DEVELOPMENT OF A HYBRID SORBENT COMPOSED OF NATURAL MATERIALS FOR THE REMOVAL OF ARSENIC FROM WATERS

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ABSTRACT

DEVELOPMENT OF A HYBRID SORBENT COMPOSED OF NATURAL MATERIALS FOR THE REMOVAL OF ARSENIC FROM WATERS

A novel sorbent has been developed by immobilizing chitosan onto pumice for As(V) sorption from waters. In order to ensure its functionality, sorption performance was determined by measuring As concentrations in water using hydride generation atomic absorption spectrometry. The success of the immobilization was checked with characterization techniques as scanning electron microscopy, thermal gravimetric analysis, and elemental analysis. Points of zero charges were determined with potentiometric mass titration. Batch type equilibration studies showed that the sorbent can be employed at a wide pH range resulting in quantitative sorption (>90%) at pH 3.0-7.0, and greater than 70% sorption at pH>8.0. These results demonstrate the advantage of immobilizing chitosan onto pumice, because, under the same conditions, pumice displays <20% sorption towards As(V) whereas chitosan gives approximately 90% sorption but only at pH 3.0. The validity of the method was verified through the analysis of ultra-pure, bottled drinking, and tap water samples spiked with arsenate; the respective sorption percentages of 93.2 (±0.7), 89.0 (±1.0), and 80.9 (±1.3) were obtained by batch type equilibration. The sorbent was applied in a column for the spiked samples of ultra-pure and tap water. Similar sorption percentages (60% at the 18th fraction) were obtained for ultra-pure water whereas the methodology gave more efficient results for tap water (90% at the 20th fraction) demonstrating the potential of the sorbent for an efficient water treatment system. Arsenic sorption was also examined in the presence of common interfering ions resulting in competing effects of PO_4^{3-} and NO_3^- on As(V) adsorption.

ÖZET

İÇME SULARINDAKİ ARSENİĞİN GİDERİMİ İÇİN DOĞAL MALZEMELERDEN OLUŞAN BİR HİBRİT SORBENT GELİŞTİRİLMESİ

Sularda bulunan As(V)'in arıtılması amacıyla kitosanın ponza üzerine immobilize edilmesi ile yeni bir sorbent geliştirilmiştir. Sorbentin işlevselliğinin görülmesi için sorpsiyon performansları As konsantrasyonlarının hidrür oluşturmalı atomik absorpsyion spektrometri ile ölçülmesi yoluyla belirlenmiştir. İmmobilizasyonun düzeyi tarayıcı elektron mikroskobu, termal gravimetrik analiz ve elemental analiz cihazları gibi karakterizasyon teknikleri ile incelenmiştir. Sorbentlerin sıfır yük noktaları gerilim ölçerli kütle titrasyonu ile saptanmıştır. Bölüt tipi dengeleme çalışmaları, yeni sorbentin geniş bir pH aralığında (3.0-7.0) etkin olduğunu (sorpsiyon>%90); pH>8'de ise %70 sorpsiyona ulaştığını göstermiştir. Aynı koşullar altında ponzanın tek başına As (V)'in %20'den daha azını tutabilmesi, kitosanın ise sadece pH 3.0'te %90 sorpsiyon sağlaması kitosanın ponza üzerine immobilize edilmesi ile elde edilen etkinliği göstermektedir. Metodun doğrulanması arsenat eklenmiş ultra-saf, şişelenmiş içme suyu ve çeşme suyu numuneleri ile yapılmış olup bölüt tipi dengeleme sonuçları sırasıyla %93.2 (±0.7), 89.0 (±1.0), ve 80.9 (±1.3) olarak saptanmıştır. Yeni sorbent, arsenat eklenmiş ultra-saf ve çeşme suyu numuneleri ile kolon çalışmalarında da denenmiştir. Ultra-saf su için benzer sorpiyon yüzdeleri (18. fraksiyonda %60 sorpsiyon) elde edilirken, çeşme suyu için bulunan daha yüksek sorpiyon (20. fraksiyonda %90 sorpsiyon) yeni sorbentin etkin bir su arıtma sistemi için potansiyelini göstermiştir. Aynı zamanda arsenik sorpsiyonu en yaygın girişim yapan iyonlar varlığında da denenmiş olup As(V) sorpsiyonunda PO_4^{3-} ve NO_3^-'ın girişim yaptığı belirlenmiştir.

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CHAPTER 1

INTRODUCTION

Water is the most significant element of human life, and in contrary to popular belief, it is a limited source. In our developing world, efficient and sustainable usage of water sources has not been obtained yet. Furthermore, sensitivity of streams and groundwater resources to the anthropogenic effects and the ever increasing needs of agriculture, industry and domestic users are resulting in a major challenge for water resources management. Among all the potential pollutants, arsenic species are one of the major groups of most toxic contaminants present in drinking water (Mohan and Pittman 2007, Nrashant Singh 2007). Arsenic is a metalloid that can contaminate waters from natural and anthropogenic sources throughout the world at varying concentrations. It is widely distributed in the earth-crust (0.00005%) in the forms of oxides, sulfides or as a salt of iron, sodium, calcium, copper, etc. (Mohan and Pittman 2007). Applications of fertilizers, preservatives and pesticides, and mining processes have been main sources of contamination of arsenic in ground waters. Arsenic and its compounds are known to be toxic and carcinogenic (Nrashant Singh 2007, Welch et al., 2000). People are exposed to arsenic from daily life needs; food, water, air, medicines, etc. Therefore, arsenic in nature forms a great concern for every living organism, bringing about the need for inexpensive, efficient and environmental friendly treatment technologies. There are many removal technologies for arsenic treatment; especially, biosorbents are the most studied materials due to their low-cost, easily applicable and non-toxic forms. However, sample pH is a significant constraint in arsenic removal by adsorption in a way that depending on the working range of the sorbent used, the solution pH must be adjusted before, and possibly, after the removal step. For instance, the most efficient removal of As(V) with activated carbon was obtained at pH 4 to 5 (Huang and Fu, 1984) while chitosan coated ceramic alumina was most effective at the pH of 4 (Boddu et al., 2008). Furthermore, the maximum sorption was obtained at pH 3.0 by Boyacı et al. (2010) in which chitosan immobilized on sodium silicate was used to remove arsenic. Consequently, there is a lack of sorbents, preferably biosorbents, for a successful sorption of arsenic at the neutral pH (6 to 8) of drinking water.

CHAPTER 2

ARSENIC IN DRINKING WATER

2.1. Chemical Proportion of Arsenic

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

2.2. Arsenic Species in the Environment

Arsenic is present in organic and inorganic forms in the nature (EPA 2000) and exists in the (-3), (0), (+3) and (+5) oxidation states (Mohan and Pittman 2007). Organic species of arsenic are monomethyl arsonic acid (MMAA), dimethyl arsinic acid (DMAA) and arseno-sugars found commonly in foodstuffs such as shellfish (EPA 2000). Inorganic species of arsenic occur in both arsenite (As(III)) which consist predominantly of arsenious acid (H_3AsO_3); and arsenate (As(V)) which consist predominantly of $H_2AsO_4^-$ and $HAsO_4^{2-}$ in natural waters (EPA 2000). Pentavalent (+5), also called arsenate species, predominate and are stable in oxygen rich aerobic environments whereas trivalent (+3), also called arsenite, predominate in moderately reducing anaerobic environments (Mohan and Pittman 2007). According to the environmental conditions such as redox potential (Eh), the presence of complexing ions like ions of sulfur, iron, and calcium, pH and microbial activity, arsenic valence and speciation may change (EPA 2000). Figure 2.1 displays the distribution of arsenic species with respect to pH and Eh.

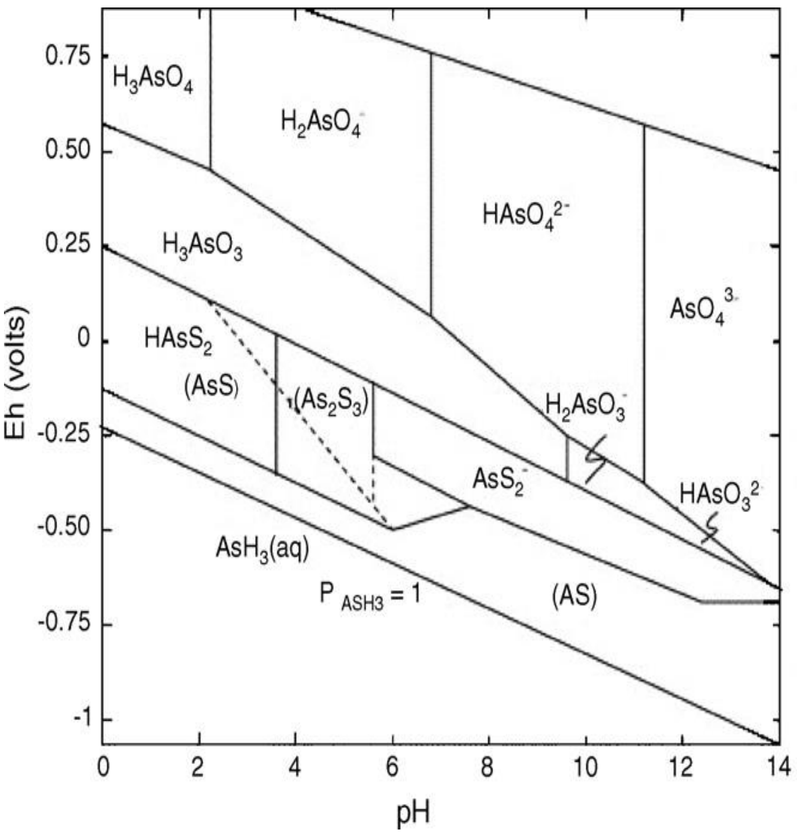


Figure 2.1. The Eh-pH diagram for arsenic at 25 ºC and 101.3 kPa
(Source: Mohan and Pittman 2007)

2.3. Effects of Arsenic Species on Environment and Health

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

Arsenic is widely present in nature; however, it is one of the least plentiful elements in the earth’s crust. The percentage of arsenic in the crust is comparable to that of tin and molybdenum. Natural activities such as volcanic action, erosion of rocks, and forest fires, can release arsenic into the environment (EPA 2000). Virgin soils usually contain a few parts of arsenic per million, but the concentration often increases several hundredfold after several years of application of geological and anthropogenic activities. Arsenic is also found in concentrations of several tenths per million parts in seawater. It exists in minerals such as arsenide, arsenite, and arsenate, all of which are more frequently found in nature when compared with the deposits of elemental arsenic.

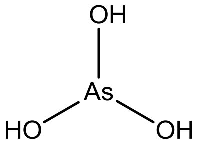
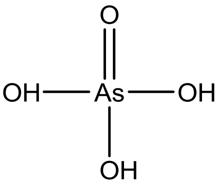
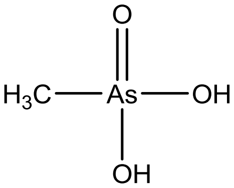
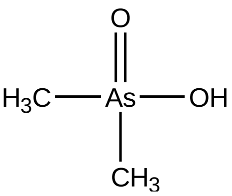
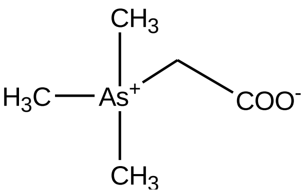
Arsenic is mostly introduced into the environment by means of both geological activities such as weathering of rocks, followed by leaching of metals, lead to the introduction of arsenic into soil and water (Butcher 2007). Moreover, the dissolution of mineral sand ores from arsenic containing rocks and sediments is also related to the presence of arsenic in natural waters (Choong et al. 2007). Another significant source of arsenic in the environment is the anthropogenic activities, which can be exemplified as mining activities, coal combustion processes, and application of pesticides and herbicides. For example, lead arsenate and calcium arsenate have been employed in orchards as horticultural pesticides (Dambies et al. 2002, Mahimairaja 2005). The oxidation state of arsenic compounds can change with respect to environmental conditions, and their toxicity level decreases with methylation (Butcher 2007).

