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DEVELOPMENT OF SORBENTS FOR ARSENIC REMOVAL FROM DRINKING WATER

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ÖZET

İÇME SULARINDAN ARSENİK GİDERİLMESİ İÇİN SORBENT GELİŞTİRİLMESİ

Deniz Çiftçi, Tülin

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As(III) ve As(V) türlerinin giderilmesi için demir hidroksit tutturulmuş silikajel, termal yöntemle demir hidroksit tutturulmuş pomza ve nikel nanopartikül tutturulmuş reçine ile çalışılmıştır.

Demir(III) hidroksitle arsenik gidermek amacıyla, safsızlıkların yanılgıya neden olmaması için laboratuar kalitesi silikajel kullanılmıştır. Demir(III) hidroksit değişik pH'lerde çöktürülmüştür ve oldukça düşük olan pH 6.0 tercih edilmiştir. Çünkü bu pH'de üst çözelti berraktı ve en yüksek giderme kapasiteli ve giderme verimi elde edilmiştir. Arsenik türleme çalışmalarından, eser düzeydeki As(III)'ün adsorplanma sırasında kısmen As(V)'e yükseltgenmeden adsorplandığı görülmüştür. Bu konuda literatürde farklı yorumlarla krşılaşılmaktadır. Beç yöntemde çözeltinin başlangıç pH'sinin 3.1-9.7 aralığında As(III) ve As(V) giderilmesinde etkisi olmadığı görülmüştür. Bunun nedeni, bu pH aralığındaki çözelti pH'sinin dengede pH 5 civarında sabitlenmesine bağlanmıştır. Giriş derişimi 1.00 mg/L arsenik olduğunda, kolon kapasiteleri 1.32 mg As(III)/g adsorban ve 1.21 mg As(V)/g adsorban olarak belirlenmiştir.

Destek maddeleri üzerine demir hidroksit tutturmak için termal yöntem geliştirilmiştir. Destek maddesi olarak pomza kullanıldığında en yüksek adsorpsiyon kapasitesi elde edilmiştir. Adsorban hazırlamada optimal sıcaklık 220 ^{0}C olarak belirlenmiştir.

As(III) ve As(V)'in giderilmesi için yeni bir adsorban olan nikel nanopartikül tutturulmuş reçine kullanılmıştır. Adsorbanın optimal hazırlama koşulları belirlenmiş ve en uygun kurutma sıcaklığı oda sıcaklığı olarak seçilmiştir. Bu koşulda As(III) giderme verimi 99.7% ve arsenik alım kapasitesi

3.50mg/g olarak hesaplanmıştır. Beç yöntemle, çözeltinin 3.3-11.5 pH aralığındaki başlangıç değerinin arsenik giderme verimine etkisi görülmemiştir. En düşük adsorban miktarında dahi çok yüksek arsenik giderme verimleri elde edilmiştir. 16g/L adsorban dozunda As(III) ve As(V) için sırasıyla 99.2% ve 100.3% giderme verimleri elde edilmiştir. Langmuir, Freundlich ve DR izotermleri çizilmiş ve sorpsiyonun Langmuir ve Freundlich izotermlerine uyduğu bulunmuştur. DR izotermi ise adsorpsiyonun fiziksel ve istemli olduğunu göstermiştir. Rejenerasyon çalışmalarından As(III) ve As(V)'in adsorbandan desorbe edilebildiği ve böylece birçok kez kullanılabileceği görülmüştür.

Anahtar Sözcükler: arsenik, giderme, demir(III) hidroksit, termal yöntem, nanopartikül, nikel.

ABSTRACT

DEVELOPMENT OF SORBENTS FOR ARSENIC REMOVAL FROM DRINKING WATER

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Removal of As(III) and As(V) species using ferric hydroxide supported on silicagel, thermally supported ferric hydroxide on pumice and nickel nanoparticle impregnated resin were studied.

For arsenic removal with ferric hydroxide, laboratory reagent quality silicagel was used to avoid confusions that may be caused by the impurities. Ferric hydroxide precipitation was realized at various pH values and a relatively low pH 6.0 was chosen because, at this pH, the highest arsenic removal capacity and removal efficiency were obtained and clear supernatant solution was observed. It was also shown by arsenic speciation analysis at trace level that As(III) is adsorbed onto ferric hydroxide partly without oxidation to As(V); it was a controversial point in the literature. In the batch method, initial pH change of the solution did not significantly affect the arsenic removal efficiencies for As(III) and As(V) in the pH range of 3.1-9.7. This was attributed to the decreases of the initial pH values to around 5 at equilibrium. The column capacities of 1.32 mg As(III)/g sorbent and 1.21 mg As(V)/g sorbent were found for initial concentration of 1.00 mg/L arsenic.

A thermal method was developed for the preparation of ferric hydroxide on support materials. Maximum adsorption capacities were obtained by pumice as the support material. Optimum temperature was 220 ^{0}C for the preparation of the adsorbent.

A novel adsorbent nickel nanoparticle impregnated resin was used for the removal of both As(III) and As(V). Optimal preparation conditions of Ni nanoparticle impregnated resin were determined. Optimum drying temperature was chosen as room temperature. Removal efficiency of As(III) was 99.7% and arsenic uptake was 3.50mg/g at 20^{0}C. In the batch method, initial pH did not significantly affect the arsenic removal efficiencies for As(III) and As(V) in the pH range 3.3-11.5. Even at the lowest adsorbent dose used, very high arsenic removal efficiencies were observed. 99.2% and 100.3% removal efficiencies were obtained for As(III) and As(V), respectively, at 16g/L adsorbent dose. The plots of adsorption isotherms Langmuir, Freundlich and DR were drawn. Adsorption process was found to obey Langmuir and Freundlich equations and DR isotherms showed that the adsorption is physical and favorable. Regeneration studies showed that As(III) and As(V) could be desorbed from the adsorbent therefore the adsorbent can be used several times.

Keywords: arsenic, removal, iron (III) hydroxide, thermal method, nanoparticle, nickel.

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ABBREVIATIONS

Abbreviations	Explanations
AAS	Atomic absorption spectrometry
AC	Activated carbon
AE	Anion exchange
AES	Atomic emission spectrometry
AFS	Atomic fluorescence spectrometry
AM3	Absorptionsmittel3
As	Arsenic
As(III)	Arsenite (AsO_3^{3-})
As(V)	Arsenate (AsO_4^{3-})
ASV	Anodic stripping voltammetry
CA	Chronoamperometry
CCSA	Constant current stripping analysis
CE	Cation exchange
CSV	Cathodic stripping voltammetry
DMA(III)	Dimethylarsinous acid
DMMTA(V)	Dimethylmonothioarsenic
DNA	Deoxyribonucleic acid

ABBREVIATIONS (continue)

DR	Dubinin-Radushkevich
EDX	Energy-dispersive X-ray spectroscopy
EPA	The Environmental Protection Agency
Fe^0	Zero valent iron
FHSS	Ferric hydroxide supported on silicagel
FI	Flow injection
GF	Graphite furnace
GFAAS	Graphite furnace atomic absorption spectrometry
GFH	Granular ferric hydroxide
GIH	Granulated iron hydroxide
HG	Hydride generation
HG-AAS	Hydride generation atomic absorption spectrometry
HGAFS	Hydride generation atomic fluorescence spectrometry
HPLC	High pressure liquid chromatography
IC	Ion chromatography
ICP	Inductively coupled plasma
ICPMS	Inductively coupled plasma mass spectrometry
ICZ	Iron coated zeolite

ABBREVIATIONS (continue)

IEP	Isoelectric point
KP	Knotted reactor
LD_{50}	Lethal Dose (50%)
LOD	Limit of detection
MCL	Maximum contaminant level
MMA(III)	Monomethylarsonous acid
MS	Mass spectrometry
NAA	Neutron activation analysis
NAA	Neutron activation analysis
Ni-NPIR	Nickel nanoparticle impreganted resin
NP	Nanoparticle
PAHs	Polycyclic aromatic hydrocarbons
PDC	Pyrolidinedithiocarbamate complex
RSD	Relative Standard Deviation
SAMMS	Self-assembled monolayers on mesoporous supports
SE	Solid extraction
SEM	The scanning electron microscope
SPE	Solid phase extraction

ABBREVIATIONS (continue)

SWCSV	Square wave cathodic stripping voltammetry
WHO	The World Health Organisation
XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectroscopy
XPS	X-Ray photoelectron spectroscopy
Zr-AC	Zirconium loaded activated carbon

1. CHAPTER ONE - INTRODUCTION

1.1. Arsenic

Arsenic is a heavy metal with a name derived from the Greek word *arsenikon*, meaning potent. It is ubiquitous and ranks 20th in natural abundance, comprising about 0,00005% of the earth's crust, 14th in the sea water, and 12th in the human body. It is a silver gray brittle crystalline solid with atomic weight 74.9; atomic number 33; valence -3, 0, +3, +5, specific gravity 5.73; melting point 817 ^{o}C (at 28 atm); boiling point 613 ^{o}C and vapor pressure 1 mm Hg at 372 ^{o}C (Weast, 1974).

1.1.1. Sources and Occurrence of Arsenic

Arsenic is a rare crystal element comprising about five hundred-thousandths of 1% of the earth crust and the average concentration of arsenic in igneous and sedimentary rocks is 2 mg/kg. Iron deposits, sedimentary iron ores and manganese nodules were rich in arsenic. Arsenic naturally occurs in over 200 different mineral forms, of which approximately 60% are arsenates, 20% sulfides and sulfosalts and the remaining 20% includes arsenides, arsenites, oxides, silicates and elemental arsenic (As) in the earth crust (Mandal and Suzuki, 2002).

Arsenic is found at low concentration in natural water. In seawater, the concentration of arsenic is usually less than 2 μg/L (Ng, 2005; Mandal and Suzuki, 2002). The levels of arsenic in unpolluted surface water and groundwater vary typically from 1-10 μg/L. In freshwater, the variation is in the range of 0.15-0.45 μg/L (Bissen and Frimmel, 2003: a,b). In thermal waters, concentrations of upto 8.5 mg/L and 1.8–6.4 mg/L have been reported in New Zealand and Japan, respectively (Ritchie, 1961; Nakahara et al., 1978). The presence of arsenic in natural water is related to the process of leaching from the arsenic containing source rocks and sediments (Robertson, 1989). It is generally associated with the geochemical environments such as basin-fill deposits of alluviallacustrine origin, volcanic deposits, inputs from geothermal sources, mining wastes and landfills (Welch et al., 1988; Korte and Fernando, 1991). Also biological actions, and geochemical reactions help to mobilize arsenic into groundwater.

Arsenic is also used in production of semiconductors, pigments, glass manufacturing, pesticides, rodenticides and fungicides (Hathaway et al., 1991) and as an ingredient of drugs for the treatment of some diseases (e.g., sleeping sickness, chronic myeloid leukemia; Nevens et al., 1990; Luh et al., 1973). Because of its usefulness and exploitation, arsenic contamination is now widespread in the environment.

1.1.2. Species of Arsenic

The term 'speciation' in analytical chemistry, refers to the determination of different oxidation states of an element that prevail in a certain specimen or to the identification and quantification of the biologically active compounds to which the element is bound. Sparingly, in the investigation of toxic effects, the speciation of small molecules (organometallic compounds) is of concern, while for the study of the biological functions, the determination of large molecules has priority. This knowledge could help to explain the mobility, storage, retention and toxicity of the different species in different environments including the human body.

Arsenic rarely occurs in free state, it is largely found in combination with sulphur, oxygen and iron (Jain and Ali, 2000). Two forms of arsenic are common in natural waters; arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}), referred to as As(III) and As(V). These anions have acidic characteristics, and the stability and dominance of a specific species depend on the pH of the solution, as shown in Figure 1.1. Under atmospheric or more oxidizing environment, the predominant species is As(V), which, in the pH range of 6-9, exists predominantly as deprotonated oxyanions, namely, $H_2AsO_4^-$ or $HAsO_4^{2-}$ (DeMarco et al., 2003) ($pK_1 = 2.2$, $pK_2 = 7.1$, $pK_3 = 11.5$). The ionic form of the pentavalent arsenic is easier to remove (Korngold et al., 2001). Under mildly reducing conditions, As(III) is thermodynamically stable, predominant and exists predominantly as H_3AsO_3 (pK_1 9.22, $pK_2 = 12.3$, $pK_3 = 13.4$) (or $HAsO_2$) at pH below 9.0. If Eh values below −250 mV exist in the environment, arsenic compounds such as As_2S_3 in the presence of sulfur or hydrogen sulfide can be formed but these conditions are not environmentally relevant. Under very strong reducing conditions, arsine and elemental arsenic are formed but again, only rarely, if ever in the natural environment (Sharma and Sohn, 2009). Also, arsenic cannot be easily destroyed and can only be converted into different forms or transformed into insoluble compounds in combination with other elements, such as iron (Choong et al., 2007).

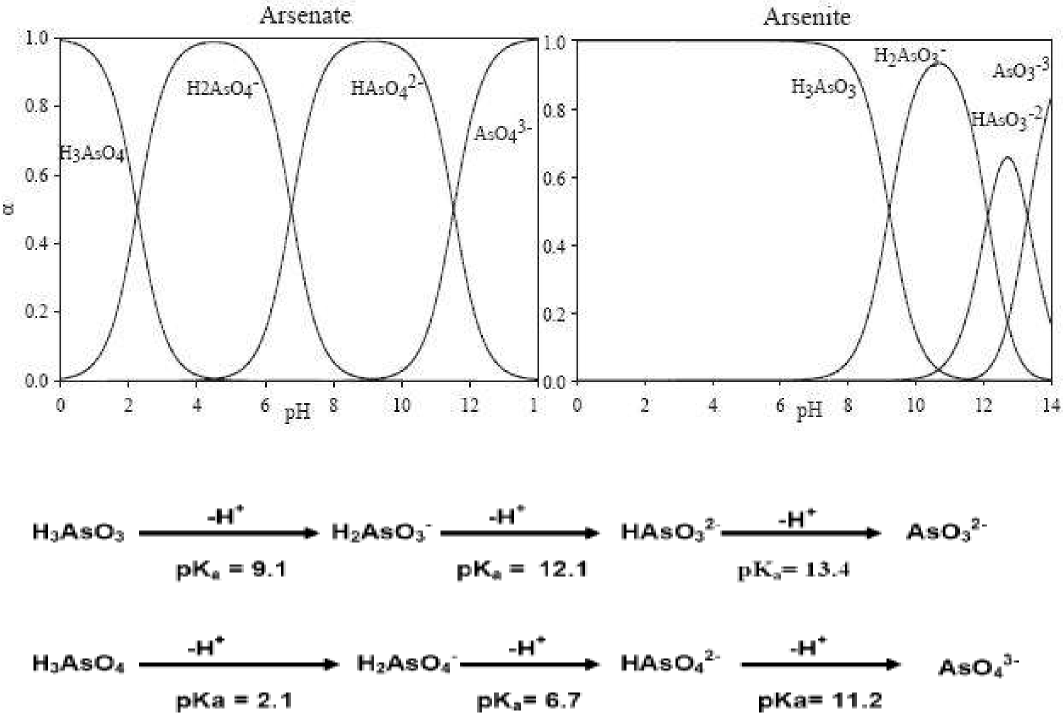


Figure 1.1. Distribution of arsenate and arsenite as a function of pH. (*Ghimire et al.,2003*)

1.1.3. Toxicity of Arsenic

Arsenic is toxic to both plants and animals and inorganic arsenicals are proven carcinogens in humans (Ng, 2005). The chemical forms and oxidation states of arsenic are more important as regards to toxicity. Toxicity also depends on other factors such as physical state, gas, solution, or powder particle size, the rate of absorption into cells, the rate of elimination, the nature of chemical substituents in the toxic compound, and, of course, the pre-existing state of the patient. It is commonly accepted that inorganic As(III) compounds are approximately 60-80 times more toxic to humans than As(V) and inorganic arsenic compounds are about 100 times more toxic than organic ones (Ferguson and Gavis, 1972; Villaescusa and Bollinger, 2008). Recent studies found that MMA(III) and DMA(III) are more acutely toxic and more genotoxic than their parent compounds. These trivalent arsenicals are more toxic than iAs(V), MMA(V), and DMA(V) in vitro. This may be related to more efficient uptake of trivalent methylated arsenicals than of pentavelent arsenicals by microvessel endothelial cells. Recently, LC_{50} values were calculated as 571, 843, 5.49, and 2.16 μM for iAs(V), DMA(V), iAs(III), and DMA(III), respectively, for human cells. This study also showed that dimethylmonothioarsenic (DMMTA(V)) is much more toxic than other pentavelent nonthiolated arsenicals (Sharma and Sohn, 2009).

Goswami and Das (2002) ordered the toxicity of arsenic compounds as;

Arsine> Arsenite>Arsenate>Alkyl Arsenic Acids>Arsonium Compounds
and Metallic Arsenic

1.1.4. Health Effects

The toxicology of arsenic is a complex phenomenon as arsenic is considered to be an essential element also. However arsenic (e.g., As(III)) can be toxic through its interaction with sulfhydryl groups of proteins and enzymes (to denature the proteins and enzymes within the cells) and through an increase of reactive oxygen species in the cells, consequently causing cell damage. (Duker et al., 2005).

The results of clinical findings for arsenic poisoning from drinking arsenic contaminated water show the presence of almost all the stages of arsenic clinical manifestation (Hotta, 1989). After the intake of arsenic into the human body, approximately 50% of the arsenic is excreted in the urine, with the small portions through the feaces, skin, hair, nails and lungs (Das et al.,1995). The oral LD_{50} for inorganic arsenic ranges from 15–293 mg(As)/kg and 11–150 mg(As)/kg bodyweight in rats and other laboratory animals respectively (Done and Peart, 1971; Ng, 2005). Exposure to arsenic trioxide by ingestion of 70–80 mg has been reported to be fatal for humans (Vallee et al., 1960).

Two types of toxicity; acute and sub-acute are known from long time. The acute arsenic poisoning requiring prompt medical attention usually occurs trough ingestion of contaminated food or drink. The major early manifestation due to acute arsenic poisoning include burning and dryness of the mouth and throat, dysphasia, colicky abnormal pain, projectile vomiting, profuse diarrhea, and hematuria. The muscular cramps, facial edema and cardiac abnormalities, shock can develop rapidly as a result of dehydration (Done and Peart, 1971). Sub-acute arsenic poisoning mainly involves the respiratory, gastro-intestinal, cardio-vascular, nervous systems. It may cause loss of appetite, nausea and some vomiting, dry throat, shooting pains, diarrhea, nervous weakness, tingling of the hands and feet. Longer exposure resulted in dry, falling hair, brittle loose nails, darken skin exfoliation and a hormy condition of the palms and soles (Holmquist, 1951; Pinto and Mcgill, 1953). Long term exposure to arsenic via drinking water causes cancer of skin, lungs, urinary bladder, and kidney, as well as other skin changes such as pigmentation changes and thickening (hyperkeratosis) (WHO, 2001). In general, there are four recognized stages of arsenicosis, or chronic arsenic poisoning (Choong et al., 2007):

- *Preclinical*: the patient shows no symptoms, but arsenic can be detected in urine or body tissue samples.

- *Clinical*: various effects can be seen on the skin at this stage. Darkening of the skin (melanosis) is the most common symptom, often observed on the palms. Dark spots on the chest, back, limbs or gums have also been reported. Oedema (swelling of hands and feet) is often seen. A more serious symptom iskeratosis, or hardening of skin into nodules, often on palms and soles. WHO estimates that this stage requires 5–10 years of exposure to arsenic.

- *Complications*: clinical symptoms become more pronounced and internal organ are affected. Enlargement of liver, kidneys and spleen have been reported. Some research indicates that conjunctivitis (pinkeye), bronchitis and diabetes may be linked to arsenic exposure at this stage.

- *Malignancy*: tumors or cancers (carcinoma) affect skin or other organs. The affected person may develop gangrene or skin, lung or bladder cancer.

1.1.5. Permissible Limits of Arsenic

The World Health Organization (WHO) revised the guideline for arsenic from 0.05 to 0.01 mg/L in 1993 (WHO, 1993). As the results, Germany has lowered its permissible limit of arsenic to 0.01 mg/L in 1996, while the Australian drinking water limits were also lowered from 0.050 to 0.007 mg/L. The French current standard is 0.015 mg/L, Mexican standard is 0.05 mg/L. In the European Union, the arsenic standard level is now set to 10 µg/L. Ng et al. (2003) reported the guidelines for arsenic in some countries (Table 1.1). The Environmental Protection Agency (EPA) has also eventually implemented the reduction of permissible values of arsenic in drinking water from 50 to 10 µg/L in light of the epidemiological evidence to support the carcinogenic nature of the ingested arsenic and its connection with liver, lung and kidney diseases and other dermal effects (EPA, 2001). Many US water utilities protested the EPA adoption of the WHO recommendation to revise the arsenic standard of 10 µg/L. Naturally occurring arsenic, adsorbed from rocks through which water passes, is present in some 4,000 sites in the US, mainly in the southwest and northeast states. Utilities supplying water complied with earlier EPA standards of a 50 µg/L maximum contaminant level (MCL), but the revised compliance levels that reduced this to 10 µg/L MCL represented a big change. The Malaysia Environmental Quality Act (1974) has stated that limit of sewage and industrial effluents for arsenic ranged between 0.05– 0.1 mg/L.

Table 1.1. Arsenic contamination in groundwater and population at risk around the world (Ng et al., 2003)

Country or area	Population at risk	Groundwater concentration (µg As/L)	Guidelines (µg As/L)	Discovery Date
Argentina	2 000 000	100-1000	50	1981
Bangladesh	50 000 000	<1-4700	50	1980s
Bolivia	20 000		50	1997
Chile	437 000	900-1040	50	1971
China, Guizhou	20 000	100-10 000 (mg/kg)	8 mg/kg	1950s
China, Inner Mongolia	600 000	1-2400	50	1990s
China, Xinjiang Province	100 000	1-8000	50	1980s
Hungary	220 000	10-176	10	1974
India, West Bengal	1 000 000	<10-3900	50	1980s
Mexico	400 000	10-4100	50	1983
Nepal	Unknown	Up to 456	50	2002
Peru	250 000	500	50	1984
Romania	36 000	10-176	10	2001
Taiwan	200 000	10-1820	10	1950s
Thailand, Ronpibool	1000	1-5000	50	1980s
USA	Unknown	10-48 000	10	1988
Vietnam	Millions	1-3050	10	2001

1.1.6. Arsenic in the World

In recent years, the presence of dissolved arsenic in contaminated groundwater has emerged as a major concern on a global scale. Soil is high in arsenic compounds and well water contain as much as 300-4000 µg/L of arsenic in Bangladesh. A world away, over 70 million people in Bangladesh and in other regions of Indian subcontinent are routinely exposed to arsenic poisoning through drinking groundwater. The problem of arsenic contamination in groundwater of West Bengal has been claimed as the biggest calamity in the world (Mandal et al., 1996) and several other countries such as New Zealand, USA, Pakistan, Taiwan, Japan, etc. have also been impacted by arsenic contaminated water (WHO, 2001).

Arsenic in Turkey

Arsenic occurs in Turkey mainly in the form of realgar and orpiment. Arsenopyrite, another form of arsenic occurrence, is associated with gold. It is found within the gold-arsenic province of the Menderes block in the west, in association with wein deposits.

High arsenic concentrations were determined in waters of some cities of Turkey for example İzmir, Manisa and Balıkesir. A comprehensive arsenic survey has not been studied yet. Figure 1.2 shows the map of arsenic affected areas of Turkey in 1970. The most arsenic affected region is Aegean as shown in Figure 1.2.

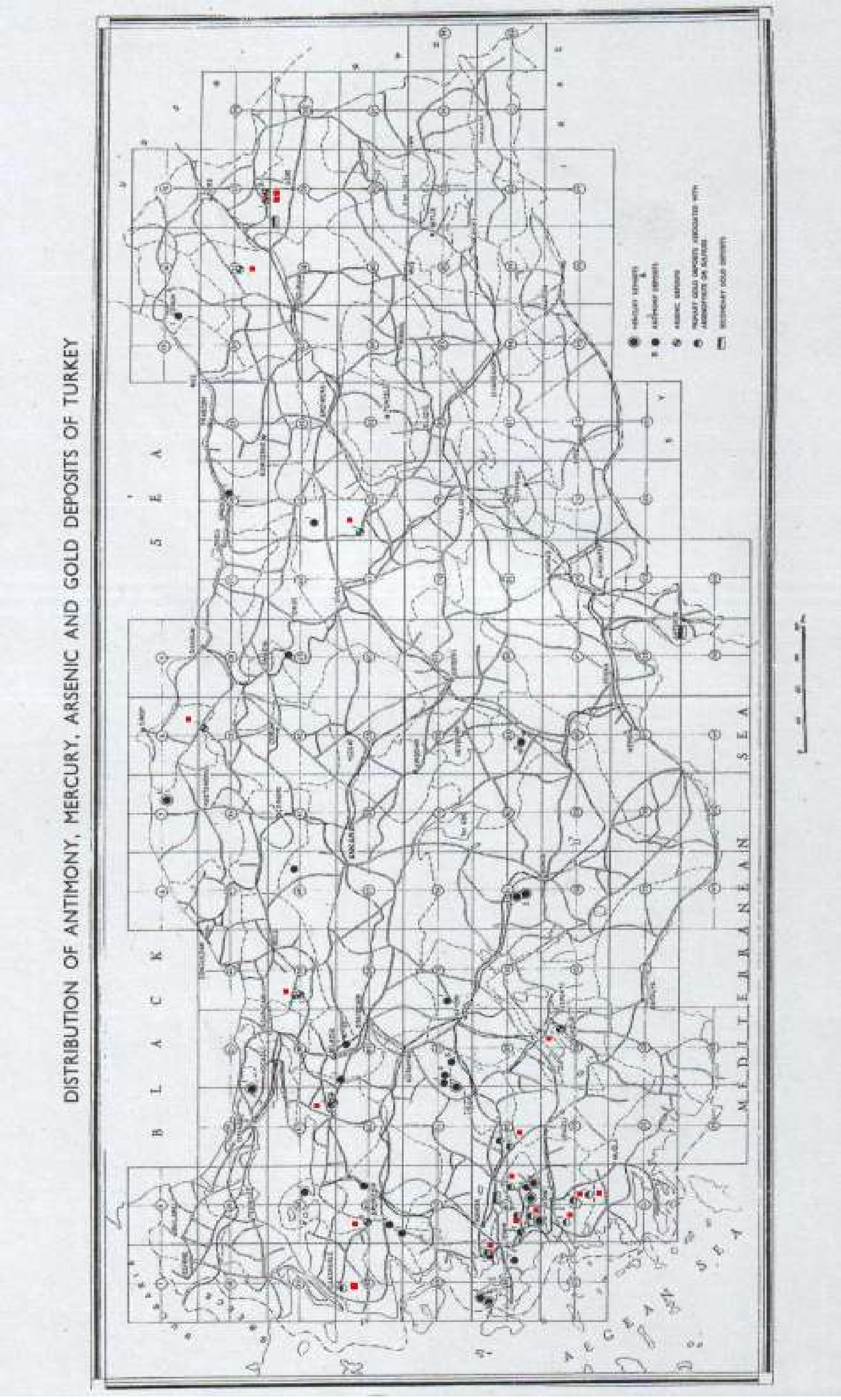


Figure 1.2. Distribution of antimony, mercury, arsenic and gold deposits of Turkey (Publications of MTA, 1970).

1.1.7. Determination Methods of Arsenic Species

Numerous instrumental methods have been developed either for the determination of total arsenic or its methylated and inorganic forms in soils and sediments, water, air and biological fluids and tissues. Inorganic forms of arsenic are more toxic than organic species, with As(III) being more toxic than As(V) (Ferguson and Gavis, 1972; Villaescusa and Bollinger, 2008). Therefore, in order to evaluate arsenic risk of drinking water, it is necessary to determine the species of arsenic in natural waters. Several techniques for the determination of arsenic species have been published in the literature (Hung et al., 2004).

Inductively coupled plasma mass spectrometry (ICPMS) has become a favored detection technique in arsenic analysis. It provides ultra sensitivity, multi element capability, and can be combined with the separation techniques for speciation analysis (Richter et al., 1998).

Hydride generation atomic absorption spectroscopy (HG-AAS) is perhaps the most widely used method for the determination of arsenic since Holak (1969) first reported it in 1969. HG allows extremely low detection limits. Hydride generation atomic fluorescence spectrometry (HGAFS) (Le et al., 1996), graphite furnace atomic absorption spectrometry (GFAAS) (Anezaki et al., 1999), neutron activation analysis (NAA) (Rottschafer et al., 1972) are the other spectrometric determination techniques of arsenic.

Determination of arsenic by HG-AAS easily can be performed using $NaBH_4$ solutions, if it is present as As(III). However, pentavalent arsenic, As(V) is partly reduced and, therefore needs to be reduced to As(III) state before reduction with $NaBH_4$. The total inorganic arsenic content detection is normally based on the concentration of As(III) after converting all the arsenic species to the trivalent form. Selective reduction procedures are based on the highly pH dependent reduction reaction between arsenic species and sodium tetrahydroborate ($NaBH_4$) to generate arsenic in HG-AAS systems. The most popular reagent for prereductant of As(V) to As(III) is potassium iodide, which can be used with ascorbic acid, in order to prevent the oxidation of iodide to triiodide by air, or with oxidants such as iron(III) and copper(II) (Chen et al., 1992). Potassium iodide can reduce As(V) only in a strong acidic media (Welz and Sucmanova, 1993). At acid concentrations less than 0.3 M, iodide failed to reduce As(V) to

As(III) completely. Other reagents used for the reduction of As(V) are mercaptoacetic (Anderson et al., 1986) acid and L-cysteine (Chen et al., 1992).

Recent studies were published about the speciation of arsenic in the literature. Sigrist and Beldomenico (2004) studied the speciation of inorganic arsenic species with variable sodium tetrahydroborate concentrations. As(V) interference was 6% in the case of water samples with 6 μg/L As(III) in the presence of 54 μg/L As(V). When the As(V) content of the sample increased, analytical error in As(III) determination was increased, too. As(V) gave signal at 0.1% and higher $NaBH_4$ concentrations because of particular reduction to As(III) under the study conditions. Coelho et al. (2002) also reported the determination of As(III) and total arsenic without pre-reduction step. They have chosen the $NaBH_4$ concentration as 0.1% but As(V) signal was about 5%. Similar results were obtained by Behari and Prakash (2006) and Anthemidis et al. (2005). As(III) and As(V) speciaiton was done by selective sorption of As(V) by aluminium hydroxide precipitate in the presence of As(III) (Tuzen et al., 2009). However, As(III) was also sorbed with 10% efficiency. Similarly As(III) was adsorbed by biomass coated resin in the presence of As(V) and the same interference was observed.

Table 1.2. Analytical parameters obtained by various detection techniques for arsenic in water samples (Hung et al., 2004).

