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DEVELOPMENT OF PRECONCENTRATION TECHNIQUES FOR CHEMICAL ANALYSIS

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ÖZET

KİMYASAL ANALİZ İÇİN ÖNDERİŞTİRME YÖNTEMİ GELİŞTİRME

İŞLEK COŞKUN, Yasemin

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Tezin birinci bölümünde Ni/Ni$_x$B adsorbanı hazırlamakta kullanılan nikel tuzları türünün arsenik önderiştirmesine etkisi incelenmiştir. Bu nanosorbentler nikel tuzlarının NaBH$_4$ ile reaksiyona sokulmasıyla sentezlenmiştir. Sentezlenen nanopartiküllerin arsenik sorpsiyon verimleri ve kapasiteleri beç (kesikli) çalışmalarla ölçülmüştür. Optimizasyon çalışmaları yapılmıştır. Langmuir, Freundlich ve Dubinin Radushkevic izotermleri çizilmiş ve adsorpsiyonun hem Langmuir hem de Freundlich izotermlerine uyduğu görülmüştür. Langmuir izoterminden hesaplanan sorpsiyon kapasitesi literatürdeki değerlerle kıyaslandığında çok büyük olup 2.5 g As(III)/g sorbent olarak bulunmuştur. DR izotermi sorpsiyonun istemli ve fiziksel olduğunu göstermiştir. Arsenik tayini için HGAAS kullanılmış ve arsenik tayinlerinde sorbentin çözünmesinden gelen nikel girişimi KI ve sitrik asit karışımı kullanarak önlenmiştir. Arsenik tayini için bulunan belirtme sınırı literatürde kullanılan diğer yöntemlerin belirtme sınırıyla kıyaslanabilinir düzeydedir. Geliştirilen yöntem çeşitli su örneklerinde toplam arseniğin HGAAS ile tayini öncesi önderiştirilmesinde başarı ile uygulanmıştır.

İkinci bölümde, fluorimetrik eser aluminyum tayini için tayin öncesi Ni/Ni$_x$B adsorbanı ile önderiştirme yöntemi geliştirilmiştir. Bu çalışmada sorbent, nikel sülfat tuzunun inert ortamda NaBH$_4$ ile indirgenmesiyle hazırlanmıştır. SEM-EDX, kimyasal analiz, TGA, XPS ve izoelektrik noktası ölçümleri ile sorbentin yapısı incelenmiştir. Elde edilen taneciklerin küresel yapıda olduğu görülmüştür. Optimizasyon çalışmaları yapılmıştır. pH 3-10 aralığındaki başlangıç pH'larında Al(III)'un nicel olarak tutulduğu bulunmuştur. Adsorpsiyon hızlıdır ve ilk beş dakikada sorpsiyon veriminin %98.9 olduğu hesaplanmıştır. 250 mL örnek hacmine kadar geri kazanımların nicel olduğu görülmüştür. Beç çalışmaları ile sorpsiyon kapasitesi 0.394 g Al(III)/g sorbent olarak hesaplanmıştır. Bulunan kapasite değerinin izoterm çalışmalarında bulunan değerle uyumlu olduğu görülmüştür. Yöntem hemodiyaliz suyu ve çeşitli gerçek su örneklerine başarı ile uygulanmıştır.

Anahtar sözcükler: Arsenik, Alüminyum, Nanopartiküller, Hidrür Oluşturmalı-Atomik Absorpsiyon Spektrometresi (HGAAS), Fluorimetre

ABSTRACT

DEVELOPMENT OF PRECONCENTRATION TECHNIQUES FOR CHEMICAL ANALYSIS

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In the first chapter of thesis, the effect of nickel salt type used for the preparation of Ni/Ni_xB adsorbent on the arsenic preconcentration was investigated. The nanosorbents were synthesized by reacting $NaBH_4$ with nickel salts. Arsenic sorption efficiencies and capacities of the synthesized nanoparticles were measured in batch studies. Optimization studies were carried out. Langmuir, Freundlich, and Dubinin-Radushkevich (DR) isotherm models were tested and it was found that the sorption was fitted both Langmuir and Freundlich isotherms. The sorption capacity which was obtained from Langmuir isotherms was very high according to literature and was found to be 2.5 g As(III)/g sorbent. DR isotherms showed that sorption is physical and favourable. Hydride generation atomic absorption spectrometer (HGAAS) was used for the determination of arsenic. Nickel interferences which occurred due to the dissolution of the sorbent were eliminated by using a mixture of KI and citric acid. The limit of detection for arsenic determination was comparable with that obtained by other established methods. The developed method was applied to the preconcentration of arsenic in various water samples prior to determination of total arsenic by using HGAAS with satisfactory results.

In chapter two, a preconcentration technique by using Ni/Ni_xB sorbent was developed for trace aluminum determination prior to the fluorimetric determination. The sorbent was synthesized by reducing sulfate salts of nickel with $NaBH_4$ in inert atmosphere. Characterization studies were executed by the aid of SEM-EDX, chemical analysis, TGA, XPS and, point of zero charge measurement. It was found that the obtained particles were spherical. Optimization studies were realized. Sorption efficiencies for Al(III) at studied initial pH values between 3-10 were found quantitative. Adsorption rate was quite high and in five minutes sorption efficiencies reached 98.9%. The recovery of

Al(III) was found quantitative (>95%) for sample volumes up to 250 mL. The sorption capacity was found to be 0.394 g Al(III)/g sorbent in batch studies. The sorption capacity obtained from batch studies was compatible with that obtained by isotherm studies. The proposed method was applied to the preconcentration of Al(III) in haemodialysis solutions and various real water samples with satisfactory recoveries.

Keywords: Arsenic, Aluminium, Nanoparticles, Hydride Generation-Atomic Absorption Spectrometer, Fluorimeter

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CONTENTS

CONTENTS (Continue)

Page

CONTENTS (Continue)

CONTENTS (Continue)

Page

CONTENTS (Continue)

CONTENTS (Continue)

LIST OF FIGURES

Figure Page

LIST OF FIGURES (Continue)

Figure Page

LIST OF FIGURES (Continue)

LIST OF FIGURES (Continue)

Figure Page

LIST OF TABLES

Tables Page

LIST OF TABLES (Continue)

SYMBOLS and ABBREVIATIONS

Abbreviations	Explanations
AD	Alzheimer’s disease
AsB	Arsenobetaine
AsC	Arsenocholine
ASCP	Anodic stripping chronopotentiometry
CPE	Cloud point extraction
CRM	Certified reference material
DLLME	Dispersive liquid liquid microextraction
DMAA	Dimethylarsinic acid
DR	Dubinin-Radushkevich
EPA	US Environmental Protection Agency
ETAAS	Electrothermal atomic absorption spectrometry
FAAS	Flame atomic absorption spectrometry
GFAAS	Graphite furnace atomic absorption spectrometry
HG	Hydride generation technique
HGAAS	Hydride generation atomic absorption spectrometry

SYMBOLS and ABBREVIATIONS (Continue)

Abbreviations	Explanations
HGAFS	Hydride generation coupled to atomic fluorescence spectrometry
ICPOES	Inductively coupled plasma optical emission spectrometry
IPCS	International Programme On Chemical Safety
ISO	International Organization For Standardization
LD	Lethal dose
LLE	Liquid–liquid extraction
LOD	Limit of detection
LOQ	Limit of quantification
LPME	Liquid phase microextraction
MMAA	Monomethylarsonic acid
MWCNTs	Multi-walled carbon nanotubes
SEM	Scanning electron microscopy
SFODME	Solidified floating organic drop microextraction
SPE	Solid phase extraction

SYMBOLS and ABBREVIATIONS (CONTINUE)

Abbreviations	Explanations
TGA	Thermo gravimetric analysis
WHO	World Health Organization
XPS	X–ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence spectrometry
WHO	World Health Organization

CHAPTER ONE

INVESTIGATION OF THE EFFECT OF NICKEL SALT TYPE USED FOR THE PREPARATION OF Ni/Ni_xB ADSORBENT ON THE ARSENIC PRECONCENTRATION AND APPLICATION OF THE SELECTED SORBENT FOR ARSENIC ANALYSIS IN CONJUCTION WITH THE HYDRIDE GENERATION-ATOMIC ABSORPTION SPECTROMETRY

1. INTRODUCTION

1.1 Historical Background of Arsenic

Arsenic was known since ancient times. Ancient Chinese, Greek, and Egyptian people mined various compounds of arsenic (Mohan and Pittman Jr., 2007). At the beginning of the Bronze Age the role of arsenic in metallurgical development is documented. Application of arsenical bronze was more extensive. In the third millennium it was used by ancient Egyptians. In ancient China, it was used for producing a silvery surface on mirrors and statues (Carapella, 2002). The people who made such artifacts would have been affected by arsenic fumes. The bronze makers and their families would have exposured to arsenic. Many copper, gold and lead ores contain significant amounts of arsenic. Most of the arsenic went into the smoke which was inhaled by the people and contaminated the surrounding areas. Orphiment (As_2S_3, the yellow arsenic sulfide) and realgar (As_4S_4) were also used as depilatories in the leather industry with a high probability of exposure of ancient workers. In ancient times orphiment was also used as pigment. A linen bag which was found in King Tutankhamun's tomb and wall paintings of the Theban necropolis were found to contain orphiment (Nriagu, 2002). Arsenic was also used in medical equipment in ancient cultures. Orphiment and realgar were used by Hippocrates as escharotics to remove fungal flesh. Realgar was also used to heal various ulsers, with oil to destroy lice, with resin for chronic cough and shortness of breath. Ancient Indian and Chienese cultures were also used arsenic minerals for medical purposes (Nriagu, 2002).

In Medieval times attempts for isolating and studying elemental arsenic were increased. In eighth century, white arsenic was obtained by heating orphiment by Geber (Jabir ibn-Haiyan) who was an Arabian alchemist. White, yellow, and red arsenic were differentiated by Avicenna (Ibn-i Sina) (980-1038)

(Wertime, 1962). Albertus Magnus (1193-1280) was thought that he was the first person who discovers metallic arsenic. In 1540, Biringuccio was made a clear distinction between elemental arsenic and arsenic minerals. In 1641 Shroeder obtained elemental arsenic after reducing white arsenic with charcoal. N. Lemery obtained metallic arsenic after heating arsenic trioxide with soap and potash in 1683. In 1773, Brand showed that white arsenic was arsenic oxide. Scheele was discovered arsine (AsH_3) in 1775 (Wertime, 1962; History magazine, 2001).

The main areas for arsenic usage were in chemistry, painting, and medicine. Orphiment was used in paintings for gold colour. Various coloured dyes were obtained by mixing orphiment and pigments. The painters who used golden orphiment in their palatte suffered from arsenic poisoning (Nriagu, 2002).

During the 1800s, Scheele's green (copper arsenite) as a pigment became very popular for wall and textile products. Afterwards it was found that this pigment cause of household poisoning (Haslam, 2013)

Arsenic became part of the social and politicial life as poison in Middle Ages. Due to it is tasteless, odorless, cheap and fatal even in small doses; it was used by families to eliminate the rivals (Nriagu, 2002). The Medici and Borgia families assassinated their rivals by arsenic compounds were documented. It was claim that Napoleon's death was the result of arsenic poisoning (Cullen, 2008). After developing a chemical test which identifies arsenic in the body by James Marsh, usage of arsenic as a poison was decreased in the 18th century (Gilbert, 2014). In general, according to this method, the sample was mix with zinc and sulfuric acid, after heating this mixture in a vessel a silvery film was occurred on the surface of the vessel. Marsh Test can detect 0.02 mg arsenic.

Arsenical compounds were used for treating syphilis up to usage of penicillin became common in the 1940s. In 1960 after understanding the health effects of lead arsenic for people who worked in orchard and increasing arsenic residues were a public concern, usage of lead arsenic was diminished and finally prohibited in 1988 (Hughes et al., 2011).

Arsenic contained pesticides still use. Chromated copper arsenate has been used for wood preservative and to keep away both insects and microbial agents. Chromated copper arsenate is still using in utility poles, marine plants (pilings and structures), and sand highway structures (EPA, 2008).

Toxicity of arsenic is well understood owing to uses of it in products, pharmaceuticals, and industry since old times. Recently, concern in toxicology of arsenic focuses on exposuring naturally occurring arsenic via food, water, and soil. The most important research area related to arsenic is to understand the environmental levels causing public health concern (Hughes et al., 2011).

1.2 Arsenic

Arsenic (atomic number 33; atomic mass 74.92) has an outer electron configuration of $4s^2 4p^3$ and belongs to subgroup V of the Periodic Table. It is often described to be a metalloid. Arsenic has three allotrope (grey arsenic, black arsenic, and yellow arsenic). Grey arsenic is the most stable one and use in industry. Arsenic exist in four oxidation numbers in the environment: As(V), As(III), As(0) and As(−III) (Lobinski and Marczenko, 1998).

1.3 Arsenic Sources

Arsenic, which exist naturally, is found throughout the environment, even if in small quantities, in all rock, soil, dust, ash, water and air. Primarily responsible for the emission of arsenic into the atmosphere, soil, groundwater systems and, food chain are natural sources (weathering of minerals, biological and, volcanic activity) along with anthropogenic events. Contamination caused by industrial activities due to emissions of arsenic by the smelting industry, industrial and animal wastes, burning of fossil fuels have fairly increased (Thorton, 1996; EPA, 2012; Vahter, 2008).

Abundance of arsenic is 3 µg/mL in the crust of the Earth. In the presence of argillaceous substances concentrations of arsenic may increase (Thorton,1996). Arsenic is related to sulphurous minerals of iron and various other metals (especially gold, silver, copper, antimony, nickel and cobalt). The most known are orpiment (As_2S_3), arsenopyrite (FeAsS) and realgar (As_4S_4) (Onishi, 1969; Lobinski and Marczenko, 1998). Hydrothermal environments contain arsenic on account of recent or ancient volcanic activity (Wakao et al., 1988).

Active volcanos emit arsenic compounds via magma and volcanic dusts (Vingradov, 1959). The spread of arsenic into the environment from human activities are not negligible. Although in several countries arsenic containing insectisides and pesticides are banned, residual arsenic content keeps cycling in the biosphere and thus continuing to contamine soil, crop, surface and groundwaters, etc. Arsenic as sodium arsenite has been widely used in agriculture as fungicide to protect grapevines was indeed used until 2001 (Grillet et al., 2004). Arsenic contamination in air is mainly result of consuming fossil fuels which high in arsenic. It causes releasing arsenic oxide (As_2O_3) to the air. This compounds are highly toxic and can retain in the air up to 10 days. In the industrial areas the amount of atmospheric arsenic have been existed to be highest (Cullen et al., 1989).

As content in non contaminated soils are in the range of 1-40 mg/kg, while arsenic in agricultural soils which contaminated by arsenical pesticides may be present 2550 mg/kg (Moore and Ramamoorthy, 1984; Gallardo et al., 2001). Moreover, arsenic concentrations in mining sites and old industrial areas may reach 20 g/kg (Gallardo et al., 2001). In surface water, arsenic concentrations are ranged from 0.2 to 2 μg/mL. Under some local conditions geothermal inputs contains arsenic up to 1000 μg/mL (Smedley and Kinniburgh, 2002).

Generally, dusts which emitted to environmental contain arsenic as As_2O_3. The solubility of this compound based on primarily pH of the environment. In environments containing hydrochloric acid the solubility of the arsenic will increase by virtue of the chloro-complexes formation. The arsenic solubility (As_2O_3) in basic conditions is higher than at neutral pH (Gao and Burau, 1997).

1.4 Arsenic Species

In the natural environment there are four oxidation number for arsenic: As(III), As(V), As(0), and As(-III). Arsenic toxicity and mobility are affected by its oxidation number (Meng et al., 2003). Therefore, characteristics of the water assign which species of the arsenic will be dominant. In groundwater, abiotic conditions, majority of arsenic are As(III) and As(V), and minority are methyl and dimethyl arsenic compounds. As(III) is more toxic and soluble than As(V). As(III) is turned into As(V) by oxidation mechanism (Liévremont et al., 2009). Arsenic also occurs in inorganic and organic forms. Compounds of organic arsenic are less toxic than compounds of inorganic arsenic (IPCS, 2001).

Mostly encountered arsenic compounds in nature are arsenate-As(V), arsenite-As(III), arsine, monomethylarsonic acid, dimethylarsinic acid, arsenobetaine, arsenocholine. Arsenic-containing compounds have different toxicities (IPCS, 2001). The frequently encountered arsenic species are shown below.

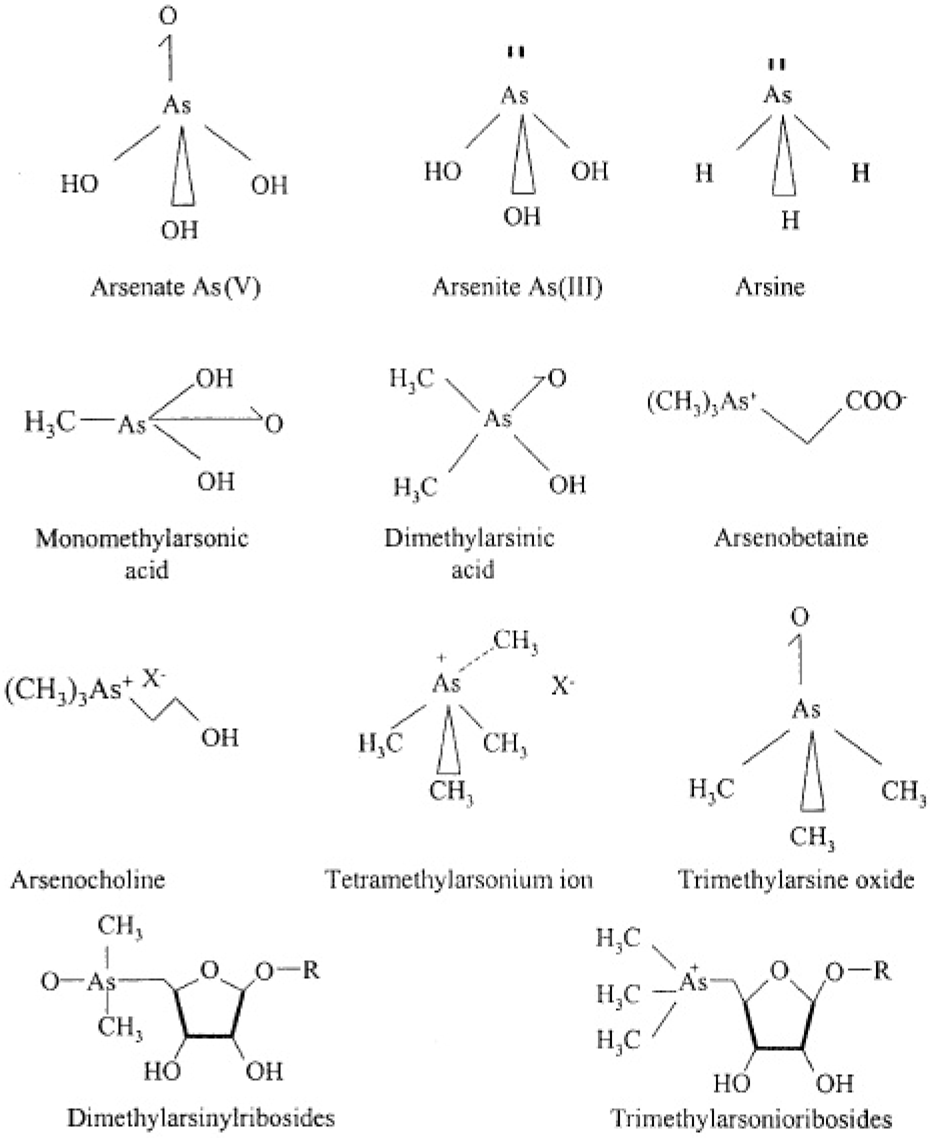

Arsenate As(V)
Arsenite As(III)
Arsine
Monomethylarsonic acid
Dimethylarsinic acid
Arsenobetaine
Arsenocholine
Tetramethylarsonium ion
Trimethylarsine oxide
Dimethylarsinylribosides
Trimethylarsonioribosides

Figure 1.1. Arsenic-containing compounds often found in the environment (Fodor, 2001).

The form of arsenic depends on the type/amount of the component of the soil, pH and, redox conditions (Eh/pH). Under reducing conditions the predominant species is As(III), which exists as arsenious acid (H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$). Under oxidizing conditions arsenate As(V) exists as oxyanions of arsenic acid ($H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}). As(III) is more soluble, more mobile and so more toxic than arsenate [As(V)] (Rochette et al., 1998).

Mostly encountered species are $H_2AsO_4^-$ and $HAsO_4^{2-}$ under oxidizing conditions, in the pH between 4 and 8 in natural environments. H_3AsO_4 may be present in immensely acidic pH values, while AsO_4^{3-} in intensely alkaline media. Under reducing media and pH below 9 (approximately), H_3AsO_3 become dominant. Arsenate is a weak triprotic acid. The respective deprotonation dissociation constants (pKa) are 2.20 (H_3AsO_4/ $H_2AsO_4^-$), 6.97 ($H_2AsO_4^-$/ $HAsO_4^{2-}$) and 11.53 ($H_2AsO_4^-/AsO_4^{3-}$). Arsenite is a hydroxo-acid, with pKa values of 9.22 ($H_3AsO_3/H_2AsO_3^-$), 12.13 ($H_2AsO_3^-/HAsO_3^{2-}$), and 13.40 ($HAsO_3^{2-}/AsO_3^{3-}$) (Alloway, 1990). The distribution diagram of arsenite and arsenate species vs pH is shown in Figure 1.2.

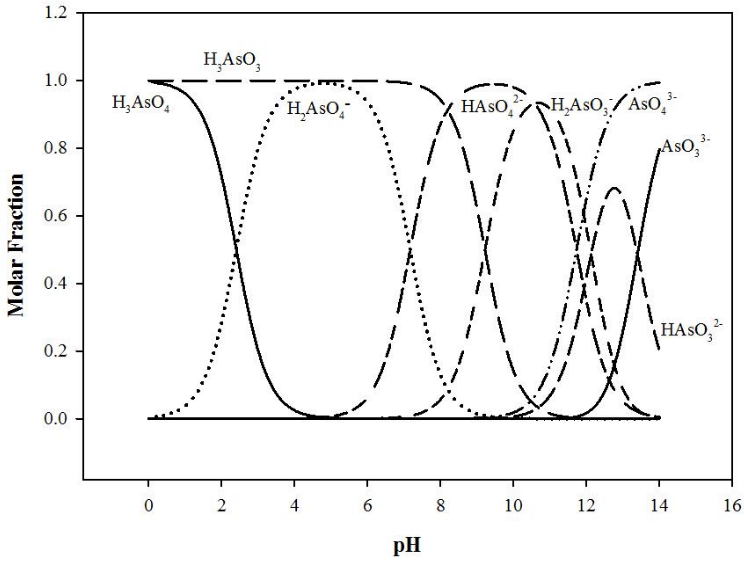


Figure 1.2. Speciation of Arsenate and Arsenite vs pH.

The existence of the organoarsenic species monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) in soil are the result of microbial-mediated methylation processes of inorganic arsenic Arsenite is formed after reducing arsenate by microbial activity. Monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) occur as a result of further methylation of arsenite. Aerobic microorganisms can reduce the formed compounds to the corresponding arsines (Cullen and Reimer, 1989). These arsines, which are highly volatile, are transferred from the soil to the atmosphere where an oxidation process follows. the arsines are transformed to inorganic arsenic. The cycle is completed because atmospheric arsenate returns to the soil via dry deposition or rain (Pongratz, 1998). Biological transformations within the arsenic cycle are shown in Figure 1.3.

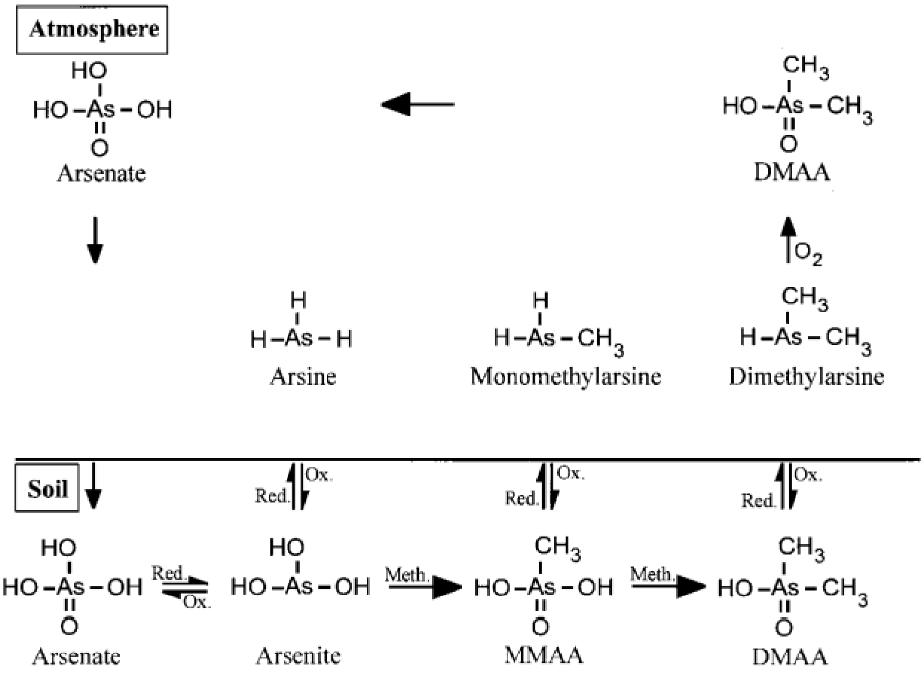


Figure 1.3. Biological transformations of arsenic (Pongratz, 1998).

1.5 Health Effect and Toxicity of Arsenic and Arsenic Compounds

Arsenic exposure is a daily event because of spreading widely throughout environment (Hughes, 2002). Arsenic entered the environment via pesticides, fertilizers, metallurgic industrial waste, melting and mining operations. Food and water are the main arsenic source for human (Grotti et al., 2006; Pantuzzo et al., 2009).

As(III) and As(V) are oxidation numbers of inorganic arsenic (Campillo et al., 2008; Shah et al., 2009). Organic arsenic is less toxic than inorganic arsenic, as pentavalent arsenite is 100 times less toxic than trivalent one (Pal et al., 2009; Sounderajan et al., 2007). Methylated arsenic, such as monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) are less toxic and arsenic compounds, such as arsenocholine (AsC) and arsenobetaine (AsB) are considered as nontoxic (Chatterjee et al., 1995; Lamble and Hill, 1996; Zhang et al., 1996). Monomethylarsonic acid (MMA^V) and dimethylarsinic acid (DMA^V) are stable methylated mammalian metabolites of inorganic arsenic and are mainly excreted in the urine. These species are used as herbicides (Hughes, 2002).

Chemical form and oxidation number of arsenic determines acute arsenic toxicity. Trivalent arsenic has greater acute toxicity than pentavalent one. The lethal dose of inorganic arsenic is evaluated as 1–3 mg As/kg for human adult (Ellenhorn, 1997). Contaminated drinking water, usage of it for food preparation, usage of contaminated irrigation water, industrial processes, consuming contaminated food and smoking tobacco are the pathways of exposure high levels of inorganic arsenic. The symptoms of serious acute arsenic toxicity in humans are gastrointestinal discomfort, vomiting, diarrhea, bloody urine, anuria, shock, convulsions, coma, and death. Long-term exposure to inorganic arsenic can lead to chronic arsenic poisoning, especially by means of drinking of contaminated water, eating of food prepared with this water and eating food irrigated with arsenic-rich water. The most characteristic effects are skin lesions (hyperpigmentation, hyperkeratosis, and hypopigmentation) and skin cancer (WHO, 2011; Mandal et al., 2001; Hughes, 2002).

Mechanism of arsenic toxicity is thought that arsenite binds to the sulphydryl groups of the enzymes and cause functional corruption of enzymes. Because of arsenic is structural of the phosphate ion, arsenate competes with phosphate ion, hinders in particular with the oxidative phosphorylation process, inhibiting the energy metabolism of the cells. It might exchange the phosphate in the DNA double helix, which might cause the mutagenic, carcinogenic and teratogenic effects of arsenic (Moore et al., 1983; Abernathy et al., 1999; Mandal and Suzuki, 2002).

Limit values for drinking water are possibly given as total arsenic because of these forms are thermodynamically unstable under natural conditions. In 1958, the World Health Organisation set the maximum permissible arsenic level in drinking water as 0.2 mg/L; this was lowered to 0.05 mg/L in 1963 and this was again lowered to 0.01 mg/L in 1993. The present limit value, which has been reduced twenty-fold, is indicative of the importance of arsenic intake via drinking water (WHO, 2011).

In the world encountered severe arsenic problems are in Argentina, Bangladesh, Chile, China, Hungary, India (West Bengal), Mexico, Romania, Taiwan, Vietnam, many parts of the USA, Nepal, Myanmar and Cambodia (Mandal and Suzuki, 2002; Bhattacharya et al., 2007; Gan et al., 2014; Sharma and Sohn, 2009).

Izmir Bay has been polluted by untreated or partially treated domestic and industrial wastewater discharges, urban and agricultural run-off, discharges from ships and sediments and contaminated waters from rivers, dredging activities in the harbor, and the disposal of the dredged material to the outer bay for several years. The important sources of water pollution are both domestic wastes and industrial wastes. Gediz River is polluted by both domestic and industrial wastewater as well (Balci and Kucuksezgin, 1994). Arsenic concentrations in sediments in İzmir Bay were reported to be 8–31 μg/g by Atalar et al. (2013). Sediments in Izmir Bay is found to contain 8.87–28.3 μg/g dry wt total arsenic by Gonul (2015). The main groundwater supply of İzmir City is formed by Gediz Plain (Çolak, 2012). The Gediz River, which flows to the outer part of İzmir, is contaminated by industrial sources, sewage and agricultural runoff (Minareci et al. 2009). Çolak (2012) found that near central Salihli arsenic values were highest (4.7–83 mg/kg) in soil due to the operation of a tannery. Geothermal groundwater in İzmir has concentration of arsenic between 0.7 and 170 mg/L (Aksoy et al., 2009).

1.6 Applications of Arsenic

Arsenic is used since ancient times. Greek, Chinese, and Egyptian people mined compounds of arsenic (Mohan and Pittman, 2007). Arsenic has been used in mining of precious metals, manufacturing of pharmaceutical, processing of wood, industry of glassmaking and electronics, chemical weapons, etc (Han et al., 2003; Köhler et al., 2001).

Compounds of arsenic have often been used in agriculture. Especially, sodium arsenite was used until 2001. It used to utilize as fungicide to protect grapevines against excoriosis (Grillet et al., 2004). Arsenic rich fossil fuel is used but it causes to emit arsenic oxide (Cullen and Reimer, 1989). Arsenic is also used in the hide tanning process and, to a limited extent, in pesticides, feed additives and pharmaceuticals. Smoking tobacco can increase intake of natural inorganic arsenic content from tobacco. Tobacco plants take the arsenic from naturally present in the soil (WHO, 2011).

In China and India, traditional medicines which include metals such as As, Hg, and Pb are used (Cooper et al., 2007; Kumar et al., 2006; Liu et al., 2008; Saper et al., 2008). The arsenical minerals orpiment, realgar, and arsenolite (essentially arsenic trioxide) are present in Chinese traditional medicines to heal heat stroke, dizziness, headache, and nausea (Liu et al., 2008).

Arsenic has had use in dentistry to lighten dental pain and for root canal therapy (Hyson, 2007). At the end of 1800s arsenic usage in dentistry decreased. Nevertheless, the use of arsenicum album (diluted arsenic trioxide) for the treatment of tooth ache is still suggested in homeopathic dentistry (Wander, 2010).

One of the arsenic uses is treatment of acute promyelocytic leukemia. Even though the treatment with arsenic trioxide decreased in China between 1950 and 1960, it reemerged in 1970s. At the end of the 1990s the United States started to use it as an anti-leukemia agent. The Food and Drug Administration approved of the use of arsenic trioxide for treatment of refractive acute promyelocytic leukemia in 2001 (Westervelt et al., 2001).

Majority of herbicides and pesticides had arsenic in the past. People have been exposed to arsenic in high level via transporting, applying, working around these products. The United States prohibited pesticides which contain compounds of inorganic arsenic in 1993. However, usage of pesticides containing organic compounds (with one exception used on cotton plants) is reduced gradually since 2013. Arsenic still treats people work in places where using arsenic in copper or lead smelting and wood treating. Regulations in place can reduce this workplace exposure (WHO, 2011; American Cancer Society, 2014).

1.7 Determination Methods for Arsenic

Various methods have been developed to determine arsenic species in biological and environmental samples including water, plant, sea food, rice, blood, saliva, nail and, hair (Chen et al., 2014). Majority provide limits of detection below 10 μg/L which of the WHO arsenic quideline value. The plenty of arsenic species exist in the environment and they affect metabolism of living organisms in an extensive manner and show toxicity. On account of this, speciation studies have a vital importance. Highly sensitive methods are needed for reliable measurements because of the arsenic species exist at very low concentrations (Burguera and Burguera, 1997).

Vast variety of instrumental methods has been used for total arsenic, organic and inorganic arsenic species determination in biological and environmental samples.

The arsenomolybdenum blue method is a colorimetric method, based on the reaction between arsenic(V) and ammonium molibdate result a colourless molybdoarsenic heteropolyacid. Molybdoarsenic heteropolyacid is reduced using tin(II) chloride to arsenomolybdenum blue. Then, the absorbance is measured at 730 nm. Methods based on ion associates of molybdoarsenate with basic dyes are more sensitive (Matsubara et al., 1987). Interference of phosphates and silicates hinders the method. The silver diethyldithiocarbamate method is a popular spectrophotometric arsenic determination method. According to the method, arsine (AsH_3) is formed either by sodium borohydride in acidic solutions or reaction between zinc and hydrochloric acid. The formed arsine is sent into diethyldithiocarbamate solution in pyridine or pyridine/chloroform. Measurement of the red colored complex is occured at 520 nm. The method is selective for arsenite. The silver diethyldithiocarbamate method is mainly used for arsenic determination in water samples (Goessler and Kuehnelt, 2002). However, colorimetric methods do not give results at trace level (Burguera and Burguera, 1997).

Several electrochemical methods are available for trace arsenic determination. Majority suffers from matrix interferences. Direct-current polarography is able to determine arsenite at concentrations above 0.7 mg/L. The detection limit for arsenite of differential pulse polarography is about 20 µg/L (Greschonig and Irgolic, 1992).

The widespread used methods in the literature are graphite furnace atomic absorption spectrometry (GF AAS) for inorganic As determination in fish and seafood (Zmozinski et. al., 2015), hydride generation atomic absorption spectrometry (HG AAS) (Çiftçi and Henden, 2015), hydride generation coupled to atomic fluorescence spectrometry (HG-AFS) for determination of arsenic in real water samples (Zou et al., 2016), inductively coupled plasma optical emission spectrometry (ICP-OES) for inorganic arsenic in real water samples (Chen et al., 2009), HPLC-ICP-MS for analysis of As metabolites in human cancer cell (Stice et al., 2016), anodic stripping chronopotentiometry (ASCP) for inorganic As species in water samples (Jedryczko et al., 2016), X-ray fluorescence (XRF) spectrometry (Hagiwara et. al., 2015).

Hydride generation (HG) is the most preferred technique for trace arsenic determination. Fundamental of the method is formation of volatile arsines either by sodium borohydride/acid mixtures or zinc/hydrochloric acid. An inert gas flushes through the volatile arsines to the detection system. When the pH of the hydride generation reaction is carefully controlled, differentiation between As(III) and As(V) is possible. At pH 5, only As(III) compounds can be reduced to volatile arsines. At pH<1, arsenic acid, dimethylarsinic acid, and methylarsonic acid also form volatile arsines (Goessler and Kuehnelt, 2002).

1.8 Preconcentration Methods for Arsenic

In environmental samples the most determined species are arsenic(III) and arsenic(V). Species of organic arsenic are generally found in biological tissues and fluids. Most of the present techniques do not have enough sensitivity for detecting arsenic. Thus, it is necessary to preconcentrate arsenic prior to its determination (Burguera and Burguera, 1997). Furthermore, analyte is separated from the majority of the matrix components by preconcentration techniques. Various preconcentration methods have been used for trace arsenic preconcentration such as liquid–liquid extraction (LLE) (Kanke et al., 1991), cloud point extraction (CPE) (Li et al., 2015), solid phase extraction (SPE) (Erdoğan et al., 2011), liquid phase microextraction (LPME) (Jiang et al., 2009), precipitation and coprecipitation (Zhang et al., 2001).

Dispersive liquid liquid microextraction (DLLME) was associated with electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). The developed technique was simultaneously carried out speciation of inorganic arsenic, tellurium, and selenium. Sodium diethyldithiocarbamate (DDTC) was utilized to be both chelating reagent and chemical modifier (Liu et al., 2015). The limits of detection was 2.5 ng/L for As(III). The enrichment factor was found to be 61. Speciation of inorganic arsenic, tellurium, and selenium was simultaneously occurred in various water samples including lake, river, and well water.

Zhang et al. (2004) determined trace As(III) and As(V) in water samples by adding Ni–ammonium pyrrolidine dithiocarbamate (APDC) complex at the pH range of 2–3. At the studied pH range As(III) was the only species which coprecipitated. The obtained coprecipitates were directly measured by electrothermal atomic absorption spectrometry (ETAAS) using the solid sampling technique. The concentration factor was obtained as 40,000 after coprecipitation procedure when carrier element (nickel) and volume of the water sample was selected as 2 mg and 500 ml, respectively. The detection limit was 0.02 ng/mL in the method.

Castor et al. (2016) was developed preconcentration method for arsenic determination in corn and rice samples. The main concept behind the method was arsenic preconcentration by cloud point extraction (CPE) using o,o-diethyldithiophosphate (DDTP) complex, which was generated from an in vitro extract using polyethylene glycol tert-octylphenyl ether (Triton X-114) as a surfactant. Hydride generation atomic fluorescence spectrometer was used for determination. A multivariate approach was used for optimization of cloud point extraction method. The limits of detection were 1.34 µg/kg and 1.90 µg/kg for rice ans corn samples, respectively. The preconcentration factors were calculated as 15.4 for rice and 10.9 for corn sample.

1.8.1 Adsorbents used for arsenic preconcentration

The most commonly used technique for preconcentration is the sorption which collected analyte on solid materials. Analyte is eluted from the solid by using appropriate inorganic acids or organic solvents. Afterwards, determination of the preconcentrated analyte is carried out by a suitable technique.

In order to reach highest preconcentration factor, the highest sample volume and the lowest volume of eluent should be selected. Solid phase extraction has many advantages over other separation techniques such as low usage of solvent, reducing extraction times, low disposal costs, increasing efficiency, elimination of some of the glassware, separating of analytes from large volumes of sample with minimal or zero evaporation losses, reduced exposure of analysts to organic solvents, more reproducible results (Türker, 2007).

The retention mechanism of analytes on solid phases is related to the nature of the solid phase and the species to be retained. The process is generally based on metal adsorption at the sorbent surface by aid of interactions with functional groups, exchange of ions, chelation and ion-pair formation processes. It is affected by the experimental conditions including temperature, pH and concentrations of metal ion. During the sorption process, the equilibrium is established between the species adsorbed on the surface of sorbent and the species remaining in the solution. The mass of species accumulated on the sorbent usually increases up to a value of sorption capacity of a sorbent, with increasing the concentration of species in the solution and reaches a plateau. The sorption capacity is defined as the maximal amount of species adsorbed per unit mass of sorbent (Türker, 2012). The material to prepare is expected to have good performance, showing high resistance to acids and bases, selectivity for analytes, large surface area and high capacity of adsorption (Samuels et al., 2010). The frequently used adsorbents are activated carbons, activated alumina, ion exchange resins, clay minerals, metal oxides, wastes, biomaterials, and their modified forms for preconcentration purposes (Ungureanu et al., 2015).

Kubota et al. (1998) was preconcentrated arsenic(V) on activated carbon as molybdoarsenate 200 fold. For the detection of arsenic, graphite furnace atomic absorption spectrometry was used. The adsorption was occurred in the range of pH 1-3. The detection limit of the method was 0.02 µg/L. The method was applied to well and sea water.

Zhang et al. (2005) used titanium dioxide to preconcentrate arsenic, selenium, and antimony. The species were detected by graphite furnace atomic absorption spectrometry. The detection limit was 0.21 µg/L. The factor of enrichment was found to be 20. Real water samples (tap and river) were analysized by the developed method.

Dimercaptosuccinic acid chemically modifying mesoporous titanium dioxide was prepared as a packing material for micro-column for the determination of inorganic arsenic and antimony species by Huang et al. (2007). Flow injection on-line microcolumn separation/preconcentration coupled to inductively coupled plasma optical emission spectrometry was used. 0.5 mol/L was selected for desorption. The preconcentration of arsenic took for four minutes and enrichment factor was 10. The detection limit for As(III) was found as 0.53 ng/mL and 0.11 ng/mL for online and offline mode, respectively. The method gave good results for determination of arsenic in pond, lake and ancient well water.

Cetyltrimethylammonium bromide (CTAB)-modified alkyl silica sorbent in the absence of chelating reagent was developed for the preconcentration and determination of inorganic arsenic and selenium species by Xiong et al. (2008). Inductively coupled plasma-optical emission spectrometer was used for determination of the species. It was observed that, As(V) was adsorbed quantitatively when pH above 6 while As(III) was not adsorbed in the all studied pH range. Nitric acid was selected for desorption of the species from the sorbent. The limit of detection and the enrichment factor were 0.15 µg/L and 26.7 for As(V), respectively. The method was applied to the determination of trace and total arsenic/selenium in natural water samples such as river water, lake water, well water, rain water, pool water and tap water.

Separation and preconcentration of inorganic arsenic were carried out by using 3-(2-aminoethylamino) propyltrimethoxysilane modified ordered mesoporous silica micro-column (Chen et al., 2009). Inorganic arsenic species in natural water samples were determined by inductively coupled plasma optical emission spectrometry. 1 mol/L hydrochloric acid was selectes as eluent. Enrichment factor was 100. The detection limit for As(V) was 0.05 µg/L. The adsorption capacity was found to be 10.3 mg/g. The method was applied lake and well water.

