UNIVERSIDADE FEDERAL DE MINAS GERAIS
Curso de Pós-Graduação em Engenharia Metalúrgica e de Minas

Dissertação de Mestrado

"Especiação de arsênio em meio aquoso através da imobilização de As(III) e As(V) em diferentes sistemas de extração em fase sólida"

Autora: Graziele Duarte
Orientadora: Profª. Virgínia S. T. Ciminelli
Co-orientadora: Mônica Cristina Teixeira

Fevereiro de 2006

UNIVERSIDADE FEDERAL DE MINAS GERAIS
Curso de Pós-Graduação em Engenharia Metalúrgica e de Minas

Graziele Duarte

"Especiação de arsênio em meio aquoso através da imobilização de As(III) e As(V) em diferentes sistemas de extração em fase sólida"

"Arsenic speciation in aqueous environment by As(III) and As(V) immobilization onto different solid phase extraction systems"

Dissertação de Mestrado apresentada ao Curso de Pós-Graduação em Engenharia Metalúrgica e de Minas da Universidade Federal de Minas Gerais

Área de Concentração: Tecnologia Mineral
Orientadora: Profª. Virgínia S. T. Ciminelli
Co-orientadora: Profª. Mônica Cristina Teixeira- UFOP

Belo Horizonte
Escola de Engenharia da UFMG
2006

AGRADECIMENTOS

Enfim mais uma etapa cumprida, mais uma meta atingida, mais um sonho realizado... E se venho conseguindo alcançar o sucesso em meus projetos, devo isso em grande parte ao apoio e exemplo de pessoas muito especiais que de alguma maneira contribuíram em muito para a minha formação pessoal e profissional.

Por isso gostaria de agradecer, em primeiro lugar, aos meus pais, senhor Tarcízio e dona Lourdes, meus primeiros e eternos mestres, por tanto amor e dedicação. E especialmente hoje, por sempre incentivarem a mim e às minhas irmãs a enfrentar nossos desafios, nos ensinando que para vencê-los a nossa melhor ferramenta seria o estudo. Vocês só não imaginavam que levaríamos esse conselho tão a sério!

Agradeço às minhas irmãs Dê, Nete, Paty e Aline, por sempre estarem ao meu lado, mesmo que à distância em alguns momentos, torcendo por mim, vibrando com meus sucessos e me consolando nas horas difíceis. Enfim, por mais do que irmãs serem também minhas grandes amigas. Falando em amigas, agradeço à presença constante em minha vida de Michelle, Denise, Carol e Cynthia. Sem vocês esses últimos sete anos não teriam sido tão especiais...

Aos meus sobrinhos, Larissa, Caio, Alice, Clara, Cecília, João Pedro e Theo, pelo prazer de tê-los como minhas eternas crianças e por encherem, literalmente, nossa casa e nossos corações de alegria.

Aos amigos do Laboratório de Processamento Aquoso, Ilda, João, Fernando, Bruno, Maycon, Rodrigo, Matheus, Júlio, Christina, Cláudia e Michelle (mais uma vez), pelo ótimo ambiente de trabalho, pelas valiosas contribuições ao meu projeto e, principalmente, pelos bons momentos de descontração que compartilhamos durante todo esse período. À minha querida Mônica, por me ensinar que não existem fronteiras para o conhecimento e pelo empenho em me ajudar durante todo o desenvolvimento deste trabalho. À minha orientadora, professora Virgínia Ciminelli, pelos ensinamentos, pelo exemplo, pelo suporte e principalmente, por me apresentar de maneira tão brilhante o “maravilhoso mundo” do processamento aquoso, que me trouxe de vez para a vida acadêmica.

RESUMO

O estudo da especiação de arsênio tornou-se uma ferramenta essencial para o conhecimento dos efeitos toxicológicos e da biodisponibilidade das espécies arsenicais em meio aquoso. Uma das etapas mais importantes nesse processo é o preparo da amostra, onde a extração em fase sólida (SPE - *Solid Phase Extraction*) é considerada como a técnica mais adequada, permitindo a preservação da composição original e do estado de oxidação dos compostos de arsênio durante o estudo de especiação. Neste trabalho, um novo sistema para especiação de arsênio foi desenvolvido usando uma resina tiólica quelante para remoção de As(III), ressaltando-se que as micro-colunas para SPE usadas atualmente têm afinidade pela espécie pentavalente. De forma comparativa, os desempenhos do novo sistema e de um produto comercial foram avaliados. Foram utilizados micro-colunas de troca de aniônica contendo sílica impregnada com amina quaternária como grupo funcional - LC-SAX (Supelco, PA - Bellefonte) e micro-colunas preparadas com a resina Amberlite GT73 (Rohm e Haas), contendo o grupo funcional tiol. A eficiência na remoção das espécies e a seletividade das resinas foram avaliadas em diferentes condições de pH, vazão e na presença de espécies competidoras. A caracterização das resinas carregadas com arsênio foi realizada usando-se análises de Espectroscopia de Absorção de raios-X. A análise de XANES (*X-ray Absorption Near Edge Structure*) demonstrou os diferentes estados de oxidação das espécies adsorvidas pelas diferentes resinas. A técnica EXAFS (*Extendend X-ray Absorption Fine Structure*) permitiu identificar a estrutura molecular de adsorção do arsênio pela resina Amberlite GT73, que envolve a coordenação do arsênio trivalente com três átomos de enxofre. Tanto o cartucho LC-SAX como o Amberlite GT73 mostraram-se eficientes na especiação de arsênio, retendo as espécies As(V) e As(III), respectivamente, em uma ampla faixa de pH e vazão de até 5,0 mL min^{-1}. A presença de íons competidores não alterou a imobilização de As(III) pela resina Amberlite GT73 e a retenção de As(V) pelos cartuchos LC-SAX (exceto quando 250 mg L^{-1} de sulfato foi usado). Porém, a seletividade de ambas as resinas foi significativamente afetada pela presença de íons sulfato e fosfato, além dos cátions de ferro (Fe^{2+} e Fe^{3+}). Os resultados obtidos confirmaram que a metodologia desenvolvida usando a resina Amberlite GT73 pode ser aplicada para especiação de arsênio em águas superficiais, tanto em laboratório como em campo, surgindo como uma alternativa única para a espécie trivalente, complementando assim as técnicas de resinas de troca aniônica atualmente utilizadas.

ABSTRACT

The study of the arsenic speciation has become an essential tool for the assessment of the toxicological effects and bioavailability of arsenic species in aqueous environment. One of the most important steps for an efficient arsenic speciation is the sample preparation, which requires the preservation of the original arsenic compounds and their oxidation state. Among the methods used for sample preparation, the solid phase extraction (SPE) can be considered as the most commonly applied sample handling technique. In this work, a new system for inorganic arsenic speciation was developed using a thiol chelating resin packed into a disposable syringe. In this system, As(III) is the immobilized species, in contrast to other SPE cartridges currently available, which remove the pentavalent species. The performances of two SPE cartridges for inorganic arsenic speciation were evaluated: a silica-based anion exchange cartridge, LC-SAX (Supelco, PA – Bellefonte), and a tailor-made cartridge filled with the Amberlite GT73 resin (Rohm and Haas), a thiol chelating resin. The As removal and selectivity of these cartridges were assessed under different conditions of pH, flow rate and in the presence of competing species. The characterization of the two resins loaded with arsenic was carried out using X-ray Absorption Spectroscopy. The different oxidation state of the adsorbed species by the two resins was demonstrated by XANES (X-ray absorption near edge structure) analyses. In addition, EXAFS (Extended X-ray absorption fine structure) resolved the molecular structure of sorbed arsenic onto the Amberlite GT73 loaded resin, showing a coordination of one atom of arsenic with three sulfur atoms. Both the LC-SAX and Amberlite GT73 cartridges were able to efficiently separated the inorganic arsenic species, As(V) and As(III), in a broad pH range (above 2.1 for LC-SAX and below 10 for Amberlite GT73), and at flow rates up to 5.0mL min^{-1}. The presence of competing ions have not altered the As(III) and As(V) immobilization by the Amberlite GT73 and LC-SAX cartridges, except when 250 mg L^{-1} of sulfate was used. However, the selectivity of both resins was significantly affected by the presence of sulfate and phosphate ions, as well as iron (Fe^{2+} and Fe^{3+}) in the experiments with Amberlite GT73. The present results show that the developed protocol using Amberlite GT73 resin can be applied for arsenic speciation in surface waters for both laboratory and field work purposes, thus arising as a novel alternative for As(III) speciation and a useful complement to the available anion exchange methods.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF SYMBOLS

AAS	Atomic Absorption Spectrometry
ADP	Adenosine diphosphate
ATP	Adenosine Triphosphate
DMA	Dimethylarsonic acid
EXAFS	Extended X-ray absorption fine structure
HPLC	High Performance Liquid Chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IGAM	Instituto Mineiro de Gestão das Águas
MMA	Monomethylarsinic acid
n	Coordination number
pka	Acid dissociation constant
R	Interatomic distance
SPE	Solid Phase Extraction
USEPA	United States Environmental Protection Agency
XANES	X-ray absorption near edge structure
XAS	X-ray Absorption Spectroscopy

1. INTRODUCTION

Arsenic is an extremely toxic metalloid that adversely affects human health in acute or sub-acute forms. An acute form of arsenic poisoning usually occurs by ingestion of contaminated food or drink while the sub-acute arsenic poisoning occurs by inhalation or by straight contact with the skin (Mandal and Suzuki, 2002; Jain and Ali, 2000).

The toxicity of compounds containing arsenic is strongly dependent on the valence of the arsenic species, as well as on the physical and chemical properties of As-bearing compound. Arsenite species are 10 times more toxic than arsenate species and 70 times more toxic than the methylated species (Kumaresan and Riyazunddin, 2001). The higher toxicity of the former is explained by the inactivation of enzyme systems, through interaction of the trivalent arsenic species with proteins by bonding to the -SH and -OH groups. As(V) needs first to be reduced to As(III) in order to exert a similar toxic effect. The toxicity of arsenate species for the living beings is more related to its competition with phosphate groups. Pentavalent arsenic can disrupt the oxidative phosphorylation - the process by which ATP is formed - by the production of an arsenate ester of ADP. This process is known as arsenolysis. Among the other factors that also affect the toxicity of arsenical compounds one may quote the physical state, the particle size, the rates of absorption and elimination by the cells (Mandal and Suzuki, 2002).

Arsenic is one of the most important global environmental pollutants and its occurrence is a result of natural processes, such as weathering reactions, biological activity and volcanic emissions, as well as of anthropogenic activities. It is found in soil, sediments, water, air and living organisms. Arsenic naturally occurs in several different minerals, such as arsenates, sulfides and sulfosalts. In relatively minor abundance one may found arsenides, arsenites, oxides, silicates and elemental arsenic. The arsenic minerals are present in large concentrations in mineralized areas, usually in association with the transition metals as well as with Cd, Pb, Ag, Au, Sb, and Mo. The arsenopyrite, FeAsS, is the most abundant arsenic ore mineral (Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002).

In aqueous environments, high concentrations of arsenic are found in groundwater throughout the world. These sources include aquifers under both oxidizing and

reducing conditions, and also areas affected by geothermal, mining and industrial activity. In a large number of aquifers in various parts of the world, like Bangladesh, India, USA, China, Chile, Mexico, Argentina, Poland, Canada and Japan, problems from As occurring at concentrations above 50 µg L^{-1} have been reported in recent years. The arsenic found on earth's atmosphere is mainly of natural origin. Its concentrations are usually low but have been increased by inputs from smelting and other industrial operations, fossil fuel combustion and volcanic activity (Jain and Ali, 2000; Smedley and Kinniburgh, 2002). In addition to the natural occurrences, which are the largest source of environmental contamination, arsenic can be released from several anthropogenic sources. These sources include the manufacturing of metals and alloys, petroleum refining, pharmaceutical manufacturing, pesticide manufacturing and application, chemical manufacturing, burning of fossil fuels, and waste incineration (Ning, 2002).

1.1. Arsenic species in water

Arsenic mobilization takes place at pH values typically found in groundwaters, usually between 6.5 and 8.5, and also, under both oxidizing and reducing conditions. Arsenic may occur in a variety of oxidation states, such as -3, 0, +3 and +5. In natural waters, it is mainly found in inorganic forms derived from the arsenious acid (H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-}) and arsenic acid (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}). With respect to the organic arsenic forms, the main species are the derived forms of the dimethylarsinc acid, $DMA_{(III)}$ and $DMA_{(V)}$ ($(CH_3)_2AsOH$ and $(CH_3)_2OAsOH$, respectively) and from the monomethylarsonic acid, $MMA_{(III)}$ and $MMA_{(V)}$ ($CH_3As(OH)_2$, and $CH_3OAs(OH)_2$, respectively). These species are generally produced by biological activity and are rarely quantitatively important. However, the presence of these organic arsenic forms is becoming more significant in areas where waters are considerably impacted by industrial pollution. The dissociation reactions for the arsenious and arsenic acids as well as their pKa_s (acid dissociation constants) are presented in the Equations from 1.1 until 1.6, and the distribution of the inorganic species as a function of pH are shown by Figure 1.1 and Figure 1.2 (Smedley and Kinniburgh, 2002; O'Day, 2006).

$H_3AsO_3 \leftrightarrows H^+ + H_2AsO_3^-$ ($pKa_1 = 9.23$) (1.1)

$H_2AsO_3^- \leftrightarrows H^+ + HAsO_3^{2-}$ ($pKa_2 = 12.13$) (1.2)

$HAsO_3^{2-} \leftrightarrows H^+ + AsO_3^{3-}$ ($pKa_3 = 13.40$) (1.3)

$H_3AsO_4 \leftrightarrows H^+ + H_2AsO_4^-$ ($pKa_1 = 2.20$) (1.4)

$H_2AsO_4^- \leftrightarrows H^+ + HAsO_4^{2-}$ ($pKa_2 = 6.97$) (1.5)

$HAsO_4^{2-} \leftrightarrows H^+ + AsO_4^{3-}$ ($pKa_3 = 11.53$) (1.6)

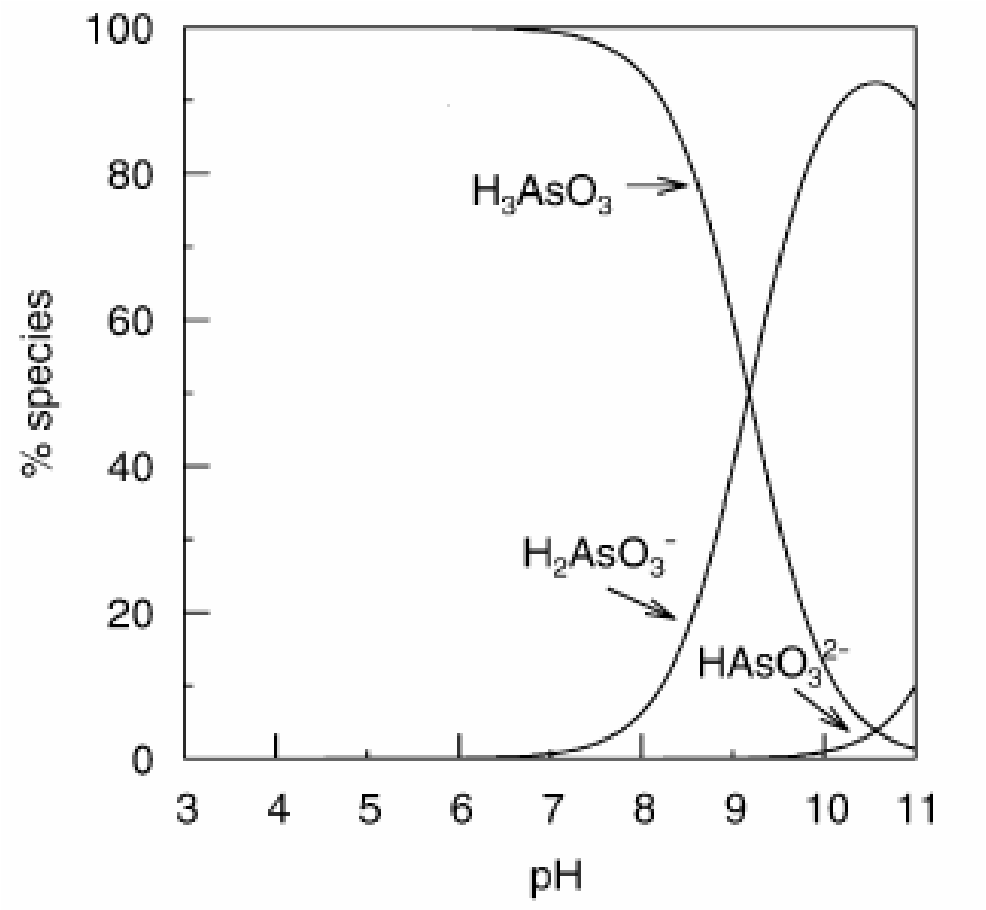

Figure 1.1: Arsenite speciation as a function of pH – ionic strength of about 0.01mol L^{-1} (Smedley and Kinniburgh, 2002).

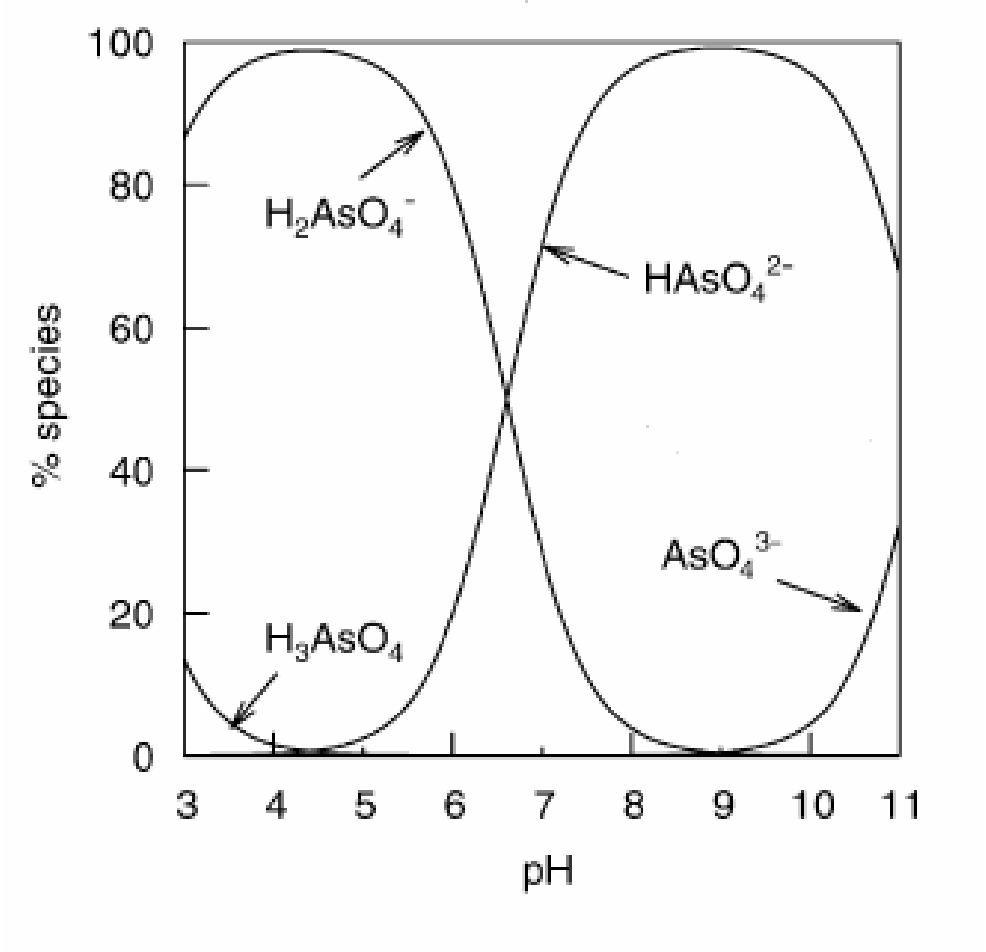

Figure 1.2: Arsenate speciation as a function of pH -ionic strength of about 0.01mol L^{-1} (Smedley and Kinniburgh, 2002).