Species	Pre concentration/ separation	Derivatisation	Detection	LOD (μg/L)
Atomic Spectrometry				
As(III)		HG	AAS	0.6
As(V)				0.5
As(III)	FI-SE	HG	AAS	0.05
As(V)				2
As(III)	FI	HG	AAS	0.037
As(III)	FI-KR: PDC	HG	AFS	0.023
As(III)		HG	AFS	0.67
As(III)	IC	HG	AFS	4
As(III)	SPE		GFAAS	0.11
As(V)				0.15
As(III)	PDC		GFAAS	0.02
As(III)	AE-resin: PDC		GFAAS	6.6
As(III)	SPE		GFAAS	0.04
ICP Techniques				
As(III)		HG	ICP-AES	0.7
As(III)	FI-KR		ICP-MS	0.021
As(V)				0.029
As(V)	SPE		ICP-MS	0.008
As(III)		HG	ICP-MS	0.003
As(III)	HG-GF		ICP-MS	0.002
As(III)	HPLC		ICP-MS	0.02
As(III)	HPLC		ICP-MS	0.06
Nuclear Techniques				
As(III)	PDC		NAA	0.001
As(III)	CE		NAA	0.02
Electrochemistry				
As(III)			CSV	0.52
As(III)			CA	0.15
As(III)			CCSA	3
As(V)				0.5
As(III)			ASV	0.19

1.1.7.1. HG-AAS

Hydride generation atomic absorption spectrometry is one of the most widely used methods for arsenic speciation due to its high sensitivity, low detection limit and high selectivity. The process of formation of arsine from

As(V) suggests that there are two steps in the reaction: the reduction of As(V) to As(III) and the subsequent formation of AsH_3 (Burguera and Burguera,1997).

$$As(V) \rightarrow As(III)$$

$$As(III) \rightarrow AsH_3$$

$$4H_2AsO_3^- + 3BH_4^- + 7H^+ \rightarrow 4AsH_3 + 3H_3BO_3 + 3H_2O$$

1.2. Removal of Arsenic

World Health Organization (WHO) published 10 µg/L as the drinking water guideline for arsenic in 1993 (WHO, 2001). According to this arsenic limit, many of the drinking water sources all over the world have became unacceptable. Therefore, research interest in arsenic removal from drinking water using low cost, simple and cheap methods has greatly increased.

1.2.1. Arsenic Removal Methods

Many treatment technologies like ion exchange, precipitation, coagulation and filtration, reverse osmosis, electro dialysis, lime softening and oxidation-filtration have been published for the removal of arsenic from water. Low removal capacity, toxic residual and high costs are the main limiting factors for the arsenic removal techniques. Moreover, for the removal of As(III), pre-oxidation to As(V) is necessary with most of the arsenic removal techniques. However, technologies based on adsorption remains attractive and promising, because of their simplicity, ease of operation and handling sludge free operation. An adsorptive material is desired to have some properties such as low cost, removal ability of both As(III) and As(V), selectivity, high physical strength, practical usage for small and big water treatment facilities. Removal of arsenic from water by adsorption on granular ferric hydroxide (GFH) (Driehaus et al., 1998), activated carbon (Natale et al., 2008), zero valent iron (Bang et al., 2005), synthetic zeolites (Chutia et al., 2009), activated red mud (Altundoğan et al., 2002), iron oxide coated sand (Hsu et al., 2008) have been reported. Yadanaparthi et al., (2009) have listed the optimal conditions and uptake capacities of the removal methods for As(III) and As(V) , respectively.

The most widely used sorbents are iron(III) oxides that are produced by different methods. Generally, ferric salts are precipitated at high pH usually with NaOH and the products vary in chemical structure, composition, and physical characteristics with the methods of precipitation. Most of these sorbents can remove both As(III) and As(V) (Ferguson and Gavis, 1972; Altundogan et al., 2000; Roberts et al., 2004; Saha et al., 2005, Wilkie and Hering, 1996) and, therefore, have commonly been preferred for arsenic removal because of the cost effectiveness and high adsorption capacities. As(V) is adsorbed as ionic species, whereas controversial reports on the mechanism of As(III) adsorption have been published; some reports stating the oxidation of As(III) to As(V) by the ferric oxides before adsorption (Sun and Doner, 1998; Malik et al., 2009; Lenoble et al., 2005; Sarkar et al., 2005) and the others reporting As(III) adsorption as the molecular species of H_3AsO_3 (Choong et al., 2007; Sarkar et al., 2008). X-ray absorption near edge structure (XANES) analysis indicated that As(III) remained stable on the goethite surface toward heterogenous oxidation to As(V) (Manning et al., 1998). X-ray absorption spectroscopy (XAS) studies by Farquar et al. (2002) confirmed that the adsorbed As(III) and As(V) remained original oxidation states on the surfaces of goethite and lepidocrocite. However, such instrumental methods are usually limited due to their comparatively high detection limits (Wang and Mulligan, 2008).

Amorphous Fe-O-OH was found to have the highest adsorption capability since it has the highest surface area (Mohan and Pittman, 2007; Lim et al., 2009). Most of the iron oxides are available only as fine powders or are generated in-situ as gels or suspensions in aqueous solution. These forms of iron oxide retain their strong affinities to As(III) and As(V) but are limited to reactor configurations incorporating large sedimentation and filtration units which cause difficulty in solid/liquid separation (Lo and Chen, 1997). Thus, they are not suitable for column adsorption in water and wastewater treatment. Furthermore, iron(III) oxide alone is not suitable as filter medium due to its low hydraulic conductivity Theis et al., 1992). Daus et al. (2004) studied As(III) and As(V) adsorption onto five different sorbents; activated carbon(AC), zirconium loaded AC (Zr-AC), zero valent iron (Fe^0), granulated iron hydroxide (GIH) , and a sorption medium with the trade name 'Absorptionsmittel3'(AM3). Highest removal of As(V) was obtained by Zr-AC and of As(III) by AC. Streat et al. (2008) have reported that GFH in water treatment was distinctly advantageous since the process involves little maintenance or manpower, and there is no pre-treatment required other than chlorination. A method was also described to remove arsenic by oxidation of

Fe(II) to iron(III) hydroxide by aeration (Roberts et al., 2004). Application of Fe(II) instead of Fe(III) was reported to be advantageous, because partial oxidation of As(III) to As(V) by aeration occurs at the same time. However, another study has reported that Fe(III) is more effective and economical than Fe(II) due to required lower coagulant dose and pH (Baskan and Pala, 2009). Iron coated zeolite (ICZ) and iron coated sand were also used as the adsorbent. The capacity of ICZ for As(V) was fifteen times higher than that of iron coated sand (Jeon et al., 2009). The adsorption capacity of iron oxide impregnated onto activated alumina was also reported to be higher than the values for iron oxide coated sand and ferrihydrite (Singh and Pant, 2006).

Table 1.3. Comparison of main arsenic removal technologies (Mohan and Pittman, 2007)

Major oxidation/ precipitation Technologies	**Advantages**	**Disadvantages**
Air oxidation	Relatively simple, low-cost but slow process; in-situ arsenic removal; also oxidizes other organic and inorganic constituents in water	Mainly removes As(V) and accelerate the oxidation process
Chemical oxidation	Oxidizes other impurities and kills microbes; relatively simple and rapid process; minimum residual mass	Efficient control of the pH and oxidation step is needed
Major coagulation/	**Advantages**	**Disadvantages**
Alum coagulation	Durable powder chemicals are available; relatively low capital cost and simple in operation; effective over a wider range of pH	Produces toxic sludges; low removal of arsenic; pre-oxidation may be required
Iron coagulation	Common chemicals are available; more efficient than alum coagulation on weigh	Medium removal of As(III); sedimentation and filtration needed
Lime softening	Chemicals are available commercially	Readjustment of pH is required
Major sorption and ion-exchange technologies	**Advantages**	**Disadvantages**
Activated Alumina	Relatively well known and commercially available	Needs replacement after four to five regeneration
Iron coated sand	Cheap; no regeneration is required; remove both As(III) and As(V)	Not standardized; produces toxic solid waste
Ion-exchange resin	Well-defined medium and capacity; pH independent; exclusive ion spesific resin to remove arsenic	High cost medium; high-tech operation and maintenance; regeneration creates a sludge disposal problem; As(III) is difficult to
Major membrane technologies	**Advantages**	**Disadvantages**
Nanolfiltration	Well-defined and high-removal efficiency	Very high-capital and running cost, pre-conditioning; high water rejection
Reverse osmosis	No-toxic solid waste is produced	High tech operation and maintenance
Electrodialysis	Capable of removal of other contaminants	Toxic wastewater produced

1.2.2. Support Materials

Sand (Hsu et al., 2008), zeolite (Jeon et al., 2009), pumice (Reddy and Turner, 2007) , silicagel (Deniz Çiftçi et al., 2010), cement (Kundu and Gupta, 2007), pottery (Dong et al., 2009), alumina (Kuriakose et al., 2004), resin (Matsunaga et al., 1996) were used as the support material of iron(III) hydoxide for arsenic removal. The strength of the adsorbent was increased when a support material used. Red color was observed on the paper when a stress was applied on GFH which had no support material. Any decomposition was observed with ferric hydroxide supported on silicagel (FHSS) (Deniz Çiftçi et al., 2010). Another advantage of the supporting material is being suitable for column studies.

1.2.2.1. Deposits of Perlite, Pumice in Turkey

Turkey is very rich about the deposits of perlite and pumice. Deposits of perlite and pumice in Turkey are shown in Figure 1.3.

Figure 1.3. Deposits of perlite and pumice in Turkey

1.2.2.2. Chemical and Physical Properties of Pumice, Perlite, Zeolite and Purolite C-100 Resin

<u>**Perlite**</u>

Perlite is a vitreous substance that contains 2-6% water. It has gray, silver dark, dark brown and black colors. Perlite is a lightweight material because it can expand 10-30 times of its volume when heated between 800 and 1150 ^{o}C. Expanded perlite was first used in USA, and spread all over the world owing to its lightweight, heat and sound insulator properties. In Turkey 8 billion tons of perlite exists, it is 70% of world reserves. The chemical and physical properties of perlites given in the literature have been tabulated in Table 1.4.

Table 1.4. Chemical and physical properties of perlites

Component	**Weight ratio (%)**	**Property**	
SiO_2	71.0–76.5	**Color**	White
Al_2O_3	12.4–16.0	**Melting point**	1300 °C
Na_2O	2.90–4.00	**Specific heat**	0.20 kcal/kg °C
K_2O	4.00–7.00	**Unit weight**	2.2–2.4 g/cm^3
CaO	0.20–1.30	**Rough density**	30–190 kg/m^3
Fe_2O_3	0.50–1.45	**Heat conductivity**	0.034–0.040 kcal/mh°C
H_2O	3.05–5.16	**Sound insulating**	18 db (125 Hz)

Figure 1.4. SEM micrograph of Perlite

Pumice

Pumice (pumicite) is a light-coloured natural sponge-like material of volcanic origin composed principally of high silica, low iron and magnesium content. In particular, it is found in the Mediterranean area. Italy, is the biggest pumice producer in the world (44% in total) and Turkey is the second (9% in total). Pumice is used in many applications such as in the chemical, dental, cosmetic, abrasives, cement, concrete, ceramic and glass industries because of being an inexpensive and widespread geological raw material. Worldwide, over 50 countries produce pumice products.The chemical and physical properties of pumices given in the literature have been tabulated in Table 1.5. The SEM picture of pumice is shown in Figure 1.4.

Table 1.5. Chemical and physical properties of pumices

Components	**Weight ratio (%)**	**Property**	
SiO_2	52.00-75.51	**Color**	White – Light gray
CaO	0.25-8.00	**Melting point**	900 °C
Al_2O_3	9.94-17.50	**Specific heat**	0.24-0.28 kcal/kg °C
Fe_2O_3	0.50-13.20	**Unit weight**	1.9-2.65 g/cm^3
Na_2O	1.60-6.80	**Heat conductivity**	0.12-0.20 kcal/m h °C
K_2O	2.25-11.27	**Sound insulating**	40-55 db

Figure 1.5. SEM micrograph of pumice

Zeolite

Zeolites are microporous crystalline materials with a uniform pore size distribution at molecular scale, a well defined ordered structure, tuneable pore structure and exchange capability. Besides their classical applications, the possibility of zeolite pores to host different ions, atoms, molecules and clusters have opened up numerous opportunities as advances nanomaterials. The chemical and physical properties of zeolites given in the literature have been tabulated in Table 1.6.

Table 1.6. Chemical and physical properties of zeolites

Components	**Weight ratio (%)**	**Property**	
SiO_2	48.6-71.29	**Color**	White – Light gray
Al_2O_3	11.30-21.36	**Melting point**	1200 ^{o}C
Fe_2O_3	0.99-2,06	**Specific heat**	0.18-0.27 kcal/kg ^{o}C
K_2O	0,4-4.2	**Unit weight**	2.2-3.1 g/cm^3
Na_2O	0-1.04	**Heat conductivity**	0.10-0.26 kcal/m h ^{o}C
CaO	0.56-1,99	**Sound insulating**	39-64 db

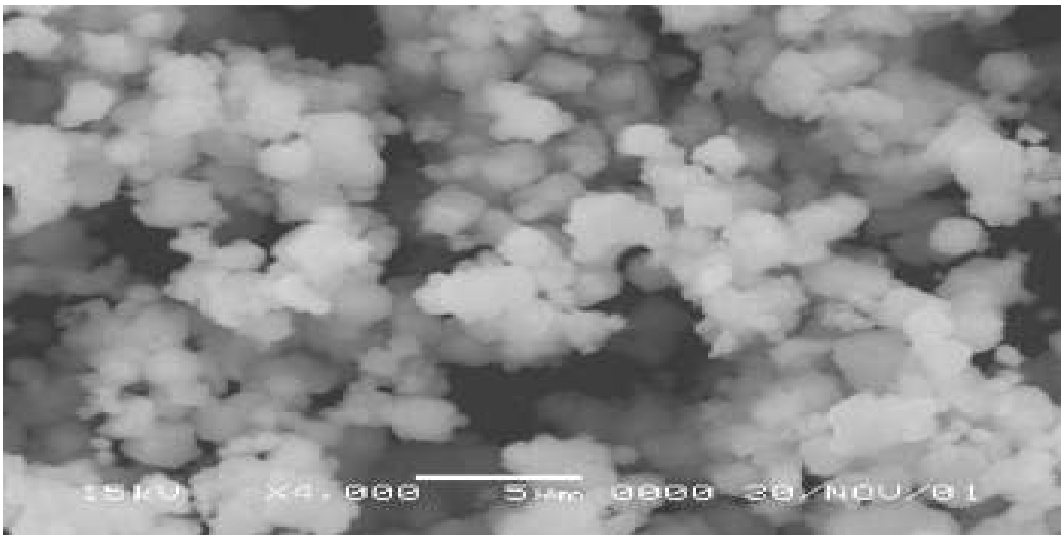


Figure 1.6. SEM micrograph zeolite

Silicagel

Silicagel is a granular, vitreous, highly porous form of silica made synthetically from sodium silicate. Despite its name, silica gel is a solid. It is a naturally occurring mineral that is purified and processed into either granular or beaded form. As a desiccant, it has an average pore size of 24 angstroms and has a strong affinity for water molecules. The chemical and physical properties of silicagel given in the literature have been tabulated in Table 1.7.

Table 1.7. Chemical and physical properties of silicagel

Components	**Weight ratio (%)**	**Color**	White
SiO_2	98.7	**Melting point**	1200-1610 ^{o}C
Al_2O_3	0.7	**Unit weight**	1.9-2.1 g/cm^3
Na_2O	0.3	**Heat conductivity**	0.02-0. 1kcal/m h ^{o}C

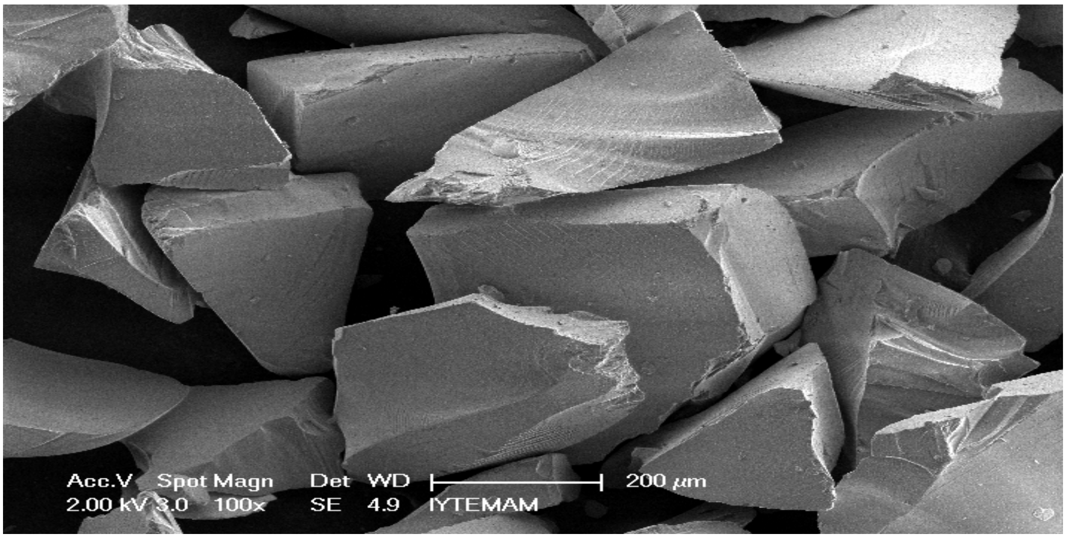


Figure 1.7. SEM micrograph of silicagel

Purolite C-100 Resin

Purolite C-100 is supplied in the sodium form and it is primarily used in coflow regenerated industrial softening or when regenerated with mineral acids (hydrochloric or sulfuric acids) as the cation resin in demineralization plants used in industrial water treatment.

Table 1.8. Chemical and physical properties of Purolite C-100 Resin

Poymer Structure	Gel polystyrene crosslinked with DVB
Physical form	Amber, clear spherical beads
Functional groups	Sulfonic
Ionic form, as shipped	Na^+
Moisture retention, Na+ form	44-48%
Particle Size range	300 - 1200 µm
Maximum temperature limit	120°C
Specific gravity, Na+ form	Approx. 1.29g/cm^3

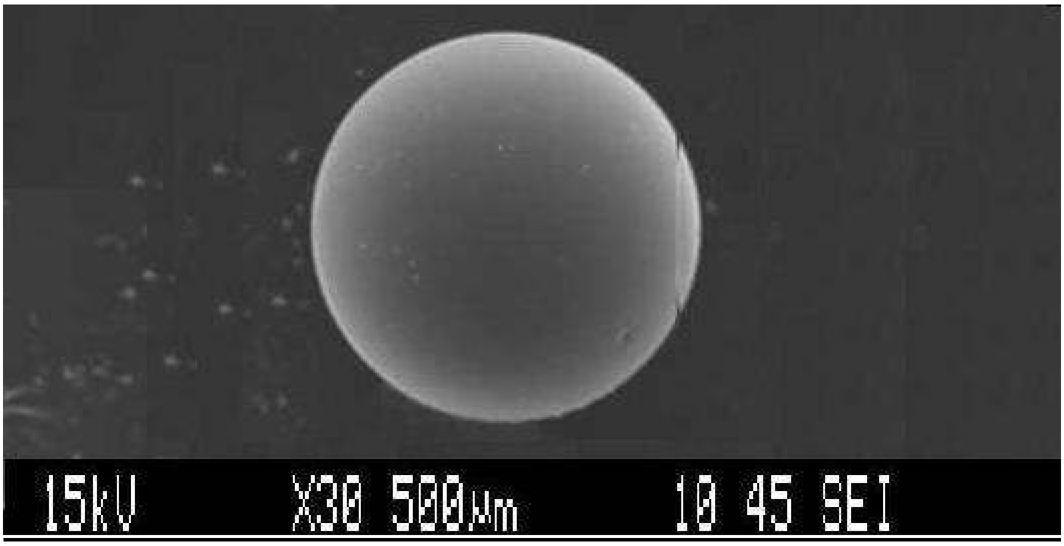


Figure 1.8. SEM micrograph of Purolite C-100 Resin

1.3. Nano Materials

A nanometer is one billionth of a meter (10^{-9} m) about one hundred thousand times smaller than the diameter of a human hair, a thousand times smaller than a red blood cell, or about half the size of the diameter of DNA. In general, nanoparticles are smaller than 100 nanometers, contain 20–15,000 of atoms, and exist in a realm that straddles the quantum and Newtonian scales. They can be produced from different materials in different shapes such as spheres, rods, wires and tubes. Figure 1.9 shows how the nanoparticle (NP) fit into other size-dependent categories that have been used for many decades.

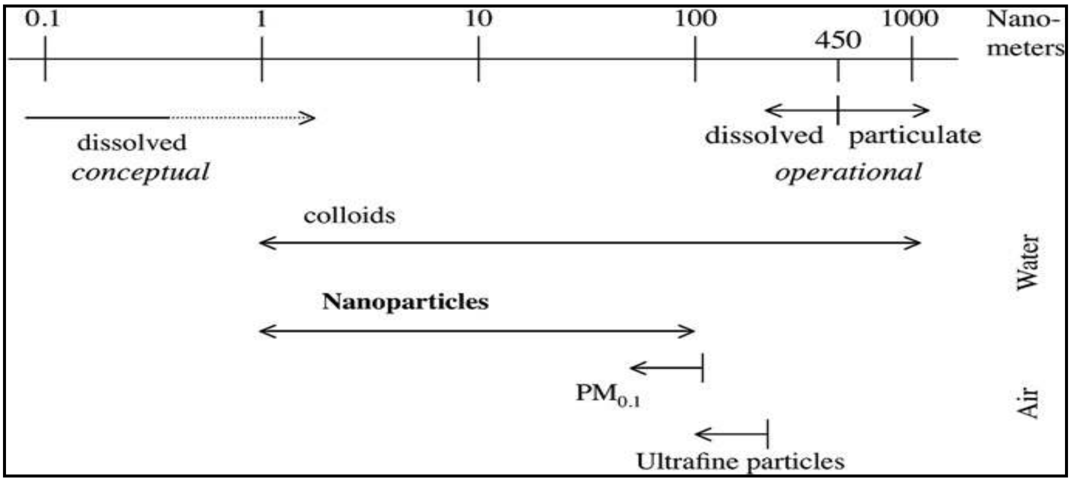


Figure 1.9. Definitions of different size classes relevant for nanoparticles

The definition of nanotechnology does not include unintentionally produced nanomaterials, such as diesel exhaust particles or other friction or airborne combustion byproducts, or nanosized materials that occur naturally in the environment, such as viruses or volcanic ash. Where information from incidentally formed or natural nanosized materials (such as ultrafine particulate matter) may aid in the understanding of intentionally produced nanomaterials.

Nanotechnology is the manipulation of matter for use in particular applications through certain chemical and / or physical processes to create materials with specific properties. The unique properties of various types of intentionally produced nanomaterials give them novel electrical, catalytic, magnetic, mechanical, thermal, or imaging features that are highly desirable for applications in commercial, medical, military, and environmental sectors. As new uses for materials with these special properties are identified, the number of products containing such nanomaterials and their possible applications continues to grow (Penn et al., 2003; West and Halas, 2000).

There are many types of intentionally produced nanomaterials, and a variety of others are expected to appear in the future. For the purpose, most current nanomaterials could be organized into four types:

1- Carbon-based materials. These nanomaterials are composed mostly of carbon, most commonly taking the form of a hollow spheres, ellipsoids, or tubes. Spherical and ellipsoidal carbon nanomaterials are referred to as fullerenes, while cylindrical ones are called nanotubes. These particles have many potential applications, including improved films and coatings, stronger and lighter materials (Bianco and Prato, 2003; Biasaga and Pyrzynska, 2006).

2- Metal-based materials. These nanomaterials include quantum dots (Gao et al., 2004), nanogold (Li et al., 2005), nanosilver (Morones et al., 2005) and metal oxides, such as titanium dioxide (Giammar et al., 2007). A quantum dot is a closely packed semiconductor crystal comprised of hundreds or thousands of atoms, and whose size is on the order of a few nanometers to a few hundred nanometers. Changing the size of quantum dots changes their optical properties.

3- Dendrimers. These nanomaterials are nanosized polymers built from branched units. The surface of a dendrimer (Duncan and Izzo, 2005) has numerous chain ends, which can be tailored to perform specific chemical functions. This property could also be useful for catalysis. Also, because three-dimensional dendrimers contain interior cavities into which other molecules could be placed, they may be useful for drug delivery.

4- Composites combine nanoparticles with other nanoparticles or with larger, bulk-type materials. Nanoparticles, such as nanosized clays (Yaron-Marcovich et al., 2005) are already being added to products ranging from auto parts to packaging materials, to enhance mechanical, thermal, barrier, and flame-retardant properties.

Table 1.9. Examples of products that use nanotechnology and nanomaterials (USEPA, 2007)

Health and Fitness	**Electronics**	**Home and Garden**	**Food and Beverage**	**Other**
Wound derssing	Computer display	Paint	Non-stick coatings for pans	Coatings
Pregnanacy test	Games	Antimicrobial pillows	Antimicrobial refrigerator	Lubricants
Toothpaste	Computer hardware	Stain resistant cushions	Canola oil	
Golf club				
Tennis racket				
Skis				
Antibacterial socks				
Waste and stain resistant pants				
Cosmetics				
Air filter				
Sunscreen				

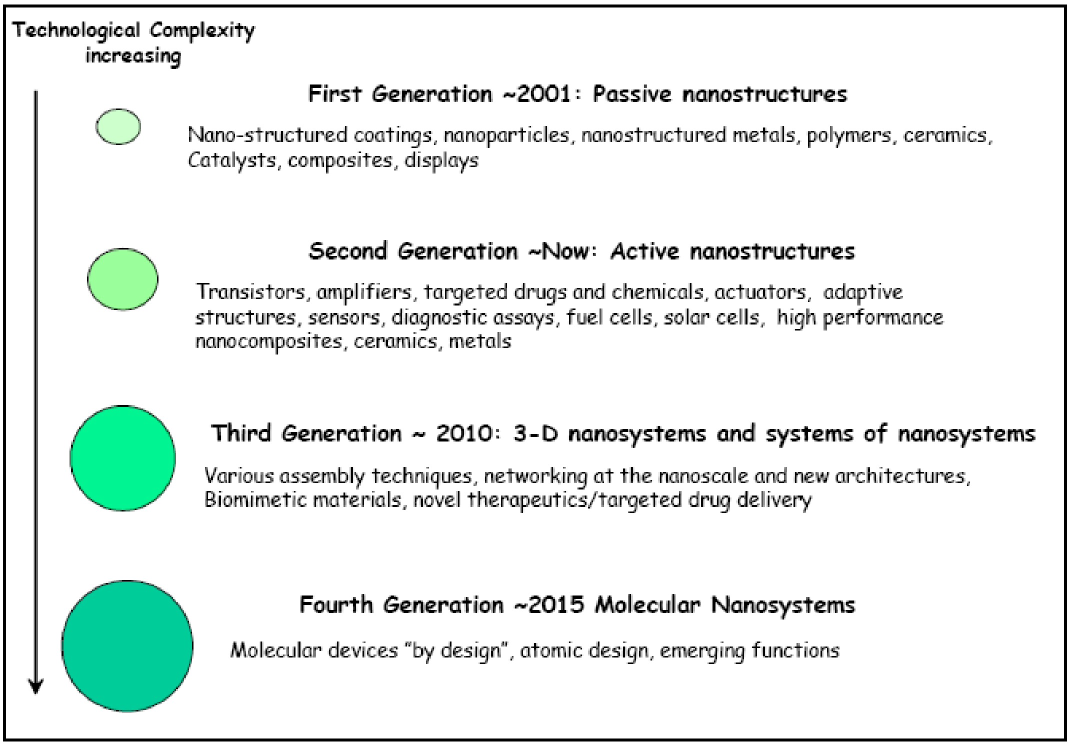


Figure 1.10. Projected stages of nanotechnology development (USEPA, 2007)

1.3.1. Health Effects

Altough nanoparticles have received much attention for their applications in biological studies, various studies have shown the potential adverse effects of nanoparticles on human health and the environment (EPA, 2005). The small particle size, a large surface area and the ability to generate oxygen species play a major role in toxicity of nanoparticles (Nel et al., 2006). Nanoparticles can be simply absorbed on to the surface of cell membranes, and possibly digested in cells and degraded, leading to cytotoxic effects. Nanowires and nanotubes can behave similarly to microneedles, damaging cell walls and impairing cell growth (Liu, 2006; Nowack and Bucheli, 2007). This may be a beneficial characteristic for such uses as targeted drug delivery and other disease treatments, but could result in unintended impacts in other uses or applications. Inhaled nanoparticles may become lodged in the lung or be translocated, and the high durability and reactivity of some nanomaterials raise issues of their fate in the environment. It may be that in most cases nanomaterials will not be of human health or ecological concern. However, at this point not enough information exists to assess environmental exposure for most engineered nanomaterials.

1.3.2. Remediation

The unique structure and electronic properties of some NP can make them especially powerful adsorbents. Enhanced retention or solubilization of a contaminant may be helpful in a remediation setting. Nanomaterials may be useful in decreasing sequestration of hydrophobic contaminants, such as polycyclic aromatic hydrocarbons (PAHs), bound to soils and sediments. Using the information, Tungittiplakorn et al. (2004) used nanoparticles for the remediation of soil.

Metal remediation has also been proposed, using zero-valent iron and other classes of nanomaterials. Morgada et al. (2009) investigated the effect of UV light and humic acid on As(V) removal. Also Deliyanni et al. (2009) studied the removal of cadmium and arsenic using iron-based nanoadsorbents. Nanoparticles such as poly(amidoamine) dendrimers can serve as chelating agents, and can be further enhanced for ultrafiltration of a variety of metal ions (Cu (II), Ag(I), Fe(III), etc.) by attaching functional groups such as primary amines, carboxylates, and hydroxymates (Diallo, 2005). Self-assembled monolayers on mesoporous supports (SAMMS) are nanoporous ceramic materials that have been developed to remove mercury or radionuclides from wastewater (Mattigod, 2003).

Nanomaterials have also been studied for their ability to remove metal contaminants from air. Certain nanostructured sorbent processes can be used to prevent emission of nanoparticles and create byproducts that are useful nanomaterials (Biswas et al., 2005)

Table 1.10. Outcomes for Sustainable Use of Major Resources and Resource Systems

Water	sustain water resources of quality and availability for desired uses
Energy	generate clean energy and use is efficiently
Materials	use material carefully and shift to environmentally preferable materials
Ecosystems	protect and restore ecosystem functions, goods, and services
Land	support ecologically sensitive land management and development
Air	sustain clean and healty air

1.3.2.1. Arsenic Removal by Using Nanoparticle

Iron and iron based adsorbents were very effective for arsenic removal. Zhu et al. (2009) combined two arsenic removal agents; nano zero-valent iron and activated carbon. Nanoscale zero-valent iron was supported onto activated carbon by impregnating carbon with ferrous sulfate followed by chemical reduction with $NaBH_4$. Adsorption capacities were calculated from Langmuir isotherm as 18.2 and 12.0 mg/g for As(III) and As(V), respectively. Protonated titanate nanotubes (Niu et al., 2009) were also used arsenic removal. More than 80% of As(III) and 95% of As(V) were adsorbed on the adsorbents.