Zhang et al. (2010) developed egg shell membrane as SPE adsorbents for enrichment of arsenic(V) from water samples. The off-line SPE followed by HGAFS method were used for detecting arsenic in samples. Elution of adsorbed As(V) on egg shell membrane was occurred by using 2 mol/L nitric acid. The preconcentration factor (PF) and the adsorption capacity was found to be 33.3 and 3.9 µg/g for arsenic(V). The developed adsorbent was successfully applied to various aqueous environmental water samples.

Aluminium hydroxide gel was used to enrich and separate trace total inorganic arsenic from environmental water by Deng et al., (2013). Adsorption of arsenic species on aluminium hydroxide gel was completed in 10 minutes. After dissolution of the sorbent in concentrated hydrochloric acid, hydride generation atomic fluorescence spectrometer was used for the determination of arsenic. The enrichment factor was calculated as 167. The limit of detection was 3 ng/L.

Natural clay minerals were also used for arsenic preconcentration as an adsorbent. Anjos et al. (2014) were used montmorillonite and vermiculite for arsenic(V) preconcentration. Determination of arsenic was carried out by inductively coupled plasma optical emission spectroscopy (ICP OES). Arsenic desorption was carried out by nitric acid. Extracted arsenic concentrations of untreated and modified clay minerals were 6.7 and 1.8 µg/g, respectively.

For preconcentration of silver, aluminium, arsenic and chromium before their inductively coupled plasma-optical emission spectroscopy determination a dual-bed resin solid phase extraction (SPE) was developed by Nomngongo and Ngila (2015). Dowex 50 W-x8 and Dowex 1-x8 were packed in the same column and used as a sorbent. The obtained enrichment factor was 130. The limit of detection was calculated as 0.18 μg/L. The developed procedure was used in silver, aluminium, arsenic and chromium determination in ten real gasoline samples.

1.8.2 Preconcentration of arsenic with nanoparticles

1.8.2.1 Nanoparticles

Nanoparticles are the particles that a size less than 100 nm in at least one dimension. This size provides particles unique features because surface to volume ratio increase (Jiang et al., 2012). For comparison, width of a single human hair, a red blood cell and a water molecule is nearly 80,000 nm, 7,000 nm and 0.3nm, respectively. As a particle size diminishes, number of atoms on the surface increases. For instance, a particle of size 30 nm has 5% of its atoms on its surface, at 10 nm 20% of its atoms, and at 3 nm 50% of its atoms. Therefore, surface area per unit mass of nanoparticles is greater than larger particles (The Royal Society, 2004).

Having large specific surface area provides nanoparticles a number of unique applications. High surface area/volume ratio and the homogenous distribution of nanoparticles improve catalysis and give strong interactions between the nanoparticles and the solid matrix in which they may be incorporated. Also, particle size and surface functionalization of nanoparticles affects the absorption and/or emission wavelengths, hence nanoparticles show interesting optical features. Moreover, getting smaller size of nanoparticles, decrease the temperature of sintering and melting. Some metals and metal oxides display magnetic behavior in comparison with bulk states (Nagarajan and Hatton, 2008; Pyrzynska, 2013; Türker, 2007).

Nanoparticles can be prepared using physical and chemical methods. Conversely, preparation procedure can be categorized into three basic groups as liquid, gas and solid phase procedures. The gas phase procedure contains gas phase evaporation procedure (resistance heating, laser heating, high frequency induction heating, plasma heating, electric heating evaporation method, electron beam heating, vacuum deposition), chemical vapor reaction (plasma enhanced chemical vapor reaction, laser induced chemical vapor reaction), sputtering method and chemical vapor deposition. The advantage of gas phase method is low contamination. Temperature, evaporation rate and gas environment control the particle size. Liquid phase methods consist of hydrolysis, precipitation, spray, solvent thermal method (high temperature and pressure), emulsion, solvent evaporation pyrolysis, oxidation-reduction (room pressure), sol-gel processing, and radiation chemical synthesis. These methods are superior to gas phase methods for controlling the shape of nanoparticles. Solid phase methods comprise stripping and milling, spark discharge, thermal decomposition, and solid state reactions (Wang and Hong, 2011; Kaur and Gupta; 2009).

The most encountered nanoparticles are categorized into metallic, silica, and carbon based.

Metallic nanoparticles:

Metal oxides (TiO_2, Al_2O_3, ZrO_2, CeO_2 and MnO, e.g.) have unique features (easy modification, large specific surface area, and high adsorption capacity). Their adsorption depends on shape, crystal structure and surface area (Pyrzynska, 2013; Acebal et al., 2013).

Silica Nanoparticles:

Silica nanoparticles offer cheap, chemically inert and thermally stable adsorbent material. Their selectivity towards analytes is improved by modifications of the silanol groups on the surfaces of silica nanoparticles with functional groups containing some donor atoms (phosphorus, sulfur, oxygen and nitrogen) (Pyrzynska, 2013; Acebal et al., 2013).

Carbon based nanoparticles:

Carbon based nanoparticles include fullerenes, carbon nanotubes, and carbon nanofibers. Fullerenes are closed-cage carbon molecules where the carbon atoms arranged in pentagonal and hexagonal rings. Fullerens shows the lowest tendency to aggregate compared to other carbon based nanoparticles.

Carbon nanotubes are formed by graphene sheets rolled into cylinder shape (Garcia-Calzón and Diaz-Garcia, 2012). Specific surface and area π-π electrostatic interactions make them attractive in adsorption studies (Valcárcel et al., 2008). Multiwalled carbon nanotubes are preferred to single wall carbon nanotubes, because it proves better interactions with analyte (Valcárcel et al., 2007).

Carbon nanofibers have same chemical and mechanical features with carbon nanotubes, however they do not posses hollow cavity and are larger in the size of diameter (El-Sheikh et al., 2012).

Nanoparticles are employed in many applications, such as catalysts, as metallurgy, in health care and fitness, in electronics, electronics and computers, home and garden, automotive, food and beverage, products for children, etc (Nagarahan and Hatton, 2008). Examples of present and potential applications of nanoparticles are shown in Table 1.1.

Table 1.1 Examples of present and potential applications of nanoparticles (Nagarahan and Hatton, 2008).

Biomedicine	Antibacterial creams and powders (Ag) Bone growth promoters (hydroxyapatite ceramics) Dental composites Biosensors (metal oxide, polymer nanoparticles, CNT)
Consumer goods and personal care products	Anti-bleaching, sctratch resistance additives in paints Glass coatings for anti-glare, anti-misting mirrors (TiO_2) Sunscreens (ZnO, TiO_2) Tennis balls, rackets (nanoclays, carbon nanotubes)
Electronics	Electronic circuits (Cu, Al) Coatings and joining materials for optical fibers (Si)
Environmental	Controlled delivery of herbicides and pesticides Self cleaning glass (TiO_2 based coatings) Water treatment (photo- catalyst treatments, TiO_2)
Food	Food pathogen sensing Food packaging materials (nanoclays, SiO_2, TiO_2, Ag)

1.8.2.2 Nanoparticles used for arsenic preconcentration

Nanoparticles present various benefits compared to the frequently used sorbents for the separation/preconcentration of trace metals; high chemical activities, high adsorption capacities, prominent adsorption speed and mechanical and chemical stability (Türker, 2007). The features mentioned above makes nanoparticles attractive sorbent materials for preconcentration (Kaur and Gupta, 2009).

In the literature it is easy to find a great number of works related to arsenic preconcentration and arsenic removal by using nanoparticles. Some of them are mentioned below.

Nano zirconium dioxide–boron oxide (ZrO_2/B_2O_3) was prepared by Erdoğan et al. (2011). The particle size of the ZrO_2/B_2O_3 is below 100 nm. Inorganic arsenic species in water samples are speciated and determined by HGAAS. The nano sorbent could preconcentrate arsenic species 20 fold. Desorption was occurred using 3 mol/L HCl. The analytical detection limit was 9.25 ng/L. Capacity of adsorption for As(V) was found as 98.04 mg/g. The stability of the prepared sorbent was high (100 cycles). Between pH 2.0 and 3.0 As(V) was adsorbed quantitatively while the lower recovery (below 5%) was obtained for As(III). One of the advantages of the sorbent was allowing to study in the acidic media.

Tavakkoli et al. (2014) developed a method based on the solid phase extraction of the As(III)-sodium diethyldithiocarbamate (As-NaDDTC) chelate on multi-walled carbon nanotubes (MWCNTs). For arsenic determination, GFAAS was used. The detection limit of the procedure was found as 0.008 ng/mL with enrichment factor of 125. The capacity of adsorption of MWCNTs for As(III) was 79.8 mg/g. The column can be reused up to at least 20 cycles of adsorption-elution. The sorbent was selective for arsenic and can be used in various samples. This procedure was carried out for separating and determining of As(III) in rice straw and its ash, drinking water, mineral water and well water samples.

A silica-coated magnetic nanoparticles (SCMNPs) was modified with AAPTS (3-(2-Aminoethylaminopropyltrimethoxysilane) and utilized to enrich As(V) 300 fold by Huang et al. (2011). TEM results represented that the average diameter of the sorbent was 70–90 nm. In the pH range between 3 and 8, As(V) adsorbed on amino-modified silica-coated magnetic nanoparticles while As(III) did not adsorb. Tolerance limit of ions for potential interferences are greater than those typically found in environmental water samples. The detection limit is 0.21 ng/L. Adsorption capacity for As(V) was 13.1 mg/g.

Studies about preconcentration and removal of metal ions by nanoparticles in the literature are listed in Table 1.2.

Table 1.2 Preconcentration and removal of metal ions by nanoparticles.

Nanoparticles	Reagent	Analyt	Sorption Efficiency (%)	Capacity (mg/g)	Preconcentration factor	Ref.
Dithizone modified Silica-coated magnetic Fe_3O_4	Dithizone	Cr(III) Cu(II) Pb(II) Zn(II)	~100	20.7 20.5 60.9 15.4	100	Cheng et al., 2012
Magnetic ɤ-Fe_2O_3 nanoparticles coated with poly-L-cysteine	L-Cysteine	As(III) Cd(II) Cu(II) Ni(II) Pb(II) Zn(II)	~100	-	-	White et al., 2009
DTC-Fe_3O_4	Dithio carbamate	Hg(II)	~100	112	-	Figueira et al., 2011
Silica coated magnetite	Dithio carbamate	Hg(II)	74	25.10-3	-	Girginova et al., 2010
ZrO_2/B_2O_3		Co(II) Cu(II) Cd(II)	~100	32.2 46.5 109.9	10 10 15	Yalçınkaya et al., 2011
B_2O_3/TiO_2		Cd(II)	~100	49	100	Kalfa et al., 2009
Cupric oxide (CuO)		As(III) As(V)	90 99	26.9 22.6	-	Martinson and Reddy, 2009
TICB (TiO_2-impregnated chitosan bead)		As(III) As(V)	>97 >67	2.10 2.05	-	Miller and Zimmerman, 2010
TICB with UV irradiation (TiO_2-impregnated chitosan bead)		As(III) As(V)	- -	3.54 2.99	-	Miller and Zimmerman, 2010
Nickel coated resin		As(III) As(V)	98.9 98.7	23.4 17.8	-	Çiftçi and Henden,2015
Zero Valent Iron (ZVI)		As(III) As(V)	~100	18.2 12.0	-	Zhu et al., 2009

Nodeh et al. (2016) synthesized silica-coated magnetic nanoparticles modificated graphene oxide ($Fe_3O_4@SiO_2/GO$) and then, applied to magnetic solid-phase extraction to enrich As(III) and As(V) as 23 fold. ICP-MS was used for determination of arsenic. TEM image indicated that the size of $Fe_3O_4@SiO_2$ nanoparticles, where the core (Fe_3O_4) size were approximately in the range of 7-15 nm and the size of the shell (SiO_2) was approximately 3 nm. At pH 4.0 maximum adsorption capacities were 7.51 and 11.46 mg/g for As(III) and As(V), respectively. Preconcentration of arsenite and arsenate were carried out using magnetic solid-phase extraction (MSPE) method. The method was studies at pH 9.0. The limits of detection for As(III) and As(V) were 7.9 pg/mL and 28.0 pg/mL, respectively.

Carboxylic graphene oxide (GO-COOH) is modified by akaganeite (β-FeOOH) and, thus β-FeOOH@GO-COOH nanocomposite was prepared obtained. Atomic fluorescence spectrometer is employed for arsenic determination. The nanocomposite adsorbed As(III) and As(V) in pH the range between 3 and 10, giving high adsorption capacities of 77.5 mg/g for As(III) and 45.7 mg/g for As(V), respectively. The detection limit for arsenate was 29 ng/L. No apparent interference is observed in the presence of 10,000-fold excess of Fe^{3+}, Al^{3+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and Ag^{+}. Therefore, the developed method can be directly applied for the preconcentration and determination of As(V) (Chen et al., 2015).

Diverse biological materials including microorganisms, fungi, bacteria, algae, yeast, etc. have been used on biosorption studies. Streptococcuspyogenes is found in the throat and nose of asymptomatic individuals rather than in the respiratory tract. S. pyogenes is one of the most frequent pathogens of humans. As normal flora, S. pyogenes can infect when defenses are compromised or when the organisms are able to penetrate the constitutive defenses. When the bacteria are introduced or transmitted to vulnerable tissues, a variety of types of suppurative infections can occur Streptococcus pyogenes modified on Sepabeads SP 70 resin was prepared as a biosorbent for solid phase extraction method. The arsenic determination was carried out by HGAAS. Arsenic(III) was adsorbed quantitatively on the sorbent in pH values between 6.0 and 7.0 while As(V) did not adsorbed in the pH range 2-9. The capacity of the biosorbent was 7.3 mg/g for arsenic(III). The preconcentration factor and limit of detection were 36 and 13 ng/L, respectively. The biosorbent was not influenced by the matrix ions which found in high levels in the solution (Uluozlu et al., 2010).

It is known that signals from the hydride-forming elements are suppressed by the transition metal ions, especially Ni, in the determination step when hydride generation atomic spectroscopy is used. It has been thought in the last 40 years black particles formed during the reaction of nickel(II) with sodium borohydride sorbs or decompose the AsH_3 and the other volatile analyte hydrides during their determination with the HGAAS. However, Henden et al. (2011) clarified that the particles obtained after reducing nickel(II) with sodium borohydride sorbed arsenic ions. Contrary to the popular belief that arsine is not adsorbed or decomposed by these particles. It was also found that the black particles were composed of nickel and nickel boride nanoparticles.

According to Glaave et al. (1994) under inert conditions reactions of Ni(II) and $NaBH_4$ formed Ni_2B and trace amount of metallic nickel. However, the same reactions gave metallic nickel under ambient conditions. Also, nickel gave Ni_2B in aqueous media, but Ni(s), Ni_2B, and Ni_3B in nonaqueous media. In the presence of air, products were also mixture of metal and metal oxides.

Reaction of Ni(II)(aq) and BH_4^- (aq) in water;

$$2Ni^{2+}\ (aq) + 4BH_4^- + 9H_2O \rightarrow Ni_2B + 12.5H_2 + 3B(OH)_3\ (+NaCl)$$

$$Ni_2B + 3O_2 \rightarrow 8Ni + 3B_2O_3$$

$$B_2O_3 + 2H_2O \rightarrow 2B(OH)_3$$

Water could convert the B_2O_3 to boric acid (6.35 g/100mL water) which can be separated by water washing (Glaave et al., 1992).

Wang and Bartholomew (1988) reported that metal borides prepared with $NaBH_4$ contain prominent Na^+ impurities (Glaave et al., 1992).

Çiftçi and Henden (2015) have used nano Ni/Ni_xB-coated resin for arsenic removal from water by using column. Arsenic adsorption capacities were found to be 23.4 mg/g and 17.8 mg/g for As(III) and As(V), respectively.

İşlek Coşkun et al. (2016) have synthesized Ni/Ni_xB nanosorbent by using nickel nitrate salt for the preconcentration of As(III) and As(V) under ambient air. HGAAS was used for determination of arsenic. It was found that the adsorption efficiencies were above 99% in the pH range of 4-10. Adsorption rate was fairly high, in the first 10 min adsorption efficiencies reached 95%. 2 mol/L HCl was used in order to recover adsorbed As(III) and As(V) from the sorbent. The adsorption efficiencies were not affected in the presence of 100-fold excess interferencing ions (Cd^{2+}, Cu^{2+}, Mg^{2+}, Zn^{2+}, K^{+}, SiO_4^{4-}, SO_4^{2-}, and PO_4^{3-}). The adsorption capacity was found 2.19 g As(III)/g sorbent in the batch studies and 2.5 g As(III)/g sorbentin the isotherm studies. It was found the adsorption efficiencies were not affected up to 250 mL sample volume. Repeatability of the method was studied applying the preconcentration procedure. After preconcentrating 10 times, the relative standard deviation was found as 3.4% (n=7), with the continuous flow method. Characterization studies of Ni/Ni_xB were carried out by SEM, EDX, XRD, XPS, TGA, and elemental analysis. The structure of the adsorbent was suggested as Ni_xB and Ni(0), and also $Ni(OH)_2$ possibly formed on the particles surface (Henden et al., 2011).

1.9 Aim of This Study

As we know it today, it is the first time, Ni/Ni_xB nanoparticles have been used for arsenic preconcentration by our group. Accordingly, the purpose of this study was to investigate the effect of varios nickel salts on preconcentration procedure for trace arsenic determination in water using Ni/Ni_xB nanoparticles as a sorbent and prepare an oxidation resistant sorbent.

Additionally, various nickel salts effects on the arsenic sorption efficiencies and capacities were studied. The amounts of ions released during arsenic sorption were examined. The chemical analyses of the prepared sorbents were investigated. The sorption models were also executed. The procedure was also applied to bottled water, tap water, and various mineral water samples.

2. EXPERIMENTAL

2.1 Apparatus and Operating Conditions

A GBC 904 PBT model atomic absorption spectrometer was used. A quartz tube atomizer, a laboratory made batch type hydride generation system and the HG 3000 automatic continuous flow hydride generator were employed. Nüve water bath shaker equipped with a thermostat was used for sorption studies. Mettler Toledo Five Go FG-2 pH meter was carried out for pH measurements. pH meter was calibrated against buffer pH 4 and pH 7 before every measurements. Nüve NF 800 Centrifuge was used in order to separate sorbent and supernatant at 3500 rpm for 5 min.

In automated system, the acidified sample, blank, or standard, is continuously pumped and mixed with a pumped stream of sodium borohydride, to produce the gaseous hydrides. A flow of nitrogen is added to this mixture and the hydrides are stripped into the gas phase. A gas/liquid separator allows the gaseous, hydride containing phase, to enter the quartz tube atomizer in air-acetylene flame, and allows the remaining liquids to be pumped to waste. The flow chart of automated system is shown in Figure 2.1.

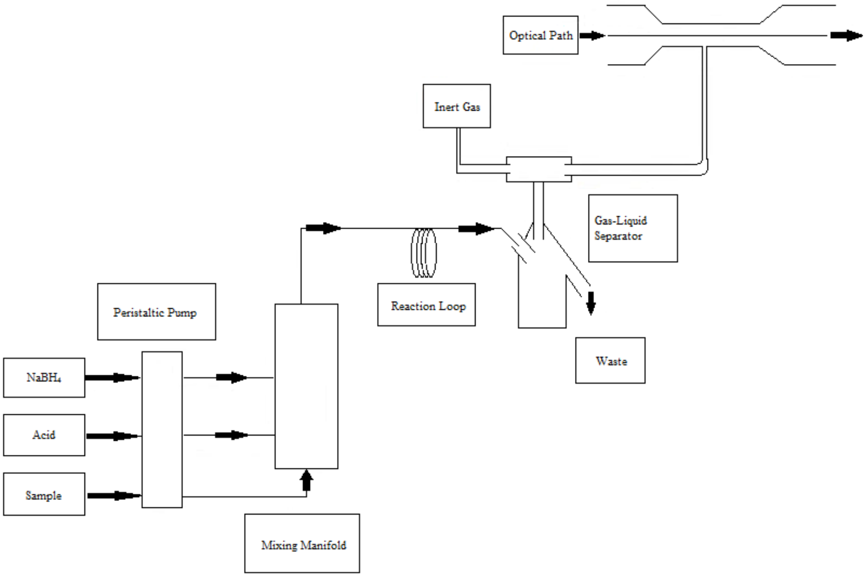


Figure 2.1. Automated hydride generation atomic absorption spectrometer.

The experimental conditions for batch type and automated hydride generation AAS system are listed in Table 2.1.

Table 2.1 Operating parameters for instrumental measurement by HG-AAS for determination of arsenic.

	Batch Type	Automated Type
Element	As	As
Matrix (mol/L HCl)	0.1	1.7
Lamp Current(mA)	8.0	8.0
Wavelenght(nm)	193.7	193.7
Slit Width(nm)	1.0	1.0
Slit Height	Normal	Normal
Instrument Mode	Absorbance BC on	Absorbance BC on
Sampling Mode	Manuel Sampling	Pump Sampling
Flame Type	Air-Acetylene	Air-Acetylene
Acetylene Flow(L/min)	1.59	1.59
Air Flow(L/min)	10.6	10.6
Read Time(s)	60	10
Measuring Mode	Peak Area	Peak Area
Carrier Gas	Nitrogen	Nitrogen

Sorption effeciencies in arsenic measurements, effect of KI and citric acid on elimination of Ni(II) interference on arsenic determination, sorption isotherm models, limit of detection and limit of quantification and application to real samples studies were carried out by automated hydride generation AAS system, while in arsenic capacities studies, batch type AAS system was used.

2.2 Reagents

All reagents and chemicals were analytical grade. Glassware was cleaned by soaking them in dilute nitric acid (10%) (v/v) and rinsed with distilled water prior to use.

Arsenite [As(III)] Stock Standard Solution (1000.0 µg/mL): Prepared by dissolving 0.3301 g As_2O_3 (Merck) in concentrated HCl (Merck). It is diluted to 250 mL with distilled water. Final acid concentration of stock solution was 2 mol/L.

Arsenate [As(V)] Stock Standard Solution (1000.0 µg/mL): Prepared by dissolving 1.04 g $Na_2HAsO_4.7H_2O$ (Merck) in concentrated HCl (Merck). It is diluted to 250 mL with distilled water. Final acid concentration of stock solution was 2 mol/L.

Standard Arsenite [As(III)] Solution (I) (10 µg/mL): Prepared by diluting 1 mL arsenite stock solution and making up 100 ml with distilled water.

Standard Arsenate [As(V)] Solution (I) (10 µg/mL): Prepared by diluting 1 mL arsenate stock solution and making up 100 ml with distilled water.

Standard Arsenite [As(III)] Solution (II) (0.5 µg/mL): Prepared by diluting 5 mL standard arsenite solution (I) and making up 100 ml with distilled water.

Standard Arsenate [As(V)] Solution (II) (0.5 µg/mL): Prepared by diluting 5 mL standard arsenate solution (I) and making up 100 ml with distilled water.

Working [As(III)] and [As(V)] Standards (2.5 / 5.0 / 10.0 / 20.0 µg/L): Standard arsenic solutions were prepared by appropriate dilution of the standard solutions I or II.

Ni(II) solution (25%) (w/v): Prepared by dissolving adequate amount of $Ni(NO_3)_2.6H_2O$ (Carlo Erba), $NiCl_2.6H_2O$ (Merck), $NiSO_4.7H_2O$ (Merck) in distilled water and adjusting the final acidity to 1 mol/L with HCl and completing the volume to 100 mL.

2.5% (v/v) of Ni(II) solutions were prepared by diluting apropriate volume of 25% Ni(II) solution with distilled water.

Automated system solutions:

Sodium tetrahydroborate(III) Solution (0.6% in 0.6% NaOH) (w/v): 1.0 g sodium tetrahydroborate(III) (Merck) and 1.0 g sodium hydroxide (Merck) dissolved in 166 mL distilled water.

HCl for carrier solution (10.2 mol/L): Prepared by diluting appropriate volume of concentrated HCl (Merck).

2.3 Procedure of Arsenic Determination

Since arsine formation efficiency from As(V) is low, for the determination of As(V), it was reduced to As(III) before reduction with $NaBH_4$. In order to reduce As(V) to As(III), 1 mL of concentrated HCl, 2 mL of 50% KI and appropriate amount of ascorbic acid (to reduce I_2 formed) were added on to 9 mL of arsenic solution. Final KI concentration was 8.3%. Prereduction time used was 15 min.

Because of the possibility of As(III) oxidation in the solutions to As(V) during various treatments, for total arsenic determination, pre–reduction with KI was always done before hydride generation with $NaBH_4$.

2.4 Preparation of Ni/Ni_xB Nanoparticles Under Nitrogen Atmosphere

A 250 mL polyethylene bottle with three holes on the lid was used as the reaction vessel. Two of the holes were for nitrogen gas inlet and $NaBH_4$ solution flow, separately, and the last one was for gas outlet. First, 2.5% (w/v) of Ni(II) (25 mL) in 0.2 mol/L HCl was added to the bottle. Afterwards, nitrogen gas was passed while nickel solution was stirred on a magnetic stirrer. Then, 25 mL of 4% (w/v) sodiumborohydride solution was added dropwise from a burette for nine minutes. After the first drop of $NaBH_4$, the black precipitate formed. Particles were separated by ultracentrifugation. Particles were then washed and centrifuged at 3500 rpm for 10 min at least three times with 20 mL portions of distilled water. In order to remove water. The same washing procedure was repeated using acetone. Drying process of the synthesized particles was realized in a water bath at 75°C for two hours under nitrogen atmosphere.

3. RESULTS AND DISCUSSION

3.1 Preparation of Ni/Ni_xB by Various Nickel Salts

In previous studies, it was seen that the colour of the sorbent was turned to grey-green by time. After sorption process when the sorbent was prepared using $Ni(NO_3)_2.6H_2O$, the sorbent was all converted to grey-green colour in a few weeks. For preparing oxidation resistant sorbent, various nickel salts were tested. The sorption efficiencies and capacities of newly prepared sorbent were also investigated.

2.5% (w/v) of Ni(II) solutions were prepared by $Ni(NO_3)_2.6H_2O$ (Carlo Erba), $NiCl_2.6H_2O$ (Merck), and $NiSO_4.7H_2O$ (Merck). After reduction with 4% $NaBH_4$ under nitrogen atmosphere, final pH was measured as 8.42, 8.23, 8.25 for the sorbents prepared by nitrate, chloride, and sulfate salts, respectively. The particles were washed and centrifuged for 4 times; three times with 15 mL portions of distilled water, and then 10 mL portion of acetone to remove the remaining water. The water bath at 85^{o}C was used for drying the nanoparticles for 2 hours under N_2 atm. Nanoparticles prepared by $Ni(NO_3)_2.6H_2O$ (Merck) were very fine and diffucult to wash and ultracentrifuge. Appearance of nanoparticles prepared from $NiCl_2.6H_2O$ (Merck) and $NiSO_4.7H_2O$ (Merck) were black leaf-like and black granular, respectively. These nanoparticles appear to be larger than the sorbent prepared by nitrate salts. It was easy to wash these nanoparticles and separate by decantation. All these particles were dried under nitrogen atmosphere.

3.2 Sorption Efficiencies and Arsenic Capacities

To find out sorption efficiencies of the sorbents, 25 mL of 100 ng/mL As(III) and As(V) solutions (pH~ 6) were separately by adding on 10 mg sorbent and shaking for 30 min. After separating sorbent and supernatant, arsenic in the supernatants were determined by HG-AAS.

The capacity experiments were carried out by batch method. 50 mL 500 µg/mL arsenic solution (pH~ 6) was added on 10 mg sorbent in falcon tubes and shaken for 18h. Ultracentrifuge technique was used for separating phases. 5 mL 2 mol/L HCl was utilized in order to dissolve the sorbents. The results were also verified by determining arsenic in the supernatant solutions. The results were summarized in Table 3.1.

Table 3.1 Sorption efficiencies and arsenic capacities of sorbents (10 mg sorbent was used) (n=3).

Nickel salts used for preparation of the sorbent	% Sorption Efficiency		Capacity (g arsenic/g sorbent)	
	As(III)	As(V)	As(III)	As(V)
Nitrate	99.5±0.4	99.9±0.7	1.93±0.04	2.02±0.03
Chloride	99.6±0.9	99.5±0.6	2.01±0.05	1.80±0.06
Sulfate	99.7±0.5	99.9±0.8	2.00±0.12	2.12±0.04

There were no significant differences in the sorption and capacity results among nickel salts used for preparation of the sorbent. On the other hand, the particles prepared by chloride and sulfate salts provide convenience in terms of separation from the solution and thus save time and labour. Moreover, after sorption it was seen that the colour of the sorbent obtained by nitrate salt turned black to green by time while the sorbents obtained by sulfate and chloride salts preserved their original black colour.

The stability of the synthesized sorbents was observed for more than two years. The sorbent prepared using nickel nitrate is converted more easily to grey-green colour in time; this may be due to the nitrate impurities remaining in the sorbent after washing that may oxidize the sorbent, Ni_2B. Whereas, sorbent prepared using nickel sulfate and nickel chloride kept their original dark colour for more than two years.

Therefore, granular like nickel sulfate were used for sorbent preparation in the subsequent/further studies unless otherwise stated.

3.3 Chemical Analysis of Sorbents

10.0 mg of the sorbent were added into beaker for the chemical analysis of the prepared nickel particles and dissolved in 5 mL 2 mol/L HCl for determination of total nickel and boron amount. After several dilutions, Ni(II) concentration was determined by AAS and boron was complexed with Azomethine-H, then determined with a spectrophotometer. The results are shown in Table 3.2.

Table 3.2 Chemical analysis results of 10 mg of sorbent prepared by various nickel salts for nickel and boron (n=3).

Nickel salts used for preparation of the sorbent	Ni(II), mg	Ni(II), mol	B, mg	B, mol	Mol ratio (Ni/B)	
					Ni(II)	B
Nitrate	4.78±0.18	0.081	0.64±0.09	0.059	1.37	1
Chloride	8.42±0.21	0.143	0.41±0.03	0.038	3.74	1
Sulfate	9.25±0.19	0.158	0.62±0.04	0.058	2.74	1

As mentioned by Glaave (1994), particles obtained by synthesis under nitrogen in water primarily consist of Ni_2B. After exposing to air majority turns to metallic nickel. According to mol ratios (nickel/boron) in Table 3.2, the sorbent prepared by nickel nitrate salts may consist of NiB structure, while those prepared by sulphate salts may consist of mainly Ni_2B, and some nickel. The chloride salts may comprise mixture of Ni_2B and metallic Ni.

3.4 The Amount of Ions Released During Sorption

In order to find the amount of nickel and boron released from the sorbents in arsenic containing solutions, 15 mL of 0, 100, 200, 300, and 500 μg/mL As(III) and As(V) were added on 10 mg sorbents and shaken for 18h at 25^oC. pH of the arsenic solutions were adjusted to about 4, by adding dilute NaOH before adding onto the sorbent. After shaking with arsenic containing solutions, all the sorbents were still black, except prepared from $Ni(NO_3)_2.6H_2O$, where the colour of the sorbent turned from black to green. Then, the supernatants were separated by ultracentrifuging. Amount of nickel and boron remained in the supernatants and held by the sorbents were analyzed by AAS and Azomethine-H method, respectively. The results are shown in Table 3.3, 3.4, 3.5, 3.6 and 3.7. According to these results, amount of boron and nickel released from sorbent is independent from arsenic concentration in the solution.

Table 3.3 The amount of nickel remained in the sorbents after arsenic sorption for 18h (n=3).

Nickel salts used for preparation of the sorbent	Nitrate		Chloride		Sulfate	
As concentration(µg/mL)	Ni(II) undissolved, mg		Ni(II) undissolved, mg		Ni(II) undissolved, mg	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
0	2.24±0.24		5.45±0.04		6.97±0.20	
100	3.02±0.32	3.78±0.78	7.77±0.33	6.47±0.32	6.65±0.33	7.12±0.24
200	3.40±0.18	4.55±0.16	6.29±0.43	6.27±0.32	6.27±0.16	6.14±0.21
300	3.32±0.32	2.71±0.15	5.98±0.52	6.87±0.43	6.65±0.31	7.82±0.16
500	3.48±0.23	3.23±0.30	6.36±0.32	5.83±0.11	5.53±0.18	6.98±0.17

*Amount of nickel present in 10 mg unused sorbent are shown in Table 3.2.

Table 3.4 The amount of nickel in the supernatants after arsenic sorption for 18h (n=3).

Nickel salts used for preparation of the sorbent	Nitrate		Chloride		Sulfate	
As concentration(µg/mL)	Ni(II) dissolved, mg		Ni(II) dissolved, mg		Ni(II) dissolved, mg	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
0	2.44±0.16		2.85±0.20		2.16±0.22	
100	1.48±0.20	0.89±0.13	0.13±0.05	1.85±0.16	2.36±0.25	2.10±0.24
200	0.95±0.14	0.12±0.38	1.67±0.13	1.55±0.18	2.22±0.23	1.85±0.14
300	1.11±0.23	1.82±0.16	1.69±0.22	1.47±0.23	1.98±0.19	1.10±0.15
500	0.96±0.20	1.18±0.21	1.19±0.11	2.28±0.20	2.84±0.16	1.94±0.16

Table 3.5 The amount of nickel in 10 mL washing solution after arsenic sorption (n=3).

Nickel salts used for preparation of the sorbent	Nitrate		Chloride		Sulfate	
As concentration(µg/mL)	Ni(II), mg		Ni(II), mg		Ni(II), mg	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
0	0.16±0.03		0.15±0.001		0.15±0.003	
100	0.43±0.02	0.16±0.03	0.62±0.001	0.16±0.05	0.20±0.08	0.082±0.04
200	0.46±0.05	0.16±0.04	0.50±0.08	0.56±0.06	0.68±0.06	0.16±0.07
300	0.44±0.02	0.35±0.03	0.72±0.01	0.15±0.01	0.58±0.01	0.14±0.06
500	0.47±0.10	0.35±0.08	0.78±0.06	0.29±0.08	0.76±0.08	0.20±0.04

Table 3.6 The amount of boron in the supernatants after arsenic sorption for 18h (n=3).

Nickel salts used for preparation of the sorbent	Nitrate		Chloride		Sulfate	
As concentration(µg/mL)	B dissolved, mg		B dissolved, mg		B dissolved, mg	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
0	0.28±0.03		0.07±0.04		0.064±0.001	
100	0.35±0.09	0.36±0.26	0.11±0.09	0.10±0.07	0.13±0.004	0.21±0.01
200	0.35±0.06	0.41±0.13	0.22±0.06	0.14±0.06	0.22±0.02	0.15±0.01
300	0.45±0.12	0.35±0.27	0.22±0.009	0.20±0.05	0.28±0.05	0.20±0.03
500	0.41±0.17	0.58±0.17	0.29±0.04	0.38±0.01	0.37±0.01	0.04±0.05

Table 3.7 The amount of boron remained in the sorbents after arsenic sorption for 18h (n=3).

Nickel salts used for preparation of the sorbent	Nitrate		Chloride		Sulfate	
As concentration(µg/ mL)	B undissolved, mg		B undissolved, mg		B undissolved, mg	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
0	0.17±0.01		0.17±0.03		0.53±0.04	
100	0.18±0.02	0.16±0.03	0.14±0.05	0.28±0.04	0.30±0.04	0.32±0.07
200	0.10±0.05	0.13±0.07	0.06±0.03	0.21±0.05	0.23±0.08	0.27±0.12
300	0.12±0.09	0.12±0.05	0.04±0.08	0.13±0.01	0.17±0.06	0.23±0.03
500	0.13±0.01	0.10±0.10	0.12±0.09	0.10±0.03	0.06±0.04	0.21±0.09

3.5 Effect of KI and KI+7% Citric Acid on Elimination of Ni(II) Interference on Arsenic Determination

It is known that hydride generation technique is suffered from the transition metal interferences (Kirkbright and Taddia, 1978; Welz and Melcher, 1984). Different mechanisms have been suggested for the interference effects observed (Welz and Schubert-Jacobs, 1986; Bax et al., 1988). It is thought that the main interference mechanism is probably due to the reaction between interfering transition metal ions and the $NaBH_4$ reductant, and the precipitate which is formed is able to capture and catalytically decompose the evolved hydrides (Welz and Schubert-Jacobs, 1986). However, Henden et al. (2011) showed that interferences of nickel on arsenic determination are due to the adsorpion of AsO_3^{3-} and AsO_4^{3-} by the black precipitate formed (Ni/Ni_xB) before the arsine formation by the borohydride reduction.

Nickel has a strongly depressing effect on the signal of arsenic and antimony. Pohl and Zyrnicki (2002) reported that at 10 fold greater concentration of Ni(II) than the analyte concentration, arsenic, bismuth, antimony, selenium and tin were already suppressed by one order on average, in comparison to the signals obtained for the solution free from the matrix. In order to eliminate its interfering effect one of the proposed method masking agents have been suggested (Welz and Melcher, 1984). Used complexing agents in the literature were thiocyanate (Welz and Melcher, 1984), acetate and citrate at pH 4 (Aggett and Aspell, 1976), diethylenetriaminepentaacetic acid (DTPA) (Wickstrøm et al., 1995), EDTA (Henden, 1982) and potassium iodide (Yamamoto et al., 1981; Pohl and Zyrnicki, 2002). The forming a complex eliminated the reduction of the interfering metal ions by sodium borohydride (Wickstrøm et al., 1995). Kavas (2010) eliminated the interferences of 400 µg/mL nickel(II) on 15 ng/mL of antimony signals by using mixture of KI and 7% citric acid succesfully.

Ni(II) forms complex with citric acid (pK_a: 2.94, Li et al., 1959) and therefore, its interference on arsenic determination possibly be avoided by masking with citric acid. Bye (1985) reported 1600 µg/mL of nickel(II) interferences on 10 ng/mL selenium were eliminated by citric acid.

Effect of ′′KI′′ and ′′KI+7% citric acid′′ on elimination of Ni(II) interferences was investigated in the presence of 0, 5, 25, 50, 100, 300 and, 500 µg/mL Ni(II) and 10 ng/mL As(III) containing solutions. Calibration graphs obtained in the presence and absence of Ni(II) are shown in Figure 3.1. Deviation in the arsenic concentrations measured for 10 ng/mL As(III) are shown in Table 3.8.

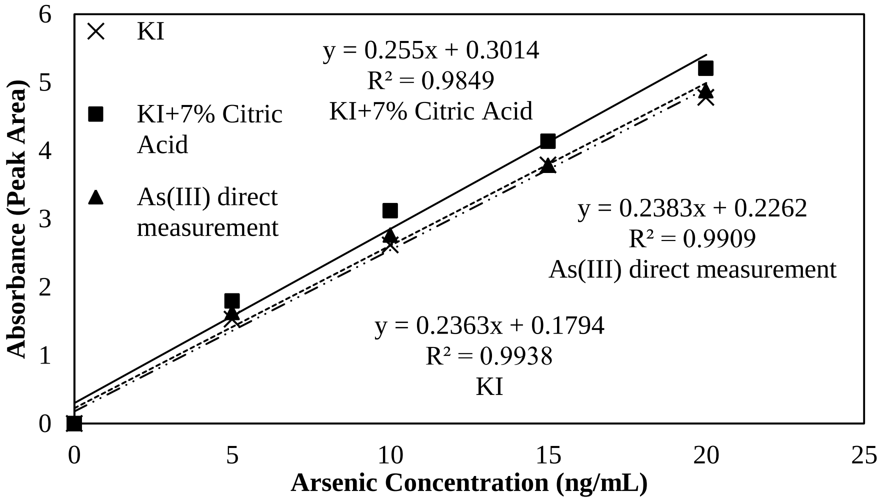


Figure 3.1. Calibration graphs obtained in the absence of Ni(II) with direct measurement of As(III) solution and after adding KI and KI+7% Citric acid.

Table 3.8 Effect of KI and KI+7% Citric Acid on 10 ng/mL arsenic determination in the presence of Ni(II) (n=3).

Variation in the measured As(III) concentration (%)			
Ni(II), µg/mL	KI	KI+ 7% Citric Acid	Direct measurement
0	0.000	0.00	0
5	-0.08±0.19	2.34±2.79	-0.26±0.75
25	0.24±0.54	3.85±0.89	-2.36±0.34
50	0.41±2.64	5.60±1.22	-13.8±0.22
100	-2.68±2.17	3.01±0.63	-50.4±4.18
200	-9.34±2.27	5.94±0.55	-86.5±1.74
300	-17.79±1.28	4.10±2.47	-96.0±0.23
500	-21.36±1.76	-9.45±1.60	ND

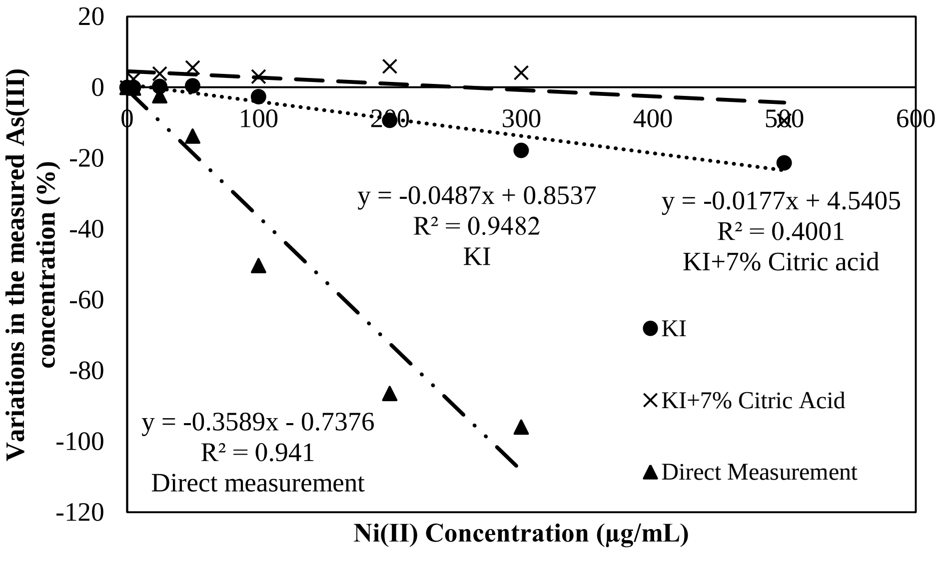


Figure 3.2. Effect of KI and KI+7% Citric Acid addition on the Ni(II) interferences on arsenic determination.

As seen in Figure 3.1, there were no significant differences among the calibration graphs. According to Table 3.8 and Figure 3.2 which were obtained using the data in Table 3.8., the results indicate that KI and KI+7% citric acid avoids interference up to 100 µg/mL and 300 µg/mL Ni(II) on the determination of As(III), respectively.