Arsenic is one of the most complex oxyanion-forming elements in the environment, due to its relative mobility over a wide range of redox conditions. With regard to the fundamental variables in the speciation of arsenic, redox potential (Eh) and pH are the most important. Figure 1.3 shows the speciation of arsenic in aqueous environment under various pH and redox conditions. As it may be seen, the dominant species under oxidizing conditions and at pH less than 6.9 is $H_2AsO_4^-$. At pH higher than 6.9, $HAsO_4^{2-}$ becomes dominant, whilst the species H_3AsO_4 and AsO_4^{3-} only appear in extremely acidic and alkaline conditions, respectively. On the other hand, under reducing conditions and at a wide range of pH (until pH values around 9.2) the uncharged arsenite species, H_3AsO_3, will predominate; the charged arsenite species only appear at pH higher than 9.2 (Smedley and Kinniburgh, 2002).

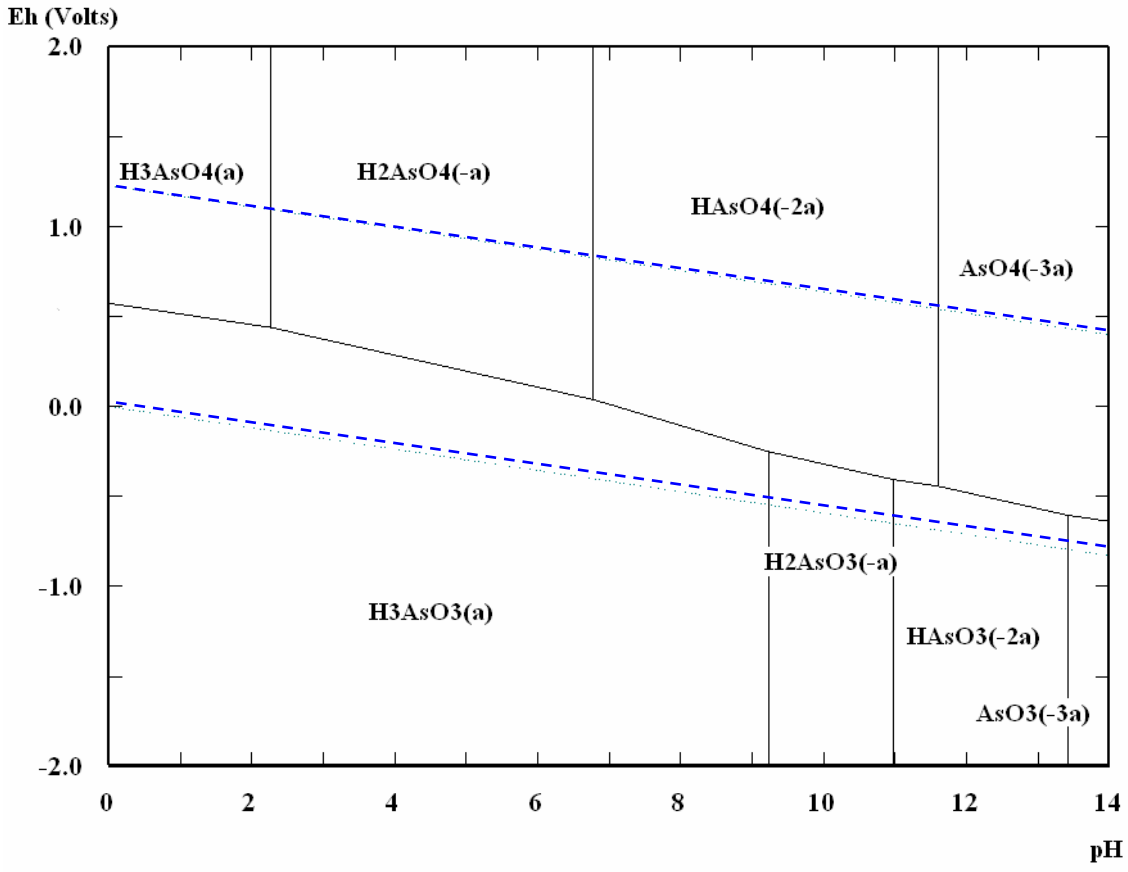

Figure 1.3: Eh-pH diagram for aqueous As species in the system As–H_2O at 25ºC and 1.0 mol kg $_{H20}^{-1}$ (obtained using the software HSC Chemistry 4.0).

1.2. Speciation analysis of arsenic in aqueous environment

The speciation analysis of an element in water is defined as the determination of the concentration of the different physical-chemical forms of the element and its total concentration in the sample. The speciation of arsenic in aqueous environments is of large interest due to differing levels of toxicity exhibited by the various species as well their different response to remediation methods (Kumaresan and Riyazunddin, 2001). In recent years, the use of arsenic speciation analysis has increased substantially, and the main techniques commonly involve a combination of chromatographic separation with spectrometric detection (B'Hymer and Caruso, 2004).

1.2.1 The major separation and detection technologies

Regarding the chromatographic methods, HPLC (High Performance Liquid Chromatography) is the mostly used one, the Ion-Exchange Chromatography and Ion-Pair Chromatography being the most important available techniques. The Ion-Exchange Chromatography can be used only for ionic species separation, and the mechanism is based on the exchange equilibrium between a stationary phase, containing ions in its surface, and the mobile phase which contain oppositely charged ions. This technique can be used at both anion and cation-exchange separation modes. The more important parameters that affect the separation and retention of analytes in ion-exchange HPLC are the ionic strength of the solute, the pH of the mobile phase, the ionic strength and concentration of the buffer, the temperature and the flow rate of the mobile phase. The Ion-Pair Chromatography makes use of aqueous solutions containing organic modifiers as the mobile phases. In this technique, the separation of the species is carried out using stationary phases that have a surface less polar than the mobile phase. To the mobile phase is added a counter-ion, causing the establishment of a secondary chemical equilibrium that is used to control the retention and selectivity during the analyses. An important advantage of ion-pair HPLC is to allow not only the separation of ionic species, but also the speciation of uncharged molecular species (Gong *et al*., 2002; B'Hymer and Caruso, 2004).

With respect to the detection technique for arsenic quantification, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) has become an attractive option, since it can provide high-sensitivity (arsenic detection limit around 2.0 µg L^{-1}), multi-element capability and can be also combined with separation techniques for speciation analysis. Another usual detection technique applied to arsenic speciation is hydride generation, which allows working with very low detection limits. A disadvantage of this technique is that not all arsenic species are able to form hydrides, and thus the use of decomposition techniques is commonly required (Gong *et al*., 2002; Bednar *et al.,* 2004; B'Hymer and Caruso, 2004).

1.2.2 Sample Preparation

The sample preparation is one of the most important steps in arsenic speciation, since it is fundamental to preserve the original compound and the arsenic oxidation state in the samples to be analyzed. In this context, several methods have been attempted to maintain the arsenic species distribution in water samples. Among these methods, the solid phase extraction (SPE) can be considered as the most applied sample handling technique (Camel, 2003; Gong *et al.,* 2002; Liska, 2000).

SPE Processes

The first step in the SPE processes is the solid phase conditioning, where an appropriate solvent is passed through the sorbent, followed by the same sample solvent. This essential step provides the pre-wetting of the packed material, removing the air present in the column, and also enables the solvation of the functional groups. The second step is the percolation of the sample through the sorbent. The sample is allowed to flow through the column by gravity, pumping or vacuum, basically. An important parameter in this step is the sample flow-rate, which needs to be low enough to reach an efficient immobilization of the analytes and, at the same time, high enough to optimize the process time. An optional step is the washing of the solid with an appropriate solvent (low elution capacity) with the aim of eliminating impurities that have been immobilized onto the sorbent. The final step is the elution with an appropriate solvent to efficiently recover the retained species (Camel, 2003).

Due to their breakthrough properties and loading capacity, the use of SPE cartridges became one of the most suitable options for aqueous sample preparation, replacing the preparation of laboratory-made columns (Liska, 2000). The mechanism of analyte retention by the SPE cartridges depends on the nature of the solid phase, where ion exchange and chelation processes are the most important. In the ion exchange mechanism, the sorbent usually contains cationic or anionic functional groups that can exchange the associated counter-ion. When the ion-exchange sites are active at any pH value, the sorbent is known as a strong cation or anion exchanger. On the other hand, if the ion exchange sites are active only at pH values greater or lower than the pKa value, the sorbent is called a weak cation or ion exchanger. The most important strong sites are the sulfonic acid groups, which presents a cation exchanger character,

and the quaternary amines, recognized by their anion exchanger character. The weak sites are mainly represented by the carboxylic acid groups (cation exchanger) or primary, secondary and tertiary amines (anion exchanger) (Camel, 2003).

The importance of separation and concentration techniques involving chelating sorbents has risen substantially in the last years, since these chelating resins are usually more selective than simple ion exchangers (Matsunaga *et al*., 1996). The advantages of these sorbents are that they can provide a concentration factor up to several hundred folds, better separation of interfering ions and high efficiency of removal (USEPA, 2000). The chelating elements most frequently used are nitrogen (amines, azo groups, amides, nitriles), oxygen (carboxylic, hydroxyl, phenolic, ether, carbonyl, phosphoryl groups) and sulfur (present in thiols, thiocarbamates, thioethers).

Some solid phase extraction cartridges containing anion and cation exchange resins have been proposed for arsenic speciation in aqueous samples. Le *et. al* (2000) had developed a system for the speciation of trace levels of arsenic in water, where the sample collection was incorporated with on-site arsenic species separation. This method was based on selective retention of arsenic species on specific solid phase cartridges followed by selective elution and hydride generation atomic fluorescence analysis of the arsenic species. Yalcin and Le (2001) carried out a comparison of many solid phase extraction cartridges for arsenic immobilization and subsequent elution. According to these authors, alumina cartridges are not suitable for speciation analysis because all the arsenic species studied - As(V), As(III), monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) are retained. However, they were very efficient for removal and preconcentration purposes. As regards to the speciation processes, a resin-based, strong cation exchange cartridge was used to retain the DMA, which were eluted with 1.0 mol L^{-1} HCl. Both As(V) and MMA were retained on a silica-based strong anion exchange cartridge and eluted with 60 mmol L^{-1} acetic acid (for MMA) and 1.0 mol L^{-1} HCl (for As(V)). The trivalent specie, As(III), was not immobilized by none of the cartridges, thus remaining in solution.

A promising option for retention of arsenic in the trivalent form is the thiol group (-SH). Teixeira and Ciminelli (2005) demonstrated the large affinity of thiol groups by As(III) in acid environment. This work introduced an original approach for the treatment of arsenic-containing aqueous environments based on biochemical and toxicological

fundamentals that explain arsenic toxicity. The investigated biomass was chicken feathers - a waste material from the poultry industry. This material was evaluated under different pH conditions (2 to 10), presence of competitors ions (phosphate and As(V)), and sorbent preparation. The results demonstrated that the cysteine-rich biomass is highly selective for arsenic in its trivalent form, without important effects of the studied competitor ions on the solid's adsorption capacity. The sulphydril reduced groups were shown to be the active groups involved in arsenic biosorption, each arsenic atom being directly bound to three sulfur atoms available in the cysteine-reduced residues present in the keratin protein constituent of the biomass. These results led us to propose that trivalent arsenic species could be similarly sorbed by thiol chelating resins, which contain the sulphydril (-SH) as functional group. It is important to elucidate that thiol resins are widely known and commercialized, however, their application has been indicated to remove metallic contaminants such as mercury (Hg^{2+}), cadmium (Cd^{2+}) and lead (Pb^{2+}) during processes of water and wastewater treatments. Hence, the use of thiol resins for the immobilization of arsenic species in aqueous environments arises as an innovator proposal for the application of these chelating resins.

Considering the aforementioned context, this work is aimed to developing a new methodology for inorganic arsenic speciation through the immobilization of the trivalent species on a thiol chelating resin. In addition, the inorganic arsenic speciation by the Amberlite GT73 cartridges (prepared by packing the thiol resin into a disposable syringe) and the commercial LC-SAX cartridges (a silica-based anion exchange cartridge containing a quaternary amine as a functional group) were compared. The behavior of these two solid phase extraction cartridges during the separation of the inorganic arsenic species As(III) and As(V) were assessed with respect to pH, flow rate and competing ion influences. The mechanism of speciation was investigated in a molecular level by X-ray absorption analyses.

2. Evidences from X-ray Absorption Spectroscopy for As(III) selective immobilization by a thiol chelating resin.

2.1. Introduction

The immobilization of arsenic species in natural environments or in water treatment process is greatly influenced by the As oxidation state. In aqueous solutions, the main inorganic species are the trivalent, As(III), and pentavalent arsenic, As(V), derivatives of the arsenous (H_3AsO_3) and arsenic (H_3AsO_4) acids, respectively. Under oxidizing conditions, the predominant species is the pentavalent arsenic, which is mainly present in the form of the oxianions $H_2AsO_4^-$ and $HAsO_4^{2-}$. On the other hand, under slightly reducing conditions, As(III) is the thermodynamically stable species, present as neutral H_3AsO_3, in a wide pH range (pKa_1 H_3AsO_3 = 9.2). As a consequence of its neutral feature, As(III) is more mobile than As(V) in natural environments. Hence, for an efficient arsenic retention, the conventional techniques for water and effluent treatment require a previous oxidation of As(III) to As(V) (Teixeira and Ciminelli, 2005; Smedley and Kinniburgh, 2002).

X-ray Absorption Spectroscopy (XAS) has become the most powerful characterization tool for arsenic speciation on solid samples. This method can provide, in a molecular level, a precise identification of the chemical conditions around the arsenic element, thus contributing for assessing and understanding the mobility of arsenic species in the environment (Ladeira *et al.* 2001). XAS analyses are conventionally divided into two regions: X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). Through XANES analysis it is possible to identify the arsenic oxidation state, the atom type and its coordination. The EXAFS part of the spectrum can be used to establish the local structure, supplying important information such as near-neighboring, coordination number and chemical bond distance. (Smith *et al*., 2005;).

Teixeira and Ciminelli (2005) demonstrated the large affinity of thiol groups by As(III) in acid and circumneutral environments. The work introduced an original approach for the treatment of arsenic-containing aqueous environments based on biochemical and toxicological fundamentals that explain arsenic toxicity. The biomass investigated was

chicken feathers - a waste material from the poultry industry. This material was evaluated under different pH conditions (2 to 10), presence of competitors ions (phosphate and As(V)), and sorbent preparation. The results demonstrated that the cysteine-rich biomass is highly selective for arsenic in its trivalent form, without important effects of the studied competitor ions on the solid's adsorption capacity. The sulphydril reduced groups were shown by XAS analyses to be the active groups responsible for arsenic biosorption. Each arsenic atom was found to be directly bound to three sulfur atoms available in the cysteine-reduced residues in the keratin protein constituents of the biomass.

The results obtained by Teixeira and Ciminelli (2005) led to the hypothesis that trivalent arsenic species could be similarly sorbed by thiol chelating resins containing the functional sulphydril (-SH) group. Thus, the main objectives of the present work were: (i) to verify the As(III) immobilization by thiol chelating resin, determining the equilibrium time and arsenic loading capacity at batch systems; (ii) to identify the oxidation state of the arsenic loaded onto the Amberlite GT73 resin through XANES analyses; and (iii) to obtain the coordination parameters for As(III) immobilized by Amberlite GT73 resin using EXAFS analyses. The obtained results are evaluated according to the assumption that the sorption process presents a mechanism similar to that proposed by Teixeira and Ciminelli (2005). With the aim to elucidate the performance of this resin for As(III) retention, the experiments were carried out at two different pH conditions. An important outcome of the work with thiol chelating resins for arsenic speciation is the possibility of its usage in a form of disposable, solid phase extraction cartridges.

2.2. Experimental

2.2.1 Reagents

Stock arsenate solution was prepared from sodium arsenate ($Na_2HAsO_4.7H_2O$ at 99% purity - Fluka). Chemically pure sodium meta-arsenite ($NaAsO_2$) of 99.99% purity (Fluka) was used to make stock arsenite solution. The other reagents used in the experiments (all of them of analytical grade) were 18MΩ cm Milli-Q water, acetic acid (Synth), ammonium hydroxide (QM Reagents), hydrochloric acid (VETEC), sodium hydroxide (VETEC), thioglicolic acid (VETEC).

2.2.2 Arsenic sorption onto a thiol chelating resin

Resin preconditioning

First, Amberlite GT73 resin (Rohm and Haas), a macroreticular polystyrene–divinylbenzene resin containing chelating thiol as functional group, was dried at 40ºC (FANEM, Model 320-SE) for 2 hours. The next step was the resin activation in accordance with the methodology used by Teixeira and Ciminelli (2005), where 10.0mL of a 5% (w/v) basic ammonium thioglycolate solution were added to the erlenmeyer flask (250mL) containing 0.5g of resin and kept under agitation at 150 rpm during two hours. After this pre-treatment step, the resin was filtered, washed with 5.0mL of 1.0molL^{-1} HCl solution to acidify the system and with 100mL of Milli-Q water to remove the Cl^- impurities.

Batch Sorption

Prior to the isotherm curve acquisition, the arsenic sorption onto thiol chelating resins was measured as a function of the time in batch experiments, with the aim of to determine the equilibrium time. In others words, it was assessed the necessary time to reach the maximum loading of arsenic by the resin. Hence, 0.5g of the preconditioned Amberlite GT73 resin was shaken with 100 mL of 200.0 mgL^{-1} As(III) solution, at pH 5.0, 25 ºC and 150 rpm, during times varying from 5.0 minutes until 24 h. A curve of the remnant arsenic concentration in the solution, measured by Atomic Absorption Spectrometry (Perkim Elmer Analyst A300), against the time of arsenic-resin contact was plotted (Figure 2.1). The equilibrium time of this process was assumed to be the point where the concentration of arsenic in solution became constant.

For the assessment of the arsenic immobilization onto Amberlite GT73, 0.5g of the preconditioned resin was shaken with 100 mL of 50.0, 100.0, 150.0 and 200.0mgL^{-1} As(III) solutions, separately, at erlenmeyer flasks (250mL), at 25ºC and 150 rpm, using a controlled environment incubator shaker (New Brunswick Scientific CO. INC.). After 6 hours, the loaded resin was filtered. The remainder arsenic in the solution was analyzed by Atomic Absorption Spectrometry (Perkim Elmer Analyst A300), and then, an isotherm curve was obtained plotting the arsenic loading against the arsenic equilibrium concentration (Figure 2.2). The experiment containing 100mL of As(III) at

100.0mgL^{-1} was repeated at pH 5.0 and pH 10.0 for the resin characterization by X-ray Absorption Spectroscopy.

X-ray Absorption Spectroscopy (XAS) Analyses

The analyses of X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) for the As(III) loaded onto Amberlite GT73 resin were performed using the synchrotron facilities at the Laboratório Nacional de Luz Synchrotron (LNLS), in Campinas, Brazil. XANES and EXAFS data from the arsenic K edge (11868eV) were obtained at XAS workstation, under operation conditions of 1.37GeV and beam currents of about 250mA. The spectra were recorded at room temperature using a Si (111) double crystal monochromator with an upstream vertical aperture of 0.3mm and calibrated with Au L1-edge (11918eV). The solid samples were fixed onto acrylic holders, sealed with Kapton tape film, and the arsenic K-edge X-ray absorption spectra were measured in the transmission and fluorescence modes for the pH 5.0 and pH 10.0 experiments, respectively. For the fluorescence measurements, the sample was placed at an angle of 45° to the incident beam and the signal was monitored using a 15-element Ge detector (Canberra Industries). The energy resolutions were 2 eV between 11760 and 11835 eV, 0.5 eV between 11835 and 11878 eV (XANES region), 2eV in the 11878 – 12170 eV region, 3 eV in the 12170-12250 eV region, and 4 ev in the 12250-12400 eV region. Counting times of 2 s were kept constant in the pH 5.0 experiments. For the pH 10.0 experiments were used counting times of 4.0 s in the first energy region (11760-11835 eV), 7.0 s in the XANES region (11835 – 11878 eV) and 10.0 for the subsequent energy regions. XANES and EXAFS spectra were obtained simultaneously. XANES spectra were analyzed using the Origin 6.0 software, and collected data from EXAFS were analyzed by using the Winxas 2.0 software. EXAFS data fit was obtained using phase and amplitude parameters calculated with the FEFF 6.01 software.