1.3.3. Synthesis of Ni-NP

Nickel nanoparticles are potential candidates for catalysts, magnetic materials, conducting inks, and ferrofluids (Zhang et al., 2004). Varied preparation conditions of nickel nanoparticle (Ni-NP) were published in recent years. Khanna et al. used sodium borohydride and sodium formaldehyde sulfoxylate as reducing agent. Optimum formation temperature was obtained betwen 50-100 ^{o}C. 70% Ni and 30% C, S and O contained in the yield. Wu et al. (2009) also prepared nickel nanoparticle by using hydrazine. They have synthesized pure metallic nickel nanoparticle, spherical in shape by the chemical reduction of nickel chloride with hydrazine at room temperature without any protective agent and inert gas protection.

1.4. Purpose of This Study

The purpose of this study was to investigate and develop sorbents for As(III) and As(V) removal.

Iron(III) hydroxide supported on silicagel (FHSS) was used. Preparation of the iron(III) hydroxide at pH 6.0 was found to be the best for arsenic removal. The FHSS developed in this study was found to have advantages over traditionally used iron oxides, such as sorption of both As(III) and As(V) with high removal efficiencies and relatively high capacities, elimination of the elaborate filtration step in the batch method of arsenic removal, ease of preparation and suitability for column use.

In order to minize the costs and simplify supporting procedure of the sorbent, iron(III) oxide thermally supported on pumice was also studied for arsenic removal.

A novel adsorbent named ‘nickel nanoparticle impregnated resin’ (Ni-NPIR) was used for arsenic removal for the first time in the literature. It was effective for both As(III) and As(V) removal without any need for oxidation of As(III). The adsorbent could be used many times for arsenic removal by regeneration.

2. CHAPTER TWO - EXPERIMENTAL

2.1. Reagents

All the reagents were of analytical-reagent grade and glass distilled water was used throughout.

1000 mg/L arsenic(III) and arsenic(V) stock standard solutions: prepared by dissolving As_2O_3 (Merck) and $Na_2HAsO_4.7H_2O$ (Merck), respectively, in concentrated HCl (Merck) and diluted with distilled water. As(III) and As(V) stock solution contained 2 M HCl. More dilute standard solutions were prepared daily by dilution of the stock solutions.

8.3 % KI solution: prepared by dissolving 8.3 g of KI (Merck) in distilled water and diluted to 100 mL with distilled water.

0.6 % and 4 %$NaBH_4$ solutions: prepared by dissolving $NaBH_4$ (Merck) pellets in 0.01 M NaOH. 0.01 M EDTA (Merck) was used for masking interferences in arsenic determination.

2 M Fe(III) solution: prepared by dissolving 54.06 g $FeCl_3.6H_2O$ (Merck) in 0.01 M HCl and diluting to 100mL with distilled water.

2 M CH_3COOH/CH_3COO^- buffer: $CH_3COONa.3H_2O$ was dissolved in distilled water and the pH values of the solutions were adjusted to the required values by adding 2 M HCl.

NH_4^+/NH_3 buffer solution: prepared by adding HCl solution onto NH_3 (Merck) solution.

Silicagel (Acros Organics): 0.200-0.500 mm in diameter with a pore diameter of ca. 4nm.

Perlite (Cuma Ovası, Etibank), pumice (Soylu Group Ltd. Şti.) and zeolite: ground and sieved (0.250-0.500mm). Particles were heated with 100mL 2 M HCl for about 2 h, two times. It was then cooled, filtered and washed with distilled water until filtrate gave negative reaction for Cl^-, and dried in an oven at 110 ^oC.

Ni nanoparticles impregnated particles:

3% Ni^{2+} solution: prepared by dissolving $NiSO_4.6H_2O$ (Merck) in 0.01 M HCl.

4% $NaBH_4$ solution was prepared by dissolving $NaBH_4$ (Merck) in distilled water.

The support material: Purolite C-100 cation exchange resin.

2.2. Apparatus

pH was measured by Jenway 3040 model pH meter. For the determination of Fe^{3+}, Jenway 6105 model UV/Vis. spectrophotometer was used. Nuve ST-402 model shaker with thermostatic bath was used for shaking at fixed temperature. 3.0 model Zeta-Meter was used for the determination of zero charge of the adsorbent. The characterization of ferric hydroxide supported silica gel (FHSS) and Ni-NPIR were performed by using a scanning electronic microscope combined with X-Ray energy dispersive spectrometer (Philips XL-30S FEG; JEOL JSM-6060, respectively). Thermo Scientific K–Alpha model X-Ray photoelectron spectroscopy used for the characterization of Ni-NPIR.

A GBC 904 PBT model atomic absorption spectrometer was used for arsenic determination. The experimental conditions for hydride generation AAS system are listed in Table 2.1. HG-3000 model automated hydride generation system was used for total arsenic determination.

Table 2.1. Instrumental operating parameters for HG-AAS in arsenic determination.

System type	Flame
Element	As
Lamp curent (mA)	8.0
Wavelength (nm)	193.7
Slit width (nm)	1.0
Slit Height	Normal
Instrument Mode	Absorbance BC on
Flame Type	Air-Acetylene
Measuring Mode	Peak Area
Carrier Gas	N_2

2.3. Procedure for Arsenic Determination

For the determination of total arsenic, the continuous flow HGAAS system (Figure 2.1) was used. In this system, the sample (8 mL/min), 10.2 M HCl solution (2 mL/min) and 0.6% $NaBH_4$ solution (2 mL/min) are continually pumped with a peristaltic pump into a mixing coil where hydrides are formed and then separated from the liquid phase in the gas liquid separator and swept into the quartz tube atomizer with a nitrogen flow for atomic absorption measurements. Conversion of As(V) to arsin was not quantitative under these conditions. Therefore, it was necessary to reduce As(V) to As(III) using 8.3 % KI in 1 M HCl prior to reduction with sodium tetrahydroborate(III) to AsH_3. The relative standard deviation for the determination of 20 µg/L arsenic was 1.4 % (n=7). The limit of detection for arsenic was 0.5 µg/L.

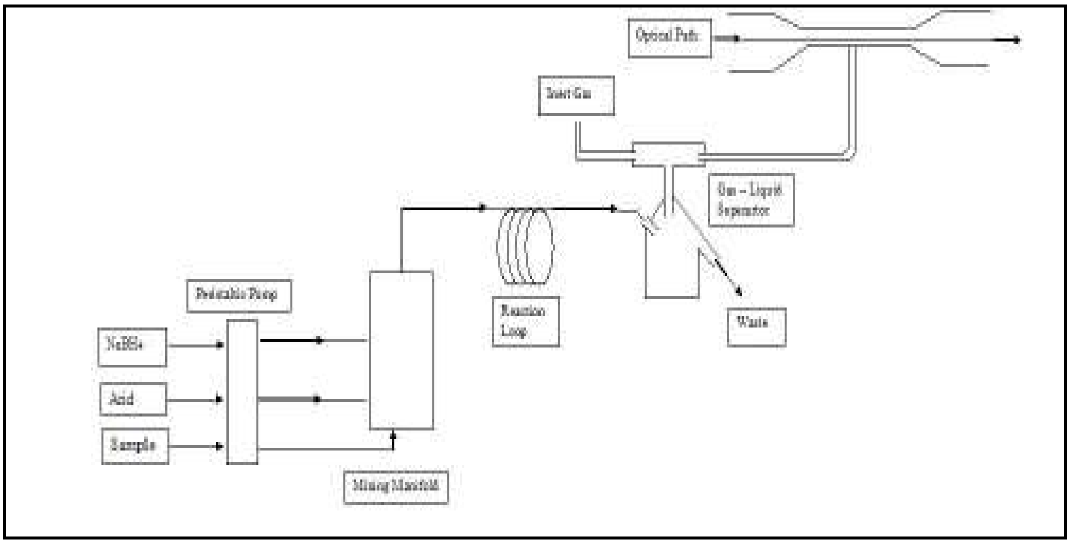


Figure 2.1. Continuous flow HGAAS system

Also, As(III) and As(V) species were determined in admixtures by using batch type HGAAS (Figure 2.2) (Erdem and Henden, 2004). 1 mL of the sample or standard solution of arsenic in 0.1 M HCl was injected into the reaction vessel of 20 mL volume containing 1 mL of 4 % $NaBH_4$ solution. The generated arsine was swept by a nitrogen flow (134 mL/min) through $CaCl_2$ and $CaSO_4$ containing drying tube into the quartz tube atomizer. Arsenic absorption at 193.7 nm was measured. The relative standard deviation for the determination of 30 µg/L As(III) was found to be 4.76 % (n=7). The limit of detection was found to be 1.2 µg/L. For the determination of As(V), it was reduced to As(III) with KI prior to borohydride reaction as above. Analytical performance for As(V) was similar to that obtained for As(III).

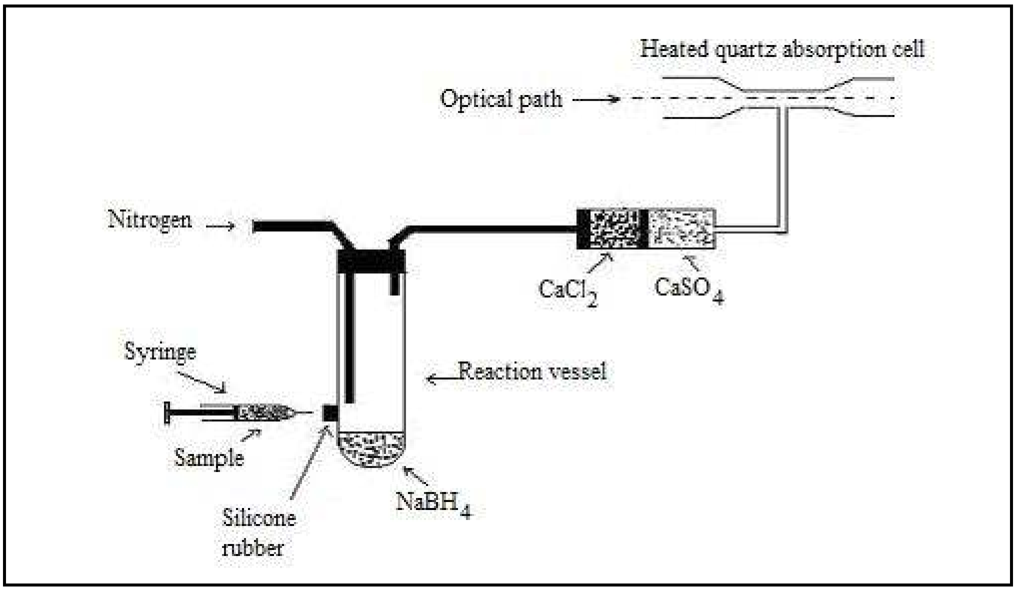


Figure 2.2. A laboratory-made hydride generation system.

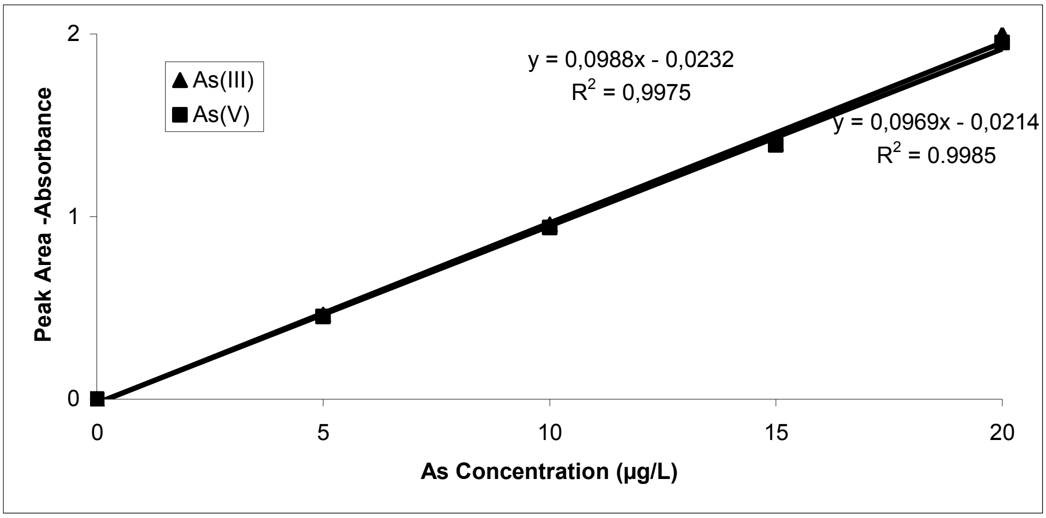


Figure 2.3. Calibration graphs for As(III) and As(V).

2.4. STUDY OF ARSENIC(III) AND ARSENIC(V) REMOVAL FROM WATERS USING FERRIC HYDROXIDE SUPPORTED ON SILICAGEL (FHSS) PREPARED AT LOW pH

2.4.1. Procedure for the Preparation of FHSS

1.0 g silicagel was weighed in a 100 mL volumetric flask. 25 mL of 2 M Fe(III) in 0.01 M HCl was added onto silicagel and shaken for 24 h at 25 °C. After decanting the solution, Fe(III) ions on the silicagel were precipitated by the addition of 25 mL 2 M CH_3COOH/CH_3COO^- buffer (pH 6.0) and shaken for another 24 h. The supernatant liquid was decanted. FHSS particles were washed with distilled water by decantation repeatedly until the aqueous washings, tested with acidic NH_4SCN solution, became iron-free.

2.4.2. Effect of the Precipitation Conditions on the Capacity and the Removal Efficiency of FHSS

It is known that when the precipitated iron(III) hydroxide contains colloids, arsenic removal efficiency seriously decreases. In such cases, an elaborate microfiltration step is added to the system in order to remove the arsenic containing colloids, and thus, improve the efficiency. It is again well known that the pH of the precipitation solution seriously affects the particle size of the hydrated iron(III) oxide precipitates. Therefore, we have studied the effect of the precipitation pH on the total arsenic removal capacity.

0.1 M NaOH, NH_4^+/NH_3 buffer of pH 9.0, and CH_3COOH/CH_3COO^- buffers of pH 4.0, 5.0, and 6.0 were used for the preparation of the adsorbent. For this purpose, 0.1g silicagel was weighed and continued as described earlier. When NaOH and NH_4^+/NH_3 buffers were used for the precipitation cloudy suspensions were formed, whereas CH_3COOH/CH_3COO^- buffer formed clear supernatant solution. 25 mL 100 mg/L As(III) or As(V) solutions were added onto the prepared adsorbents and shaken for 24 h. Amount of arsenic adsorbed was found by measuring unadsorbed arsenic in the solution. Also for the removal efficiency studies, 25 mL 200 µg/L As(III) or As(V) solutions were added onto the adsorbents prepared using 0.5g silicagel (much below the capacity).

2.4.3. The Effect of Shaking Time of Silicagel with $FeCl_3$ on Removal Capacity

Portions of 0.1 g silicagel were weighed and added onto 2 M 10 mL $FeCl_3$ solutions in beakers (for the absorbtion of $FeCl_3$ into the pore). The beakers were shaken for different times (1; 4; 7; 13; 18; 24h). At the end of the times, solutions were decanted and 10 mL pH 6.0 buffer added into the beakers and shaken for 24 h at 25 ^oC. 24 h later, solutions were decanted and the adsorbents were washed with distilled water untill obtaining colorless solution. For arsenic uptake of the adsorbent, 15 mL 100 mg/L As(III) and As(V) solution were added onto the adsorbents and shaken for 24 h at 25 ^oC.

2.4.4. The Effect of Shaking Time of Fe(III) Impregnated Silicagel With CH_3COOH/CH_3COO^- buffer pH 6.0 on Arsenic Uptake

Portions of 0.1 g silicagel were weighed and added onto 2 M 10 mL $FeCl_3$ solutions in beakers. The beakers were shaken for 1h. Solutions were decanted and 10 mL pH 6.0 buffer added into the beakers (for the precipitation of Fe^{3+}) and shaken for different times (1; 2; 5; 16; 24h) at 25 ^oC. 24 h later, solutions were decanted and the adsorbents were washed with distilled water untill obtaining colorless solution. 15 mL 100 mg/L As(III) and As(V) solution were added onto the adsorbents and shaken for 24 h at 25 ^oC.

2.4.5. Effect of Adsorbent Dose

Various amounts of silicagel were weighed and the adsorbents were prepared as described earlier. 25 mL of 200 µg/L As(III) or As(V) solutions wereadded onto the adsorbents and shaken for 24 h at 25 °C. The effect of the adsorbent dose on the removal of As(III) and As(V) were determined by following the unadsorbed arsenic in the solutions.

2.4.6. Characterization of FHSS

For the identification of the adsorbent, SEM and EDX analysis were done. 25 mL volumes of 800 mg/L As(III) and As(V) solutions were added onto separate portions of 0.25 g FHSS and shaken for 72 h. The particles were washed with distilled water and dried at 40 °C for 90 minutes. Parallel experiments were also carried out using silicagel without iron. The surface morphology and chemical composition of the FHSS were determined by SEM-EDX analysis.

2.4.7. Investigation of pH Dependence of As(III) and As(V) Removal

The uptake of As(III) and As(V) by the adsorbent at various initial pH levels was studied in order to determine the optimum pH for arsenic removal. 25 mL 100 µg/L As(III) or As(V) solutions with pH in the range of 3.1-11.2 was added onto 0.5 g of FHSS and shaken for 24 h. Unadsorbed arsenic in each solution was determined by HGAAS and arsenic removal efficiencies were calculated.

2.4.8. Zeta Potential of the Adsorbents

Electrophoretic mobility was used to determine the surface electrical characteristics of FHSS particles at various pH values. Silicagel particles (0.20-0.50mm) were grinded to powder. 18 portions of 0.1 g powder silicagel were weighed and placed to different beakers. Six portions of the silicagel were shaken with distilled water for blank. 5 mL 2 M $FeCl_3$ solutions were added onto each 12 portions and shaken 24 h at 25 °C (in the thermostated water bath). Supernatant solutions were decanted. 5 mL CH_3COOH/CH_3COO^- buffer (pH 6.0) solutions were added into the each beakers and shaken for 24 h at 25 °C (in the thermostated water bath). 24 h later, adsorbents were washed with distilled water until the supernatant solution was clear.

A-10 mL 0.01 M HCl were added into separate beakers and pHs of these solutions (pH 3.5 - 8.5) were adjusted by adding 0.01 M NaOH. These solutions were transferred into volumetric flasks and diluted to 100 mL with water. 30 mL of the solutions in the pH range 3.5-8.5 were added onto the adsorbents. pH of supernatant solution was measured again. Final pHs were, 3.80; 4.26; 5.08; 6.15; 7.80 and 8.50 for blank and 3.20; 4.23; 5.03; 6.18; 7.81 and 8.50 for the adsorbents.

B- FHSS particles were diluted in 100 mL of 0.01 M $NaNO_3$ solution at different pHs. The pHs of these solutions (pH 3.2 - 8.5) were adjusted either by 0.1 mol/L NaOH or HNO_3 solution.

The electrophoretic mobility was observed at room temperature with a Zeta-meter. The ζ-potentials of FHSS were determined as a function of pH using 0.01 M $NaNO_3$ as the supporting electrolyte.

2.4.9. Study of As(III) sorption

Sorption of As(V) onto hydrated iron(III) oxides from natural waters is mainly due to the ionic adsorption of $H_2AsO_4^-$ and $HAsO_4^{2-}$, the main species existing at natural water pH. However, there are controversial approaches in the literature for the mechanism of adsorption of As(III) onto hydrated iron(III) oxide. In one approach, it is stated that As(III) is oxidized to As(V) by Fe(III) in the sorbent before the adsorption (Sun and Doner, 1998; Malik et al., 2009; Lenoble et al., 2005; Sarkar et al., 2005). In another approach, physical adsorption is caused mainly by Van Der Waals forces and electrostatic forces between adsorbate molecules, and the atoms which compose the adsorbent surface (Choong et al., 2007; Sarkar et al., 2008). Such explanations are usually based on theoretical approaches.

We have, therefore, carried out studies in order to identify experimentally the arsenic species adsorbed during the removal of As(III) by FHSS, based on the separate determination of As(III) and As(V) species. A series of experiments were carried out in order to make clear whether As(III) is adsorbed onto FHSS as As(III) species or oxidized to As(V) by Fe(III) in the FHSS before the adsorption. For this purpose, As(III) was adsorbed by the FHSS by column study and batch study.

Column Study: 30 mL of 400 mg/L As(III) solution was passed through the column containing 2 mL adsorbent . The column was washed well with distilled water, column fillings were then transferred into a beaker and iron(III) hydroxide in the FHHS was dissolved by heating with 20 mL of 2 M HCl. Iron and arsenic ions were passed into the solution. The solution was transferred to a volumetric flask and the silicagel was washed with water until white color was obtained. The washing solutions were also added into the volumetric flask and diluted to 100 mL with distilled water. 1mL of the solution was diluted to 50 mL and was then passed through 15 mL cation exchange resin (IR- 120) containing column. Iron(III) in the solution was held by the resin and, therefore, arsenic containing colorless eluate was obtained. 5 mL of the eluate was completed to 100 mL with distilled water. As(III) in this solution was measured using EDTA as the interference masking agent with batch type HGAAS. Presence of As(V) in the eluate was controlled in the same way after reducing As(V) to As(III) with KI. Parallel experiments were carried out throughout the procedure using As(V) in order to check if it is reduced to As(III) by any means before the determination step.

Batch Study: Arsenic adsorption experiments were repeated with the batch method. 25 mL of 500 μg/L As(III) solution was added onto 1.25 g adsorbent and shaken for 24 h at 25 °C. The adsorbent was then dissolved in 2 M HCl, and the concentrations of arsenic species in the solution were determined.

2.4.10. Determination of Column Capacity for Arsenic Removal

Column capacities were determined for both As(III) and As(V). The adsorbent was prepared using 5.5 g dry silicagel. For capacity determination, 1000 μg/L As(III) solution was made flow through the arsenic removal column containing FHSS. Arsenic in the eluent solutions were determined by HG-AAS. The same procedure was also applied for As(V).

2.4.11. Adsorption of As(III) and As(V) Depending on Time and Temperature

The adsorbents were prepared by using portions of 0.5 g of silicagel. Shaking time was 1 h for both Fe(III) solution and pH 6.0 buffer for the preparation of the adsorbent. 250 mL of 100 μg/L As(III)and As(V) solutions (pH

6.0 buffer included) were added onto the adsorbents and shaken at 20 ^oC, 25 ^oC and 30 ^oC, respectively. 20 minutes later, 2 mL of these solutions were taken out and As(III) and As(V) were determined by HG-AAS. The same procedure was applied for 45; 90; 150; 180; 220 and 1320 minutes.

Because of lack adsorption, the experiment was repeated to obtain faster removal. For this purpose, 0.5 g silicagel was weighed and 25 mL of 2 M Fe(III) in 0.01 M HCl was added onto silicagel and shaken for 24 h at 25 ^oC. After decanting the solution, Fe(III) ions on the silicagel were precipitated by the addition of 25 mL 2 M CH_3COOH/CH_3COO^- buffer (pH 6.0) and shaken for another 24 h. The supernatant liquid was decanted. FHSS particles were washed with distilled water by decantation repeatedly. 250 mL of 100 µg/L As(III) and As(V) solutions (pH 6.0) were added onto the adsorbents and shaken at 25 ^oC. 10 minutes later, 2 mL of these solutions were taken out and As(III) and As(V) were determined by HG-AAS. The same procedure was applied for 30; 60; 130; 210 and 240 minutes.

2.4.12. Supporting of Ferric Hydroxide on Different Particles

In order to decrease the cost of the adsorbents; pumice, perlite, zeolite were used as the support material.

2.4.12.1. Preparation of Sorbents

Perlite, pumice, and zeolite were firstly ground and sieved using 250 and 500 µm sieves. ~ 20 g portions of paticles were heated with 100 ml 3 M HCl, for about 2 h, two times. It was then cooled, filtered and washed with distilled water until filtrate gave negative reaction for Cl^-, and dried in an oven at 110 ^oC. Silicagel used was 0.200-0.500 mm in diameter and with a pore diameter of ca 4 nm. The products were ready for supporting.

2.4.12.2. Preparation of Ferric Hydroxide Supported on the Particles

0.1 g of dry perlite, pumice, zeolite and silicagel (0.250-0.500 mm) was weighed. 10 ml 2 M Fe(III) solution (in 0.01 M HCl) was added onto the particles and shaken for 24 h at 28 ^oC. Also 0.01 M HCl solution was added onto the particles as blank and the same procedure was applied them, too. The solution above the particles was decanted. Hydrated iron(III) oxide were precipitated by the addition of acetic acid-sodium acetate buffer (pH 6.0) solution. Then, again shaken for 24 h at 28 °C. The supernatant liquor was decanted together with the suspending ferric hydroxide and the remaining gel were washed with distilled water by decantation repeatedly until the aqueous washings became iron-free in water.

2.4.12.3. Determination of Iron on the Adsorbents (Precipitated with pH 6.0 buffer)

20 mL 2 M HCl solution was added onto the ferric hydroxide on sorbents (1 g). On warming the precipitate was dissolved and iron ions passed into the solution. This solution was diluted to 100 mL with distilled water. Iron ions were determined by spectrophotometric method. Absorbances of the solutions were measured.

2.5. STUDY OF ARSENIC(III) AND ARSENIC(V) REMOVAL FROM WATERS USING FERRIC HYDROXIDE SUPPORTED ON SILICAGEL (FHSS) PREPARED BY THERMAL METHOD

Generally, Fe(III) was precipitated by a reagent such as NaOH. We know that, Fe(III) can be oxidized by the air in a heated media. Ferric Hydroxide obtaining by thermal method would decrease the reagent spent. Therefore we have studied the thermally ferric oxide preparation on silicagel. Oven and furnace (Figure 2.4) were used to form ferric hydroxide at stepwise and fixed temperatures.

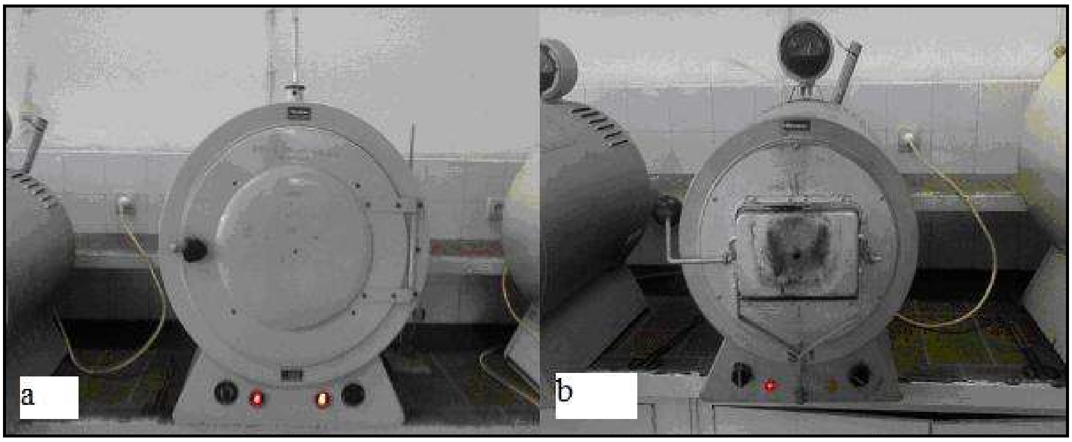


Figure 2.4. a) Oven b)Furnace photography

2.5.1.Supporting Ferric Hydroxide on Silicagel at Different Temperatures (Thermal Method)

The adsorbents were prepared thermally by two methods: stepwise and fixed temperature.

2.5.1.1. Stepwise heating: 8.0 g of silicagel were weighed. 100 mL 2 M $FeCl_3$ was added onto the silicagel and shaken for 24 h at 30 ^oC (in a thermostated water bath). Supernatant solution was decanted and the silicagel was divided into 14 portions. All of them were placed into a gravimetric furnace with air tube open at 190 ^oC. It was seen that all were red 10 minutes later. 3 h later one pair of them was taken out from the furnace and the temperature was increased to 230 ^oC. 3 h later, again one more pair was taken out and the temperature was increased to 290 ^oC. This procedure was applied to the others at 350, 400, 450 and 500 ^oC. The same procedure was repeated in an oven at 30, 45, 90, 130, 180 and 200 ^oC. Adsorbents were washed with distilled water with the wash solutions did not give red colour with NH_4SCN and dried at room temperature.

2.5.1.2. Heating at one fixed temperature: 100 mL 2 M $FeCl_3$ was added onto 6.0 g of silicagel in 250 mL beaker, in the thermostated water bath at 30 ^oC, and shaken for 24 h. Supernatant solution was decanted and silicagel with iron was divided into 12 portions. One pair of them was waited at room temperature (30 ^oC). Temperature of the oven was fixed to 90 ^oC and one pair was placed into the oven. 3 h later, these adsorbents were taken out and temperature of the oven was increased to 130 ^oC. One other pair was placed into the oven at 130 ^oC. This procedure was repeated at 180, 200 (oven) and 500 ^oC (furnace).

2.5.2. Determination of Iron on Silicagel (prepared by Thermal Method)

Iron contents of the adsorbents prepared were determined. For this pupose, 10 mL 2 M HCl was added onto the adsorbents (0.1 g). On warming the precipitate was dissolved and iron ions passed into the solution. This solution was diluted to 100 mL with distilled water. 1mL of this solution, 5 mL 2 M HCl and 8 mL 3 M NH_4SCN were mixed and diluted to 50 mL with distilled water. Fe^{3+} was determined by absorption photometric method at 460 nm wavelength.

2.5.3. Arsenic Adsorption by Thermally Prepared Ferric Hydroxide Supported on Silicagel

0.1 g adsorbent was put into beakers. 20 mL of 100 mg/L As(III) (pH 7.0) was added onto each beaker. The top of the beaker was stretched closed with parafilm and shaken for 24 h at 30 ^{o}C (in the thermostated water bath). Arsenic concentration in the supernatant solution was measured.

Adsorbents were also prepared at 100 ; 200 ; 300 ; 400 ; 500 ; 600 ; 700 ^{o}C (for 3 h at fixed temperature). As(III) adsorption experiments were studied as descibed above.

2.5.4. Arsenic Removal by Thermally Ferric Hydroxide Supported on Perlite, Pumice, Zeolite and Silicagel

In order to decrease the costs, perlite, pumice and zeolite were used as the support material for the preparation of adsorbent by thermal method.

