Chitosan-Immobilized Pumice for the Removal of As(V) from Waters

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Abstract A novel sorbent, chitosan-immobilized pumice, has been prepared for the sorption of As(V) from waters prior to its determination by hydride generation atomic absorption spectrometry. 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. Batch-type equilibration studies have shown that the novel 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 toward As(V), whereas chitosan gives approximately 90 % sorption only at pH 3.0. The validity of the method was verified through the analysis of ultrapure, 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. 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.

Keywords Arsenic · Chitosan · Pumice · Removal · Biosorbent

1 Introduction

Trace metal contamination, especially in water, is a great concern for every living organism, which brings about the need for efficient and environmentally friendly treatment techniques. Among the metal treatment techniques, development of new biosorbents is a significant research area. There are many kinds of recently developed biosorbents for this purpose such as *Spirulina platensis* (Şeker et al. 2008), *Escherichia coli* biofilm supported on kaolin (Quintelas et al. 2009), *Ulva lactuca* (Schijf and Ebling 2010), and carbonate hydroxylapatite (CHAP) prepared from eggshell waste (Zhang et al. 2011).

Among all the biosorbents, chitosan has importance due to its many features like being one of the most abundant natural biopolymers, hydrophilic, nontoxic, biodegradable structure, regeneration, and recycling potential and having the ability to form complexes with metals (Elwakeel 2010; Hasan et al. 2008). As a consequence

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of 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 (Chatterjee and 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 wastewater using thiocarbamoyl chitosan; Miretzky and 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.

Pumice stone is a type of light, highly porous (pore volumes up to 85 %) (Kitis and Kaplan 2007), and low-cost volcanic stone with high silica content (generally 60–75 % SiO_2) (Baytak et al. 2008) found abundantly in Turkey. On account of its highly porous structure, it provides a large number of possible attachment sites for pollutants (Alemayehu and Lennartz 2009; Ersoy et al. 2010). Thus, it takes place 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 a filtration medium and biofilm support in environmental engineering (Kitis et al. 2005) in addition to its use as a sorbent. For example, 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 pH 6.0 (Alemayehu and Lennartz 2009; Yavuz et al. 2008). Asgari et al. (2012) studied fluoride adsorption onto functionalized pumice stone and obtained 96 % removal at pH 6.

As a result of natural and anthropogenic activities, inorganic arsenic is released into natural waters resulting in human exposure via ingestion of contaminated drinking water and foods (Boddu et al. 2008; Choong et al. 2007; Kavcar et al. 2009). Long-term exposures to even very low concentrations have highly toxic effects on human health resulting in skin, lung, liver, kidney, and bladder cancer risks (Boddu et al. 2008; Luu et al. 2009). The World Health Organization (WHO) recommends the standard of arsenic in drinking water as 10 $\mu g\ L^{-1}$, and the US, the EU, and Turkey promulgate it (Kavcar et al. 2009).

Although arsenic cannot be destroyed easily, it can be converted into different forms or can be transformed into insoluble compounds in combination with other elements. Arsenic removal is expensive, especially when it coexists with other impurities, such as lead, iron, and

selenium (Choong et al. 2007; Hansen et al. 2008). In the arsenic treatment, membrane filtration systems such as reverse osmosis and nanofiltration are very effective; however, those systems have high treatment costs which pose an obstacle for a wide use (Choong et al. 2007). At this point, the need for efficient and cost-effective treatment techniques arises, and adsorption of arsenic onto relatively inexpensive and natural biosorbents is a favorable alternative (Boyacı et al. 2010; Choong et al. 2007). 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. 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. On the other hand, the presence of interfering ions such as Mg^{2+}, Ca^{2+}, Fe^{3+}, NO_3^-, and PO_4^{3-} may have competing effects on adsorption of arsenic from natural waters (Kundu et al. 2004; Rau et al. 2003).

