgL^{-1} As(V) solution, pH 7.0, 50.0 mg sorbent, 25.0 °C reaction temperature)

3.3.6. Effect of Initial As(III) and As(V) Concentrations

The sorption efficieny of unmodified IRA 458 and ZVI-IRA 458 as a function of initial As(III) and As(V) concentrations was tested at pH 7.0.

The results for different concentrations of As (III) are given in Table 3.7. As shown in the table, IRA 458 showed no sorption whereas ZVI-IRA 458 had very high sorption affinity for As(III). The modified resin indicated > 95% sorption, even at a 10.0 mgL^{-1} concentration. By increasing the concentration to 100.0 mgL^{-1}, the sorption decreased to 16%, which indicates that the saturation capacity of the sorbent is exceeded in the applied experimental conditions. It is noteworthy that the amount of resin used in the experiments was 50.0 mg and this amount of resin contained only 1.45 mg iron.

Table 3.8 shows the experimental results performed with As(V). Both IRA 458 and ZVI-IRA 458 showed almost 90% sorption affinity for As(V) up to concentrations of 60.0 mgL^{-1}. Despite the fact that the sorption results decreased at 100.0 mgL^{-1} concentration, the values obtained for IRA 458 and ZVI-IRA were 71% and 89%, respectively. These results which were quite different compared to As(III) sorption behaviour results, showed that the quaternary ammonium functional groups of strong anion exchange resin was active in the sorption of As(V). The results also indicated the high sorption capacity of IRA 458 and ZVI-IRA 458.

Table 3.7. Effect of initial As(III) concentration on the sorption efficiency for IRA 458 and ZVI-IRA 458. (50.0 mg sorbent amount, at pH 7.0 in 20.0 mL As(III) solution, 60 min shaking time, 25.0 °C reaction temperature)

As(III)	Sorption (%)	
Concentration (mgL^{-1})	IRA 458	ZVI-IRA 458
0.010	~ 0	85.2 (±0.4)
0.10	~ 0	86.3 (±0.8)
1.0	~ 0	97.0 (±2.9)
10.0	~ 0	96.7 (±0.1)
30.0	~ 0	91.1 (±0.7)
60.0	~ 0	84.4 (±1.9)
100.0	~ 0	15.7 (±3.9)

Table 3.8. Effect of initial As(V) concentration on the sorption efficiency for IRA 458 and ZVI-IRA 458. (50.0 mg sorbent amount, at pH 7.0 in 20.0 mL As(V) solution, 60 min shaking time, 25.0 °C reaction temperature)

As(V)	Sorption (%)	
Concentration (mgL^{-1})	IRA 458	ZVI-IRA 458
0.010	85.4 (±0.5)	87.6 (±0.8)
0.10	87.7 (±0.4)	88.2 (±0.3)
1.0	97.4 (±3.6)	98.6 (±0.9)
10.0	98.9 (±1.5)	99.4 (±3.3)
30.0	86.7 (±0.7)	94.2 (±2.4)
60.0	81.3 (±1.3)	93.2 (±3.1)
100.0	71.4 (±0.8)	89.2 (±0.6)

3.3.7. Effect of Reaction Temperature

Temperature effect on the sorption of arsenic was studied at 25, 40 and 60 °C. As(III) and As(V) sorption percentages of ZVI-IRA 458 as a function of temperature are given in Figure 3.19. As shown in the figure, ZVI-IRA 458 showed no change in the sorption with the increase in temperature for both As(III) and As(V). Therefore, 25 °C was chosen as a optimum value for further experiments.

In order to understand the effect of temperature on the adsorption better, it is important to study the thermodynamic parameters such as standard Gibbs free energy change, ΔG^{o}, standard enthalpy change ΔH^{o}, and standard entropy change, ΔS^{o}. The magnitude of the change in free energy can be used to determine the type of adsorption. The summary of thermodynamic parameters are given in Table 3.9.

Table 3.9. Thermodynamic parameters of ZVI-IRA 458.