2.5.4.1. Preparation of the Adsorbents from Perlite, Pumice, Zeolite and Silicagel Particles

1 g of the perlite were weighed into beakers and 30 mL 2 M $FeCl_3$ was added onto the each portions. The beakers were shaken for 24 h at 25 ^{o}C (in the thermostated water bath). Supernatant solution was decanted. Perlite containing $FeCl_3$ solution was placed into the furnace at 100 ^{o}C. 1 h later, temperature was increased to 150 ^{o}C, and then, one more hour later temperature was increased to 200 ^{o}C. At the end of this time, adsorbents were taken out from the furnace. The same procedure was applied to pumice, zeolite and silicagel.

2.5.4.2. Determination of As(III) Sorption Capacity

20 mL of 100 mg/L As(III) (pH 7.0) solutions were added onto 0.1 g adsorbents prepared as described above. The top of the beaker was stretched closed with parafilm and shaken for 24 h at 30 ^{o}C (in the thermostated water bath). Unadsorbed arsenic was measured by manuel HG-AAS.

2.5.5. Preparation of Thermally Supported Ferric Hydroxide on Pumice

As desribed earlier, pumice was chosen as the porous material. The pumice was provied commercially. Pumice was operated with 2 M HCl by heating 3 times and washed with distilled water until became Cl^- free. After drying at room temperature, portions of 0.5 g pumice were weighed. 10 mL 2 M $FeCl_3$ solution was added onto the pumice and shaken for 24 h. The supernatant solution was decanted and the pumice (containing Fe^{3+}) was placed onto the watch-glass. Oven and furnace were used to form ferric hydroxide at stepwise and fixed temperatures. Temperatures were; 100; 200; 300; 400; 500 ^oC for the furnace and 50; 90; 140; 180; 200 ^oC for the oven. The adsorbents were taken out 2 h later and washed with distilled water and dried at room temperature.

0.1 g of the prepared sorbents were weighed and 20 mL of 100 mg/L As(III) and As(V) solutions were added onto the adsorbents and shaken for 24 h at 25 ^oC. 24 h later, the concentrations of the solutions were determined and the capacities were calculated.

2.6. STUDY OF ARSENIC(III) AND ARSENIC(V) REMOVAL FROM WATERS USING NICKEL NANOPARTICLES IMPREGNATED RESIN (Ni-NPIR)

2.6.1. Preparation of Ni Nanoparticles Impregnated Support Particles

Perlite, pumice, zeolite, silicagel and Purolite C-100 resin were used for the support material. 0.5 g of the materials were weighed, 5 mL 4% Ni^{2+} solutions were added and shaken for 24 h at 25 ^oC. After decanting the solution, Ni impregnated support materials were washed with distilled water (until gave no reaction with dimethylglyoxime). Then, 2.5 mL of 4% $NaBH_4$ solution was added onto the materials (in a fume cupboard). Black and gaseous solution was observed. After waiting the end of gas output, the adsorbents were washed with distilled water. It was seen that, nanoparticles were formed out of the particles excluding C-100 resin.

2.6.2. Effect of Drying Temperature of the Adsorbent on Removal Efficiency and Arsenic Uptake

In order to understand the effect of drying temperature of the adsorbent on arsenic removal, prepared adsorbents were dried at 20, 40, 60, 80 and 100 ^{o}C. For the comparison, a pair of adsorbent were used wet. 0.1g of the adsorbents were used for arsenic uptake and also 0.4 g of the adsorbents were used for removal efficiency. 100 mg/L and 100 g/L As(III) solutions were added onto the adsorbents, respectively and shaken for 24 h at 25 ^{o}C.

2.6.3. Effect of Nickel(II) Concentration Used for the Adsorbent Preparation on Removal Efficiency and Arsenic Uptake

Different concentrations of Ni^{2+} were used for the preparation of the adsorbents. 5mL nickel(II) solutions at 0.1; 1.0; 3.0; 6.0 and 12.5% concentrations were added onto the resin and shaken for 24 h at 25 ^{o}C and the same procedure was applied.

2.6.4. Effect of $NaBH_4$ Concentration Used for the Adsorbent Preparation on the Arsenic Removal Efficiency and Arsenic Uptake

Different concentrations of $NaBH_4$ were used for reducing Ni^{2+} to Ni^{0}. 0.25; 0.5; 1.0; 2.0; 4.0 and 6.0% concentrations of $NaBH_4$ were added onto Ni^{2+} impregnated resin and washed until achieving clear supernatant solution. The adsorbents were dried at room temperature.

2.6.5. Time Effect of Shaking the Resin with Nickel(II) on the Removal Efficiency and Arsenic Uptake

In order to understand the effect of shaking time of the resin with Ni^{2+} on removal efficiency and arsenic uptake, resin particles were shaken with Ni^{2+} solution for different times (20; 60; 150; 390; 960 and 1350min). 0.4 g of prepared adsorbents were used for removal efficiency and also 0.1 g of the adsorbents were used for arsenic uptake.

2.6.6. Investigation of the Adsorption pH Dependence of As(III) and As(V) Removal Efficiencies

The uptake of As(III) and As(V) by the adsorbent at various initial pH levels was studied in order to determine the optimum pH for arsenic removal. Unbuffered As(III) or As(V) solutions with initial pH in the range of 3.3-11.5 were added onto the adsorbents and the mixture was shaken for 24 h. Arsenic removal efficiencies were calculated by measuring unadsorbed arsenic in the solution.

2.6.7. Characterization of Nickel Nanoparticles Impregnated Resin

25 mL volumes of 500 mg/L As(III) and As(V) solutions were added onto separate portions of 0.25 g adsorbents and shaken for 72 h. The particles were washed with distilled water and dried at room temperature (about 35 ^{o}C). Parallel experiments were also carried out without arsenic. The surface morphology and chemical composition of the adsorbents were determined by SEM-EDX and XPS analysis. Acquisition parameters for XPS analysis were:

Parameter	
Total acq. time	57.3 secs
No. Scans	6
Source Type	Al K Alpha
Spot Size	400 μm
Lens Mode	Standard
Analyser Mode	CAE : Pass Energy 30.0 eV
Energy Step Size	0.100 eV
No. of Energy Steps	191

2.6.8. Adsorption Isotherms

In order to identify the adsorption type and determine the maximum arsenic capacities, adsorption isotherm graphs were drawn. Various portions of adsorbent were weighed (0.05; 0.1; 0.2; 0.3; 0.5; 0.8 and 1.25 g). 50 mL 10 mg/L As(III) or As(V) solutions were added onto the adsorbents and, shaken at 25 ^{o}C for 24 h. Unadsorbed arsenic in the solution phase was determined by HGAAS.

Isotherm equations are;

$1/q = (1/bq_mC_e) + 1/q_m$ Langmuir Equation (1)

$\log (x/m) = \log K + 1/n \log Ce$ Freundlich Equation (2)

q:	Amount of adsorbed arsenic (g) / Amount of the adsorbent (g)
b:	Langmuir constant (L/mg)
q_m:	Adsorption capacity (mg/g)
C_e:	Equilibrium concentration of the solution (mg/L)
x:	Amount of adsorbed arsenic (g)
m:	Amount of the adsorbent (g)
K:	Freundlich constant (mg/g)
n:	Freundlich constant (dimensionless)

Langmuir and Freundlich isotherms do not give any idea about adsorption mechanism. In order to understand the adsorption type, equilibrium data was applied to Dubinin-Radushkevich (DR) isotherm which has the following form.

$\ln Q = \ln Q_m - k\varepsilon^2$ DR Equation (3)

Where ε (Polany Potentiali) is $[RT \ln(1+1/C_e)]$, Q the amount of As(III) and As(V) adsorbed per unit weight of adsorbent (mg/g), Q_m the adsorption capacity (mg/g), C_e the equilibrium concentration of arsenic species in aqueous solution, k a constant related to adsorption energy, R the gas constant and T the temperature (K).

The mean free energy of adsorption (E), defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the adsorbent was calculated from the k value using the Equation 4.

$$E=-(2k)^{-0.5} \tag{4}$$

In order to predict the adsorption efficiency of the process, the dimensionless equilibrium parameter was determined by the following equation:

$$r = \left(\frac{1}{1 + bC_1} \right) \tag{5}$$

2.6.9. Adsorption of As(III) and As(V) on Ni-NPIR Depending on Time

250 mL of 100 µg/L As(III) solution was added onto the 5 g of the adsorbents and shaken for 24 h at 30 °C. 20 minutes later 2 mL of this solution was taken out and arsenic was determined by HG-AAS. Taking of sample from the supernatant solution was repeated for 60, 180, 270, 500, and 1440 minutes. The same procedure was applied for As(V).

2.6.10. Effect of Some Ions on As(III) and As(V) Sorption

5 mg/L P, 20 mg/L Cl, 20 mg/L S, 10 mg/L Si anionic solutions were contained 500 µg/L As(III) and As(V). The mixture solutions were added onto 0.5 g adsorbent and shaken for 24 h at 25 °C.

2.6.11. Regeneration Studies of Ni-NPIR

Arsenic could be desorbed from FHSS (Deniz Çiftçi et al., 2010) using 2% NaOH and 3% NaCl mixture. Using this information an experiment was done. 2 g of the adsorbent were packed into a 1.0 cm i.d. glass column as to have 4.5mL packing volume and fitted with glass wool at the bottom and top. A 25 mL of 100 µg/L As(III) or As(V) solutions were passed through the column at a constant speed (1.5mL/min) at room temperature. The column was washed with distilled water. 50 mL of 2% NaOH and 3% NaCl mixture solution was passed through the column at 1.5 mL/minutes. Then, again 25 mL of 100 µg/L As(III) or As(V) solutions were passed through the column at a constant speed (1.5 mL/min) at room temperature and arsenic species were desorbed using the same procedure. Sorption and desorption studies were repeated six times.

3. RESULTS AND DISCUSSION

3.1 STUDY OF ARSENIC(III) AND ARSENIC(V) REMOVAL FROM WATERS USING FERRIC HYDROXIDE SUPPORTED ON SILICAGEL (FHSS) PREPARED AT LOW pH

3.1.1. Effect of the Precipitation Conditions on the Capacity and the Removal Efficiency of FHSS

The amount of adsorbed arsenic was calculated by the difference of the initial and residual amounts of arsenic in solution. The results are shown in Figures 3.1 and 3.2. The adsorbent was prepared by precipitation with CH_3COOH/CH_3COO^- buffer at pH 6.0 had the highest total batch capacity and removal efficiencies for both As(III) and As(V). When CH_3COOH/CH_3COO^- buffers with pH 4.0 and 5.0 were used for the precipitation, the colors of the adsorbent were yellowish and orange, respectively. When the adsorbent was prepared by using pH 6.0 buffer, the color was dark-red. The adsorbent color changed from dark-red to pale yellow as the pH values varied as follows: 6.0>5.0>9.0>13.0>4.0.

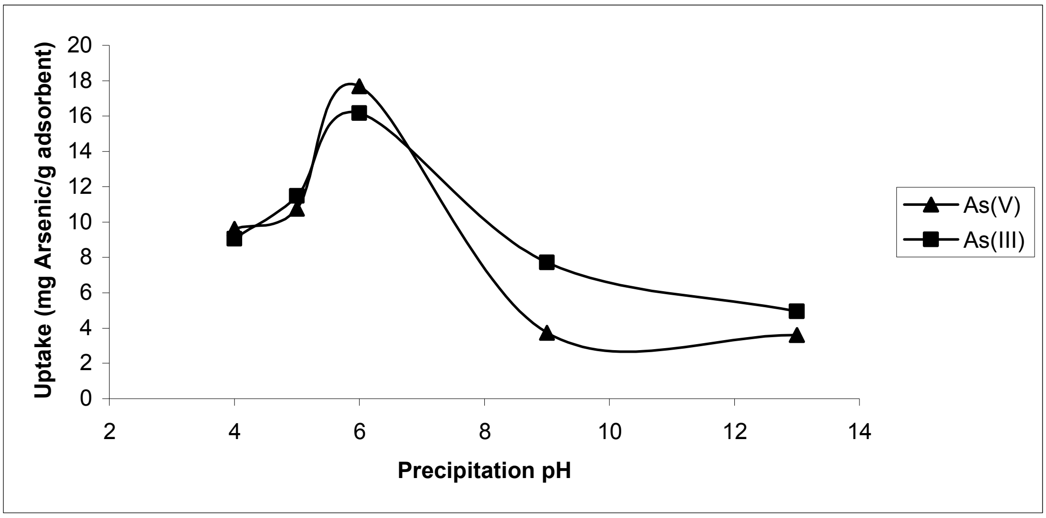


Figure 3.1. Effect of the pH of precipitation on the total batch capacity (Initial As concentration: 100 mg/L, adsorbent dose: 4 g/L, sorption: 24 h at 25 °C).

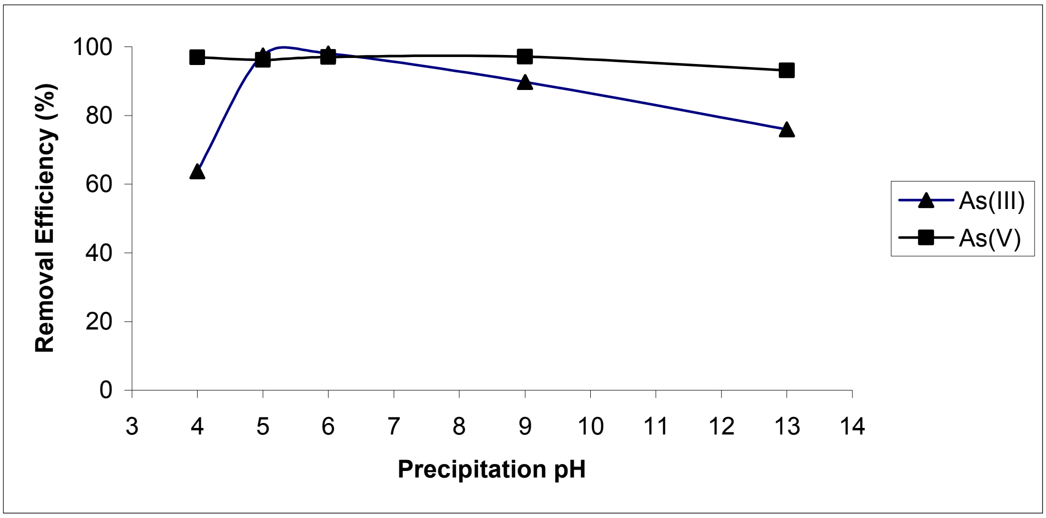


Figure 3.2. Effect of the pH of precipitation on the removal efficiency (Initial As concentration: 200 µg/L, adsorbent dose: 20 g/L, sorption: 24 h at 25 ^{o}C).

Figure 3.2 showed that when the adsorbent was prepared by using pH 4.0 and 13.0 buffers, removal efficiencies of these adsorbents were poor for As(III), but very good for As(V).

Maximum arsenic uptake and removal efficiencies were observed at pH 6.0 (precipitating pH). It could be the result of maximum iron content of the adsorbent. Therefore, we have determined the iron content of the adsorbents obtained at different pHs. For this purpose, after the determination of arsenic, the adsorbent was dissolved in concentrated HCl and the iron contents were determined by Flame-AAS. Results were shown in Figure 3.3.

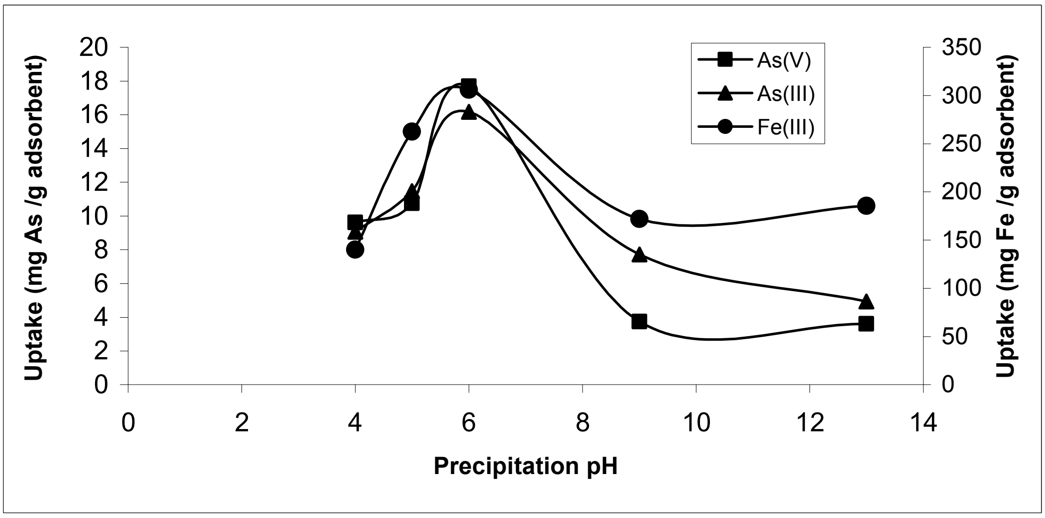


Figure 3.3. Iron contents and arsenic uptakes of the adsorbents prepared at different pHs.

It can be seen that, maximum arsenic uptake was obtained by precipitating Fe(III) at pH 6.0. This result could be explained by the iron content of the adsorbent. Therefore, pH 6.0 buffer was selected as the precipitation solution while preparing FHSS.

3.1.2. The Effect of Shaking Time of Silicagel with $FeCl_3$ on Removal Capacity

Calibration graphs were drawn for As(III) and As(V), respectively and the concentration of the supernatant solutions were determined. Adsorbed arsenic was calculated. As shown in Figure 3.4, shaking time of silicagel with $FeCl_3$ did not effect the arsenic uptake. $FeCl_3$ was placed into the pores of the silicagel even at the lowest shaking time.

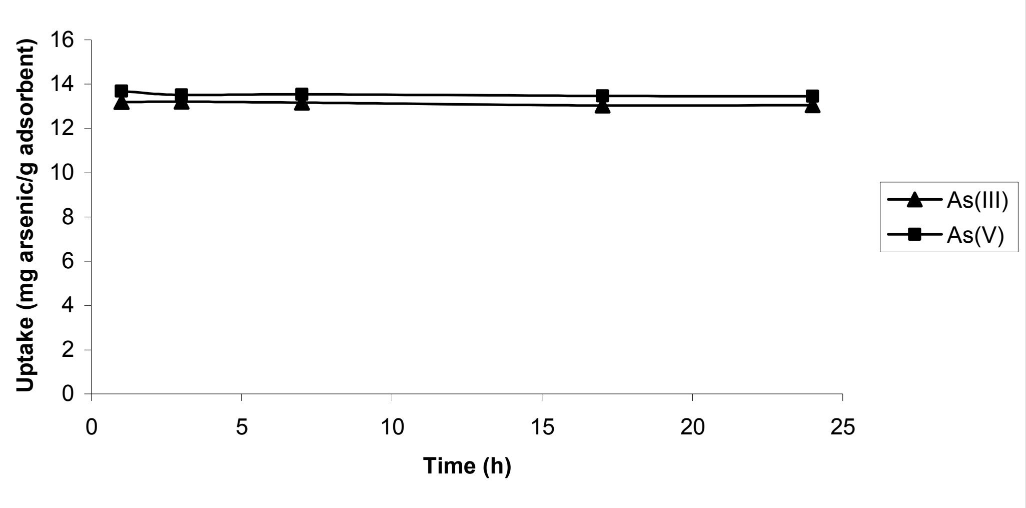


Figure 3.4. The effect of shaking time of silicagel with $FeCl_3$ (Initial As concentration: 100 mg/L, adsorbent dose: 7 g/L, sorption: 24 h at 25 ^{o}C).

3.1.3. The Effect of Shaking Time of Fe(III) Impregnated Silicagel With CH_3COOH/CH_3COO^- buffer pH 6.0 on Arsenic Uptake

The concentration of the supernatant solutions were determined. The graph of the arsenic uptake versus shaking time with pH 6.0 buffer was drawn and shown in Figure 3.5.

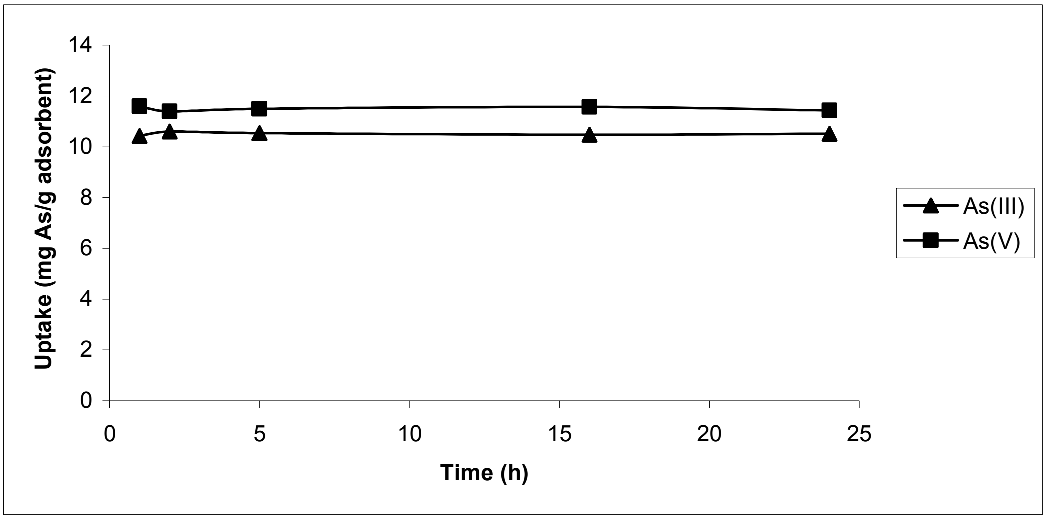


Figure 3.5. The effect of shaking time of Fe(III) impregnated silicagel with the buffer (Initial As concentration: 200 µg/L, adsorbent dose: 20 g/L, sorption: 24 h at 25 ^{o}C).

It was obvious that time of shaking with $FeCl_3$ and the pH 6.0 buffer did not effect to the capacity.

3.1.4. Effect of Adsorbent Dose

Even at the lowest adsorbent dose used, very high arsenic removal efficiencies were observed. 97.3±4.3% and 98.7±3.7% removal efficiencies were obtained for As(III) and As(V), respectively, at 2.5 g/L adsorbent dose. Beyond 5.0 g/L adsorbent dose the removal efficiencies of both As(III) and As(V) were more than 99.5% for the initial As(III) and As(V) concentration of 200 µg/L.

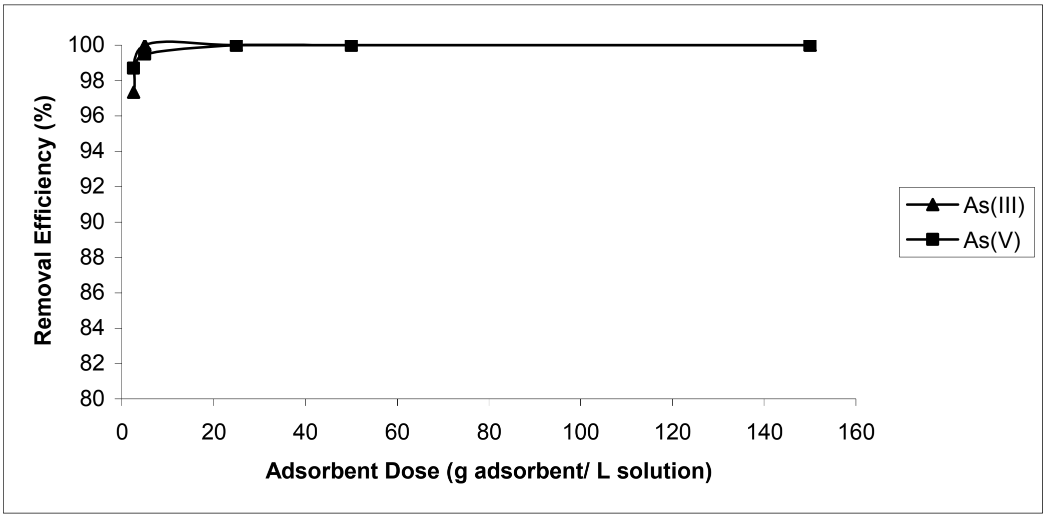


Figure 3.6. Arsenic removal efficiencies of FHSS depending on the adsorbent dose (Initial As concentration: 200 µg/L, sorption: 24 h at 25 ^{o}C).

The adsorbent was also analyzed for hydrated iron(III) oxide content by taking the difference of FHSS and silicagel, dried at the same temperature, 40 ^{o}C. The results showed that, 20.0±0.9% (w/w) of the adsorbent was ferric hydroxide (n=9, RSD= 4.6%).

3.1.5. Characterization of FHSS

SEM and EDX data showed that all the FHSS materials are robust and granular, not aggregated (Figure 3.7). Silicagel alone contained no detectable iron, while iron on FHSS could clearly be seen (Figure 3.8). After the adsorption of As(III) and As(V), arsenic peak was determined on the FHSS (Figures 3.9 and 3.10). However, arsenic peak has not been seen on silicagel alone. The experimental data has proven that silicagel without iron does not sorb arsenic significantly.

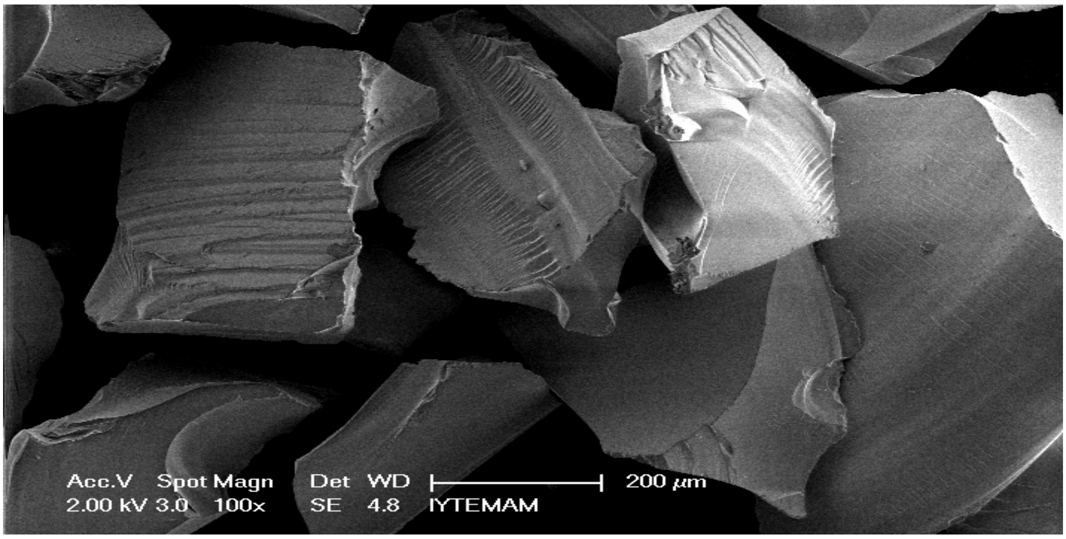
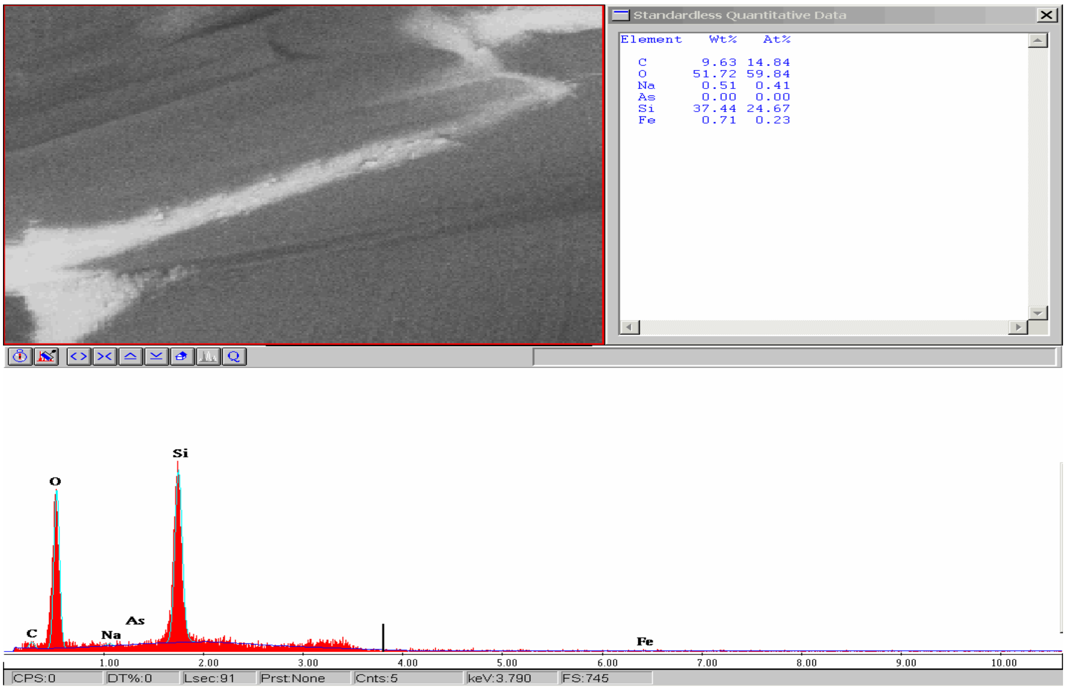


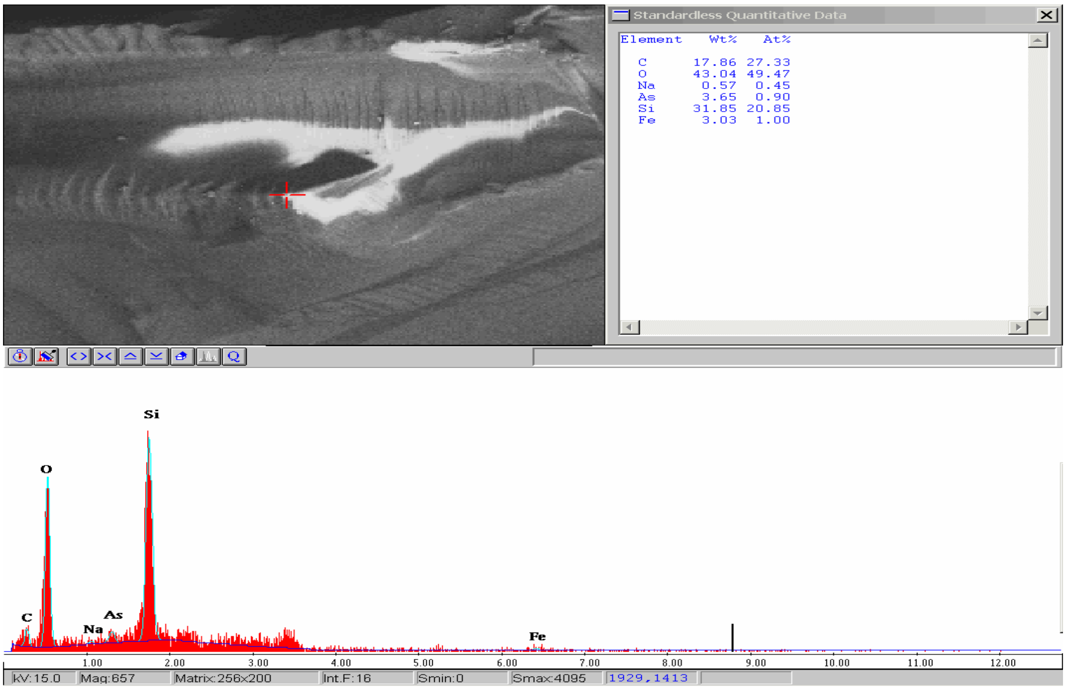
Figure 3.7. SEM image of FHSS.



```
Element    Wt%    At%

  C       9.63  14.84
  O      51.72  59.84
  Na      0.51   0.41
  As      0.00   0.00
  Si     37.44  24.67
  Fe      0.71   0.23
```

Figure 3.8. SEM-EDX image of Silicagel (without iron and arsenic).