2.3. Results and Discussion

2.3.1 Batch sorption

Figure 2.1 shows the concentration of As(III) in the resin as a function of the contact time in batch sorption experiments. The concentration becomes constant at an averaged value of 28.1 ± 2.3 mg g^{-1} after passed approximately 6 hours, which was selected as the equilibrium time for the subsequent batch sorption experiments.

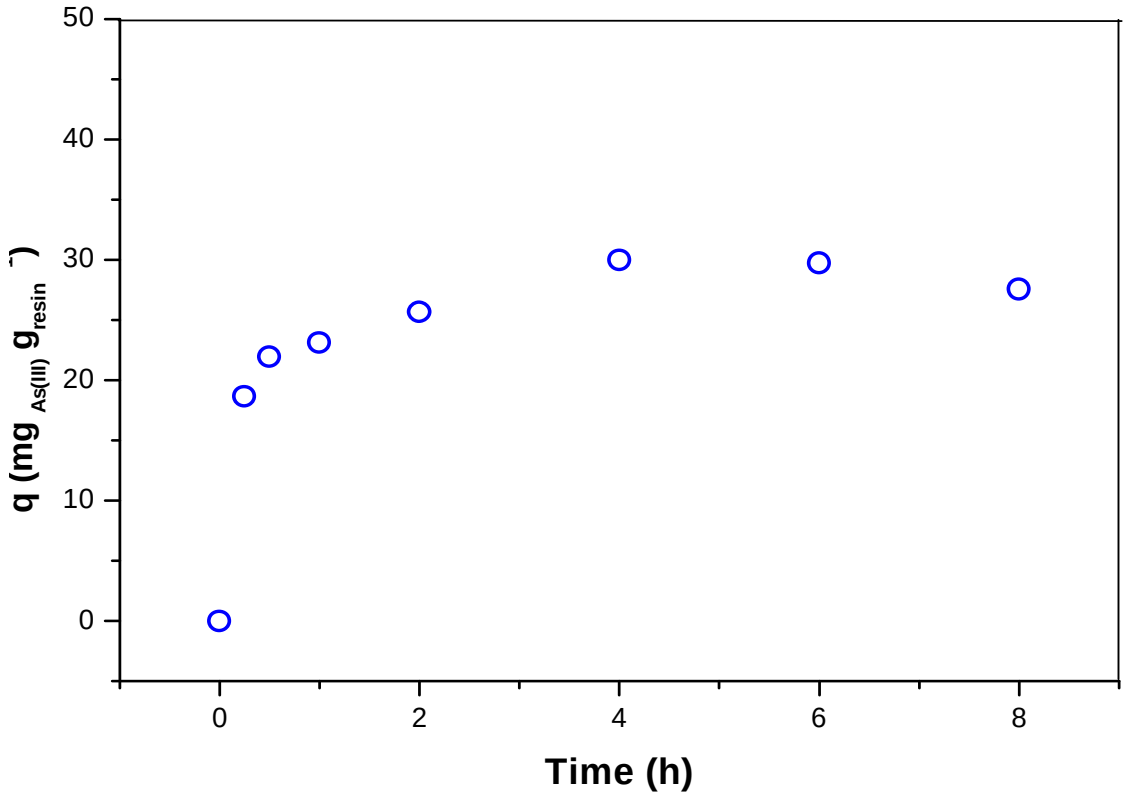

Figure 2.1: Determination of the equilibrium time for As(III) adsorption onto Amberlite GT73 resin. Conditions: 0.5 g of dried resin, 100.0 mL of As(III) solution at initial concentration of 200 mg L^{-1}, pH 5.0, 25 ºC, 150 rpm.

The isotherm that represents the As(III) immobilization onto Amberlite GT73 resin is illustrated in Figure 2.2. Under the evaluated conditions, the experimental loading capacity of As(III) onto this resin was q = 32.63 ± 0.28 mg g^{-1}, which corresponds to approximately 0.4 Eq of A(III) per liter of dried resin.

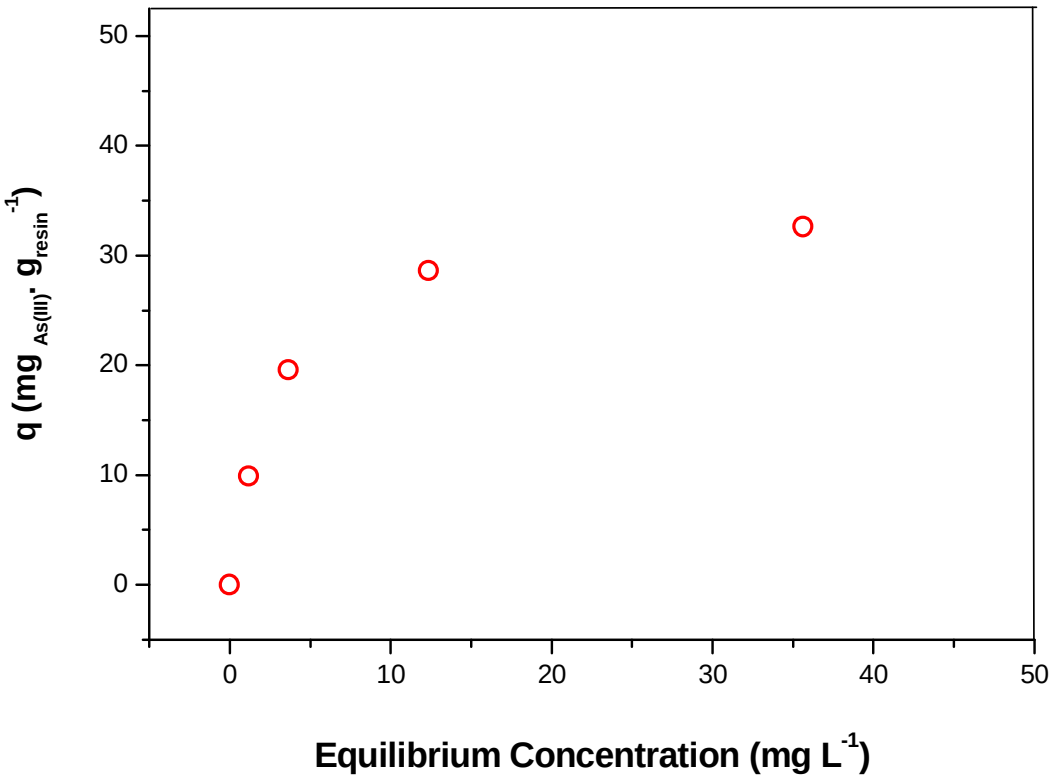

Figure 2.2: Isotherm for As(III) adsorption onto Amberlite GT73 resin. Conditions: 0.5g of dried resin, 100.0mL of As(III) solution at initial concentrations of 50.0, 100.0, 150.0 and 200.0mg L^{-1}, pH 5.0, 25ºC, 6h under agitation of 150 rpm.

With the aim of to obtain the adsorption parameters Q_{max} and k, the experimental data showed in the Figure 2.2 were adjusted to a linear expression of the Langmuir equation:

$$C_{eq} q^{-1} = k Q_{\max}{}^{-1} + C_{eq} Q_{\max}{}^{-1} \quad (7)$$

The linearized experimental curve is shown in the Figure 2.3 where the line curve indicates the fit by Langmuir equation. The obtained parameters were Q_{max} = 33.9 ± 1.5 mg g^{-1} and k = 0.02.

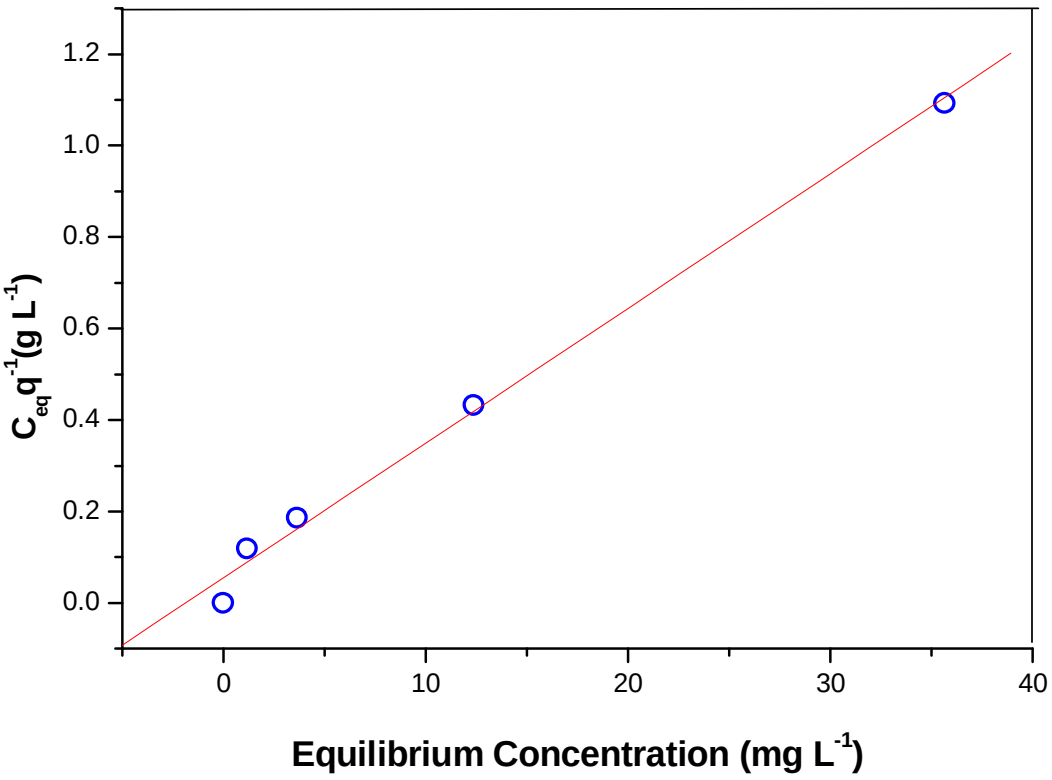

Figure 2.3: Linearized experimental data (scatter) adjusted to linear Lagmuir equation (line); theoretical Q_{max} = 33.9 ± 1.5 mg g^{-1}.

2.3.2 X-ray Absorption Spectroscopy (XAS) Analyses

The first step in the XAS analyses was to verify the oxidation state of the arsenic species adsorbed onto the Amberlite GT73 resin through X-ray absorption near edge structure (XANES) analyses. The XANES spectra were obtained for the As(III) standard ($NaAsO_2$); the loaded Amberlite GT73 resin at pH 5.0 and 10.0 and for the As(V) standard (Na_2HAsO_4). The results are shown in Figure 2.4.

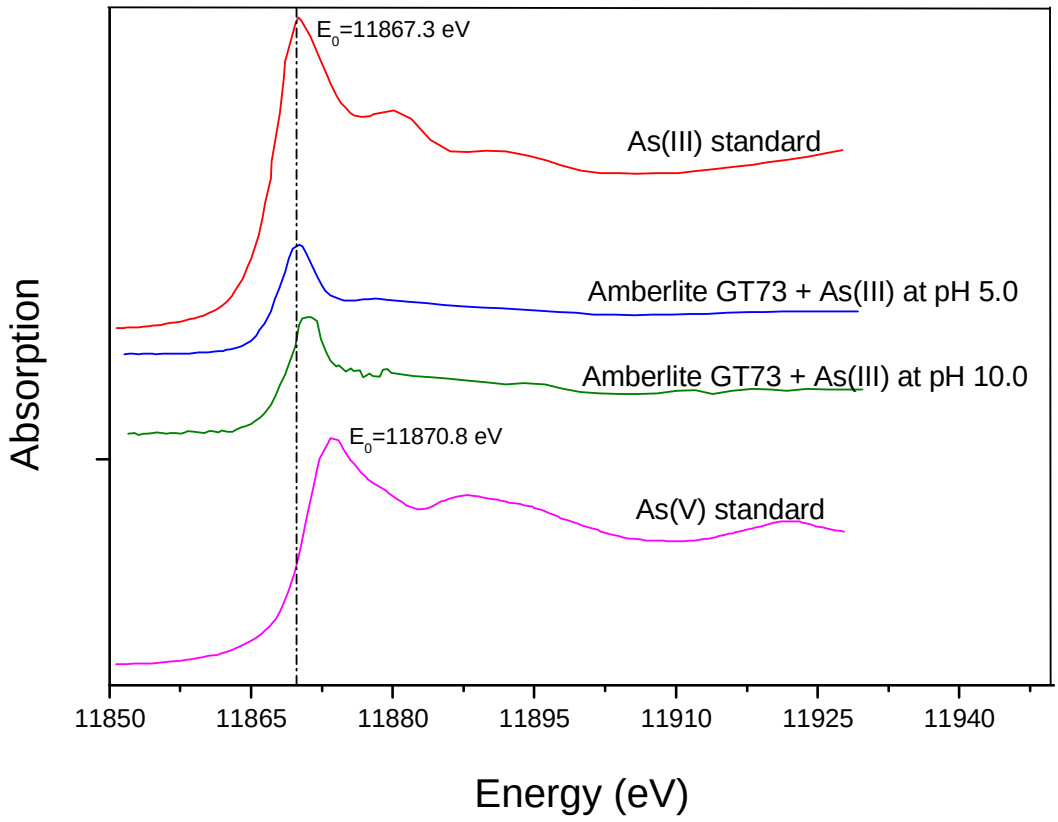

Figure 2.4: XANES spectra for As(III) standard (NaAsO2); As(III) adsorbed onto Amberlite GT73 at pH 5.0; As(III) adsorbed onto Amberlite GT73 at pH 10.0 and As(V) standard ($Na_2HAsO_4.7H_2O$).

The analyses of these spectra indicate that arsenic is loaded onto the Amberlite GT73 resin in its trivalent form at both pH values assessed. The E_0 found through the second derivative of the curves (using the Origin 6.0 software) was 11867.3 eV for the As(III) standard; 11867.1 eV for the arsenic loaded onto Amberlite GT73 resin at pH 5.0; 11867.5 eV for the arsenic loaded onto Amberlite GT73 resin at pH 10.0 and 11870.8 eV for the As(V) standard. The slight displacement in the energy peak at pH 10.0, also shown in Figure 2.4, can indicate a partial oxidation of the trivalent arsenic during the experiment.

The EXAFS analyses were based on the average of five and seven different spectra of the experiments carried out at pH 5.0 and pH 10.0, respectively, in addition to the average of three spectra of the As(III) standard. These average data were converted to the eV energy unit and then submitted to the background line extraction. The experimentally obtained E_o values were found as 11 867 eV for pH 5.0 and 11867.7 eV pH 10.0. For the As(III) standard sample, the E_o value was found as 11867.3 eV, which confirm that the arsenic species remained in the trivalent oxidation state during immobilization onto Amberlite GT73 resin, and thus confirming the results obtained by XANES analyses. The EXAFS spectra obtained for As(III) immobilization onto Amberlite GT73 resin at pH 5.0 and pH 10.0, after the background correction, are presented in Figure 2.5 and Figure 2.6, respectively.

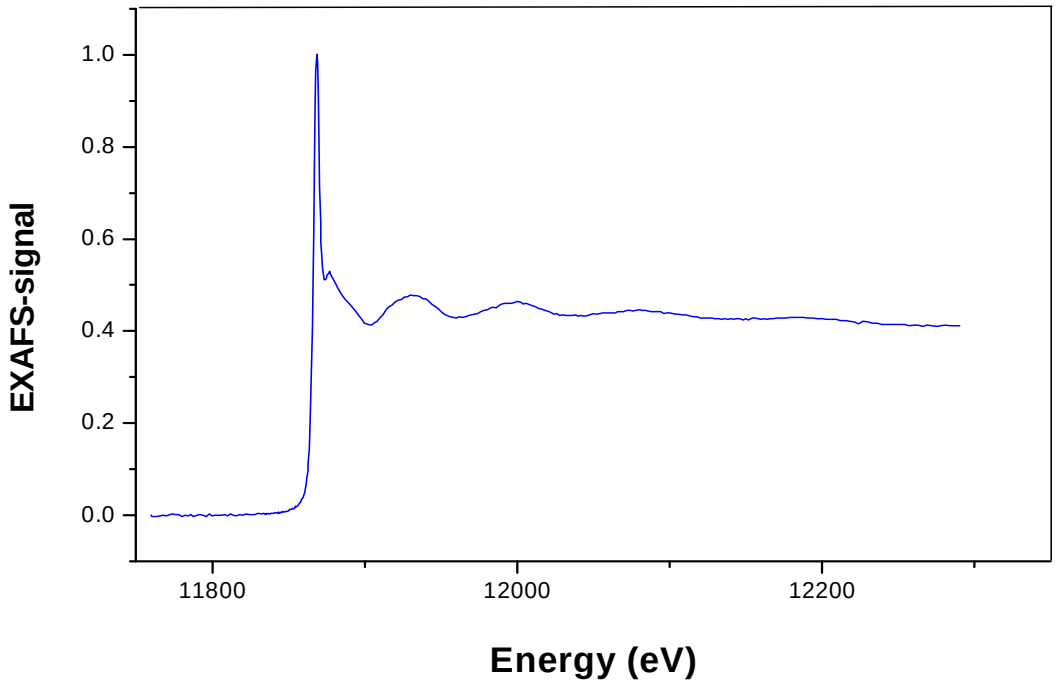

Figure 2.5: EXAFS spectrum of As(III) adsorbed onto Amberlite GT73 resin at pH 5.0, after background correction.

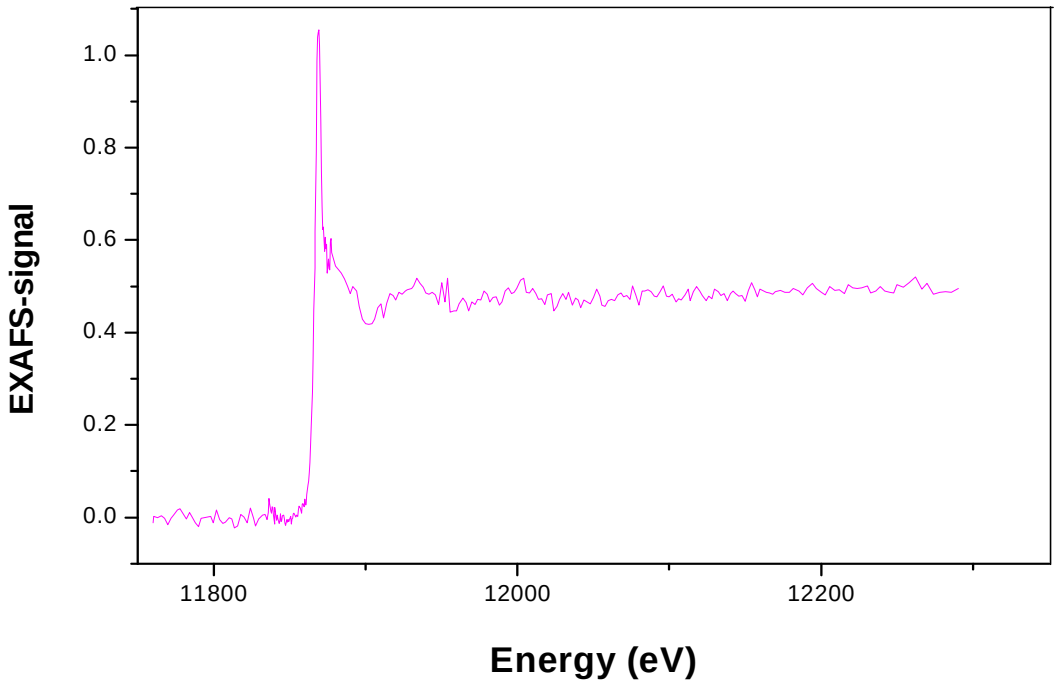

Figure 2.6: EXAFS spectrum of As(III) adsorbed onto Amberlite GT73 resin at pH 10.0, after background correction.