The majority of human exposure to arsenic occurs via food and water ingestion (Terlecka 2005). As a consequence of the fact that arsenic in food is generally in organic forms; contaminated water is one of the most considerable risk for human being (Butcher 2007). Therefore, the major pathway to human exposure to arsenic is drinking contaminated groundwater (Boddu et al. 2008, Choong et al. 2007, Kavcar et al. 2009). However, for the regions with less water contamination risk, food ingestion, such as rice, is another great source of As exposure (Sofuoglu et al. 2014). Exposure to As is considered as one of the most significant environmental causes of cancer in the world (Kapaj et al. 2006). Long-term exposure to the consumption of arsenic in drinking water causes skin, lung, kidney, bladder, and liver cancers as well as pigmentation changes and skin thickening (hyperkeratosis) (Mohan and Pittman 2007; Boddu et al. 2008, Luu et al. 2009). These effects differ from acute poisoning, which typically causes vomiting, oesophageal and abdominal pain, and “rice water” diarrhea (Mohan and Pittman 2007). Other potential long-term effects include neurologic impairment (Lomaquahu and Smith 1998), neurobehavioral effects in adolescence, even memory and intellectual functions (Kapaj et al. 2006).

In order to minimize the health effects of arsenic, the World Health Organization (WHO) adopted a maximum contaminant level (MCL) for arsenic in drinking water at 10 µgL^{-1}(ppb), replacing the old standard of 50 ppb (0.05 mgL^{-1}) WHO, 2011). Also, the United States Environmental Protection Agency (USEPA) set the permissible value of arsenic in drinking water to 0.01 mgL^{-1}(10 ppb-µgL^{-1}) as a provisional standard on the basis of treatment performance and analytical achievability (Choong et al. 2007, USEPA 2001).

The toxicity of arsenic is dependent upon its chemical forms and oxidation states. The decreasing of the toxicity of arsenicals occurs in the following order, As(III) > As(V) > As (Mandal and Suzuki 2002). Table2.1 displays the structures and acidity dissociation constants of arsenic species used throughout this study.

Table 2.1. Chemical structure of the arsenic species

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

2.4. Arsenic Determination Methods

Various instrumental techniques have been developed to determine arsenic concentration in different matrices. Inductively coupled plasma-mass spectrometry (ICP-MS) is one of the most widely used systems for arsenic determination. Furthermore, samples are continuously introduced into the plasma and ICP-MS is relatively easy to interface with most chromatographic systems for the speciation of arsenic. Moreover, it offers excellent sensitivity and long linear dynamic ranges (Butcher 2007). On the other hand, a major disadvantage of it is that it is affected from spectral interference of $^{40}Ar^{35}Cl$ on the monoisotopic ^{75}As signal in the chloride-containing matrixes. This interference effect can be eliminated by matrix separation provided by hydride generation (Menegario and Gine 2000; Sabarudin et al. 2005), or can be corrected with the use of interference-correction equations. Hydride generation atomic absorption spectrometry (HGAAS) is another instrumental technique which is applied after a suitable pre-treatment step or directly (Menegario and Gine 2000, Bundaleska et al. 2005). Hydride generation has an advantage for the determination of the different forms of arsenic (different oxidation states and forms a bond to organic matter) on the basis of different kinetics of hydride generation by each species (Niedzielski et al. 2002).

Lastly, inductively coupled plasma-atomic emission spectrometry (ICP-AES) and HG-ICP-AES are the other instrumental techniques used for the determination of arsenic (Dambies 2004, Faria et al. 2002). High-pressure liquid chromatography (HPLC) in combination with ICP-MS can be used to determine various arsenic species (Afton et al. 2008; Ammann 2010).

2.5. Arsenic Removal Methods

Drinking water is generally treated to remove color, turbidity, and fecal microorganisms using suitable combination of coagulation-flocculation-sedimentation-filtration and disinfection processes. However, if the removal of chemicals like arsenic from water is expected, more complex methods are required (Esparza 2006).In order to remove arsenic from drinking water, precipitative processes, adsorption processes, ion exchange processes, separation (membrane) processes, and other alternative methods are used (EPA 2000). As a consequence of the uncharged state of the arsenite species under pH 9 (H_3AsO_3), all processes are limited with lower efficiency for the removal of arsenite. For this reason, if arsenite is the predominant species present, oxidation to arsenate may be required to achieve the desired removal (EPA 1999).

2.5.1. Precipitative Processes

Coagulation/filtration, direct filtration, coagulation assisted microfiltration, enhanced coagulation, lime softening and enhanced lime softening are the precipitative methods used most frequently to treat arsenic contaminated water. Coagulation/filtration process uses ferric salts, (e.g. ferric chloride, ferric sulfate, ferric hydroxide), aluminum sulfate and alum (aluminum hydroxide) as a coagulant. This process is used not only to remove solids from drinking water supplies but also to change some dissolved species (e.g., natural organics, inorganics, and hydrophobic synthetic organic compounds to insoluble by means of the metal salt coagulants (typically aluminum sulfate, ferric chloride, or ferric sulfate) (EPA 2000, Wickramasinghe et al. 2004). Coagulation is a two-stage process used to remove the suspended or dissolved compounds. In the first stage, the compound in water is destabilized by altering its physical/chemical properties; and, in the second stage, the destabilized compound is removed by filtration. Removal extremely relies on the coagulant type, dosage of coagulant, coagulation pH, initial arsenic concentration and the valence of the arsenic species (As(III) or As(V)) (EPA 2000). This process is mainly preferred as it is simple in operation and the compounds used are commonly available. However; efficient pH control requirement and toxic sludge occurrence are the main disadvantages of this process (Mohan and Pittman 2007).

2.5.2. Membrane Processes

Membrane filtration processes separate contaminants from water passing through a semi-permeable barrier or membrane. The membrane allows some constituents to pass through while blocking the passage of others (EPA 2002).A driving force is required for the movement of constituents across a membrane and according to the type of driving force (e.g., pressure, concentration, electrical potential, and temperature), membrane processes are classified. Among all these methods, pressure-driven membrane processes are the most frequently used for the removal of arsenate. They are classified into four categories: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). In addition these methods can be categorized by the size of the particles which can pass through the membranes or by the molecular weight cut off (i.e., pore size) of the membrane (EPA 2002).The pore size of the membrane is strongly dependent on the applied pressure. If two solutions are separated by a semipermeable membrane, the solvent will naturally pass from the lower-concentration solution to the higher-concentration solution. This process is known as osmosis. It is also possible to change the flow of solvent in the opposite direction, from the higher to the lower concentration, by increasing the pressure on the higher-concentration solution (WHO 2011). Reverse osmosis and nanofiltration, which remove constituents primarily through chemical diffusion, have relatively small pore sizes and a high pressure application. Therefore, these two processes are capable of removing significant portions of the dissolved arsenic compounds in natural waters due to their small pore size. Nanofiltration is a reliable arsenic removal process for groundwater which contains up to 90% dissolved arsenic (AWWARF, 1998). Moreover, in another study RO was combined with NF and the results showed that the removal of arsenic is independent of the pH, and arsenic removal efficiency reaches up to 90% (Johnston et al. 2001, Esparza 2006). On the other hand, relatively lower pressure is applied in ultrafiltration and microfiltration and removal is achieved through physical sieving. A main drawback of the membrane filtration is reported to be the high cost among the other methods (Choong et al. 2007). Furthermore, high technology requirement inconveniences the operation and maintenance of the system (Mohan and Pittman 2007).

2.5.3. Ion Exchange Processes

Ion exchange is a process in which ions are held electrostatically on the surface of a solid phase exchanged for ions in the feed water. This solid phase is typically a resin made from synthetic organic materials, inorganic materials, or natural polymeric materials containing specific ionic functional groups to which exchangeable contaminant ions are attached. The pH independence of this system is one of the main reasons of preference. The resin is usually packed into a column and while contaminated water is passing through the column, contaminant ions are exchanged for other ions. Furthermore, ion exchange resins must be periodically regenerated to remove the adsorbed contaminants, as a result the sludge disposal problems occur (EPA 2002, Mohan and Pittman 2007). Strong acid-weak acid, strong base-weak base types of media have been used for ion exchange. Strong and weak acid resins exchange cations while strong and weak base resins exchange anions. Weak base resins tend to be effective over a smaller pH range and strong base resins are typically used for arsenic treatment because dissolved arsenic is usually in an anionic form. Furthermore, cation exchange can be used for both water softening and removal of heavy metals. Also, anionic resins are generally used in the removal of nitrate, arsenic and selenium species (EPA 2002). As cation exchange resins, Ce(IV)-loaded resins, Cu(II)-loaded resins, Fe(III)-loaded resins, La(III)-loaded resins, Y(III)-loaded resins and Zr(IV)-loaded resins were used to remove of As(V) in some research, and macroreticular chelating resins and anion exchange resins were used for the same purpose (Mohan and Pittman 2007). In another study for arsenic removal by ion exchangers, Dominguez et al. (2003) synthesized fiber like ion exchange resin from vinylbenzyl chloride and found that the fiber ion exchange resin showed preferable kinetic performance compared to commercial resins.

2.5.4. Alternative Technologies

All the above mentioned methods for arsenic removal have limitations due to their cost or health hazard effects. As a consequence of this fact, need of environmentally safe alternative methods arises. Application of different biomasses in sorption studies for arsenic removal has a significant role with their advantages of low cost and being environmentally friendly in nature. In various processes, bacterial activity may play a significant role as a catalyst for arsenic removal, but little is known about the viability of biological processes in eliminating arsenic from water (Johnston et al. 2001; Esparza 2006). *Spirulinplatensis* (Şeker et al. 2008), *E. coli* biofilm supported on kaolin (Quintelas et al. 2009), ulvalactuca (Schijf and Ebling 2010) and carbonate hydroxylapatite (CHAP) prepared from eggshell waste (Zhang et al. 2011) are some examples of biosorbents developed for this purpose.

CHAPTER 3

LITERATURE REVIEW

3.1. Sorption Studies

In adsorptive processes, the adsorption media is usually packed into a column. While the contaminated water is passed through the column, contaminants are adsorbed by the media. When adsorption sites become filled, the column must be regenerated or replaced with new media (EPA 2002, Banerjee et al. 2008).

Out of various types of sorbents such as activated carbon, activated alumina, copper-zinc granules, granular ferric hydroxide, iron oxide coated sand, greensand filtration ($KMnO_4$ coated glauconite), and surfactant-modified zeolite, activated alumina is the most commonly used one to remove arsenic from drinking water (EPA 2002). Because, arsenic ions in feed water can be sorbed by the oxidized activated alumina surface. Although the chemical reactions involve exchange of contaminant ions (such as fluoride, arsenic, selenium, and silica) with the surface hydroxides on the alumina, activated alumina is considered to be working based on adsorption process. Furthermore, iron oxide coated sand was used for the removal of arsenic where the ions are exchanged with the surface hydroxides (EPA 2000, Lin and Wu 2001).

Nevertheless, sample pH is an important constraint in arsenic removal by adsorption in a way that depending on the working range of the sorbent used; the solution pH must be adjusted before, and possibly, after the removal step. For example, the maximum removal of As(V) with activated carbon was obtained at pH 4 to 5 (Huang and Fu 1984), while chitosan coated ceramic alumina was most effective at the pH of 4 (Boddu et al. 2008). Furthermore, the maximum sorption was obtained at pH 3.0 by Boyacı et al. (2010) in which chitosan immobilized on sodium silicate was used to remove arsenic.

3.2. Supporting Surfaces in Sorption Studies

In sorption studies, the biosorbents are generally coated on the surfaces of some physical supports in order to enhance active sides which are responsible for the high adsorption potentials for metals (Hasan et al. 2008). In order to increase the adsorption capacity of chitosan, it is widely spread on physical supports that help to enhance the accessibility of metal binding amine sites (Dambies et al. 2002, Elwakeel 2010, Guibal et al. 1998). Furthermore, an adsorbent developed by chitosan supported on porous glass beads was used for heavy metal adsorption (Shen et al. 2013).

Among all the physical support materials, pumice stone is one of the most prevalent biosorbent supports. It is a type of light material with highly porous (pore volumes up to 85%) (Kitis and Kaplan2007) structure with high silica content (generally 60-75% SiO_2) (Baytak et al. 2008).Its skeleton structure allows ions and molecules move and settle with ease. It is a highly preferred support material in many treatment studies due to its rough surface and porous structure which provides various possible attachment sites for pollutants (Alemayehu and Lennartz 2009). This low-cost volcanic stone is found abundantly in Turkey. Kitis and co-workers (2005) have reported the physicochemical characteristics of pumice samples from the most abundant pumice sources in Turkey (Table 3.1.). As a consequence of its highly porous structure, it provides a large number of possible attachment sites for pollutants (Alemayehu and Lennartz 2009, Ersoy et al. 2010). Moreover, it is used in environmental applications as supporting material in catalytic removal of trace metals (Baytak et al. 2008, Kitis and Kaplan 2007). It also plays a role as filtration medium and biofilm support in environmental engineering (Kitis et al. 2005).