As(III)	ΔG (kJ/mol)		ΔH (kJ/mol)	ΔS(J/molK)	
	298 K	313 K		298 K	313 K
ZVI-IRA 458	-24.75	-31.04	100.15	419.12	419.13

As(V)	ΔG (kJ/mol)		ΔH (kJ/mol)	ΔS(J/molK)	
	298 K	313 K		298 K	313 K
ZVI-IRA 458	-26.88	-27.15	-21.49	18.087	18.083
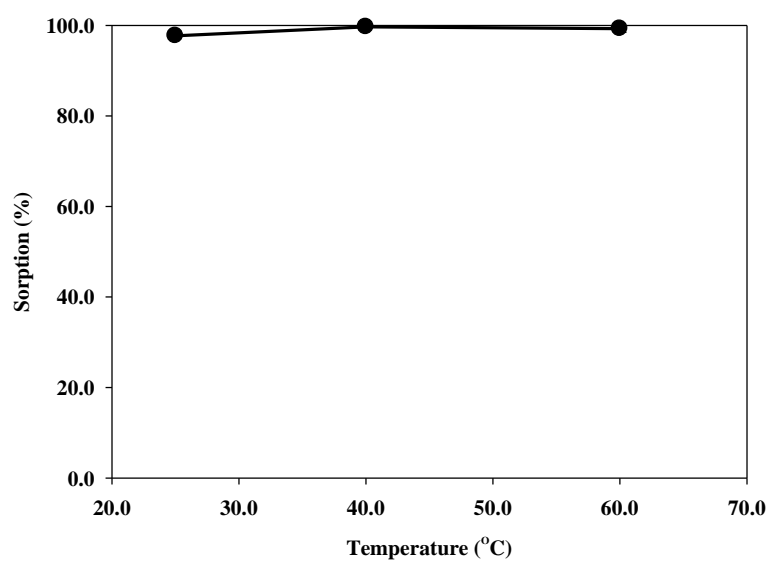
(a)
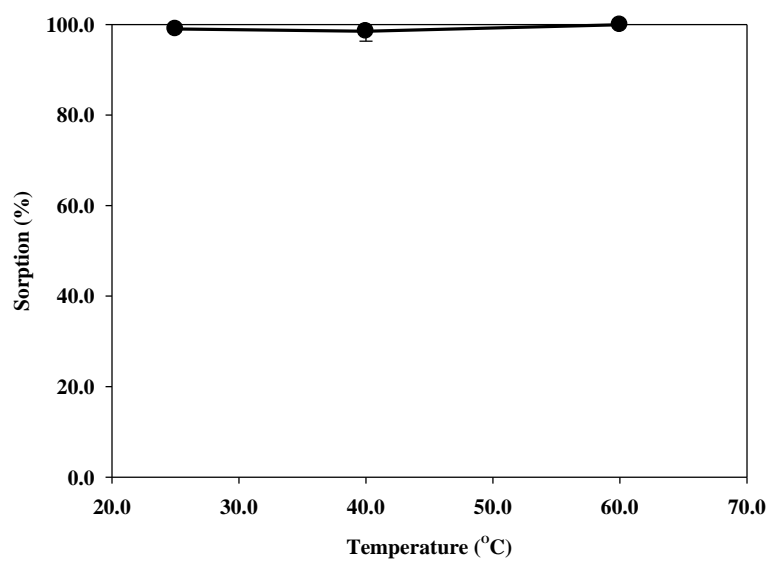
(b)

Figure 3.19. Effect of sorption temperature on the sorption of (a) As(III) and (b) As(V) for ZVI-IRA 458 (20.0 mL and 100.0 μgL^{-1} As solution, at pH 7.0, 60 min shaking time, 50.0 mg sorbent)