The EXAFS spectrum obtained for the pH 10.0 experiments presents a relatively noisier signal than the spectra from pH 5.0 experiments. This may indicate a different adsorption mechanism, probably related to the presence of the negatively charged ions, $H_2AsO_3^-$ and $HAsO_3^{2-}$ at pH higher than the first pka value of the arsenious acid (pKa_1 H_3AsO_3 = 9.2).

The Fourier transform (k = 3) of the EXAFS spectrum obtained at pH 5.0 experiments is shown in Figure 2.7. It is possible to observe the oscillations caused by all of the atoms in the neighboring coordination shells; the amplified peak corresponds to the first arsenic coordination shell.

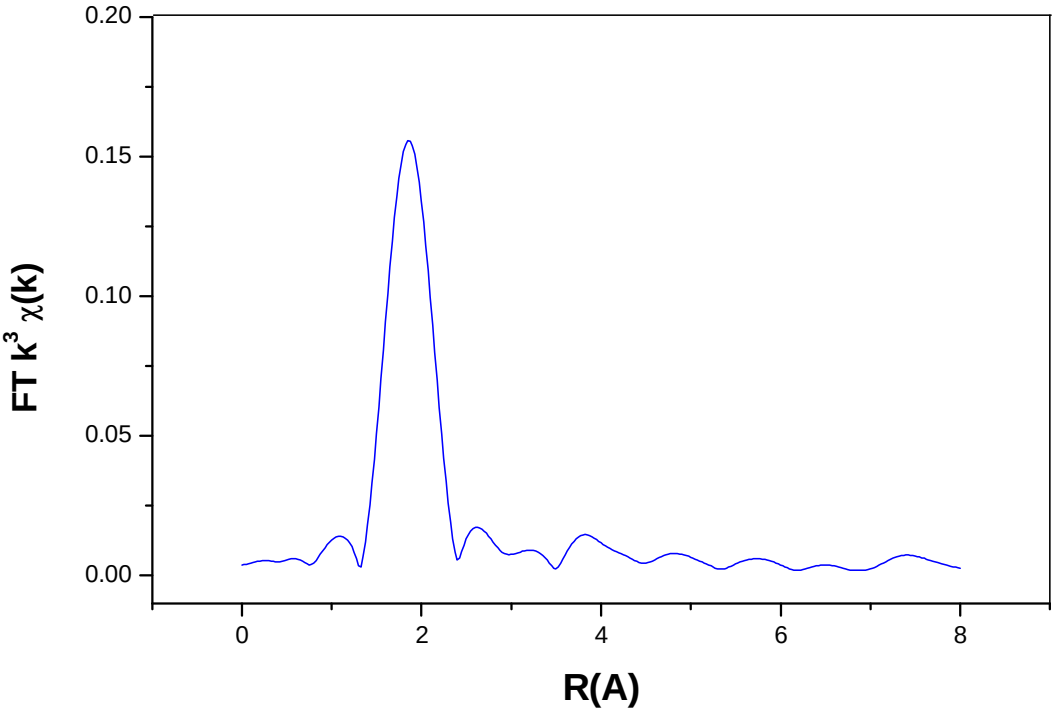

Figure 2.7: Fourier transform amplitude (K = 3). Radial distribution functions for As(III) adsorbed onto Amberlite GT73 resin at pH 5.0.

The Fourier transform of the EXAFS spectrum obtained at pH 10 is shown in Figure 2.8. As it can be observed, the amplitude of the Fourier transform was significantly lesser in this case if compared with the pH 5.0 experiment. Also, the width of the amplified peak was relatively higher at pH 10.0, which may indicate the presence of more than one atom in the arsenic neighborhood. In view of this feature, the structural parameters of the trivalent arsenic loaded onto the Amberlite GT73 resin were calculated only for the pH 5.0 experiments.

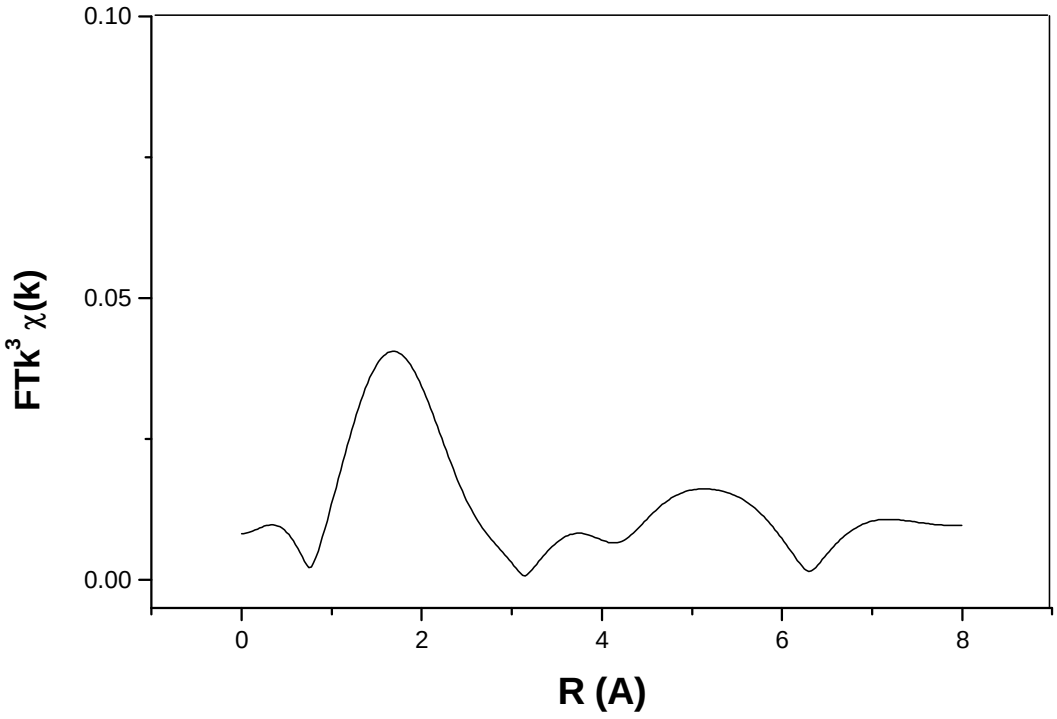

Figure 2.8: Fourier transform amplitude (K = 3). Radial distribution functions for As(III) adsorbed onto Amberlite GT73 resin at pH 10.0.

For the determination of the structural parameters such as the interatomic distance between As and atoms in the first coordination shell, the coordination number, and also the first neighbor atom, the signal obtained previously (Figure 2.7) was submitted to a second Fourier transform treatment. The resultant spectrum (Figure 2.9) shows a scattered curve, highlighting only the oscillation caused by the atoms in the As first coordination shell. The next step was the calculation of the structural parameters, adjusting the experimental data with the theoretical model provided by the FEFF program. These adjustments confirmed that sulfur is the retro-scattering atom and each arsenic atom is bound to three sulfur atoms, with an As-S interatomic distance, R = (2.2366 $\pm$ 0.0003) and a coordination number, n = (3,06 $\pm$ 0.05).

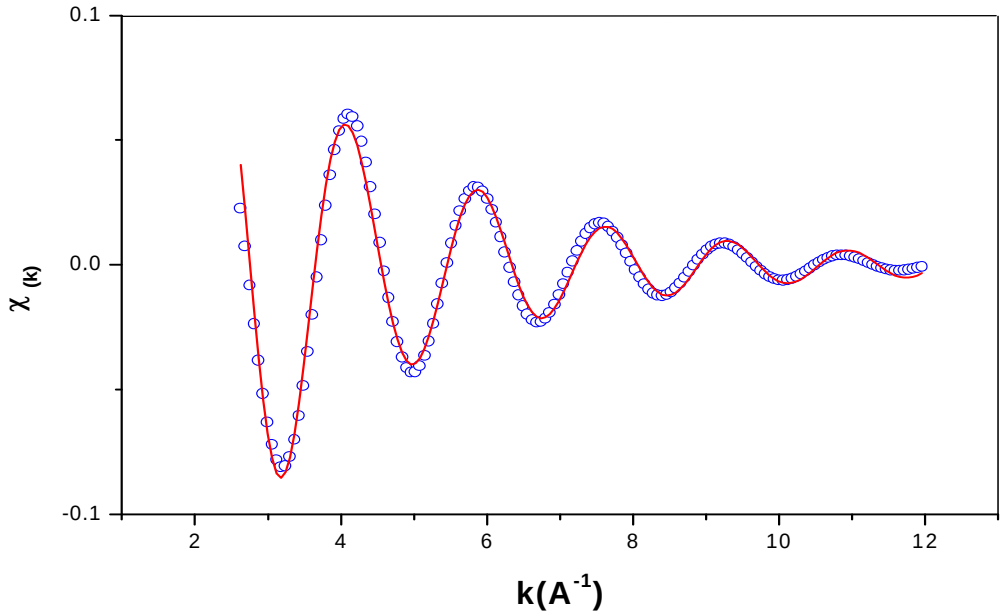

Figure 2.9: Back Fourier transform (K-space), first coordination shell. Best fit of EXAFS data to As(III) adsorbed onto Amberlite GT73 resin. Experimental data were fitted to hypothetical As/S complex using FEFF 6.0. Scatter and line curves represent experimental and theoretical data, respectively. The structural parameters are n = (3.06 ± 0.05) and R = (2.2366 ± 0.0003).

Comparing these results with those obtained by Teixeira and Ciminelli (2005) it is possible to state that the mechanism of As(III) immobilization by Amberlite GT73 resin at pH 5.0 is similar to the trivalent arsenic adsorption onto the cystein-rich biomass, where the thiol (or sulphydril) group is the active site for the As(III) retention process.

2.4. Conclusions

The Amberlite GT73 resin was shown to be able to efficiently retain the trivalent arsenic species at pH 5.0-10, and room temperature. Under saturation conditions, corresponding to an equilibrium time of approximately 6h, the resin showed an arsenic loading capacity of 30mg of As(III) per gram of dried resin.

X-ray Absorption Spectroscopy-XANES analyses showed that the arsenic loaded onto the Amberlite GT73 resin was not oxidized during the sorption process, remaining in its trivalent form. This is an unique feature since the usual sorption-based processes for arsenic immobilization remove only As(V). EXAFS analyses indicated that the trivalent arsenic species are coordinated to three sulfur atoms in the resin's thiol groups at pH 5.0, showing an interatomic As-S distance of R = (2.2366±0.0003) and a coordination number of n = (3.06±0.05).

2.5. References

LADEIRA, A. C. Q.; CIMINELLI, V. S. T.; DUARTE, H. A.; ALVES, M. C. M. and RAMOS, A. Y. (2001). Mechanism of anion retention from EXAFS and density functional calculations: Arsenic (V) adsorbed on gibbsite. *Geochimica et Cosmochimica Acta,* vol. 65, p. 1211–1217.

SMEDLEY, P. L. and KINNIBURGH, D. G. (2002). A review of the source, behavior and distribution of arsenic in natural waters. *Applied Geochemistry,* vol. 17, p. 517-568.

SMITH, P. G.; KOCH, I.; GORDON, R.; MANDOLI, D. F.; CHAPMAN, B. D. and REIMER, K. N. J. (2005). X-ray Absorption Near-Edge Structure Analysis of Arsenic Species for Application to Biological Environmental Samples. *Environmental Science and Technology,* vol. 39, p. 248-254.

TEIXEIRA, M. C. and Ciminelli, V. S. T. (2005). Development of a Biosorbent for Arsenite: Structural Modeling Based on X-ray Spectroscopy. *Environmental Science and Technology,* vol. 39, p. 895-900.

3. Inorganic arsenic speciation through As(III) and As(V) immobilization into solid phase extraction cartridges

3.1. Introduction

Arsenic speciation in natural waters and effluents is increasingly important for the assessment of toxicity and bioavailability of arsenic species in an aqueous environment. Among the methods for arsenic speciation, HPLC is the most usually applied, while other technologies such as gas chromatography, supercritical fluid chromatography and capillary electrophoresis have also been used, but with relatively lesser importance. For arsenic immobilization and consecutive speciation assessment, both anion and cation exchange chromatography techniques can be used, however, anion exchange is the most applied one (Bednar *et al.,* 2004; Impellitteri, 2004; Gong *et al.,* 2002). Prior to the analyses, the chemical species in the original sample may suffer unwanted alterations due to inadequate sample preservation. Several methods have been attempted in order to preserve the original arsenic species distribution in water samples. Among these methods, solid phase extraction (SPE) appears as the main technique, considering the benefit of arsenic species separation in the field, immediately after sample collection, and its efficient conservation, thus minimizing the possible undesirable effects of using sample preservatives (Camel, 2003; Gong *et al.,* 2002; Liska, 2000).

Regarding the materials for arsenic immobilization by SPE processes, ion exchange resins have been used as the most suitable alternative. These can be easily employed and, also, they are a useful option for field work (Impellitteri, 2004). Parker and Ciminelli (2005) investigated a flow system for inorganic arsenic speciation using a quaternary amine resin, LC-SAX, coupled on-line with the ICP-MS. The results indicated that this simplified system was very efficient for the preconcentration of As(V) and its separation from As(III), reaching a enrichment factor of approximately 4 and a recovery in the range of 99 to 110% for natural waters samples.

In recent years, the use of solid phase extraction cartridges containing anion and cation exchange resins have been proposed for arsenic speciation in aqueous samples. Le *et. al* (2000) developed a system for the speciation of trace levels of arsenic in water,

where the sample collection was incorporated with in-site arsenic species separation. This method was based on selective retention of arsenic species on solid phase cartridges - a resin-based cation-exchange cartridge (Alltech, Missisauga, ON, Canada) and a silica-based anion-exchange cartridge (Supelco, Missisauga, ON, Canada) sequentially connected, followed by selective elution and hydride generation atomic fluorescence analysis of the arsenic species. Yalcin and Le (2001) carried out a comparison of many solid phase extraction cartridges for arsenic immobilization and subsequent elution. According to these authors, alumina cartridges are not suitable for speciation analysis because all the arsenic species studied - As(V), As(III), monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) are retained. However, they were very efficient for removal and preconcentration purposes. As regarding to the speciation processes, a resin-based, strong cation exchange cartridge was used to retain the DMA, which was subsequently eluted with 1.0 $molL^{-1}$ HCl. Both As(V) and MMA were retained on a silica-based strong anion exchange cartridge and eluted with 60$mmolL^{-1}$ acetic acid (for MMA) and 1.0 $molL^{-1}$ HCl (for As(V)). The trivalent species, As(III), was not immobilized by none of the cartridges, thus remaining in solution.

A promising option for retention of arsenic in the trivalent form arose from the work of Teixeira and Ciminelli (2005), who demonstrated the large affinity of thiol groups by As(III). In an original approach for the treatment of arsenic-containing aqueous environments, the authors based their biomass selection on biochemical and toxicological fundamentals that explain arsenic toxicity. The results demonstrated that the cysteine-rich biomass was highly selective for arsenic removal in its trivalent form, without important effects of the studied competitor ions on the solid's adsorption capacity. The sulphydril reduced groups were shown to be the active groups involved in arsenic biosorption, each arsenic atom being directly bound to three sulfur atoms available in the cysteine-reduced residues present in the keratin-rich, protein constituent of the biomass. These results led us to propose that trivalent arsenic species could be similarly sorbed by thiol chelating resins, containing the sulphydril (-SH) as functional group. A potential practical advantage of using these resins for As(III) immobilization is the possibility of the resin's assemblage into solid phase extraction cartridges, thus providing an option to the anion exchange resins that have been currently used for As(V) retention.

Although the use of solid phase extraction cartridges filled with anion exchange resins for arsenic speciation has been the focus of many investigations (Le *et al*., 2000; Yalcin and Le, 2001; Impellitteri, 2004), there is not enough information about the effects of pH, flow rate and competing ions on the efficiency of these processes. Therefore, the objectives of this work are: (i) to develop a methodology for inorganic arsenic speciation in aqueous environment using Amberlite GT73, a chelating thiol resin, packed into a disposable syringe, as a SPE cartridge; (ii) to evaluate the effects of the initial pH of feed solution, percolation flow rate and presence of competing ions on arsenic speciation by the prepared Amberlite GT73 cartridge and also by the commercial LC-SAX cartridge. The latter is a silica-based anion exchange resin (quaternary amine as functional group and Cl^- as counter-ion) used for As(V) separation. The contributions of this work include the development of an arsenic speciation procedure based on the immobilization of the trivalent species on SPE cartridges filled with thiol resins. Another contribution is the evaluation of the interferences caused by relevant competing ions present in the aqueous environment on both SPE materials.

3.2. Experimental

3.2.1 Instruments

A peristaltic pump (Milan Scientific Equipments, Model 202) was used to allow the feed solutions flow through the cartridges. LC-SAX cartridges (Supelco, Bellefonte – PA, USA) were used to carry out arsenic speciation by anion exchange resins and Amberlite GT73 (Rohm and Haas) was applied in the arsenic speciation by thiol resins.

The quantitative determination of the arsenic in each experiment was carried out using an ELAN ® 9000 ICP-MS instrument (Perkin Elmer SCIEX, Concord, Ontario, Canada), except in the loading capacity determination tests, for which Atomic Absorption Spectrometer equipment (Perkin Elmer Analyst A300) was used.

3.2.2 Reagents

Stock arsenate solution was prepared from sodium arsenate ($Na_2HAsO_4.7H_2O$ at 99% purity - Fluka). Chemically pure sodium meta-arsenite ($NaAsO_2$) of 99.99% purity (Fluka) was used to make stock arsenite solution. The other reagents used in the experiments (all of them of analytical grade) were 18MΩ cm Milli-Q water, acetic acid (Synth), ammonium hydroxide (QM Reagents), calcium carbonate (Reagen), hydrochloric acid (VETEC), hydrogen peroxide (Synth), iron (II) sulfate (Reagen), iron (III) sulfate (Reagen), magnesium hydroxide (ISOFAR), nitric acid (QM Reagents), sodium hydroxide (VETEC), sodium phosphate (QEEL), sodium sulfate (VETEC), thioglicolic acid (VETEC).

3.2.3 Arsenic speciation using an anion exchange resin

Cartridge preconditioning

Before each experiment the cartridges were preconditioned with 2 mL of methanol solution at 50% (w/v), and followed by 2 mL of Milli-Q water, in accordance with the manufacturer's orientations.

Retention stage

50mL of arsenic solution containing 100 µg L^{-1} of As(III) and 100 µg L^{-1} of As(V), without competing ions and at pH 5.0, was allowed to flow through the LC-SAX cartridge, which contains a silica-based anion exchange resin with a quaternary amine as functional group and the chloride as the counter-ion. A flow rate of 1.0 mL min^{-1} was kept during this process using a peristaltic pump. Between the two main inorganic forms of the arsenic - As(V) and As(III), the LC-SAX cartridge was only able to retain the anionic As(V) species (derived from arsenic acid - $H_2AsO_4^-$, $HAsO_4^{2-}$) at pH used in this process. The trivalent specie of arsenic (as the neutral form H_3AsO_3) remained in the solution. Continuing the experiment, the cartridge effluent was collected at fractions of 10mL in 50 mL polyethylene tubes and subsequently submitted to quantitative As analysis using ICP-MS.

For the pH influence evaluation, this procedure was repeated at pH values of 1.8 and 7.5. As regard the assessment of the flow rate effects, the retention stage was also performed at a flow rate of 5mL min^{-1}. With the aim of estimating the interferences caused by competing ions, the feed solution containing As(III) at 100µgL^{-1} or As(V) at 100µgL^{-1} was prepared in the presence of sulfate and phosphate anions, separately. The initial concentrations evaluated for each species were chosen in accordance with the Monitoring Report of the Surface Waters at the Rio das Velhas, Minas Gerais state, Brazil (IGAM, 2005). The other higher concentrations were used with the aim of to elucidate the effects of these ions, so the sulfate anion influence was evaluated at 10.0, 50.0, 100.0 and 250.0mgL^{-1} and phosphate anion at 10 and 50mgL^{-1}. All of these tests were carried out in duplicates.