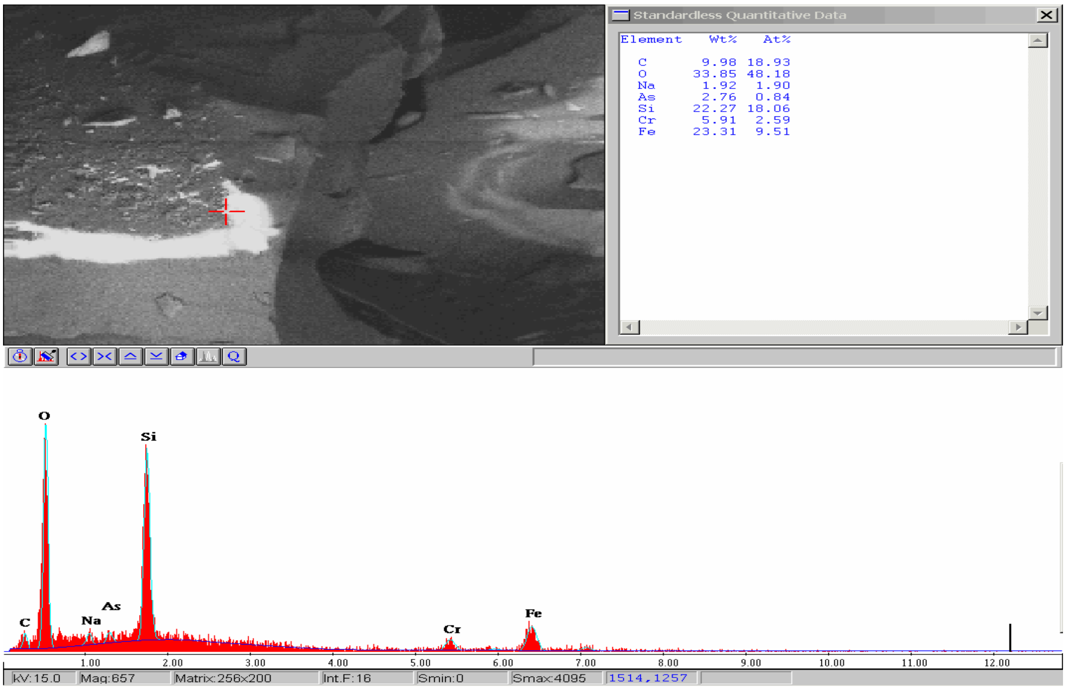


Standardless Quantitative Data

Element	Wt%	At%
C	17.86	27.33
O	43.04	49.47
Na	0.57	0.45
As	3.65	0.90
Si	31.85	20.85
Fe	3.03	1.00

kV:15.0 Mag:657 Matrix:256x200 Int.F:16 Smin:0 Smax:4095 1929,1413

Figure 3.9. SEM-EDX image of FHSS + As(III).



Standardless Quantitative Data

Element	Wt%	At%
C	9.98	18.93
O	33.85	48.18
Na	1.92	1.90
As	2.76	0.84
Si	22.27	18.06
Cr	5.91	2.59
Fe	23.31	9.51

kV:15.0 Mag:657 Matrix:256x200 Int.F:16 Smin:0 Smax:4095 1514,1257

Figure 3.10. SEM-EDX image of FHSS + As(V).

3.1.6. Investigation of pH Dependence of As(III) and As(V) Removal

In the batch method, initial pH did not significantly affect the arsenic removal efficiencies for As(III) and As(V) in the pH range 3.1-9.7 (Figure 3.11). The removal efficiencies varied in the range 96.0-99.8% for As(III) and 95.6-99.9% for As(V). It is clear that there is a decrease in both As(III) and As(V) removal efficiencies at pH 11.2.

It was observed that pH of the sorption medium decreased by time. Equilibrium pHs measured after 24 h against initial pHs are shown in Figure 3.12. Under the experimental conditions used initial pH values between 3.1 - 9.7 decreased to equilibrium pH values of between 3.1 and 5.1, correspondingly. The decrease of the pH values at equilibrium explains why the variations in the initial solution pH did not significantly affect arsenic removal efficiencies.

The pH of the solution with initial pH 11.2 decreased to 10.6 at equilibrium. When the pH is above 9.2, negatively charged arsenic species becomes predominant whereas the adsorbent surface also becomes negatively charged. Thus, electrostatic repulsion between FHSS and arsenic anions resulted in a decrease of arsenic adsorption.

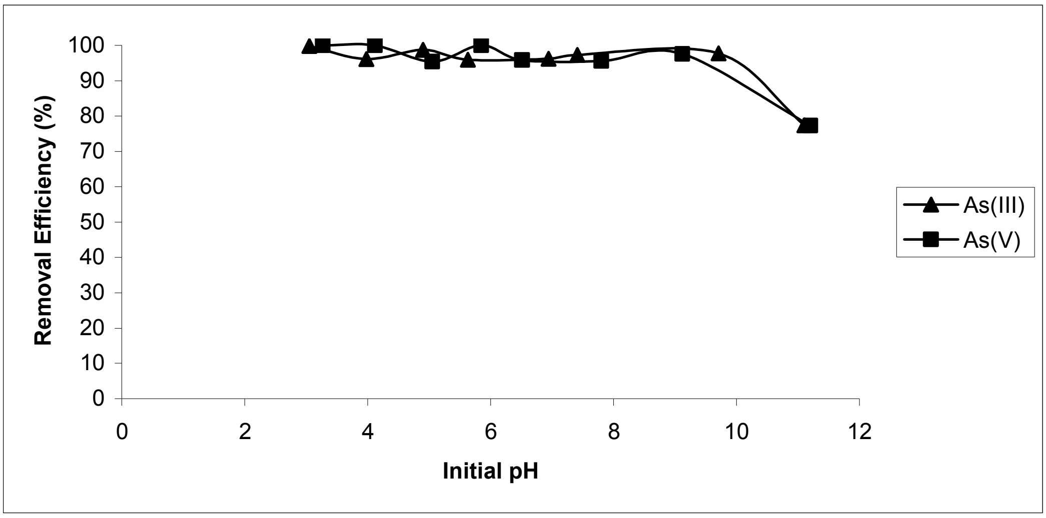


Figure 3.11. Effect of initial pH of the solution on As(III) and As(V) removal efficiency. (Initial As concentration: 100 μg/L, adsorbent dose: 20 g/L, sorption: 24 h at 25 ^{o}C).

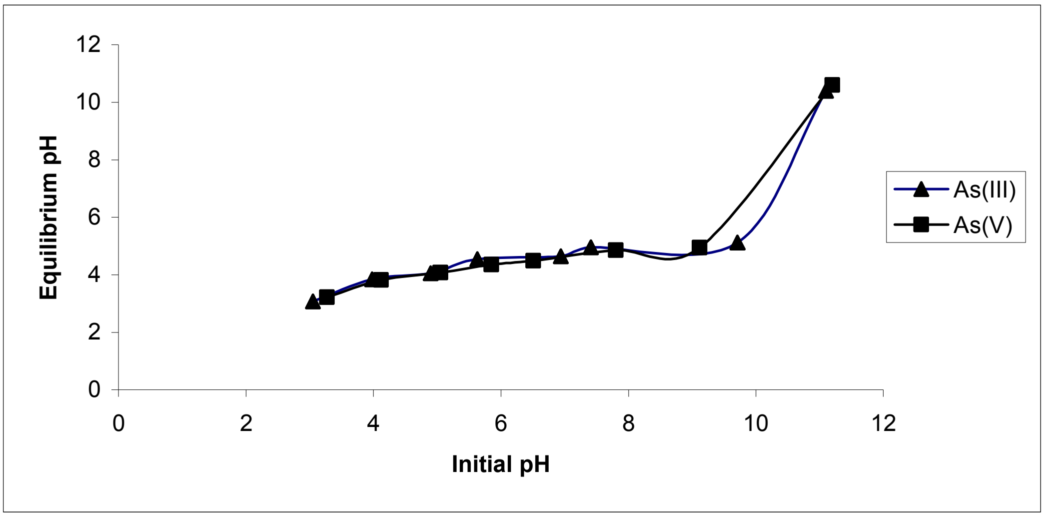


Figure 3.12. Variation of equilibrium pH with the initial pH of the solution (Initial As concentration: 100 µg/L, adsorbent dose: 20 g/L, sorption: 24 h at 25 ^{o}C).

3.1.7. Zeta Potential of the Adsorbents

A- The obtained results are shown in Figure 3.13.

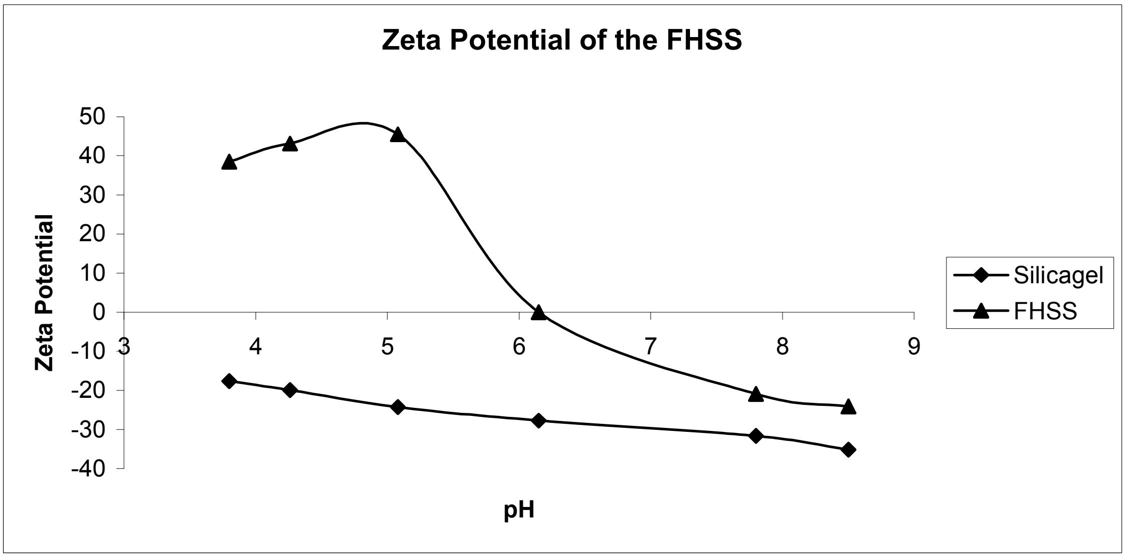


Figure 3.13. A- Zeta potentials of the adsorbents (in NaCl solution)

It was excepted that, the potential would be decreased by pH increase. However a slight potential increase was observed at pH from 3.8 to 5.0 for FHSS. Therefore the experiment was repeated in NaNO$_3$ media.

B- The repeated experiment results are shown in Figure 3.14.

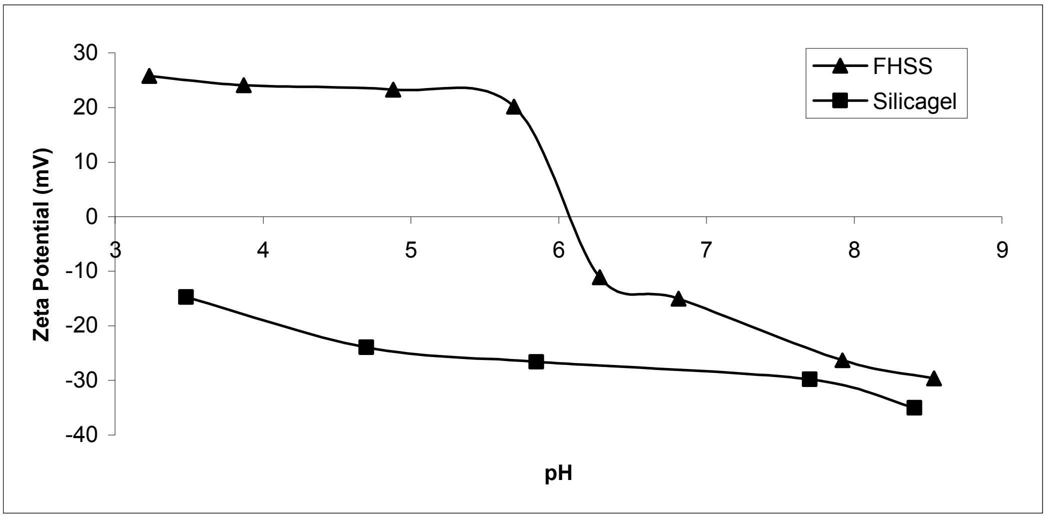


Figure 3.14. B- Zeta potentials of the adsorbents (in $NaNO_3$ solution)

As the results of two experiments, it was found that the isoelectric point (IEP) occurred at pH 6.2. It means that the surface of the adsorbent was neutral at pH 6.2.

3.1.8. Study of As(III) sorption

Column Study: More than 99 % of the arsenic in the solution was found to be still in As(III) oxidation state when sorption was realized in the column with 7 ml/min solution flow rate, and relatively high arsenic concentration (400 mg/L) was used. However, when more dilute As(III) solution (500 µg/L) was passed through the column relatively slow (1.5 mL/min), 62±2.9% of As(III) was oxidized to As(V).

Batch Study: 99±4.7% of As(III) was found to be oxidized to As(V). It means that, when the adsorbents were shaken with relatively low concentration of arsenic solution for a long time, all the As(III) species were oxidized to As(V).

The results above show that As(III) can be adsorbed even at trace level without oxidation to As(V) by FHSS. Part of the As(III) was found to be oxidized either by FHSS or Fe(III) passed into the solution after dissolving FHSS in HCl. Mechanism of As(III) sorption on ferric oxide appears to be dependent on the experimental conditions and arsenic concentration.

3.1.9. Determination of Column Capacity for Arsenic Removal

Column capacities were determined for both As(III) and As(V). The results are shown in Figure 3.15. Arsenic was determined in the effluents after 296 BV and 318 BV for As(III) and As(V), respectively. Total capacities of the arsenic removal column can be calculated from these values for As(III) and As(V). Total capacities are 1.32 and 1.21 mg/g for As(III) and As(V), respectively.

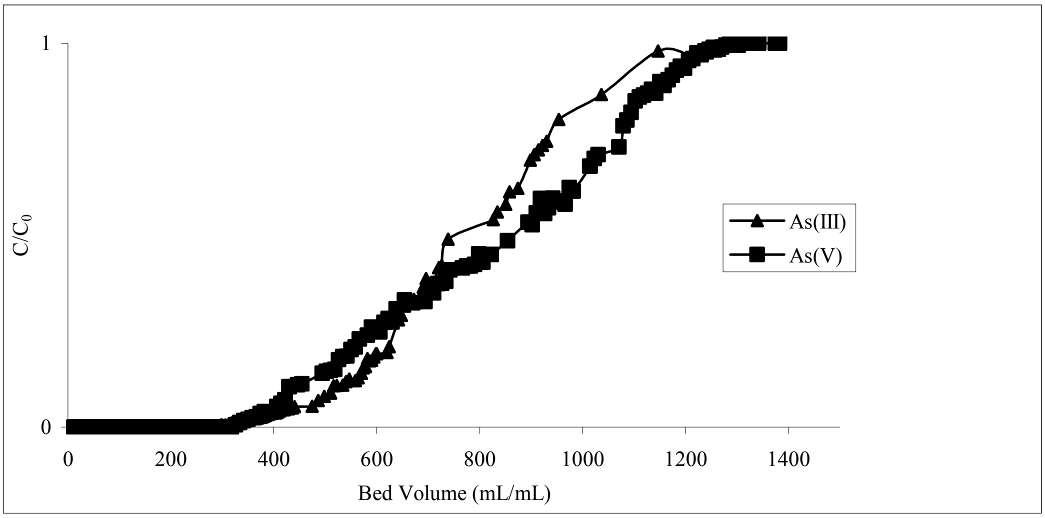


Figure 3.15. Breaktrough curves of As(III) and As(V) (Initial As concentration: 1000 μg/L, adsorbent amount: 5.5 g).

3.1.10. Adsorption of As(III) and As(V) Depending on Time and Temperature

As shown in Figures 3.16 and 3.17, it can be thought that As(III) was removed while As(V) was not. However, As(III) was oxidized to As(V) and it seemed to be removed. The reason of the lack adsorption was; the adsorbent was prepared by shaking the Fe(III) impregnated silicagel with the pH 6.0 buffer for only 1 h. Therefore the precipitate was not formed well, as the result, iron(III) hydroxide colloids come to the solution with arsenic. The experiment was repeated to obtain faster removal. For this purpose, $FeCl_3$ impregnated silicagel was shaken with the buffer 6.0 for 24 h to obtain stable precipitation. The results are shown in Figure 3.18.

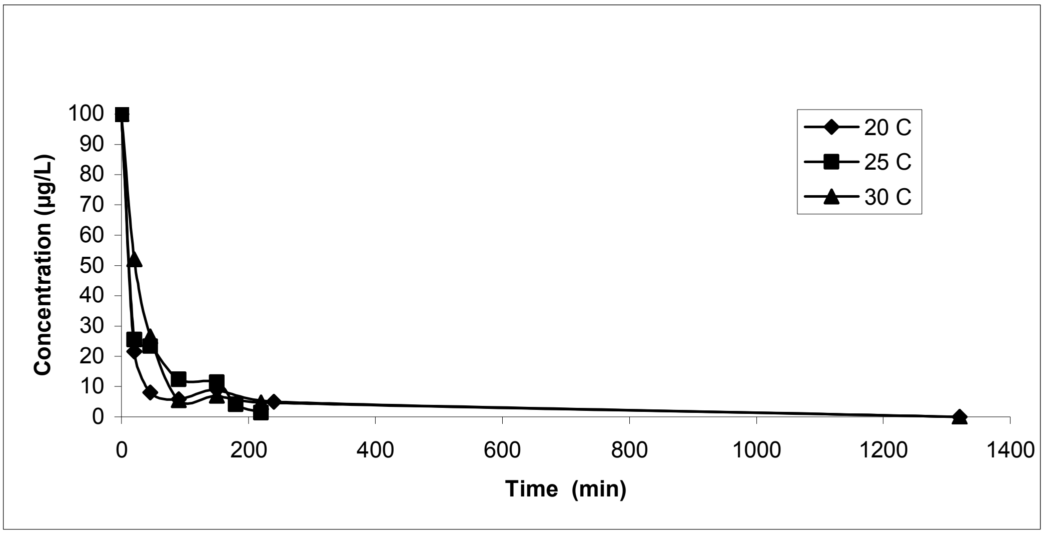


Figure 3.16. As(III) adsorption at 20; 25 and 30 °C depending on time (Initial As(III) concentration: 100 µg/L, adsorbent dose: 2 g/L, sorption: 24 h at 20, 25, 30 °C).

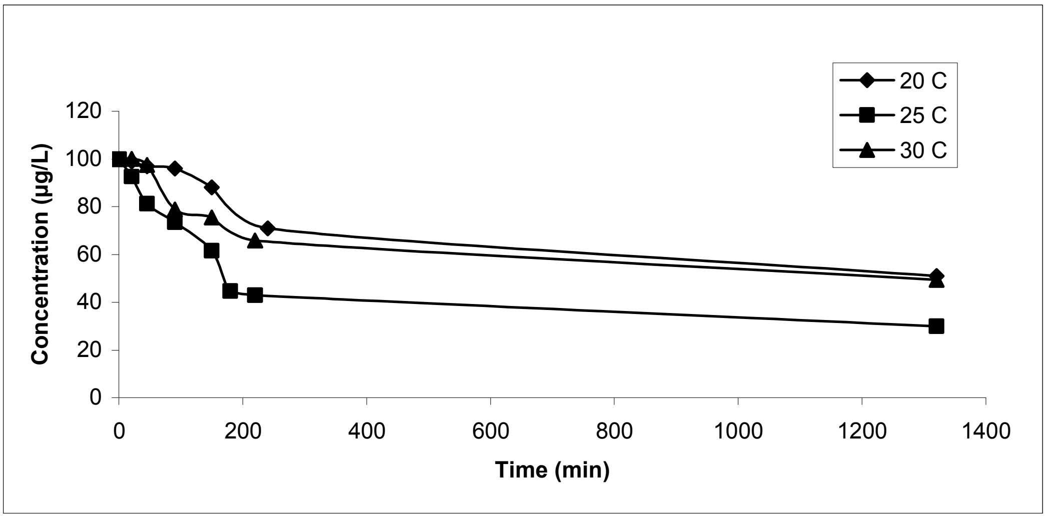


Figure 3.17. As(V) adsorption at 20; 25 and 30 °C depending on time (Initial As (V) concentration: 100 µg/L, adsorbent dose: 2 g/L, sorption: 24 h at 20, 25, 30 °C).

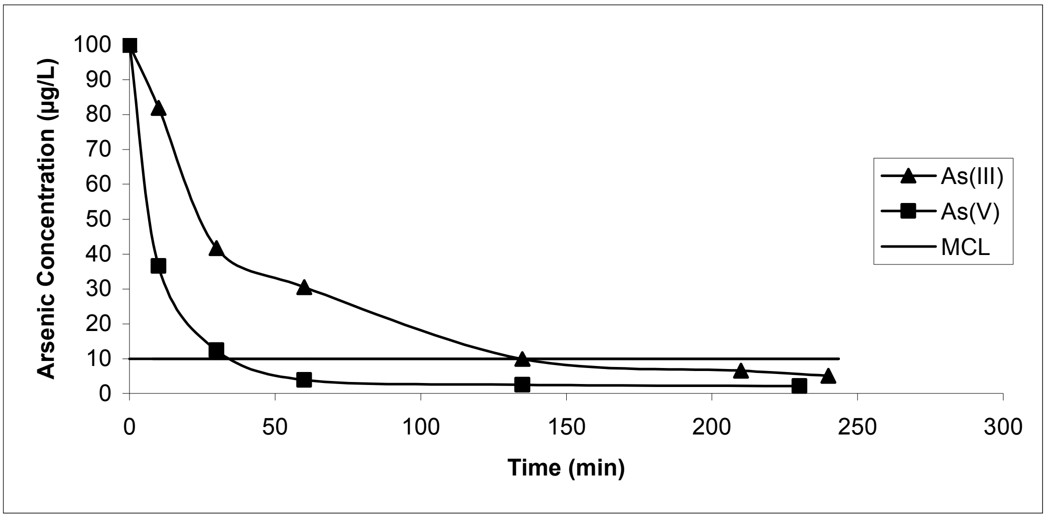


Figure 3.18. As(III) and As(V) adsorption at 25 °C depending on time (Initial As concentration: 100 µg/L, adsorbent dose: 2 g/L, sorption: 24 h at 25 °C).

As(III) removal rate was slightly low using FHSS. While As(V) was reduced under the Maximum Contaminant Limit (0.01 mg/L) in 35 minutes, As(III) was reduced under 0.01 mg/L in 135 minutes. It could be explain by the nature of As(III) that is neutral at the experimental condition.

3.1.11. pHs of the precipitation buffer onto particles before and after the precipitation

In order to understand whether the pH of the buffer changed or not, pHs of the buffer solution (6.0) on particles were measured before and after the precipitation and showed in Table 3.1. CH_3COOH/CH_3COONa buffer was used for the precipitation (pKa=4.76). A slight decrease of the buffer solution could be explain by the low buffer capacity.

Table 3.1. pHs of the supernatant liquor on particles before and after the precipitation.

Particle	Initial pH	Equilibrium pH
Perlite	6.0	5.2
Pumice	6.0	5.1
Zeolite	6.0	5.6
Silicagel	6.0	5.5

3.1.12. Determination of Iron on the Adsorbents (Precipitated with pH 6.0 buffer)

The averages of dry adsorbent capacities are shown in Table 3.2. The results of the experiments show that the highest capacity for ion adsorption is that of pumice. Pumice is natural, cheap and easily found material. Some authors have used pumice as an heavy metal (i.e. Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and Cr^{3+}) and basic dye adsorbent. In this work the first opinion is to use pumice as the supporting material. The capacity of perlite is good. However, the capacity of zeolite is poor, as compared.

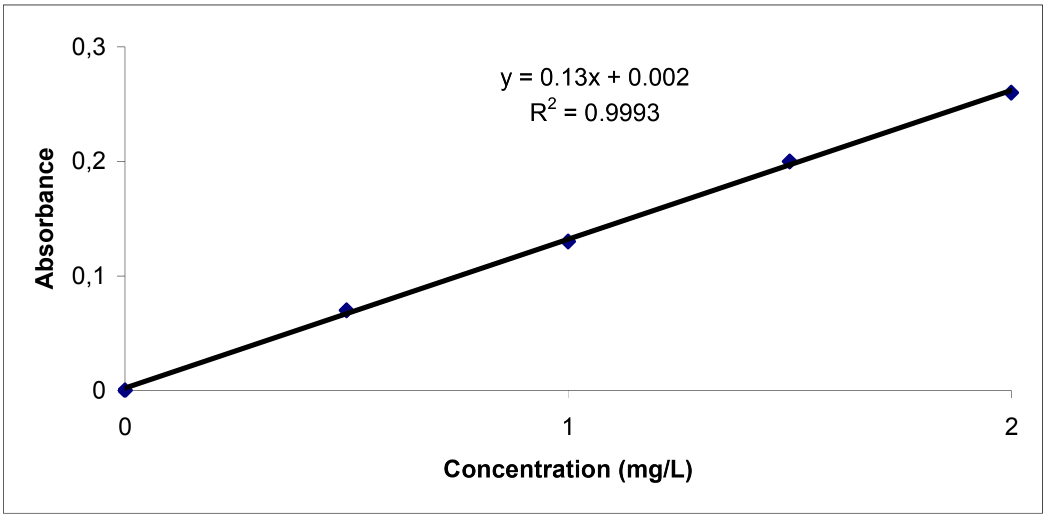


Figure 3.19. Calibration Graph for Fe^{3+} Ion of spectofotometric determination using NH_4SCN.

Table 3.2. The averages of iron contents of the supports after the precipitation as hydrated iron(III) oxide.

Supports	**Capacity** (mg Fe^{3+}/g support)
Perlite	44.0±2.2
Pumice	78.0±3.2
Zeolite	11.7±0.3
Silicagel	72.8±2.9

3.2. STUDY OF ARSENIC(III) AND ARSENIC(V) REMOVAL FROM WATERS USING FERRIC HYDROXIDE SUPPORTED ON SILICAGEL (FHSS) PREPARED BY THERMAL METHOD

3.2.1. Determination of Iron on Silicagel (prepared by Thermal Method)

Iron contents of the adsorbents prepared at different temperatures and techniques are shown in Figures 3.20, 3.21 and 3.22. Iron contents were increased by temperature. While increasing temperature, more ionic iron(III) was transformed to iron(III) oxide. Therefore, iron(III) oxide was stable in the silicagel pores and the iron uptakes were high for both stepwise and fixed temperature techniques in the oven and the furnace.

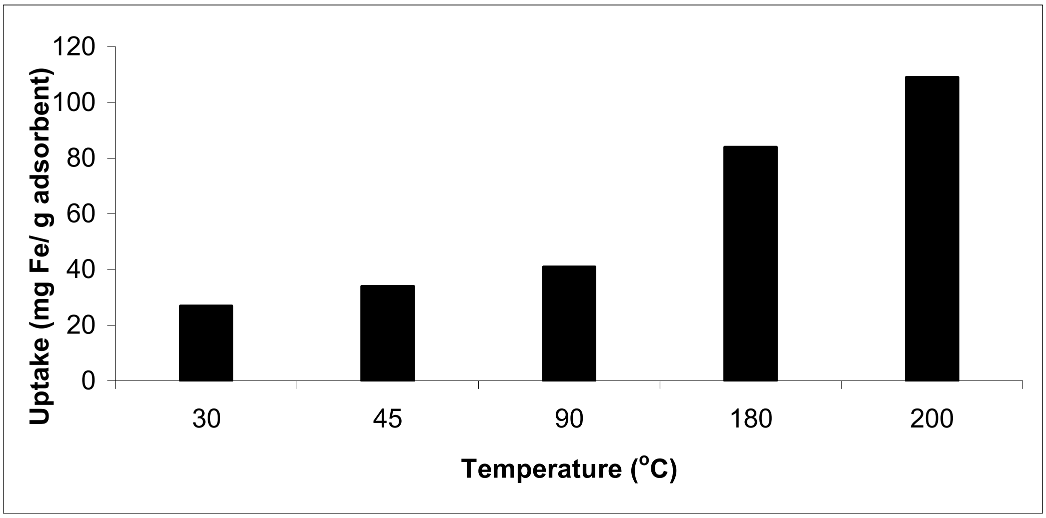


Figure 3.20. Iron contents of the adsorbents prepared by **stepwise** heating in the **oven**.