3.4. Desorption Studies

Desorption studies for ZVI-IRA 458 were performed as described in section 2.5.1.7. The efficiency/feasibility of the various eluents for the desorption of As(III) and As(V) were investigated. Table 3.10 summarizes the desorption percentages of various desorbing matrices for As(III) and As(V). At first, HNO_3, KH_2PO_4, $(NH_4)(NO_3)$, NH_3 and NaOH were used for the elution of As(III) or As(V) from ZVI-IRA 458 by the batch method. It was shown that except for KH_2PO_4, NaOH and NaOH+NaCl, other eluents did not give any promising desorption for arsenic. According to these results 2% (m/v) NaOH + 3% (m/v) NaCl and 5% (m/v) NaOH + 3% (m/v) NaCl solutions are suitable desorbing solvent for As(III) and As(V), respectively.

Table 3.10. Percent desorption values of various eluent matrices for As. (The sorption parameters; 100.0 μgL^{-1} concentration of As(III) or As(V), shaking time of 60 min or 120 min, 50.0 mg sorbent amount, solution volume of 20.0 mL, reaction temperature of 25.0 °C, solution pH of 7.0)

	Desorption %	
Eluents	**As(III)**	**As(V)**
0.1 M NaOH	2.3 (±0.8)	3.2 (±0.3)
0.5 M NaOH	59.3 (±3.2)	52.1 (±3.4)
0.1 M $(NH_4)(NO_3)$	~ 0	2.3 (±3.0)
0.1 M HNO_3	7.8 (±2.2)	6.7 (±2.2)
0.1 M KH_2PO_4	16.7 (±3.6)	9.5 (±3.6)
0.5 M KH_2PO_4	49.6 (±1.8)	54.1 (±3.1)
1.0 M KH_2PO_4	43.6 (±2.2)	33.9 (±1.7)
0.5 M NH_3	3.3 (±0.2)	1.9 (±2.1)
2% NaOH + 3% NaCl (m/v)	96.3 (±1.6)	56.1 (±0.6)
5% NaOH + 3% NaCl (m/v)	89.5 (±0.7)	64.5 (±1.2)

3.5. Method Validation

ZVI-modified strong ion exchanger resin Amberlite IRA 458 (ZVI-IRA 458) was used for the removal of arsenic from water samples of different matrices. In order to investigate the sorption efficieny of sorbents, five different water samples (tap water from İYTE, tap water from Gülbahçe, river water from İYTE, rain and sea water) were spiked with As(III) or As(V). Firstly the sorption performance of the sorbent was checked and the results are summarized in Table 3.11. As shown in the table, the sorbent displayed very efficient performances towards As(V) at the indicated pH for all water samples except the rain water. The sorption of As from rain water (which can be considered relatively clean compared to other types of water) was about 60%. On the other hand, the sorption percentages from other heavy matrix waters were about 100% which was unexpected. Similar results were also observed for the sorption of As(III). These results indicated that inorganic As species can be removed from various water types, also the speciation of As can be done in sea water. These results have been decided to be the topic of further studies.

Table 3.11. Percent sorption of spiked arsenite and arsenate in rain water, river water (from İYTE), tap water (from Gülbahçe), tap water (from İYTE) and sea water for ZVI-IRA 458. (Sorption parameters; As concentration: 100.0 μgL^{-1}, pH: 7.0, shaking time: 60 min, amount of sorbent: 50.0 mg, solution volume: 20.0 mL, temperature: 25.0 ºC)

Water Type	Sorption %	
	As(III)	As(V)
Rain Water	59.1 (±0.5)	61.5 (±0.2)
River Water	92.8 (±0.9)	100.0 (±0.8)
Tap Water (from Gülbahçe)	100.0 (±4.3)	100.0 (±0.9)
Tap Water (from İYTE)	100.0 (±1.1)	100.0 (±2.7)
Sea Water	~ 0	100.0 (±2.4)

3.6. Studies for the Removal of Boron

Sorption and optimization of sorbent experiments highlighted another important issue; the control of the boron concentration which passed into the solution. Use of $NaBH_4$ as a reductant caused the formation of borate salts and the increase of boron amount passing from the resin surface to the solution during sorption studies. The results indicated that the amount of boron reached above the maximum contamination limit in drinking water. In order to eliminate this high amount of boron from the solution, the studies were concentrated on the use of IRA 743 resin due to its selectivity towards boric acid and borate ion. At that point, three different methods were used for the optimization of boron removal (as described in Section 2.6.8.2).