3.6 Interference Studies

The effect of diverse ions on arsenic meaurements were investigated. 25 mL solution containing 50 µg of diverse ions (Cd^{2+}, Cu^{2+}, K^{+}, Mg^{2+}, Zn^{2+}, SiO_4^{4-}, SO_4^{2-}, and PO_4^{3-}) and 500 ng As (III) was added on 10 mg Ni/Ni_xB nanoparticles. The solution was shaken for an hour, and then, the adsorbent and liquid phases were separated by centrifugation. The adsorbents were dissolved in 5 mL, 2 mol/L HCl. Final volume of the solution was diluted to 10 mL. By measuring the unadsorbed and adsorbed arsenic, it was found that the adsorption efficiencies were more than 99%. No significant interferences were observed on the arsenic determination in the presence of 100 fold excess of the possible interfering ions.

3.7 Sorption Isotherm Models

The sorption isoterms for As(III) and As(V) sorption on Ni/Ni_xB nanoparticles were obtained at 25 °C by varying the arsenic concentrations (50-4000 µg/mL) in the solution while keeping other sorption parameters constant (20 mL of sample solution, pH~6, 10 mg sorbent and 120 min shaking time).

The concentrations of As(III) and As(V) in the supernatant solutions were determined by HG-AAS.

The Langmuir, Freundlich and Dubinin-Radushkevich models are among the most frequently used isoterm models.

Isotherm equations are;

$$\frac{C}{q} = \frac{1}{Q_{max}b} + \frac{C}{Q_{max}} \qquad \text{Langmuir Equation}$$

$$\log q = \log K + n \log C \qquad \text{Freundlich Equation}$$

C: Equilibrium concentration of the solution (mg/L)

q: Amount of sorbed arsenic(mg)/amount of sorbent (g) b: Langmuir constant (L/mg),

Q_{max} = The monolayer adsorption capacity (mg/g),

K: Freundlich constant, adsorpton capacity (mg /g),

n: Freundlich constant, intensity of the adsorbent (dimensionless).

Sorption mechanism can not be understood by using Freundlich and Langmuir isotherms. Since DR isotherm defines the sorption type, equilibrium data was applied to DR isotherm which was the following form.

$$\mathbf{\ln Q = \ln Q_m - k\mathcal{E}^2} \qquad \text{DR Equation}$$

Where Ɛ(Polany potential) is (RTln(1+1/C_2)), Q the amount of As(III) and As(V) sorbed per unit weight of sorbent (mol/g), Q_m the sorption capacity (mol/g), C_2 the equilibrium concentration of arsenic species in aqueous solution (mol/L), k is a constant related to adsorption energy (mol^2/kJ^2), R the gas constant (kJ/mol.K), and the T absolute temperature (K).

The mean free energy of sorption (E) (kJ/mol), defined as the free energy change when one mole of ion is transferred to the surface of the solid from infinity in solution can be calculated from the k value using the equation:

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

The type of adsorption is predicted by using the value of E. The E values lower than 8 kJ/mol indicates that the adsorption is physical in nature, while the values between 8 and 16 kJ/mol, adsorption is occurred by chemisorptions or exchange of ions.

The adsorption efficiency of the adsorption process is predicted by the dimensionless equilibrium parameter by using the following equation:

$$\mathbf{R_L = (\frac{1}{1 + bC_0})}$$

where C_0 is the initial concentration and b is the Langmuir isotherm constant. R_L values below 1 indicate favorable adsorption and values higher than

1 show unfavorable adsorption.

After sorption, unadsorbed As(III) and As(V) in the supernatants were measured. The graphs are shown in Figures 3.3, 3.4, 3.5, 3.6, and 3.7. It was found that both Langmuir and Freundlich isotherms are fitted the equilibrium for As(V) and As(III) by taking into account high R^2 values. It indicates that both monolayer and multilayer adsorption were occurred.

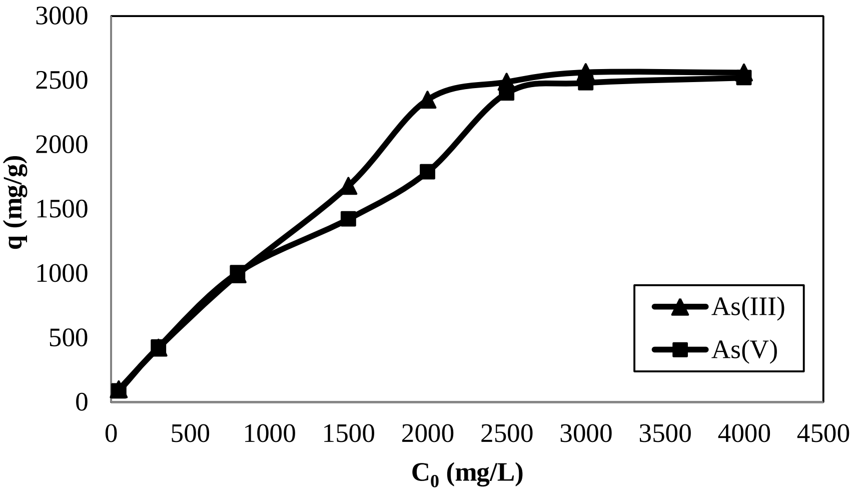


Figure 3.3. Initial arsenic concentration against adsorbed arsenic amount at equilibrium by Ni/Ni_xB (20 mL of 50; 300; 800; 1,500; 2,000; 2,500; 3,000; 4,000 mg/L As(III) and As(V) solution added on 10 mg adsorbent at 25°C).

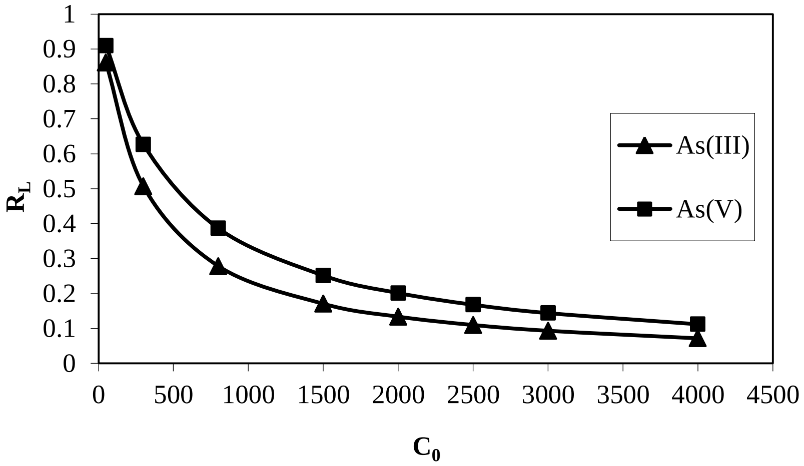


Figure 3.4. The R_L values as a function of initial arsenic concentrations.

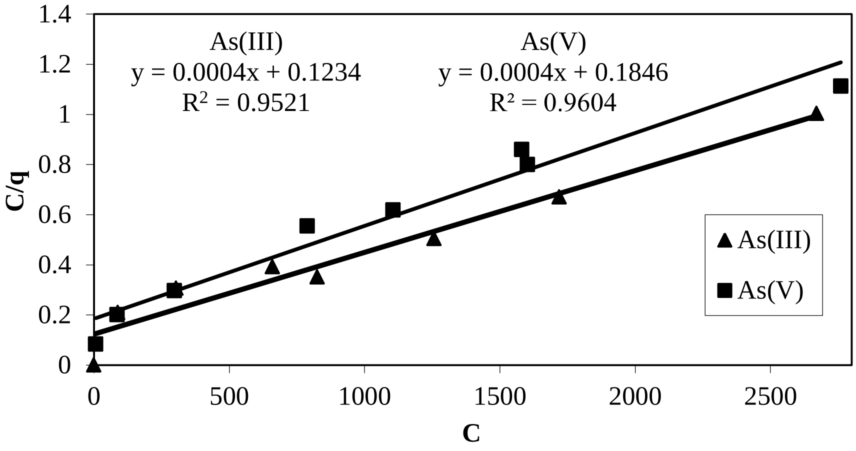


Figure 3.5. Langmuir isotherm plots for the arsenic adsorption on Ni/Ni$_x$B (20 mL of 50; 300; 800; 1,500; 2,000; 2,500; 3,000; 4,000 mg/L As(III) and As(V) solution added on 10 mg adsorbent at 25°C).

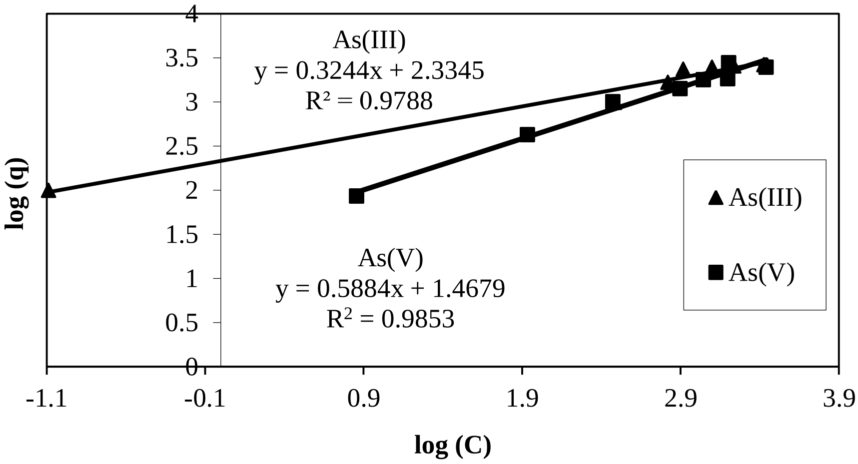


Figure 3.6. Freundlich isotherm plots for arsenic adsorption on Ni/Ni$_x$B (20 mL of 50; 300; 800; 1,500; 2,000; 2,500; 3,000; 4,000 mg/L As(III) and As(V) solution added on 10 mg adsorbent at 25°C).

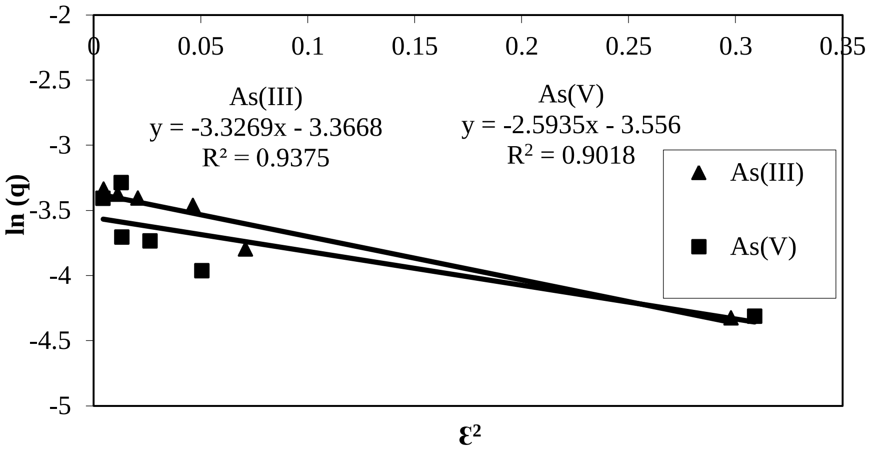


Figure 3.7. D–R isotherm plots for arsenic adsorption on Ni/Ni$_x$B (20 mL of 50, 300, 800, 1,500, 2,000, 2,500, 3,000, 4,000 mg/L As(III) and As(V) solution added on 10 mg adsorbent at 25°C).

Table 3.9 Parameters of Freundlich, Langmuir, and D–R isotherm.

	Related Equation	As(III)	As(V)
Freundlich Isotherm	log q = log K+ n log C		
n		0.3244	0.5884
K, mg/g		216.0	29.37
R^2		0.9788	0.9853
Langmuir Isotherm	$\frac{C}{q} = \frac{1}{Q_{\max} b} + \frac{C}{Q_{\max}}$		
$Q_{max,}$ mg/g		2500	2500
b, L/mg		0.003241	0.002167
R^2		0.9521	0.9604
D-R Isotherm	$\ln Q = \ln Q_m - k\varepsilon^2$		
E, kj/mol		0.39	0.44
Q_m, g/g		2.585	2.139
Q_m, mol/g		0.0345	0.0286
k, mol^2/kJ^2		3.3269	2.5935
R^2		0.9375	0.9018

R_L values lower than 1 indicates that adsorption is favorable, while adsorption is unfavorable when $R_L>1$. The values of R_L for various initial concentrations are plotted in Fig. 3.4. The values noticed that highly favorable adsorption. Table 3.9 shows calculated E values to be 0.39 kJ/mol and 0.44 kJ/mol for As(III) and As(V), respectively. Both E values indicate the adsorption was physical since they were below 8 kJ/mol.

3.8 Limit of Detection and Limit of Quantification

In order to determine the instrumental detection limit for arsenic, 25 mL of 1.5 ng/mL arsenic solution was added on 10 mg sorbent. The sorbent and arsenic solutions were shaken for an hour, and then, 5mL 0.1 mol/L HCl was used for dissolving the sorbents. Sorbed arsenic was determined (n=7).

The instrumental detection limit, based on three times the standard deviation of the blank ($LOD_i=3\sigma/m$, where m is the slope of the calibration curve) were found to be 0.48 ng/mL for As(III) and 0.67 ng/mL for As(V) without preconcentration for the sorbent obtained from the nickel sulfate, 0.46 ng/mL As(III) and 0.88 ng/mL As(V) for the sorbent obtained using nickel nitrate and 0.60 ng/mL As(III) and 0.77 ng/mL As(V) for the sorbent obtained using nickel chloride salt. The analytical limit of detection (LOD_a) (Dubiella-Jackowska et al., 2009; Yalcınkaya et al., 2012) has been calculated by dividing the instrumental detection limit by the enrichment factor (50). The enrichment factor was found by dividing initial volume of the sample to final eluent volume (Wang et al., 2012). The enrichment factor was calculated as 50 when the initial sample volume and final volume of eluent were chosen as 250 mL and 5 mL, respectively. The LOD_a were 0.0096 ng/mL for As(III) and 0.0134 ng/mL for As(V) for the sorbent obtained by sulfate salt, 0.0092 ng/mL As(III) and 0.0176 ng/mL As(V) for the sorbent obtained by nitrate salt, and 0.012 ng/mL As(III) and 0.015 ng/mL As(V) for the sorbent obtained by chloride salt. The instrumental quantification limit based on ten times the standard deviation of the blank ($LOQ_i=10\sigma/m$, where m is the slope of the calibration curve) were found to be 1.6 ng/mL for As(III) and 2.23 ng/mL for As(V) without preconcentration for the sorbent obtained from the sulfate salt, 1.53 ng/mL As(III) and 2.93 ng/mL As(V) for the sorbent obtained from the nitrate salt, and 2.00 ng/mL As(III) and 2.60 ng/mL As(V) for the sorbent obtained using the chloride salt. The analytical limit of quantification of the method (LOQ_a) (Dubiella-Jackowska et al., 2009; Yalcınkaya et al., 2012) has been calculated by dividing the instrumental quantification limit by the enrichment factor (50). The LOQ_a were 0.032 ng/mL As(III) and 0.045 ng/mL As(V) for the sorbent obtained using the sulfate salt, 0.031 ng/mL As(III) and 0.059 ng/mL As(V) for the sorbent obtained using the nitrate salt, and 0.004

ng/mL As(III) and 0.052 ng/mL As(V) for the sorbent obtained using the chloride salt. The relative standard deviation of the methods were calculated as 5.54 % for the sorbent obtained fom the sulfate salt, 3.40% for the sorbent obtained from the nitrate salt and 4.90 % for the sorbent obtained from the chloride salt (n=7).

3.9 Application to Real Samples

The developed method was applied to the preconcentration of arsenic prior to total arsenic determination in various real water samples (mineral, tap and commercially bottled drinking water). The sample pH was set to 6.0. Subsequently, 25 mL of 5 and 10 ng/mL of As(III) and As(V) spiked samples as well as unspiked samples were added individually to 10 mg adsorbent. After shaking for an hour, adsorbent was separated by filtration. In order to dissolve the adsorbents 5 mL 2 mol/L HCl was used. The results in Table 3.10 indicated that the recoveries were quantitative for trace arsenic analysis, ranging from 98.2 to 112.1%.

The analysis of certified reference material (CRM) (EnviroMAT Drinking water-Low, EP-L-2) utilizing the adsorption and recovery procedures in order to appraise the validation of the presented procedure. The results found were in good agreement with the certified values of CRM and are shown in Table 3.10.

Table 3.10 Application of the method to CRM and some real water samples (CRM: EnviroMAT Drinking water-Low, certified value for total arsenic 0.010 mg/ L)

Samples	Certified Value, mg/L	Added, µg/L		Found, µg/L		Recovery, %	
		As(III)	As(V)	Total As		Total As	
CRM	0.010	-	-	0.0099±0.0003		99.0	
Bottled water		-	-	BLD	-	-	-
		5	-	5.39±0.13	-	107.8	-
		-	5	-	5.52±0.075	-	110.4
		10	-	10.90±0.31	-	109.0	-
		-	10	-	11.21±0.32	-	112.1
Tap water		-	-	4.60±0.70	-	-	-
		5	-	9.86±0.84	-	105.2	-
		-	5	-	9.70±1.02	-	102.0
		10	-	15.27±1.16	-	106.7	-
		-	10	-	14.69±0.82	-	100.9
Mineral water 1		-	-	8.67±0.51	-	-	-
		5	-	13.65±0.56	-	99.6	-
		-	5	-	13.94±0.54	-	105.4
		10	-	18.71±0.35	-	100.4	-
		-	10	-	18.72±0.40	-	100.5
Mineral water 2		-	-	2.98±0.39	-	-	-
		5	-	8.39±0.55	-	108.2	-
		-	5	-	8.33±0.32	-	107.0
		10	-	12.92±0.23	-	99.4	-
		-	10	-	12.80±0.83	-	98.2
Distilled water		-	-	BLD	-	-	-
		5	-	5.25±0.03	-	105.0	-
		-	5	-	5.54±0.14	-	110.8
		10	-	10.93±0.29	-	109.3	-
		-	10	-	10.39±0.15	-	103.9

4. CONCLUSION

The effects of various nickel salts used for Ni/Ni_xB sorbent ($Ni(NO_3)_2.6H_2O$, $NiCl_2.6H_2O$ and, $NiSO_4.7H_2O$) on the arsenic sorption efficiency and arsenic capacity were studied. It was observed that the particles size was influenced by the kind of the initial nickel salt solutions. Larger particles were obtained when $NiSO_4.7H_2O$ was used. The particles prepared by $NiCl_2.6H_2O$ and, $NiSO_4.7H_2O$ were more resistant to oxidation than the particles prepared by $Ni(NO_3)_2.6H_2O$. $NiSO_4.7H_2O$ salts were selected for sorbent preparation.

Arsenic sorption efficiencies and arsenic capacities of synthesized Ni/Ni_xB nanoparticles were investigated. The capacity experiments were studied by batch method. The sorption capacities were found to be 2.00 g As(III)/g sorbent and 2.12 g As(V)/g sorbent for particles obtained using the sulfate salts. Three isotherm models, namely, Langmuir, Freundlich, and Dubinin-Radushkevich were tested for identifying the type of adsorption and determining the maximum arsenic capacities of sorbent. Adsorption process was found to obey Langmuir and Freundlich equations and DR isotherms showed that sorption is physical and favourable.

In order to eliminate nickel interferences on arsenic determination, KI+7% citric acid was used whenever necessary. The results indicate that KI and KI+7% citric acid avoids interference until 100 µg/mL and 300 µg/mL Ni(II) on the determination of As(III), respectively.

Nickel and boron release in the arsenic containing and non-arsenic containing aqueous solution from prepared Ni/Ni_xB nanoparticles were investigated. There is no correlation between Ni(II) and boron release and arsenic concentration.

The LOD of this method was comparable with that obtained by other established methods. The method was implemented to the total arsenic determination in various real water samples with satisfactory results.

The aim of the method was preconcentration of the trace arsenic before arsenic determination. However, because of the very high adsorption capacity, the studied adsorption technique can also be suggested for the minimization of arsenic waste water volume and, also for preconcentration prior to X-ray fluorescence spectroscopic arsenic analysis directly in the sorbent without sorbent dissolution.

CHAPTER TWO

INVESTIGATION OF ALUMINIUM PRECONCENTRATION

5. INTRODUCTION

5.1 Aluminium

Aluminium (Al) is the second element in Group IIIA of the periodic table; it has an atomic number of 13, an atomic weight of 26.98, and a valence of 3. It is the third most abundant element in the earth's crust. However, it is a trace element in the biosphere due to having low solubility of its ores in natural waters (Lobinski and Marczenko, 1996).

Aluminium is an odourless, relatively soft, durable, lightweight, ductile, malleable, and silvery-white metal. Aluminium possesses high electrical and thermal conductivity. It is a corrosion resistance metal. It forms a thin surface layer after exposing to air which protect it for further oxidation (Vargel, 2004). The oxide film on the surface of the aluminium protects it from some acids such as nitric acid, and hinders further chemical attack on the metal. On the contrary, some acids such as hydrochloric or hot sulfuric acids can dissolve the protective oxide film. Moreover, alkaline solutions subject the metal to further reactions. Aluminium is often alloyed with other metals. Being light, strong and malleable are characteristics of aluminium alloys (WHO, 1997). Aluminium has eight radioactive isotopes and ^{26}Al is the most stable with a half-life of 7.4×10^5 years (Frank et al., 1985). Aluminium shows amphoteric character, so it reacts with mineral acids and strong alkali solutions (Sax and Lewis, 1987).

5.2 Sources of Aluminium

Aluminium is the third most abundant element in the Earth’s crust. The average abundance of aluminium in the earth’s crust is 8.1%; in soils is 0.9 to 6.5%; in streams is 400 μg/L; in United States drinking waters is 54 μg/L, and in groundwater is <0.1 μg/L (Clesceri et al., 1999).

Aluminium has a strong affinity to oxygen. Therefore, it is not found as a free metal in the environment. It occurs primarily in soluble aluminium silicate minerals. Aluminium is present in the earth’s crust in combination with silicon and oxygen to form feldspars, micas, and clay minerals (Csuros and Csuros, 2002). The weathering of the clay yields bauxite, the chief ore of aluminium. Bauxite contains aluminium in the form of hydrated oxide ($Al_2O_3.xH_2O$) (Csuros and Csuros, 2002).

Both natural processes and anthropogenic sources cause to release aluminium to the environment. The contribution of natural processes is more efficient than anthropogenic sources since aluminium is a major constituent of the earth's crust. Acid rains or the releasing of acid mine drainage result in decreasing pH, and thus mobility of the monomeric forms of aluminium increased. The atmosphere is affected by direct anthropogenic releases of aluminium compounds which are associated with industrial processes such as smelting. Moreover, usage of aluminium and its compounds in preparation, packaging, preservation steps of food products and in drinking-water treatment as flocculants may cause to increase their aluminium contents (ATSDR, 1992).

Both natural and human activities such as erosion, mining or agricultural activities, volcanic eruptions, coal combustion provide a pathway for entering aluminium to the atmosphere. In street dust in urban areas aluminium concentrations are between 3.7 and 11.6 μg/kg. Atmospheric aluminium concentrations in Antarctica are 0.5 ng/m^3 while in industrialized areas it is over 1000 ng/m^3. In natural waters aluminium are found to be both monomeric and polymeric forms. Dominant aluminium species are determined by pH, concentrations of dissolved organic carbon (DOC), fluoride, sulfate, phosphate and suspended particulates.

In the neutral pH values, dissolved aluminium concentrations for water vary from 1.0 to 50 ng/mL, but in more acidic water, it rises to 500-1000 ng/mL. pH of water exposed to acid mine drainage is extremely low, and dissolved aluminium levels have been measured up to 90 μg/mL (WHO, 1997). The concentrations of aluminium in drinking-water depend on the aluminium concentrations present in the source water and aluminium coagulants used for water treatment (WHO, 2003). In drinking water treatment Al-based coagulants such as aluminium sulphate ($Al_2(SO_4)_3$) (alum) or polyaluminium chloride (PACl) are generally used in order to increase the removal of particulate, colloidal, and dissolved substances. The use of alum as a coagulant in water treatment causes to increase the aluminium concentration in treated water. Alum which is added to the raw water for water treatment is not removed during treatment and remains as residual aluminium in the treated water (Srinivasan et al., 1999).

Aluminium occurred in foods naturally or from the use of aluminium-containing food additives. Foods such as potatoes, spinach, and tea naturally contains high amount of aluminium. The addidion of the aluminium based food additives to nutrients increase the aluminium level. Moreover, the use of aluminium containing materials such as cookware, utensils, and wrappings for preparing foods causes to increase the aluminium level in food (WHO, 1997).

5.3 Aluminium Species

pH and finely suspended mineral particles determine predominant aluminium species in natural water. Below pH 4, the predominant species is Al(III) cation. The cationic aluminium hydroxycomplexes $Al(OH)^{2+}$ and $Al(OH)_2^+$ are present above at pH 4. pH values above 6, $Al(OH)_3$ species are formed. Above neutral pH, the predominant dissolved form is $Al(OH)_4^-$. The $Al(OH)_4^-$ species are became dominant at pH 8-9 (Clesceri et al., 1999; Matúš et al., 2009). In Figure 5.1 speciation diagram for aluminum at a given pH (the total aluminum species denotes as α can be seen (Holt, 2002).

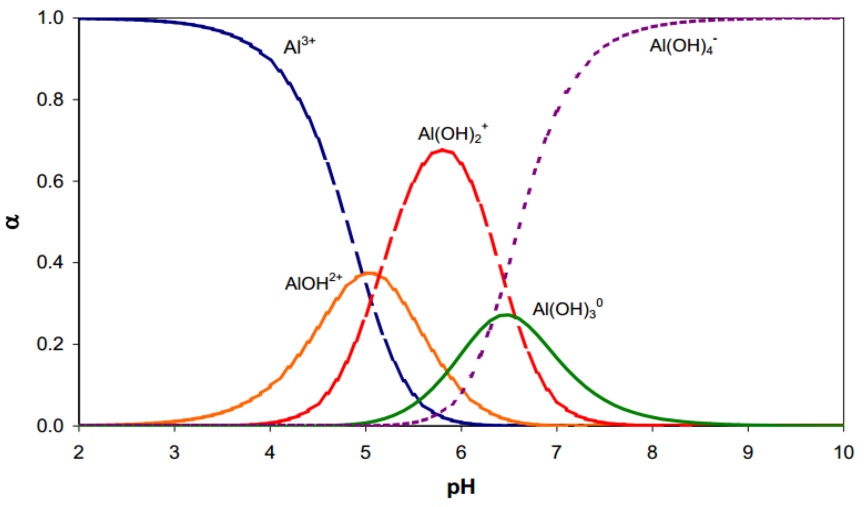


Figure 5.1. Speciation diagram for aluminum in aqueous solution as a function of pH (Holt, 2002).

Labile cationic aluminium hydroxy complexes are acceptable as toxic. Aluminium complexes with organic ligands are accepted almost non toxic (Matúš et al., 2009).

The levels of dissolved aluminium in waters are generally between 0.001 and 0.05 µg/mL at pH values close to neutral pH. However, the levels of dissolved aluminium increase to 0.5–1 µg/mL in highly acidic waters or rich organic matter water. pH of water exposed to acid mine drainage is extremely low, and dissolved aluminium levels have been measured up to 90 µg/mL (WHO, 1997).

Aluminium speciation studies for drinking water contain suspended, colloidal and monomeric forms of Al species. The sum of suspended, colloidal and monomeric forms of aluminium gave total aluminium. Particulate aluminium is the sum of suspended and colloidal aluminium. Monomeric aluminium consists of non-labile aluminium and labile aluminium. Non-labile aluminium is related to dissolved organic carbon. Labile aluminium contains aqua (Al^{3+}), hydroxide, fluoride, and sulphate complexes of aluminium (Srinivasan et al., 1999). The scheme of various species of aluminium is shown in Figure 5.2.

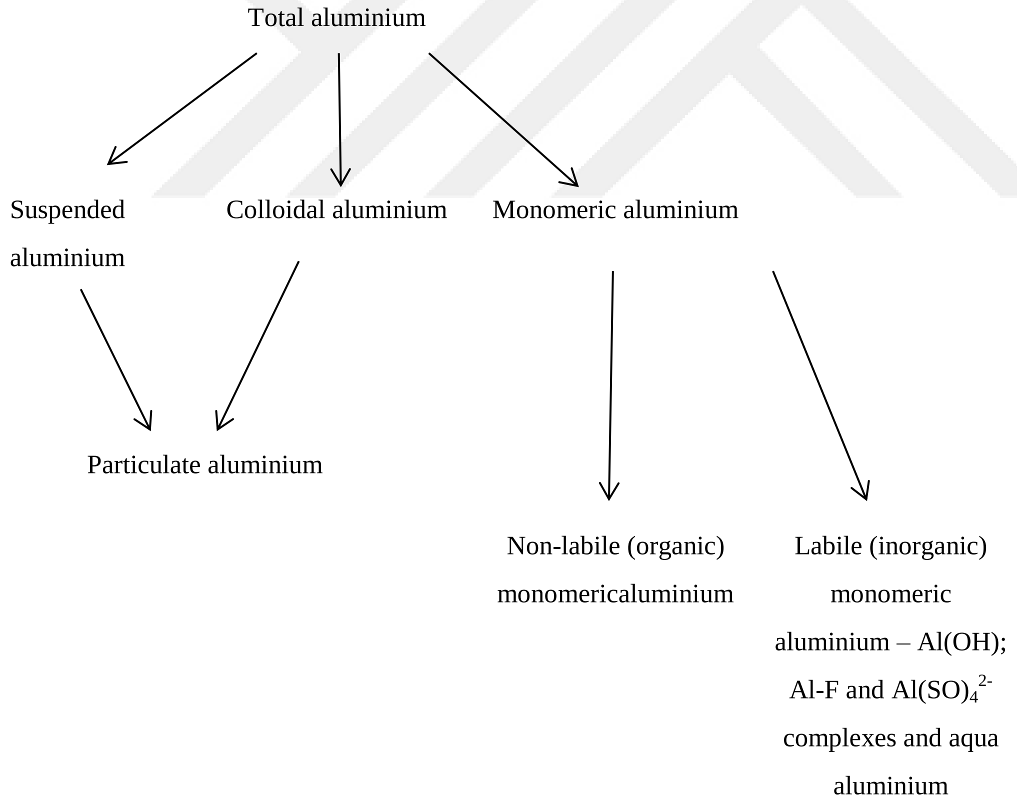


Figure 5.2. Various species of aluminium (Srinivasan et al., 1999).

In drinking water Al is found in a mononuclear form as free Al (Al^{3+}) or its complexes of other dissolved inorganic constituents (such as OH^-, F^-, SO_4^{2-}). Alum which is added to the raw water for water treatment is not removed during treatment and remains as residual aluminium in the treated water. Residual aluminium includes dissolved and particulate species. An efficient operation can easily remove particulate aluminium, while dissolved aluminium which consist of complexes of natural organic matter, fluoride, phosphate, sulphate, and hydroxyl ion can not (Srinivasan et al., 1999).

5.4 Health Effects of Aluminium

Aluminium is both nonessential and toxic for humans. Aluminium is not soluble and the amount of aluminium in most neutral natural waters is low. Water acidification, waste discharge, and soils extract from acidic rain increase the released amount of Al(III) into the environment. In drinking water treatment Al-based coagulants such as aluminium sulphate ($Al_2(SO_4)_3$) (alum) or polyaluminium chloride (PACl) are generally used. The usage of these chemicals causes to increase the aluminium concentration in treated water. The maximum permissible content of Al(III) in drinking water determined as 200 ng/mL (WHO, 1997).

The other pathways of aluminium intake are inhalation and dietary. The contribution of air to the total exposure is generally negligible. Aluminium is found in nutrients naturally or by adding aluminium-containing food additives (aluminium oxides) (Krewski et al., 2007). The aluminium level of some vegetables and fruits such as potatoes, spinach, and tea is high (up to 150 mg/kg). Aluminium compounds are used for storing and processing food (e.g., soy-based infant formula, preservatives, colouring agents, baking powder, cooking vessels, and metal foil). High aluminium intake is the result of the use of packaging, aluminum cooking vessels, aluminum foil, and aluminum containing antacids. Long term usage of antacids, buffered aspirins and other medical preparations are the major intake ways (Csuros and Csuros, 2002; Krewski et al., 2007). The dietary intakes of aluminium (mg/day) for adults are 1.9–2.4, 6.78–11, 4.5, 3.1, 13, 4.4, 3.9, 7.1–8.2 for Australia), Finland, Germany, Japan, Netherlands, Sweden, Switzerland, United Kingdom, and USA, respectively (WHO, 1997).

Solubility, pH, and chemical species determine the aluminium intake. The complex forming compunds such as citrate increase intake of aluminium.

Aluminium accumulates in the bones once it absorbed. Excess aluminium is removed by urine and by bile from the body. The oral LD_{50} of aluminium nitrate, chloride, and sulfate in mice and rats ranges from 200 to 1000 mg of aluminium per kg of body weight (WHO, 1997).

The symptoms including nausea, vomiting, diarrhoea, mouth ulcers, skin ulcers, skin rashes, and arthritic pain are seen after acute aluminium exposure. Long term exposure is resulted in weakness, bone pain and anorexia (Carol and Arnold, 1990).

Alzheimer’s disease, dialysis encephalopathy, renal osteodystrophy, and Parkinson's disease have been associated with aluminium. It is realized that particularly in patients with chronic renal failure suffered from dementia when their dialysis fluid has 80 ng/mL of aluminium. After removing aluminium from the dialysis solution, it was seen that the symptoms of dementia minimized (Shokrollahi et al., 2008). In addition, the sources of trace aluminium contamination are salts and water which used for preparation of the dialysis concentrates (Narin et al., 2004). The European Committee established that diluted dialysis fluids should not contain aluminium concentrations higher than 10 ng/mL (WHO, 2003).

5.5 Applications of Aluminium

Aluminium has many uses ranging from aluminium foil to airplane construction. Having low density and moderate strength makes aluminium essential for structural purposes such as construction, electric cables, packaging and containers (Csuros and Csuros, 2002). In addition, aluminium alloys are used in the aerospace and automotive industries for the same reason (Safavi et al., 2009). One of the interesting usages of aluminium is drain cleaners (Csuros and Csuros, 2002).

Since aluminium is ductile and malleable metal, beverage cans, pots, pans, siding and roofing, and foil is made of it. Powdered aluminum metal is often used in explosives and fireworks. Many consumer products such as antacids, astringents, buffered aspirin, food additives, antiperspirants, cosmetics contain aluminium. Furthermore, flour, baking powder, coloring agents, anticaking agents may comprise aluminum compounds (ATSDR, 1992).

Some countries as France, Italy, Poland, Finland, Romania, Israel, and the former Yugoslavia used coins made of aluminium or aluminium-copper alloy (Wikipedia, 2015).

One of the significant aluminium componds is aluminium hydroxide ($Al(OH)_3$). This compound is the main component of antiacids. In order to neutralize base components of soils, potassium aluminium sulfate ($KAl(SO_4)_2.12H_2O$) is used. Aluminium chloride ($AlCl_3$) is used for both as a catalyst and for isolating aluminium from bauxite. Papers gain water resistant features after treating with Aluminium sulfate ($Al_2(SO_4)_3$). In addition, in water treatment plants, aluminium sulfate is used along with lime (CaO). Calcium oxide makes water alkaline, and thus, aluminium hydroxide precipitates. Suspended solids and certain bacteria are also precipitates in that condition (Csuros and Csuros, 2002).

5.6 Determination Techniques of Aluminium

Up to now it was thought that aluminium did not have a toxic effect. Al(III) are entered body via different routes (drinking waters, food, and medicines) and may be accumulated in the brain. The normal activities of nervous system are interfered (Arain et al., 2015). Additionally, after observing the people who suffers from Alzheimer’s disease has high aluminium content in certain brain cells, research of high aluminium intake is become important (Csuros and Csuros, 2002). Trace aluminium determination has been substantial because of its negative effect on human life.

Various methods are used for the determination of trace levels of aluminium in food, biological fluids and environmental samples. These methods can be classified as electrochemical methods, chromatographic methods, and spectrometric methods. Especially, spectrometric methods such as flame atomic absorption spectrometry (FAAS) (Yalçınkaya et al., 2012; Safavi et al., 2009), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma optical emission spectrometry (ICP-OES) (Sombra et al., 2003), graphite furnace atomic absorption spectrometry, spectrophotometry (Shokrollahi et al.,2008; Luo and Bi, 2003), and fluorimetry (Buratti et al., 2006; Khan et al., 2009; Kazi et al., 2009; Goon et al., 1953; Khan et al., 2011) were commonly used for aluminium determination.

Flame and graphite furnace atomic absorption spectrometric (AAS) methods can determine the concentration of aluminium in water in the range of 5–100 μg/mL with detection limit of 0.1 μg/mL and 0.01–0.1 μg/mL, respectively. Working with diluted sample or small sample volume can increase the linear dynamic range of the graphite furnace AAS (ISO, 1997). The limit of detection for the determination of aluminium by inductively coupled plasma optical emission spectroscopy ranges from 40 to 100 ng/mL (ISO, 1996). Having excellent sensitivity and specificity makes ETAAS preferred. Detection limit and working range are 3 ng/mL and 20-200 ng/mL, respectively. It is very hard to use the method in clinical chemistry on account of the complexity of instrumental requirements and, expensive maintanence of the instrument (Buratti et al., 2006).

The atomic absorption spectrometric methods and the inductively coupled plasma methods are free from such common interferences as fluoride and phosphate, are preferred for aluminium determination (Clesceri et al., 1999). On the other hand, serious matrix interferences are disadvantages of these methods. Moreover, the equipment for these methods is much more expensive and accurate determination of Al requires considerable expertise (Sutheimer and Cabaniss, 1995).

Compared to these methods, spectrofluorimetry has advantages such as low cost, simple operation, easy spread and wide applications. Several reagents have been reported for the spectrofluorimetric determination of aluminium. For these purpose, the widely used reagents are 8-hydroxyquinoline (Buratti et al., 2006), morin (Al-Kindy et al., 2002), lumogallion (Hoch, 1999), quercetin (Lian et al., 2004), Alizarin red (dos Santos et al., 2003) and morin (Hernandez and Escriche, 1984).

5.7 Preconcentration Techniques of Aluminium

The direct determination of trace aluminium by techniques such as FAAS, ETAAS etc. is generally difficult because of the low concentration of aluminium and possible matrix interference problems. These problems can be eliminating by using a preconcentration and/or separation procedure before determination.

A number of separation and preconcentration procedures for preconcentration and/or separation of aluminium involving cloud point extraction (Khan et al., 2009; Kazi et al., 2009; Khan et al., 2011) solid phase extraction

(Khan et al., 2009; Yalçınkaya et al., 2012; Safavi et al., 2009), coprecipitation (Bulut et al., 2010) and liquid–liquid extraction (Buratti et al., 2006) have been proposed to overcome this problem.

Komarek et al. (1998) preconcentrated and determined aluminium in dialysis concentrates using continuous flow solvent extraction (CFE) and by ET-AAS. 8-hydroxyquinoline and methylisobutylketone were used as complexing agent and extraction solvent, respectively. Limits of detection of 0.3 ng/mL were obtained.

Bulut et al. (2010) developed a preconcentration method based on 8-hydroxyquinoline–cobalt(II) coprecipitation system for trace aluminium determination in water samples and dialysis concentrates. Detection was occurred by UV–vis spectrophotometry. Aluminium was coprecipited by using 8-hydroxyquinoline (8-HQ) as a chelating agent and Co(II) as a carrier element. Obtained precipitate was dissolved in nitric acid and after appropriate dilution, trace aluminium was determined by Erio Chrome Cyanine-R/UV–vis Spectrophotometry. The analysis of haemodialysis concentrate was achieved after dilution 1:20 with the distilled water. The preconcentration factor found to be 50. The limit of detection was 0.2 ng/mL.

Dispersive liquid–liquid microextraction method was developed for the preconcentration and determination of aluminium by Rezaee et al. (2010). The determination was carried out inductively coupled plasma-optical emission spectrometry (ICP-OES). Morin was used as complexing agent. After aluminium and morin formed complex, the mixture of acetone and 1-undecanol was added into the sample, afterwards, a cloudy solution was formed. After centrifugation, the test tube was cooled for 5 min. The solidified solvent (1-undecanol) was transferred into a vial and dissolved by 1-propanol. Then, concentration of the sample was determined. The enhancement factor was found as 128. The detection limit was calculated to be 0.8 ng/mL. The method was successfully applied to tap, well and, sea water.

Temperature controlled dispersive liquid–liquid microextraction (TIL-DLLME) for preconcentration of trace levels of aluminium in scalp hair samples of Alzheimer’s disease (AD) patients was used by Arain et al. (2015) and enhancement factor found as 85. 1-butyl-3-methylimidazolium hexafluorophosphate was used as an extractant solvent. After complexing with 8-

hydrooxyquinoline (oxine) and 3,5,7,2′-4′ pentahydroxy flavone (morin) separately, the aluminium extracted by solvent at temperature (50±2.0 ^{o}C). The detection limits (3 s) were 0.56 ng/mL and 0.64 ng/mL, while enhancement factor were 85 and 73 for oxine and morin, respectively. The method was applied to the aluminium determination in acid digested scalp hair samples of AD patients and healthy controls. The resulted data shows significant higher level in scalp hair samples of AD male patients with related to referents of same age and socioeconomic status.

A solidified floating organic drop microextraction (SFODME) procedure was used for preconcentration of ferric iron and aluminium from water samples by Moghadam et al. (2015). The method based on floating organic solvent which has a low melting point in the range of 10–30 ^{o}C on the surface of an aqueous solution. The aqueous phase is stirred for a few minutes, and the sample is transferred into the ice bath. After the organic solvent is solidified, it is transferred into a small conical vial and the melted organic solvent is used for the determination of the analyte. The cationic complexes between Fe(III) and Al(III) and 3,5,7,2′,4′-pentahydroxyflavone (morin) were extracted into 1-undecanol as ion pairs with perchlorate ions. The absorbance of the extracted complexes was measured in the wavelength range of 300–450 nm. The orthogonal signal correction–partial least squares (OSC–PLS) calibration method was used in order to determine the concentration of each metal ion. Obtained enhancement factor was 96 for Al(III). The method was applied for determination of iron and aluminum in steam and water samples of thermal power plant. The accuracy of the method was evaluated by electrothermal atomic absorption spectroscopy (ETAAS).