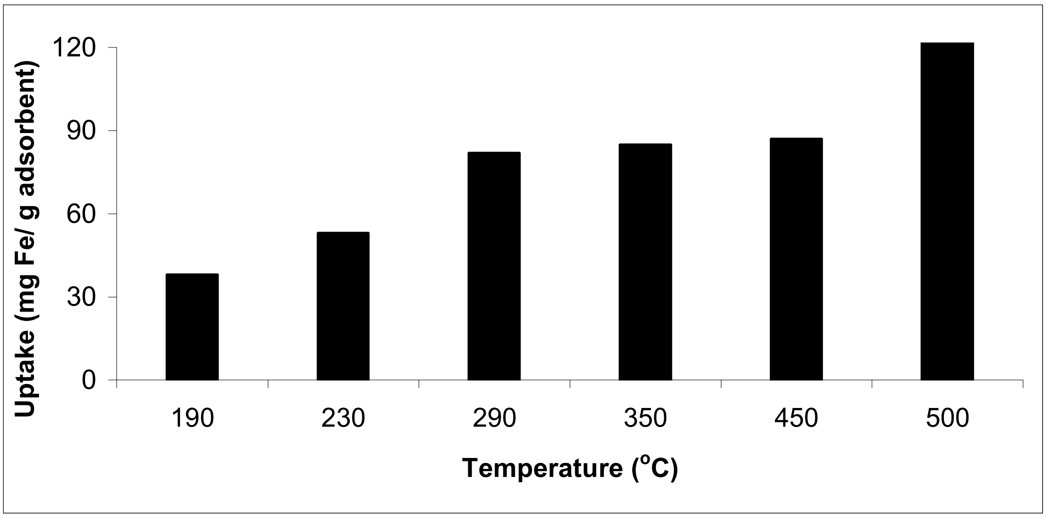


Figure 3.21. Iron contents of the adsorbents prepared by **stepwise** heating in the **furnace.**

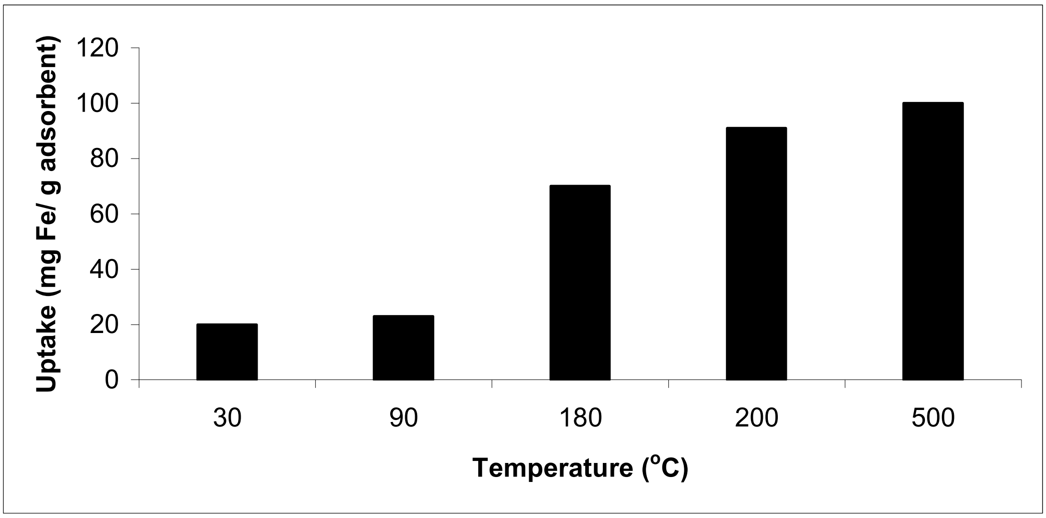


Figure 3.22. Iron contents of the adsorbents prepared by heating at **fixed temperature.**

3.2.2. Arsenic Adsorption by Thermally Prepared Ferric Hydroxide Supported on Silicagel

Arsenic uptakes of the prepared adsorbents were determined and the results are shown in Figures 3.23, 3.24 and 3.25. In Figure 3.23, a decrease was observed at higher then 350 ^{o}C. Because of the decomposition of iron(III) hydroxide higher than 190 ^{o}C, arsenic adsorption was decreased. Similarly, in Figure 3.25, arsenic uptakes were decreased by the temperature increasing because of the decomposition. At lower temperatures than 180 ^{o}C, iron(III) hydroxide particles in the pores of the adsorbents passed trough the solution. As a result, the iron contents were lower and arsenic uptakes had been low (Figure 3.24).

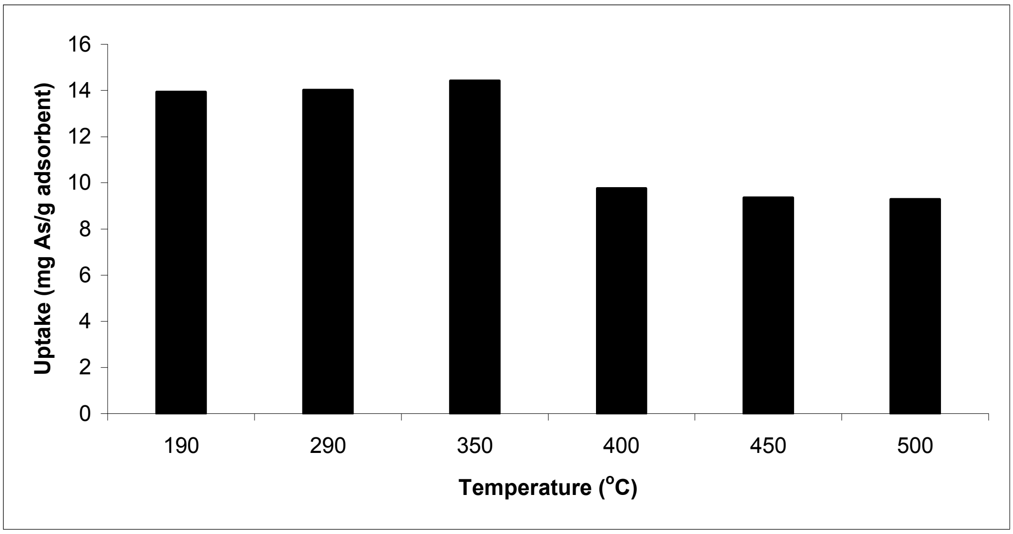


Figure 3.23. Adsorption capacities of the adsorbents (Adsorbents were prepared in the **furnace** by **stepwise heating**) (Initial As concentration: 100 mg/L, adsorbent dose: 5 g/L, sorption: 24 h at 25 °C).

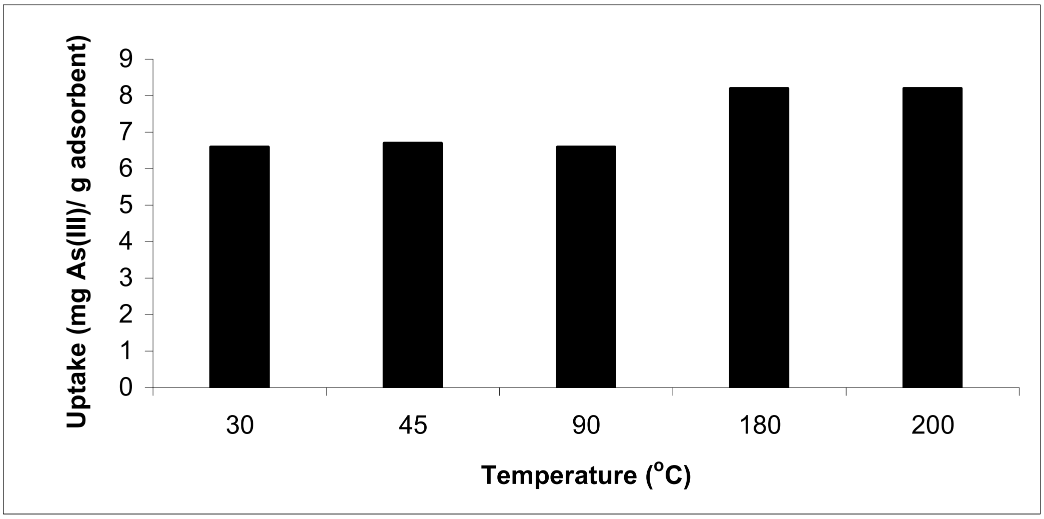


Figure 3.24. Adsorption capacities of the adsorbents (Adsorbents were prepared at the **oven** by **stepwise heating**) (Initial As concentration: 100 mg/L, adsorbent dose: 5 g/L, sorption: 24 h at 25 °C).

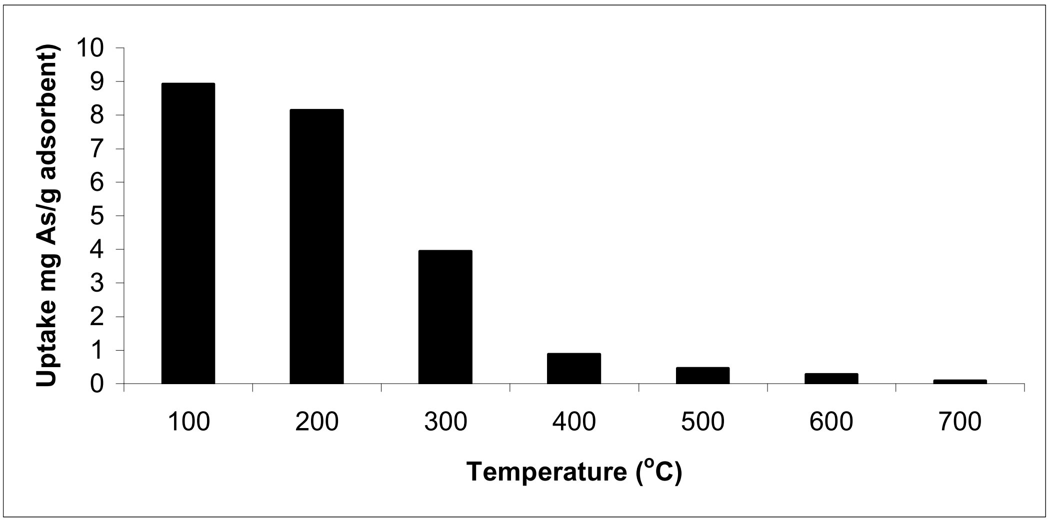


Figure 3.25. Uptakes of the adsorbents were prepared by heating for 3 h at **fixed** temperature (Initial As concentration: 100 mg/L, adsorbent dose: 5 g/L, sorption: 24 h at 25 °C).

3.2.3. Standard Deviations of the Arsenic Uptakes

As(III) adsorption procedure was applied to the adsorbents prepared by stepwise temperature technique at 200 °C. Standard deviations of the arsenic uptakes for six samples were calculated. Relative standard deviation is found to be 0.97% (n=6).

3.2.4. Arsenic Removal by Thermally Ferric Hydroxide Supported on Perlite, Pumice, Zeolite and Silicagel

Various particles were used as the support material. The arsenic uptakes of the adsorbents were shown in Figure 3.26. Pumice had the highest arsenic uptake relatively. Therefore pumice was chosen as the support material.

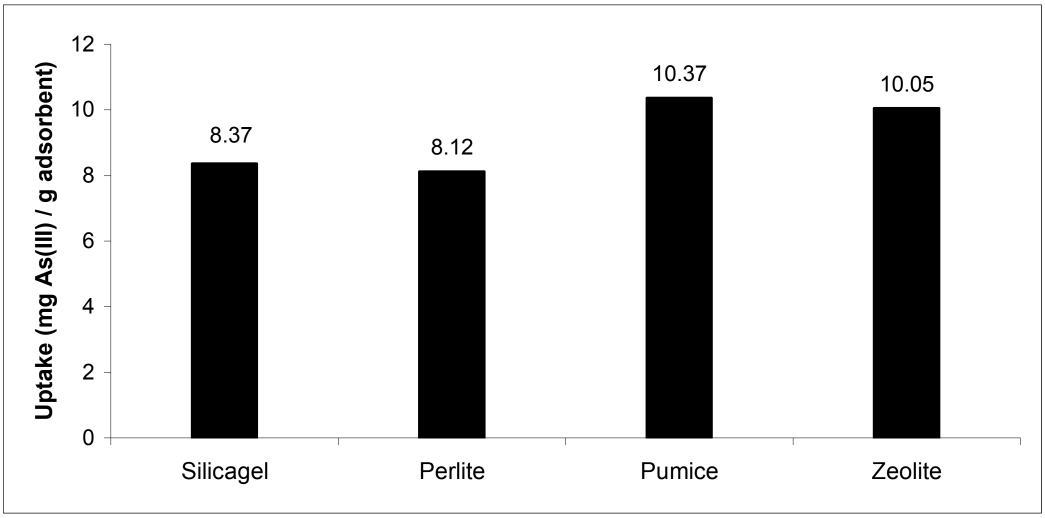


Figure 3.26. As(III) sorption capacities of the adsorbents prepared at 200 °C **fixed** temperature. (Initial As concentration: 100 mg/L, adsorbent dose: 5 g/L, sorption: 24 h at 25 °C).

3.2.5. Preparation of Thermally Supported Ferric Hydroxide on Pumice

The concentrations of the solutions were determined and the capacities were calculated. The results are shown in from Figures 3.27 to 3.30. Similar results were obtained with silicagel. Because of the decomposition of iron(III) hydroxide at high temperatures than 190 °C, relatively, arsenic uptakes were lower.

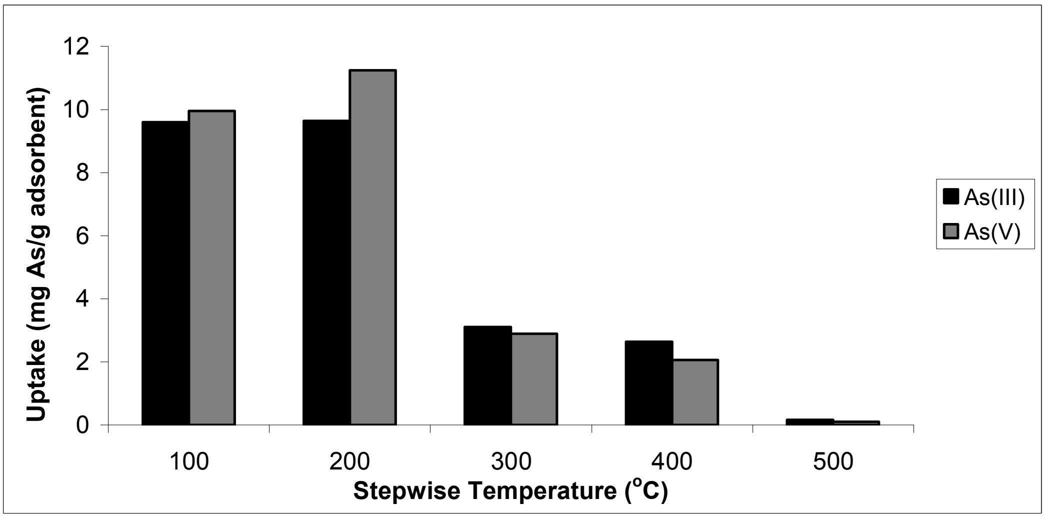


Figure 3.27. Total batch capacities of the adsorbent that prepared by **stepwise** temperature increase (heating in the **furnace**). (Initial As concentration: 100 mg/L, adsorbent dose: 5 g/L, sorption: 24 h at 25 °C).

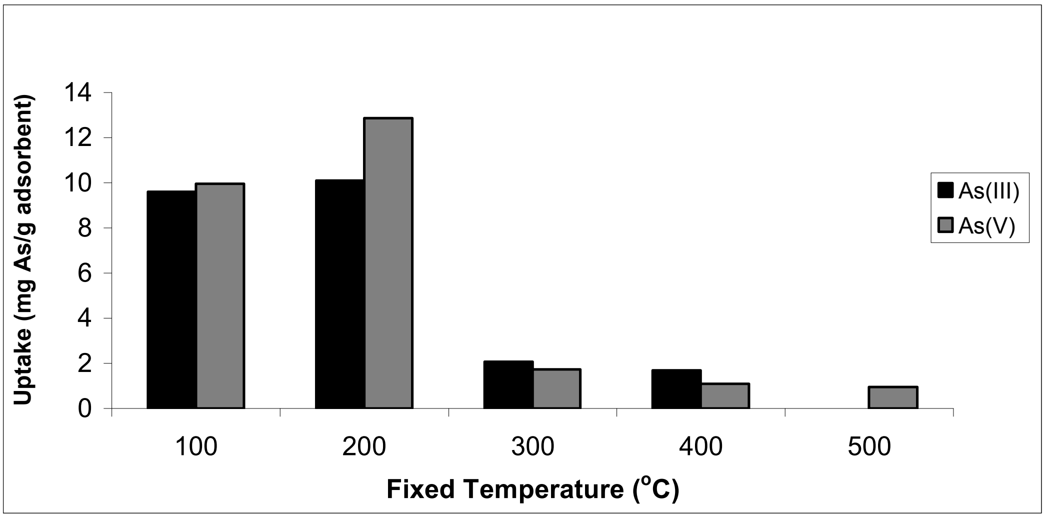


Figure 3.28. Total batch capacities of the adsorbent that prepared by **fixed** temperature (heating in the **furnace**) (Initial As concentration: 100 mg/L, adsorbent dose: 5 g/L, sorption: 24 h at 25 °C).

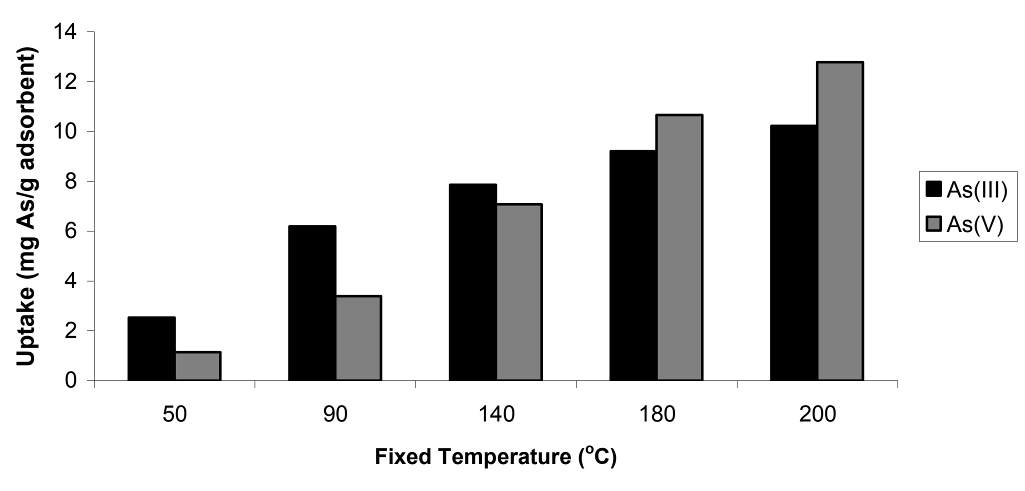


Figure 3.29. Total batch capacities of the adsorbent that prepared by **fixed** temperature (heating in the **oven**) (Initial As concentration: 100 mg/L, adsorbent dose: 5 g/L, sorption: 24 h at 25 °C).

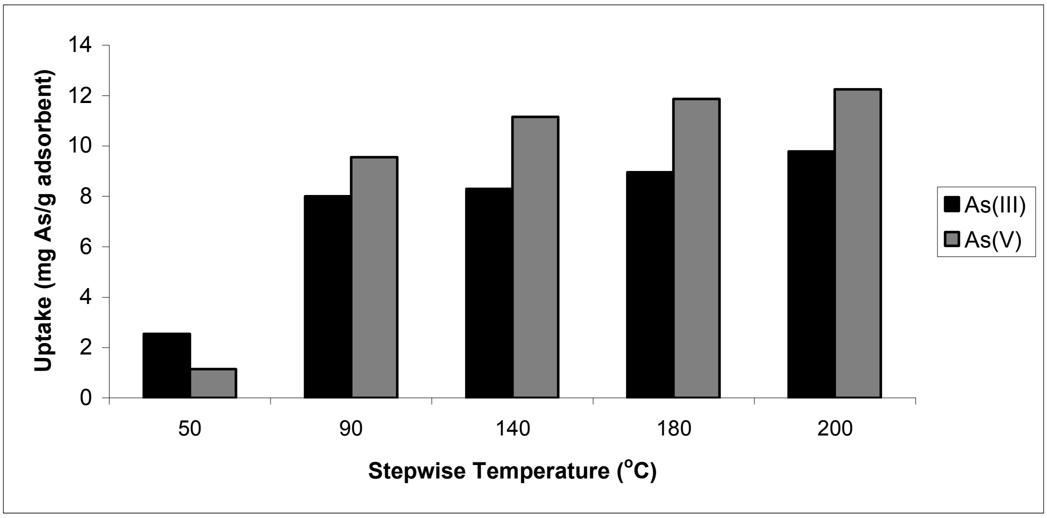


Figure 3.30. Total batch capacities of the adsorbent that prepared by **stepwise** temperature increase (heating in the **oven**) (Initial As concentration: 100 mg/L, adsorbent dose: 5 g/L, sorption: 24 h at 25 °C).

Stepwise and fixed temperature techniques showed the similar result that, optimal temperature was found to be nearby 200 °C. In order to determine the exact temperature, the experiment was repeated at between 190-310 °C. The results are shown in Figure 3.31. Optimum temperature was chosen as 220±5.2 °C.

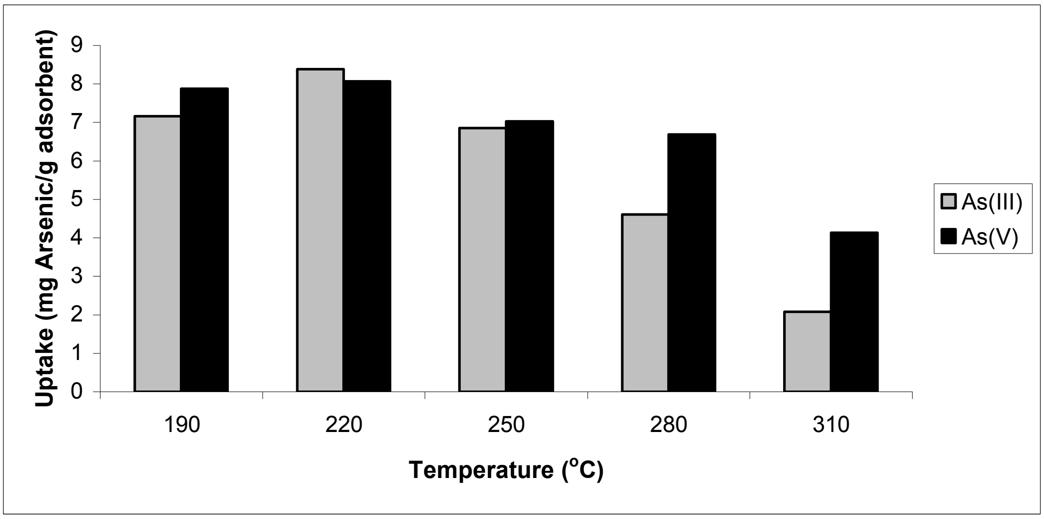


Figure 3.31. Arsenic uptakes of the adsorbents that was prepared by heating at a **fixed** temperature. (heating in the **furnace**) (Initial As concentration: 100 mg/L, adsorbent dose: 5 g/L, sorption: 20 h at 25 °C).

3.3. STUDY OF ARSENIC(III) AND ARSENIC(V) REMOVAL FROM WATERS USING NICKEL NANOPARTICLES IMPREGNATED RESIN (Ni-NPIR)

3.3.1. Preparation of Ni Nanoparticles Impregnated Support Particles

After the preparation, 24 h later, black nanoparticles were decomposed and the colors were green for perlite, pumice, zeolite and silicagel. However, the resin was still black and stable. Purolite C-100 cation exchange resin was chosen as the support material.

3.3.2. Effect of Drying Temperature of the Adsorbent on Removal Efficiency and Arsenic Uptake

In order to understand the effect of drying temperature of the adsorbent on arsenic removal, prepared adsorbents were dried at 20, 40, 60, 80 and 100 °C. The results are shown in Figures 3.32 and 3.33. Ni barks were seperated from the resin when the temperature was higher than 40 °C.

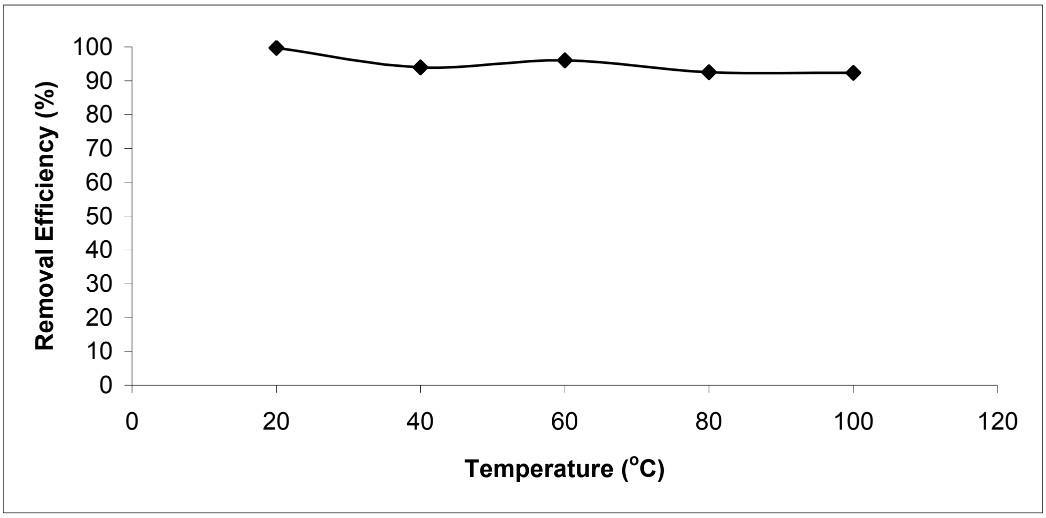


Figure 3.32. Effect of drying temperature of the adsorbent on arsenic removal efficiency (Initial As(III) concentration: 100 µg/L, adsorbent dose: 16 g/L, sorption: 24 h at 25 °C).

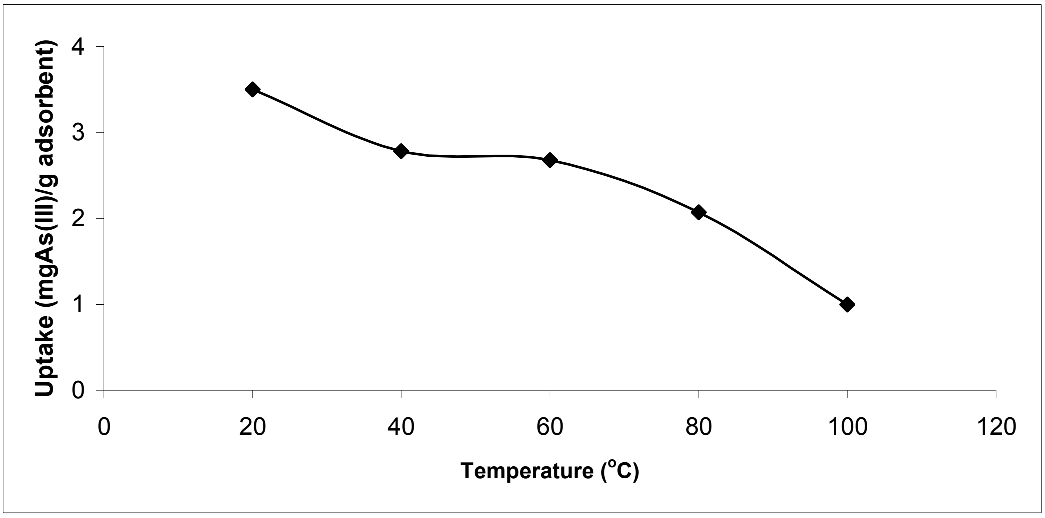


Figure 3.33. Effect of drying temperature of the adsorbent on arsenic uptake (Initial As(III) concentration: 100 mg/L, adsorbent dose: 4 g/L, sorption: 24 h at 25 °C).

As shown in Figures 3.32 and 3.33, room temperature was chosen as the drying temperature. Wet adsorbents gave very similar results with room temperature. (3.5±0.3 mg/g uptake and 99.5±3.1% removal efficiency)

3.3.3. Effect of Nickel(II) Concentration Used for the Adsorbent Preparation on Removal Efficiency and Arsenic Uptake

Removal efficiency and arsenic uptake graphs are shown in Figures 3.34 and 3.35. A plateu was obtained at higher Ni^{2+} concentrations than 10 g/L for removal efficiency. Arsenic uptake values had a plateu at higher Ni^{2+} concentrations than 30 g/L studies. Therefore, 30 g/L Ni^{2+} concentration was chosen.

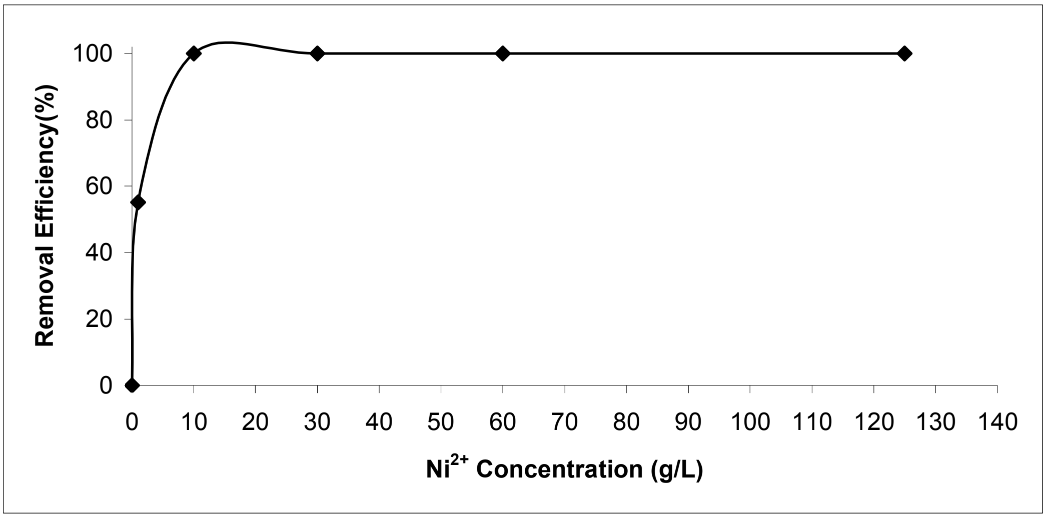


Figure 3.34. Effect of nickel(II) concentration on arsenic removal efficiency (Initial As(III) concentration: 100 µg/L, adsorbent dose: 16 g/L, sorption: 24 h at 25 °C).

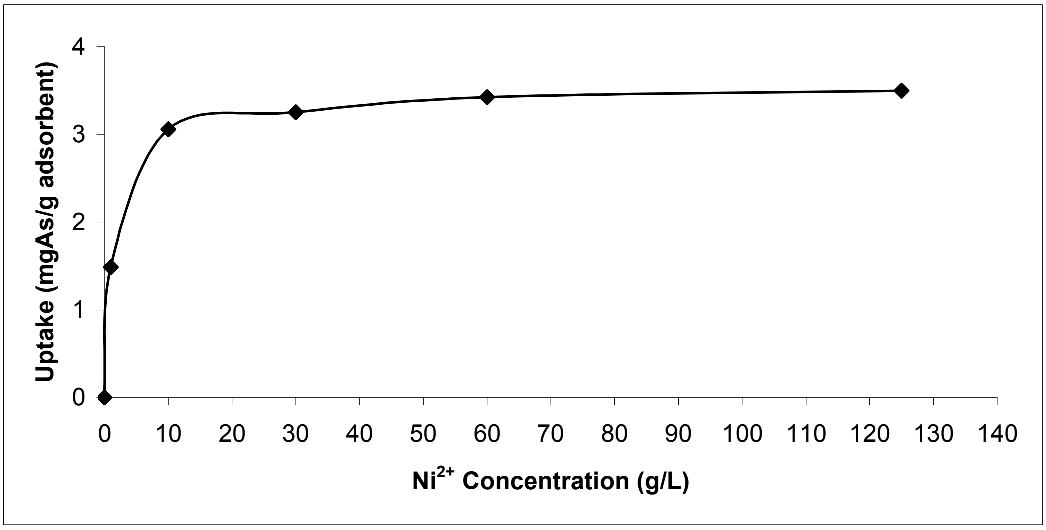


Figure 3.35. Effect of nickel(II) concentration on arsenic uptake (Initial As(III) concentration: 100 mg/L, adsorbent dose: 4 g/L, sorption: 24 h at 25 °C).