In the first method, sample was treated with the zero-valent iron modified-IRA 458 (batch type) and IRA 743 (column type), respectively. While the first resin provided the removal of arsenic, the use of the second resin was planned to prevent boron from passing into the solution by adsorption.

In the second method, the column was filled with equal amounts of ZVI-IRA 458 and IRA-743. Solution passing through the column first interacted with ZVI-IRA 458 and then with IRA 743.

In the last method, the column was filled with a homogenous mixture of equal amounts of ZVI-IRA 458 and IRA 743.

According to these three methods mentioned above, arsenic sorption results and amounts of boron were summarized in Table 3.12 and Table 3.13, respectively. It was observed that with all three methods, a successful decrease in the released boron concentration was obtained. In the second and third method, the boron concentration was even below the maximum contaminant level (MCL) (1.0 mgL^{-1}).

As shown in the Table 3.13, all three methods have reduced the boron concentration appreciably. The initial boron concentrations were 46.9 mgL^{-1} and 53.6 mgL^{-1} for As(III) and As(V) solutions, respectively. Still, method 1 was not convenient since there was approximately 8.4 - 10.5 mgL^{-1} boron for As(III) and 6.8 - 9.8 mgL^{-1} boron for As(V), respectively, in the final solution. On the other hand, 2nd and 3rd methods were more efficient in reducing the released amount of boron in a way that, 2nd method decreased the boron concentration below MCL after the second treatment, whereas in 3rd method only one treatment was sufficient.

Table 3.12. Arsenic sorption studies with three different methods. (20.0 mL and 100.0 mgL^{-1} As solution, flow rate 1.0 mL/min, pH 7.0, 60 min shaking time, 100.0 mg sorbent, 25.0 °C reaction temperature)

	Sorption %	
	As(III)	As(V)
1st Method	89.0	74.3
2nd Method	100.0	100.0
3rd Method	99.0	100.0

Table 3.13. Boron removal studies with three different methods. (20.0 mL and 100.0 mgL^{-1} As solution, flow rate 1.0 mL/min, pH 7.0, 60 min shaking time, 100.0 mg sorbent, 25.0 °C reaction temperature)

	Boron concentration (mgL^{-1})	
	0.10 mgL^{-1} As(III)	0.10 mgL^{-1} As(V)
Initial Boron concentration (mgL^{-1})	**46.9**	**53.6**
1st Method	8.4	6.8
	9.0	8.6
	10.5	9.8
2nd Method	11.7	9.3
	2.2	1.9
	0.9	1.0
3rd Method	4.8	5.6
	1.0	0.9
	0.5	0.4

3.7. Sorption of Organoarsenic Species

Sorption behaviour of unmodified IRA 458 and ZVI-IRA 458 for organoarsenicals was investigated for DMA, MMA and AsB. The solution pH was adjusted to 4.0, 5.0, 7.0, 8.0 and 10.0.

As shown in Figure 3.20, maximum sorption of DMA was observed by ZVI-IRA 458 at pH 4.0 where unmodified resin showed around 20% sorption. At other pHs,

ZVI-IRA 458 has higher sorption efficiency than unmodified IRA 458; however, the diference was not so high to be significant for further studies.

As displayed in Figure 3.21 both unmodified IRA 458 and ZVI-IRA 458 show high sorption efficiencies at all pHs tested for MMA species. However, ZVI-IRA 458 resin still has higher sorption efficiencies than unmodified IRA 458.

On the other hand, both unmodified IRA 458 and ZVI-IRA 458 sorbents show almost no sorption for AsB species at the investigated pHs, as illustrated in Figure 3.22.