Elution stage

Immediately after the retention stage, each cartridge was eluted with 10 mL of 1 mol L^{-1} HNO_3 solution. Another eluent fraction of 5 mL was passed through the cartridge to guarantee a complete elution. The eluent was collected in fractions of 5 mL and subsequently submitted to As quantification by ICP-MS. The nitric acid was chosen as the eluent solution based on the work of Parker and Ciminelli (2005). The hydrochloric acid, which is the eluent indicated by the manufacturer, was rejected due to the interferences during the ICP-MS analysis.

Determination of the As(V) loading capacity into LC-SAX cartridges

For the arsenic loading capacity determination, 45 0mL of 20 mg L^{-1} As(V) solution was passed through the LC-SAX cartridge at a flow rate of 2 mL min^{-1}. The cartridge effluent was collected at fractions of 20 mL in 50 mL polyethylene tubes and the arsenic content analyzed by Atomic Absorption Spectrometry.

3.2.4 Arsenic speciation using a chelating thiol resin

The first step of this experiment was to prepare the Amberlite GT73 cartridge. So, the Amberlite GT73, a macroreticular polystyrene–divinylbenzene resin containing chelating thiol as functional group, was dried at 40ºC (FANEM, Model 320-SE) for 2 hours. It is important to elucidate that this drying have not affected the resin performance since were carried out tests with wet and dried resins and both presented the same behaviors. Following this drying stage, the next step was to pack the cartridge and thus, 0.5 g of the dried resin was placed into a 5 mL disposable syringe, and the ends of the resin bed were closed with 0.45 µm pore-size membranes (Cole-Parmer Instrument Company).

Cartridge preconditioning

Once prepared the cartridges, the next step was their preconditioning using a procedure based on the pretreatment step used by Teixeira and Ciminelli (2005), in which the oxidized SH groups were reduced by ammonium thioglycolate solution. Thus in this experiment, 30 mL of a 5% (w/v) ammonium thioglycolate solution were percolated through the cartridge at a flow rate of 1.0 mL min^{-1}, followed by 15.0 mL of 1.0 mol L^{-1} HCl solution and 50 mL of Milli-Q water.

Retention stage

Immediately after the resin preconditioning was passed through the prepared Amberlite GT73 cartridge 50mL of an arsenic solution containing 100.0µg L^{-1} of As(III) and 100.0µg L^{-1} of As(V), free of competing ions, at pH 5.0. A flow rate of 1mL min^{-1} was reached with the aid of a peristaltic pump. The Amberlite GT73 cartridge was expected to efficiently retain the neutral As(III) species (H_3AsO_3) at pH used in this process. The pentavalent species of arsenic remained in the solution. Following, the cartridge effluent was collected at fractions of 10.0mL in 50.0mL polyethylene tubes and subsequently submitted to quantitative analysis using ICP-MS.

As well as for the silica-based anion exchange cartridge experiments, the influences of pH, flow rate and competing ions were evaluated. The retention stage was also performed at a flow rate of 5.0mL min^{-1} and the pH influences was assessed at initial

pH 12.0 and pH 10.0 in addition to the pH 5.0. As regard to the competing ions, in addition to sulfate (SO_4^{2-}, at 50.0, 100.0 and 250.0mg L^{-1}) and phosphate (HPO_4^{2-}, at 10.0 and 50.0mg L^{-1}), the interferences of calcium (Ca^{2+}, at 10.0mgL^{-1}), magnesium (Mg^{2+}, at 5.0mgL^{-1}) and iron (Fe^{2+} and Fe^{3+} both at 0.2 mgL^{-1}) were analyzed. Also, these initial concentrations were chosen in accordance with the Monitoring Report of the Surface Waters at the Rio das Velhas, Minas Gerais state, Brazil (IGAM, 2005). All of these tests were carried out in duplicates.

Elution stage

The elution stage was carried out using a 10% (w/v) hydrogen peroxide solution according to the following procedure: a fraction of 5.0mL of the eluent solution was kept in contact with the loaded resin into the cartridge for 5.0min. After this time, the solution was allowed to flow through the cartridge and this fraction was thus collected. Next, 30.0mL of the same eluent solution were percolated through the cartridge, being recycled for 3 times. After the recycle, the cartridge eluent was collected in 3 fractions of 10.0mL and thus, another fraction of 5.0mL was passed through the cartridge to guarantee a complete elution. In the end, all fractions of cartridge eluent were referred for arsenic quantification by ICP-MS.

Determination of the As(III) loading capacity

850mL of 20.0mg L^{-1} As(III) solution was allowed to flow through the Amberlite GT73 cartridge at a flow rate of 2.0mL min^{-1}. As well as for the LC-SAX cartridges, the effluent solution was collected at fractions of 20.0mL in 50.0mL polyethylene tubes and the arsenic that remained in solution was analyzed by AAS - Atomic Absorption Spectrometry.

3.3. Results and Discussion

3.3.1 Arsenic speciation using an anion exchange resin

This experiment was carried out with the aim of to verify and optimize the inorganic arsenic speciation by the LC-SAX cartridges. Thus, the data obtained of total arsenic loading (%) into the cartridges were plotted as a function of the cumulative volume (mL) of feed solution passed through them at different values of pH and flow rate. In the Figure 3.1 are shown the results obtained for arsenic speciation at three different pH values.

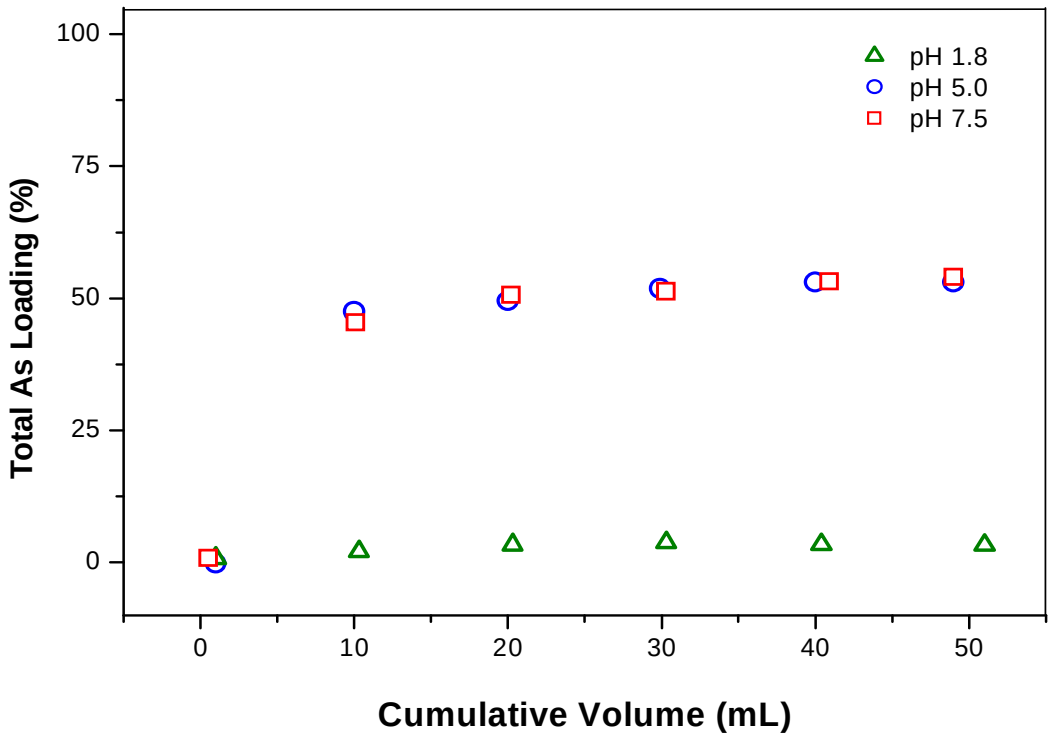

Figure 3.1: Effect of initial pH on the inorganic arsenic speciation by LC-SAX cartridges. Feed solution concentration of 200µg L^{-1} (As(III) at 100µg L^{-1} + As(V) at 100µg L^{-1}) and flow rate of 1.0mL min^{-1}.

As the feed solution contained the same concentrations of both As(III) and As(V) species (100µg L^{-1}), the results indicate, based on mass balance, that arsenic speciation proceeded successfully at pH 5.0 and pH 7.5. The percentage of arsenic loaded remained around 50% in both experiments, thus indicating that half of the original arsenic in the feed was retained into the cartridge while the other half was left in solution. The standard deviation was of 2.1% of 52.8%, for the pH 5.0 experiments and 1.8% for an arsenic loading of 49.7% for the pH 7.5. Furthermore, the elution stage using 1mol L^{-1} HNO_3 solution was able to recover 100% of the immobilized As(V) in the under the two pH conditions. Due to their anion exchange characteristics, the LC-SAX cartridges are only able to retain the pentavalent arsenic species at pH values above 2.1 (pKa_1 of arsenic acid, H_3AsO_4). Thus, as expected, the immobilization of As(V) by LC-SAX is not indicated for solutions at pH below 2 (Figure 3.1). Figure 3.2 show the results obtained for arsenic speciation at feed solution flow rates of 1mL min^{-1} and 5mL min^{-1}.

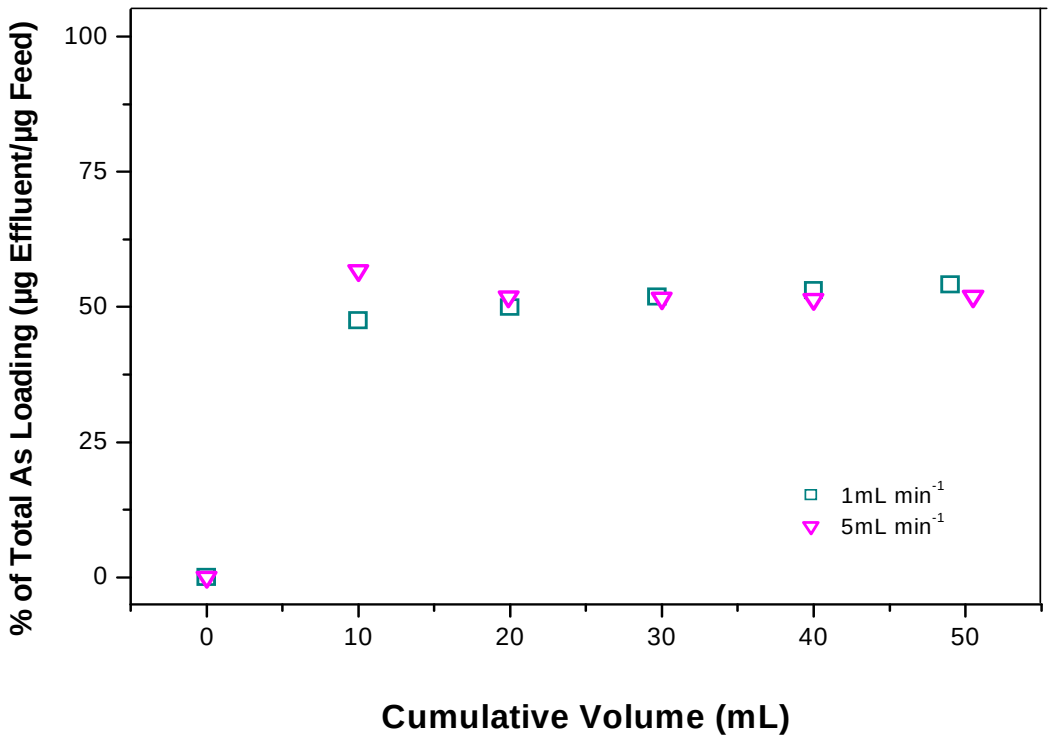

Figure 3.2: Effect of percolation flow rate on the inorganic arsenic speciation by LC-SAX cartridges. Feed solution concentration of 200µg L^{-1} (As(III) at 100µg L^{-1} + As(V) at 100µg L^{-1}) and pH 5.0.

These results demonstrate that arsenic speciation by LC-SAX cartridges is not significantly affected by an increase in the flow rate from 1.0mL min^{-1} to 5.0mLmin^{-1}. The average arsenic loading was 52.8 % with a standard deviation of 2.1% for a flow rate of 1.0mL min^{-1}, and for the higher flow rate, the average arsenic loading was 49.7%, with a standard deviation of 4.3%. The results indicate that small fluctuation in the operational flow rates suggested by the manufacturer, which vary from 1mL min^{-1} until 2mL min^{-1}, will not affect the performance of the resin with respect to arsenic speciation.

Effects of Competing Ions

For the assessment of the influences of sulfate and phosphate anions on arsenic speciation by the LC-SAX cartridges, three different values of sulfate concentration (50mgL^{-1}, 100mgL^{-1} and 250mgL^{-1}) and two values of phosphate concentration (10mgL^{-1} and 50mgL^{-1}) were selected. Figure 3.3 and Figure 3.4 show the sulfate interference on the As(V) and As(III) immobilization, respectively, using the LC-SAX cartridges.

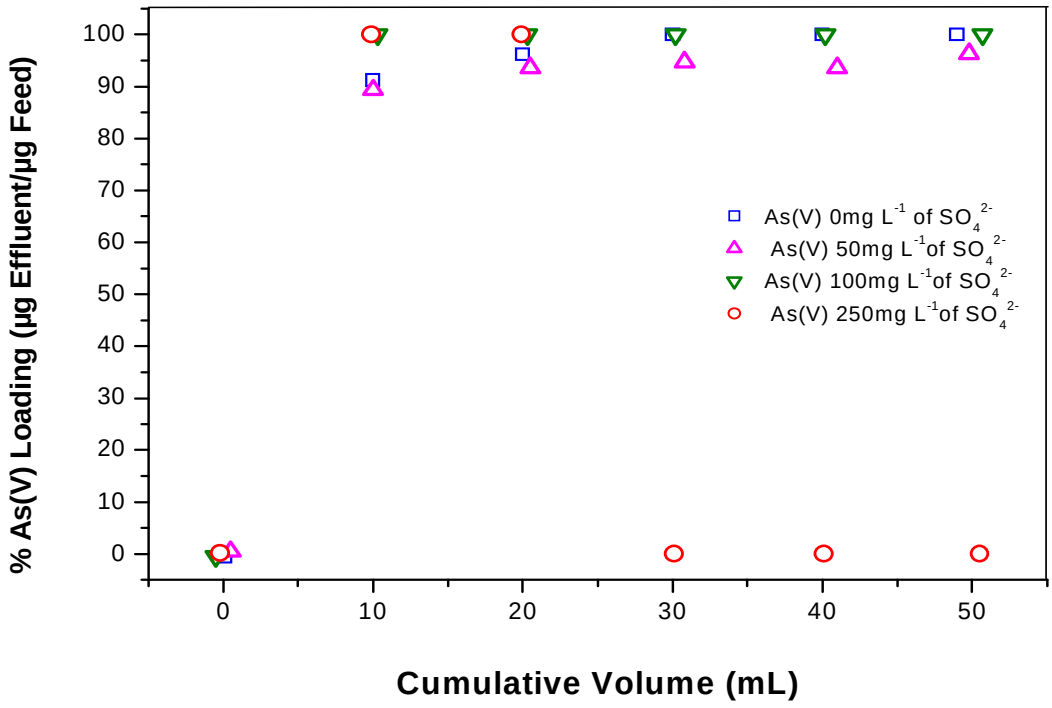

Figure 3.3: Effect of sulfate concentrations on As(V) retention by LC-SAX cartridges. Feed solution concentration of As(V) at 100µg L^{-1}; flow rate of 1mL min^{-1} and pH 5.0.

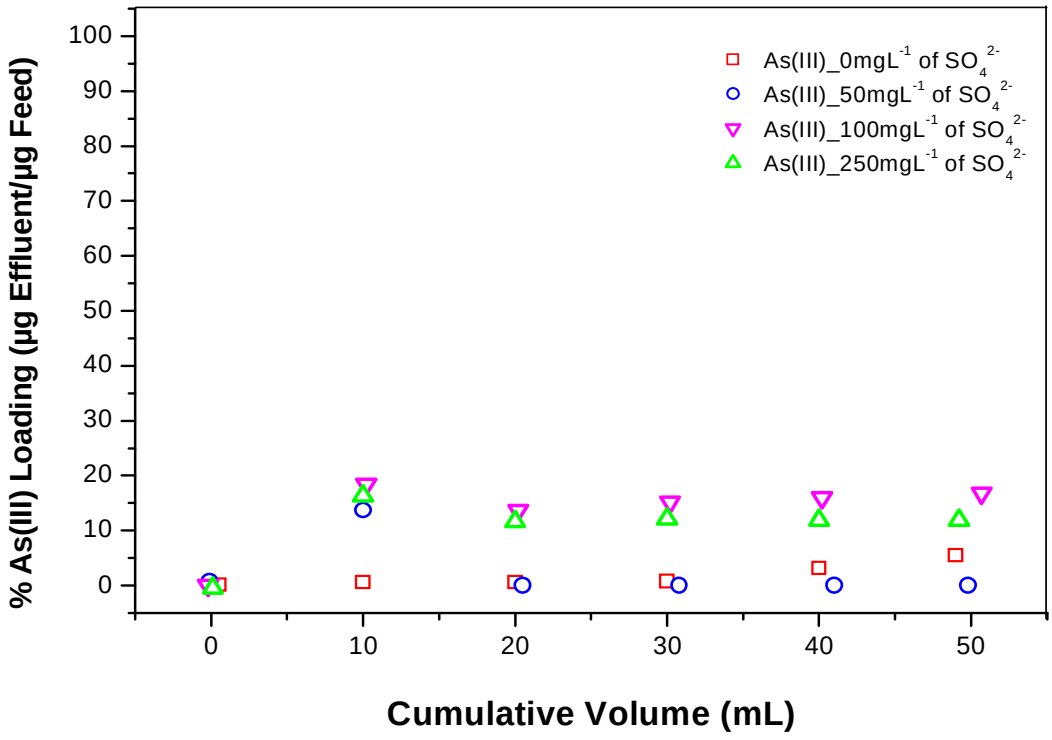

Figure 3.4: Effect of sulfate concentrations on As(III) retention by LC-SAX cartridges. Feed solution concentration of As(III) at 100µg L^{-1}; flow rate of 1mL min^{-1} and pH 5.0.

Figure 3.3 shows that As(V) retention by the LC-SAX cartridge was virtually unaffected by the presence of sulfate ions up to a sulfate concentration of 250mg L^{-1}. In this case, a breakthrough point was reached at a cumulative volume of 30mL approximately. In the case of As(III) immobilization (Figure 3.4) no alterations were observed at a sulfate concentration of 50mg L^{-1}. However, when sulfate concentration was increased to 100mgL^{-1} and 250mgL^{-1}, As(III) loading reached 16% (standard deviation of 1.8%) and 12% (standard deviation of 1.9%), respectively.

Figure 3.5 shows the results obtained for As(V) and As(III) retention into LC-SAX cartridges in the presence of phosphate ions. Similarly to the effect of sulfate, the results illustrate that the As(V) immobilization was not altered by the presence of phosphate ions in the range of concentrations evaluated here.