3.3. Chitosan and Pumice for Arsenic Removal

Chitin is one of the most abundant organic compounds in the earth, with the largest amounts of production per year (Kurita 2006). Chitin (Figure 3.1) is a type of polymer consisting of 2-acetamido-2-deoxy-β-D-glucose through a β (1→4) linkage (Kumar 2000). Chitin can be obtained from fungi, algae, protozoa, etc.; but exoskeletons are the most easily accessible sources of chitin. The shells of marine crustaceans such as crabs and shrimps are available as waste from the seafood processing industry and used for commercial production of chitin. The shells contain chitin, proteins, $CaCO_3$, lipids and pigments (Kurita 2006). Extraction of chitin from shells requires demineralization with HCl and further treatment with NaOH for deproteinization (Planas 2002). Chitosan (Figure 3.2) is the N-deacetylated form of chitin which is produced by thermochemical alkaline treatment of chitin. It has a high nitrogen content (7%) which makes it as a useful chelating agent (Kurita 2006, Tolaimate et al. 2000). Chitin and chitosan are attractive materials with unique properties of non-toxicity, film and fiber forming properties, adsorption of metal ions, coagulation of suspensions or solutes, and distinctive biological activities (Kurita 2006).

Table 3.1. Physicochemical characteristics of the original pumice samples (Source: Kitis et al. 2005)

Parameter	Chemical characteristics (% mass)[a]		
	Nevsehir	Kayseri	Isparta
SiO_2	74.1	68.5	59.0
Al_2O_3	13.5	14.9	16.6
Fe_2O_3	1.4	3.1	4.8
CaO	1.2	2.9	4.6
MgO	0.4	0.95	1.8
Na_2O	3.7	4.1	5.2
K_2O	4.1	2.8	5.4
SO_3	ND[b]	ND	0.4
TiO_2	0.07	0.2	0.6
Ash content	1.7	2.6	1.6
Particle size (μm)	Internal porosity (%)[c]		
250-500	58.5	69.2	46.3
500-1000	62.5	73.3	55.3
1000-2000	66.5	76.9	61.5
Specific gravity (without pores) (g/cm^3)[d]	2.33	2.21	2.47

[a] Obtained from XRD analysis
[b] Below detection limit
[c] Includes all interconnected open and closed pores
[d] Bulk densities (with pores) for all above crushed pumices are generally 0.5-1.0 g/cm^3

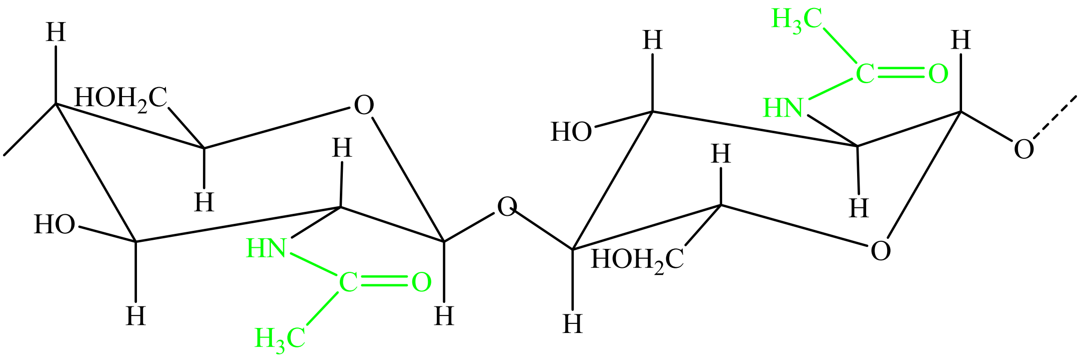


Figure 3.1. Structure of chitin repeating unit

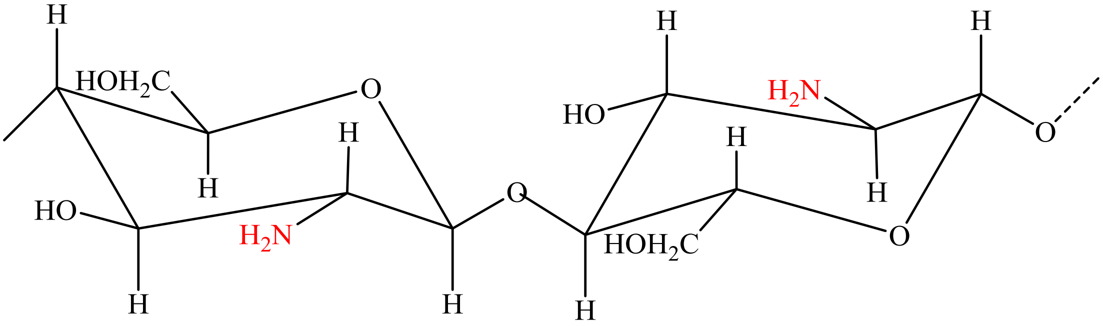


Figure 3.2. Structure of chitosan repeating unit

Among all the biosorbents, chitosan and its modified forms have importance due to its many features like being one of the most abundant natural biopolymers, hydrophilic, non-toxic, biodegradable structure, regeneration and recycling potential, and having the ability to form complexes with metals (Elwakeel 2010, Hasan et al. 2008). Due to the last feature, many studies regarding the removal of metal ions from water can be found in the literature. For instance, chitosan hydrogel beads were studied for removal of nitrate (Chatterjeeand Woo 2009) and protonated chitosan beads were used for fluoride (Viswanathan et al. 2009). Chaunhan et al. (2012) studied the removal of cadmium and hexavalent chromium from electroplating waste water using thiocarbamoyl chitosan; Miretzkyand Cirelli (2009) studied Hg(II) removal from water not only by chitosan but also its derivatives; and Chen and Chung (2006) evaluated the removal of As(III) and As(V) from water by chitosan itself due to its excellent biological properties. Also, in column studies, chitosan is used as a resin for the sorption of arsenic with improved resistance to shrinkage which was obtained by 3, 4-diamino benzoic acid functionalized cross linked chitosan (Sabarudin et al. 2005).

Furthermore, Boddu et al. (2008) used chitosan dip coated ceramic alumina for As(III) and As(V) removal in column with improved sorption capacity for As(III).

Last but not least, pumice can also be used as a sorbent itself in addition to its supporting material properties. For instance, Panuccio et al. (2009) concluded that cadmium adsorption on pumice can be performed at pH 7.5 with 90% efficiency. A sorption of 80% was reported for Cu^{2+} and Cr^{3+} at pH 8.0, and 90% for cadmium at pH6.0 (Alemayehu and Lennartz 2009, Yavuz et al. 2008). Asgariet al. (2012) studied fluoride adsorption onto functionalized pumice stone and obtained 96% removal at pH 6.0.

3.4. Motivation and Aims

According to the literature review, there is a lack of sorbents, preferably biosorbents, for a successful sorption of arsenic at the neutral pH (6.0 to 8.0) of drinking water. On the other hand, the presence of interfering ions such as (Mg^{2+}, Ca^{2+}, Fe^{3+}, NO_3^-, $PO_4)^{3-}$ may have competing effects on adsorption of arsenic from natural waters (Kundu et al. 2004; Rau et al. 2003). Therefore, the main objective of this study was to develop a new biosorbent for arsenic removal from drinking water. In order to accomplish this goal, a novel biosorbent was developed by immobilizing chitosan onto pumice. In the next step, characterization of the novel sorbent was checked with scanning electron microscopy, thermal gravimetric analysis, elemental analysis, and potentiometric mass titration for the points of zero charge. The optimization of working parameters for arsenate sorption by the chitosan-immobilized pumice was performed a working pH, amount of sorbent, reaction time, ionic strength, and, reaction temperature.

In order to verify the method validity, the sorbent was also used for the ultra-pure, bottled drinking, and tap water samples spiked with arsenate. Lastly, sorption studies were also carried out with column application, and in the presence of interfering ions.

CHAPTER 4

MATERIALS AND METHODS

4.1. Instrumentation and Apparatus

In arsenic determination; a Thermo Elemental Solaar M6 Series atomic absorption spectrometer (Cambridge, UK) with an air-acetylene burner was used; utilizing the Segmented Flow Injection Hydride Generation (SFI-HGAAS) unit (Figure 3.1). An arsenic hollow cathode lamp at the wavelength of 193.7 nm and a deuterium lamp were employed as the source line and for background correction, respectively. In HGAAS, the quartz tube atomizer was 10 cm long, 8 mm in internal diameter and 10mm in external diameter with a 4 mm bore inlet tube fused at the middle for sample introduction. Air-acetylene flame was used for heating the quartz tube externally and nitrogen was used as the carrier gas. Operating parameters for the HGAAS system are given in Table 4.1.

In batch sorption studies, GFL 1083 water bath shaker (Burgwedel, Germany) equipped with microprocessor thermostate was used to provide efficient mixing. The elemental composition of chitosan was determined by LECO-CHNS-932 elemental analyzer (Mönchengladbach, Germany). Molecular weight determinations were performed in Petrotest capillary viscosimeter (Dahlewitz, Germany). Crystallographic properties were obtained with Philips X'Pert ProX-Ray Diffractometer (Eindhoven, The Netherlands). Interference studies were performed with Agilent 7500ce Series (Tokyo, Japan) inductively coupled plasma mass spectrometer (ICP-MS). IR measurements were performed with Perkin Elmer Spectrum 100 FTIR Spectrometer (Shelton, USA) with pike Miracle Single Reflection Horizontal ATR Accessory. The Diamond/KRS-5 Lens Single Reflection ATR plate was used as a sample holder. Spectra of samples were recorded in the range of 4000-450 cm^{-1} with a resolution of 4 cm^{-1} and scan number of 4.pH adjustments were performed with Ino Lab Level 1 pH meter (Weilheim, Germany). Images of sorbents were taken with Philips XL-30S FEG scanning electron microscope (Eindhoven, The Netherlands). Thermal properties of sorbents were analyzed with Perkin Elmer Pyris Diamond TG/DTA (Boston, MA, USA). Mastersizer 2000, Hydro 2000S (Malvern Worcs, U.K.) was used for determination of size distribution of oxalic acid treated pumice, and chitosan immobilized pumice. Point of zero charge of chitosan flakes was determined with a potentiometric mass titration method (Bourikas et al. 2003).

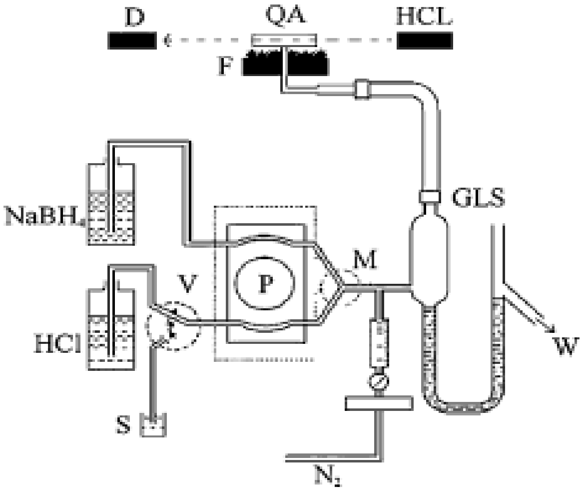


Figure 4.1. Segmented Flow Injection HGAAS system used in arsenic determinations. D: deuterium lamp, QA: quartz atomizer, HCL: hollow cathode lamp, F: flame, GLS: gas-liquid separator, W: waste, P: peristaltic pump, V: three way valve and S: sample (Source: Yersel, et al. 2005)

Table 4.1. Operating parameters for the segmented flow injection (SFI-HGAAS) system

Operating parameters	
Carrier gas (N_2) flow rate	200 mLmin^{-1}
HCl flow rate	6.1 mLmin^{-1}
HCl concentration	2.0 % (v v^{-1})
$NaBH_4$ concentration	1.0 % (m/m) stabilized with 0.10 % (m/m) NaOH
$NaBH_4$ flow rate	3.0mLmin^{-1}
Sample flow rate	7-8 mLmin^{-1}

4.2. Reagents and Solutions

All chemicals used during this study were of analytical reagent grade. Ultra-pure water (18.2 MΩ) was used throughout the study. Glassware and plastic containers were cleaned by soaking in 10% (v/v) nitric acid for 24 h and rinsed with deionized water prior to use. Table 4.2 shows all the reagents used with their concentrations.