Figure 3.20. Effect of solution pH on the sorption of DMA for (●) IRA 458, (▼) ZVI-IRA 458. (20.0 mL and 100.0 μgL^{-1} DMA solution, 60 min shaking time, 50.0 mg sorbent, 25.0 °C reaction temperature)

These results have shown that both the unmodified and nZVI-modified strong anion exchange resins can be used in the separation of DMA and MMA. This topic will be the subject of further studies.

Figure 3.21. Effect of solution pH on the sorption of MMA for (●) IRA 458, (▼) ZVI-IRA 458. (20.0 mL and 100.0 µgL^{-1} MMA solution, 60 min shaking time, 50.0 mg sorbent, 25.0 °C reaction temperature) Inset: The same data with different y-scale.

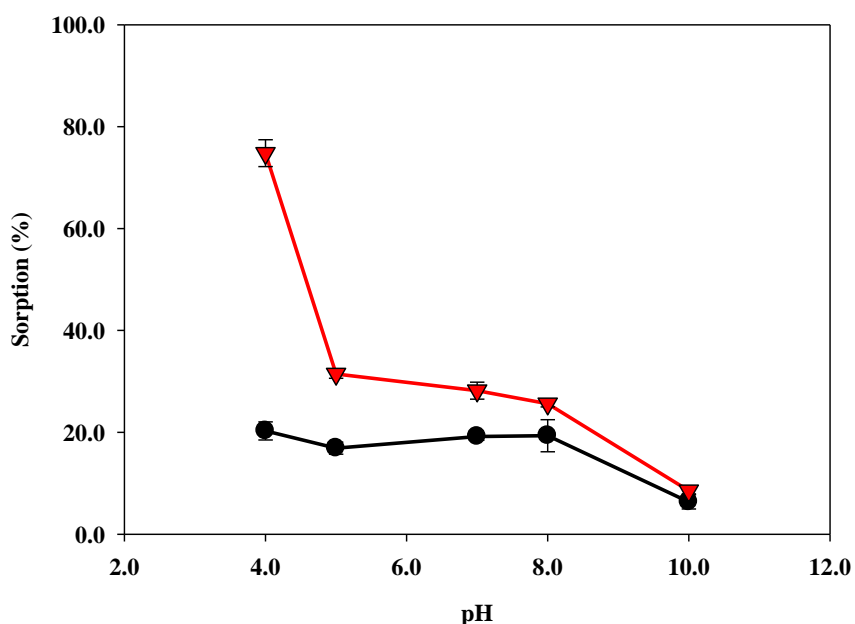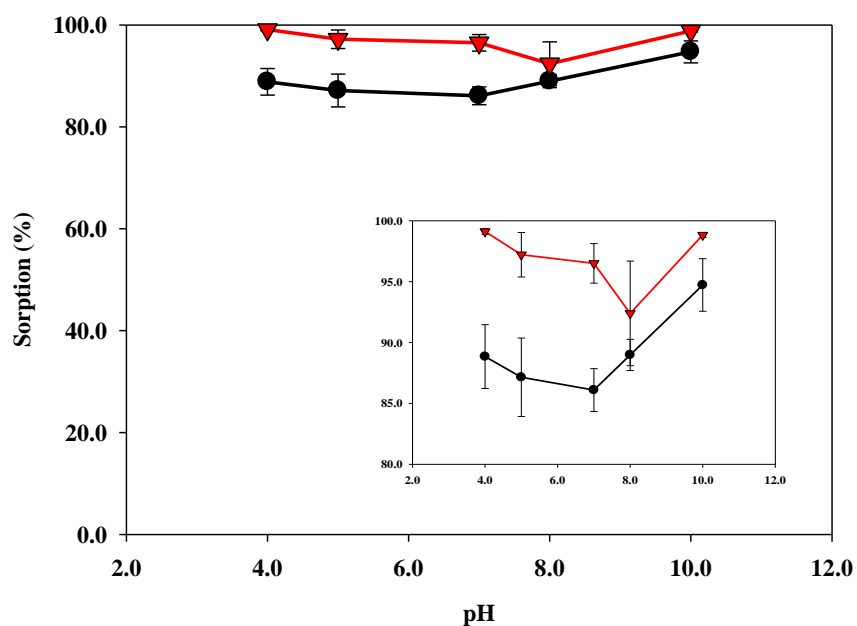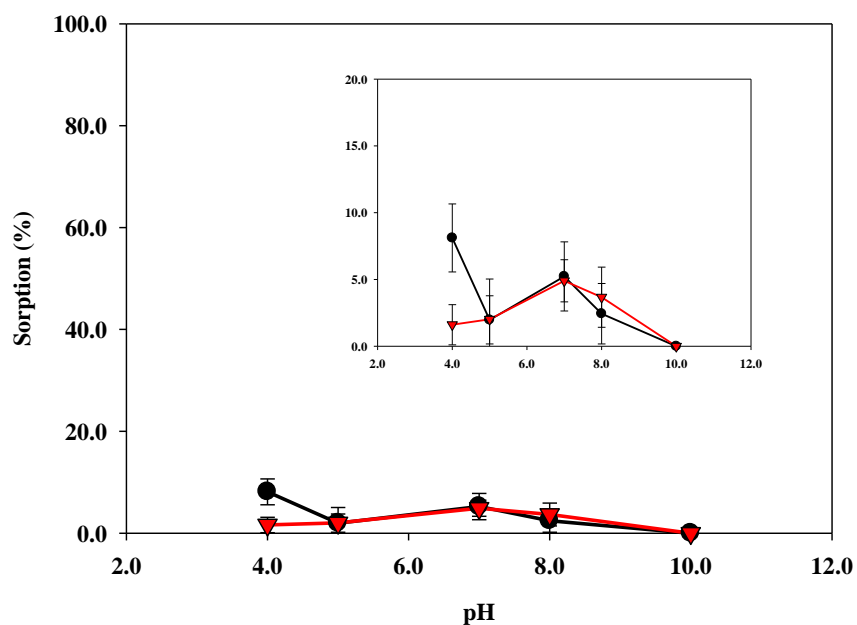Figure 3.22. Effect of solution pH on the sorption of AsB for (●) IRA 458, (▼) ZVI-IRA 458. (20.0 mL and 100.0 µgL^{-1} AsB solution, 60 min shaking time, 50.0 mg sorbent, 25.0 °C reaction temperature) Inset: The same data with different y-scale.