Ulusoy et al. (2011) developed a cloud point extraction (CPE) method based on the complex of Al(III) with Xylidyl Blue (XB) and then entrapped in non-ionic surfactant Triton X-114. Al(III) determination was carried out by flame atomic absorption spectrometry. Obtained enrichment factor was 50. Detection limit of the method was 1.43 µg/L. The method was applied to the certified reference materials, drinking waters and, mineral water samples.

5.7.1 Adsorbents used for aluminium preconcentration

Separation and the preconcentration of trace metals by solid phase extractions on different materials are became significant (Narin et al., 2004). For this purpose, resins, activated carbon, cellulose, modified silica gel, polymeric resin, biomaterials, and nano particles are generally used adsorbents for preconcentration/separation of metal ions (Ciftci et al., 2015).

The chelating ion-exchange Chelex-100 resin was applied for the preconcentration of aluminium and copper ions (Knežević et al., 1998). The limit of detection for aluminium and copper in dialysis concentrates after 2 fold preconcentrated were calculated as 0.5 ng/mL and 0.2 ng/mL, respectively. Aluminium was detected by electrothermal atomic absorption spectrophotometer and also spectrophotometer with spectrophotometric 8-hydroxyquinoline method at 395 nm. The detection limit was 5 ng/mL for spectrophotometric measurements. Before sample analysis, concentrate dialysis fluids were diluted with pure water 35 times.

Pyrocatechol violet was attached on Amberlite XAD-1180 resin by Narin et al. (2004). The prepared sorbent was used for aluminium preconcentration. Determination of aluminium was realized by graphite furnace atomic absorption spectrometer. Adsorbed aluminium on the sorbent was eluted by 2 mol/L hydrochloric acid. The capacity of sorbent was calculated as 6.45 mg/g. The limit of detection was 0.021 ng/mL. The highest preconcentration factor was found as 150. The method was applied to tap water, river water, acidic dialysis fluid and, basic dialysis fluid samples. The haemodialysis concentrates were used after dilution 1:35 with a de-ionised water obtained in hospitals.

In order to preconcentrate aluminium, biosorbent was also used. Tuzen and Soylak (2008) immobilized Pseudomonas aeruginosa (aerobic rods) on Chromosorb 106 as a biosorbent. The limit of detection was 30 ng/L. The capacity of biosorbent was found to be 10.5 mg/g. The preconcentration factor is calculated as 50. The developed method was applied to natural water samples and food samples.

In biological samples, trace aluminium determination was carried out after preconcentrion of aluminium by L-methionine on controlled pore glass (Pacheco et al., 2008). L-methionine was loaded on the surface of controlled pore glass.

Determination of trace aliminium was executed by inductively coupled plasma optical emission spectrometry connected to ultrasonic nebulization system. The maximum sorption efficiency for 50 ng/mL of aluminium was reached at pH 12.5. The sorption of aluminium on controlled pore glass without L-methionine was also investigated. No sorption was occurred. It was understood that sortion of aluminium on the sorbent actualized owing to L-methionine. The maximum desorption efficiencies were reached by using nitric acid. The limit of detection was 25 ng/L. Total enhancement factor was found 1600 when inductively coupled plasma optical emission spectrometry connected to ultrasonic nebulization system was used. The method was used for the determination of aluminium concentrations of urine, saliva, and hair samples. The results were found as 5.5 and 93 ng/mL for urine and saliva, respectively, while 19 µg/g for hair.

Safavi et al. (2009) used glycerol-bonded silica gel for preconcentration of aluminum prior to analyzing by flame atomic absorption spectrometer and achieved the preconcentration of aluminium by 500 fold. The detection limit was 2 ng/mL. The capacity of sorbent was 0.4 mg/g. Eluent was hydrochloric acid. The method was applied for the determination of aluminum in mineral water, hair and green tea samples. It was found that mineral water, hair and green tea samples contained 28.94, 33.7 and, 142.5 ng/mL of aluminium.

Khan et al. (2009) separated and preconcentrated trace aluminium from pharmaceutical solutions and bottled mineral water samples. Interfering ions is eliminated by complexing with 2-methyl-8-hydroxyquinoline (quinaldine) adsorbed onto activated silica gel. The preconcentration step of aluminium was realized by cloud point extraction (CPE) using 8-hydroxyquinoline as complexing reagent, the resulted complex was entrapped in a non-ionic surfactant octylphenoxypolyethoxyethanol (Triton X-114). The preconcentrated aluminium in sample was determined by spectrofluorimetry at λexcitation 370 nm and λemission 510 nm. The enrichment factor and the limit of detection of aluminium for the preconcentration of 50 ml of pharmaceutical solutions and bottled mineral water were found to be 100 and 0.25 µg/L, respectively.

Khan et al. (2011) developed a similar separation/preconcentration method for trace aluminium determination in environmental and biological samples. Activated silica was modified by 2-methyl-8-hydroxyquinoline (quinaldine) and then, interfering ions was complexed with quinaldine on the activated silica. 3,5,7,2′-4′ pentahydroxy flavone (morin) was complexed with trace aluminium, complex was trapped in non-ionic surfactant octylphenoxypolyethoxyethanol (Triton X-114). Aluminium was determined by spectrofluorimetry at λexcitation 440 nm and λemission 505 nm. The detection limit found to be 0.24 μg/L.

Ciftci et al. (2015) preconcentrated Al(III) by 100 fold using SPE/XAD-761 resin. Duolite XAD-761 is a macroporous organic ester acrylic polymer. It was used as an adsorbent. The 4-(2-pyridylazo) resorcinol was used as a chelating agent for adsorption of aluminum ions from aqueous solutions on Duolite XAD-761 polymeric resin. Determination of aluminium was carried out by high resolution-continuum source flame atomic absorption spectrometer. The method was applied haemodialysis solutions after diluting by deionized water five fold. Then, the preconcentration procedure was applied to the sample solutions. The maximum recovery efficiencies were obtained at pH 5.5. 5 mL of 2 mol/L of HCl solution was selected as an eluent. According to Langmuir isotherm model monolayer adsorption capacity was estimated as 22.5 mg/g. The analytical limit of detection was 0.18 μg/L. The method was utilized for the analysis of aluminium in dialysis fluids and some water samples.

Şahan et al. (2015) realized to preconcentrate of aluminium in dialysis concentrates by solid phase extraction with Lewatit TP-207 resin and electrothermal atomic absorption spectrometry. Lewatit TP-207 resin was a weakly acidic, macroporous cation exchanger with chelating iminodiacetate groups. This on-line flow injection procedure method applied to determine the amount of aluminium in dialysis concentrates. The method applied to 10 fold diluted dialysis concentrates. The preconcentration factor found to be 40. The limit of detection was 7.4 ng/L. The results of the analysis of the certified reference material (CRM403) are in good agreement with the certified value.

5.7.2 Nanoparticles used for aluminium preconcentration

Having most of the atoms are on the surface provide nanoparticles unique features such as high adsorption capacity. The atoms on the surface of the nanoparticle are unsaturated. Thus, they tend to bind other atoms. There have been reports in the literature on the preconcentration and separation of trace aluminium (Zheng et al. 2011)

Liang et al. (2003) was used nano titanium dioxide nanoparticles attached 8-hydroxyquinolin for the preconcentration of trace aluminium(III) and chromium(III) before detection by inductively coupled plasma optical emission spectrometry (ICP-OES). The sorbent prepared by a dynamical method. Acccording to the method, titanium dioxide nanoparticles were transferred into PTFE microcolumn. To clean the column HCl acid and distilled water were passed through the column. A solution of 8-hydroxyquinoline was passed through the microcolumn. Then, distilled water was passed through the column in order to remove excess reagents. It was observed that the sorption efficiency of aluminium was above 90%. Elution of the aluminium was realized by 0.5 mol/L of hydrochloric acid. The adsorption capacity for aluminium was 5.23 mg/g. The enrichment factor was calculated as 50. The detection limit was found to be 1.96 ng/mL. The method was applied for the determination of trace Al(III) and Cr(III) in biological samples and lake water with satisfactory results.

Nanometer-sized titanium dioxide was applied to preconcentration of aluminium as a solid-phase extractant before its determination by electrothermal atomic absorption spectrometry (ET AAS) and inductively coupled plasma optical emission spectrometry (ICP OES) by Matúš et al. (2009). The adsorption capacity of TiO_2 was obtained from isotherm 4.1 mg/g. The detection limit and preconcentration factor were found to be 0.11 ng/mL and of 20. The method applied to natural lake water samples.

Zheng et al. (2011) prepared nano sized adsorbent consisted of titanium dioxide and silica which was chemically modified with 4-aminophenylarsonic acid. The optimum pH value for aluminium was found as 3. It was found that the bare nano titanium dioxide/silica was not adsorbed aluminium at studied pH. Thus, by modifying the sorbent, selectivity was improved. 2 mL of 0.5 mol/L HCl acid was used as an eluent. The enrichment factor was found 150 when 300 mL of sample volume was selected. The adsorption capacity in batch study was 56.58 mg/g. under optimum conditions limit of detection was 0.06 ng/mL. The method was applied to spiked water samples and human urine.

Yalçınkaya et al. (2012) used hybrid nano zirconium dioxide–boron oxide (ZrO_2/B_2O_3) sorbent in order to preconcentrate aluminium. After aluminium sorption on the sorbent, elution was occurred by using nitric acid. Determination of aluminium was carried out flame atomic absorption spectrometry. The analytical detection limit of Al(III) was 7.71 ng/mL. The adsorption capacity was found as 107.7 mg/g. The preconcentration factor was 10. The method was applied to dam water samples.

Mashhadizadeh and Amoli-Diva (2013) developed a preconcentration method for trace aluminium in biological and environmental samples. 3-mercaptopropionic acid attached silica modified Fe_3O_4 magnetic nanoparticles were used. Determination of aluminium was performed by graphite furnace atomic absorption spectrometry. The detection limits of 0.09. The enrichment factor was 99. The maximum adsorption capacity was found to be 64.7 mg/g. The method was applied for determination of trace aluminium in tap water, mineral water, human plasma and, human urine.

Chitosan film loaded with silver nanoparticles (CS-AgNPs) as an adsorbent for solid phase extraction of Al(III), Cd(II), Co(II), Cu(II), Ni(II), Pb(II) and Zn(II) was used before determination by inductively coupled plasma massspectrometry (ICP MS) (Djerahov et al., 2016). In order to prepare chitosan film loaded with silver nanoparticles, two methods were used. In the first one, silver nanoparticles were formed in chitosan solution. The disadvantages of the method were obtained particles had a wide distrubition range and was not shown uniform shapes. In the second method, firstly, silver nanoparticles and chitosan solution were prepared separately, and then prepared silver nanoparticles and chitosan solution were mixed vigorously until having homogeneous mixture. The method provided smaller particle size and higher stability. The second method was selected. It was observed that the particle size of the chitosan film loaded with silver nanoparticles were 28.9 nm. The sorption efficiencies of chitosan film and chitosan film loaded with silver nanoparticles were found as 46 and 98% for 12 hours, respectively. Concentrated nitric acid at 80^oC was used for quantitative eluation. It was the evidence of the metal ions penetrated into the sorbent structure. The enhancement factor was calculated as 125. The limit of detection for aluminium was found 0.05 ng/mL. The method was applied to lake water samples.

5.8 The Aim of This Study

It is considered that usage of aluminium containing water can cause possible health effects. Especially the kidney dialysis patients suffer from dementia when the dialysis fluid contained aluminium. The European Committee established that diluted dialysis fluids should not contain aluminium concentrations higher than 10 μg/L. The qualitative and quantitative determinations of such trace concentrations of aluminium are difficult. Thus, the preconcentration of aluminium before its determination is very important. The fluorimetric technique is rapid, reliable, and low cost technique. Therefore, this study aimed to develop a fast, reliable and simple preconcentration technique for the determination of aluminium at such low trace level based on flourimetric measurements after preconcentration. For this purpose, preconcentration of trace aluminium using a nickel/nickel boride adsorbent prior to the determination by means of the fluorimetric method using morin as the complexing agent was developed. Working conditions for the preconcentration and fluorimetric aluminium determination were optimized, possible interferences were studied. The method developed was applied succesfully to the determination of aluminium in water samples and dialysis fluids.

6. EXPERIMENTAL

6.1 Apparatus and Operating Conditions

Fluorescence intensity measurements were made on a Shimadzu RF-5301 PC model spectrofluorimeter. Shimadzu UV-160A UV-Visible Recording Spectrophotometer was used. Jenway PFP7 model flame photometer was used for sodium determination. For the determination of metal ions Varian SpectrAA 220 Fast Sequential modal Atomic Absorption Spectrometer was used. BIOSAN OS-10 orbital shaker was used at 350 rpm for sorption studies. Zeiss Ultra Plus Field Emission Scanning Electron Microscope, Perkin Elmer Pyris Diamond TG/DTA (Japan), and Thermo Scientific K-alpha (source Al Kα) XPS were used for characterization studies.

The pH measurements were performed by using a Mettler Toledo Five Go FG-2 pH meter. pH meter was calibrated against buffer pH 4 and pH 7 before every measurements.

Nüve NF 800 Centrifuge was used in order to separate sorbent and supernant at 3500 rpm for 5 min.

The experimental conditions for spectrofluorimeter are listed in Table 6.1.

Table 6.1 Instrumental operating parameters for spectrofluorimeter in Al(III) determination.

Lamp Source	Xe lamp
Spectrum Type	Emission
Sensitivity	High
Excitation Slit Width (nm)	3
Emission Slit Width (nm)	3
Scanning Speed	Fast
Excitation Wavelength (nm)	418
Emission Wavelength (nm)	495

6.2 Reagents

All reagents and chemicals used were analytical grade. Ultrapure water was used in the preparation of solutions. Glassware and falcon tubes were cleaned by soaking them in dilute nitric acid (10%) for a night and rinsed with distilled water prior to use.

Absolute ethanol (Merck), Methanol (Merck), Isobuthymethylketone (IBMK) (Merck), Morin hydrate (Fluka) were used.

A stock solution of Al(III) (1000 µg/mL aluminium) in 4% HCl acid was obtained from Merck. More diluted standard solutions (0.4, 1.0, 1.6, 2.0 µg/mL and 5-20 ng/mL aluminium) were prepared daily by dilution of the stock solutions.

0.5% (w/v) Morin: 0.5 g morin was dissolved in ethanol and diluted to 100 mL.

0.0125% (w/v) Morin Solution: Prepared by dissolving 0.0125 g morin hydrate in 86 mL absolute ethanol, 9 mL methanol and 5 mL ultrapure water.

Acetic acid/acetate buffer (0.1 M): 2.86 mL acetic acid (Merck) and 6.8 g sodium acetate (Merck) was dissolved in water and diluting to 500 mL.

HCl-KCl solution at pH 2 was prepared by adding appropriate amount of 0.2 mol/L HCl to 50 mL 0.2 mol/L KCl solution and diluting to 200 mL.

6.3 Aluminium Determination Procedure

Al(III) in the solution can be determined by measuring the fluorescence intensity of Al(III)-morin complex. The ratio of aluminium to morin in the complex is 1 to 3 (Al-Kindy et al., 2002). Structure of aluminium morin complex is shown in Figure 6.1.

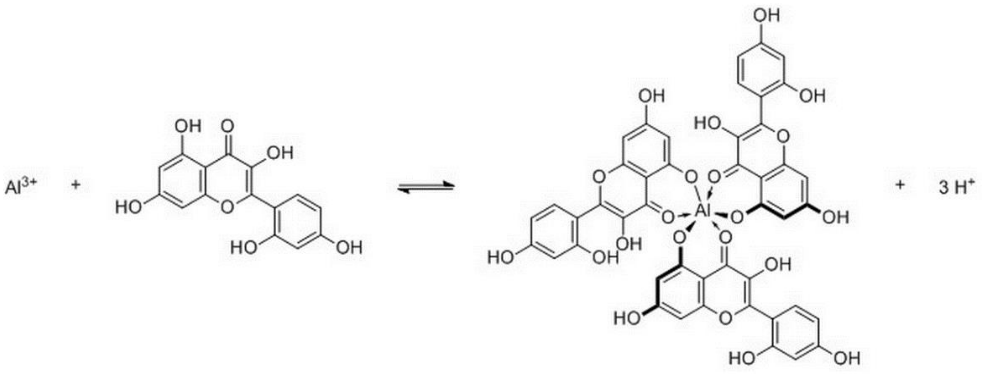


Figure 6.1. Structure of Aluminium morin complex (Wikipedia, 2015).

Procedure 1:

Measurements of aluminium were realized using two different determination procedures. At µg/mL levels of aluminium, following procedure was used. Aliqout amount of aluminium was placed in 25 mL volumetric flask and 0.5 mL 0.5% morin, 14 mL ethanol and 5 mL acetic acid/acetat buffer were added. After 30 minutes fluorescence intensity was measured by exciting at 465 nm and measuring the emission at 516 nm. The obtained fluorescence spectrum and related calibration graph are shown in Figure 6.2 and 6.3, respectively.

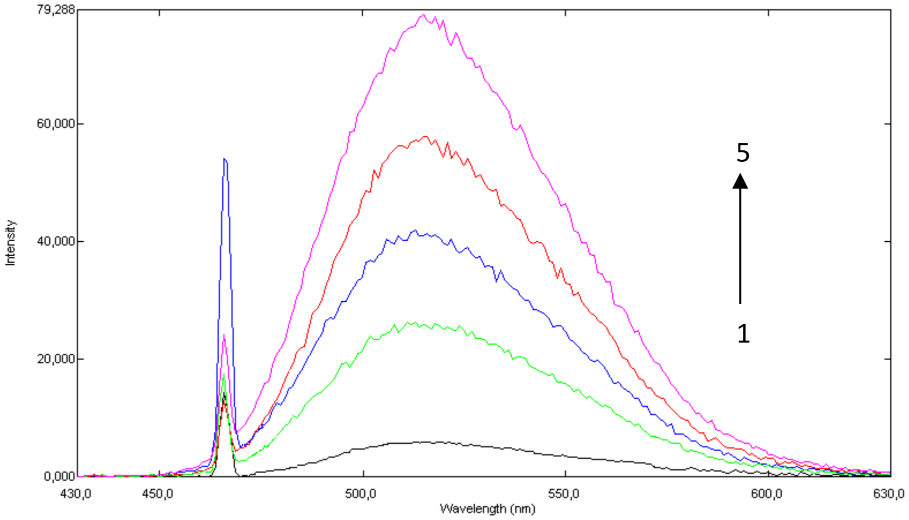


Figure 6.2. Fluorescence spectrum for Al(III)-morin complex at µg/mL levels (λexc 465 nm, λem 516 nm, slit 1.5 nm, concentrations of Al(III) in 1; blank, 2; 0.5 µg/mL, 3; 1 µg/mL, 4; 1.5 µg/mL, 5; 2 µg/mL).

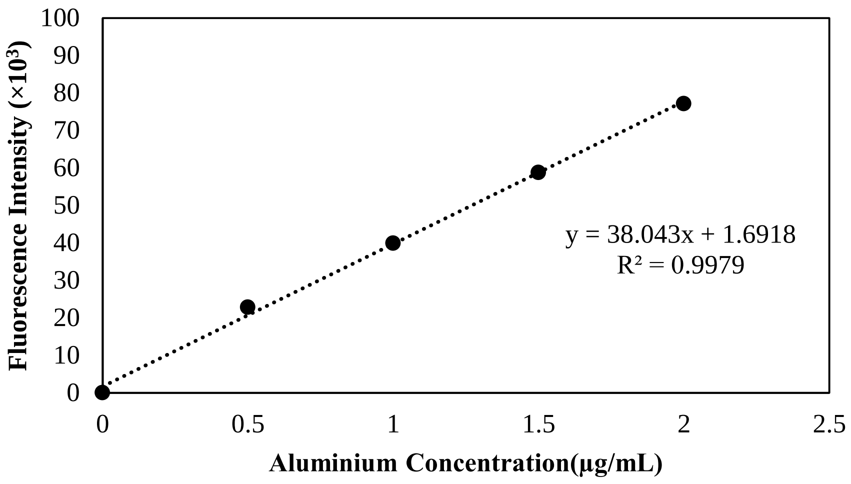


Figure 6.3. Calibration graph for Al(III)-morin µg/mL levels (λ_{exc} 465 nm, λ_{em} 516 nm, slit 1.5 nm, concentration range: 0.5-2.0 µg/mL).

Procedure 2:

Significant signals were not obtained for determination of aluminium at ng/mL levels when this procedure was used. Second procedure which adapted from Hernandez and Escriche (1984) was used to determine aluminium at ng/mL levels. A 4 mL of IBMK and 4 mL of the morin solution (0.0125%) were placed in a beaker and aliquot of aluminium solution was added. The pH of the solution was set between 3.55-3.95 by adding HCl-KCl solution. Fluorescence intensity was measured at 495 nm, after excitation at 418 nm. The obtained fluorescence spectrum and related calibration graph are shown in Figure 6.4 and 6.5, respectively.

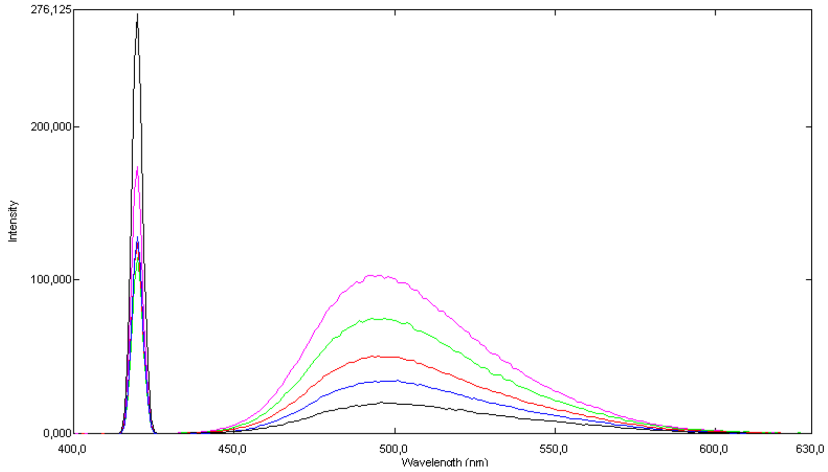


Figure 6.4. Fluorescence spectrum of Al(III)-morin/IBMK-ethanol-water system (at pH~3.60, λexc 418 nm, λem 495 nm, slit 3 nm, concentration range: 5-20ng/mL).

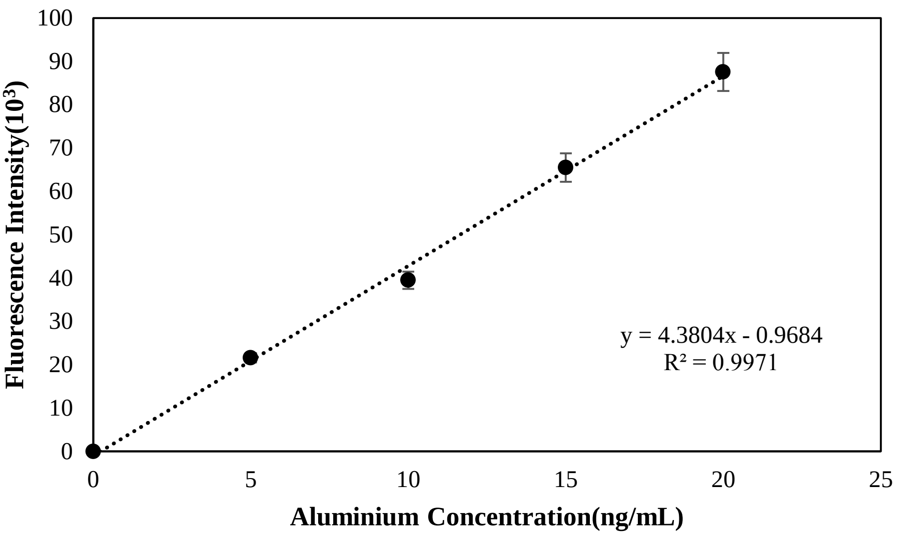


Figure 6.5. Calibration graph of Al(III)-morin/IBMK-ethanol-water system (at pH~3.60, λexc 418 nm, λem 495 nm, slit 3 nm, concentration range: 5-20 ng/mL, n=3).

6.4 Preparation of Ni/Ni$_x$B from NiSO$_4$.7H$_2$O

As described in chapter one, preparation of adsorbent Ni/Ni$_x$B using nickel sulfate salt (NiSO$_4$.7H$_2$O) has advantages compared to the use of nickel nitrate (Ni(NO$_3$)$_2$.6H$_2$O) salt, while showing similar sorption properties, nickel sulfate were used for sorbent preparation in the further studies.

Although ultracentrifuge was used, solution and sorbent are not always separated effectively. It affects sorption efficiencies. The particles of sorbents prepared by sulphate salts are larger and their separation by centrifuge is easy. Clesceri et al. (1999) reported that majority of aluminium is adsorbed by filter paper, absorbent cotton, or glass wool. Therefore, filter paper was not used in the experiments.

A 250 mL polyethylene bottle with three holes on the lid was used for providing inert atmosphere. Two of the holes were for nitrogen and NaBH$_4$ solution flow, separately, and the last one was for gas outlet. First, 2.5% (w/v) of Ni(II) (25 mL) solution as NiSO$_4$.7H$_2$O (Merck) in 0.1 mol/L HCl was added to the bottle. Afterwards, nitrogen gas was passed while nickel solution was stirred on a magnetic stirrer. Then, 20 mL of 4% (w/v) sodiumborohydride solution was dropped. After the first drop of NaBH$_4$, the black precipitate formed. It was observed that when 20 mL of NaBH$_4$ was added, final pH value was reached 9.25. Particles were separated by ultracentrifugation.The particles were washed and centrifuged for 6 times, the first with 15 mL portions of water and then 5 mL portions of ethanol to remove all the water. A water bath at 95 °C was used for drying the nanoparticles for 2 hours under nitrogen atmosphere. Appearance of nanoparticles were black granular. It was easy to wash, centrifuge and dry.

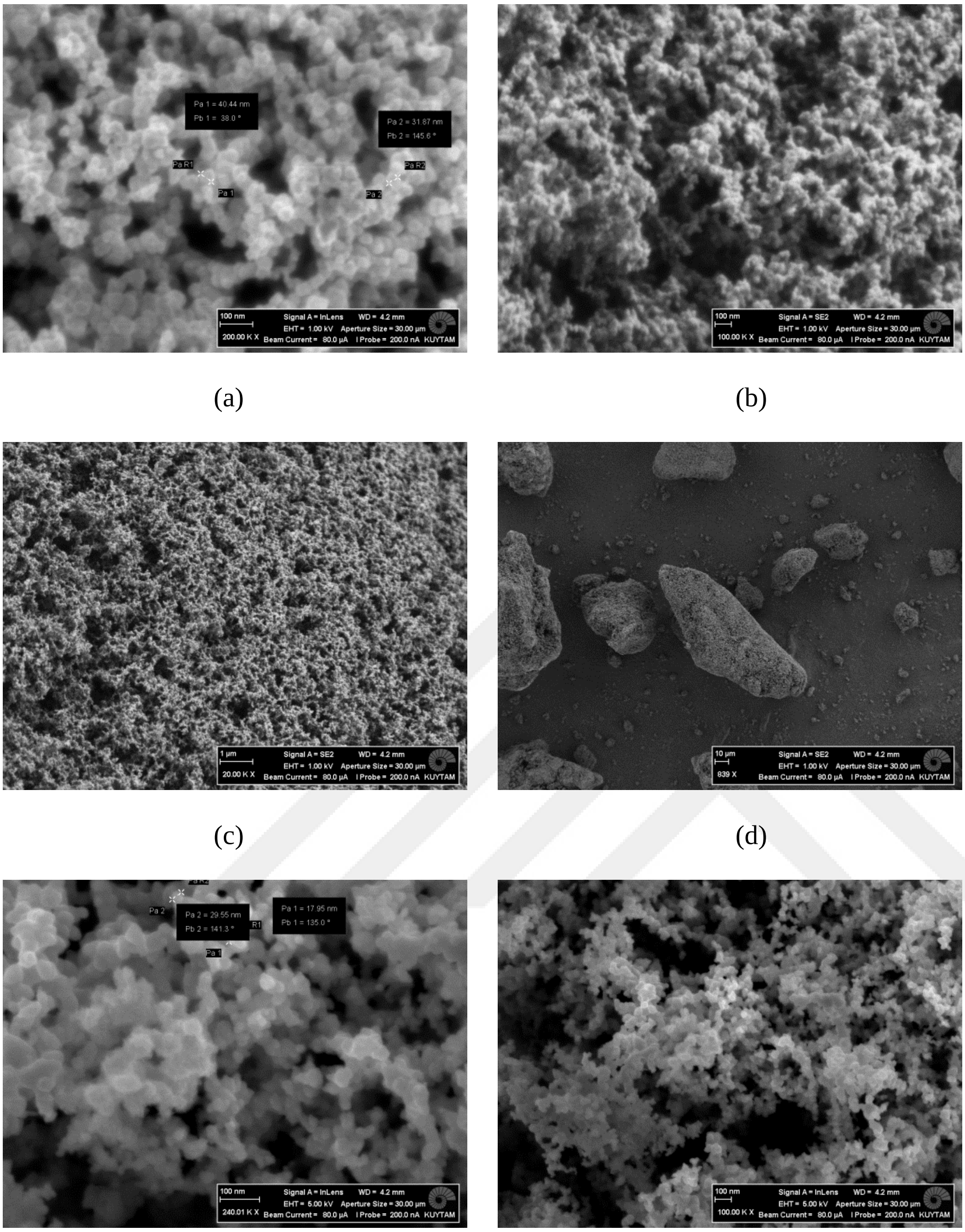
7. RESULTS AND DISCUSSION

7.1 Characterization of Sorbent

Characterization studies help us to understand structure of the sorbent, elements into its chemical structure/elements and functional groups which it has. Characterization of the sorbent was executed using scanning electron microscopy (SEM-EDX), chemical analysis, thermo gravimetric analysis (TGA), X–ray photoelectron spectroscopy (XPS) and, point of zero charge measurements.

7.1.1 Scanning electron microscopy (SEM-EDX)

The SEM images of the newly prepared sorbent are represented in Figure 7.1. The particles of the sorbent prepared by nickel sulfate salts were observed that their shapes were spherical. The particles align to form long chain like structure. The particles were 30-50 nm in diameter.



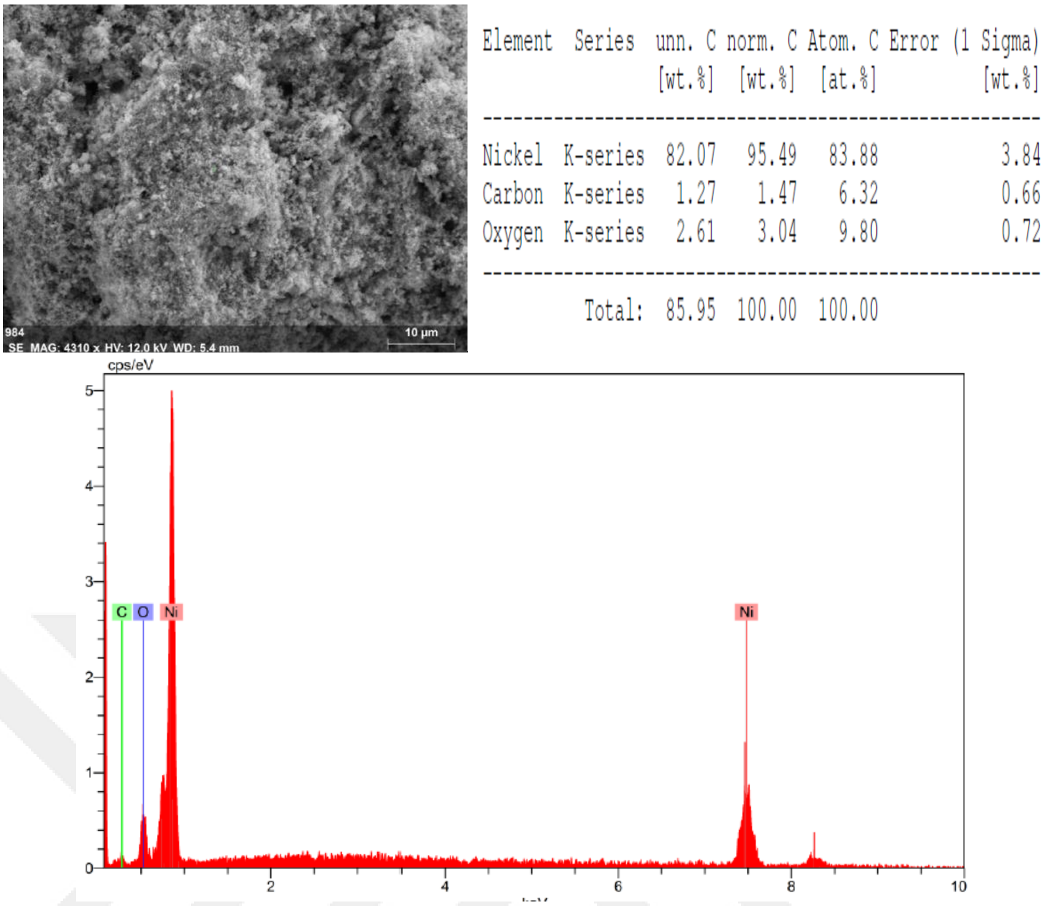
(a) (b)

(c) (d)

(e) (f)

Figure 7.1. Typical SEM images of Ni/Ni$_x$B sorbent (a) 200.00 K X, (b) 100.00 K X, (c) 20.00 K X, (d) 839 X, (e) 240.01 K X, (f) 100.00 K X.

The samples were also analyzed with EDX by randomly selected area on the sorbent surface. Figure 7.2 displays EDX spectrum.



```
Element  Series  unn. C norm. C Atom. C Error (1 Sigma)
                 [wt.%]  [wt.%]  [at.%]          [wt.%]
-----------------------------------------------------
Nickel  K-series  82.07   95.49   83.88           3.84
Carbon  K-series   1.27    1.47    6.32           0.66
Oxygen  K-series   2.61    3.04    9.80           0.72
-----------------------------------------------------
           Total:  85.95  100.00  100.00
```

Figure 7.2. EDX spectrum of Ni/Ni_xB sorbent.

EDX analysis indicated that the majority of the sorbent was nickel and the minority was oxygen. The presence of carbon attributed to the usage of ethanol in the washing step of synthesis of the sorbent. The characteristic X-ray peak of boron is expected to appear at 0.183 eV. There is not any clear boron peak in the EDX spectrum. However, boron may not be detected due to inefficient sensitivity of the instrument (Berlin et al., 2011).

7.1.2 Chemical analysis

Approximately 10 mg portions of the sorbent were taken and dissolved in 5 mL 1 mol/L HCl. After several dilutions, amount of nickel, boron, sulphate, nitrate and, sodium in sorbents were analyzed by AAS, Azomethine-H photometric method, turbidimeter, UV-Vis spectrometer and, flame photometer, respectively. The results are shown in Table 7.1.

Table 7.1 Chemical analysis of the sorbent (%) (n=3).

Sample no	Nickel	Boron	Nitrat	Sulphate	Sodium
I	93.12	3.76	1.28	0.514	0.165
II	89.24	3.62	1.24	0.505	0.133
III	88.57	3.52	1.14	0.610	0.076
	90.30±2.43	3.65±0.107	0.832±0.578	0.542±0.055	0.127±0.0472

Corresponding mol numbers are 0.1637 mmol Ni^{2+}, 0.03595 mmol B, 0.002085 mmol nitrate, 0.0005999 mmol sulfate, 0.0005882 mmol Na^{+}. The mol ratio of Ni to B was calculated as 4.55. This can be indicating the structure as a mixture of elementel nanonickel and Ni_2B, as mentioned by Glavee et al. (1994), where they reported that synthesized particles obtained under nitrogen atmosphere in water primarily consist of Ni_2B. After exposing to air majority turns to metallic nickel.

7.1.3 Thermo gravimetric analysis (TGA)

TGA graph of $Ni(OH)_2$ in nitrogen atmosphere is shown in Figure 7.3. It showed three steps of weight loss. The first weight loss in a temperature range of 25–100°C can be ascribed to the evaporation of adsorbed water molecules and water of crystallization. The second and third weight losses in the range of 200–400°C are due to thermal decomposition of $Ni(OH)_2$ to NiO nanoparticles. When temperature is above 400°C, weight loss becomes fairly slight; indicating the formation of NiO nanoparticles is nearly complete (El-Kemary et al., 2013; Liu et al., 2015). Therefore, prepared Ni/Ni_xB nanoparticles were not contained nickel hydroxide.

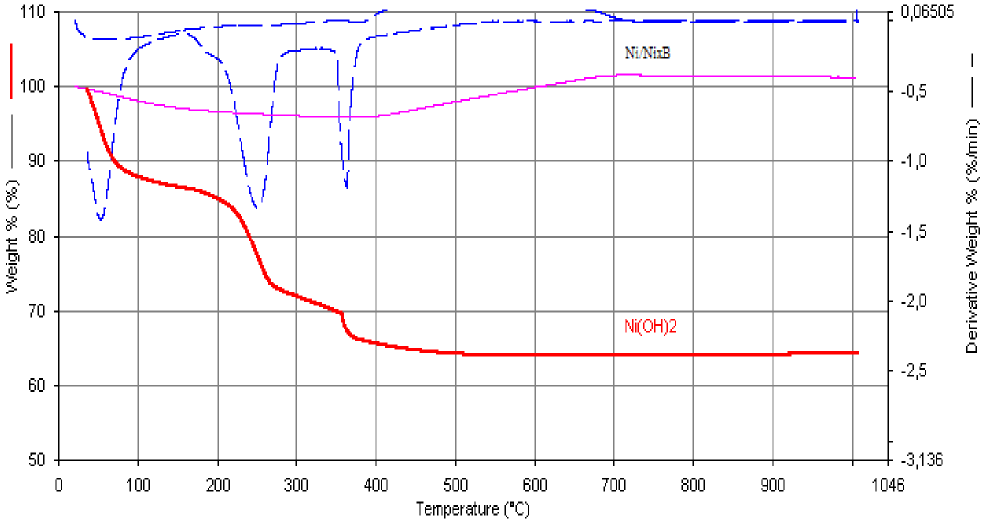


Figure 7.3. TGA of Ni/Ni$_x$B and Ni(OH)$_2$.

7.1.4 X–ray photoelectron spectroscopy (XPS)

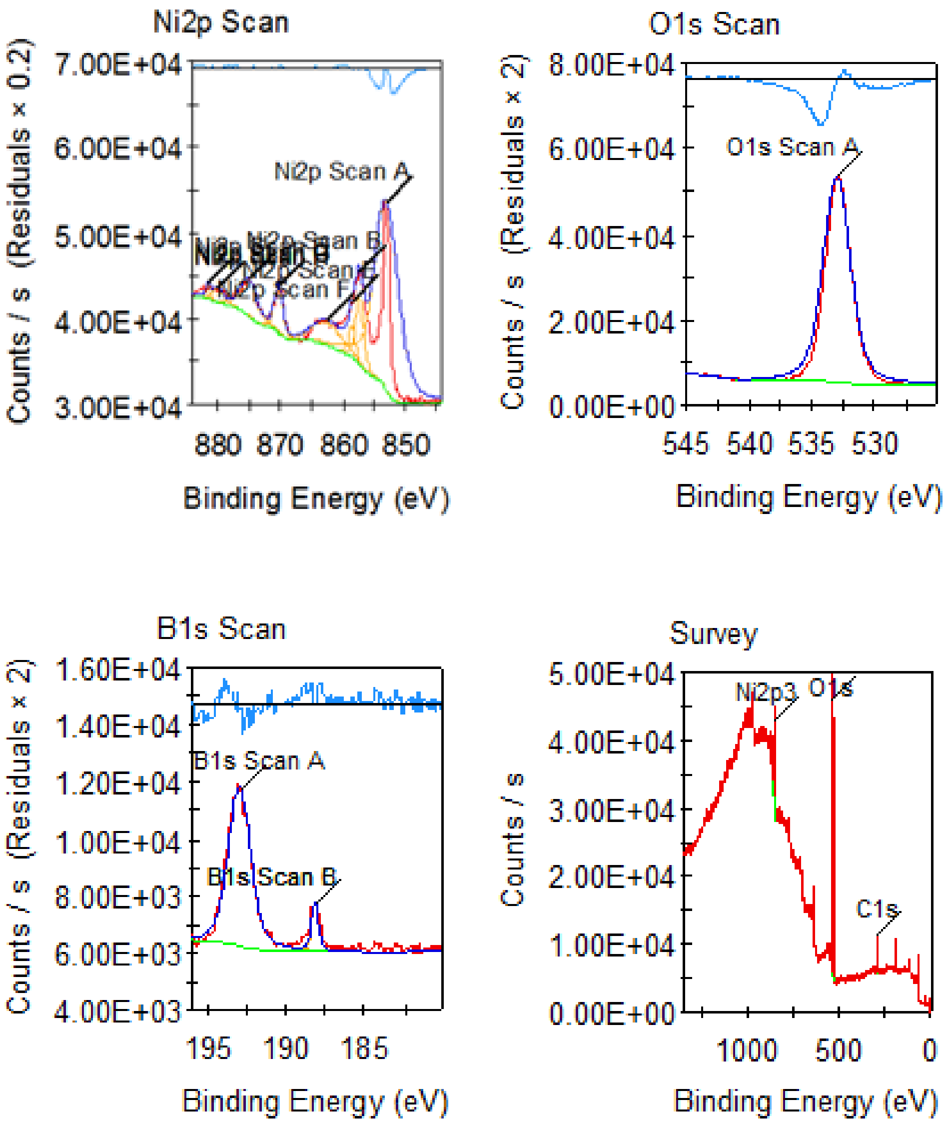
To obtain further insight into the aluminium sorption on the Ni/Ni$_x$B sorbent, XPS spectra of the sorbent before and after Al(III) sorption have been examined. The O 1s, B 1s, Ni 2p, Al 2p, and survey scans are illustrated in Figure 7.4.