Stock standard solutions of As(V) and As(III), 2000.0 mg/L, were prepared by dissolving As_2O_5 (Merck, product code: 1.09939, CAS no: [1303-28-2]) and As_2O_3 (Fischer, CAS no: [1327-53-3]), respectively, in ultra-pure water. Oxalic acid (Carlo Erba, product code: 408737, CAS No: [6153-56-6]) solution was prepared in a concentration of 10.0% (w/v) for dissolution of chitosan in immobilization step. Chitosan flakes (910 kDa) were synthesized from practical grade chitin (Sigma, product code: C9213, CAS no: [1398-61-4]) by refluxing a mixture of chitin containing 40.0% (m/m) NaOH (Merck, product code: 1.06498, CAS no: [1310-73-2]) solution. L-cysteine (Merck, product code: 1.02838, CAS no: [52-90-4]) was used as reducing agent for As(V) to As(III) prior to arsenic determination by HG-AAS in a concentration of 0.50% (m/v).

The interference studies were carried out with stock solutions of $Mg(NO_3)_2.6H_2O$ (Merck, product code:1058550050, CAS no: [13446-18-9]), $Ca(NO_3)_2.4H_2O$ (Merck, product code: 1021230100, CAS no: [13477-34-4]), $Fe(NO_3)_3.9H_2O$ (Sigma, product code: 24855367, CAS no: [7782-61-8]), NaCl (Riedel-de Haen, product code: 13423,CAS no: [7647-14-5]), HNO_3 (Sigma, product code: 24845344, CAS no: [7697-37-2]), and H_3PO_4 (Sigma, product code: 24868686, CAS no: [7664-38-2]) in ultra-pure water.

Calibration standards were prepared daily by preparing buffer stock solution of the stock standards. pH adjustments were done by using different concentration (0.01 M, 0.1 M, 1.0 M) of NH_3 and HNO_3solutions for ICP-MS and NaOH and HCl solutions for HGAAS determinations.

Table 4.2. Reagents used throughout the study

Reagent	Concentration used	Company	Product Code	CAS no.	Purpose of use
Chitin (practical grade, from crab shell)		Sigma	C-923	[1398-61-4]	Chitosan synthesis and used as a sorbent
$NaBH_4$ (granular)	1.0 % (m/v)	Merck	8.06373	[16940-66-2]	AsH_3 generation in HGAAS
NaOH (pellets)	0.10 % (m/v)	Merck	1.06498	[1310-73-2]	Stabilization of $NaBH_4$ solution
L-cysteine	0.50 % (m/v)	Merck	1.02838	[52-90-4]	Reduction of As(V) to As(III)
NaCl	0,0001-0.01 M	Riedel-de Haen	13423	[7647-14-5]	Determination of effect of ionic strength on sorption of As(V) by chitosan
HNO_3 (65%)		Sigma	24845344	[7697-37-2]	Acidification, preparation of NO_3^- stock solution for interference and sorption study

(cont. on next page)

Table 4.2 (Cont.)

Reagent	Concentration used	Company	Product Code	CAS no.	Purpose of use
NaCl	0.01 M	Riedel-de Haen	13423	[7647-14-5]	Preparation of NaCl stock solution for interference and sorption study
NaOH	40.0 % (m/m)	Merck	1.06498	[1310-73-2]	Chitosan synthesis
NaOH	0.100 M	Merck	1.06498	[1310-73-2]	Extraction of inhibitor from styrene and titration of chitosan solution (determination of D.D.)
Acetic acid	2.0 % (v/v)	Riedel-de Haen	27225	[64-19-7]	Preparation of chitosan solution and various desorption solutions
Oxalic acid	0.01M	Carlo Erba	408737	[6153-56-6]	Activation of chitosan, activation of pumice
SRM (Trace elements in natural water)		NIST	1640		Method validation

(cont. on next page)

Table 4.2 (Cont.)

Reagent	Concentration used	Company	Product Code	CAS no.	Purpose of use
As_2O_5		Merck	1.09939	[1303-28-2]	Preparation of As(V) stock solution
As_2O_3		Fischer		[1327-53-3]	Preparation of As(III) stock solution
$Mg(NO_3)_2.6H_2O$		Merck	1058550050	[13446-18-9]	Preparation of Mg stock solution for interference and sorption study
$Ca(NO_3)_2.4H_2O$		Merck	1021230100	[13477-34-4]	Preparation of Ca stock solution for interference and sorption study
$Fe(NO_3)_3.9H_2O$		Sigma	24855367	[7782-61-8]	Preparation of Fe stock solution for interference and sorption study

4.3. Preparation of the Chitosan-Immobilized Pumice as a Sorbent

4.3.1. Synthesis of Chitosan

Chitosan flakes were synthesized from chitin under inert atmosphere by the method of Rigby and Wolfrom given in the monograph by Muzzarelli (1973). Chitin (15.0 g) was treated with 720 mL of 40.0% (m/m) aqueous NaOH solution in a one liter three-necked round bottomed flask with reflux condenser connected to its middle neck. A thermometer was connected to control the temperature during reaction and N_2 gas was bubbled through the solution from the side arm to provide inert atmosphere in the reaction medium. Constant reflux was obtained at 115℃ and continued for 6 hours. After cooling the alkaline mixture to room temperature, chitosan flakes were washed with distilled water until a neutral filtrate was obtained. Resulting chitosan flakes were dried at 60℃ for 2 h before use.

4.3.2. Batch Type Immobilization on Pumice

Chitosan is known to have a tendency to form a gel or agglomerate in aqueous media, and its amine groups are generally considered as main active sites which are responsible for the high adsorption potential for metals (Hasan et al. 2008). In order to increase the adsorption capacity of chitosan, it is widely spread on physical supports that help to enhance the accessibility of metal binding amine sites (Dambies et al. 2002, Elwakeel 2010, Guibal et al. 1998).

Pumice has a skeleton structure allowing ions and molecules move and settle with ease. As a consequence of its rough surface and porous structure which provides various possible attachment sites for pollutants, it is a highly preferred support material in many treatment studies (Alemayehu and Lennartz 2009). Turkey is one of the leading pumice and pumicite producing countries with 32% of the world total production in 2012 which is followed by Italy (18%) (US Geological Survey, 2014). Furthermore, pumice is also a low cost material, which makes it highly preferable in sorption studies (Ahmaruzzaman, 2008, Yavuz et al. 2008, Kitis et al. 2007).

Therefore, chitosan was immobilized onto pumice with slight modification of the method applied by Boddu et al. (2008) in the immobilization of chitosan onto ceramic alumina. The pumice was obtained from Isparta (Turkey) and had a particle size range of 250-1000 μm. Acid treatment was required in order to remove organic and inorganic extractable contaminants (Yavuz et al. 2008) which may affect the sorption capacity of the sorbent. Moreover, acid treatment step would facilitate adherence of chitosan onto pumice. For this purpose 5.0 g of pumice was stirred with 100 mL of 10.0% (m/v) oxalic acid for 4 h at room temperature. Acid-treated pumice was filtered, washed with deionized water until being neutral, and dried in an oven at 70 °C for 24 h. Supporting particles were further ground to prevent them to settle down from the reaction mixture. In another vessel, chitosan flakes were dissolved in 20.0 mL of 10.0% (m/v) oxalic acid in order to obtain a 5% (m/v) chitosan solution. To assist the mixing of highly viscous solution, heat was applied at 40-50°C until a clear solution was observed as a result of complete dissolution of flakes. About 5.0 g of the acid-treated pumice was added slowly to the diluted gel and stirred for 2 h at the same mixing temperature. Excess oxalic acid in the composite biosorbent was neutralized by the addition of 1.0 M NaOH solution followed by filtration and washing with deionized water until a neutral filtrate was obtained. After the immobilization procedure, the chitosan-immobilized pumice was dried at 60°C overnight and ground by mortar and pestle prior to use.

4.4. Characterization Studies

A variety of methods were applied for the characterization of synthesized chitosan flakes, pumice and chitosan-immobilized pumice. The elemental compositions of the sorbents were determined by a LECO-CHNS-932 elemental analyzer (Mönchengladbach, Germany). For determination of the degree of deacetylation, potentiometric titrimetry and elemental analysis were employed as described elsewhere (Tolaimate et al. 2000). Images of pumice, chitosan, and chitosan-immobilized pumice were obtained with a Philips XL-30S FEG scanning electron microscope (SEM) (Eindhoven, The Netherlands). In addition, thermal gravimetric degradation behavior was examined with Perkin Elmer Pyris Diamond TG/DTA (Boston, MA, USA). Particle size distribution of oxalic acid-treated pumice and chitosan-immobilized pumice was determined by Mastersizer 2000, Hydro 2000S (Malvern Worcs, U.K.). Point of zero charge (PZC) for pumice and the novel sorbent were determined with a potentiometric mass titration method (Bourikas et al. 2003).

4.4.1. Degree of Deacetylation

For the determination of deacetylation degree of chitosan, two methods, namely potentiometric titration and elemental analysis were performed for comparison.

4.4.1.1. Potentiometric Titration

Potentiometric method depends on the titration of chitosan with standardized NaOH solution which is used to deprotonate positively charged amine groups in chitosan. For this purpose, 250.0 mg portion of chitosan were dissolved in 10.0 mL of 0.30 M HCl and after being diluted to 50.0 mL with ultrapure water, it was titrated with 0.100 M NaOH. The consumed volume of NaOH which corresponds to the amount of amine groups in chitosan is obtained from the difference between two inflection points of acid-base titration (Tolaimate 2000). Equation 4.1 describes the formulation used in the calculation of degree of acetylation (AD). In this equation, 161 is the molecular weight of glucosamine unit of chitosan, 42 is the difference in the molecular weights of chitin and chitosan repeating units, m is the mass of the chitosan sample taken, ΔV is the volume and M is the molarity of NaOH solution. Degree of deacetylation (DD) was calculated from Equation 4.2.

$$AD = \frac{\left(1 - 161 \times \frac{\Delta V \times M}{m}\right)}{\left(\frac{\Delta V \times M}{m} \times 42 + 1\right)} \tag{4.1}$$

$$DD = 1 - AD \tag{4.2}$$

4.4.1.2. Elemental Analysis

Elemental analysis provides the percent concentrations of C, N, H and S in a compound. Deacetylation process removes two carbon atoms and one oxygen atom from chitin structure. Chitosan and chitin structures differ in their C and O contents while N remains constant in both structures. Therefore, C/N ratios are used in the determination of degree of deacetylation by using Equation 4.3 (Kasaai et al. 2000). Here, 5.145 is the ratio of C/N in completely N-deacetylated chitosan repeating unit and 6.816 is that of N-acetylated chitin repeating unit.

$$D.D. = \left(1 - \frac{C/N - 5.145}{6.816 - 5.145}\right) \times 100 \tag{4.3}$$

4.4.2. Point of Zero Charge Determination

Point of zero charge (PZC) for pumice and the novel sorbent were determined with a potentiometric mass titration method (PMT) (Bourikas et al. 2003). PMTs were performed, under an N_2 atmosphere, for a blank solution and suspensions of three different masses of the pumice and chitosan-immobilized chitosan (0.125, 0.250, and 0.500 g) were immersed oxide at constant ionic strength (0.03 M). A small amount of base, 1 M NaOH, was then added to deprotonate a significant part of the surface sites, rendering the surface negative, and then the suspension was titrated by adding small volumes of an aqueous HNO_3 solution. The pH value was recorded after each addition of the acidic solution as a function of its volume. A similar titration procedure was followed for the blank solution.