CHAPTER 4

CONCLUSION

In this study, commercial and newly modified sorbents were used for the sorption/speciation of arsenite (As(III)) and arsenate (As(V)) prior to determination by atomic spectrometric techniques. Characterization of the sorbents was realized using SEM, XRD, TGA, and the obtained results demonstrated the success of the modification procedure. Characterization studies were followed by the examination of the sorption performance of the unmodified and the modified sorbents towards arsenic species.

This study demonstrated that various commercial ion-exchange resins and zero-valent iron modified ion-exchange resins can effectively be employed in the sorption/speciation of As(III) and As(V) in waters. The results obtained from sorption studies clearly showed that commercial anion-exchange resins can be used only for the removal of As(V). On the other hand, zero-valent iron modified ion-exchange resins gave promising results for both As(III) and As(V) sorption. Among the investigated sorbents, the high sorption efficiency of IRA-458 also led to the search for new zero-valent iron containing sorbents for the same purpose. Therefore, the sorption and the optimization experiments in the thesis were only carried out with this sorbent.

The results of the sorption studies performed with ZVI-IRA 458 revealed that for the speciation of arsenic, ZVI-IRA 458 resin and unmodified IRA 458 should be used together. The most important advantage of this sorbent is that it does not require a pre-adjustment step or various preliminary works such as fixing oxidation step in waters, especially containing unknown arsenic species. Also, by applying the method to various water samples, this sorbent can be considered to be widely effective for the removal of arsenic from waters only by exception of water samples that has heavy matrix such as sea water.

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