Position of the O1s level core, around 533 eV, indicates the presence of B-O bond regarding B_2O_3 (Legrand et al., 2002). The binding energies of 532.99 and 533.05 eV which belong to O1s scan could indicate presence of B_2O_3, in the spectra obtained both before and after sorption, respectively. Furthermore, after aluminium sorption, it was found that the atomic ratio of this peak increased from 49.52 to 61.42%. This increase indicate that B_2O_3 were involved in Al(III) sorption (Li et al., 2010; Wagner et al., 2003).

As mentioned by Legrand et al. (2002) B_2O_3 is a byproduct of the Ni_2B oxidation. B1s spectra for B_2O_3 and Ni_2B, corresponding B-O and B-Ni bond, show peaks at 193.8 eV and 188 eV, respectively (Legrand et al., 2002). In Figure 7.4, B1s spectra had two binding energies of 193.18 and 188.18 eV. Therefore, these peaks may be related to structure of B_2O_3 and nickel borides. After sorption, it can be seen that B1s spectra had peaks at 194.48, 193.48, 192.68, and 184.38 eV. These binding energies again may depict $Na_2B_4O_7$, B_2O_3, $(Al_2O_3)_9(B_2O_3)_2$/ B/Al_2O_3 and nickel-borides, respectively (Strohmeier, 1989; Legrand et al., 2002; Stranick et al. 1987).

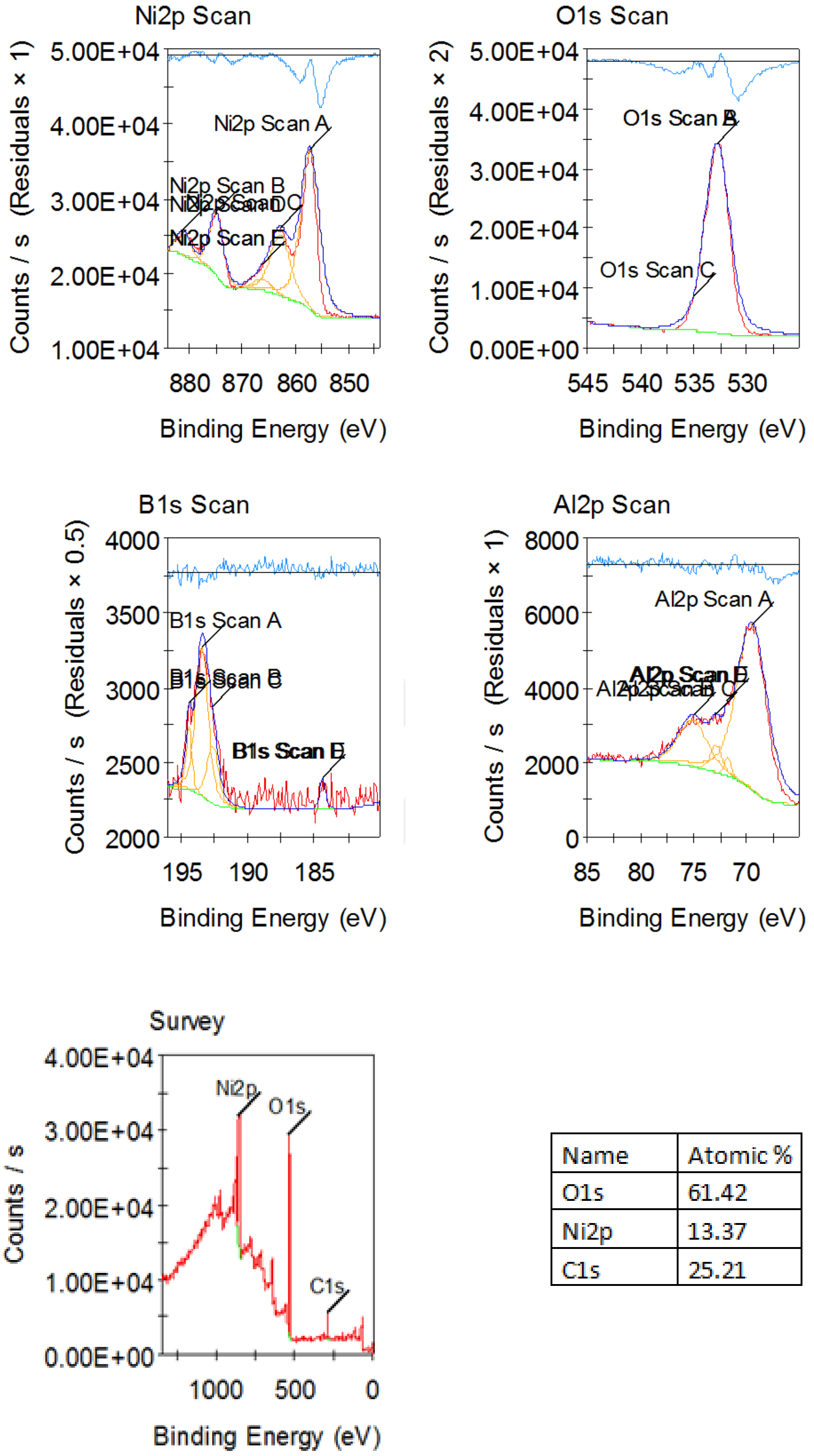
$Ni2p_{3/2}$ binding energies of 852.7, 853.40, 854.0, 856.2 and, 858.2 eV related to Ni metal, Ni_2B, NiO, $Ni(OH)_2$ and NiOOH, respectively (Luo et al., 1996; Legrand et al., 2002; Arfelli et al., 1990; Venezia et al., 1995). In Figure 7.4, Ni2p spectra binding energies having 852.98, 870.38, 875.08, 862.98, 881.58 and, 879.08 eV were seen. These binding energies may indicate the presence of metalic Ni, NiO, Ni_2B, and/or Ni_2O_3. Because of O1s peak assigned to hydroxide (531eV) was not seen, hydroxide might not be in the structure of the sorbent. This is also verified by the absence of $Ni(OH)_2$ and NiOOH peaks in Ni2p spectrum at 856.2 and 858.2 eV, respectively. After sorption, peak at 857.18 eV in Figure 7.5, Ni2p scan may be indicating the presence of $NiAl_2O_4$ structure (Kasztelan et al., 1983).

In Figure 7.5, survey spectra of Al loaded sorbent and Al2p scan spectra are shown. It was reported that binding energies of 71.90, 72.80, 75 eV indicated AlB_2, metallic Al, and Al-oxides, respectively (Wagner et al., 2003). Peaks at 71.78, 72.88 and, 75.08 eV in Al2p spectra of Al adsorbed sorbent might be belonging to AlB_2, metallic Al and, Al-oxides, respectively.



Name	Atomic%
B 1s	24.28
C 1s	16.96
N 1s	2.3
O 1s	49.52
Ni2p	6.94

Figure 7.4. XPS spectra of Ni/Ni$_x$B before aluminium sorption.



Name	Atomic %
O1s	61.42
Ni2p	13.37
C1s	25.21

Figure 7.5. XPS spectra of Ni/Ni$_x$B after aluminium sorption.

7.1.5 Determination of point of zero charge by immersion technique

To clarify the point of zero charge of the sorbent, various methods (potentiometric mass titration, mass titration, and immersion technique) were used in the literature (Mahmood et al., 2011; Fiol and Villaescusa, 2009; Preočanin and Kallay, 2006). The point of zero charge (pH_{pzc}) defined as the pH value which the charge of the positive surface sites is equal to the negative ones. Determining the point of zero charge gives information about possible electrostatic interactions between sorbent and metal species. The surface of the sorbent is negatively charged when the pH is higher than pH_{pzc} and could interact with metal positive species, whereas at pHs lower than pH_{pzc} surface of the sorbent is positively charged and could interact with negative species (Fiol and Villaescusa, 2009).

The point of zero charge was determined by immersion technique (salt addition technique). Initially, 25 mL 0.1 mol/L KNO_3 solutions adjusted at different pH values by HCl or NaOH addition were added on 10 mg sorbents and shaken for 24h to reach equilibrium pH. The change of pH (ΔpH) during equilibration was calculated by substracting the initial pH values from final pH values. Then, ΔpH values were plotted against the initial pH values. The minimum ΔpH value indicates the point of zero charge. The relevant plot is shown in Figure 7.6.

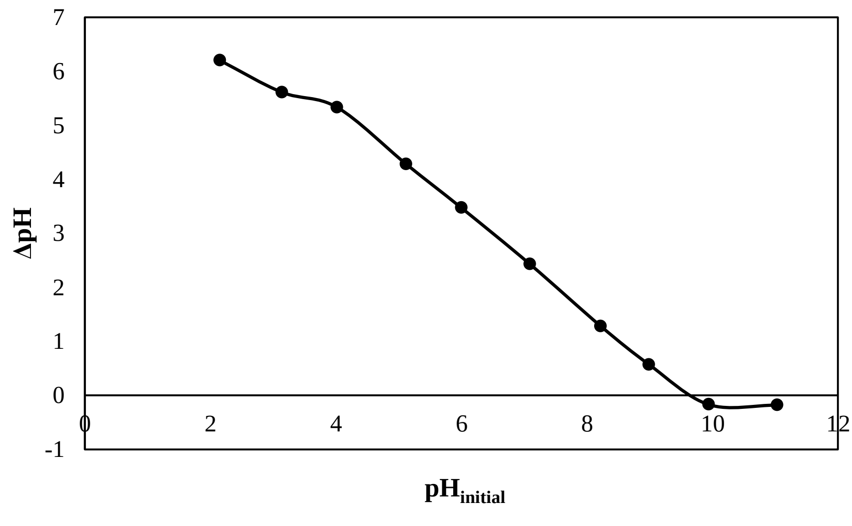


Figure 7.6. Plot of ΔpH vs initial pH values obtained by immersion technique.

The pH_{pzc} value was found as 9.66. This result means that pH values below 9.66, surface of the sorbent is positively charged and interacts negatively charged species. Above this value surface is negatively charged and attracts positively charged species. Taking into account the diagram of distribution for Al species, after pH 8 dominant species are $Al(OH)_4^-$. It was thought that aluminium was sorbed as $Al(OH)_4^-$ before pH_{pzc}. Theorically, in this condition, after pH_{pzc}, repulsion was expected between aluminate species and negatively charged sorbent. On the contrary, in studies about the effect of pH on sorption efficiencies, it was seen that the sorption efficiencies were independent of pH values of the solution in the range studied, pH 3-10. Hence, there could also be another different mechanism other than electrostatic forces for the Al(III) sorption.

7.2 The Effect of Time on Fluorescence Intensity

According to Hernandez and Escriche (1984), fluorescence measurements are made with little variations after 1 h when pH is between 3.55 and 3.95. In order to investigate the time effect, variations in the fluorescence intensity of 10 ng/mL Al(III) standard was measured during 90 min using the procedure for Al(III) measurement at ng/mL level. The effect of time on fluorescence intensity is shown in Figure 7.7.

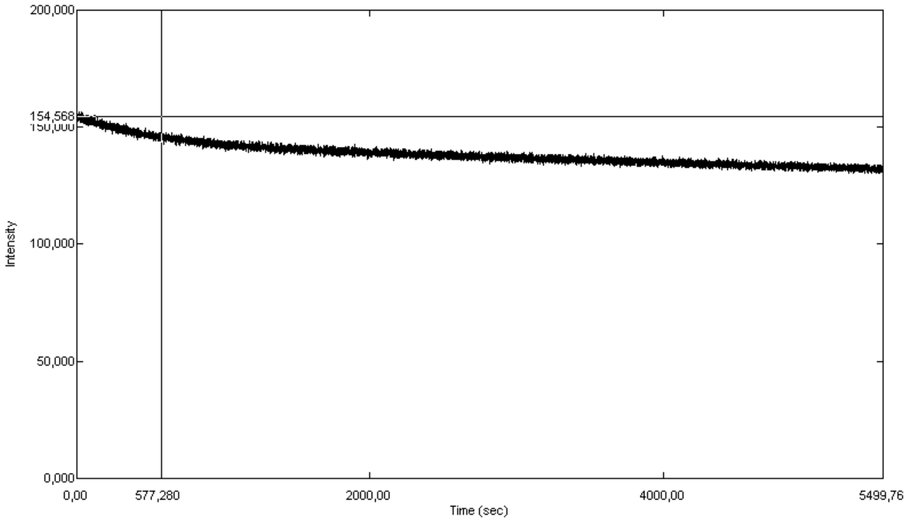


Figure 7.7. The effect of time on fluorescence intensity (10 ng/mL of Al(III)-morin/IBMK-ethanol-water, λ_{exc} 418 nm, λ_{em} 495 nm, slit 3 nm).

In the first 50 min. the fluorescence intensity decreased by 12.78% then, it became relatively stable and decreased slowly in the following 40 min. Therefore, the fluorescence measurement was made at 50 min.

7.3 Some Preliminary Studies

To make the sorbent selective for aluminium, the sorbent was tried to coat with morin. Firstly, 0.2 g of sorbent was weighed, and then 40 mL 0.1 mol/L morin solution was added on it and, shaken for a night. After then, sorbent was washed with ultrapure water until excess morin receded. Finally, the morin coated sorbent was dried in air atmosphere. 25 mL of 100 ng/mL Al(III) at pH 4.53 was added on 10 mg of morin coated sorbent and shaken for an hour. Final pH rose to 7.50 after sorption. Sorption efficiencies were found to be only 21.95%. It was known aluminium-morin complex could form at pH 5 quantitatively. At pH 7.50 the complex between Al(III) and morin may not be formed. Therefore, sorption efficiencies of Al were not quantitative.

7.4 Sorption Procedure

For sorption; 25 mL 100 ng/mL Al(III) solution at pH~4 was added on 10 mg sorbent and was shaken in orbital shaker at 25°C for half an hour. After sorption, solutions were centrifuged and remaining Al(III) was measured in the solution. All the results given are the mean of three measurements otherwise stated.

The sorption percentage of aluminium was calculated using equation below. C_i and C_f indicates the initial and final Al(III) concentrations in supernatant.

$$\boldsymbol{Sorption}(\%) = \frac{\boldsymbol{C_i - C_f}}{\boldsymbol{C_i}} \times \mathbf{100}$$

7.4.1 Preliminary experiments for Al(III) sorption on Ni/Ni_xB

In preliminary experiments sorption efficiencies of Al(III), Al(III)-morin complexes, and morin on Ni/Ni_xB were investigated.

Firstly, 25 mL of 10 µg/mL Al(III) solution at pH~4 was added on 10 mg Ni/Ni_xB. After shaking 2 h, sorbent and solution phases were separated by ultracentrifuge at 3500 rpm for 5 min. The remaining Al(III) in the solution was measured using the fluorimetric method. Amount of Al(III) remaining unadsorbed in the solution was below the detectable concentration.

7.4.2 Sorption of trace Al(III) on Ni/Ni$_x$B

The sorption efficiency of 25 mL 100 ng/mL of Al(III) solution at pH~4 was determined. After shaking for 2 h, phases were separated. The remaining Al(III) in the solutions were analyzed by the method which suggested by Hernandez and Escriche (1984). Unadsorbed aluminium in the solution was below the detectable concentration.

7.4.3 Sorption of trace Al(III)-Morin complex on sorbent

25 mL 50 ng/mL of Al(III)-morin complex in IBMK-ethanol-methanol solution were added on 10 mg sorbent and shaken for 20 min., and then separated by ultracentrifuge. Unadsorbed Al(III) concentration was determined in the supernatant by means of measuring fluorescence intensity of Al(III)-morin complex. The complex was quantitatively adsorbed and unadsorbed aluminium in the solution was below the detectable concentration.

7.4.4 Sorption of Morin on Ni/Ni$_x$B

To test whether the sorbent adsorbs morin in solution, 10 mL 0.0125% morin in solution (EtOH:MetOH:water/86:9:5mL) was added on 10 mg sorbent and shaken for 30 min. then, fluorescence spectrum was obtained. The relevant spectra are shown in Figure 7.8 indicating that morin was also quantitatively (97.46%) adsorbed by Ni/Ni$_x$B.

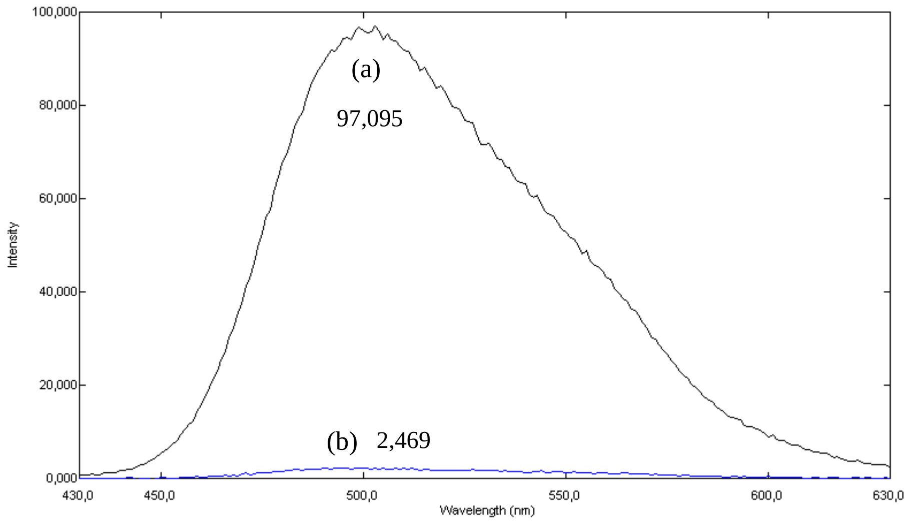


Figure 7.8. Fluorescence spectrum for 0.0125% morin solution before sorption (a) (Fluorescence intensity: 97,095) and after sorption (b) (Fluorescence intensity: 2,469) (λ_{exc} 418 nm, λ_{em} 495 nm, slit 3 nm).

The pH values of the 10 mL of 0.0125% morin solution were measured as 5.07 before sorption and 5.80 after sorption in this medium.

7.5 The Effect of pH on Al(III) Sorption Efficiency and the Aluminium Species Adsorbed

The pH effect on the sorption of the sorbent was investigated in the range pH 3-10. Initial pH of solutions was prepared adjusted using HCl and NaOH solutions by controlling with a pH meter. After sorption, sorbent was separated by ultracentrifuge. Remaining Al(III) in the solution was measured by fluorimeter. Variation in the percent sorption versus initial pH of the solution is shown in Figure 7.9. As seen from the figure, the sorbent offered quantative sorption in the studied pH range. Initial pH was selected as 4 for the following studies.

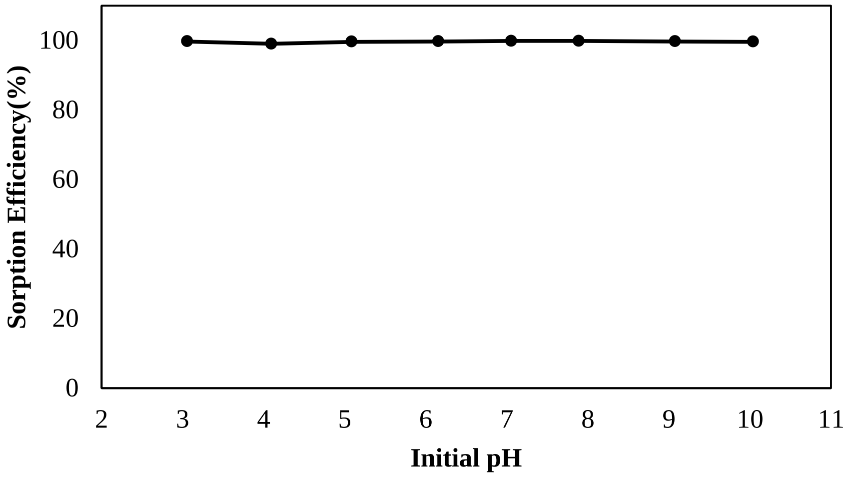


Figure 7.9. The effect of pH on Aluminium sorption (25mL, 100ng/mL Al(III), 10 mg sorbent, 1 h contact time, n=3).

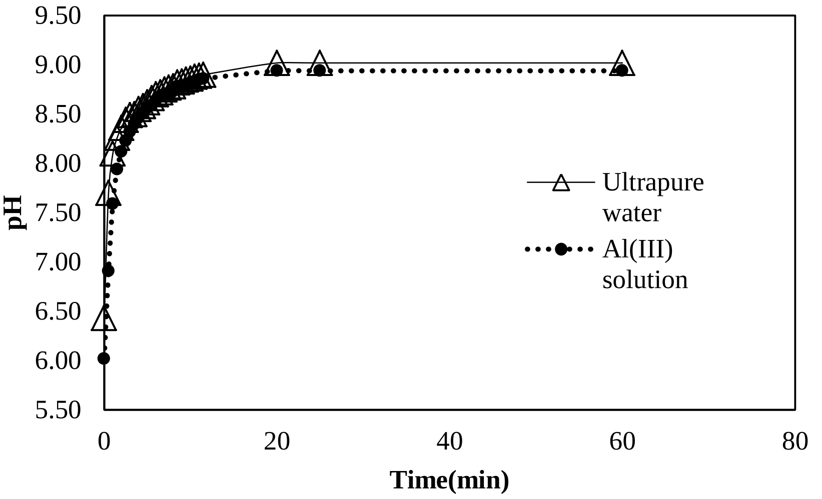


Figure 7.10. Diagram of time dependent pH change after adding 10 mg Ni/Ni$_x$B sorbent into 25 mL ultrapure water and 25 mL 100 ng/mL Al(III).

Time dependent pH variations were also investigated. 25 mL water and 25 mL 100 ng/mL Al(III) solutions were added on 10 mg sorbent and shaken for 1800 seconds. Initial pHs were 5.75 for ultrapure water and 5.45 for Al(III) solution. pH increased to about 8 in about a minute and in first 270 seconds pH reached 8.50 for both water and aluminium solution.

Similar to the studies done before for arsenic (İşlek Coşkun et. al., 2016), pH increased to ~9 after sorption independent to the initial pH. It is indicated that the initial pH value is actually about 9. Therefore, the sorption efficinecies were not affected by the initial pH values between 3 and 10.

According to the species distribution diagram in Figure 5.1, after pH 8 the dominant aluminium species is $Al(OH)_4^-$. Since equilibrium pH varies between 8.52-9.40, and pH rises to above in less than a minute, as shown in Figure 7.10, the species sorbed by the Ni/Ni$_x$B is $Al(OH)_4^-$. The Ni/Ni$_x$B sorbs aluminium as $Al(OH)_4^-$.

To find out whether Al(III)-morin complexes forms at pH 9, after setting pH of the 0-2 mg/L Al(III) standard solutions to the desired value by adding 0.1 mol/L NaOH, morin and ethanol were added to these solutions. After 30 min, fluorescence intensities of the standards were measured using Procedure 1. No significant difference between the measured values of standards and blank solution could be observed. Thus, it was concluded that the complex of Al(III)-

morin did not form at pH 9.

7.6 The Effect of Sorbent Dose on Al(III) Sorption Efficiency

The dependence of Al(III) sorption on the amount of Ni/Ni$_x$B was studied. Different sorbent doses (0.1, 0.2, 0.4, 0.6, 0.8, and 1.2 g/L) corresponding to in the range of 2.5 mg and 30 mg were used for 25 mL of 100 ng/mL Al(III) sorption. Sorption efficiencies were very high for all the sorbent doses experienced. After separation by ultracentrifuge, remaining Al(III) was determined by fluorimeter. The effect of sorbent dose on the sorption of Al(III) is depicted in Figure 7.11. It was observed that the sorption was quantitative even for sorbent dose 0.1 g/L (2.5mg sorbent). 0.4 g/L (10 mg sorbent amount) was chosen to make sure sorption was quantitative. Nevertheless to decrease the concentration of nickel ion on the determination of Al, 4 mg of the sorbent could be selected for some studies.

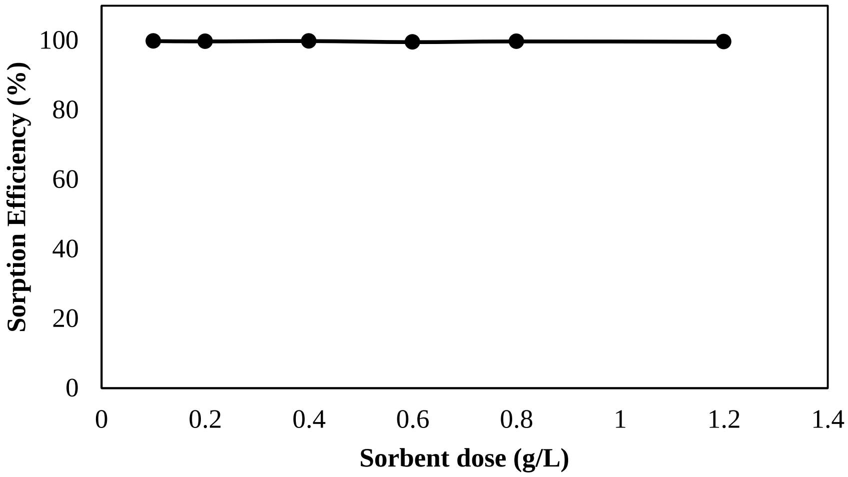


Figure 7.11. The effect of the sorbent dose on Aluminium sorption (25mL, 100ng/mL Al(III), pH~4, 1 h contact time, n=3).

7.7 The Contact Time Effect on Al(III) Sorption

Samples were shaken for 5, 10, 15, 30, 60 and 120 minutes to understand the effect of contact time on sorption. Other parameters were kept constant at 25 mL sample volume, 100 ng/mL Al(III) concentration, 4 mg and 10 mg sorbent amount. Sorption experiments were carried out at pH~4. The remaining Al(III) was analyzed by the fluorimetric method after separating by ultracentrifuge. The effect of contact time on aluminium sorption is shown in Figure 7.12.

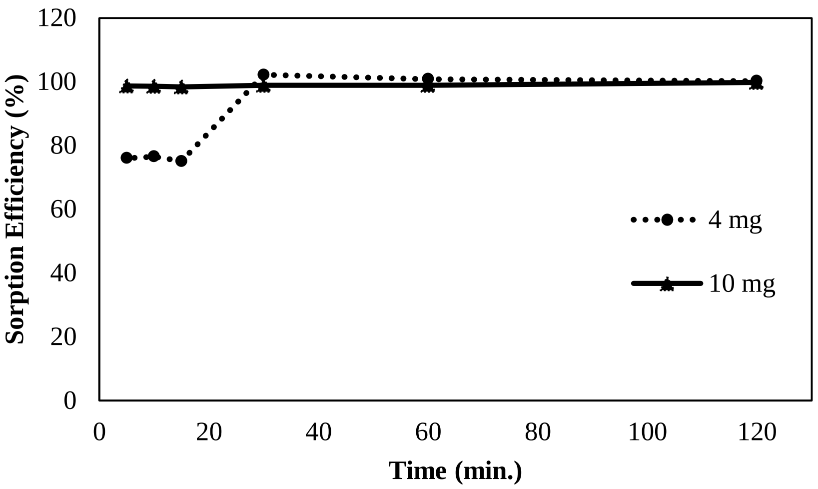


Figure 7.12. The effect of contact time on Aluminium sorption (25mL, 100ng/mL Al(III), pH ~4, n=3).

As can be seen in Figure 7.12, sorption efficiency reached 100% after 30 minutes for 4 mg sorbent. Therefore, 40 minutes contact time was selected when 4 mg of sorbent was used.

The higher the amount of sorbent, the less time require for sorption. Sorption was completed in first five min when 10 mg sorbent was used. In order to reduce contact time, 10 mg of sorbent was selected in the following studies.

7.8 The Effect of of Sample Volume and Enrichment Factor

In order to determine the maximum volume of sample solution that can be used, the effect of the volume of sample solution on the recovery of the Al(III) was investigated. For this purpose, 25, 50, 100, 150 and 250 mL solutions containing 1000 ng Al(III), corresponding to concentrations of 40, 20, 10, 6.67 and 4 ng/mL, respectively were prepared. The contact time was choosen for half an hour. The recovery of Al(III) was quantitative (>95%) for sample volumes up to 250 mL. The graph is shown in Figure 7.13.

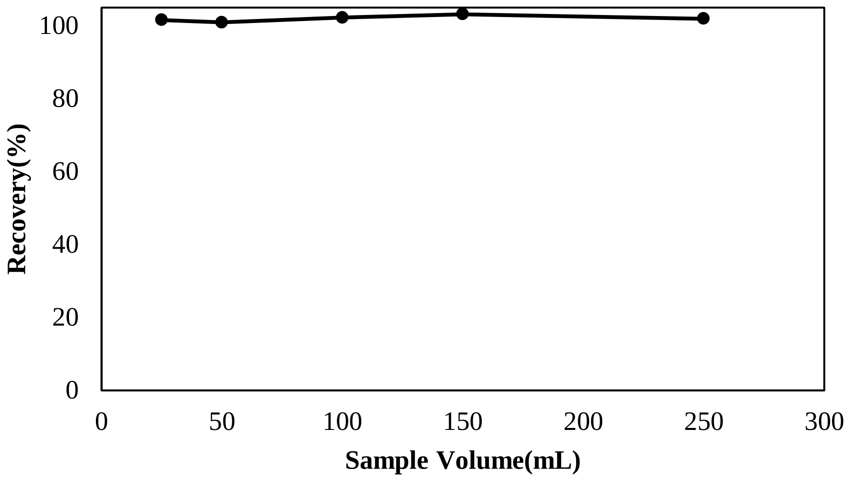


Figure 7.13. Recovery of Al(III) vs sample volume (25, 50, 100, 150 and 250 mL containing 1000 ng Al(III), pH ~4, 10 mg sorbent, n=3).

After the preconcentration of 250 mL sample solution, if 5 mL of 0.1 mol/L HCl solution was used for dissolving the sorbent, the enrichment factor was found to be 50 for Al(III). The enrichment factor was found by dividing initial volume of the sample to final eluent volume (Dubiella-Jackowska et al., 2009, Wang et al., 2012).

7.9 Recovery of Aluminium from the Sorbent

After sorption of aluminium by sorbent, its recovery from the sorbent was investigated. For this purpose morin solution, NaOH, mixture of NaCl+NaOH, EDTA, and HCl solutions were tried.

Since aluminium forms complex with morin, it was thought that morin could be used as an eluent. First, 25 mL of 100 ng/mL of Al(III) solution was adsorbed on the sorbent. Then, 10 mL of 0.0125% morin solution was added onto the sorbent and shaken for 30 min. Finally, fluorescence intensity of the solution was measured. As mentioned in section 7.4.4, morin was also sorbed by the sorbent, but it could not desorp adsorbed Al(III) from the sorbent. Therefore, morin was not effective for aluminium recovery.

For the recovery of Al(III) from the sorbent 2% (w/v) NaOH and a mixture of 2% (w/v) NaOH and 3% (w/v) NaCl were used. However, both solutions were ineffective for the recovery of Al(III). According to variations of aluminium species with pH data (Figure 5.1), aluminate was dominant species after pH 8. At the end of the shaking process, the pH of the aluminium solution was increased to about 9. That is, aluminium was sorbed as aluminate by the sorbent. This may be the reason why the solutions were uneffective for the recovery of Al(III).

For the recovery of Al(III) by means of using EDTA was also tried. 5 mL 0.1 mol/L EDTA solution was used for desorbing the aluminium from the sorbent. Al(III) containing sorbent was shaken for one hour with EDTA solution. It was observed that majority of the sorbent was dissolved by EDTA. The calibration graph could not be obtained when 0.1 mol/L EDTA was used. Therefore, the concentration of the EDTA solution was reduced to 10^{-4} mol/L EDTA. The solution was shaken for one hour and also overnight. Moreover, the sorbent and EDTA solution were heated at boiling temperature. The calibration graph could be obtained in the presence of 10^{-4} mol/L EDTA. However, in this case, no aluminium could be recovered. This may be due to back adsorption of the Al(III) and/or AlEDTA complex is occurred during the dissolution of the sorbent. The stability constants of EDTA complex and morin complex of aluminium are 16.13 (Sillén et al., 1964) and 16.96 (Pavun et al., 2009), respectively. The stability constant of Ni-EDTA complex is 18.56 (Sillén et al., 1964). However, recovery with EDTA could be suggested when aluminium is determined by atomic absorption spectrometric methods.

In order to desorp aluminium, 5 mL of HCl was selected. The Al(III) adsorbed adsorbent was shaken with HCl solutions or it was dissolved on hot plate to get aluminium from sorbent. The results were shown in Table 7.2.

Table 7.2 Dissolution of aluminium from the sorbent by HCl (25mL of 100 ng/mL aluminium was added to 10 mg of sorbent) (n=3).

Concentration of HCl (mol/L)	Dissolution type of the sorbent	Contact time with 5 mL HCl solution(min.)	Aluminium Recovery(%)	Amount of dissolved Ni(II) from the sorbent after shaking with HCl (mg)
0.2	Partial dissolution of the sorbent after shaking 5 mL HCl	30	77.30	4.82
0.2	Partial dissolution of the sorbent after shaking 5 mL HCl	60	85.75	7.85
0.2	Complete dissolution by heating with 5 mL HCl	-	99.41	9.91
0.1	Partial dissolution of the sorbent after shaking 5 mL HCl	30	56.74	4.62
0.1	Partial dissolution by heating with 5 mL HCl	60	88.44	7.98
0.1	Complete dissolution by heating with 5 mL HCl	300(5h)	106.50	9.84
0.1	Complete dissolution by heating with 5 mL HCl	180(3h)	102.71	9.79
0.05	Complete dissolution by heating with 5 mL HCl	420(7h)	109.02	9.42

As seen in the table above, shaking the sorbent with HCl solutions were not efficient for recovery of aluminium unless all the sorbent were dissolved. The efficient recovery results were obtained by dissolution of the sorbent on the hot plate. Usage of 0.2 mol/L HCl arised some difficulties while setting the desired pH in preparation of aluminium solutions. Therefore, the optimal conditions attained for 0.1 mol/L HCl and complete dissolution for 180 min.

7.10 The Effect of Foreign Ions

The preconcentration method can be affected by the ions which found in the sample; as a result the recovery of aluminium species can be affected. Therefore, the effects of the possible interfering ions of the samples on the proposed procedure should be investigated.

In order to examine the effect of other constituent on the recovery of Al(III), the possible interfering elements (Ca^{2+}, Cu^{2+}, Cr^{3+}, Fe^{3+}, Mg^{2+}, Pb^{2+}, Zn^{2+}, Cl^{-}, HCO_3^{-}, NO_3^{-}, PO_4^{3-}, SO_4^{2-}) were added to 50 mL of model solutions containing 500 ng of Al(III) (10 ng/mL), as their potassium, sodium, sulfate, chloride or nitrate salts. 4 mg of sorbent was used. The contact time was chosen as one hour. Interfering ion concentrations causing ±5% deviation in recovery of the Al(III) is considered as the tolerance limit. The results are shown in Table 7.3.

Table 7.3 Effects of foreign ions for the determination of 10 ng/mL Al(III) (n=3).

Ion	Concentration of Interfering Ion(μg/mL)	Recovery(%)of Aluminium Ion	Tolerable Concentration of Interfering Ion (μg/mL) for 2 ng/mL Al (*20 ng/mL Al) (Hernandez and Escriche, 1984)
Cu^{2+}	100	BDL	0.05
	10	BDL	0.07*
	1	103.2±5.3	
Cr^{3+}	100	91.6±12.7	>10
	10	104.6±4.4	
	1	105.1±4.4	
Fe^{3+}	100	BDL	0.07
	10	BDL	0.06*
	1	93.9±3.2	
Pb^{2+}	100	512.2±33.0	0.08
	10	182.4±1.3	1*
	1	108.6±1.9	
Zn^{2+}	100	1110.9±29.5	0.07
	10	260.5±3.9	0.1*
	1	106.2±5.6	
Ca^{2+}	5000	BDL	>5
	500	98.5±.5.5	
	100	99.7±3.8	
	10	99.4±4.1	
	1	100.3±5.3	
Mg^{2+}	700	BDL	>10
	100	99.0±5.4	
	10	103.4±2.7	
	1	98.2±4.6	
Cl^{-}	5000	BDL	-
	1000	98.8±2.9	
	100	99.7±4.3	
	10	103.9±3.1	

Table 7.3 Effects of foreign ions for the determination of 10 ng/mL Al(III) (n=3) (Continue)

Ion	Concentration of Interfering Ion(µg/mL)	Recovery(%)of Aluminium Ion	Tolerable Concentration of Interfering Ion (µg/mL) for 2 ng/mL Al (*20 ng/mLAl) (Hernandez and Escriche, 1984)
HCO_3^-	1000	BDL	-
	100	98.1±4.1	
	10	99.7±3.2	
NO_3^-	100	BDL	>10
	10	110.9±2.1	
	1	100.3±6.2	
PO_4^{3-}	100	BDL	0.8
	10	23.1±5.1	
	1	93.3±4.9	
SO_4^{2-}	100	BDL	>1
	10	39.4±2.7	
	1	95.4±2.9	
Without another added interfering ion (Ni^{2+} from dissolution of the sorbent)	80	103.5±4.9	>5

Detection limit was found as 0.011 ng/ml.

The sorption efficiencies of 100 µg/mL interfering ions were found to be above 95% for Cu^{2+}, Cr^{3+} and Fe^{3+}; 40.2% for Zn^{2+}, and 53.7% for Pb^{2+}. The sorption efficiencies of Cl^- were 35.4% for 5000 µg/mL, 86.2% for 1000 µg/mL, 99.7% for 100 µg/mL, and 99.2% for 10 µg/mL. The sorption efficiencies of HCO_3^- were above 99% at the studied concentrations. Ca^{2+} and Mg^{2+} were not adsorbed at studied concentrations by the sorbent. By dissolution of the sorbent, after sorption, the concentrations of these ions in the final solution that is used for Al(III) determination were measured as 99.0 µg/mL, 95.7 µg/mL, 97.6 µg/mL, 41.0 µg/mL and, 51.7 µg/mL for Cu^{2+}, Cr^{3+}, Fe^{3+}, Zn^{2+}, Pb^{2+}, respectively.

Concentrations of unadsorbed aluminium in the supernatant solutions were found to be below the detection limit. When these results were compared with that reported in the literature by Hernandez and Escriche (1984), it can be said that the use of Ni/Ni$_x$B is also higly effective for eliminating or reducing interfences such as Cu^{2+}, Cr^{3+}, Fe^{3+}, Zn^{2+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, PO$_4^{3-}$ on the fluorimetric aluminium determination as well as preconcentration. However, both studies had similar tolerable concentrations for Pb^{2+}, NO$_3^-$, and SO$_4^{2-}$.

As seen in Table 7.3 Pb(II) and Zn(II) had positive interferences on 10 ng/mL of Al(III). Therefore, the formation of the morin complexes of Pb(II) and Zn(II) were also examined. Calibration graphs (0.0-0.1-1.0-5.0 µg/mL) that belong to these complexes were plotted in Figure 7.14, Figure 7.15 and Figure 7.16. Fluorescence intensities were measured at the aluminium measuring conditions at 495 nm for both complexes and also their fluorescence peak maximum, 505 nm for Pb(II)-morin, and 499 nm for Zn(II)-morin. It was seen that morin complexes of Pb(II) and Zn(II) gave raise to spectral interferences on aluminum signal.

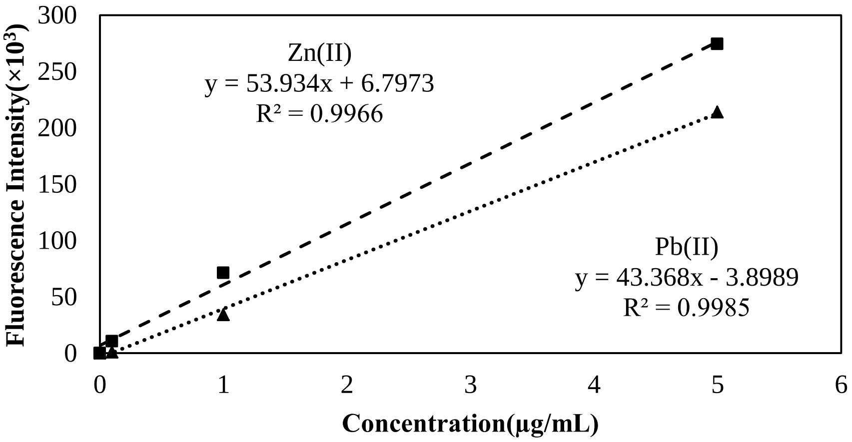


Figure 7.14. Calibration graph of Pb(II)-morin and Zn(II)-morin for emissions at 495 nm.