4.5. Sorption Studies

Sorption studies were performed for all the sorbents through batch process; namely, chitosan, pumice, and chitosan-immobilized pumice. Solution pH was adjusted with Ino Lab Level 1 pH meter (Weilheim, Germany) using various concentrations of HCl and NH_3. The batch sorption studies were carried out in GFL 1083 water bath shaker (Burgwedel, Germany) equipped with a microprocessor thermostat. Effect of solution pH, amount of sorbent, reaction time, ionic strength, and reaction temperature were investigated. Investigated parameters are summarized in Table 4.3. Batch sorption was followed by filtration of the mixture through blue-band filter paper. Each sorption was achieved in triplicate trials. All samples and standard solutions were acidified with concentrated HCl to produce 1.0% (v/v) HCl in the final solution. A Thermo Elemental Solaar M6 Series atomic absorption spectrometer (Cambridge, UK) with an air-acetylene burner was used in arsenic determination utilizing the Segmented Flow Injection Hydride Generation (SFI-HGAAS) unit. An arsenic hollow cathode lamp (193.7 nm) and a deuterium lamp were employed as the source line and for background correction, respectively. Operating parameters for the HGAAS system were as follows: 200 $mLmin^{-1}$ carrier gas (N_2) flow rate, 6.1 $mLmin^{-1}$ HCl flow rate, 2.0% (v/v) HCl concentration, 3.0 $mLmin^{-1}$ $NaBH_4$ flow rate, 1.0% (m/v) $NaBH_4$ concentration (stabilized with 0.1% (m/v) NaOH), 7–8 $mLmin^{-1}$ sample flow rate. Using the optimized parameters, calibration equation was $y= 0.0046x + 0.0278$, $R^2= 0.992$, limit of detection (LOD_{3s}) and limit of quantification (LOQ) was 0.79 μgL^{-1} and 2.61 μgL^{-1}, respectively. The percent arsenic sorption was calculated using Equation 4.4, where C_i is the initial and C_f is the final concentration in the solution.

$$Sorption\,\% = \frac{C_i - C_f}{C_i} \times 100 \tag{4.4}$$

Table 4.3. Studied parameters and ranges

Parameters investigated	Range
pH of solution	2.0, 3.0, 4.0, 6.0, 7.0, 8.0 and 10.0
Amount of sorbent (mg)	25.0, 50.0, 75.0, 100.0, 150.0, 200.0 and 250.0
Reaction time (min)	15, 30, 60, 120, 240, 360 and 720
Ionic strength (M of NaCl)	0.0001, 0.001, and 0.01
Sorption temperature (ºC)	25, 50 and 75

4.5.1. Effect of Solution pH

Solution pH is one of the most important factors affecting the sorption of As species (arsenite As(III) and arsenate As(V)). Initial experiments were carried out with each sorbent; chitosan, pumice, and chitosan-immobilized pumice in order to investigate the interaction between the species of arsenic and the functional groups on the sorbents, and to find the optimum pH for sorption. 100 μgL^{-1} As(III) or As(V) standard solutions were prepared and the initial pH of these solutions was adjusted to 2.0, 3.0, 4.0, 6.0, 7.0, 8.0, and 10.0 with dilute HNO_3 or NH_3. After pH adjustment step, 50.0 mg sorbent was added into the 50 mL centrifuge tube containing 30.0 mL of $100.0 \mu gL^{-1}$ As(V)or $40.0 \mu gL^{-1}$As(III) solution. The mixture was placed in a thermostated water bath shaker and was shaken for 30 minutes which is followed by a filtration step. The filtrate was analyzed for its arsenic content by HGAAS.

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

Effect of amount of chitosan, pumice, and chitosan-immobilized pumice on the sorption was investigated for 25.0, 50.0, 75.0, 100.0, 150.0, 200.0, and 250.0 mg. Arsenate ion concentration, solution volume, shaking time, solution pH, and reaction temperature were 100.0 $\mu g\ L^{-1}$, 20.0 mg, 4 h, pH=7.0, and 25℃, respectively.

4.5.3. Effect of Reaction Time

Effect of reaction time on the sorption of arsenate ion by chitosan, pumice, and chitosan-immobilized pumice was investigated for time intervals of 15, 30, 60, 120, 240, 360 and 720 min. Arsenate ion concentration, solution volume, sorbent amount, solution pH and reaction temperature were 100.0 μgL^{-1}, 20.0 mL, 200.0 mg, pH=7.0, and 25℃, respectively.

4.5.4. Effect of Ionic Strength

Effect of ionic strength on the sorption of arsenate ion by chitosan, pumice, and chitosan-immobilized pumice was investigated in 0.0001, 0.001, and 0.01 M NaCl solution. Arsenate ion concentration, solution volume, shaking time, solution pH, sorbent amount, and reaction temperature were 100.0 μgL^{-1}, 20.0 mL, 200.0 mg, 4 h, pH=7.0, and 25℃, respectively.

4.5.5. Effect of Reaction Temperature

Effect of reaction temperature on the sorption of arsenate ion by chitosan, pumice, and chitosan-immobilized pumice was investigated at 25, 50 and 70℃ sorption temperatures. Arsenate ion concentration, solution volume, shaking time, solution pH, and sorbent amount were 100.0 μgL^{-1}, 20.0 mL, 4 h, pH=7.0, and 200.0 mg, respectively.

These results were also used to investigate the thermodynamic parameters of sorption (ΔG^o, ΔS^o and ΔH^o) utilizing the equations 4.5, 4.6 and 4.7 (Atkins and de Paula 2002; Yersel, et al. 2005):

$$\Delta G^o = -RT \ln R_d \tag{4.5}$$

$$\Delta H^o = R \ln \frac{R_d(T_2)}{R_d(T_1)} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^{-1} \tag{4.6}$$

$$\Delta S^o = \frac{\Delta H^0 - \Delta G^o}{T} \tag{4.7}$$

where ΔG^o (kJmol^{-1}) is the Gibbs free energy which can be written in terms of enthalpy change, ΔH^o (kJmol^{-1}), and the entropy change, ΔS^o (J$mol^{-1}K^{-1}$)with respect to temperature R_d (mLg^{-1})is the ratio of arsenate ion distributed between solid (sorbent) and liquid (aqueous solution of arsenate) phase at equilibrium and is defined by Equation 4.8 as

$$R_d = \frac{C_{solid}}{C_{liquid}} \tag{4.8}$$

where, C_{solid} is the concentration of arsenate in sorbent (mgg^{-1}) and C_{liquid} is the concentration of arsenate ion in solution after sorption (mgL^{-1}).

4.5.6. Application to Natural Samples

In order to demonstrate the applicability of the developed method, two natural water samples were chosen, namely, commercial bottled spring water and tap water from the campus of İzmir Institute of Technology (IZTECH), Urla, İzmir. Each sample was spiked with 100.0 μgL^{-1} arsenate. Solution volume, shaking time, solution pH, and sorbent amount were 20.0 mL, 4 h, pH=7.0, and 25℃, respectively.

4.6. Column Application

In order to show the applicability of chitosan-immobilized pumice in the continuous removal of arsenic from water, the column sorption was also carried out. A 50 mm height fluorinated ethylene propylene (FEP) tubing with internal diameter of 1.5 mm was used in the preparation of microcolumns. The particle size of the chitosan-immobilized pumice was sieved to a range of 125-150 μm. The microcolumn was filled with the sorbent to obtain 25 mm active filling. The 100.0 μgL^{-1} As(V) solution was passed through the column in an upward flow at a flow rate of 0.8 mLmin^{-1} using a peristaltic pump. In addition to spiked ultra-pure water, spiked tap water samples from IZTECH campus were also used. The effluent was collected in 1.0 mL volume intervals.

4.7. Interference Studies

Interference studies were performed for Mg^{2+}, Ca^{2+}, Fe^{3+}, NO_3^-, $PO_4)^{3-}$ions. Interfering effects of selected ions during the removal of As(V) were examined under optimized sorption conditions. For this purpose, 15 solutions (pH 7.0), all containing 100.0 μgL^{-1}As(V) and varying amount of each interfering ion(0.1 mgL^{-1}, 1 mgL^{-1}, and 10 mgL^{-1}) were prepared separately and used in sorption study.

CHAPTER 5

RESULTS AND DISCUSSION

5.1. Characterization of the Sorbents

Images of chitosan flakes, pumice and chitosan-immobilized pumice obtained by scanning electron microscopy are given in Figure 5.1. As shown, pumice is highly porous as compared to chitosan. The image of chitosan-immobilized pumice indicates that chitosan was well dispersed on the surface of pumice stone, and this high degree of dispersion must have increased the available surface active sites of chitosan which are responsible for sorption.

Thermal gravimetric analysis (TGA) of the sorbents was carried out by flowing N_2 gas from room temperature to 800 °C. It can be seen from Figure 5.2 that weight is gradually decreased to almost 0% in the case of chitosan. The weight loss between 25 and 97°C can be ascribed to the removal of water molecules adsorbed on the surface whereas smaller weight loss between 98 and 266°C is due to the elimination of bonded water. Weight loss owing to the thermal degradation of chitosan took place between 266 and 800°C. However, within the same temperature range, pumice had a very small weight loss (5%) possibly through the decomposition of organic contaminants. The thermal behavior of chitosan-immobilized pumice was between chitosan and pumice in a way that water was lost up to 244 °C, resulting in a 15% weight loss (Figure 5.2); yet, at higher temperatures, small changes in the weight was due to the decomposition of chitosan in the composite structure leaving pumice itself.

Pumice had a particle size range of 250-1000 μm, originally. This wide range of particle size precluded its direct use due to difficulties in getting homogeneous amount of chitosan in the final sorbent. Therefore, an average particle size of 143±1,4 μm was obtained through milling after oxalic acid treatment. A final grinding of bulk chitosan-immobilized pumice resulted in an average particle size of 81±0,8 μm.

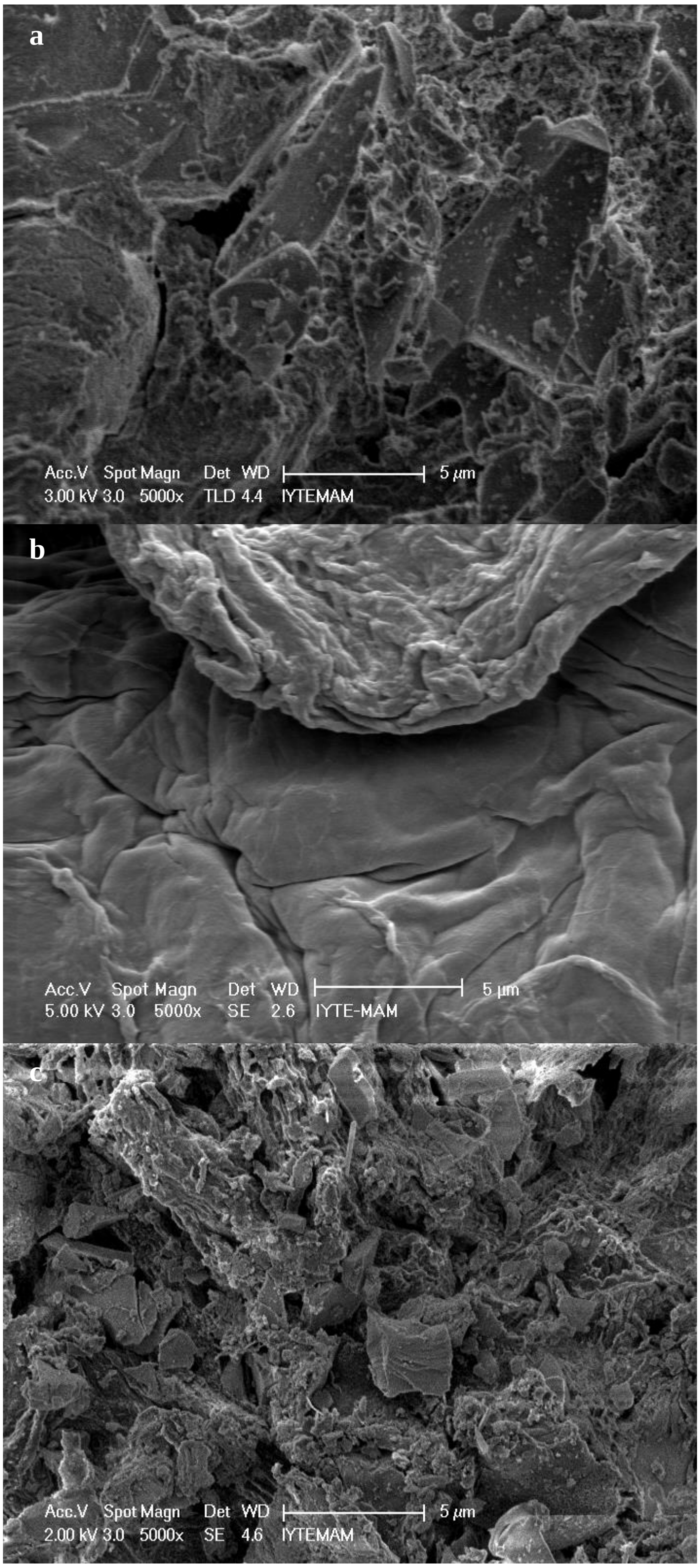


Figure 5.1. SEM images of (a) pumice, (b) chitosan, and (c) chitosan-immobilized pumice