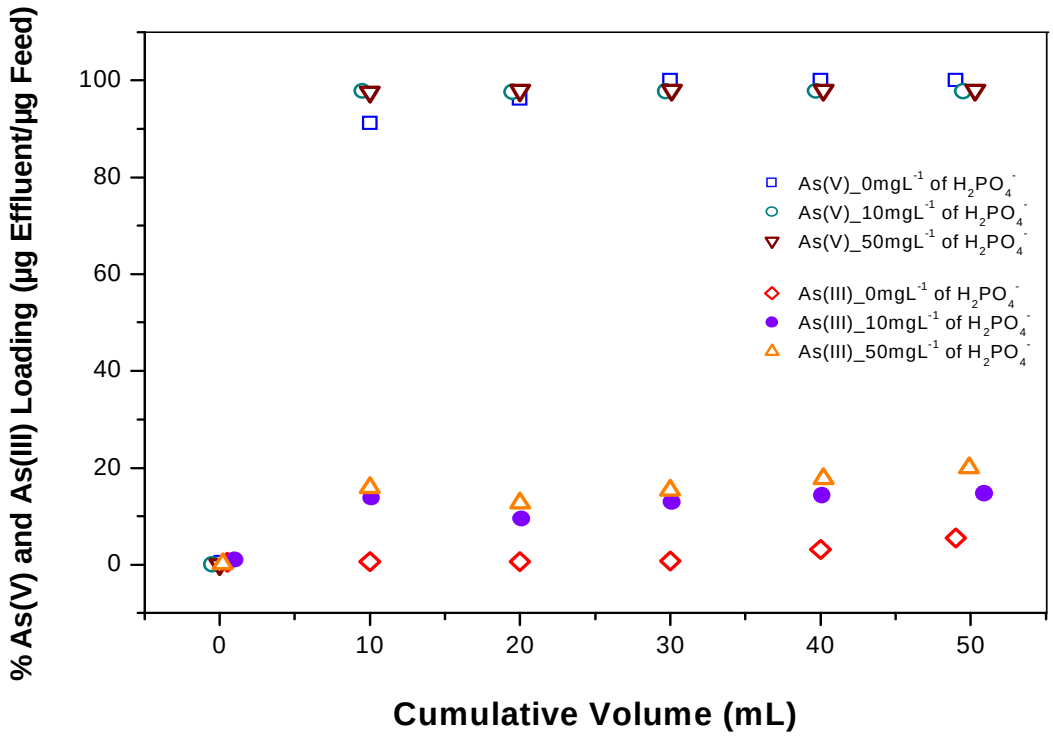

Figure 3.5: Effect of phosphate concentrations on As(V) and As(III) retentions by LC-SAX cartridges. As(III) and As(V) feed solutions concentration of 100µgL^{-1}, flow rate of 1mL min^{-1} and pH 5.0.

The As(III) species are loaded onto the LC-SAX cartridges at levels of 13.03% (standard deviation of 2.1) to 16.4% (standard deviation of 2.7) in the presence of phosphate concentrations of 10.0mgL^{-1} and 50.0mgL^{-1}, respectively. These unexpected results indicate that the inorganic arsenic speciation by the LC-SAX cartridge is hindered as a result of As(III) uptake in the presence of both phosphate (≥10 mg/L) and sulfate concentrations (≥100mgL^{-1}).

Determination of the As(V) loading capacity by LC-SAX cartridges

For the quantification of arsenic loading capacity, the LC-SAX cartridges underwent a test for the determination of the As(V) breakthrough curve. The result is shown in Figure 3.6, which indicates a breakthrough point near to 150mL of cumulative volume passed through the cartridge, corresponding to a As(V) loading capacity of 6.0mg g^{-1} by the LC - SAX resin.

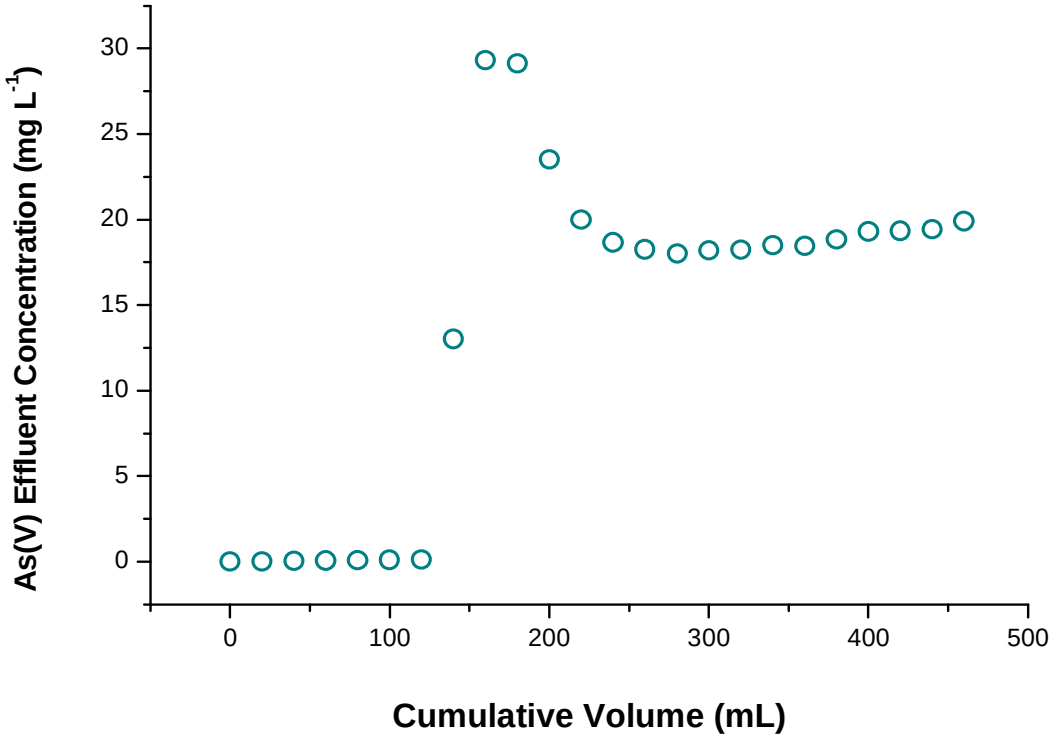

Figure 3.6: Breakthrough curve for As(V) at LC-SAX cartridges. Feed solution concentration of 20mg L^{-1}; flow rate of 2mL min^{-1} and pH 5.0.

3.3.2 Arsenic speciation using a chelating thiol resin

The use of a commercial resin for As(III) speciation required the development of a protocol of preparation and preconditioning of Amberlite GT73 cartridges prior to the retention stage, and also, a protocol arsenic elution. The first attempts to immobilize As(III) on the GT73 resin led to very low uptakes. These results were ascribed to the spontaneous oxidation of the active thiol groups. Based on a previous experience of our group (Teixeira and Ciminelli, 2005), a protocol for the regeneration of the active group was available and applied to the resin. The major challenge was the development of an adequate elution procedure. This difficulty was due to the strong chelation of As(III) by the resin, shown in Chapter 2. Various eluent solutions have been tested. Firstly, the use of strong acids such as HCl and HNO_3 was attempted in order to restore the SH group in the resin. Next, an $AgNO_3$ solution was evaluated due to the high affinity of the thiol group by the Ag^+ cation. However, none of these solutions led to an efficient recovery of the loaded As(III). The elution required the oxidation of As(III). The best elution conditions were established with the use of hydrogen peroxide solution at 10% (w/v) concentration.

The performance of the retention stage was assessed plotting the data of percentage of total arsenic loading against the cumulative volume (mL) of feed solution passed through the cartridge, at different pH and flow rates (Figures 3.7 and 3.8, respectively). The separation of the inorganic arsenic species can be efficiently accomplished by using the Amberlite GT73 cartridge. However, in this case, the trivalent arsenic is the immobilized species, as opposed to As(V) in the LC-SAX experiments. Regarding to the elution process, the optimized procedure presented recoveries in a range varying from 97 to 99%.

Figure 3.7 illustrates the results of arsenic speciation at an initial feed solution pH of 5.0, 10.0 and 12.0. Among the initial pH values assessed, the Amberlite GT73 cartridge was able to suitably separate the As(III) and As(V) at pH 5.0 and 10. At pH 5.0, the As(III) species is found originally at its neutral form, H_3AsO_3 (pKa_1 = 9.2), which is the arsenic species that presents the highest affinity by the functional thiol group (-SH) in Amberlite GT73 resins. An interesting finding was the similar recoveries obtained at pH 5 and pH 10. The high recovery at pH 10 was related to the pH variation during the experiment.

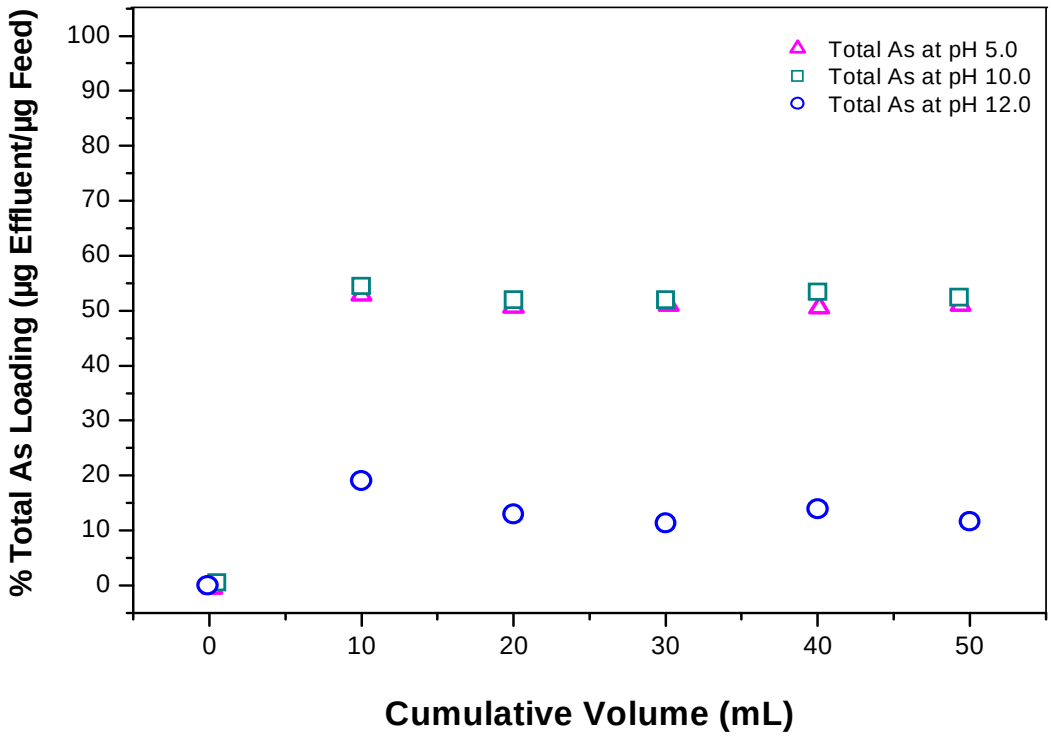

Figure 3.7: Effect of initial pH on the inorganic arsenic speciation by Amberlite GT73 cartridges. Feed solution concentration of 200µg L^{-1} (As(III) at 100µg L^{-1} + As(V) at 100µg L^{-1}) and flow rate of 1mL min^{-1}.

For all tests, the pH value was reduced during arsenic uptake. When the initial pH was 5.0, the final value was 3.0; for an initial pH of 10.0, the pH dropped to approximately 5.5. At an initial pH of 12.0, the pH initially decreased to pH 7.0, and then returned to the value of 12. These pH variations can explain the performance of the Amberlite GT73 cartridge shown in Figure 3.7. One could expect that arsenic immobilization at pH 10 would be lesser than at pH 5.0. However, the drop in the solution pH created conditions to reestablish the neutral trivalent arsenic as the predominant species in solution. For a feed pH of 12.0, the retention of arsenic by Amberlite GT73 cartridges is significantly reduced, since in this case the arsenic is found predominantly in an anionic form.

Figure 3.8 presents the results obtained with arsenic speciation by Amberlite GT73 cartridges at flow rates of 1.0mL min^{-1} and 5.0mL min^{-1}. The results showed that arsenic speciation by Amberlite GT73 cartridges undergo a slight alteration when the flow rate is increased from 1.0mL min^{-1} to 5.0mL min^{-1}. The reduction in the average arsenic loading varied from 51% to 46%, approximately, with the increase of the flow rate. It is important to emphasize that these experiments presented standard deviations of 0.7% at a flow rate of 1.0mL min^{-1} and 3.7% at a flow rate of 5.0mL min^{-1}.

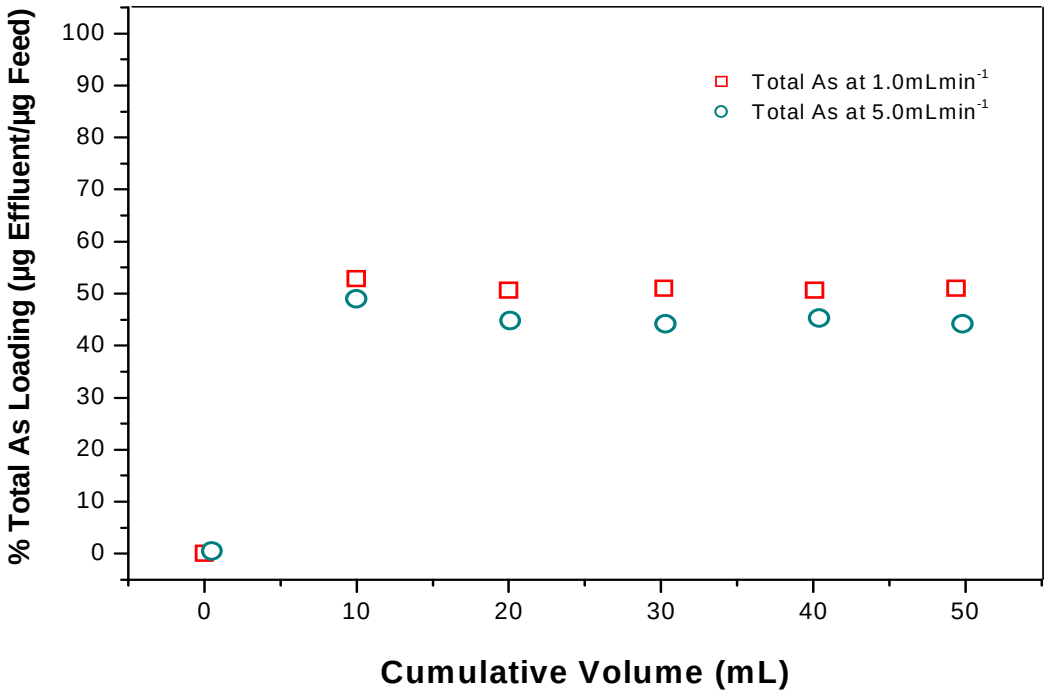

Figure 3.8: Effect of percolation flow rate on the inorganic arsenic speciation by Amberlite GT73 cartridges. Feed solution concentration of 200µg L^{-1} (As(III) at 100µg L^{-1} + As(V) at 100µg L^{-1}) and pH 5.0.

Effects of Cations

The Amberlite GT73 resin presents a weak cation exchanger character and has usually been applied to remove cations from aqueous solution. The selectivity sequence of this resin, according to its manufacturer, is: Hg > Ag > Cu > Pb > Cd > Ni > Co > Fe > Ca > Na. The fact that calcium, magnesium and iron cations are frequently present in natural waters justify the need to verify the performance of the Amberlite GT73 cartridge in the presence of these cations. Figure 3.9 and Figure 3.10 show the results for the effect of Ca^{2+} and Mg^{2+}, respectively.

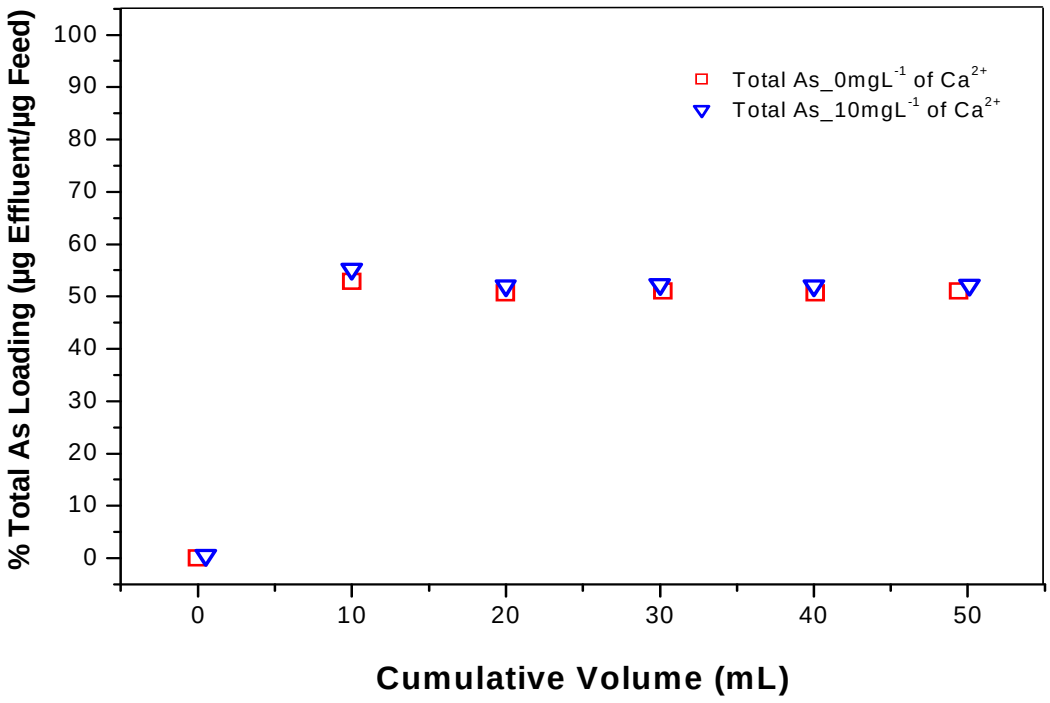

Figure 3.9: Effect of Ca^{2+} on the inorganic arsenic speciation by Amberlite GT73. Feed solution concentration of 200µg L^{-1} (As(III) at 100µg L^{-1} + As(V) at 100µg L^{-1}); flow rate of 1mL min^{-1} and pH 5.0.

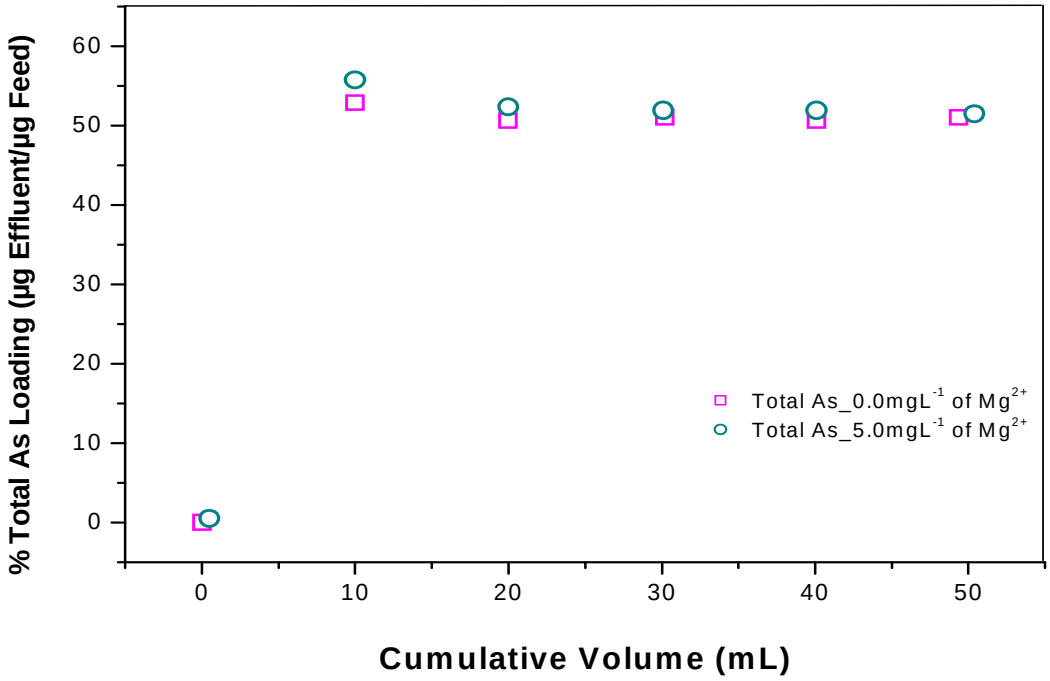

Figure 3.10: Effect of Mg^{2+} on the inorganic arsenic speciation by Amberlite GT73. Feed solution concentration of 200µg L^{-1} (As(III) at 100µg L^{-1} + As(V) at 100µg L^{-1}); flow rate of 1mLmin^{-1} and pH 5.0.