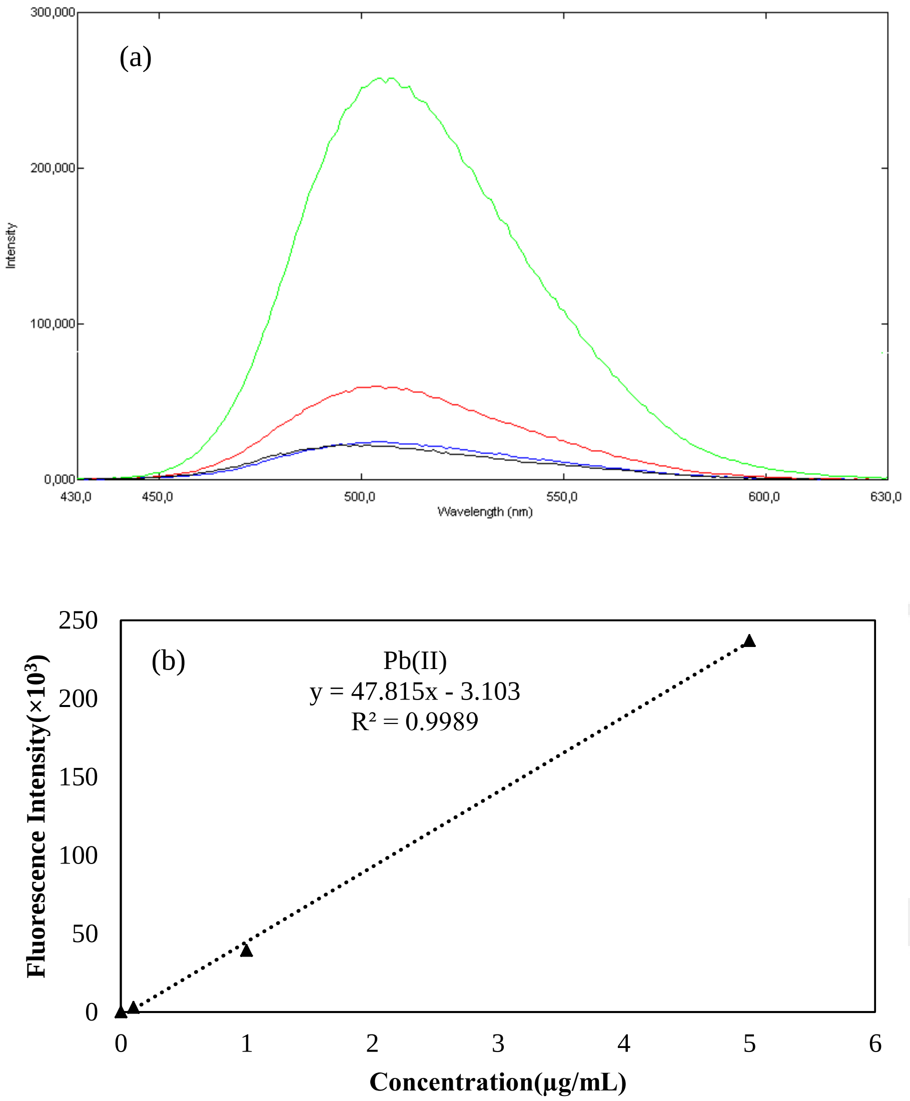
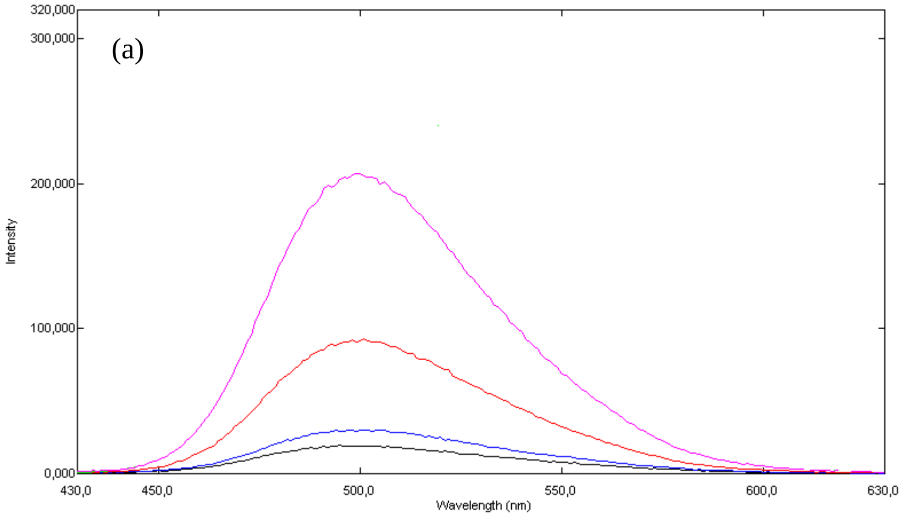


Figure 7.15. Fluorescence spectrum of Pb(II)-morin at 505 nm (a), Calibration graph of Pb(II)-morin (b).



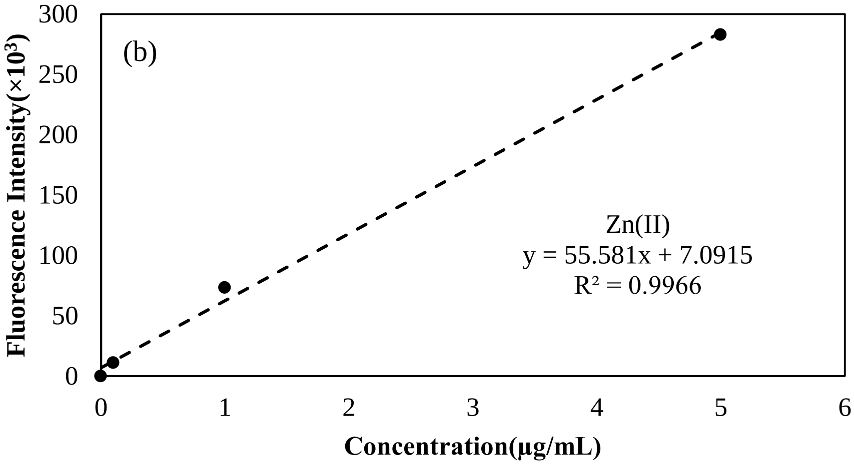


Figure 7.16. Fluorescence spectrum of Zn(II)-morin at 499 nm (a), Calibration graph of Zn(II)-morin (b).

7.11 Investigation of Sorption Efficiencies of NO_3^-, SO_4^{2-} and PO_4^{3-}

To investigate sorption efficiencies of nitrate, sulphate and phosphate ions, 25 mL various concentrations of ions were added onto 10 mg sorbent. After shaking for an hour, unadsorbed ions in the supernatants were analyzed by UV-Vis spectrophotometer. The results were shown in Table 7.4.

Table 7.4 Sorption Efficiencies of NO_3^-, SO_4^{2-} and PO_4^{3-} (n=3).

Analyte	Sorption Efficiency (%)
30 µg/mL NO_3^-	2.2±1.2
10 µg/mL NO_3^-	98.5±1.8
30 µg/mL SO_4^{2-}	11.6±1.2
10 µg/mL SO_4^{2-}	63.9±2.8
1 µg/mL SO_4^{2-}	99.6±2.0
30 µg/mL PO_4^{3-}	7.2±0.6
10 µg/mL PO_4^{3-}	24.7±2.3
1 µg/mL PO_4^{3-}	97.8±1.4

According to the Table 7.4, sorption efficiencies of sulfate and phosphate were above 5%, while nitrate did not adsorbed significantly at 30 µg/mL. The lower concentrations of these ions were adsorbed with higher sorption efficiencies showing that the sorbent had low capacity for studied ions.

7.12 Capacity of the Sorbent

Investigation of sorbent capacity was executed by shaking 10 mg sorbent with 500 µg/mL 50 mL Al(III) solution for 2 hours. After sorption, supernatant and sorbent were separated and sorbent was washed with ultrapure water twice. Then, the sorbent was dissolved by 0.1 mol/L HCl. Finally, the adsorbed Al(III) was measured. The sorption capacity was found to be 393.8±29.1 mg Al(III)/g sorbent.

7.13 Sorption Isotherm Models

The Langmuir, Freundlich and Dubinin-Radushkevich models are among the most frequently used isotherm models. The adsorption type of the Al(III) was examined by using these models.

Isotherm equations are;

$$\frac{C}{q} = \left(\frac{1}{Q_{max}}\right) C + \frac{1}{bQ_{max}} \qquad \text{Langmuir Equation}$$

$$\log q = \log K + n \log C \qquad \text{Freundlich Equation}$$

C: Equilibrium concentration of the solution (mg/L),

q: Amount of sorbed arsenic(mg)/amount of sorbent (g),

b: Langmuir constant (L/mg),

Q_{max} = The monolayer adsorption capacity (mg/g),

K: Freundlich Constant, adsorpton capacity (mg/g),

n: Freundlich Constant, intensity of the adsorbent (dimensionless).

Dubinin-Radushkevich (DR) isotherm was plotted for understanding the sorption type of Al(III) on Ni/Ni_xB.

$$\ln Q = \ln Q_{max} - k\varepsilon^2 \qquad \text{DR Equation}$$

Where ε (Polany potential) is (RTln(1+1/C_2)), Q the amount of Al(III) sorbed per unit weight of sorbent (mol/g), Q_{max} the sorption capacity (mol/g), C_2 the equilibrium concentration of aluminium in aqueous solution (mol/L), k is a constant related to adsorption energy (mol^2/kJ^2), R the gas constant (kJ/mol.K), and the T absolute temperature (K).

The mean free energy of sorption (E) (kJ/mol), defined as the free energy change when one mole of ion is transferred to the surface of the solid from infinity in solution can be calculated from the k value using the equation:

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

The value of E is used for predicting the type of adsorption. When the value is below 8 kJ/mol it means physical adsorption occures and when the values in the range of 8-16 kJ/mol, then the adsorption is actualized by chemisorptions or ion exchange.

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

$$\boldsymbol{R_L = (\frac{1}{1 + bC_0})}$$

where C_0 is the initial concentration and b is the Langmuir isotherm constant. R_L values below 1 indicate favorable adsorption and when the values higher than 1, it means adsorption is unfavorable.

Sorption capacity and sorption type were investigated by drawing sorption isotherm graphs. The concentration of aluminium was selected as 0.1, 10, 50, 100, 300, 500, 1000 and 2000 µg/mL at pH 3.30. 25 mL of these solutions were added on 10 mg of sorbent and shaken for two hours at 25 $^{\circ}$C. Unadsorbed aluminium was measured. The graphs are shown in Figures 7.17, 7.18, 7.19 and 7.20. It was found that only Langmuir isotherm has the maximum correlation coefficient for the linear regression. It indicates the monolayer sorption process was occurred. According to Langmuir isotherm, maximum capacity of aluminium was calculated as 400 mg/g by dividing slope to 1. According to D-R isotherm, the value of E indicating the type of adsorption was calculated as 15.81 kJ/mol. Since the value is in the range of 8-16 kJ/mol, then the adsorption is actualized by chemisorptions or ion exchange. The R_L values for the various initial concentrations are shown in Figure 7.21. The values obtained shows that our system is favorable. The constant values of Langmuir, Freudlich, and D-R isotherm are summarized in Table 7.5.

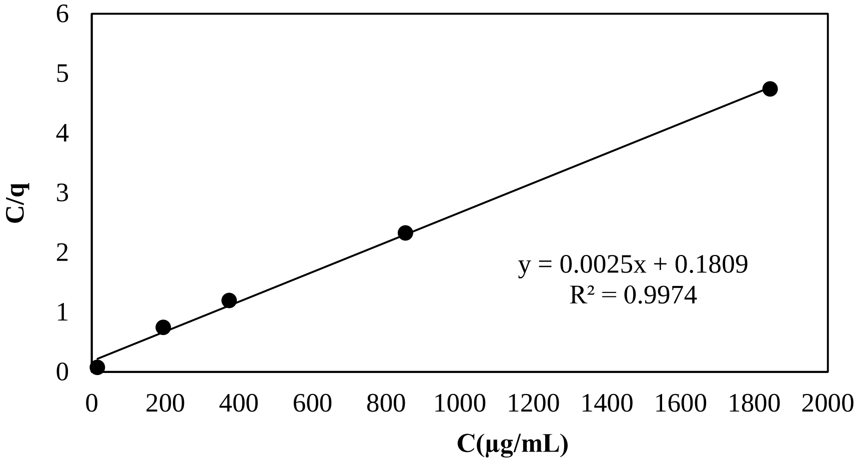


Figure 7.17. Langmuir isotherm for the sorption of Al(III) on sorbent (25 mL of 0.1, 10, 50, 100, 300, 500, 1000 and 2000 µg/mL at pH 3.30 Al(III) solution added on 10 mg adsorbent at 25°C).

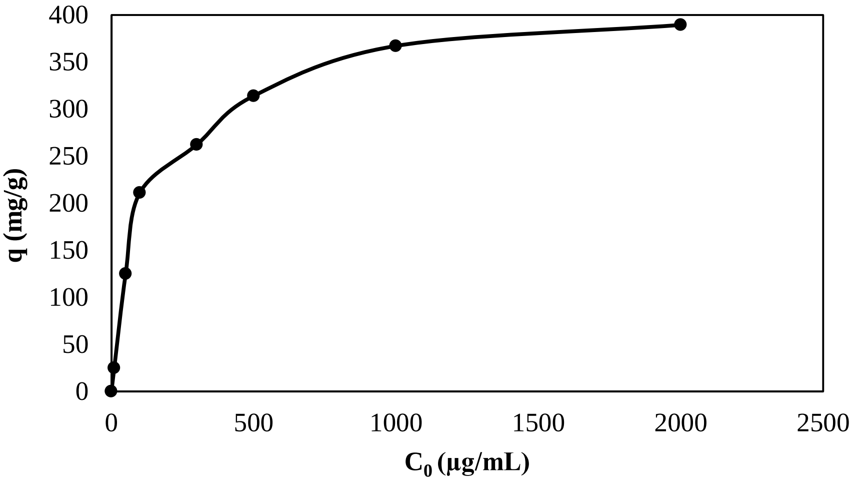


Figure 7.18. The graph of q (mg/g) versus initial aluminium concentration (µg/mL) (25 mL of 0.1, 10, 50, 100, 300, 500, 1000 and 2000 µg/mL at pH 3.30 Al(III) solution added on 10 mg adsorbent at 25°C).

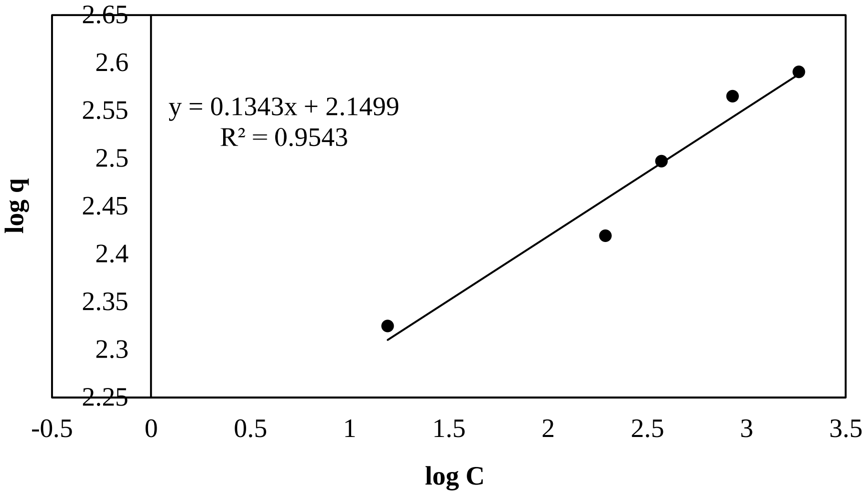


Figure 7.19. Freundlich isotherm for the sorption of aluminium on sorbent (25 mL of 0.1, 10, 50, 100, 300, 500, 1000 and 2000 µg/mL at pH 3.30 Al(III) solution added on 10 mg adsorbent at 25°C).

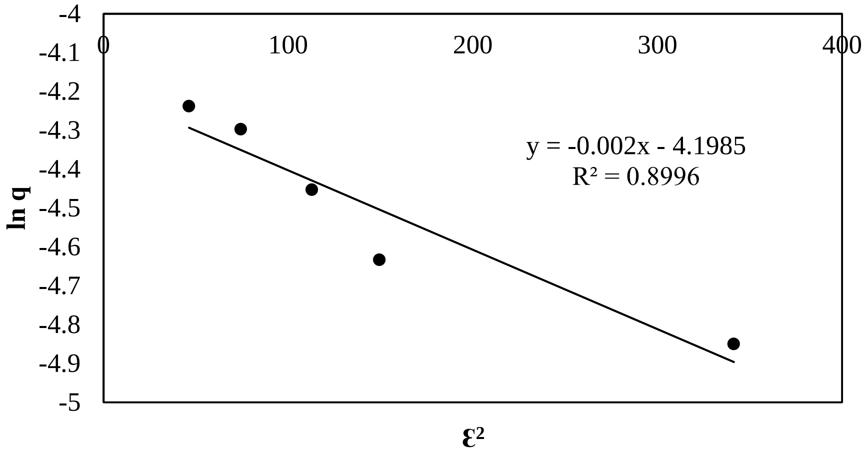


Figure 7.20. D-R isotherm for the sorption of aluminium on sorbent (25 mL of 0.1, 10, 50, 100, 300, 500, 1000 and 2000 µg/mL at pH 3.30 Al(III) solution added on 10 mg adsorbent at 25°C).

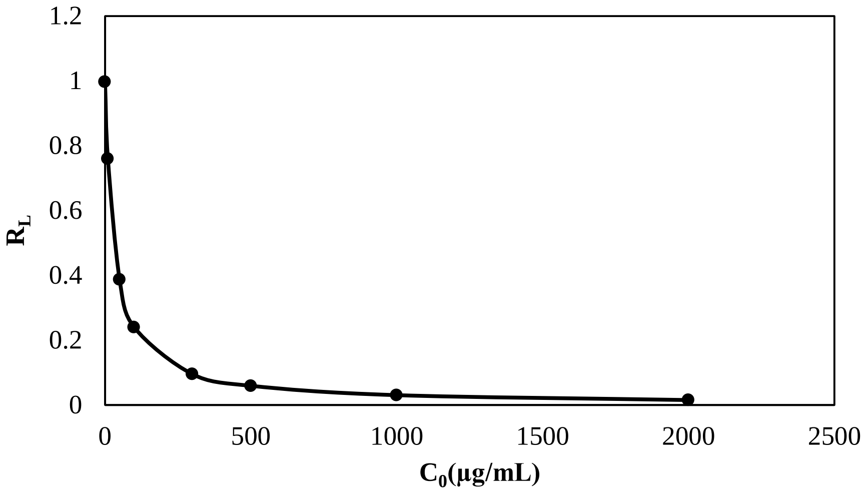


Figure 7.21. R_L values vs initial aluminium concentration.

Table 7.5 Parameters of Langmuir, Freundlich, and D-R isotherm.

	Aluminium
Langmuir Isotherm	
Q_{max} (mg/g)	400.0
b (L/mg)	0.001382
R^2	0.9974
Freundlich Isotherm	
n	0.1343
K (mg/g)	141.2
R^2	0.9543
D-R Isotherm	
E (kj/mol)	15.81
Q_m (g/g)	0.4052
Q_m (mol/g)	0.01502
k (mol^2 /kJ^2)	0.002
R^2	0.8996

7.14 The Amount of Ions Released During Sorption

In this study the amount of nickel, boron, sulphate and, sodium released from sorbent during Al(III) sorption was investigated. The supernatants obtained after adding ultrapure water on the adsorbent was used as a blank. 25 mL of 100 ng/mL aluminium was added on 10 mg sorbent at pH~4 for 30 min. were analyzed (n=3).

It was found that the supernatants contained 6.596±0.016 μg/mL nickel (it corresponds to 0.1649±0.0004 mg Ni(II)) and 7.017±0.261 μg/mL Ni(II) (0.189±0.007 mg Ni(II)) after shaking with water and, aluminium respectively.

Released boron, sulphate, nitrate and sodium amounts after shaking with water were also calculated as 0.091±0.005, 0.054±0.007, 0.021±0.003, 0.004±0.005 mg , while after shaking with aluminium 0.108±0.006 mg, 0.052±0.009 mg, 0.024±0.020 mg, 0.0047±0.0006 mg, respectively (n=3).

In order to investigate whether displacement between nickel and Al(III) takes place, 25 mL of 0-10-25-50-100 μg/mL Al(III) were added on 10 mg sorbent and the solutions have been shaken for 2 hours. After sorption, amount of nickel in the supernatants were determined (n=3). The results are shown in Table 7.6. Aluminium was quantitatively adsorbed in all the solutions. The correlation graphs for the concentrations of Ni(II) passed into the supernatant solution and initial Al(III) concentration are shown in Figure 7.22 and Figure 7.23.

Table 7.6 Variation of nickel and boron amounts passed into the solution with Al(III) amounts added on the sorbent during sorption (n=3).

Initial Al(III), µg/mL	Al(III), mmol	Ni(II), µg/mL (25 mL)	Ni(II), mmol	Net mol ratio of Ni(II)/Al(III)	B, µg/mL (25 mL)	B, mmol	Net mol ratio of B/Al(III)	Initial pH of the Al(III) solutions
0	0.0000	6.9	0.0029	-	3.619	0.0084	-	4.71
10	0.0093	52.3	0.0223	2.085	5.981	0.0138	0.590	4.70
25	0.0231	77.5	0.0330	1.299	6.774	0.0157	0.315	4.71
50	0.0463	114.3	0.0487	0.987	10.230	0.0237	0.330	4.75
100	0.0926	252.5	0.1076	1.130	11.173	0.0258	0.189	4.71

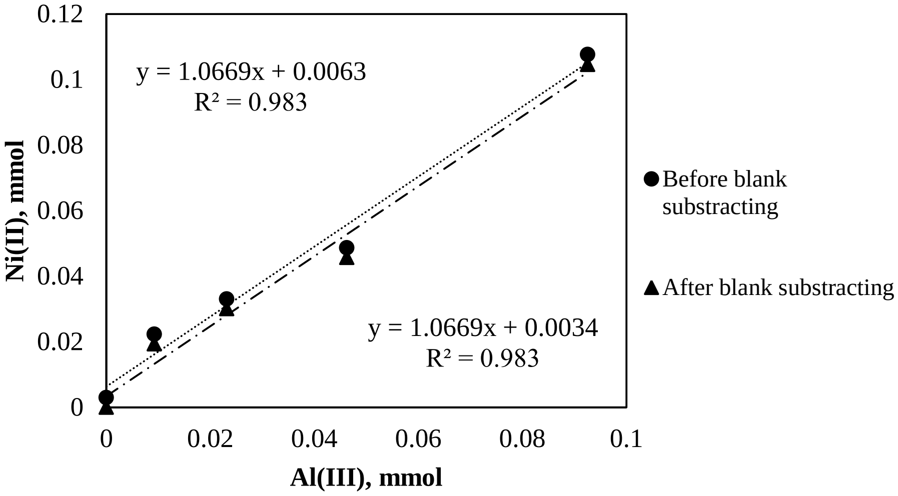


Figure 7.22. The correlation graphs for the concentrations of Ni(II) passed into the supernatant solution and initial Al(III) concentration, mmol.

Although displacement between nickel and aluminum was not salient at trace level, at the higher concentrations correlation became evident. The correlation coefficient was found to be 0.983. The mol ratio of Ni(II) dissolved to Al(III) adsorbed varies between 0.987 and 2.085. It may be assumed that some of the Al(III) is adsorbed by the nanonickel in the adsorbent and, therefore, the mol ratio is below unity.

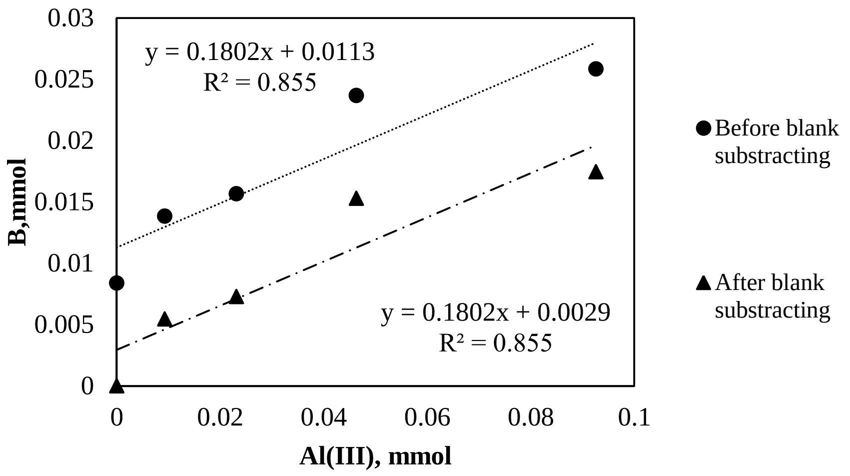


Figure 7.23. The correlation graphs for the concentrations of boron passed into the supernatant solution and initial Al(III) concentration, mmol.

The correlation coefficient between aluminium and boron concentration passed into the solution are quite low (R^2:0.855).

7.15 Calibration Graphs for Al(III) Determination

7.15.1 Calibration graph for trace Al(III) determination

In order to determine trace aluminium, the method developed by Hernandez and Escriche (1984) was used.

According to this method 4 mL of IBMK and 4 mL 0.0125% morin solution (in 86 mL ethanol+ 9 mL methanol+ 5 mL water) are placed in a 25 mL beaker and aluminium solution with final concentration between 0 and 20 ng/mL is added. The pH is adjusted to 3.55-3.95 with HCl-KCl solution and NaOH, and then the mixture is diluted to 10 mL with water. After 1 h, the fluorescence intensity is measured at 25°C, by excitating at 418 nm and measuring emission at 495 nm. The obtained fluorescence spectrum and related calibration graph are shown in Figure 7.24 and 7.25, respectively.

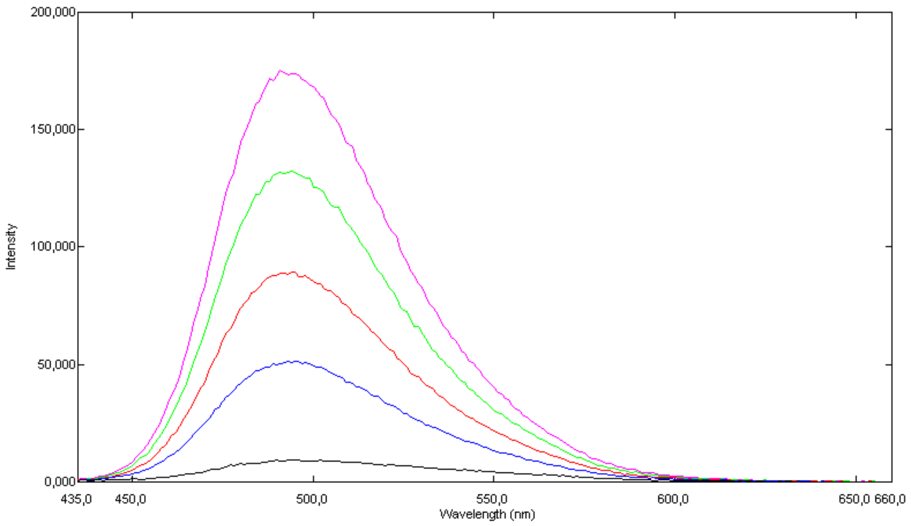


Figure 7.24. Fluorescence spectrum of Al(III)-morin/IBMK-ethanol-water system (at pH~3.60, λ_{exc} 418 nm, λ_{em} 495 nm, slit 3 nm, concentration range: 5-20ng/mL).

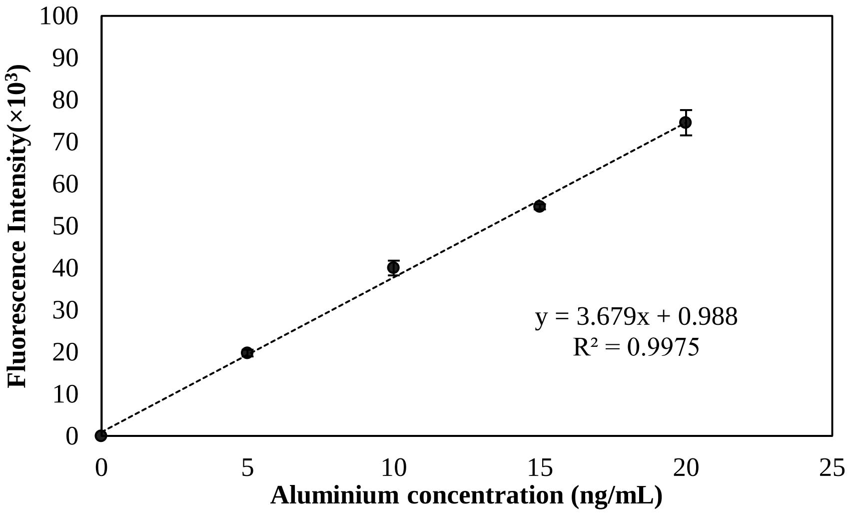


Figure 7.25. Calibration graph for Al(III)-morin/IBMK-ethanol-water system (at pH~3.60, λ_{exc} 418 nm, λ_{em} 495 nm, slit 3 nm, n=3)

7.15.2 Calibration graph for nickel containing standards

The effect of nickel on fluorescence intensity of Al(III)-morin/IBMK-ethanol-water system was examined by using various standard aluminium solutions. In sorption studies it was observed that Ni(II) ions passed into the solutions from the sorbent during shaking. After appropriate dilution, it was analyzed and calculated that the solutions that are used for measurements contains about 1.0 µg/mL Ni(II). However, in recovery studies Al(III) sorbed sorbent was dissolved completely in HCl and after appropriate dilution, it was found that the measuring solutions contains 60 µg/mL Ni(II).

Nickel-free standards (standard series) and also Al(III) standards with added 1 µg/mL and 60 µg/mL of nickel were used. For the preparation of matrix match standards that will be used for the analysis of aluminium in the supernatant solutions of the adsorption, known amount of aluminium were added on the supernatant solution of the blank sorbent. For the determination of Al(III) in the sorbent, the blank sorbent was dissolved in 0.1 mol/L HCl acid and calibration standards were prepared by adding Al(III) into these solutions to prepare matrix match standards. The related graphs are shown in Figure 7.26, Figure 7.27, Figure 7.28.

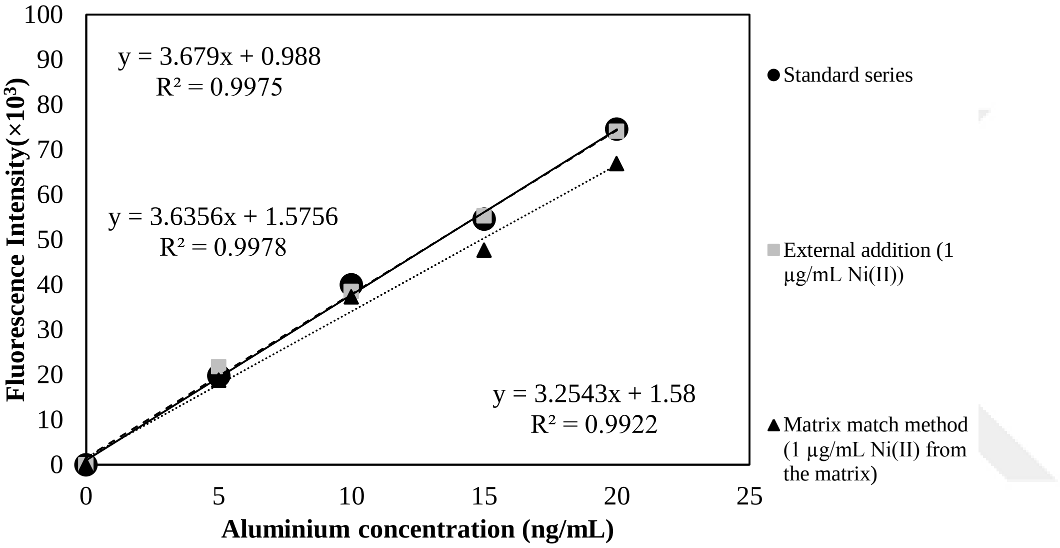


Figure 7.26. The calibration graph of 1 µg/mL nickel containing Al(III) standard series for the examination of the calibration graph for Al(III) analysis in supernatant solution.

The decrease in fluorescence intensity of aluminium were 1.2% and 12% for 1 µg/mL nickel containing standard and 1 µg/mL nickel containing standards prepared matrix match method, respectively.

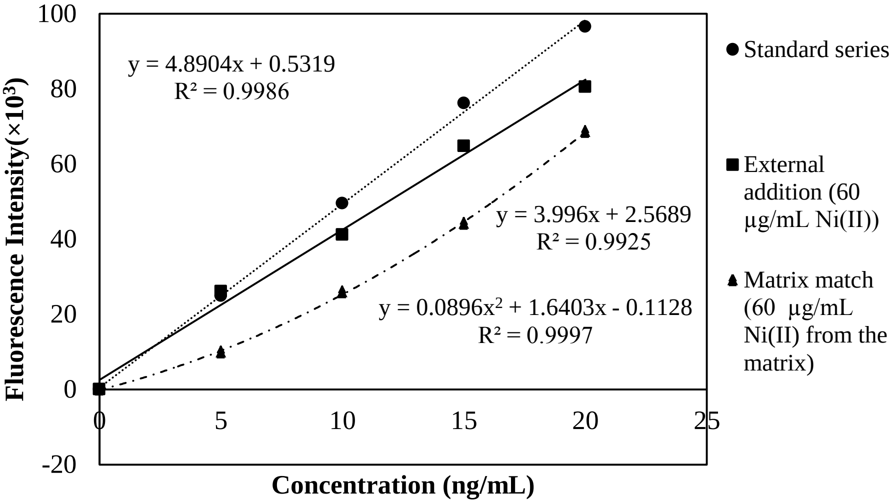


Figure 7.27. The calibration graphs of standards series and 60 µg/mL nickel containing aluminium standards prepared by external addition and by matrix match.

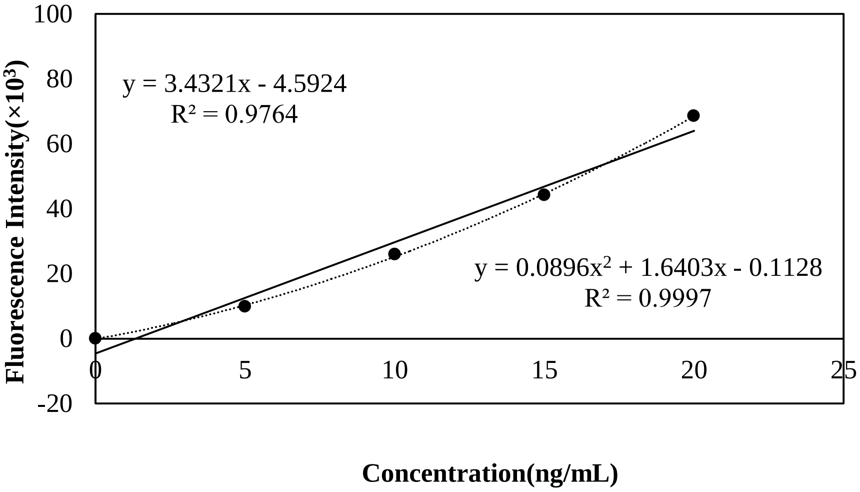


Figure 7.28. The calibration graph of 60 µg/mL nickel containing aluminium standards prepared by matrix match method.

It was understood that in the presence of 60 µg/mL of nickel (external addition), fluorescence intensity of aluminium decreased by 18%. However, in the matrix match method containing 60 µg/mL of Ni(II), suppression of the Al(III) signal increased at low concentrations of the aluminium. The suppression on the 5, 10, 15 and 20 ng/mL Al(III) signals were 60.3, 47.6, 42.0 and 29.0%, respectively.

Although 1 µg/mL of nickel containing standard and standards prepared by matrix match method included the same amount of nickel, the decrease in signal in the matrix match was bigger than that of signals obtained by external Ni(II) addition. Differences in the decreases between two series of standards may be attributed possibly to the presence of other ions in the standards prepared by matrix match method.

Furthermore, in the presence of 200 μg/mL of nickel, the signal intensity of aluminium standards can not be obtained.

Calibration graphs were also drawn by standard addition technique. In this case, aluminium standards were added directly onto equal volume of the same sample solution. The graph is shown in Figure 7.29.

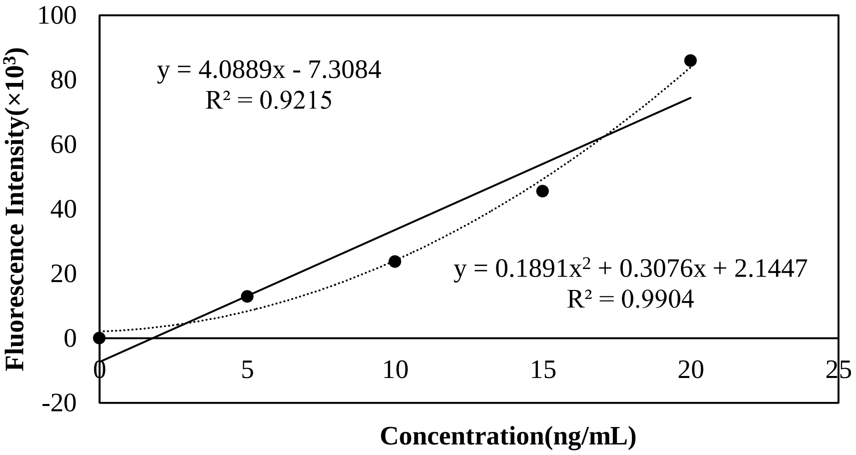


Figure 7.29. The calibration graphs obtained by adding aluminium standards to the sample solutions (standard addition technique).

Correlation coefficient of the standard addition graph is higher when graph is drawn by as a polynomial equation. Curve line structure of the graph shows again the presence of higher signal suppression at low concentration of aluminium.

7.15.3 Calibration graph obtained by adding standards onto the sorbents and following the sorption procedure

50 mL of 5, 20, 40, 70 and 100 ng/mL Al(III) standards were added on 5 mg portions of the sorbent. The solutions were shaken for an hour. The sorbents were separated from the solution by ultracentrifuge and then dissolved in 5 mL 0.1 mol/L HCl. 1 mL of this solution was taken and, diluted to 10 mL with distilled

water(contains 100 µg/mL of Ni^{2+}). The calibration graph obtained is shown in Figure 7.30 and after excluding standards of 70 and 100 ng/mL of Al(III) in Figure 7.31.

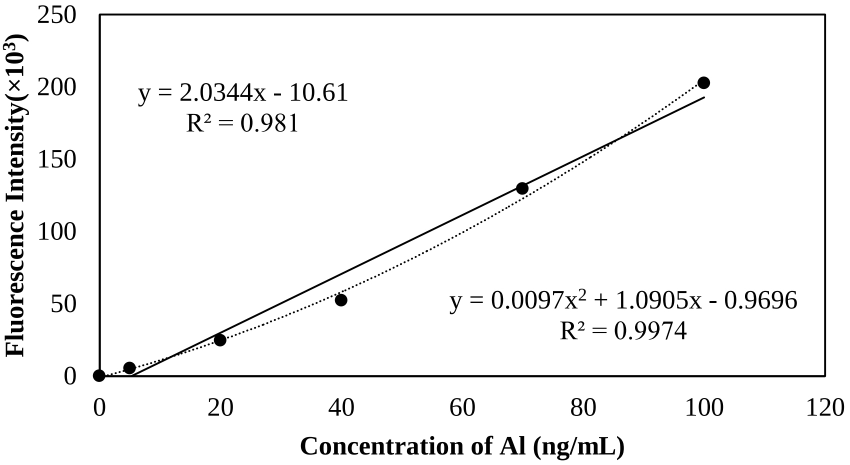


Figure 7.30. Calibration graph in the range 0 to 100 ng/mL Al(III) by adding standards on the sorbent (measuring solutions contain: 100 µg/mL Ni(II)).

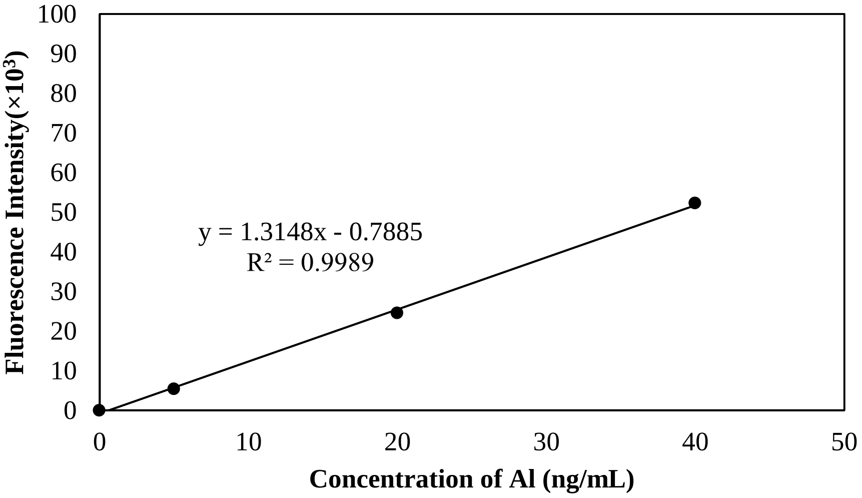


Figure 7.31. The calibration graph ranged from 0 to 40 ng/mL aluminium by dissolving sorbent after sorption of the standards (solutions contain: 100 µg/mL Ni(II)).

The decrease in the signals in the Figure 7.30 is due to the higher concentration of Ni(II) and thus, higher suppression of the signals.

7.15.4 Comparison of the calibration graphs

In this study, three kinds of calibration graphs in the range of 5-20 ng/mL were examined. The calibration graphs were prepared as standard series, matrix match (standard additions on the dissolved blank sorbent), and standards prepared by adding Al(III) on the sorbent. Final concentrations of nickel in the measuring solutions were 30 µg/mL in matrix match series and the series obtained by adding Al(III) on the sorbents.

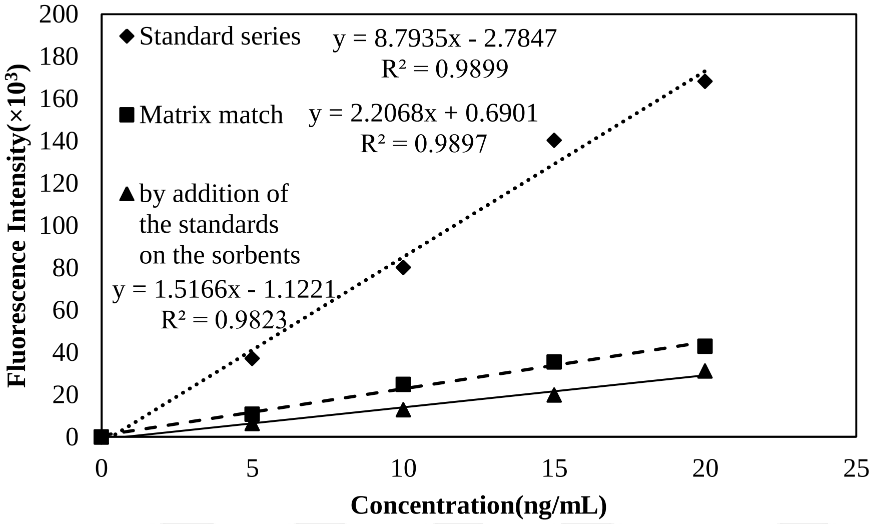
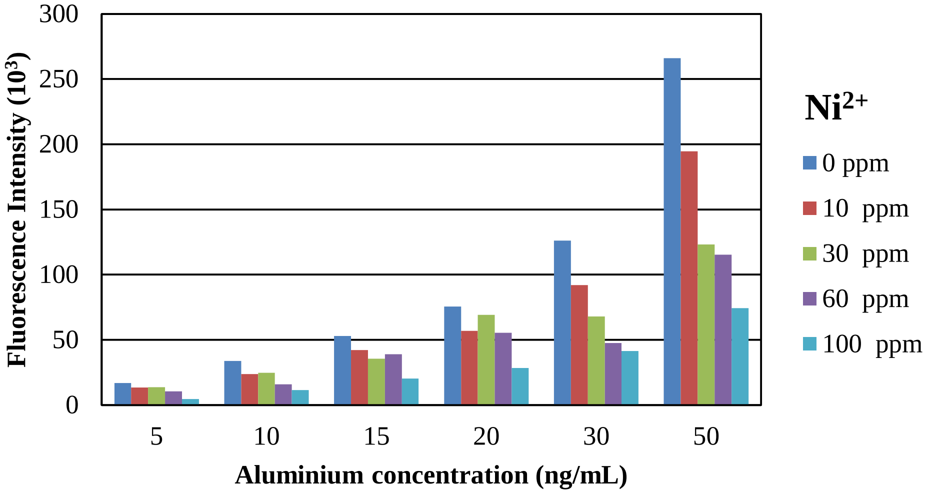


Figure 7.32. Comparison of the calibration graphs ranged from 0 to 20 ng/mL.