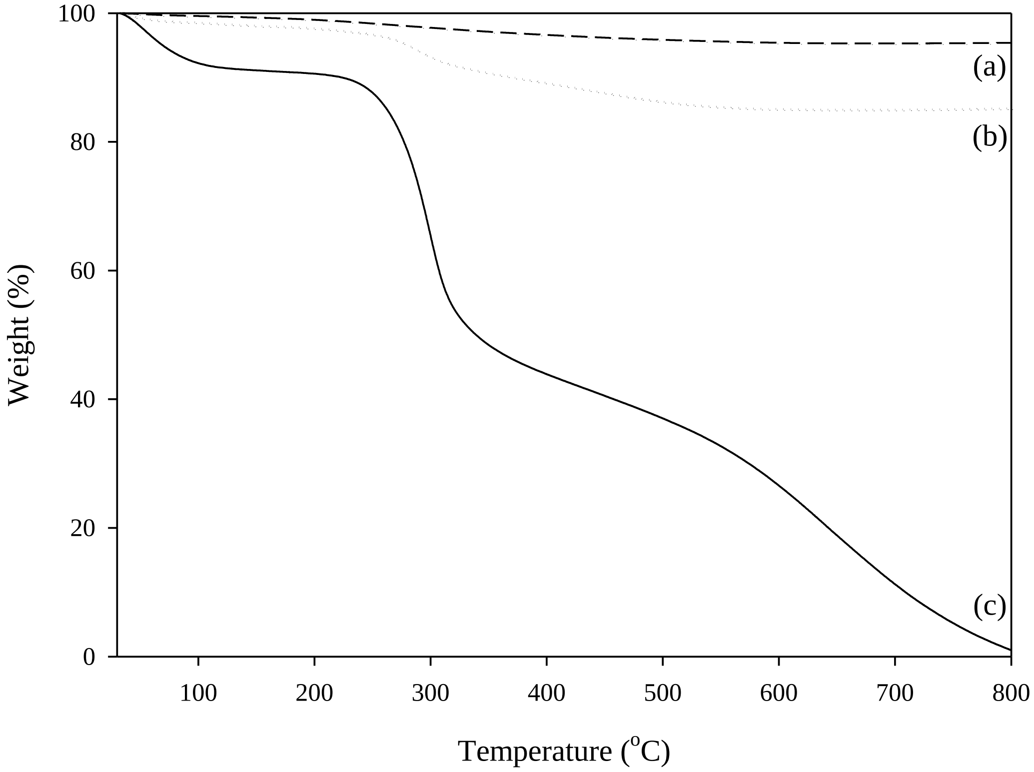


Figure 5.2. TGA curves of (a) pumice, (b) chitosan-immobilized pumice and (c) chitosan

5.1.1. Degree of Deacetylation

The elemental composition of chitosan, pumice, and chitosan-immobilized pumice are summarized in Table 5.1. The amount of acetyl groups removed from starting material (chitin) in terms of degree of deacetylation was determined by potentiometric titrimetric method studied by Tolaimate and co-workers (2000). The potentiometric titration graph of chitosan is illustrated in Figure 5.3 where the difference between two inflection points corresponds to amount of protonated amine groups in chitosan. From the titrimetric method for determination of degree of deacetylation, 87.3% removal of acetyl groups was calculated which was in agreement with the result obtained from elemental analysis (84.7%). The elemental analysis results are not only indicative of deacetylation process, but also valuable for determining the amount of chitosan immobilized onto pumice. The ratio of carbon percentage of chitosan-immobilized pumice to that of chitosan indicates that 9.3% of the material was immobilized onto pumice. This value is also in agreement with the amount determined gravimetrically after calcination of the chitosan-immobilized pumice (11.3%).

Table 5.1. Results of the elemental analysis

	%		
Sorbent	N	C	H
Pumice	0.00	0.26	0.62
Chitosan-immobilized pumice	0.60	3.78	1.19
Chitosan	7.55	40.8	7.23

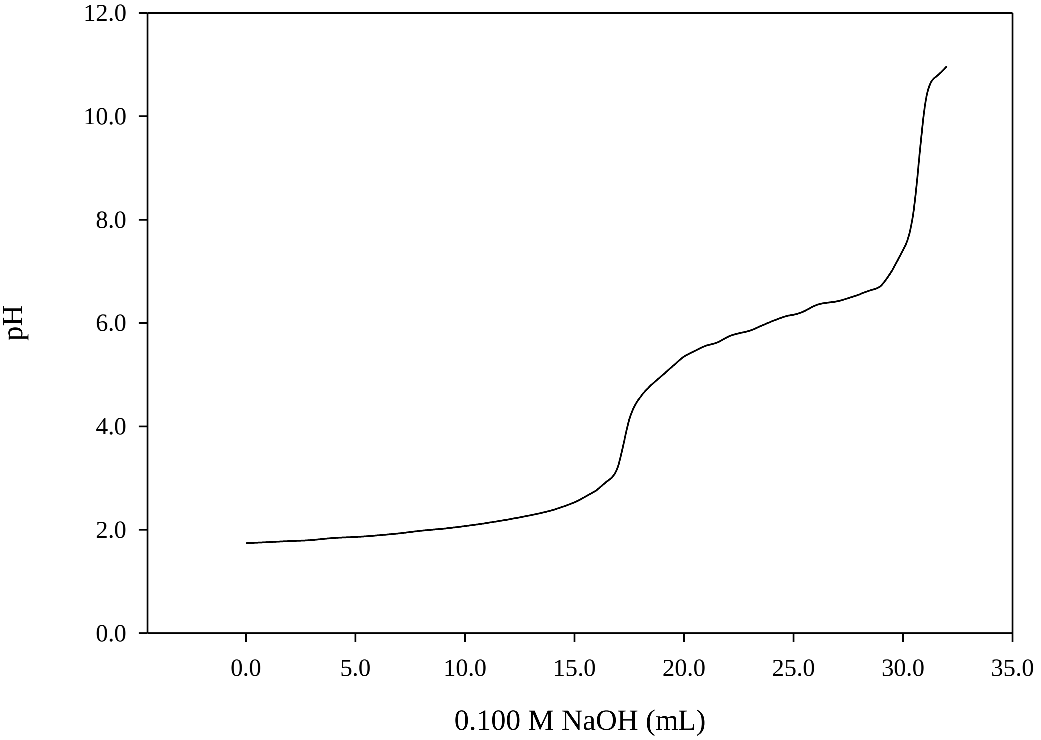
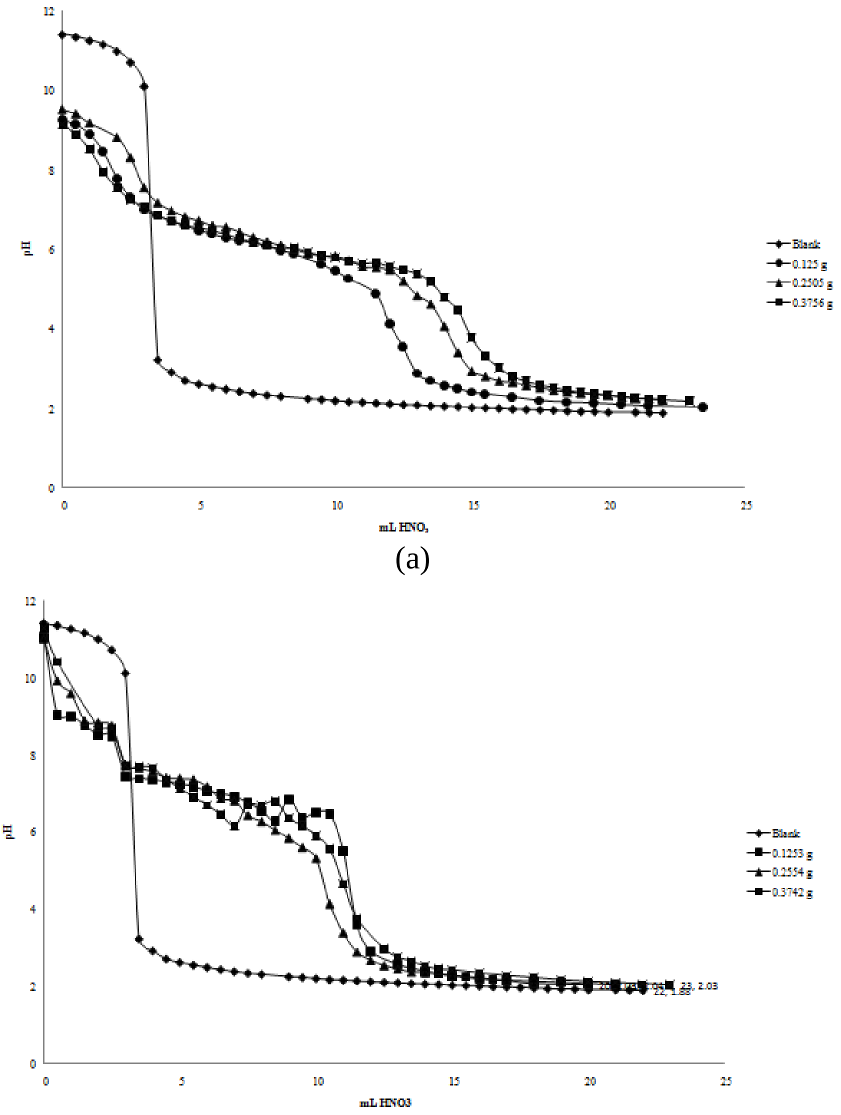


Figure 5.3. Titration curve of chitosan (dissolved in HCl) with standard NaOH solution

5.1.2. Point of Zero Charge Determination

Point of zero charge (PZC) values of chitosan-immobilized pumice and pumice were determined by application of potentiometric mass titration as described by Bourikas et al. (2003). After application of aforementioned method the PZCs of pumice and chitosan-immobilized pumice were determined to be 6.8 and 7.4; respectively. PZC can be identified from the intersection point of the curves demonstrating samples with different masses as can be seen in Figure 5.4. The PZC of pumice was determined to be about 6.8 which is close to the value (7.7) obtained by Kitis et al. (2005).



(a)

(b)

Figure 5.4. PZC curves of (a) chitosan-immobilized pumice, (b) pumice

5.2. Sorption Studies

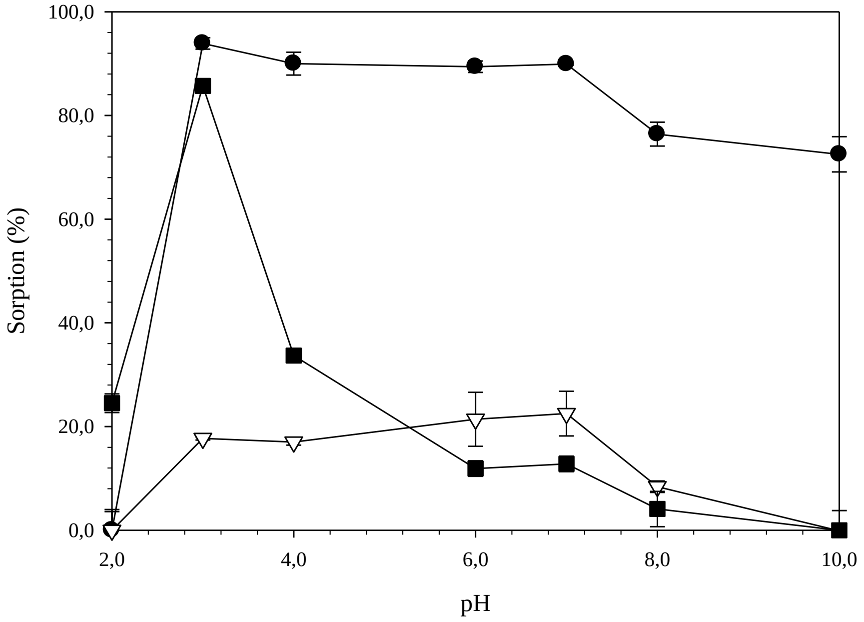
5.2.1. Effect of Solution pH

All the initial experiments were carried out to investigate sorption characteristics of chitosan-immobilized pumice as well as pumice and chitosan itself by the variation in solution pH. The sorption results for As(V) and As(III) as a function of solution pH are given in Figure 5.5. As shown in Figure 5.5a, pumice was not able to efficiently remove As(V) from the solution at any pH tested. The relatively low sorption (0-20%) of pumice can be attributed to the presence of minor amounts of Al_2O_3 (16.6%) and Fe_2O_3 (4.8%). Since these compounds, namely, activated alumina-based sorbents, and iron oxide-based nano particles, in addition to hybrid materials and commercial resins have been employed as sorbent for removal of inorganic arsenic species. In contrast to pumice, chitosan was very effective in the sorption of As(V), however only at a specific pH of 3.0, as already been demonstrated in a previous study (Boyacı et al. 2010). The specific sorption was explained to be due to the electrostatic attraction between the positively charged surface active groups on chitosan (protonated amine groups) and $H_2AsO_4^-$ ion, the predominant (about 85%) As(V) species at pH 3.0. The point of zero charge of chitosan is about 6.3, and under this pH, amine groups of chitosan are protonated. Decreasing the pH strongly increases the positive charge on the surface which supports the electrostatic nature of sorption (Boddu et al. 2008; Boyacı et al. 2010). As a consequence of the fact that chitosan flakes have the possibility to be dissolved under acidic conditions, more acidic conditions were not studied.