The results presented in Figure 3.9 and Figure 3.10 demonstrated that the arsenic speciation by Amberlite GT73 cartridge was not significantly affected by the presence of the cations Ca^{2+} and Mg^{2+}. The average of the total arsenic loading was 52.8% with a standard deviation of 1.4% in the presence of 10.0mg L^{-1} of calcium ions against the total arsenic loading of 52.7% with a standard deviation of 1.7% in the presence of 5.0 mg L^{-1}.of magnesium ions. In the absence of these ions, the average arsenic loading was 51.2% (standard deviation of 0.96%).

As regard to the iron interferences, both Fe^{2+} (Figure 3.11) and Fe^{3+} (Figure 3.12) have also not influenced As(III) retention by the Amberlite GT73 resin. However, the selectivity of the resin have been affected, since the pentavalent species became slightly immobilized onto the Amberlite GT73 cartridge in the presence of both Fe^{2+} and

Fe^{3+} cations. In the case of Fe^{2+}, this alteration was observed only after the flow of a second aliquot of 10mL (20mL total). The average As(V) loading was 7.6%, with a standard deviation of 3.2 %. In the presence of Fe^{3+}, a significant alteration was observed only in the first aliquot of 10mL, for which an As(V) loading of 14% was found.

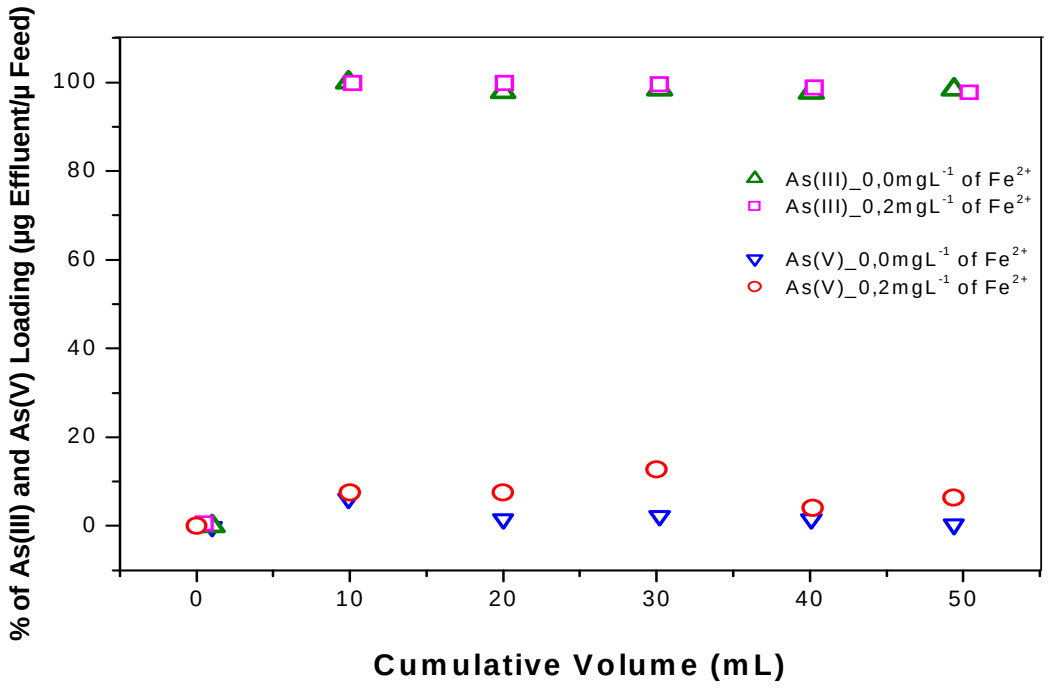

Figure 3.11: Effect of the presence of Fe^{2+} in the feed solution on the As(III) and As(V) retention by Amberlite GT73. As(III) and As(V) feed solutions concentration of 100µgL^{-1}, flow rate of 1mL min^{-1} and pH 2.0.

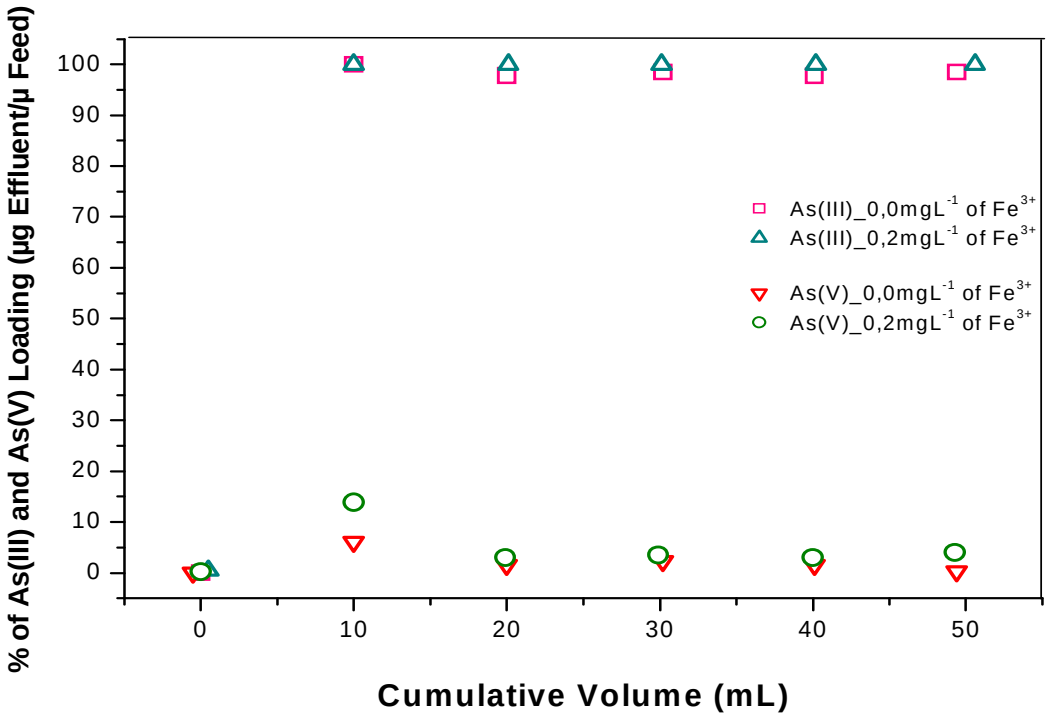

Figure 3.12: Effect of the presence of Fe^{3+} in the feed solution on the As(III) and As(V) retention by Amberlite GT73. As(III) and As(V) feed solutions concentration of 100µgL^{-1}, flow rate of 1mL min^{-1} and pH 2.0.

Effects of Anions

The experiments in the presence of sulfate and phosphate ions were carried out in the same conditions applied to the LC-SAX tests. The aim was to compare the performance of the Amberlite GT73 and the LC-SAX cartridges during arsenic immobilization. Figure 3.13 and Figure 3.14 show the results of As(III) and As(V) retention by the Amberlite GT73 cartridge, respectively, at sulfate concentrations of 50.0mg L^{-1}, 100.0mg L^{-1} and 250.0mg L^{-1}.

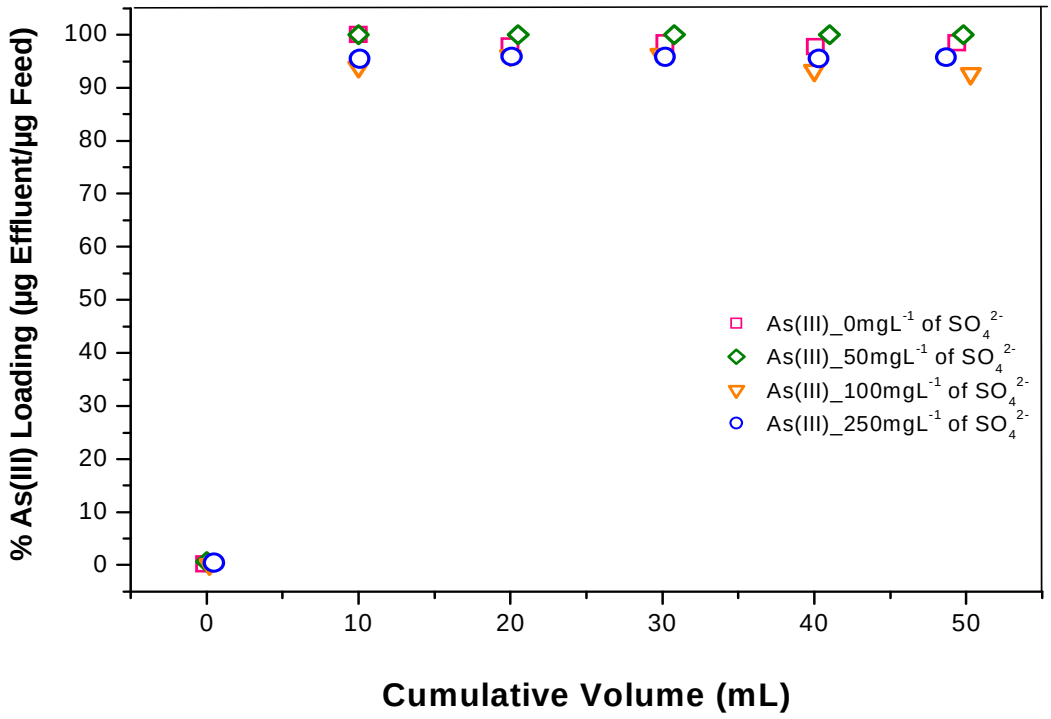

Figure 3.13: Effect of sulfate concentrations on As(III) retention by Amberlite GT73 cartridges. As(III) feed solution concentration of 100µgL^{-1}, flow rate of 1mL min^{-1} and pH 5.0.

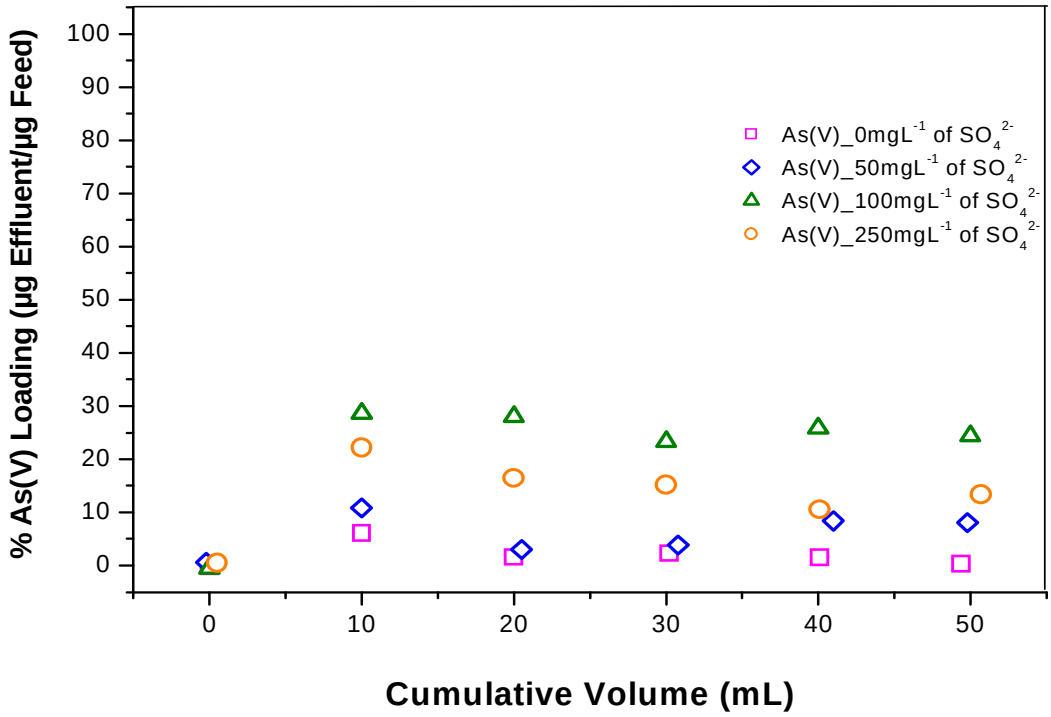

Figure 3.14: Effect of sulfate concentrations on As(V) retention by Amberlite GT73 cartridges. As(V) feed solution concentration of 100µgL^{-1}, flow rate of 1mL min^{-1} and pH 5.0.

Figure 3.13 demonstrated that the As(III) retention by Amberlite GT73 was not affected by any of the assessed sulfate ion concentrations. On the other hand, the As(V) loading onto the resin became detectable in the presence of sulfate ions, so altering the resin selectivity (Figure 3.14). The average As(V) loading onto the resin was 6.8% at 50.0mg L^{-1} (standard deviation of 3.3%); 26.0% at 100.0mgL^{-1} (standard deviation of 2.3%) and 15.5% at 250.0mg L^{-1} of sulfate ions (standard deviation of 4.3%).

The behavior of the Amberlite GT73 cartridges in the presence of phosphate anion was similar to that shown by sulfate. As shown by Figure 3.15, As(III) immobilization was not affected while As(V) retention presented an average retention of 11.9% with a standard deviation of 2.6% for a phosphate concentration of 50mg L^{-1}.

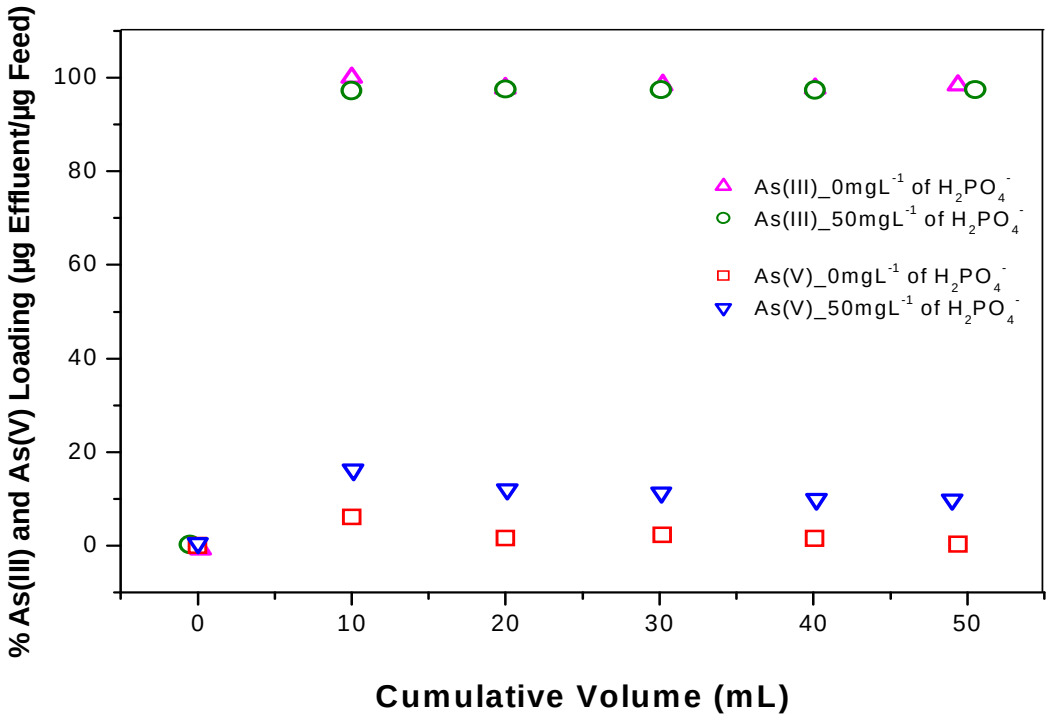

Figure 3.15: Effect of phosphate concentrations on As(III) and As(V) retention by Amberlite GT73 cartridges. As(III) and As(V) feed solutions concentration of 100µgL^{-1}, flow rate of 1mL min^{-1} and pH 5.0.

Determination of the As(III) loading capacity into Amberlite GT73 cartridges

During this experiment the equilibrium concentration between the feed and effluent solutions was not reached, since the feed solution was at 20.7 mg L^{-1} and the final effluent fraction presented a concentration of 17.7 mg L^{-1}. Therefore, through a mass balance in the system, it is possible to say that the As(III) loading capacity of the Amberlite GT73 cartridges is higher than 18mg g^{-1} of dried resin, in agreement with the loading of 30mg g^{-1} indicated by the batch experiments (Chapter 2).

3.4. Conclusions

In this work, was possible to evaluate different conditions of pH, flow rate and competing ions in the inorganic arsenic speciation by two kinds of solid phase extraction cartridges, which present completely different functional groups and mechanisms of arsenic immobilization. In the case of LC-SAX cartridges, the functional group is a quaternary amine, a strong anion exchange group, and in the Amberlite GT73 the functional group is the thiol, which presents a chelating character. Comparing the performances of these two cartridges, was possible to verify that both are efficient for inorganic arsenic speciation, with retention of As(V) specie onto the LC-SAX and the As(III) immobilization onto the Amberlite GT73 cartridges.

Regarding the pH influences, was observed that the performances of both LC-SAX and Amberlite GT73 cartridges are pH dependent. For LC-SAX experiments, it is necessary that As(V) species are present in their anionic forms ($H_2AsO_4^-$ and $HAsO_4^{2-}$) thus, the pH needs to be higher than 2.1, which is the first pka value of the arsenic acid. In the Amberlite GT73 experiments, the pH during the As(III) immobilization needs to be lesser than 9.2, (pka_1 of the arsenious acid), assuring that the trivalent species are present in its neutral form, H_3AsO_3. With regard to flow rate interferences, in the case of LC-SAX cartridges significant alterations were not observed in the arsenic speciation when it was increased from 1.0mL min^{-1} to 5.0mL min^{-1}, while in the Amberlite GT73 cartridges de efficiency of arsenic speciation undergoes a reduction of 5% approximately, when the same increase in the flow rate was applied. Considering the competing ions interferences, the As(V) immobilization by LC-SAX cartridges and the As(III) retention by Amberlite GT73 cartridges kept to unaltered at the evaluated ions concentrations, except when 250.0mg L^{-1} of sulfate ions were used in LC-SAX experiments. However, the selectivity of both cartridges was affected by the presence of sulfate, phosphate and, in the case of Amberlite GT73, also by the presence of iron ions. In the LC-SAX experiments, the presence of both sulfate and phosphate ions made possible the partial retention of the trivalent specie. The same behavior was observed for Amberlite GT73 experiments with respect to the presence of sulfate, phosphate and iron ions. However, these cartridges were able to retain only the As(III) and became able to also retain the As(V) specie. The most significant alteration was verified when 100.0 and 250.0mg L^{-1} of sulfate ions were used.

Finally, with respect to the developed protocol for the methodology using Amberlite GT73 cartridge for inorganic arsenic speciation, it is possible to believe, based on the obtained results, that it can be applied for arsenic speciation in surface waters for both laboratories and field works purposes, arising as an interesting alternative for the anion exchange resins that have been currently used.

3.5. References

BEDNAR, A. J.; GARBARINO, J. R.; BURKHARDT, M. R.; RANVILLE, J. F. and WILDEMAN, T.R. (2004). Field and laboratory arsenic speciation methods and their application to natural-water analysis. *Water Research*, vol 38, p. 355–364.

CAMEL, V. (2003). Solid phase extraction of trace elements. *Spectrochimica Acta - Part B*, vol. 58, p. 1177–1233.

GONG, Z.; LU, X.; MA, M.; WATT, C. and LE, X. C. (2002). Arsenic speciation analysis. *Talanta*, vol. 58, p. 77–96.

IGAM (2005). Relatório de monitoramento das águas superficiais na Bacia do Rio São Francisco em 2004: Sub-bacia do Rio das Velhas. *Instituto Mineiro de Gestão das Águas*. - Belo Horizonte, Minas Gerais - Brasil.