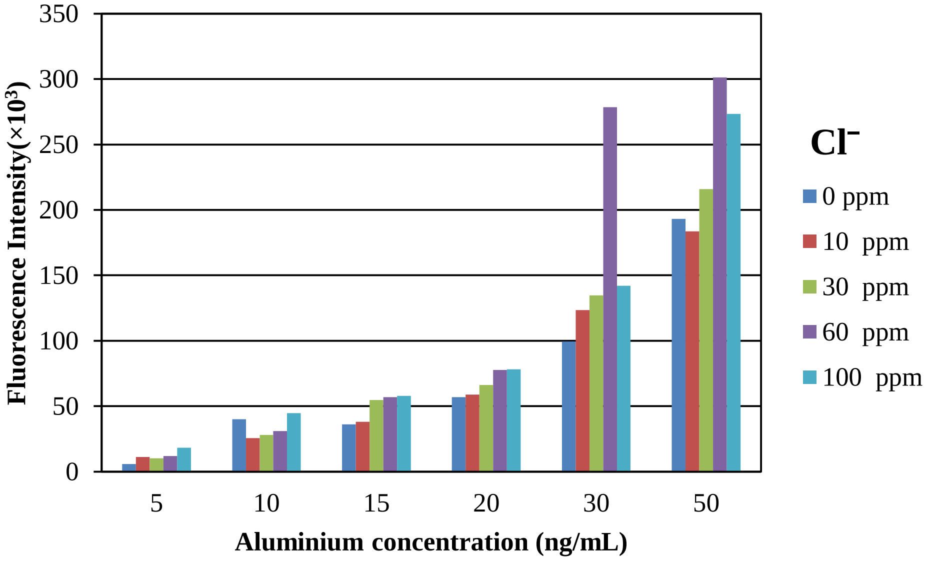
Figure 7.32 displays lineer calibration graphs in the range of 0-20 ng/mL Al(III). It was clearly seen that slopes of the graphs decreased from the standard series to graphs obtained by addition of the standards on the sorbents. Since diversity and amount of the ion in the calibration standards obtained by dissolution of the sorbent after the aluminium sorption were increased, the reducing of the slope can be expected. Although the slope of the curve was low, it represented the matrix components better and, therefore, was used in the following experiments.

7.15.5 The diverse ion effects on the calibration graphs obtained by direct fluorescence measurement without employing adsorption procedure

In order to investigate the effect of diverse ions on calibration graphs, various concentrations of Ni^{2+}, Cl^-, B, SO_4^{2-}, NO_3^-, HCO_3^- were used. The concentrations of diverse ions and Al(III) were selected as 0-10-30-60-100 µg/mL and 0-5-10-15-20-30-50 ng/mL, respectively. The results are shown in Figure 7.33, Figure 7.34 and Figure 7.35.

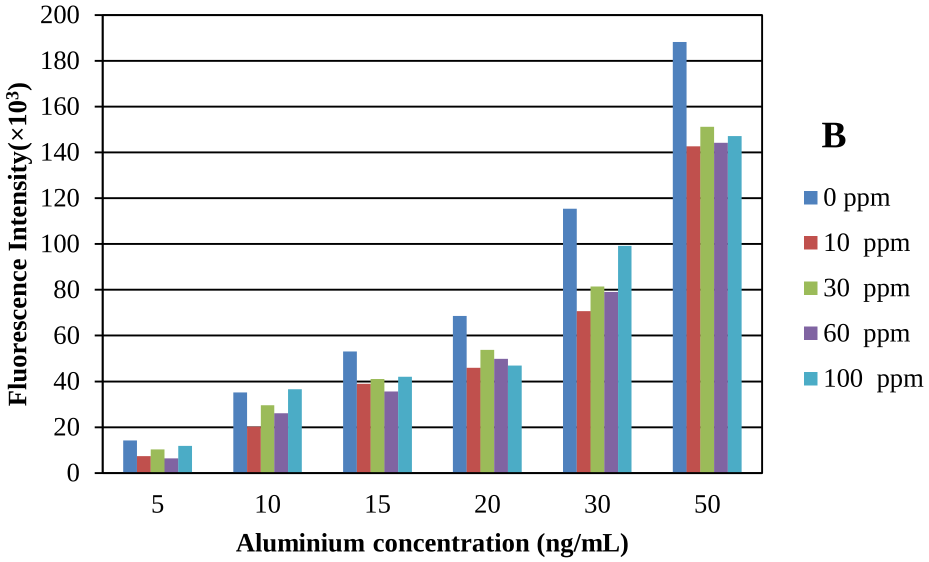


(a)

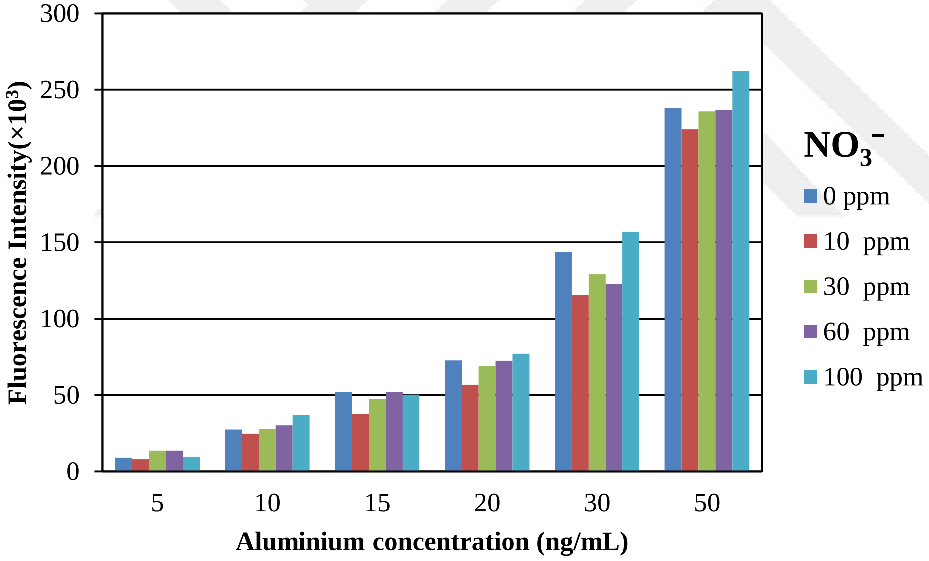


(b)

Figure 7.33. The effect of nickel ions (a) and chloride ions (b) on the calibration graph.

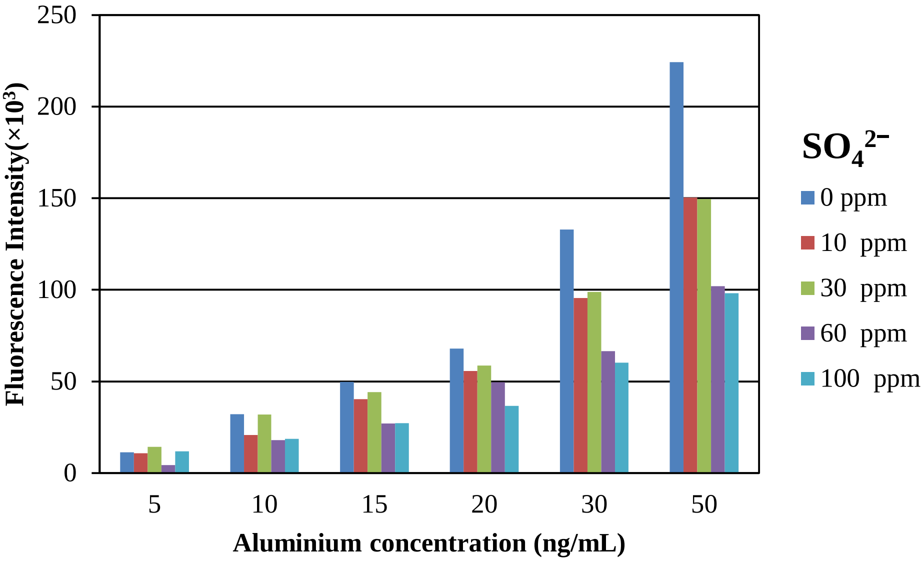


(a)

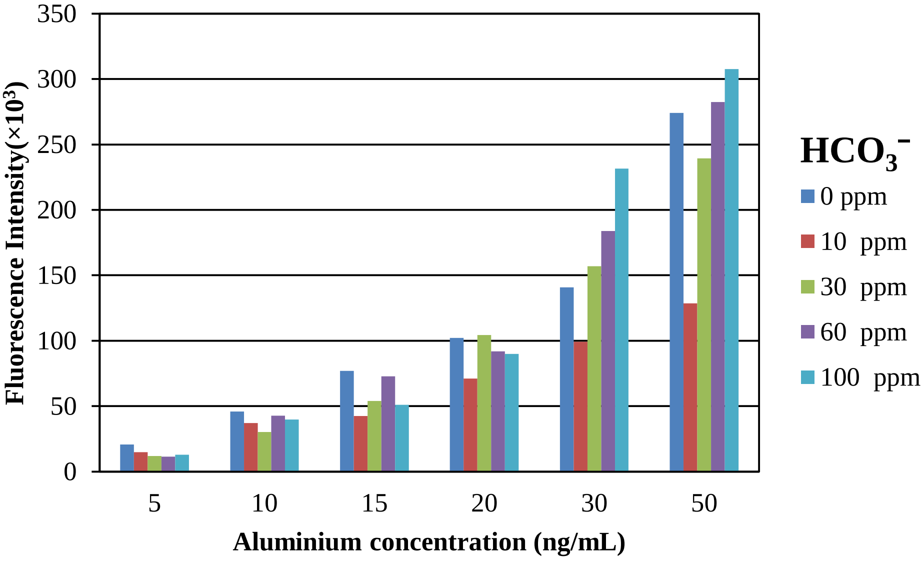


(b)

Figure 7.34. The effect of boron ions (a) and nitrate ions (b) on the calibration graph.



(a)



(b)

Figure 7.35. The effect of sulfate ions (a) and HCO_3^- ions (b) on the calibration graph.

It was observed that Ni^{2+}, SO_4^{2-}, B and NO_3^- decreased the fluorescence intensity of aluminium, on the other hand HCO_3^- effect is variable and Cl^- had enhancing effects on the signal intensity of aluminium. The interference effects increase with increasing concentration of the diverse ion as expected.

7.15.6 The effects of both Ni^{2+} and B (as H_3BO_3) on the calibration graph

After dissolution of 10 mg sorbent and appropriate dilutions, the final solution was calculated to contains approximately 60 µg/mL Ni(II) and 1 µg/mL B. The concentration of Ni(II) was also confirmed by AAS measurements. In order to examine how both ions affect the calibration graph obtained by matrix match method, standard solutions in the range of 0-20 ng/mL Al(III) were prepared by adding Ni(II) and B solutions. In the presence of Ni(II) and B, it was observed that calibration graph was linear up to 20 ng/mL of Al(III) in Figure 7.36.

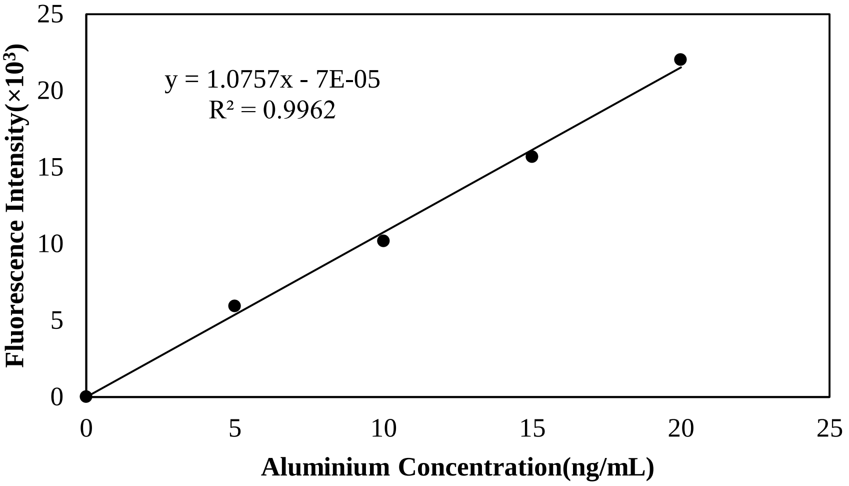


Figure 7.36. The effect of Ni(II) and B on calibration graph in the range of 0-20 ng/mL.

It was known that in the presence of Ni(II) and B ions, fluorescence intensity of aluminum decreased. When comparing Figure 7.36 with standard series in Figure 7.27, decrease in the slope was found as 78%.

7.16 Analytical Figures of Merit

Precision:

In order to examine precision of the method, 10 mg of sorbents were shaken with water (accepted as blank solution) at pH 4 and then, sorbents were dissolved in 0.1 mol/L HCl. After appropriate dilutions, the average of fluorescence intensities of these solutions was found as 13.597. The standard deviation and relative standard deviation (RSD) for the determination of the blank signal was calculated as 0.306 and 2.25% (n=7), respectively.

The standard deviations and relative standard deviations for the determination of 15 ng/L aluminium solutions (which was obtained after dissolution of 25 mL 100 ng/mL of aluminium adsorbed sorbent and dilution according to the procedure.) were 0.231 and 1.57% (n=9), respectively.

The standard deviation for the standard solution of 10 ng/mL of aluminium by preparing matrix match method was also evaluated. The standard deviation and relative standard deviation were found to be 0.655 and 1.12% (n=7), respectively.

Accuracy:

The accuracy of the proposed method was tested by determining the content of Al(III) ions in the certified reference materials (EnviroMAT^{TM} Drinking Water-Low, Lot No: EL-2) containing various elements such as As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Sr, Zn, etc. under optimal experimental conditions. After diluting the SRM solution 1000 fold, 25 mL of diluted SRM solution was added onto the 5 mg of sorbent and was shaken for an hour. Supernatant and the sorbent were separated by ultracentrifuge. The sorbents were dissolved by 5 mL 0.1 mol/L HCl. The adsorbed aluminium concentration was measured.

As seen in Table 7.7, the determined values were in good agreement with the certified values. The relative error was found about 5%.

Table 7.7 Determination of Al(III) in certified reference material, EnviroMAT^{TM} Drinking Water-Low, Lot No: EL-2, (n=3).

Analyte	Consensus Value, (µg/mL)	Confidence Interval, (µg/mL)	Tolerance Interval, (µg/mL)	Found Value, (µg/mL)	Relative Error, (%)	RSD, (%)
Al	0.10	0.10-0.11	0.07-0.13	0.0947±0.0054	-5.3	5.71

Limit of Detection (LOD) and Limit of Quantitation (LOQ):

In order to determine the instrumental detection limit for aluminium, 50 mL of 1 ng/mL Al(III) were added on 4 mg sorbent. After shaking for half an hour, sorbents were separated from the solution and dissolved in 0.1 mol/L HCl. Sorbed aluminium was determined (n=11). The instrumental detection limit based on three times the standard deviation of the blank (*LOD_i*=3σ/m, where m is the slope of the calibration curve) and limit of quantification were found to be 0.11 ng/mL and 0.36 for Al(III), respectively. The analytical limit of detection (LOD_a) (Dubiella-Jackowska et al., 2009; Yalcınkaya et al., 2012) has been calculated by dividing the instrumental detection limit by the enrichment factor. The enrichment factor was found by dividing initial volume of the sample to final eluent volume (Wang et al., 2012). The enrichment factor was found as 50 by dividing initial volume of sample (250 mL) to final sample volume (5 mL). The LOD_a were 2.2 pg/mL for Al(III) and the analytical *LOQ* (Dubiella-Jackowska et al., 2009; Yalcınkaya et al., 2012) based on 10σ/m were 7.2 pg/mL. The relative standard deviation of the method was calculated as 14% (n=11).

7.17 Application of the Method

The proposed preconcentration method was applied for the determination of aluminium in three haemodialysis solutions (concentrated acidic solution for haemodialysis (A), concentrated basic solution for haemodialysis (B) and, mixture of them diluted by 35 times with distilled water (dialysis solution) (C)). The dialysis solutions for haemodialysis were collected from Ege University, İzmir.

The concentration (g/L) of each component was as follows.

(A) Concentrated acidic solution (Medicasol) (A): NaCl 214.60; KCl 5.22; $CaCl_2$ 7.718; $MgCl_2$ 3.558; CH_3COOH 4.207 (pH:3.10)

(B) Concentrated basic solution (Medicasol) (B): HCO_3^- 84 (pH:8.48)

(C) Dialysis solution : 1:1.225:32.775 (A:B:water) (pH:8.34)

50 mL of the sample solutions were added on 4 mg sorbent and shaken for an hour. After separating, sorbents were dissolved in 5 mL 0.1 mol/L HCl on hot plate. Then, concentrations of aluminium were measured. The results are given in Table 7.8 below.

Table 7.8 Determination of Al in dialysis fluids and various water samples (n=3).

Sample	Al(III)		
	Added(ng/mL)	Found(ng/mL)	Recovery(%)
DIRECT MEASUREMENT			
Concentrated acidic solution	-	BDL	-
Concentrated basic solution	-	BDL	-
Dialysis solution	-	BDL	-
Concentrated acidic solution after dilution 35 fold	-	BDL	-
Concentrated basic solution after dilution 35 fold	-	BDL	-
Tap water	-	24.3±1.1	-
AFTER PRECONCENTRATION PROCEDURE			
Concentrated acidic solution	-	BDL	-
	5	BDL	-
	10	BDL	-
Concentrated basic solution	-	BDL	-
	5	BDL	-
	10	BDL	-
Concentrated acidic solution after dilution 35 fold	-	3.4±0.1	-
	5	8.7±0.1	105.6±1.7
	10	13.9±0.4	104.8±2.6

Table 7.8 Determination of Al in dialysis fluids and various water samples (n=3) (Continue).

Sample	Al(III)		
	Added(ng/mL)	Found(ng/mL)	Recovery(%)
Concentrated basic solution after dilution 35 fold	-	3.1±0.3	-
	5	8.4±0.1	106.3±5.6
	10	13.3±0.3	101.4±3.3
Dialysis solution 1:1.225:32.775 (A:B:water)	-	8.4±0.2	-
	5	13.8±0.1	107.8±2.3
	10	18.7±0.5	102.6±4.2
Ultra pure water	-	BDL	-
	5	4.8±0.1	96.8±2.7
	10	11.0±0.2	109.6±2.3
Tap water	-	22.1±0.4	-
	5	27.4±0.3	105.9±4.6
	10	32.1±0.3	100.7±4.0

Analytical detection limit: 0.011 ng/ml.

Low recovery of aluminium determination in the concentrated acidic or basic solutions may be due to the effect of high concentration of the salts on the aluminium preconcentration or suppression effect on the aluminium fluorescence. In order to make it clear, chemical analyses were carried out. It was found that Mg^{2+}, Ca^{2+}, Na^{+}, and K^{+} were not sorbed by the sorbent at the measurable level during the preconcentration step. Cl^{-} and HCO_3^{-} are partly sorbed by the sorbent and their concentrations in the solution obtained by dissolving the sorbent after preconcentration procedure are shown in Table 7.9. Chloride concentration was measured by Mohr titration method and HCO_3^{-} concentration was measured by titration with NaOH against methyl red and then phenolphthalein indicators. Mg^{2+}, Ca^{2+}, Na^{+}, and K^{+} analysis were realized by AAS and flame photometer.

Table 7.9 Cl^- and HCO_3^- concentrations in the solution obtained by dissolving the sorbent after preconcentration procedure (n=3) (final volume: 5 mL).

	Adsorption in Concentrated acidic solution (mol/L)	Adsorption in Concentrated acidic solution after dilution 35 fold (mol/L)	Adsorption in Concentrated basic solution (mol/L)	Adsorption in Concentrated basic solution after dilution 35 (mol/L)	Adsorption in Dialysis solution (mol/L)
Cl^-	$7.3x10^{-2}$	$2.7x10^{-2}$	-	-	$2.6x10^{-2}$
HCO_3^-	-	-	$1.5x10^{-1}$	$4.3x10^{-2}$	$3.8x10^{-2}$

Although significant amout of adsorbed HCO_3^- is converted to CO_2 and lost during the dissolution of the sorbent in cold HCl, still quite high concentration of unlost HCO_3^- was measured. HCO_3^- concentration in the dissolved sorbent was measured by titration with NaOH against methyl red and then phenolphthalein indicators separately. The concentration of HCO_3^- is given by the difference between the titrations. According to the results in Table 7.9, it is understood that Cl^- concentration in the concentrated acidic solution and HCO_3^- concentration in the concentrated basic solution were above the sorbent capacity. The high concentrations of Cl^- and HCO_3^- ions hindered the determination of Al(III) while studying with concentrated acidic solution and concentrated basic solution.

The developed method was not efficient for the aluminium determination in the concentrated haemodialysis solutions. The high concentrations of interfering ions hindered the determination of Al(III) in these solutions by causing signal suppression. The aluminium concentrations could not be measured by direct measurements without preconcentration procedure. After sorption of concentrated acidic solution the supernatant solution was diluted 35 fold and aluminium concentration in the supernatant solution was below the limit of detection that means sorption of aluminium was quantitative. However, aluminium concentrations of 35 fold diluted solutions could be measured after preconcentration procedure. The method can be directly be used to determine trace Al(III) in final dialysate solution, where the concentration of the possible interfering ions are 35 times less. In practice, the haemodialysis concentrates were used after 35-fold dilution in hospitals.

The maximum permissible concentration of Al(III) in drinking water is only 200 ng/mL (WHO, 1997). Aluminium concentration in tap water studied was found to be below the limits.

8. CONCLUSION

It is difficult to determine trace aluminium directly with the common techniques since low concentration of aluminium usually suffers from matrix constituents. The solution is to preconcentrate and/or separate the analyte from matrix before detection procedure. The fluorimetric technique was chosen for aluminium determination in this study, because it is a sensitive, rapid, reliable, and low cost technique.

In this chapter, a newly introduced sorbent was utilized for the preconcentration of aluminium before fluorimetric determination. The sorbent was synthesized by reducing Ni(II) with $NaBH_4$ in inert atmosphere. Granular particles were obtained by choosing sulfate salts of nickel and, such structure enables the easier separation during preparation of the sorbent after sorption. Initially, characterization studies of the sorbent were executed by the aid of SEM-EDX, chemical analysis, TGA, XPS and, point of zero charge. Subsequently, preliminary studies for aluminium sorption were done. Sorption efficiencies for Al(III), Al(III)-morin complexes, and morin on Ni/Ni_xB were examined and all these species were found to be sorbed by the sorbent. Optimization studies for Al(III) were realized. Sorption efficiencies for Al(III) at studied initial pH values, between 3-10, were found quantitative. Adsorption rate was quite high and in the first five minutes sorption efficiencies reached 98.9%. The recovery of Al(III) was found quantitative (>95%) for sample volumes up to 250 mL. The enrichment factor was found to be 50 for Al(III). Al(III) recovery from the sorbent was investigated trying morin solution, NaOH, mixture of NaCl and NaOH, EDTA, and HCl solutions. Best results were attained using HCl. Therefore, different kinds of acids were not tried. The sorption capacity was found to be 0.394 g Al(III)/g sorbent in batch studies. This capacity value was consistent with that calculated in isotherm studies. It was found that Langmuir isotherm has the maximum correlation coefficient (R^2=0.9974) for the linear regression and the correlation coefficient (R^2) for Freundlich isotherm was 0.9543. Displacement between nickel and Al(III) during sorption was also investigated. Although displacement between nickel and aluminum was not salient at trace level, at the higher concentrations correlation became evident. Precision and accuracy of the method were fairly good.

The proposed method was also applied to the preconcentration of Al(III) in real water samples and good recoveries were obtained as shown in Table 7.8.

When the present method is compared with the methods used for preconcentration of aluminium in the literature (Table 8.1), synthesized sorbent showed outstanding features such as high capacity and low LOD. Moreover, the preconcentration technique investigated can be combined with the atomic spectrometric techniques for possibly interference free trace determination of aluminium at trace level.

Table 8.1 Comparisons of the methods for preconcentration of aluminium.

System	Analytical Technique	LOD ng/ mL	PF[a]	Capacity mg/g	Sample	Reference
Solid phase extraction with Lewatit TP-207 resin	Electrothermal atomic absorption spectrometry (ETAAS)	7.4 ng/L	40	-	Dialysis concentrates	Şahan et al., 2015
BG-Amberlite XAD-2	ICP-AAS	2.19	10	10.8	Environmental samples	Panahi et al., 2015
3-mercaptopropionic acid grafted silica modified Fe_3O_4 magnetic Nanoparticles	GFAAS	0.09	99[b]	64.7	Biological and environmental samples	Mashhadizadeh and Amoli-Diva, 2013
Duolite XAD-761 polymeric resin	High resolution-continuum source flame atomic absorption spectrometry	0.18	100	-	Water samples and dialysis solutions	Ciftçi et al., 2015
Coprecipitation with Co^{2+}/8-hydroxyquinoline system	UV–vis spectrophotometry	0.2	50[b]	-	Sea water, river water, tap water and haemodialysis fluids samples	Bulut et al., 2010
Cloud point extraction using 3,5,7,2´-4´ pentahydroxy flavone (morin)	Spectrofluorimetry	0.24	20	-	Drinking water and biological samples	Khan et al., 2011
Ni/Ni_xB adsorbent	Spectrofluorimetry	0.011	50[b]	393.8	Tap and dialysis water	This study

[a] Preconcentration Factor ($C_{final}/C_{initial}$) (Naeemullah et al., 2012), [b] Enrichment Factor ($V_{initial}/V_{final}$) (Dubiella-Jackowska et al., 2009, Wang et al., 2012).

REFERENCES

Abernathy, C.O., Liu, Y.P., Longfellow, D.H., Aposhian, V., Beck, B., Fowler, B., Goyer, R., Menzer, R., Rossman, T., Thompson, C. and Waalkes, M., 1999, *Arsenic: Health Effects, Mechanisms Of Actions, And Research Issues*, Environmental Health Perspectives, 107:593–597pp.

Acebal, CC., Simonet, B.M. and Valcárcel, M., 2013, *Nanoparticles and Continuous-Flow Systems Combine Synergistically For Preconcentration*, Trends in Analytical Chemistry, Vol. 43:109-120pp.

Aggett, J. and Aspell, A.C., 1976, *The Determination Of Arsenic(III) And Total Arsenic By Atomic-Absorption Spectroscopy*, Analyst, 101, 1202:341-347pp.

Aksoy, N., Simsek, C. and Gunduz, O., 2009, *Groundwater Contamination Mechanism in A Geothermal Field: A Case Study Of Balcova*, Turkey, Journal Of Contaminant Hydrology, 103, 1-2:13-28pp.

Al-Kindy, S.M.Z., Badia, R. and Diaz-Garcia, M.E., 2002, *Fluorimetric Monitoring Of Molecular Imprinted Polymer Recognition Events For Aluminium*, Analytical Letters, 35, 11:1763–1774pp.

Alloway, B.J., 1990, *Heavy-Metals in Soils: Trace Metals and Metalloids in Soils and Their Bioavailability*, Springer Netherlands, Blackie, London, 83-99pp.

American Cancer Society, 2014, Arsenic, Http://Www.Cancer.Org/Cancer/Cancercauses/Othercarcinogens/Intheworkplace/Arsenic (30.01.2016).

Anjos, V.E., Rohwedder, J.R., Cadore, S., Abate, G. and Grassi, M.T., 2014, *Montmorillonite And Vermiculite As Solid Phases For The Preconcentration Of Trace Elements In Natural Waters: Adsorption And Desorption Studies Of As, Ba, Cu, Cd, Co, Cr, Mn, Ni, Pb, Sr, V, And Zn*, Applied Clay Science, 99: 289–296pp.

Arain, M.S., Arain, S.A., Kazi, T.G., Afridi, H.I., Naeemulllah, J.A., Arain, S.S., Brahman, K.D. and Mughal, M.A., 2015, *Temperature Controlled Ionic Liquid-Based Dispersive Micro-Extractionusing Two Ligands, For Determination Of Aluminium In Scalp Hair Samples Of Alzheimer's Patients: A Multivariate Study*, Spectrochimica Acta Part A: Molecular And Biomolecular Spectroscopy 137:877–885pp.

REFERENCES (Continue)

Arfelli, M., Ingo, G. M., Mattogno, G. and Beccaria A. M., 1990, *XPS Investigation On The Corrosion Behaviour Of Nickel In Sea Water*, Surface And Interface Analysis, Volume 16, Issue 1-12:299–303pp.

Atalar, A., Kucuksezgin, F., Duman, M. and Gonul, L.T., 2013, *Heavy Metal Concentrations In Surficial and Core Sediments from Izmir Bay: An Assessment of Contamination and Comparison against Sediment Quality Benchmarks*, Bulletin of Environmental Contamination and Toxicology, 91:69–75pp.

ATSDR, 1992, *Toxicological Profile For Aluminum And Compounds*, Atlanta, Georgia, Agency For Toxic Substances And Disease Registry, (TP-91/01) 136p.

Balci, A. and Kucuksezgin, F., 1994, *Heavy Metal Concentrations In Selected Organisms From Izmir Bay*, Turkey, Marine Pollution Bulletin, 28:333–335pp.

Bax, D., Agterdenbos, J., Worrell, E., and Kolmer, J.B., 1988, *The Mechanism of Transition Metal Interference In Hydride Generation Atomic Absorption Spectrometry*, Spectrochimica Acta Part B: Atomic Spectroscopy, Volume 43, Issue 9-11:1349-1354pp.

Berlin, J., Terborg, R., Salge, T., Falke, M. and Scheller, S., 2011, *EDS Analysis of Light Elements with Silicon Drift Detectors: Quantification of Boron*, International Union of Microbeam Analysis Societies V (IUMAS), Seoul – Korea, Bruker Nano GmbH, Schwarzschildstr, 12, 12489, Berlin, Germany,1p (https://www.bruker.com/fileadmin/user_upload/8-PDF-Docs/X-rayDiffraction_ElementalAnalysis/Microanalysis_EBSD/Posters/ScPos_Berlin_IUMAS_May11_A0_01.pdf) (01.06.2016).

Bhattacharya, P., Welch, A.H., Stollenwerk, K.G., Mclaughlin, M.J., Bundschuh, J. and Panaullah, G., 2007, *Arsenic In The Environment: Biology And Chemistry*, Science Of The Total Environment, 379, 2-3:109-120pp.

Bulut, V.N., Arslan, D., Ozdes, D., Soylak, M. and Tufekci, M., 2010, *Preconcentration, Separation And Spectrophotometric Determination Of Aluminum(III) In Water Samples And Dialysis Concentrates At Trace Levels With 8-Hydroxyquinoline-Cobalt(II) Coprecipitation System*, Journal Of Hazardous Materials, 182:331-336pp.

REFERENCES (Continue)

Buratti, M., Valla, C., Pelegrino, O., Rubino, F.M. and Colombi, A., 2006, *Aluminium Determination In Biological Fluids And Dialysis Concentrates Via Chelation With 8-Hydroxyquinoline And Solvent Extraction Fluorimetry,* Analytical Biochemistry, 353:63–68pp.

Burguera, M. and Burguera, J.L., 1997, *Analytical Methodology for Speciation of Arsenic in Environmental and Biological Samples,* Talanta, 44:1581–1604pp.

Bye, R., 1985, *Citric Acid as a Masking Agent for High Concentrations of Nickel in the Determination of Selenium by Hydride Generation Atomic-absorption Spectrometry,* Analyst, Volume 110:85-86pp.

Campillo, N., Peñalver, R., Viñas, P., López-García, I. and Hernández-Cordoba, M., 2008, *Speciation Of Arsenic Using Capillary Gas Chromatography With Atomic Emission Detection*, Talanta, 77: 793–799pp.

Carapella, S.C., 2002, *Arsenic and Arsenic Alloys*, Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc., 250p.

Carol, H.T. and Arnold, K.F., 1990, *Health and Aesthetic Aspect of Water Quality*, In: Pontius FW (Ed.), Water Quality and Treatment (A Handbook of Community Water Supplies by AWWA), Mcgraw-Hill, New York. 64-154pp.

Castor, J.M.R., Portugal, L., Ferrer, L., Hinojosa-Reyes, L., Guzmán-Mar, J. L., Hernández-Ramírez, A. and Cerdà, V., 2016, *An Evaluation Of The Bioaccessibility Of Arsenic In Corn And Rice Samples Based On Cloud Point Extraction And Hydride Generation Coupled To Atomic Fluorescence Spectrometry*, Food Chemistry, 204:475–482pp.

Chatterjee, A., Das, D., Mandal, B.K., Chowdhury, T.R., Samanta, G. and Chakraborti, D., 1995, *Arsenic In Ground Water In Six Districts Of West Bengal, India: The Biggest Arsenic Calamity In The World. Part I. Arsenic Species in Drinking Water and Urine of the Affected People,* Analyst, 120:643-650pp.

REFERENCES (Continue)

Chen, D., Huang, C., He, M. and Hu, B., 2009, *Separation And Preconcentration Of Inorganic Arsenic Species In Natural Water Samples With 3-(2-Aminoethylamino) Propyltrimethoxysilane Modified Ordered Mesoporous Silica Micro-Column And Their Determination By Inductively Coupled Plasma Optical Emission Spectrometry*, Journal Of Hazardous Materials, Volume 164, Issues 2–3, 30:1146–1151pp.

Chen, M.L., Ma, L.Y. and Chen, X.W., 2014, *New Procedures for Arsenic Speciation: A Revie*w, Talanta, 125:78–86pp.

Chen, M.L., Sun, Y., Huo, C.B., Liu, C. and Wang, J.H., 2015, *Akaganeite Decorated Graphene Oxide Composite For Arsenic Adsorption/Removal And Its Proconcentration At Ultra-Trace Level*, Chemosphere, 130:52–58pp.

Cheng, G., He, M., Peng, H. and Hu, B., 2012, *Dithizone Modified Magnetic Nanoparticles For Fast And Selective Solid Phase Extraction Of Trace Elements In Environmental And Biological Samples Prior To Their Determination By ICP-OES,* Talanta, 88:507–515pp.

Ciftci, H., Er, C. and Ozkan, M., 2015, *Determination Of Aluminum From Water Samples And Dialysis fluids Afterseparation/Preconcentration On Duolite XAD-761 Polymeric Resin*, Desalination and Water Treatment, 10:1–9pp.

Çiftçi, T.D. and Henden, E.,, 2015, *Nickel/Nickel Boride Nanoparticles Coated Resin: A Novel Adsorbent For Arsenic(III) And Arsenic(V) Removal*, Powder Technology, 269:470–480pp.

Clesceri, L. S., Greenberg, A.E. and Eaton, A.D.(Eds), 1999, *Standard Methods For The Determination Of Water And Wastewater*, American Public Health Association, American Water Works Association, Water Environment Federation, United Book Press, USA, 404p.

Çolak, M., 2012, *Heavy Metal Concentrations in Sultana-Cultivation Soils and Sultana Raisins from Manisa (Turkey)*, Environmental Earth Sciences, 67:695–712pp.

REFERENCES (Continue)

Cooper, K., Noller, B., Connell, D., Yu, J., Sadler, R., Olszowy, H., Golding, G., Tinggi, U., Moore, M.R. and Myers, S., 2007, *Public Health Risks From Heavy Metals And Metalloids Present In Traditional Chinese Medicines*, Journal Of Toxicology And Environmental Health Part A, 70: 1694–1699pp.

Csuros, M. and Csuros, C., 2002, *Environmental Sampling and Analysis for Metals,* CRC Press Company, USA, 372p.

Cullen, W.R. and Reimer, K.J., 1989, *Arsenic Speciation in the Environment*, Chemical Reviews, 89:713-764pp.

Cullen, W.R., 2008, *Is Arsenic An Aphrodisiac? The Sociochemistry Of An Element*, Royal Society Of Chemistry, Cambridge, U.K., 412p.

Deng, F., Dong, R., Yu, K., Luo, X., Tu, X., Luo, S. and Yang, L., 2013, *Determination Of Trace Total Inorganic Arsenic By Hydride Generation Atomic Fluorescence Spectrometry After Solid Phase Extraction-Preconcentration On Aluminium Hydroxide Gel*, Microchimica Acta, 509–515pp.

Djerahov, L., Vasileva, P., Karadjova, I., Kurakalva, R.M. and Aradhi, K.K., 2016, *Chitosan Film Loaded With Silver Nanoparticles—Sorbent For Solid Phase Extraction Of Al(III), Cd(II), Cu(II), Co(II), Fe(III), Ni(II), Pb(II) And Zn(II),* Carbohydrate Polymers 147: 45–52pp.

dos Santos, T.C.R., Aucélio, R.Q. and Campos, R.C., 2003, *Spectrofluorimetric Method for the Determination of Aluminum with Alizarin Red PS,* Microchimica Acta, 142:63–66pp.

Dubiella-Jackowska, A., Polkowska, Ż., Lech, D., Pasławski, P., Staszek, W., Namieśnik, J., 2009, *Estimation Of Platinum In Environmental Water Samples With Solid Phase Extraction Technique Using Inductively Coupled Plasma Mass Spectrometry,* Central European Journal of Chemistry, 7, 1:35–41pp.

El-Kemary, M., Nagy, N. and El-Mehasseb, I., 2013, *Nickel Oxide Nanoparticles: Synthesis And Spectral Studies Of Interactions With Glucose***,** Materials Science In Semiconductor Processing, Volume 16, Issue 6:1747–1752pp.

REFERENCES (Continue)

Ellenhorn, M.J., 1997, *Ellenhorn's Medical Toxicology: Diagnosis and Treatment of Human Poisoning,* Second Ed. Williams & Wilkins, Baltimore, 1540p.

El-Sheikh, A.H., Al-Jafari, M.K. and Sweileh, J.A., 2012, *Solid Phase Extraction And Uptake Properties Of Multi-Walled Carbon Nanotubes Of Different Dimensions Towards Some Nitro-Phenols And Chloro-Phenols From Water*, International Journal Of Environmental Analytical Chemistry, Vol. 92, No 2: 190–209pp.

EPA, 2008, *Reregistration Eligibility Decision For Chromated Arsenicals*, EPA 739-R-08–1006, 90p.**,** Https://Archive.Epa.Gov/Pesticides/Reregistration/Web/Pdf/Cca_Red.Pdf, (15/05/2016).

EPA, 2012, *Arsenic Compounds,* Http://Www3.Epa.Gov/Airtoxics/Hlthef/Arsenic.Html (12.12.2015).

Erdoğan, H., Yalçınkaya, Ö. and Türker, A. R., 2011, *Determination Of Inorganic Arsenic Species By Hydride Generation Atomic Absorption Spectrometry In Water Samples After Preconcentration/Separation On Nano* Zro_2/B_2O_3 *By Solid Phase Extraction*, Desalination, 280:391–396pp.

Figueira, P. Lopes, C.B. Daniel-Da-Silva, A.L. Pereira, E. Duarte, A.C. and Trindade, T., 2011, *Removal Of Mercury (II) By Dithiocarbamate Surface Functionalized Magnetite Particles: Application To Synthetic and Natural Spiked Waters,* Water Research, 5:5773-5784pp.

Fiol, N. and Villaescusa, I., *2009, Determination Of Sorbent Point Zero Charge: Usefulness In Sorption Studies*, Environmental Chemistry Letters, 7:79–84pp.

Fodor, P., 2001, *Chapter 11: Arsenic Speciation In The Environment, Trace Element Speciation For Environment, Food And Health*, Edited By Ebdon, L., Pitts, L., Cornelis, R., Crews, H., Donard, O.F.X. Quevauviller, P., The Royal Society Of Chemistry, Published By The Royal Society Of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge CB4 OWF, UK, 422pp.

REFERENCES (Continue)

Frank, W.B., Haupin, W.E., Dawless, R.K., Granger, D.A., Wei, M.W., Calhoun, K.J. and Bonney, T.B., 1985, *Aluminum*, In: Gerhartz W, Yamamoto YS, Campbell, F.T., Pfefferkorn, R., Rounsaville, J.F. Ed. Ullmann's Encyclopedia Of Industrial Chemistry - Volume A1: Abrasives To Aluminium Oxide, 5th Revised Ed. Weinheim, Verlag Chemie, 459-480 pp.

Gallardo, M.V., Bohari, Y., Astruc, A., Potin-Gautier, M. and Astruc, M., 2001, *Speciation Analysis Of Arsenic In Environmental Solids Referencematerials By High-Performance Liquid Chromatography–Hydridegeneration–Atomic Fluorescence Spectrometry Following Orthophosphoric Acid Extraction*, Analytica Chimica Acta, 441:257–268pp.

Gan, Y.Q., Wang, Y.X., Duan, Y.H., Deng, Y.M., Guo, X.X. and Ding, X.F., 2014, *Hydrogeochemistry and Arsenic Contamination Of Groundwater In The Jianghan Plain Central China*, Journal Of Geochemical Exploration, 138:81-93pp.

Gao, S. and Burau, R.G., *1997*, *Environmental Factors Affecting Rates Of Arsine Evolution From and Mineralization Of Arsenicals In Soil*, Journal Of Environmental Quality, 26:753–763pp.

Garcia-Calzón, J.A. and Diaz-Garcia, M.E., 2012, *Silica Nanotubes: Analytical Applications*, Trends in Analytical Chemistry., 35:27-38 pp.

Gilbert, S., 2014, *Arsenic Poisoning*, (May 30,) Http://Www.Toxipedia.Org/Display/Toxipedia/Arsenic+Poisoning, (11/5/2016).

Girginova, P.I., Daniel-Da-Silva, A.L., Lopes, C.B., Figueira, P., Otero, M., Amaral, V.S., Pereira, E. and Trindade, T., 2010, *Silica Coated Magnetite Particles For Magnetic Removal Of Hg^{2+} From Water*, Journal Of Colloid And Interface Science, 345:234–240pp.