3.3.4. Effect of $NaBH_4$ Concentration Used for the Adsorbent Preparation on the Arsenic Removal Efficiency and Arsenic Uptake

Removal efficiency and arsenic uptake graphs are shown in Figures 3.36 and 3.37. The adsorbents prepared using 0.25; 0.5 and 1.0% $NaBH_4$ solutions were still green or black-green colored. Maximum removal efficiency and optimal arsenic uptake was observed at 4% $NaBH_4$ concentration. Therefore, 4% $NaBH_4$ was chosen as the reducing agent concentration.

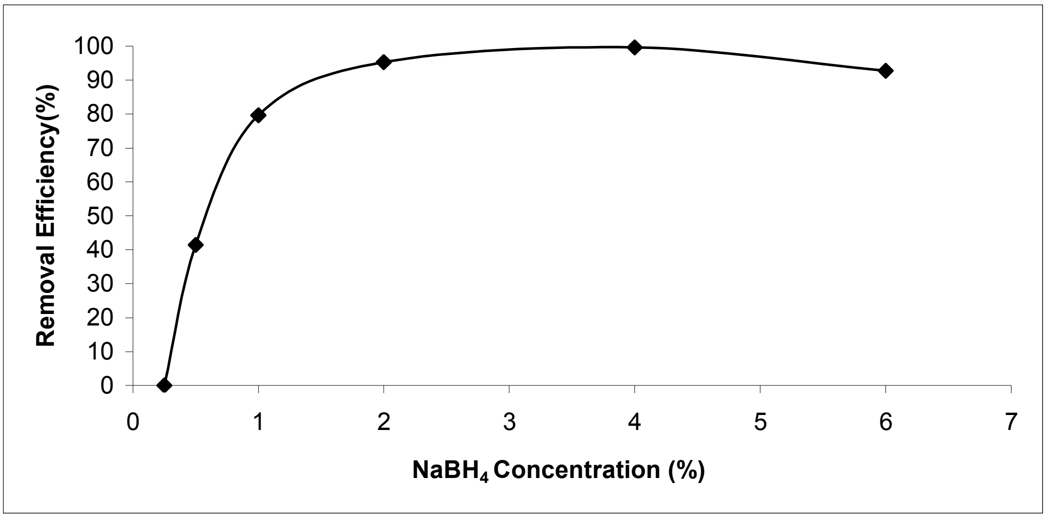


Figure 3.36. Effect of $NaBH_4$ concentration on arsenic removal efficiency (Initial As(III) concentration: 100 µg/L, adsorbent dose: 16 g/L, sorption: 24 h at 25 °C).

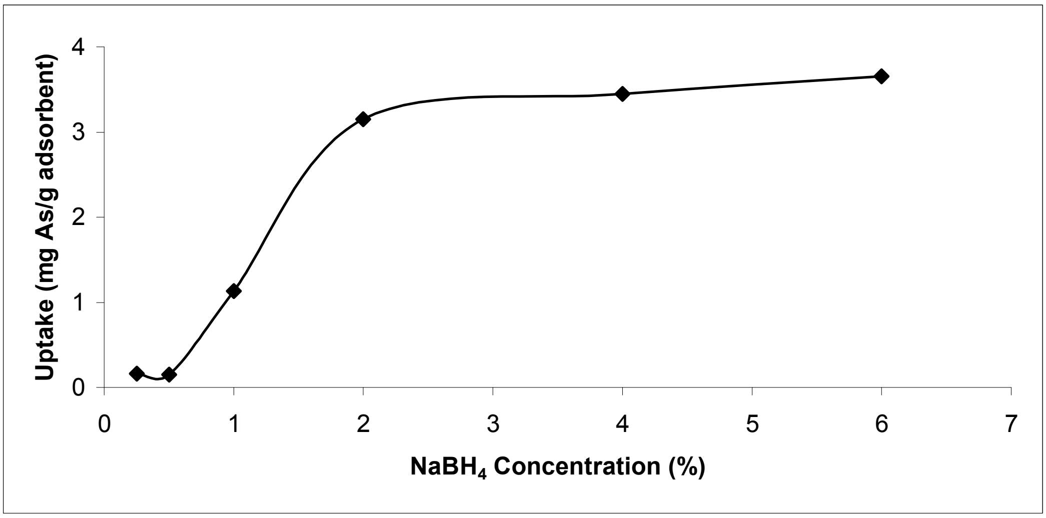


Figure 3.37. Effect of $NaBH_4$ concentration on arsenic uptake (Initial As(III) concentration: 100 mg/L, adsorbent dose: 4 g/L, sorption: 24 h at 25 °C).

3.3.5. Time Effect of Shaking the Resin with Nickel(II) on the Removal Efficiency and Arsenic Uptake

Purolite C-100 resin is a strong cation exchange resin. Therefore, H^+ exchanged with Ni^{2+}, rapidly. As a result, shaking time with nickel(II) solution did not effect both removal efficiency and arsenic uptake as shown in Figures 3.38 and 3.39, respectively.

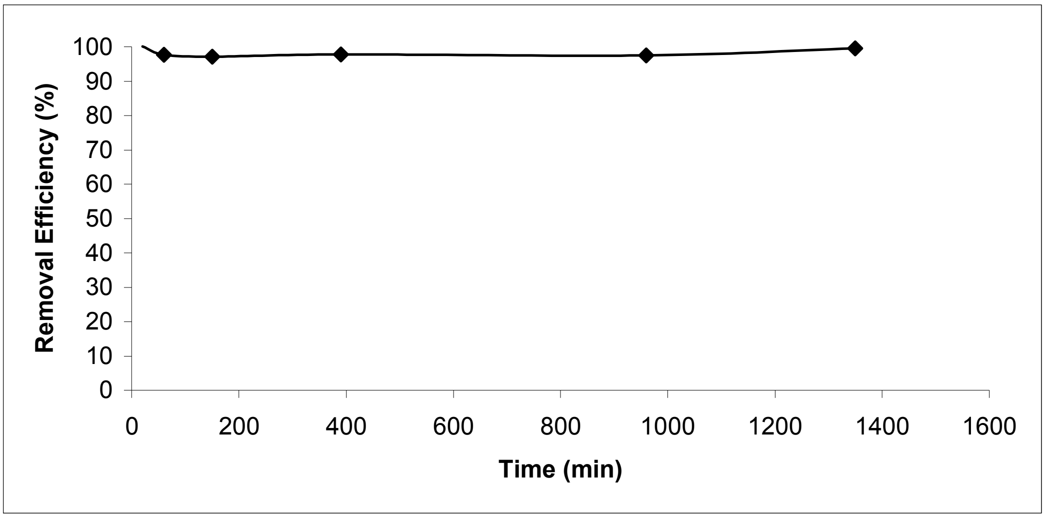


Figure 3.38. Time effect of shaking the resin with nickel(II) on arsenic removal efficiency (Initial As(III) concentration: 100 µg/L, adsorbent dose: 16 g/L, sorption: 24 h at 25 °C).

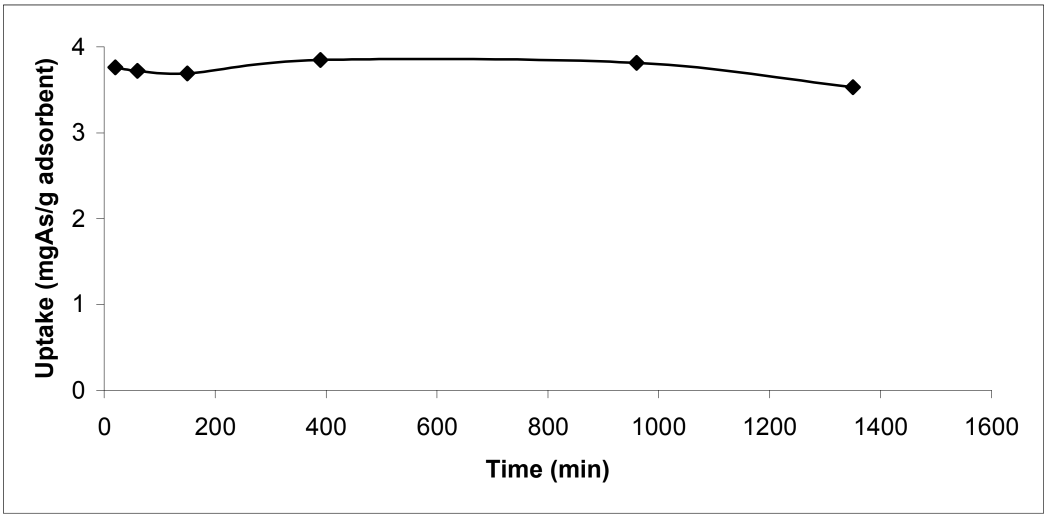


Figure 3.39. Time effect of shaking the resin with nickel(II) on arsenic uptake (Initial As(III) concentration: 100 mg/L, adsorbent dose: 4 g/L, sorption: 24 h at 25 °C).

3.3.6. Investigation of the Adsorption pH Dependence of As(III) and As(V) Removal Efficiencies

The obtained values are shown in Figure 3.40. In the batch method, initial pH did not significantly affect the arsenic removal efficiencies for As(III) and As(V) in the pH range 3.3-11.5. The removal efficiencies varied in the range 97.0-98.9% for As(III) and 93.5-98.7% for As(V).

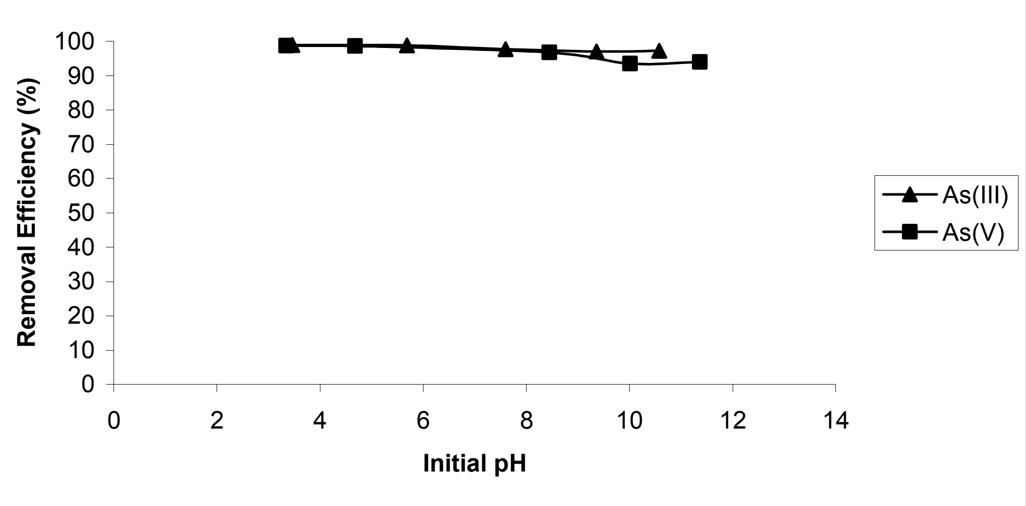


Figure 3.40. Effect of the initial pH of the solution on As(III) and As(V) removal. (Initial arsenic concentration: 100 µg/L, adsorbent dose: 20 g/L, sorption: 24 h at 25 °C)

It was observed that pH of the sorption medium increased by time. Equilibrium pH values measured after 20 h against the initial pH values are shown in Figure 3.41. Under the experimental conditions used initial pH values changed to around 9 at equilibrium and, this change of the pH values at equilibrium explains why the variations in the initial solution pH did not significantly affect arsenic removal efficiencies.

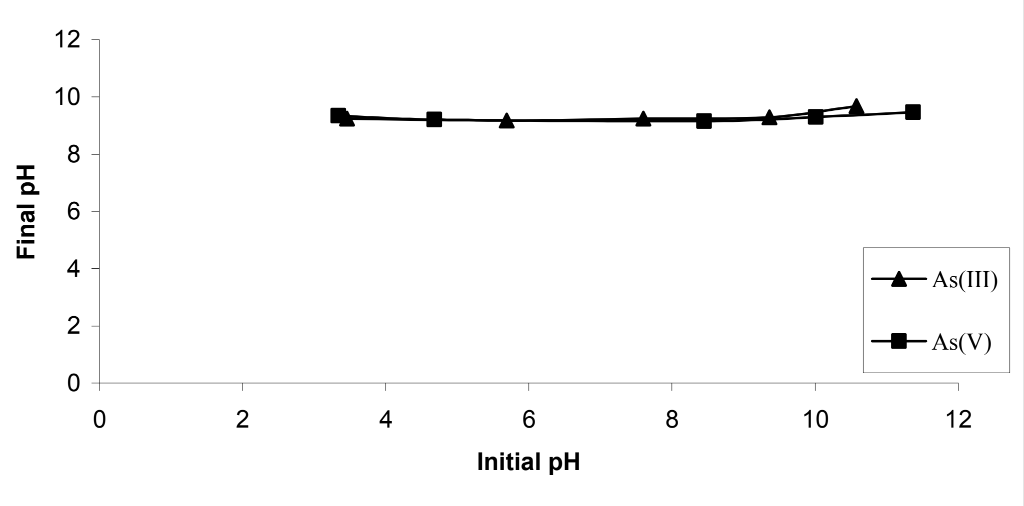


Figure 3.41. Variation of the equilibrium pH with the initial pH of the solution. (Initial arsenic concentration: 100 µg/L, adsorbent dose: 20 g/L, sorption: 24 h at 25 °C)

3.3.7. Characterization of Nickel Nanoparticles Impregnated Resin

SEM images showed that some particles of the adsorbents were damaged and nickel nanoparticle barks were seperated from the resin because of the preparation of the adsorbent to the SEM-EDX analysis (Figure 3.42). The adsorbent alone contained nickel, boron, carbon, oxygen (Figure 3.43). After the adsorption of As(III) and As(V), arsenic peak was determined on the adsorbents (Figures 3.44 and 3.45).

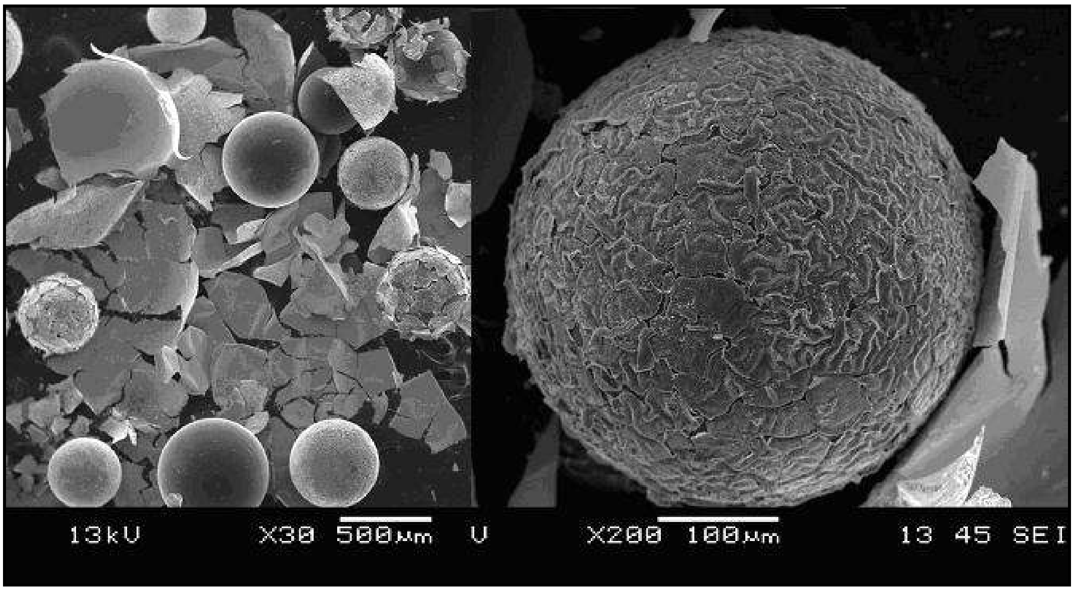
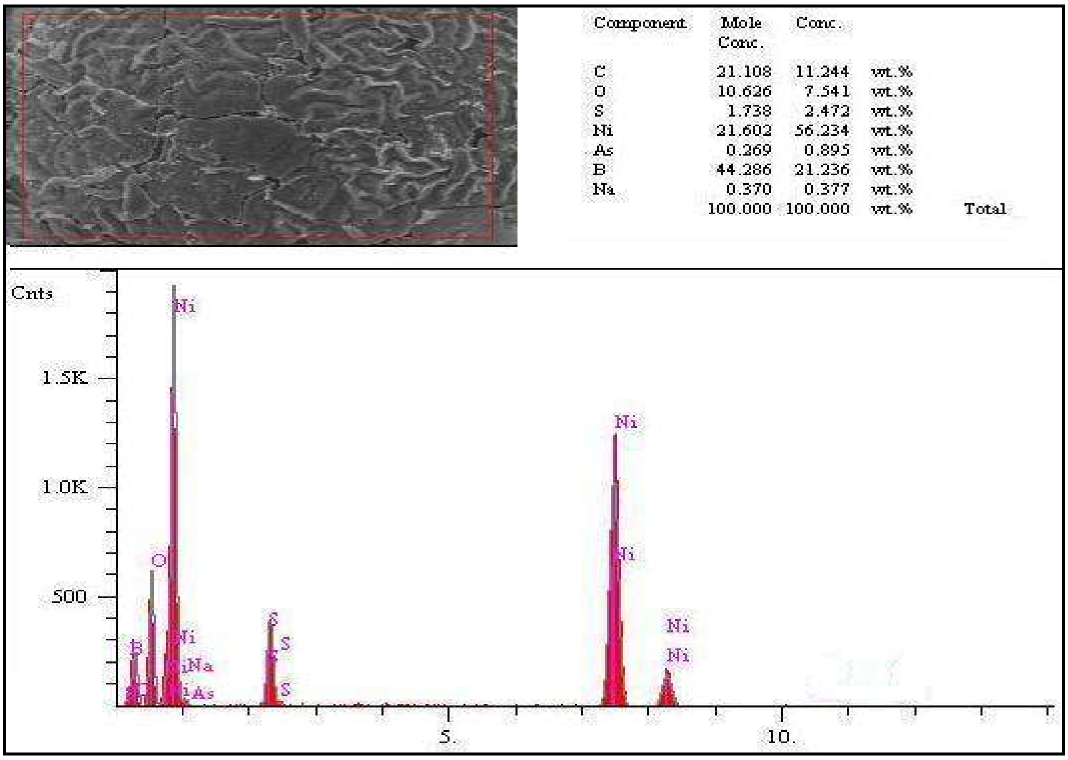
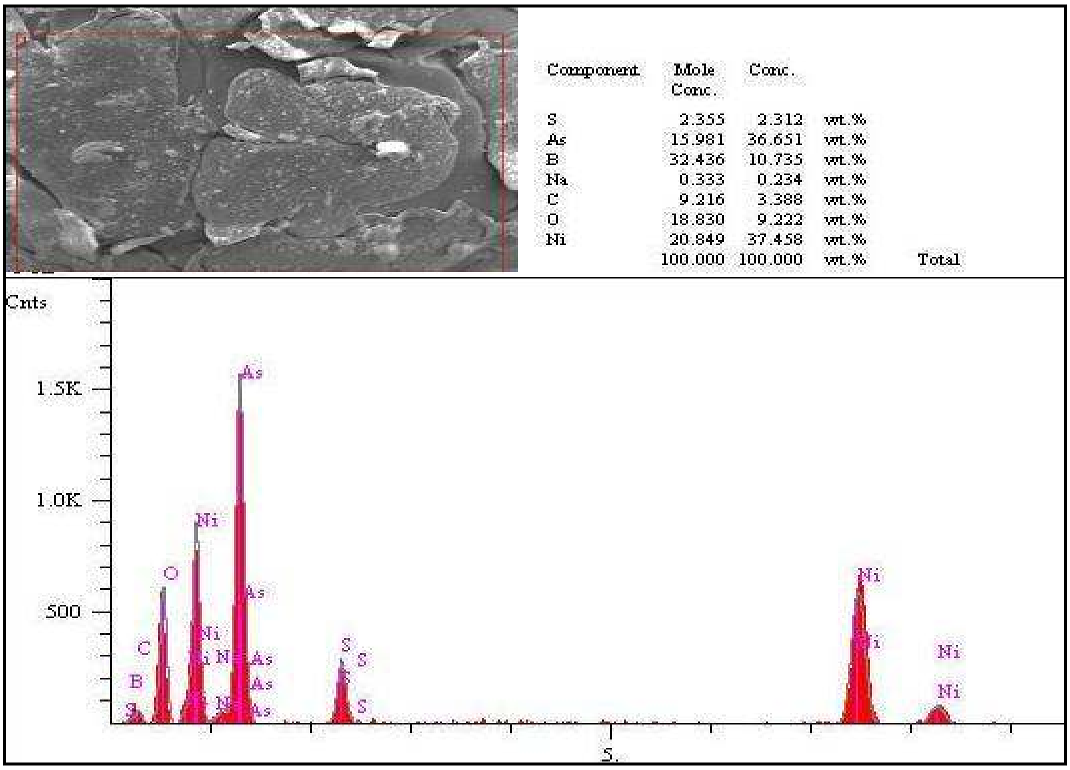


Figure 3.42. SEM image of Ni-NPIR



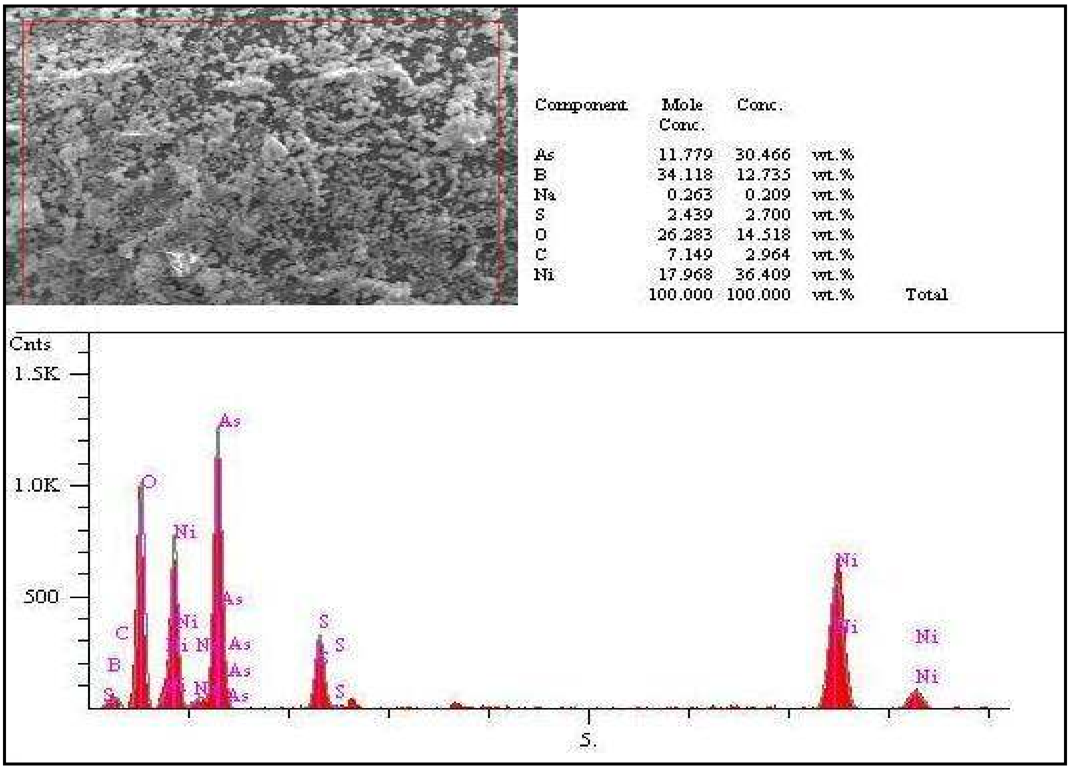
Component	Mole Conc.	Conc.		
C	21.108	11.244	wt.%	
O	10.626	7.541	wt.%	
S	1.738	2.472	wt.%	
Ni	21.602	56.234	wt.%	
As	0.269	0.895	wt.%	
B	44.286	21.236	wt.%	
Na	0.370	0.377	wt.%	
	100.000	100.000	wt.%	Total

Figure 3.43. SEM-EDX image of Ni-NPIR (Without arsenic)



Component	Mole Conc.	Conc.		
S	2.355	2.312	wt.%	
As	15.981	36.651	wt.%	
B	32.436	10.735	wt.%	
Na	0.333	0.234	wt.%	
C	9.216	3.388	wt.%	
O	18.830	9.222	wt.%	
Ni	20.849	37.458	wt.%	
	100.000	100.000	wt.%	Total

Figure 3.44. SEM-EDX image of Ni-NPIR + As(III)

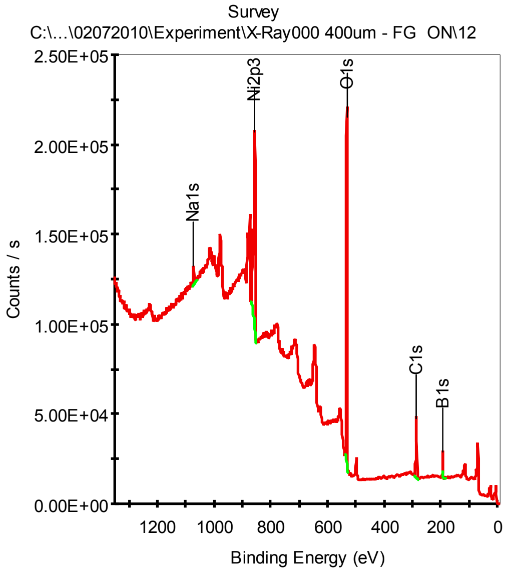


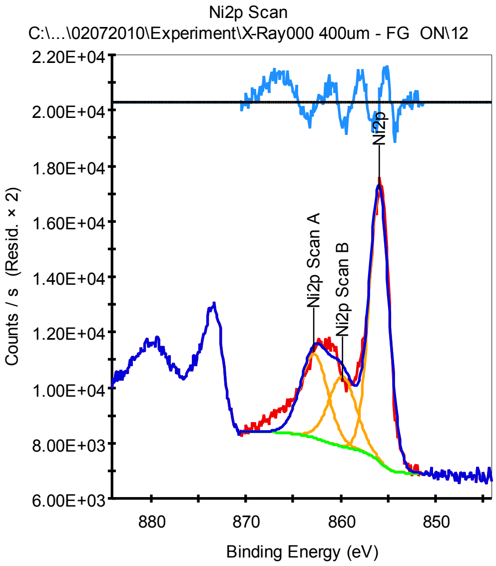
Component	Mole Conc.	Conc.		
As	11.779	30.466	wt.%	
B	34.118	12.735	wt.%	
Na	0.263	0.209	wt.%	
S	2.439	2.700	wt.%	
O	26.283	14.518	wt.%	
C	7.149	2.964	wt.%	
Ni	17.968	36.409	wt.%	
	100.000	100.000	wt.%	Total

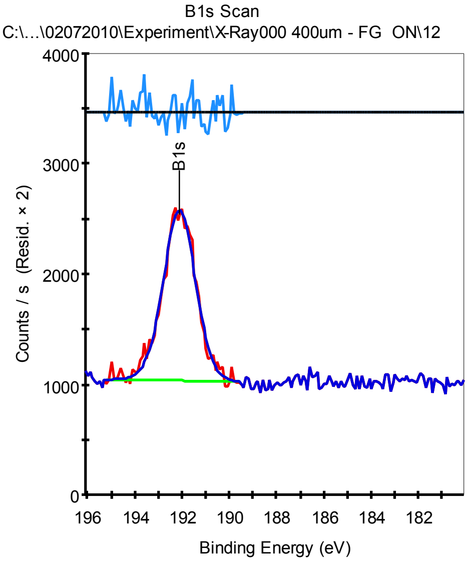
Figure 3.45. SEM-EDX image of Ni-NPIR + As(V)

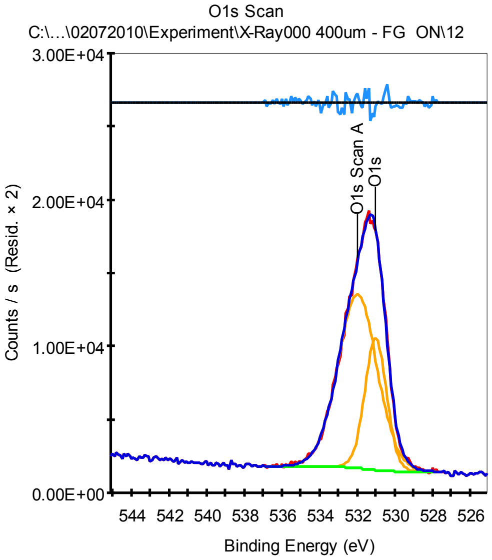
XPS Analysis of Ni-NPIR

As shown in Figure 3.46, at the surface up to 10nm depth, the major portion of the adsorbent is oxygen (51,42%). This can be explained by three reasons; 1. oxidizing conditions of the air, nickel nanoparticles on the resin could be oxidized, 2. nanoparticle compound contained oxygen, 3. XPS analysis contained a part of the resin Purolite C100 which contained oxygen. Carbon peak was confirm the first and thirth idea because the adsorbent can be affected by carbon of the air or carbon content of the resin is determined. In the literature (İşlek, 2010), it was shown that Ni-NP without resin also contained carbon and oxygen. This information confirmed the first idea that the adsorbent was effected by the air.