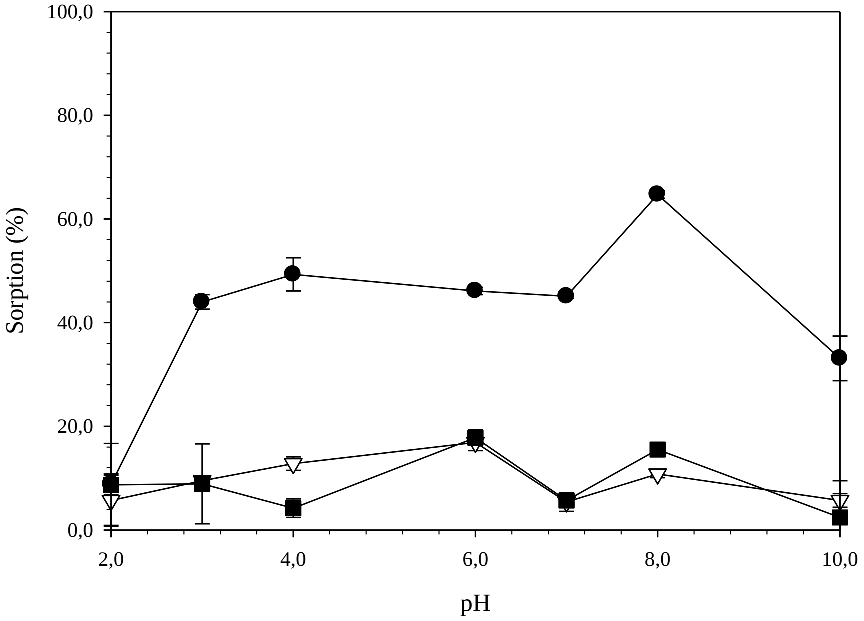
In contrast to chitosan, chitosan-immobilized pumice displayed different, more efficient sorption behavior in a way that this novel sorbent can be applied at a wider pH range, from 3.0 to 7.0 (≥ 90% removal). The sorbent can also be used between pHs 7.0 and 10.0 with a percent sorption of about 75±10. The sorption characteristics of the novel sorbent towards As(V) is completely distinctive from chitosan or pumice which suggest a predominant chelation of arsenate between chitosan functional groups and pumice surface active sites. Moreover, Mohan and Pittman (2007) stated that Al-hydroxide presence in the surface of adsorbents may be responsible for arsenic sorption at a wide pH range.

In the case of As(III), neither pumice nor chitosan were capable of removal (<20%) from solutions under the working conditions (Figure 5.5b). However, chitosan-immobilized pumice showed around 50±10% affinity for arsenite between pHs 3.0 and 8.0 where the predominant species is neutral H_3AsO_3. Above pH 9.0 to 13.0, As(III) is in the form of $H_2AsO_3^-$ and the sorption decreased below 40% at pH 10.0. At any particular point in the studied pH range, the arsenite species cannot display electrostatic interaction with the sorbent. However, some hydroxyl groups present in the biosorbent may be involved in the coordination with the sorbate. Lower arsenite sorption was also reported by Boddu et al. (2008) and Chen et al. (2008), who suggested the interaction of arsenite with the unprotonated amine groups. Furthermore, decrease in the sorption capacity of As(III) for pH >7.5 may be resulted from the competition of OH^- ions for the sorption sites, and the reversal of the surface charge of the sorbent may also be possible (Maliyekkal et al. 2009).

The high efficiency (greater than 90% sorption) of the novel sorbent towards As(V) between pHs 3.0 and 7.0 offers an important advantage since it removes the possible pH adjustment step before the application of the new methodology unless the solution pH is either too high or too low. Especially, at the approximate pH of natural waters, the novel sorbent can directly be applied without pH adjustment. Even for As(III), less probable form of the arsenic in surface waters, greater than 40% removal can be considered to be another advantage of the method. In order for the sorbent to be more applicable for removal of arsenate from natural water, the pH of 7.0 was chosen for further optimization studies.



(a)



(b)

Figure 5.5. Effect of solution pH on the sorption of 100.0 μgL^{-1} of (a) As(V) and (b) As(III). (●) chitosan-immobilized pumice, (∇) pumice and (■) chitosan (reaction time: 4 h, sorbent amount: 200.0 mg, sample volume: 20.0 mL, sorption temperature: 25 °C, n=3)

5.2.2. Effect of Sorbent Amount

The effect of the sorbent amount on As(V) sorption is demonstrated in Figure 5.6. It was found that as the amount of sorbent increased, the sorption also increased. Maximum sorption was reached at the investigated highest amount of 250.0 mg; however, increasing the amount from 75.0 mg to 250.0 mg did not have a critical effect on the sorption. This was an indication of the adequacy of the active sites for sorption even though the chitosan-immobilized pumice had only 10% (m/m) chitosan. This finding is essential for potential application of the novel sorbent for municipal water treatment since pumice has the advantage of being a low cost and naturally abundant material.

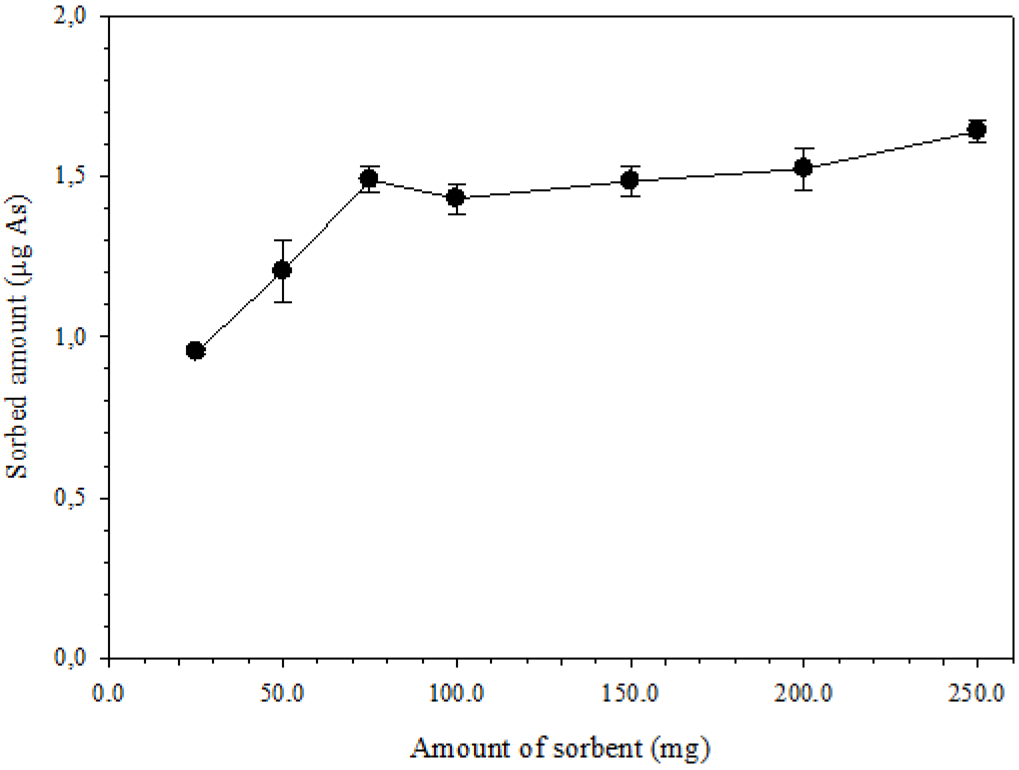


Figure 5.6. Effect of sorbent amount on the sorption of 100.0 µgL^{-1}As(V). (reaction time: 4 h, sample pH: 7.0, sample volume: 20.0 mL, sorption temperature: 25 °C, n=3)

5.2.3. Effect of Reaction Time

The effect of reaction (equilibration) time on the sorption of arsenate by chitosan-immobilized pumice was investigated for different time intervals from 15 min to 12 h. As can be seen from Figure 5.7, the optimum equilibration time for As(V) removal was determined as 240 min (4 h). However, a significant sorption of 60% was observed even in 15 min.

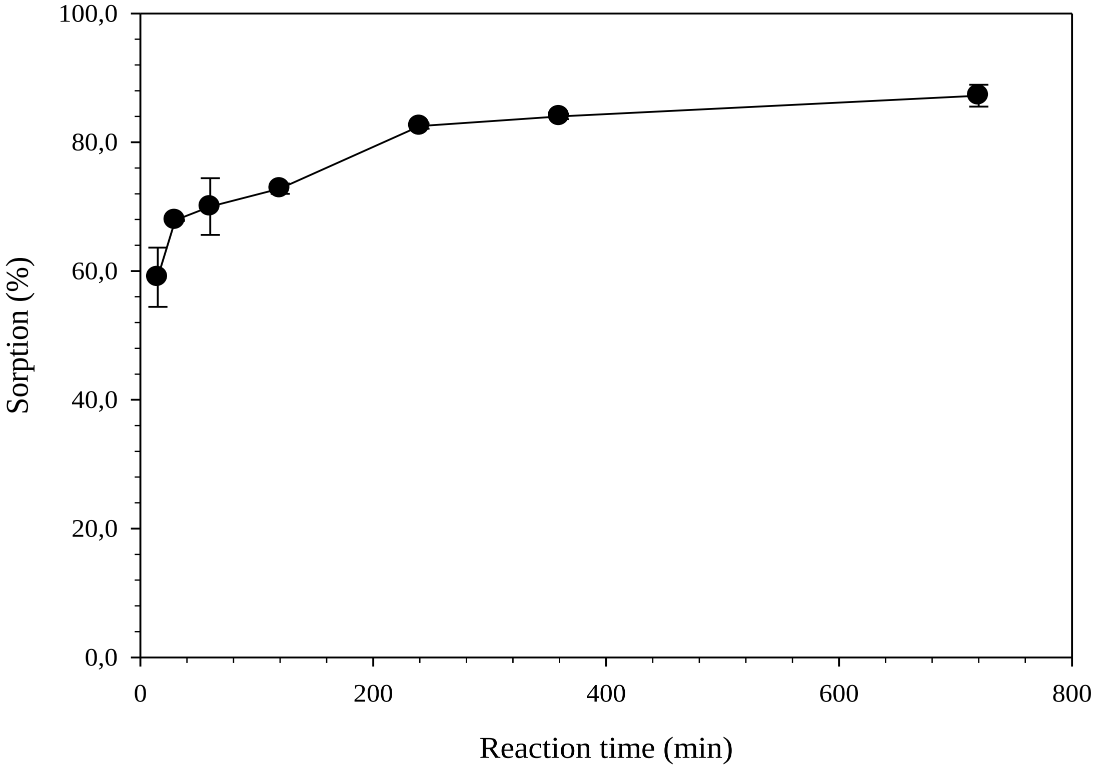


Figure 5.7. Effect of reaction time on sorption of 100.0 μgL^{-1} As(V)(sorbent amount: 200.0 mg, sample pH: 7.0, sample volume: 20.0 mL, sorption temperature: 25 °C, n=3)

5.2.4. Effect of Ionic Strength

Effect of ionic strength on the sorption performance of chitosan-immobilized pumice was investigated by addition of various concentration of NaCl into arsenic solution as illustrated in Figure 5.8. The sorption capacity was reduced to 63% in the presence of NaCl. However; no significant change was observed in the sorption characteristics of chitosan-immobilized pumice with respect to varying NaCl concentrations. This is especially important for the application of the novel sorbent to the natural waters that have varying ionic concentrations.