Glavee, G.N., Klabunde, K.J., Sorensen, C.M. and Hadjipanayis, G.C., 1992, *Borohydride Reductions Of Metal Ions. A New Understanding Of The Chemistry Leading To Nanoscale Particles Of Metals, Borides, And Metal Borates*, Langmuir, 8: 771-773pp.

REFERENCES (Continue)

Glavee, G.N., Klabunde, K.J., Sorensen, C.M. and Hadjipanayis, G.C., 1994, *Borohydride Reduction Of Nickel And Copper Ions In Aqueous And Nonaqueous Media. Controllable Chemistry Leading To Nanoscale Metal And Metal Boride Particles*, Langmuir, 10: 4726-4730pp.

Goessler, W. and Kuehnelt, D., 2002, *Chapter 2: Analytical Methods For The Determination Of Arsenic And Arsenic Compounds In The Environment, Environmental Chemistry Of Arsenic*, Edited By Frankenberger Jr., W.T., Language English, Published New York: Marcel Dekker, 391p.

Gonul, L.T., 2015, *Chemical Speciation And Ecological Risk Assessment Of Arsenic In Marine Sediments From Izmir Bay (Eastern Aegean Sea)*, Environmental Science And Pollution Research, 22:19951–19960pp.

Goon, E., Petley, J.E., Mccullen, W.H. and Wıberley, S.E., 1953, *Fluorometric Determination Of Aluminum Use Of 8-Quinolinol*, Analytical Chemistry, 25, 4: 608-610pp.

Greschonig, H. and Irgolic, K.J., 1992, *Electrochemical Methods for the Determination of Total Arsenic and Arsenic Compounds*, Applied Organometallic Chemistry, 6:565–577pp.

Grillet, J.P., Adjémian, A., Bernadac, G., Bernon, J., Brunner, F. and Garnier, R., 2004, *Arsenic Exposure In The Wine Growing Industry In Ten French Departments*, International Archives Of Occupational And Environmental Health, 77: 130–135pp.

Grotti, M., Lagomarsino, C. and Magi, E., 2006, *Simultaneous Determination Of Arsenic, Selenium And Mercury In Foodstuffs By Chemical Vapour Generation Inductively Coupled Plasma Optical Emission Spectroscopy*, Annali Di Chimica, 96: 751–764pp.

Hagiwara, K., Koike, Y., Aizawa, M. and Nakamura T., 2015, *On-Site Quantitation Of Arsenic In Drinking Water By Disk Solid-Phase Extraction/Mobile X-Ray Fluorescence Spectrometry*, Talanta, 144:788–792pp.

Han, F.X., Su, Y., Monts, D.L., Plodinec, M.J., Banin, A. and Triplett, G.E., 2003, *Assessment Of Global Industrial-Age Anthropogenic Arsenic Contamination*, Naturwissenschaften, 90:395–401pp.

REFERENCES (Continue)

Haslam, J.C., 2013, *Deathly Décor: A Short History Of Arsenic Poisoning In The Nineteenth Century*, Res Medica Journal Of The Royal Medical Society, 21:1, 76-81pp.

Henden, E., 1982, *Attempts To Eliminate Interferences In The Determination Of Arsenic, Anthimony, Tin And Germanium By Molecular Emission Cavity Analysis With The Hydride Generation Technique*, Analyst, Volume 107:872-878pp.

Henden, E., İşlek, Y., Kavas, M., Aksuner, N., Yayayürük, O., Çiftçi, T.D. and İlktaç, R., 2011, *A Study Of Mechanism Of Nickel Interferences In Hydride Generation Atomic Absorption Spectrometric Determination Of Arsenic And Antimony*, Spectrochim. Acta, Part B, 66: 793–798pp.

Hernandez F.H. and Escriche J.M., 1984, *Fluorimetric Determination Of Aluminium With Morin After Extraction With Isobuthyl Methyl Ketone*, Analyst, Vol 109, 1585-1588pp.

History Magazine, 2001, *Arsenic*, http://www.history-magazine.com/arsenic.html (26.02.2014).

Hoch, R.L., 1999, *Determination Of Aluminium In Beverages By Automated Non-Segmented Continuous Flow Analysis With Fluorescent Detection Of The Lumogallion Complex*, Analyst, 124:793–796pp.

Holt, P., *2002, Electrocoagulation Unravelling And Synthesising The Mechanisms Behind A Water Treatment* Process, Thesis (Ph. D.)- University Of Sydney, Austrália, 229p.

Huang, C., Xie, W., Li, X. and Zhang, J., 2011, *Speciation Of Inorganic Arsenic İn Environmental Waters Using Magnetic Solid Phase Extraction And Preconcentration Followed By ICP-MS*, Microchimica Acta, Volume 173, Issue 1:165-172pp.

Huang, C.Z., Hu, B. and Jiang, Z.C., 2007, *Simultaneous Speciation Of Inorganic Arsenic And Antimony In Natural Waters By Dimercaptosuccinic Acid Modified Mesoporous Titanium Dioxide Micro-Column On-Line Separation And Inductively Coupled Plasma Optical Emission Spectrometry Determination*, Spectrochimica Acta Part B, 62: 454–460pp.

Hughes, M.F., 2002, *Arsenic Toxicity and Potential Mechanisms of Action*, Toxicology Letters, 133:1–16pp.

REFERENCES (Continue)

Hughes, M.F., Beck, B.D., Chen, Y., Lewis, A.S. and Thomas, D.J., 2011, *Arsenic Exposure And Toxicology: A Historical Perspective,* Toxicological Sciences, 123:2, 305–332pp.

Hyson, J.M., 2007, *A History Of Arsenic In Dentistry,* Journal Of The California Dental Association, 35: 135–139pp.

IPCS, 2001, *Arsenic and Arsenic Compounds*, 2nd Ed. Geneva, World Health Organization, International Programme on Chemical Safety (Environmental Health Criteria 224; Http://Whqlibdoc.Who.Int/Ehc/WHO_EHC_224.Pdf).

İşlek Coşkun, Y., Çiftçi, T.D. and Henden, E., 2016, *A Novel Nanoadsorbent Ni/Ni_xB For Preconcentration Of Arsenic(III) And Arsenic(V) Before Hydride Generation-Atomic Absorption Spectrometric Determination*, Desalination And Water Treatment, 57, 43:20411-20421.

ISO, 1996, Water Quality — *Determination of 33 Elements by Inductively Coupled Plasma Atomic Emission Spectroscopy*, GENEVA, International Organization for Standardization (ISO11885:1996 (E)).

ISO, 1997, Water Quality — *Determination of Aluminium — Atomic Absorption Spectrometric Methods*, GENEVA, International Organization for Standardization (ISO 12020:1997 (E)).

Jedryczko, D., Pohl, P. and Welna, M., 2016, *Inorganic Arsenic Speciation In Natural Mineral Drinking Waters By Flow-Through Anodic Stripping Chronopotentiometry*, Talanta, 150:265–271pp.

Jiang, H.M., Hu, B., Chen, B.B., Xia, L.B., 2009, *Hollow Fiber Liquid Phase Microextraction Combined With Electrothermal Atomic Absorption Spectrometry For The Speciation Of Arsenic (III) And Arsenic (V) In Fresh Waters And Human Hair Extracts*, Analytica Chimica Acta, 634:15–21pp.

Jiang, X., Huang, K., Deng, D., Xia, H., Hou, X. and Zheng, C., 2012, *Nanomaterials in Analytical Atomic Spectrometry*, Trends in Analytical Chemistry, Vol. 39:38-59pp.

Kalfa, O.M., Yalcınkaya, O. and Turker, A.R., 2009, *Synthesis Of Nano B_2O_3/TiO_2 Composite Material As A New Solid Phase Extractor And Its Application To Preconcentration And Separation Of Cadmium*, Journal Of Hazardous Materials, 166:455–461pp.

REFERENCES (Continue)

Kanke, M., Kumamaru, T., Sakai, K. and Yamamoto, Y., 1991, *Determination Of Arsenic By Graphite Furnace Atomic Absorption Spectrometry Combined With Liquid–Liquid Extraction Of Arsenomolybdic Acid*, Analytica Chimica Acta, 247:13–18pp.

Kasztelan, S., Grimblot, J., Bonnelle, J.P., Payen, E., Toulhoat, H. and Jacquin, Y., 1983, *Preparation Of Co-Mo-ΓAl*$_2$*O*$_3$ *And Ni-Mo-ΓAl*$_2$*O*$_3$ *Catalysts By pH Regulation Of Molybdenum Solution. Characterization Of Supported Species And Hydrogenation Activities*, Applied Catalysis, 7, 1, 15: 91-112pp.

Kaur, A. and Gupta, U., 2009, *A Review On Applications Of Nanoparticles For The Preconcentration Of Environmental Pollutants*, Journal Of Materials Chemistry, 19:8279–8289pp.

Kavas, M., 2010, *Method Development for the Determination of Antimony at Trace Level*, Master of Science Thesis, Ege University, Graduate School of Natural and Applied Sciences, 70p (unpublished).

Kazi, T.G., Khan, S., Baig, J.A., Kolachi, N.F., Afridi, H.I., Kandhro, G.A., Kumar, S. and Shah, A.Q., 2009, *Separation And Preconcentration Of Aluminum In Parenteral Solutions And Bottled Mineral Water Using Different Analytical Techniques*, Journal Of Hazardous Materials, 172: 780–785pp.

Khan, S., Kazi, T.G., Baig, J.A., Kolachi, N.F., Afridi, H.I., Shah, A.Q., Kandhro, G.A. and Kumar, S., 2009, *Separation And Preconcentration Of Trace Amounts Of Aluminum Ions In Surface Water Samples Using Different Analytical Techniques*, Talanta, 80: 158–162pp.

Khan, S., Kazi, T.G., Kolachi, N.F., Baig, J.A., Afridi, H.I. and Shah, F., 2011, *Simple Separation/Preconcentration Method For The Determination Of Aluminum In Drinking Water And Biological Sample*, Desalination, 281: 215–220pp.

Kirkbright, G.F. and Taddia, M., 1978, *Application Of Masking Agents In Minimizing Interferences From Some Metal Ions In The Determination Of Arsenic By Atomic Absorption Spectrometry With The Hydride Generation Technique*, Analytica Chimica Acta, Volume 100, Issue C:145-150pp.

REFERENCES (Continue)

Knežević, S., Milačič, R. and Veber, M., 1998, *ETAAS Determination Of Aluminum And Copper In Dialysis Concentrates After Microcolumn Chelating Ion-Exchange Preconcentration*, Fresenius Journal Of Analytical Chemistry, 362: 162–166pp.

Köhler, M., Hofmann, K., Völsgen, F., Thurow, K. and Koch, A., 2001, *Bacterial Release Of Arsenic Ions And Organoarsenic Compounds From Soil Contaminated By Chemical Warfare Agents*, Chemosphere, 42: 425–429pp.

Komarek, J., Cervenka, R., Ruzicka, T. and Kuban, V., 1998, *ET-AAS Determination Of Aluminum In Dialysis Concentrates After Microcolumn Chelating Ion-Exchange Preconcentration*, Fresenius' Journal Of Analytical Chemistry, 362:162–166pp.

Krewski, D., Yokel, R.A., Nieboer, E., Borchelt, D., Cohen, J., Harry, J., Kacew, S., Lindsay, J., Mahfouz, A.M. and Rondeau, V., 2007, *Human Health Risk Assessment For Alumiınium, Aluminium Oxide, And Aluminium Hydroxide*, Journal Of Toxicology And Environmental Health, Part B: Critical Reviews, 10: 1–269pp .

Kubota, T., Yamaguchi, T. and Okutani, T., 1998, *Determination Of Arsenic Content In Natural Water By Graphite Furnace Atomic Absorption Spectrometry After Collection As Molybdoarsenate On Activated Carbon*, Talanta, 46, 6:1311–1319pp.

Kumar, A., Nair, A.G., Reddy, A.V. and Garg, A.N., 2006, *Bhasmas: Unique Ayurvedic Metallic Herbal Preparations, Chemical Characterization*, Biological Trace Element Research, 109: 231–254pp.

Lamble, K.J. and Hill, S.J., 1996, *Arsenic Speciation In Biological Samples By On-Line High Performance Liquid Chromatography-Microwave Digestion-Hydride Generation-Atomic Absorption Spectrometry*, Analytica Chimica Acta, 334:261-270pp.

Legrand, J., Taleb, A,. Gota, S., Guittet, M.-J. and Petit, C., 2002, *Synthesis And XPS Characterization Of Nickel Boride Nanoparticles*, Langmuir, 18, 4131-4137pp.

Li, N.C., Lindenbaum, A., and White, J.M., 1959, *Some Metal Complexes of Citric and Tricarballylic Acids*, Journal of Inorganic and Nuclear Chemistry, Volume 12, Issues 1–2:122-128pp.

REFERENCES (Continue)

Li, S., Wang, M., Zhong, Y., Zhang, Z. and Yang, B., 2015, *Cloud Point Extraction For Trace Inorganic Arsenic Speciation Analysis In Water Samples By Hydride Generation Atomic Fluorescence Spectrometry*, Spectrochimica Acta Part B, 111:74–79pp.

Li, Z., Deng, S., Yu, G., Huang, J. and Lim, V.C., 2010, *As(V) And As(III) Removal From Water By A Ce–Ti Oxide Adsorbent: Behavior And Mechanism*, Chemical Engineering Journal, 161: 106–113pp.

Lian, H., Kang, Y., Bi, S.P., Shao, D., Chen, Y., Dai, L., Gan, V. and Tian, L., 2004, *Direct Determination Of Trace Aluminium With Quercetin By Reversed- Phase High Performance Liquid Chromatography*, Talanta, 62:43–50 pp.

Liang, P., Yang, L., Hu, B. and Jiang, Z., 2003, *ICP-AES Detection Of Ultratrace Aluminum(III) And Chromium(III) Ions With A Microcolumn Preconcentration System Using Dynamically Immobilized 8-Hydroxyquinoline On Tio2 Nanoparticles*, Analytical Science, 19, 8:1167-71pp.

Liévremont, D., Bertin, P.N. and Lett, M.C., 2009, *Arsenic In Contaminated Waters: Biogeochemical Cycle, Microbial Metabolismand Biotreatment Processes*, Biochimie, 91:1229–1237pp .

Liu, J., Lu, Y., Wu, Q., Goyer, R.A., and Waalkes, M.P., 2008, *Mineral Arsenicals In Traditional Medicines: Orpiment, Realgar, And Arsenolite*, The Journal Of Pharmacology And Experimental Therapeutics, 326: 363–368pp.

Liu, Y., He, M., Chen, B. and Hu, B., 2015, *Simultaneous Speciation Of Inorganic Arsenic, Selenium And Tellurium In Environmental Water Samples By Dispersive Liquid Liquid Microextraction Combined With Electrothermal Vaporization Inductively Coupled Plasma Mass Spectrometry*, Talanta, 142:213–220pp.

Liu, Y., Wang, R. and Yan, X., 2015, *Synergistic Effect between Ultra-Small Nickel Hydroxide Nanoparticles and Reduced Graphene Oxide sheets for the Application in High-Performance Asymmetric Supercapacitor*, Scientific Reports, 5, 11095: 1-12pp

REFERENCES (Continue)

Lobinski, R. and Marczenko, Z., 1996, *Spectrochemical Trace Analysis For Metals And Metalloids*, Chapter 13, Wilson And Wilson's Comprehensive Analytical Chemistry, Elsevier, ISBN 0444417354, 9780444417350, 808p.

Lobinski, R. and Marczenko, Z., 1998, *Spectrochemical Trace Analysis For Metals And Metalloids*, *Chapter 15: Arsenic*, Elsevier Science, Amsterdam, 838p.

Luo, M. and Bi, S., 2003, *Solid Phase Extraction-Spectrophotometric Determination Of Dissolved Aluminum In Soil Extracts And Ground Waters*, Journal Of Inorganic Biochemistry, 97:173-178p.

Luo, P.F., Kuwana, T., Paul D.K. and Sherwood, P.M., 1996, *Electrochemical and XPS Study Of the Nickel−Titanium Electrode Surface*, Analytical Chemistry, 68, 19:3330–3337pp.

Mahmood, T., Saddique, M.T., Naeem, A., Westerhoff, P., Mustafa, S. and Alum, A., 2011, *Comparison Of Different Methods For The Point Of Zero Charge Determination Of NiO*, Industrial Engineering Chemistry Research, 50: 10017–10023pp.

Mandal, B.K. and Suzuki, K.T., 2002, *Arsenic Round the World: A Review*, Talanta, 58, 1:201-235pp.

Mandal, B.K., Ogra, Y. and Suzuki, K.T., 2001, *Identification Of Dimethylarsinous And Monomethylarsonous Acids In Human Urine Of The Arsenic-Affected Areas In West Bengal, India*, Chemical Research In Toxicology, 14: 371–378pp.

Martinson, C.A. and Reddy, K.J., 2009, *Sorption Of Arsenic(III) And Arsenic(V) By Cupric Oxide Nanoparticles*, Journal Of Colloid And Interface Science, 336:406–411pp.

Mashhadizadeh, M.H. and Amoli-Diva, M., 2013, *Atomic Absorption Spectrometric Determination of* Al^{3+} *and* Cr^{3+} *After Preconcentration and Separation on 3-Mercaptopropionic Acid Modified Silica Coated-*Fe_3O_4 *Nanoparticles*, Journal of Analytical Atomic Spectrometry, 28: 251–258pp.

Matsubara, C., Yamamoto, Y. and Takamura, K., 1987, *Rapid Determination Of Trace Amounts Of Phosphate And Arsenate In Water By Spectrophotometric Detection Of Their Heteropoly Acid--Malachite Green Aggregates Following Pre-Concentration By Membrane Filtration*, Analyst, 112, 9: 1257-1260pp.

REFERENCES (Continue)

Matúš, P., Hagarova, I., Bujdos, M., Divis, P. and Kubava, J., 2009, *Determination Of Trace Amounts Of Total Dissolved Cationic Aluminium Species In Environmental Samples By Solid Phase Extraction Using Nanometer-Sized Titanium Dioxide And Atomic Spectrometry Techniques*, Journal Of Inorganic Biochemistry, 103, 11: 1473–1479pp.

Meng, X., Jing, C. and Korfiatis, G.P., 2003, *A Review Of Redox Transformation Of Arsenic In Aquatic Environments*, ACS Symposium Series, 835: 70-83pp.

Miller, S.M. and Zimmerman, J. B., 2010, *Novel, Bio-Based, Photoactive Arsenic Sorbent: Tio2-Impregnated Chitosan Bead*, Water Research, 44:5722-5729pp.

Minareci, O., Öztürk, M., Egemen, Ö. and Minareci, E., 2009, *Detergent and Phosphate Pollution in Gediz River, Turkey*, African Journal of Biotechnology, 8, 15:3568–3575pp.

Moghadam, M.R., Haji Shabani, A.M. and Dadfarnia, S., 2015, *Simultaneous Spectrophotometric Determination Of Fe(III) And Al(III) Using Orthogonal Signal Correction-Partial Least Squares Calibration Method After Solidified Floating Organic Drop Microextraction*, Spectrochimica Acta Part A: Molecular And Biomolecular Spectroscopy, 135:929-934pp.

Mohan, D., and Pittman Jr., C.U., 2007, *Arsenic Removal From Water/Wastewater Using Adsorbents-A Critical Review*, Journal Of Hazardous Material, 142, 1-53pp.

Moore, J.W., Ramamoorthy, S. and Ballantyne, E.E., 1984, *Heavy Metals In Natural Waters: Applied Monitoring And Impact Assessment Springer Series On Environmental Management*, Springer-Verlag, Michigan Üniversitesi, Springer, New York, 268p.

Moore, S.A., Moennich, D.M. and Gresser, M.J., 1983, *Synthesis And Hydrolysis Of ADP- Arsenate By Beef Heart Sub Mitochondrial Particles*, The Journal Of Biological Chemistry, 258:6266–6271pp.

Naeemullah, Kazi, T.G., Shah, F., Afridi, H.I., Khan, S., Arian, S.S., Brahman, K.D., 2012, *A Green Preconcentration Method For Determination Of Cobalt And Lead In Fresh Surface And Waste Water Samples Prior To Flame Atomic Absorption Spectrometry*, Journal of Analytical Methods in Chemistry, 2012, 713862:1-8pp.

REFERENCES (Continue)

Nagarajan, R. and Hatton, A., 2008, *Nanoparticles: Synthesis, Stabilization, Passivation And Functionalization, Chapter 1: Nanoparticles: Building Blocks For Nanotechnology*, American Chemical Society, Distributed By Oxford University Press, 2-14pp.

Narin, I., Tuzen., M. and Soylak, M., 2004, *Aluminium Determination In Environmental Samples By Graphite Furnace Atomic Absorption Spectrometry After Solid Phase Extraction On Amberlite XAD-1180/Pyrocatechol Violet Chelating Resin*, Talanta, 63:411–418pp.

Nodeh, H.R., Ibrahim, W.A.W., Ali, I. and Sanagi, M.M., 2016, *Development Of Magnetic Graphene Oxide Adsorbent For The Removal And Preconcentration Of As(III) And As(V) Species From Environmental Water Samples*, Environmental Science and Pollution Research, 23, 10: 9759-9773pp.

Nomngongo, P.N. and Ngila, J.C., 2015, *Multivariate Optimization Of Dual-Bed Solid Phase Extraction For Preconcentration Of Ag, Al, As And Cr In Gasoline Prior To Inductively Coupled Plasma Optical Emission Spectrometric Determination*, Fuel, 139, 285–291pp.

Nriagu, J.O., 2002, *Environmental Chemistry Of Arsenic*, Ed.: William T. Frankenberger, Jr., Chapter 1: Arsenic Poisoning Through The Ages, Marcel Dekker Inc., Printed İn USA, CRC Press, 412p.

Onishi, H., 1969, *Arsenic*, In: K.H. Wedepohl (Ed.), Handbook Of Geochemistry, Springer-Verlag, New York, 33-K, 200p.

Pacheco, P.H., Gil, R.A., Smichowski, P., Polla, G., and Martinez, L.D., 2008, *Trace Aluminium Determination In Biological Samples After Microwave Digestion Followed By Solid Phase Extraction With L-Methionine On Controlled Pore Glass*, Microchemical Journal, 89: 1–6pp.

Pal, P., Bhattacharyay, D., Mukhopadhyay, A. and Sarkar, P., 2009, *The Detection Of Mercury, Cadmium And Arsenic By The Deactivation Of Urease On Rhodinized Carbon*, Environmental Engineering Science, 26:25–32pp.

REFERENCES (Continue)

Panahi, H.A., Feizbakhsh, A., Riyasati, S., Moniri, E., Nezhati, M.N. and, Galaev, I.Y., 2015, *Preconcentration And Determination Of Aluminum In Water Samples By Inductively Coupled Plasma-Atomic Emission Spectroscopy With Brilliant Green-Based Anion-Exchange Solid-Phase Extraction Support*, Desalination And Water Treatment, Volume 53, Issue 7, 1902-1908pp.

Pantuzzo, F.L., Silva, J.C.J. and Ciminelli, V.S.T., 2009, *A Fast And Accurate Microwave Assisted Digestion Method For Arsenic Determination In Complex Mining Residues By Flame Atomic Absorption Spectrometry*, Journal Of Hazardous Materials, 168:1636–1638pp.

Pavun, L., Đikanović, D., Đurđević, P., Stankov, M.J., Malešev D. and Ćirić, A., 2009, *Spectrofluorimetric and HPLC Determination of Morin in Human Serum*, Acta Chimica Slovenica, 56, 967–972pp.

Pohl, P. and Zyrnicki W., 2002, *Study Of Chemical And Spectral Interferences In The Simultaneous Determination Of As, Bi, Sb, Se And Sn By Hydride Generation Inductively Coupled Plasma Atomic Emission Spectrometry*, Analytica Chimica Acta, 468, 1:71-79pp.

Pongratz, R., 1998, *Arsenic Speciation in Environmental Samples of Contaminated Soil*, The Science Of The Total Environment, 224: 133-141pp.

Preočanin, T. and Kallay, N., 2006, *Point Of Zero Charge And Surface Charge Density Of TiO2 In Aqueous Electrolyte Solution As Obtained By Potentiometric Mass Titration*, Croatica Chemica Acta, 79, 1:95-106pp.

Pyrzynska, K, 2013, *Use Of Nanomaterials In Sample Preparation*, Trends In Analytical Chemistry, 43: 100-108pp.

Rezaee, M., Yamini, Y., Khanchi, A., Faraji, M. and Saleh, A., 2010, *A Simple And Rapid New Dispersive Liquid–Liquid Microextraction Based On Solidification Of Floating Organic Drop Combined With Inductively Coupled Plasma-Optical Emission Spectrometry For Preconcentration And Determination Of Aluminum In Water Samples*, Journal Of Hazardous Materials, 178: 766–777pp.

Rochette, E. A., Li, G. C. and Fendorf, S. E., 1998, *Stability Of Arsenate Minerals In Soil Under Biotically Generated Reducing Conditions*, Soil Science Society Of America Journal, 62, 6:1530-1537pp.

REFERENCES (Continue)

Safavi, A., Momeni, S. and Saghir, N., 2009, *Efficient Preconcentration And Determination Of Traces Of Aluminum Ion Using Silica-Bonded Glycerol Sorbent,* Journal Of Hazardous Materials, 162:333-337pp.

Şahan, S., Saçmacı,Ş., Ülgen, A., Kartal, Ş. and Şahin, U., 2015, *A New Automated System For The Determination Of Al(III) Species In Dialysis Concentrates By Electrothermal Atomic Absorption Spectrometry Using A Combination Of Chelating Resin,* Microchemical Journal, 122:57–62pp.

Samuels, W.D., Lafemina, N.H., Sukwarotwat, V., Yantasee, W., Li, X.H.S. and Fryxell, G.E., 2010, *Chloromethylated Activated Carbon: A Useful New Synthon For Making A Novel Class Of Sorbents For Heavy Metal Separations,* Separation Science And Technology, 45: 228–235pp.

Saper, R.B., Phillips, R.S., Sehgal, A., Khouri, N., Davis, R.B., Paquin, J., Thuppil, V. and Kales, S.N., 2008, *Lead, Mercury, And Arsenic In US-And Indian-Manufactured Ayurvedic Medicines Sold Via The Internet,* JAMA: The Journal Of The American Medical Association, 300: 915–923pp.

Sax, N.I. and Lewis, R.J.S.R., 1987, *Hawley's Condensed Chemical Dictionary***,** 11th Ed. New York, Van Nostrand Reinhold Company, 42-51pp.

Shah, A.Q., Kazi, T.G., Arain, M.B., Baig, J.A., Afridi, H.I., Kandhro, G.A. and Khan, S., 2009, *Hazardous Impact Of Arsenic On Tissues Of Fish Species Of The Manchar Lake And Indus River, Pakistan*, Journal Of Hazardous Materials, 167:511–515pp.

Sharma, V.K. and Sohn, M., 2009, *Aquatic Arsenic: Toxicity, Speciation, Transformations, and Remediation*, Environment International, 35, 4:743-759pp.

Shokrollahi, A., Ghaedi, M., Niband, M.S. and Rajabi, H.R., 2008, *Selective And Sensitive Spectrophotometric Method For Determination Of Sub-Micro-Molar Amounts Of Aluminum Ion*, Journal Of Hazardous Materials, 151:642-648pp.

Sillén, L.G., Martell, A.E., Bjerrum, J., 1964, *Stability constants of metal-ion complexes,* Chemical Society, The Burlington House, Special Publication No:17, 754p.

REFERENCES (Continue)

Smedley, P.L. and Kinniburgh, D.G., 2002, *A Review Of The Source, Behaviour And Distribution Of Arsenic In Natural* Waters, Applied Geochemistry, 17:517–568pp.

Sombra, L.L., Luconi, M.O., Fernández L.P., Olsina, R.A., Silva, M.F. and Martínez, L.D., 2003, *Assessment Of Trace Aluminum Content In Parenteral Solutions By Combined Cloud Point Preconcentration-Flow Injection Inductively Coupled Plasma Optical Emission Spectrometry*, Journal Of Pharmaceutical And Biomedical Analysis, 30:1451-1458pp.

Sounderajan, S., Udas, A.C. and Venkataramani, B., 2007, *Characterization Of Arsenic(V) And Arsenic(III) In Water Samples Using Ammonium Molybdate And Estimation By Graphite Furnace Atomic Absorption Spectroscopy*, Journal Of Hazardous Materials, 149:238–242 pp.

Srinivasan, P.T., Viraraghavan, T. and Subramanian, K.S., 1999, *Aluminium In Drinking Water: An Overview*, Water SA, 25,1:47-56pp.

Stice, S., Liu, G., Matulis, S., Boise, L. H. and Cai, Y., 2016, *Determination Of Multiple Human Arsenic Metabolites Employing High Performance Liquid Chromatography Inductively Coupled Plasma Mass Spectrometry*, Journal Of Chromatography B, 1009-1010: 55–65pp.

Stranick, M.A., Houalla, M. and Hercule, D.M., 1987, *Determination Of The Distribution Of Species İn Supported Metal Catalysts By X-Ray Photoelectron Spectroscopy*, Journal Of Catalysis, 103, 1, 151-159pp.

Strohmeier, B.R., 1989, *Surface Characterization Of Aluminum Foil Annealed In The Presence Of Ammonium Fluoborate*, Applied Surface Science, 40: 249-263pp.

Sutheimer, S.H. and Cabaniss, S.E., 1995, *Determination Of Trace Aluminum In Natural Waters By Flow-Injection Analysis With Fluorescent Detection Of The Lumogallion Complex,* Analytica Chimica Acta, 303:211-221pp.

Tavakkoli, N., Habibollahi, S. and Tehrani, S.A., 2014, *Separation And Preconcentration Of Arsenic(III) Ions From Aqueous Media By Adsorption On MWCNTS*, Arabian Journal Of Chemistry, Available Online, Corrected Proof — Note To Users, In Press.

The Royal Society and The Royal Academy Of Engineering, 2004, *Nanoscience And Nanotechnologies: Opportunities And Uncertainties*, Www.Nanotech.Org.Uk, (23.10.2015).

REFERENCES (Continue)

Thorton, I., 1996, *In Environmental Geochemistry and Health***,** Ed. I.D. Appleton, R. Fuge And G.H. Mccall, Geological Society Special Publication, 113:154p.

Türker, A. R., 2007, Review: *New Sorbents For Solid-Phase Extraction For Metal Enrichment,* Clean- Soil, Air, Water, 35, 6:548-557pp.

Türker, A.R., 2012, *Separation, Preconcentration and Speciation Of Metal Ions By Solid Phase Extraction*, Separation & Purification Reviews, 41:169-206pp,

Tuzen, M. and Soylak, M., 2008, *Biosorption Of Aluminum On Pseudomonas Aeruginosa Loaded On Chromosorb 106 Prior To Its Graphite Furnace Atomic Absorption Spectrometric Determination*, Journal Of Hazardous Materials, 154: 519–52 pp.

Uluozlu, O.D., Tuzen, M., Mendil, D. and Soylak, M., 2010, *Determination Of As(III) And As(V) Species In Some Natural Water And Food Samples By Solid-Phase Extraction On Streptococcus Pyogenes Immobilized On Sepabeads SP 70 And Hydride Generation Atomic Absorption Spectrometry*, Food And Chemical Toxicology, 48:1393–1398pp.

Ulusoy, H.İ., Gürkan, R., Aksoy, Ü. and Akçay, M., 2011, *Development Of A Cloud Point Extraction And Preconcentration Method For Determination Of Trace Aluminum In Mineral Waters By FAAS*, Microchemical Journal 99:76–81pp.

Ungureanu, G., Santos, S., Boaventura, R. and Botelho, C., 2015, *Arsenic and Antimony in Water and Wastewater: Overview of Removal Techniques with Special Reference To Latest Advances In Adsorption Review*, Journal Of Environmental Management, 151:326-342pp.

Vahter, M., 2008. *Health Effects of Early Life Exposure to Arsenic,* Basic Clin. Pharmacol. Toxicol. 102, 204–211pp.

Valcárcel, M. , Cárdenas, S. and Simonet, B.M., 2007, *Role Of Carbon Nanotubes In Analytical Science (Review),* Analytical Chemistry Volume 79, Issue 13:4788-4797pp.

Valcárcel, M., Cárdenas, S., Simonet, B.M., Moliner-Martínez, Y. and Lucena R., 2008, *Carbon Nanostructures As Sorbent Materials In Analytical Processes*, Trac Trends İn Analytical Chemistry, Volume 27, Issue 1:34–43pp.

REFERENCES (Continue)

Vargel, C., 2004, *Corrosion Of Aluminium*, Elsevier, 700p.

Venezia, A. M., Bertoncello, R. and Deganello, G., 1995, *X-Ray Photoelectron Spectroscopy Investigation Of Pumice-Supported Nickel Catalysts*, Surface And Interface Analysis, Volume 23, Issue 4:239–247pp.

Vingradov, A.P., 1959, *The Geochemistry Of Rare And Dipersed Chemical Elements In Soils*, 2nd Edn., New York, 65p.

Wagner, C.D., Naumkin, A.V., Kraut-Vass, A., Allison, J.W., Powell, C.J. and Rumble, J.R.Jr., 2003, *Nist Standard Reference Database 20*, Version 3.4 (Web Version) (Http:/Srdata.Nist.Gov/Xps/), (17.02.2016).

Wakao, N., Koyatsu, H., Komai, Y., Shimokawara, H., Sakurai, Y. and Shiota, H., 1988, *Microbial Oxidation Of Arsenite And Occurrence Of Arsenite-Oxidizing Bacteria In Acid Mine Water From A Sulfur-Pyrite Mine*, Geomicrobiology Journal, 6:11–24pp.

Wander, P., 2010, *Top 5 Reasons We Visit ... The Dentist*, British Homeopathic Association, Health & Homeopathy, Http://Www.Britishhomeopathic.Org/Bha-Charity/How-We-Can-Help/Conditions-A-Z/Top-5-Reasons-We-Visit-The-Dentist/ (30.01.2016).

Wang, J. and Bartholomew, C. H., 1988, Proceedings 9th International Congress on Catalysis, 2, 813-820pp.

Wang, L.S. and Hong, R.Y., 2011, *Synthesis, Surface Modification And Characterization Of Nanoparticles, Advances In Nanocomposites- Synthesis Characterization And Industrial Applications*, Dr.Boreddy Reddy(Ed.), ISBN:978-953-307-165-7, Intech, 966p.

Wang, Y., Ke, X., Zhang, J., Du, X., Ma, J., and Li, J., 2012, *A Novel Separation/Preconcentration Technique Based On Ultrasonic Dispersion Liquid-Liquid Microextraction For Determination Of Trace Cobalt By Flame Atomic Absorption Spectrometry*, Bulletin of the Chemical Society of Ethiopia, 26, 1: 9-18pp.

Welz, B. and Melcher, M., 1984, *Mechanisms of Transition Metal Interferences In Hydride Generation Atomic-Absorption Spectrometry: Part 1. Influence of Cobalt, Copper, Iron and Nickel on Selenium Determination*, Analyst, Volume 109, Issue 5:569-572pp.

REFERENCES (Continue)

Welz, B. and Melcher, M., 1984, *Mechanisms of Transition Metal Interferences In Hydride Generation Atomic-Absorption Spectrometry: Part 3. Releasing Effect of Iron(III) on Nickel Interference on Arsenic and Selenium*, Analyst, Volume 109:577-579pp.

Welz, B., and Schubert-Jacobs, M., 1986, *Mechanisms Of Transition Metal Interferences In Hydride Generation Atomic Absorption Spectrometry: Part 4. Influence Of Acid And Tetrahydroborate Concentrations On Interferences In Arsenic And Selenium Determinations*, Journal of Analytical Atomic Spectrometry, Volume 1:23-27pp.

Wertime, T.A., 1962, *The Coming Of The Age Of Steel*, The University Of Chicago, The University Of Chicago Press, Printed In The Netherlands, 335p.

Westervelt, P., Brown, R.A., Adkins, D.R., Khoury, H., Curtin, P., Hurd, D., Luger, S.M., Ma, M.K., Ley, T.J. and Dipersio, J.F., 2001, *Sudden Death Among Patients With Acute Promyelocytic Leukemia Treated With Arsenic Trioxide*, Blood, 98: 266–271pp.

White, B.R., Stackhouse, B.T. and Holcombe, J. A., 2009, *Magnetic -*Fe_2O_3 *Nanoparticles Coated With Poly-L-Cysteine For Chelation Of As(III), Cu(II), Cd(II), Ni(II), Pb(II) And Zn(II),* Journal Of Hazardous Materials, 161:848–853pp.

WHO, 1997, *Aluminium*, Geneva, World Health Organization, International Programme on Chemical Safety (Environmental Health Criteria 194).

WHO, 2003, *Aluminium in Drinking-Water Background Document for Development of WHO Guidelines for Drinking-Water Quality*, World Health Organization, Geneva. Http://Www.Who.Int/Water_Sanitation_Health/Dwq/Chemicals/En/Aluminium.Pdf (07.09.2014).

WHO, 2011, *Guidelines for Drinking-Water Quality, Arsenic*, Fourth Edition, Http://Apps.Who.Int/Iris/Bitstream/10665/44584/1/9789241548151_Eng.Pdf.

Wickstrøm, T., Lund, W., and Bye, R., 1995, *Determination Of Arsenic And Tellurium By Hydride Generation Atomic Spectrometry: Minimizing Interferences From Nickel, Cobalt And Copper By Using An Alkaline Sample Solution*, Analyst, Volume 20:2695-2698pp.

REFERENCES (Continue)

Wikipedia, *Aluminium*, Https://De.Wikipedia.Org/Wiki/Aluminium, (07.12.2015).

Xiong, C., He, M. and Hu, B., 2008, *On-Line Separation And Preconcentration Of Inorganic Arsenic And Selenium Species In Natural Water Samples With CTAB-Modified Alkyl Silica Microcolumn And Determination By Inductively Coupled Plasma-Optical Emission Spectrometry*, Talanta, 76:772–779pp.

Yalcınkaya, O., Erdogan, H., Çiftçi, H. and Turker, **A.R.**, 2012, *Preconcentration Of Aluminum On Nano* ZrO_2/B_2O_3 *And Its Determination By Flame Atomic Absorption Spectrometry*, Spectroscopy Letters, 5:344-351pp.

Yalcınkaya, O., Kalfa, O.M. and Turker, **A.R.**, 2011, *Chelating Agent Free-Solid Phase Extraction (CAF-SPE) Of Co(II), Cu(II) And Cd(II) By New Nano Hybrid Material* (ZrO_2/B_2O_3), Journal Of Hazardous Materials 195:332– 339pp.

Yamamoto, M., Shohji, T., Kumamaru, T., and Yamamoto, Y., 1981, *Masking Effect Of Potassium Iodide On The Interferences In The Atomic-Absorption Spectrophotometric Determination Of Antimony Utilizing Stibine Generation By Sodium Borohydride Tablet Reduction*, Fresenius' Zeitschrift für Analytische Chemie, Volume 305, Issue 1:11–14pp.

Zhang, L., Ishi, D., Shitou, K., Morita, Y. and Isozaki, A., 2005, *Simultaneous Multielement Analysis Of Total As, Se And Sb On Titanium Dioxide By Slurry Sampling-Graphite Furnace Atomic Absorption Spectrometry*, Talanta, 68: 336–342pp.

Zhang, Q., Minami, H., Inoue, S. and Atsuya, I., 2001, *Preconcentration By Coprecipitation Of Arsenic And Tin In Natural Waters With A Ni–Pyrrolidine Dithiocarbamate Complex And Their Direct Determination By Solid-Sampling Atomic-Absorption Spectrometry*, Fresenius J Anal Chem, 370 :860–864pp.

Zhang, Q., Minami, H., Inoue, S. and Atsuya, I., 2004, *Differential Determination Of Trace Amounts Of Arsenic(III) And Arsenic(V) In Seawater By Solid Sampling Atomic Absorption Spectrometry After Preconcentration By Coprecipitation With A Nickel–Pyrrolidine Dithiocarbamate Complex*, Analytica Chimica Acta, 508, 1:99–105pp.

REFERENCES (Continue)

Zhang, X., Cornelis, R., De Kimpe, J. and Mees, L., 1996, *Speciation Of Toxicologically Important Arsenic Species In Human Serum By Liquid Chromatography-Hydride Generation Atomic Absorption Spectrometry*, Journal Of Analytical Atomic Spectrometry, 11:1075-1079pp.

Zhang, Y., Wang W., Li, L., Huang, Y. and Cao, J., 2010, *Eggshell Membrane-Based Solid-Phase Extraction Combined With Hydride Generation Atomic Fluorescence Spectrometry For Trace Arsenic(V) In Environmental Water Samples*, Talanta, Volume 80, Issue 5:1907–1912pp.

Zheng, H., Gao, X., Song, L., Guo, H., Yang, S. and Chang, X., 2011, *Preconcentration Of Trace Aluminum (III) Ion Using A Nanometer-Sized* Tio_2*-Silica Composite Modified With 4-Aminophenylarsonic Acid, And Its Determination By ICP-OES*, Microchimica Acta, 175: 225–231pp.

Zhu, H., Jia, Y., Wu, X. and Wang, H., 2009, *Removal Of Arsenic From Water By Supported Nano Zero-Valent Iron On Activated Carbon*, Journal Of Hazardous Materials, 172:1591-1596pp.

Zmozinski, A.V., Llorente-Mirandes, T., Damin, I.C.F, López-Sánchez, J.F., Vale, M.G.R., Welz, B. and Silva, M. M., 2015, *Direct Solid Sample Analysis with Graphite Furnace Atomic Absorption Spectrometry—A Fast and Reliable Screening Procedure for the Determination of Inorganic Arsenic in Fish and Seafood*, Talanta 134:224–231pp.

Zou, Z., Wang, S., Jia, J., Xu, F., Long, Z. and Hou, X., 2016, *Ultrasensitive Determination Of Inorganic Arsenic By Hydride Generation-Atomic Fluorescence Spectrometry Using* Fe_3O_4*@ZIF-8 Nanoparticles For Preconcentration*, Microchemical Journal 124:578–583pp.

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İşlek Coşkun, Y., Çiftçi, T.D. and Henden, E., 2016, *A Novel Nanoadsorbent Ni/Ni$_x$B For Preconcentration Of Arsenic(III) And Arsenic(V) Before Hydride Generation-Atomic Absorption Spectrometric Determination*, Desalination and Water Treatment, 57, 43:20411-20421pp.