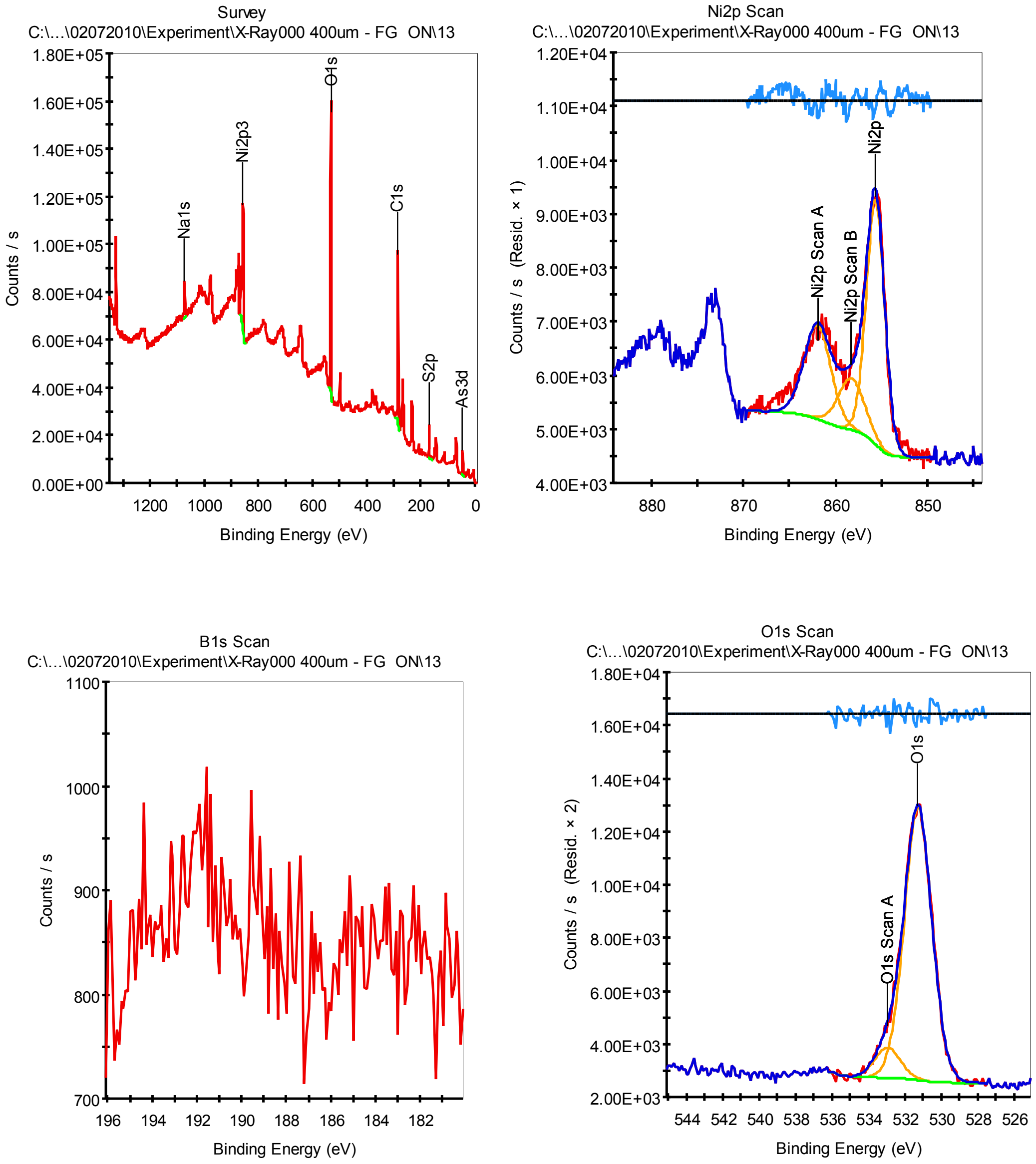
Peak Table:

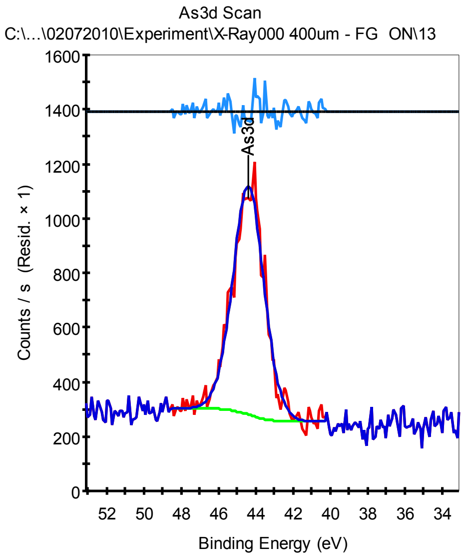
The adsorbent

Name	**At. %**
O1s	51,42
Ni2p3	13,76
C1s	22,98
Na1s	2,3
B1s	9,53

Figure 3.46. XPS analysis of Ni-NPIR (Without arsenic).

Figure 3.47 shows the XPS result of As(III) adsorbed adsorbent. Arsenic peak can be seen from the image. Also table shows the arsenic content. There was no boron peak (only noise signal), it can explain by the arsenic adsorption on the surface. While boron peak could not be determined by XPS, it was determined by SEM-EDX analysis (Figure 3.44). Because XPS analysis clarify only 5-10 nm deepth of the surface. However SEM-EDX is more sensitive analysis (1-50 nm). Binding energies were 44.4 eV and 44.8 eV for As(III) and As(V), respectively (Figures 3.47 and 3.48).



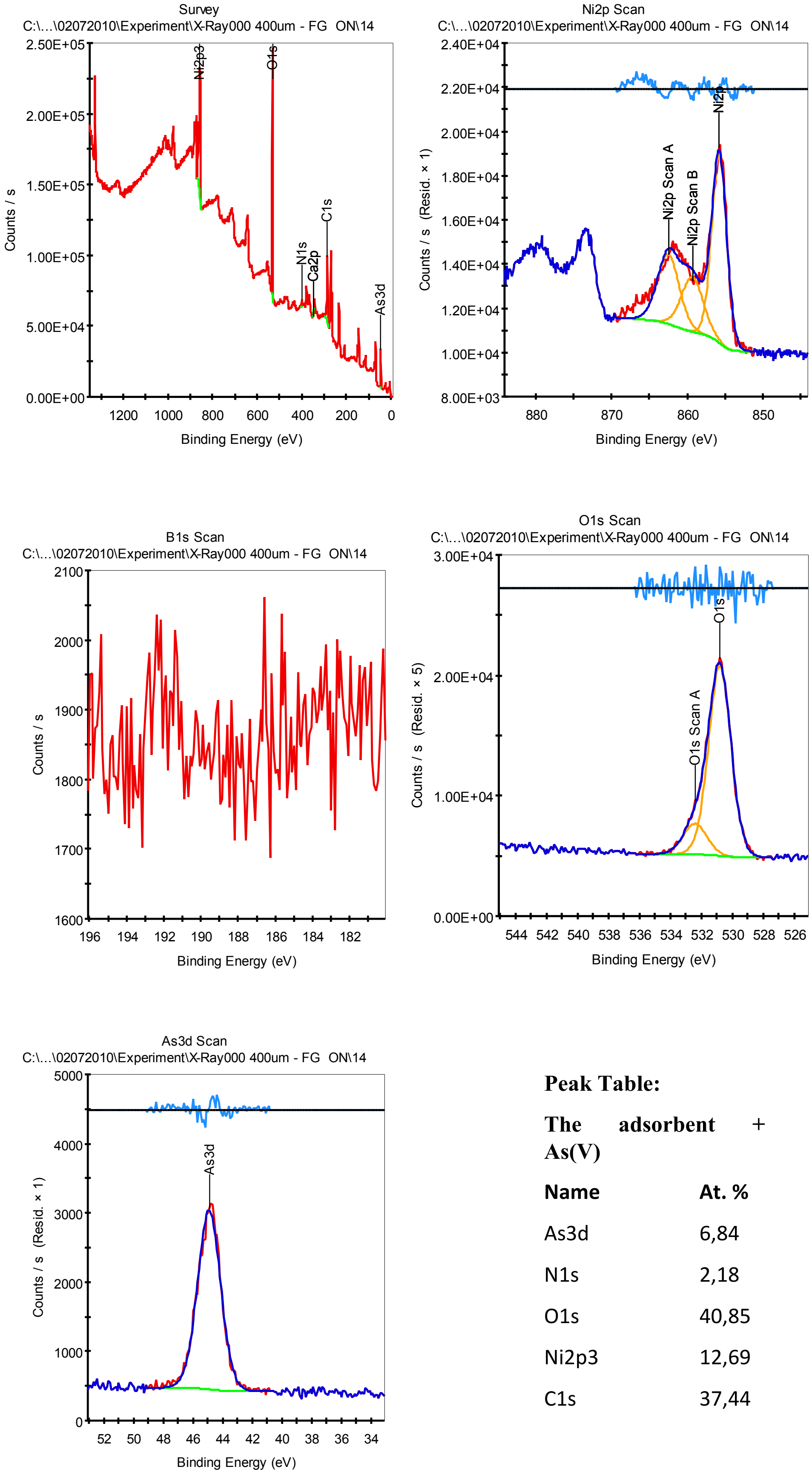


Peak Table:

The adsorbent + As(III)

Name	At. %
O1s	31,61
Ni2p3	8,31
C1s	46,62
As3d	3,59
S2p	6,41
Na1s	3,46

Figure 3.47. XPS analysis of As(III) sorbed Ni-NPIR.



Peak Table:

The adsorbent + As(V)

Name	**At. %**
As3d	6,84
N1s	2,18
O1s	40,85
Ni2p3	12,69
C1s	37,44

Figure 3.48. XPS analysis of As(V) sorbed Ni-NPIR.

3.3.8. Effect of Adsorbent Dose

The effect of the adsorbent dose on the removal efficiency of As(III) and As(V) are shown in Figure 3.49. Even at the lowest adsorbent dose used, very high arsenic removal efficiencies were observed. 82.4±2.1% and 82.3±3.2% removal efficiencies were obtained for As(III) and As(V), respectively, at 2.0 g/L adsorbent dose. Beyond 4.0 g/L adsorbent dose the removal efficiencies of both As(III) and As(V) were more than 93.8% for the initial As(III) and As(V) concentration of 200 µg/L.

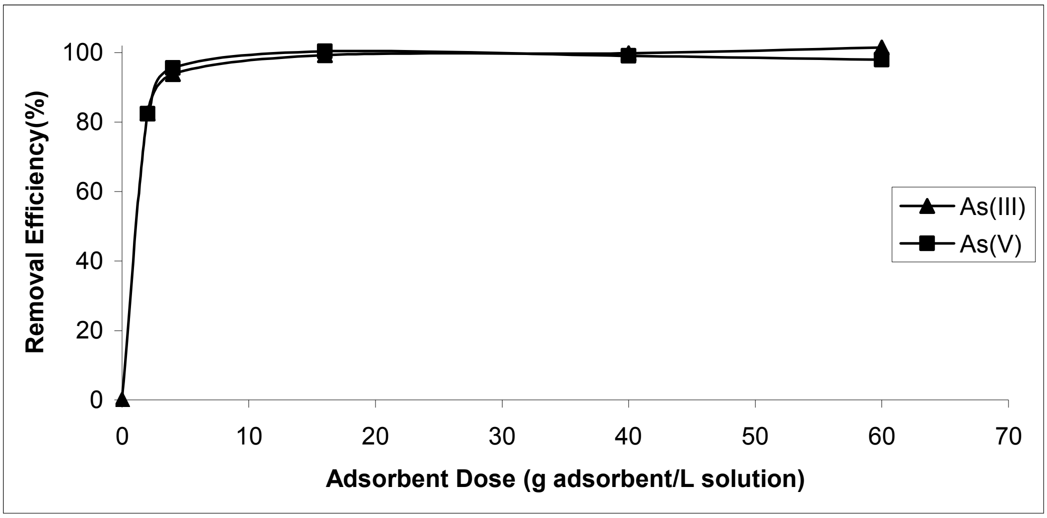


Figure 3.49. Arsenic removal efficiencies depending on the adsorbent dose (Initial As concentration: 100 µg/L, sorption time: 24 h at 25 °C).

The adsorbent was also analyzed for nickel content by taking the difference of adsorbent and resin, dried at the same temperature, 40 °C. The results showed that, 11.2±0.6% (w/w) of the adsorbent was Ni^o or its compounds. The average content of nickel on dry resin was also determined as 65.9±4.6 mg Ni/g adsorbent using Flame AAS. Also Boron analysis showed that 1 g resin contained 2.7±0.2 mg B.

3.3.9. Adsorption Isotherms

Langmuir, Freundlich and DR isotherm graphs are shown in Figures 3.50, 3.51 and 3.52.

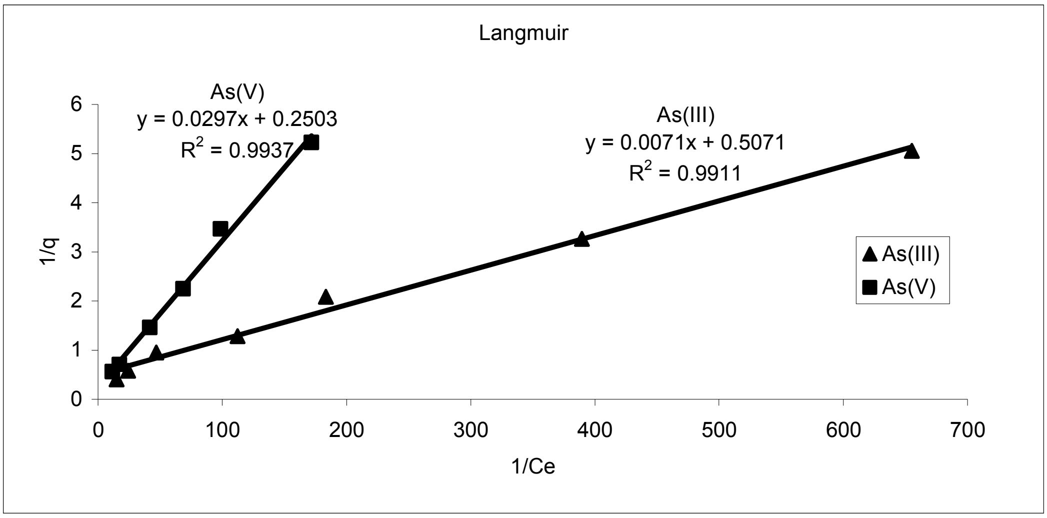


Figure 3.50. Langmuir isotherm for the adsorption of As(V) and As(III) (Initial As concentration: 10 mg/L, sorption: 24 h at 25 ^{o}C).

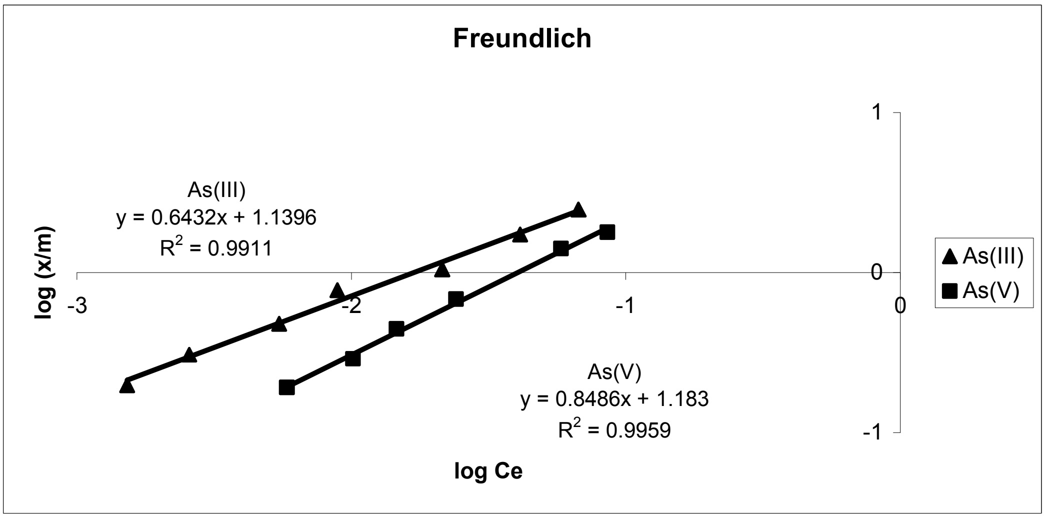


Figure 3.51. Freundlich isotherm for the adsorption of As(V) and As(III) (Initial As concentration: 10 mg/L, sorption: 24 h at 25 ^{o}C).

The correlation coefficients for the linear regression fit of Langmuir and Freundlich isotherms was found to be higher than 0.99. Figure 3.52 shows the plot of lnQ against ε^2. DR isotherm constants k and Q_m were calculated from the slope and intercept of the plot. The constant of adsorption isotherms are shown in Table 3.3.

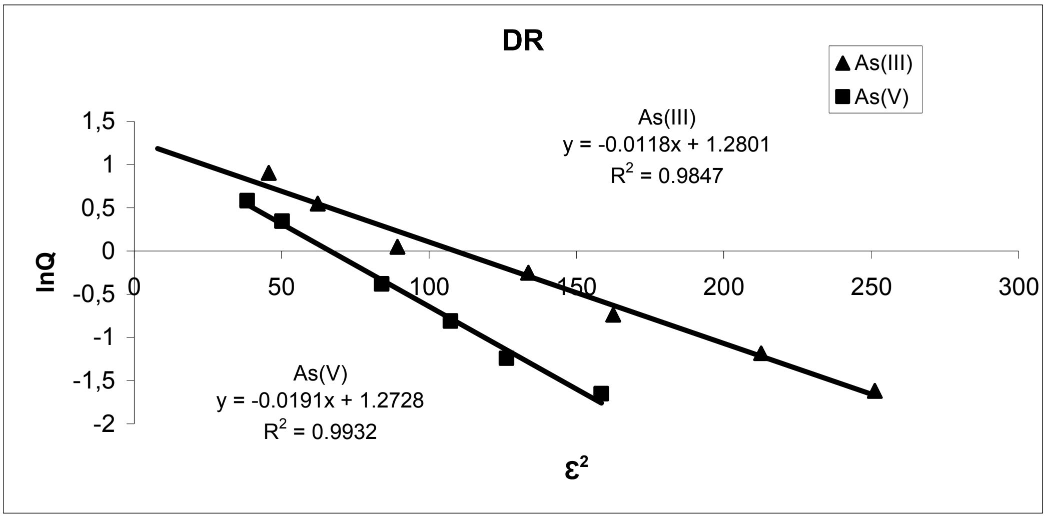


Figure 3.52. DR isotherm for As(V) (Initial As concentration: 10 mg/L, sorption: 24 h at 25 °C).

Table 3.3. Adsorption isotherm constants for As(III) and As(V) on the adsorbent

Species	**q_m (mg/g)**	**b(L/mg)**	**K(mg/g)**	**n**	**Q_m(mg/g)**	**K(mol^2/kJ^2)**
As(III)	1,97	278	13,8	1,55	3,60	0,01
As(V)	4,00	135	15,2	1,18	3,57	0,02

The calculated mean free energy of adsorption value of E was 5.04±0.2 kJ/mol for As(III) and 6.51±0.2 kJ/mol for As(V). It is known that magnitude of E is useful for estimating the type of adsorption and if this value between 8 and 16 kJ/mol adsorption type can be explained by ion exchange. But the value E found in this study is within the energy range of physical adsorption due to weak Van Der Waals forces (E < 8kJ/mol) (Mahramanlioglu et.al., 2002).

Value of r<1 represents the favorable adsorption and value greater than one represents unfavorable adsorption. The value of r for initial As(III) and As(V) were found to be 0.026±0.006 and 0.053±0.008 respectively. These values indicate highly favorable adsorption (Mahramanlioglu et.al., 2002).

The adsorption process was found to obey Langmuir and Freundlich equations and DR isotherms showed that the adsorption is physical and favorable.

Arsenic Capacities of Ni-NPIR

Nickel and boron contents of the adsorbent were indicated as 65.9±4.6 mg/g and 2.7±0.2 mg/g, respectively. Maximum arsenic capacities of the adsorbent were also determined as 3.60±0.2 mg/g for As(III) and 3.57±0.2 mg/g from the isotherms. Arsenic capacities were calculated for each Ni and B and shown in Table 3.4.

Table 3.4. Arsenic capacities calculated with respect to the amount of adsorbent nickel and boron content.

	As(III)	**As(V)**
Adsorbent (for each g)	3.60±0.2 mg	3.57±0.2 mg
Ni (for each g)	546.4±31 mg	541.8±30 mg
B (for each g)	1333±74 mg	1322±72 mg
Ni (for each mol)	0.0428±0.002 mol	0.0425±0.002 mol
B (for each mol)	0.1924±0.08 mol	0.1908±0.08 mol

3.3.10. Adsorption of As(III) and As(V) on Ni-NPIR Depending on Time

As shown in Figure 3.53, within 550 and 850 minutes, arsenic concentrations were decreased under the maximum contaminant limit for drinking water (0.01 mg/L) for As(III) and As(V), respectively. It is relatively longer time than FHSS but not for a long time for arsenic removal for batch method.

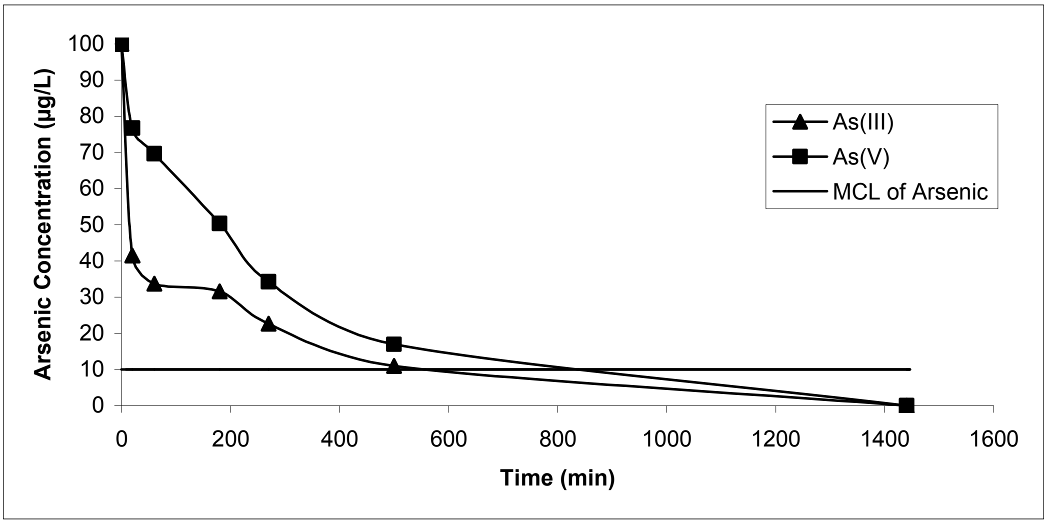


Figure 3.53. As(III) and As(V) adsorption depending on time (Initial As concentration: 100 µg/L, adsorbent dose: 20 g/L, sorption: 24 h at 30 ^{o}C).

3.3.11. Effect of Some Ions on As(III) and As(V) Sorption

The effect of some ions such as (phosphate, silicate, sulfate, nitrate, chloride) on arsenic removal was determined. In the literature, while chloride and sulfate increase the arsenic sorption, silicate and phosphate decrease (Zhang et al., 2004). Effect of the ions on arsenic removal efficiency by Ni-NPIR are shown in Figures 3.54 and 3.55 for As(III) and As(V), respectively. An efficiency decrease was observed while As(III) solution contained phospate. A little decrease was also seen for As(III) solution which contained silicate. However, none of the ions effected the As(V) removal efficiencies.

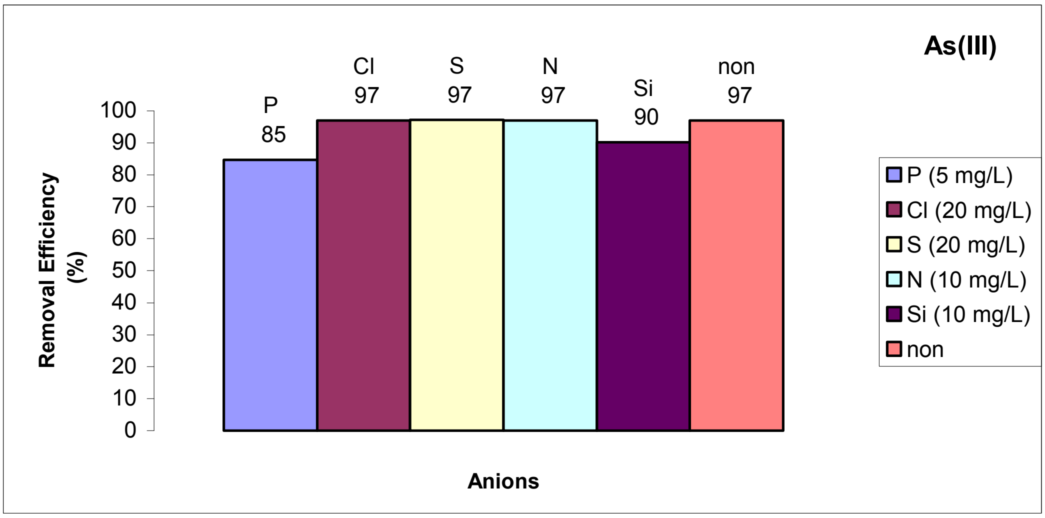


Figure 3.54. Removal efficiencies of the adsorbents in the ion contained media (Initial As concentration: 500 µg/L, adsorbent dose: 20 g/L, sorption: 24 h at 25 ^{o}C).

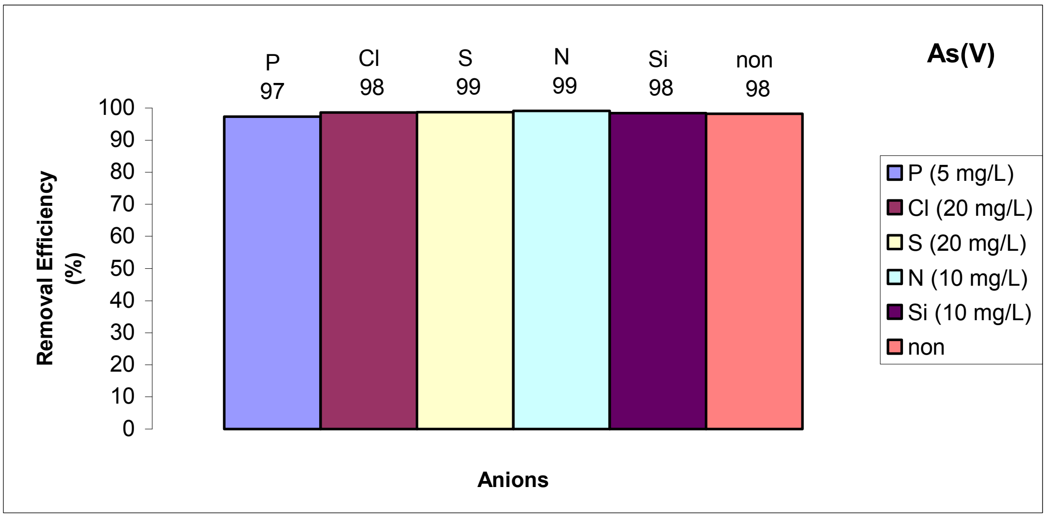


Figure 3.55. Removal efficiencies of the adsorbents in the ion contained media (Initial As concentration: 500 µg/L, adsorbent dose: 20 g/L, sorption: 24 h at 25 ^{o}C).

3.3.12. Regeneration Studies of Ni-NPIR

The results of the adsorption studies showed that 96.1±3.4% of As(III) and 97.0±3.2% of As(V) were adsorbed by the adsorbent in the column. Statistically, all of the adsorbed arsenic was desorbed for both As(III) and As(V). Sorption and desorption studies were repeated six times and the results are shown in Tables 3.5 and 3.6.

Table 3.5. Arsenic sorption studies of Ni-NPIR filled column

	Removal Efficiencies (%)					
	1	2	3	4	5	6
As(III)	>99.5±2.3	97.0±4.1	96.1±4.6	99.4±3.5	>99.5±2.1	96.9±3.2
As(V)	>99.5±1.8	98.0±2.2	97.4±2.8	100.1±2.1	>99.5±2.1	97.0±3.4

Table 3.6. Desorption studies of arsenic sorbed Ni-NPIR filled column

	Desorption Efficiencies (%)					
	1	2	3	4	5	6
As(III)	99.5±1.9	99.3±2.1	99.5±2.4	100.6±1.7	101.5±2.3	101.3±3.1
As(V)	100.9±1.1	100.1±2.2	100.3±2.1	101.1±2.0	101.4±2.5	99.9±3.5

4. CONCLUSIONS

4.1. FHSS

The FHSS developed in the study has the following advantages over traditionally used iron(III) oxides: (1) big particle size which makes it easy to separate from aqueous system after adsorption activity (2) high adsorption capacity for both As(III) and As(V) (3) high physical strength; (4) suitable for column use (5) easy for preparation since all the chemical reactions occur simultaneously in one system and furthermore. Consequently, it is believed that the FHSS developed in this study is environmentally acceptable and applicable.

Ferric oxide which was precipitated onto silicagel as support at only pH 5.0–6.5 could adsorb both As(III) and As(V) effectively. Therefore, pH 6.0 was chosen as the precipitation pH. Ferric hydroxide precipitated at pH 6.0 on silica gel and packed in a column can be used to remove As(III) and As(V) from water without any need to an oxidation step. Initial solution pH did not significantly affect the arsenic removal efficiencies in the pH range 3.1-9.7. The removal efficiencies varied in the range 96.0-99.8% for As(III) and 95.6-99.9% for As(V). Since granular ferric oxide was obtained by precipitating at relatively low pH, no colloid formation took place, and therefore there is no need for a microfiltration step to obtain high removal efficiencies. The physical strength of the system was increased by using silicagel as support material. SEM and EDX data showed that all the FHSS materials are robust and granular, not aggregated. The capacity of the column is high, and preparation of the material is easy. Adsorption of As(III) at trace level by FHSS was shown to be realized without oxidation to As(V) by means of arsenic speciation analysis with 7 ml/min solution flow rate, and relatively high arsenic concentration (400 mg/L) was used. However, when more dilute As(III) solution (500 μg/L) was passed through the column slowly (1.5 mL/min), 62 % of As(III) was oxidized to As(V).

4.2. Thermal Method

Thermal method was tried to form ferric hydroxide from Fe(III). The experiment is succesful and the adsorbent is robust, granular, not aggregated and stable. The obtained adsorbent adsorbed both As(III) and As(V). Optimal heating temperature was 220 ^{o}C. At higher temperatures than 220 ^{o}C, because of the decomposition of ferric hydroxide, the capacities were decreased. Significantly the same arsenic uptake capacities were obtained by stepwise and fixed temperature heating methods.

4.3. Ni-NPIR

Ni-NPIR developed first time in the literature was found to have advantages such as sorption of both As(III) and As(V) with high removal efficiencies and relatively high capacities, ease of preparation and suitability for column use.

Optimal preparing conditions of Ni nanoparticle impregnated resin were determined. Optimum drying temperature was chosen as room temperature. Removal efficiency of As(III) was 99.7% and arsenic uptake was 3.50 mg As(III)/g adsorbent at 20 ^{o}C. As(III) and As(V) uptakes by the nickel based adsorbent at various initial pH levels were studied in order to determine the optimum pH for arsenic removal. In the batch method, initial pH did not significantly affect the arsenic removal efficiencies for As(III) and As(V) in the pH range 3.3-11.5. Effect of the adsorbent dose was determined on the removal efficiencies. Even at the lowest adsorbent dose used, very high arsenic removal efficiencies were obtained. 99.2% and 100.3% removal efficiencies were obtained for As(III) and As(V), respectively, at 16 g/L adsorbent dose. The graph of adsorption isotherms Langmuir, Freundlich and DR were drawn. Adsorption process was found to obey Langmuir and Freundlich equations and DR isotherms showed that the adsorption is physical and favorable. Diverse ion effects study showed that phosphate decreased 12.3% the removal efficiency of As(III), also silicate 6.8% decreased the removal efficiency. The other selected ions did not effect the As(V) removal efficiency. Desorption studies showed that As(III) and As(V) could be desorbed from the adsorbent therefore the adsorbent can be used many times.

This novel adsorbent; is effective for both As(III) and As(V) removal, is suitable for column studies, has high As(III) and As(V) removal efficiency and capacities, and could be regenerated.

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