IMPELLITTERI, C. (2004). Effects of pH and competing anions on the speciation of arsenic in fixed ionic strength solutions by solid phase extraction cartridges. *Water Research*, vol. 38, p. 1207–1214.

LE, X . C.; YALCIN, S. and MA, M. (2000). Speciation of submicrogram per liter levels of arsenic in water: On-Site Species Separation Integrated with Sample Collection. *Environmental Science and Technology*, vol. 34, p. 2342-2347.

LISKA, I. (2000). Fifty years of solid-phase extraction in water analysis – historical development and overview. *Journal of Chromatography A*, vol. 885, p. 3–16.

PARKER, A. P. and CIMINELLI, V. S. T. (2005). A simplified flow system for inorganic arsenic speciation by preconcentration of As(V) and separation of As(III) in natural waters by ICP-MS. *Atomic Spectroscopy,* vol. 26, p. 131 – 136.

TEIXEIRA, M. C. and CIMINELLI, V. S. T. (2005). Development of a Biosorbent for Arsenite: Structural Modeling Based on X-ray Spectroscopy. *Environmental Science and Technology,* vol. 39, p. 895-900.

YALCIN, S. and LE, C. (2001). Speciation of arsenic using solid phase extraction cartridges. *Journal of Environmental. Monitoring*., vol. 3, p. 81-85.

4. REFERENCES

BEDNAR, A. J.; GARBARINO, J. R.; BURKHARDT, M. R.; RANVILLE, J. F. and WILDEMAN, T.R. (2004). Field and laboratory arsenic speciation methods and their application to natural-water analysis. *Water Research*, vol 38, p. 355–364.

B'HYMER, C. B. and CARUSO, J.A. (2004). Arsenic and its speciation analysis using High Performance Liquid Chromatography and Inductively Coupled Plasma Mass Spectrometry. *Journal of Chromatography A*, vol. 1045, p. 1–13.

CAMEL, V. (2003). Solid phase extraction of trace elements. *Spectrochimica Acta - Part B*, vol. 58, p. 1177–1233.

GONG, Z.; LU, X.; MA, M.; WATT, C. and LE, X. C. (2002). Arsenic speciation analysis. *Talanta*, vol. 58, p. 77–96.

IGAM (2005). Monitoring report of the surface waters at the Rio São Francisco basin: Sub-basin of the Rio das Velhas. *Instituto Mineiro de Gestão das Águas*. - Belo Horizonte, Minas Gerais state - Brazil.

IMPELLITTERI, C. (2004). Effects of pH and competing anions on the speciation of arsenic in fixed ionic strength solutions by solid phase extraction cartridges. *Water Research*, vol. 38, p. 1207–1214.

JAIN, C. K. and ALI, I. (2000). Arsenic: Occurrence, Toxicity And Speciation Techniques. *Water Research*, vol. 34, p. 4304-4312.

KUMARESAN, M. and RIYAZUNDDIN, P. (2001). Overview of speciation chemistry of arsenic. *Current Science*, vol. 80, p. 837-846.

LADEIRA, A. C. Q.; CIMINELLI, V. S. T.; DUARTE, H. A.; ALVES, M. C. M. and RAMOS, A. Y. (2001). Mechanism of anion retention from EXAFS and density functional calculations: Arsenic (V) adsorbed on gibbsite. *Geochimica et Cosmochimica Acta,* vol. 65, p. 1211–1217.

LE, X . C.; YALCIN, S. and MA, M. (2000). Speciation of submicrogram per liter levels of arsenic in water: On-Site Species Separation Integrated with Sample Collection. *Environmental Science and Technology*, vol. 34, p. 2342-2347.

LISKA, I. (2000). Fifty years of solid-phase extraction in water analysis – historical development and overview. *Journal of Chromatography A*, vol. 885, p. 3–16.

MANDAL, B. K. and SUZUKI, K. T. (2002). Arsenic round the world: a review. *Talanta,* vol. 58, p. 201-235.

MATSUNAGA, H.; YOKOYAMA, T.; ELDRIDGE, R. J. and BOLTO, B. A. (1996). Adsorption characteristics of arsenic(III) and arsenic(V) on iron(III)-loaded chelating resin having lysine-N^{α},N^{α}-diacetic acid moiety. *Reactive & Functional Polymers,* vol. 29, p. 167-174.

NING, R. Y. (2002). Arsenic removal by reverse osmosis. *Desalination,* vol. 143, p.237-241.

O'DAY, P. (2006). Chemistry and Mineralogy of Arsenic. *Elements,* vol. 2, p. 77–83.

PARKER, A. P. and CIMINELLI, V. S. T. (2005). A simplified flow system for inorganic arsenic speciation by preconcentration of As(V) and separation of As(III) in natural waters by ICP-MS. *Atomic Spectroscopy,* vol. 26, p. 131 – 136.

SMEDLEY, P. L. and KINNIBURGH, D. G. (2002). A review of the source, behavior and distribution of arsenic in natural waters. *Applied Geochemistry,* vol. 17, p. 517-568.

SMITH, P. G.; KOCH, I.; GORDON, R.; MANDOLI, D. F.; CHAPMAN, B. D. and REIMER, K. N. J. (2005). X-ray Absorption Near-Edge Structure Analysis of Arsenic Species for Application to Biological Environmental Samples. *Environmental Science and Technology,* vol. 39, p. 248-254.

TEIXEIRA, M. C. and Ciminelli, V. S. T. (2005). Development of a Biosorbent for Arsenite: Structural Modeling Based on X-ray Spectroscopy. *Environmental Science and Technology,* vol. 39, p. 895-900.

USEPA. (2000). Technologies and Costs for Removal of Arsenic from Drinking Water. Prepared by *International Consultants, Inc. Malcolm Pirnie, Inc. The Cadmus Group, Inc.* Under contract with the USEPA No. 68-C6-0039.

YALCIN, S. and LE, C. (2001). Speciation of arsenic using solid phase extraction cartridges. *Journal of Environmental. Monitoring*., vol. 3, p. 81-85.

5. APPENDICES

5.1. Appendix A: Results of the pH and flow rate experiments using LC-SAX cartridges

Efeito do pH

Testes

pH 1.8

	Volume (mL)	Conc. As na saída	Saída (µg)	Entrada (µg)	Acúm. (µg)	% Carregamento	Vol. Acumulado (mL)	Desvio Padrão	Des_Pad Med
27_A									
C200		167.00				0.00	0.0		2.30
27_a.1	10.1	163.49	1.6512	1.6867	0.0355	2.10	10.1	4.35	
27_a.2	10.2	161.41	1.6463	1.7034	0.0571	3.35	20.2	2.37	
27_a.3	10	160.75	1.6075	1.6700	0.0625	3.74	30.3	1.67	
27_a.4	10.1	161.30	1.6292	1.6867	0.0575	3.41	40.4	1.76	
27_a.5	10.6	161.51	1.7120	1.7702	0.0582	3.29	51.0	1.35	
					Média=	3.18			
27_B									
C200		218.00							
27_b.1	10.0	200.00	2.0000	2.1800	0.1800	8.26	10.0	% Carreg. Médio=	2.78
27_b.2	10.0	229.00	2.2900	2.1800	0.0000	0.00	20.0		
27_b.3	9.9	215.00	2.1285	2.1582	0.0297	1.38	29.9		
27_b.4	10.0	216.00	2.1600	2.1800	0.0200	0.92	39.9		
27_b.5	9.2	215.00	1.9780	2.0056	0.0276	1.38	49.1		
					Média=	2.39			

pH 5.0

	Volume (mL)	Conc. As na saída	Saída (µg)	Entrada (µg)	Acúm. (µg)	% Carregamento	Vol. Acumulado (mL)	Desvio Padrão	Des_Pad Med
28_A1									
C200		169.00				0.00	0.0		2.13
28_a1.1	10	88.70	0.8870	1.6900	0.8030	47.51	10.0	6.37	
28_a1.2	10	84.60	0.8460	1.6900	0.8440	49.94	20.0	2.19	
28_a1.3	10	81.40	0.8140	1.6900	0.8760	51.83	30.0	1.03	
28_a1.4	10	79.40	0.7940	1.6900	0.8960	53.02	40.0	0.94	
28_a1.5	9	77.50	0.6975	1.5210	0.8235	54.14	49.0	0.12	
					Média=	51.29			

28_A2									
C200		161.00							
28_a2.1	10.0	70.00	0.7000	1.6100	0.9100	56.52	10.0	% Carreg. Médio=	52.76
28_a2.2	10.0	75.60	0.7560	1.6100	0.8540	53.04	20.0		
28_a2.3	10.1	75.20	0.7595	1.6261	0.8666	53.29	30.1		
28_a2.4	10.1	73.50	0.7424	1.6261	0.8838	54.35	40.2		
28_a2.5	10.3	74.10	0.76323	1.6583	0.8951	53.98	50.5		
					Média=	54.24			

pH 7.5

	Volume (mL)	Conc. As na saída	Saída (µg)	Entrada (µg)	Acúm. (µg)	% Carregamento	Vol. Acumulado (mL)	Desvio Padrão	Des_Pad Med
33_A									
C200		224.41				0.00	0.0		1.79
33_a.1	10.1	122.48	1.2371	2.2665	1.0294	45.42	10.1	0.69	
33_a.2	10.1	110.85	1.1195	2.2665	1.1470	50.60	20.2	3.37	
33_a.3	10.0	108.73	1.0873	2.2441	1.1568	51.55	30.2	2.40	
33_a.4	10.7	105.07	1.1243	2.4012	1.2769	53.18	40.9	1.92	
33_a.5	8.1	103.10	0.8351	1.8177	0.9826	54.06	49.0	0.58	
					Média=	50.96			
33_B									
C200		216.00							
33_b.1	10.0	120.00	1.20	2.16	0.96	44.44	10.0	% Carreg. Médio=	49.69
33_b.2	10.2	117.00	1.19	2.20	1.01	45.83	20.2		
33_b.3	10.2	112.00	1.14	2.20	1.06	48.15	30.4		
33_b.4	10.2	107.00	1.09	2.20	1.11	50.46	40.6		
33_b.5	10.1	101.00	1.02	2.18	1.16	53.24	50.7		
					Média=	48.43			

Efeito da Vazão

Testes

1.0mL min^{-1}

	Volume (mL)	Conc. As na saída	Saída (µg)	Entrada (µg)	Acúmulo (µg)	% Carregamento	Vol. Acumulado (mL)	Desvio Padrão	Des_Pad Med
28_A1									
C200		169				0.00	0.0		2.13
28_a1.1	10	88.7	0.8870	1.6900	0.8030	47.51	10.0	6.37	
28_a1.2	10	84.6	0.8460	1.6900	0.8440	49.94	20.0	2.19	
28_a1.3	10	81.4	0.8140	1.6900	0.8760	51.83	30.0	1.03	
28_a1.4	10	79.4	0.7940	1.6900	0.8960	53.02	40.0	0.94	
28_a1.5	9	77.5	0.6975	1.5210	0.8235	54.14	49.0	0.12	
					Média=	51.29			
28_A2									
C200		161							
28_a2.1	10.0	70	0.7000	1.6100	0.9100	56.52	10	% Carreg. Médio=	52.76
28_a2.2	10.0	75.6	0.7560	1.6100	0.8540	53.04	20		
28_a2.3	10.1	75.2	0.7595	1.6261	0.8666	53.29	30.1		
28_a2.4	10.1	73.5	0.7424	1.6261	0.8838	54.35	40.2		
28_a2.5	10.3	74.1	0.7632	1.6583	0.8951	53.98	50.5		
					Média=	54.24			

d

5.0mL min^{-1}

	Volume (mL)	Conc. As na saída	Saída (µg)	Entrada (µg)	Acúmulo (µg)	% Carregamento	Vol. Acumulado (mL)	Desvio Padrão	Des_Pad Med
32_A									
C200		194				0.00	0.0		4.27
32_a.1	10	83.9	0.8390	1.9400	1.1010	56.75	10.0	7.96	
32_a.2	9.9	93.4	0.9247	1.9206	0.9959	51.86	19.9	3.56	
32_a.3	10	93.9	0.9390	1.9400	1.0010	51.60	29.9	3.10	
32_a.4	10.1	94.3	0.9524	1.9594	1.0070	51.39	40.0	2.80	
32_a.5	10.5	93.2	0.9786	2.0370	1.0584	51.96	50.5	3.92	
					Média =	52.71			
32_B									
C200		235.0				0.00	0.0	% Carreg. Médio=	49.69
32_b.1	10	128.1	1.2810	2.3500	1.0690	45.49	10.0		
32_b.2	10	124.96	1.2496	2.3500	1.1004	46.83	20.0		
32_b.3	10	124.04	1.2404	2.3500	1.1096	47.22	30.0		
32_b.4	10.1	123.54	1.2478	2.3735	1.1257	47.43	40.1		
32_b.5	10	125.94	1.2594	2.3500	1.0906	46.41	50.1		
					Média =	46.67			

5.2. Appendix B: Results of the pH and flow rate experiments using Amberlite GT73 cartridges

a

Efeito do pH

Testes

pH 5.0

37_A	Volume (mL)	Conc. As na saída	Saída (µg)	Entrada (µg)	Acúmulo (µg)	% Carregamento	Vol. Acumulado (mL)	Desv.Pad (%)	Des. Pad_Med
C200		215.93				0.00	0.0		0.67
37_a.1	10.0	101.69	1.0169	2.1593	1.1424	52.91	10.0	0.17	
37_a.2	10.0	106.61	1.0661	2.1593	1.0933	50.63	20.0	0.81	
37_a.3	10.2	105.82	1.0793	2.2025	1.1232	50.99	30.2	0.65	
37_a.4	9.9	106.65	1.0559	2.1377	1.0819	50.61	40.1	1.18	
37_a.5	9.3	105.83	0.9842	2.0082	1.0240	50.99	49.4	0.55	
					média=	51.23			
37_B									
C200		256.29							
37_b.1	10.5	120.08	1.2608	2.6910	1.4302	53.15	10.5		
37_b.2	10.0	123.59	1.2359	2.5629	1.3270	51.78	20.5		
37_b.3	10.0	123.23	1.2323	2.5629	1.3306	51.92	30.5	% carreg. médio=	51.70
37_b.4	10.1	122.31	1.2354	2.5885	1.3531	52.27	40.6		
37_b.5	10.8	123.62	1.3351	2.7679	1.4329	51.77	51.4		
					média=	52.18			

pH 10.0

39_A	Volume (mL)	Conc. As na saída	Saída (µg)	Entrada (µg)	Acúmulo (µg)	% Carregamento	Vol. Acumulado (mL)	Desv.Pad (%)	Des. Pad_Med
C200		198.00				0.00	0.0		0.98
39_a.1	10.0	90.10	0.9010	1.9800	1.0790	54.49	10.0	1.88	
39_a.2	10.0	95.10	0.9510	1.9800	1.0290	51.97	20.0	1.20	
39_a.3	10.0	95.10	0.9510	1.9800	1.0290	51.97	30.0	1.00	

39_a.4	10.0	92.20	0.9220	1.9800	1.0580	53.43	40.0	0.20	
39_a.5	9.3	94.20	0.8761	1.8414	0.9653	52.42	49.3	0.64	
					média=	52.86			
39_B									
C200		207.00							
39_b.1	10.0	88.70	0.8870	2.0700	1.1830	57.15	10	% carreg. médio=	53.55
39_b.2	10.0	95.90	0.9590	2.0700	1.1110	53.67	20		
39_b.3	10.0	96.50	0.9650	2.0700	1.1050	53.38	30		
39_b.4	10.0	95.80	0.9580	2.0700	1.1120	53.72	40		
39_b.5	9.2	96.60	0.8887	1.9044	1.0157	53.33	49.2		
					média=	54.25			

pH 12.0

62_A	Volume (mL)	Conc. As na saída	Saída (µg)	Entrada (µg)	Acúmulo (µg)	% Carregamento	Vol. Acumulado (mL)	Desv.Pad (%)	Des. Pad_Med
C200		154.50				0.00	0.0		3.14
62_a.1	10.0	125.00	2.50	3.0900	0.5900	19.09	10.0		
62_a.2	10.0	134.50	2.69	3.0900	0.4000	12.94	20.0		
62_a.3	10.0	137.00	2.74	3.0900	0.3500	11.33	30.0		
62_a.4	10.0	133.00	2.66	3.0900	0.4300	13.92	40.0		
62_a.5	10.0	136.50	2.73	3.0900	0.3600	11.65	50.0		
					média=	13.79			

Efeito da Vazão

Testes

1.0 mL min.$^{-1}$

37_A	Volume (mL)	Conc. As na saída	Saída (µg)	Entrada (µg)	Acúmulo (µg)	% Carregamento	Vol. Acumulado (mL)	Desv.Pad	Desv.Pad_Med
C200		215.93				0.00	0.0		0.67
37_a.1	10.0	101.69	1.0169	2.1593	1.1424	52.91	10.0	0.17	
37_a.2	10.0	106.61	1.0661	2.1593	1.0933	50.63	20.0	0.81	
37_a.3	10.2	105.82	1.0793	2.2025	1.1232	50.99	30.2	0.65	
37_a.4	9.9	106.65	1.0559	2.1377	1.0819	50.61	40.1	1.18	
37_a.5	9.3	105.83	0.9842	2.0082	1.0240	50.99	49.4	0.55	
					média=	51.23			
37_B									
C200		256.29							
37_b.1	10.5	120.08	1.2608	2.6910	1.4302	53.15	10.5		
37_b.2	10.0	123.59	1.2359	2.5629	1.3270	51.78	20.5		
37_b.3	10.0	123.23	1.2323	2.5629	1.3306	51.92	30.5		
37_b.4	10.1	122.31	1.2354	2.5885	1.3531	52.27	40.6		
37_b.5	10.8	123.62	1.3351	2.7679	1.4329	51.77	51.4		
					média=	52.18			
							% carreg. médio=	51.70	

d

5.0mL min.$^{-1}$

38_A	Volume (mL)	Conc. As na saída	Saída (µg)	Entrada (µg)	Acúmulo (µg)	% Carregamento	Vol. Acumulado (mL)	Desv.Pad	Desv.Pad_Med
C200		200.00				0.00	0.0		3.71
38_a.1	10.0	96.90	0.9690	1.9000	0.9310	49.00	10.0	0.85	
38_a.2	10.1	105.00	1.0605	1.9190	0.8585	44.74	20.1	0.87	
38_a.3	10.2	106.00	1.0812	1.9380	0.8568	44.21	30.3	1.56	
38_a.4	10.1	104.00	1.0504	1.9190	0.8686	45.26	40.4	2.31	
38_a.5	9.4	106.00	0.9964	1.7860	0.7896	44.21	49.8	12.97	
					média=	45.48			
38_B									
C200		200.00							
38_b.1	9.9	99.60	0.9860	1.9800	0.9940	50.20	9.9		
38_b.2	10.0	113.00	1.1300	2.0000	0.8700	43.50	19.9		
38_b.3	10.0	116.00	1.1600	2.0000	0.8400	42.00	29.9		
38_b.4	10.1	116.00	1.1716	2.0200	0.8484	42.00	40.0		
38_b.5	9.6	74.90	0.7190	1.9200	1.2010	62.55	49.6		
					média=	48.05	% carreg. médio=	46.13	

Livros Grátis

(http://www.livrosgratis.com.br)

Milhares de Livros para Download:

Baixar livros de Literatura
Baixar livros de Literatura de Cordel
Baixar livros de Literatura Infantil
Baixar livros de Matemática
Baixar livros de Medicina
Baixar livros de Medicina Veterinária
Baixar livros de Meio Ambiente
Baixar livros de Meteorologia
Baixar Monografias e TCC
Baixar livros Multidisciplinar
Baixar livros de Música
Baixar livros de Psicologia
Baixar livros de Química
Baixar livros de Saúde Coletiva
Baixar livros de Serviço Social
Baixar livros de Sociologia
Baixar livros de Teologia
Baixar livros de Trabalho
Baixar livros de Turismo