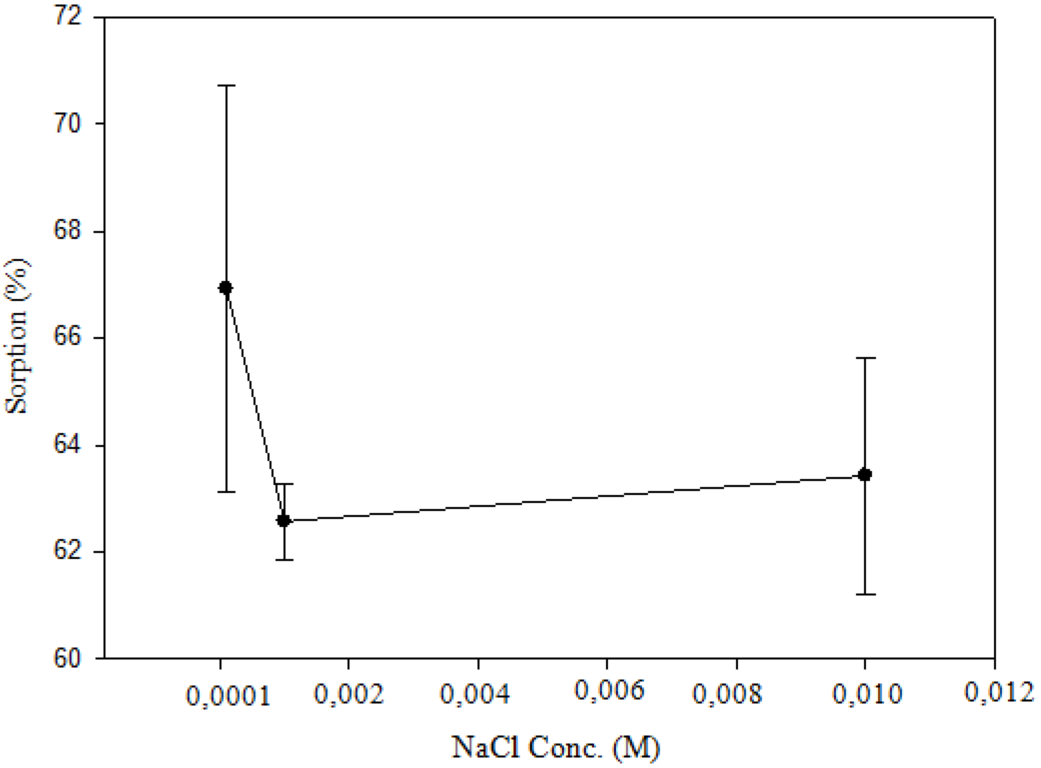


Figure 5.8. Effect of ionic strength on sorption of 100.0 μgL^{-1} As(V)(sorbent amount: 200.0 mg, sample pH: 7.0, sample volume: 20.0 mL, sorption temperature: 25 °C, n=3)

5.2.5. Effect of Reaction Temperature

In order to examine the effect of the reaction temperature on As(III) and As(V) sorption, three different temperatures, 25, 50 and 75 °C, were applied. The respective sorption percentages of 93, 88, and 74% were obtained for As(V).

According to the calculated thermodynamic parameters given in Table 5.2, the sorption of arsenate by chitosan-immobilized pumice is spontaneous at low temperatures. The exothermic nature of the arsenate sorption by chitosan-immobilized pumice can be understood from the negative ΔHº value. On the other hand, any significant effects for As(III) sorption with respect to temperature change were not observed.

Table 5.2. Thermodynamic parameters of chitosan-immobilized pumice

	ΔG ($kJmol^{-1}$)		ΔH ($kJmol^{-1}$)	ΔS ($Jmol^{-1}K^{-1}$)	
	298 K	323 K		298 K	323 K
Chitosan-immobilized pumice	-17.9	-17.7	-19.7	-6.2	-6.2

(As(V) concentration: 100.0 μgL^{-1}, reaction time: 4 h, sorbent amount: 200.0 mg, sample pH: 7.0, sample volume: 20.0 mL, n=3)

Further clarification of arsenic sorption by proposed sorbent was studied by Dubinin-Radushkevich (D-R) isotherm model (Boyacı et al. 2010). The linear correlation of the model is 0.995 suggesting that the isotherm is suitable to describe the sorption of As(V) by the sorbent. In a typical sorption study, the arsenic amount adsorbed was 0.0066 $mgAsg^{-1}$ sorbent (initial concentration of As: 100.0μgL^{-1}, solution volume: 20.0 mL and sorbent amount: 250.0 mg) and according to the maximum sorption capacity (0.3697 ($mgAsg^{-1}$sorbent)), calculated from linearized form of the isotherm, only small portion of the sorbent capacity appears to be used for sorption and sorbent is far away from saturation. In addition, the calculated value of mean free energy of sorption (3.45 $kJmol^{-1}$) is indicative of physisorption.

5.2.6. Application to Natural Samples

Natural waters spiked with arsenate were used to show the applicability of the proposed method to real samples. Percentage sorption values were 93.2 (±0.7) for the ultra-pure, 89.0 (±1.0) for the bottled drinking, and 80.9 (±1.3) for the tap water samples. The decrease in the sorption for tap water can be attributed to the presence of competitive ions for the active sites of the sorbent. However, the decrease was tolerable which was also supported by the ionic strength study where no significant effect was observed in the sorption characteristics of chitosan-immobilized pumice even after the addition of 0.01M NaCl. This is especially important for the application of the novel sorbent to the natural waters that have variable ionic concentrations.

5.4. Column Application

In order to examine the potential use of the novel sorbent, chitosan-immobilized pumice was also tried in column equilibration. The sorption was studied with both ultra-pure and tap water spiked with As(V). Each milliliter of the effluent collected off the column was analyzed for its As(V) concentration (Figure 5.9). As can be seen from the figure, there was a gradual decrease in the sorption of As(V) from the ultra-pure water. It was stabilized around 60% after 18 mL. The results obtained with tap water were more efficient in contrast to the results obtained in batch sorption. The sorption was greater than 95% even at the 15th fraction, and it was decreased to around 90% at the 20th. The higher sorption obtained with tap water can be due to the stabilization of the arsenate in tap water matrix. The increase in the sorption percentages obtained in the column study as compared to the batch can be attributed to the different mechanisms of the sorption, and to the differences in the contact time of sorbent and analyte in the two equilibration modes. The relatively long (4h) sorption time applied in the batch sorption might have resulted in the dissolution of some minerals from pumice affecting the sorption capacity. This observation can be a topic of further studies. As a conclusion, it can be argued that the application of the novel sorbent in the column mode indicate a potential for simpler water treatment systems.

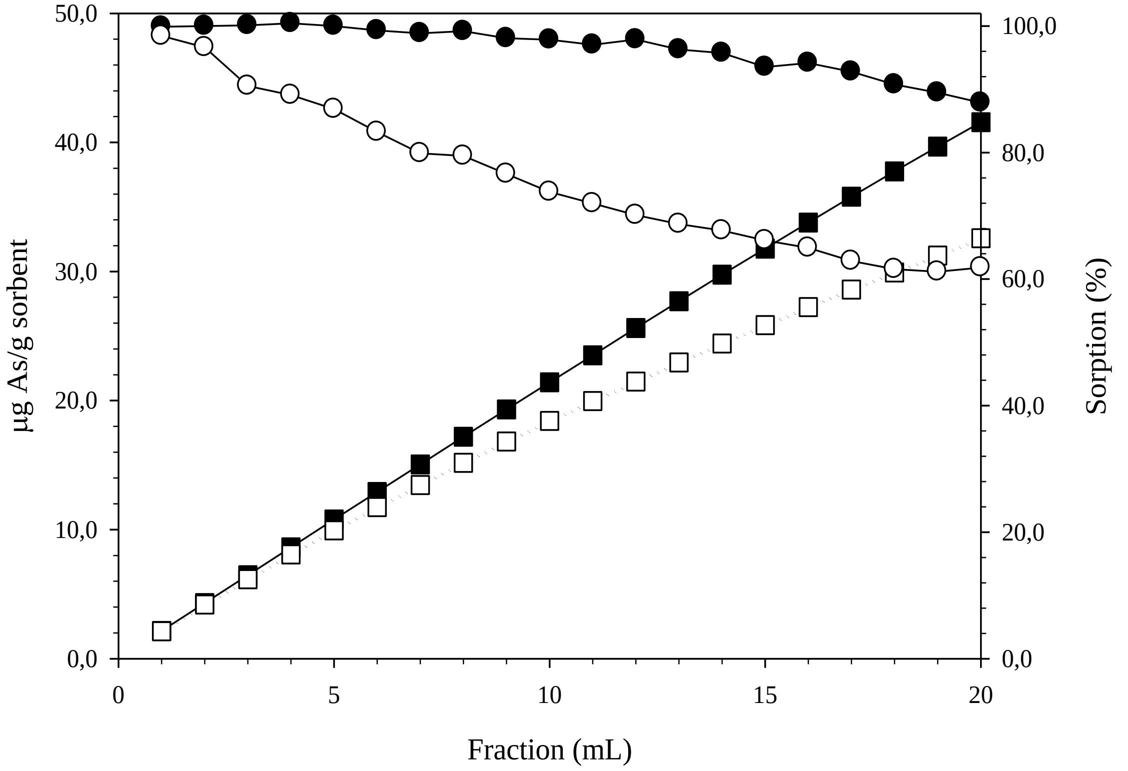


Figure 5.9. Microcolumn sorption of 100.0 μgL^{-1} As(V). Sorption (%) scale: (●) tap water and (○) ultra-pure water; μg As/g sorbent scale: (■) tap water and (□) ultra-pure water (flow rate: 0.8 mLmin^{-1}, particle size: 125-150 μm, active column height: 24 mm, column diameter: 1.6 mm, sample pH: 7.0, sample volume: 20.0 mL, sorption temperature: 25 °C)

5.5. Effect of Interfering Ions

Effect of the possible interfering ions to sorption of As(V) was studied and shown in Table 5.3. The sorption percentages for As(V) in the presence of interfering ions were determined and compared with the sorption percentage of As(V) in interference free case. Any positive or negative deviation greater than 20% was considered as an interference. The results showed that the cations, Mg^{2+}, Ca^{2+}, and Fe^{3+}, used in this study did not show interference effect. Chloride ion was not examined as possible interference in this particular study; however, the ionic strength studies have demonstrated non-interfering effects for this ion.

On the other hand, NO_3^- and PO_4^{3-} ions had interfering effects at all concentrations tested. The affinity of the novel sorbent to PO_4^{3-} and NO_3^- was similar to the results obtained by Rau et al. (2003).

Table 5.3. Effects of interfering ions on As(V) adsorption: N: no interference, I: interference (20 % decrease in the sorption)

	$0.1\ mgL^{-1}$ As (V)		
Interfering Ion	$0.1\ mgL^{-1}$	$1\ mgL^{-1}$	$10\ mgL^{-1}$
Mg^{2+}	N	N	N
Ca^{2+}	N	N	N
Fe^{3+}	N	N	N
NO_3^-	I	I	I
PO_4^{3-}	I	I	I

(As(V) concentration: 100.0 μgL^{-1}, reaction time: 4 h, sorbent amount: 200.0 mg, sample pH: 7.0, sample volume: 20.0 mL, n=3)

CHAPTER 6

CONCLUSIONS

In this study, a novel sorbent (chitosan immobilized pumice) was developed for arsenic removal from drinking waters. The success of the immobilization has been checked with such characterization techniques as scanning electron microscopy, thermal gravimetric analysis, and elemental analysis. Points of zero charge of the sorbents were determined with potentiometric mass titration. As a consequence of the batch type equilibration studies, the novel sorbent can be employed at a wide pH range resulting in quantitative sorption (>90%) of As(V) from the waters at neutral pHs. Furthermore, a wide pH range (3.0-10.0) can be used for arsenate sorption by chitosan-immobilized pumice in contrast to chitosan whose sorption was limited only to pH 3.0. The nature of the sorption of chitosan was considered to be electrostatic in nature; however, in case of chitosan-immobilized pumice chelate formation mechanism can be more appropriate. Optimized sorption parameters for the batch system were as follows; solution pH of 7.0, sorbent amount of 200 mg, reaction temperature of 25 ºC, and reaction time of 4h. Sorption of As(V) decreased with increase in solution temperature which indicates the exothermic nature of the sorption. The validity of the method was verified through the analysis of ultra-pure, bottled drinking, and tap water samples spiked with arsenate; the respective sorption percentages of 93.2 (±0.7), 89.0 (±1.0), and 80.9 (±1.3) were obtained by batch type equilibration. The sorption capacity of the novel sorbent was also observed in the column application. Arsenic sorption was also examined in the presence of common interfering ions resulting in competing effects of PO_4^{3-} and NO_3^- on As(V) adsorption.

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