The goal of the present study was to develop a biosorbent for arsenic removal from drinking water at neutral pH levels. Chitosan immobilized on pumice was studied as a new sorbent for this purpose. The characterization of the biomaterial, effects of change in the amount of sorbent, and sorption with respect to time and temperature were investigated. The novel sorbent was also employed in column experiments to investigate the potential of the proposed methodology for further applications. Lastly, interfering effects of some common ions (Mg^{2+}, Ca^{2+}, Fe^{3+}, NO_3^-, and PO_4^{3-}) to the adsorption were studied.

2 Materials and Methods

2.1 Reagents

All chemicals were of analytical reagent grade. Ultrapure water (18.2 MΩ cm) 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.

Stock standard solutions of As(V) and As(III) (2,000.0 mg L^{-1}) were prepared by dissolving As$_2$O$_5$ (Merck, product code 1.09939, CAS no. [1303-28-2]) and As$_2$O$_3$ (Fischer, CAS no. [1327-53-3]), respectively, in ultrapure water. Oxalic acid (Carlo Erba, product code 408737, CAS no. [6153-56-6]) solution was prepared in a concentration of 10.0 % (m/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 code1.06498, CAS no. [1310-73-2]) solution. L-Cysteine (Merck, product code 1.02838, CAS no. [52-90-4]) was used as a 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$_2$O (Merck, product code 1058550050, CAS no. [13446-18-9]), Ca(NO$_3$)$_2$·4H$_2$O (Merck, product code 1021230100, CAS no. [13477-34-4]), Fe(NO$_3$)$_3$·9H$_2$O (Sigma, product code 24855367, CAS no. [7782-61-8] and CAS no. [7647-14-5]), HNO$_3$ (Sigma, product code 24845344, CAS no. [7697-37-2]), and H$_3$PO$_4$ (Sigma, product code 24868686, CAS no. [7664-38-2]) in ultrapure water.

2.2 Preparation of the Chitosan-Immobilized Pumice as a Sorbent

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). On the other hand, pumice has a skeleton structure allowing ions and molecules to 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).

In the light of the experience gained in the previous studies and the literature articles, a novel hybrid sorbent was prepared. First, chitosan flakes were synthesized as it was described elsewhere (Boyacı et al. 2010). Then, 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 taken from Isparta (Turkey) and had a particle size range of 250–1,000 μm. The 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. In addition, the acid treatment step facilitated the 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.

2.3 Characterization Studies

Various methods were applied for the characterization of pumice, synthesized chitosan flakes, 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 PerkinElmer Pyris Diamond TG/DTA (Boston, MA, USA). Particle size distribution of oxalic-acid-treated pumice and chitosan-immobilized pumice was determined by Mastersizer 2000 and Hydro 2000S (Malvern Worcs, UK). Point of zero charge (PZC) for pumice and the novel sorbent were

determined with a potentiometric mass titration method (Bourikas et al. 2003).

2.4 Sorption Studies

Sorption studies were performed for all the sorbents through batch process. Solution pH was adjusted with inoLab 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 1. 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 mL min^{-1} carrier gas (N$_2$) flow rate, 6.1 mL min^{-1} HCl flow rate, 2.0 % (v/v) HCl concentration, 3.0 mL min^{-1} NaBH$_4$ flow rate, 1.0 % (m/v) NaBH$_4$ concentration (stabilized with 0.1 % (m/v) NaOH), and 7–8 mL min^{-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) were 0.79 and 2.61 µg L^{-1}, respectively.

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 of them containing 100.0 µg L^{-1} As(V) and varying amount of each interfering ion (with 100.0 µg L^{-1} As(V) solutions in separate medium containing 0.1, 1, and 10 mg L^{-1}), were prepared separately and used in sorption study.

2.5 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 µg L^{-1} arsenate. Solution volume, sorbent amount, solution pH, and reaction temperature were 20.0 mL, 200.0 mg, 7.0, and 25 °C, respectively.

2.6 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 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 µg L^{-1} As(V) solution was passed through the column in an upward flow at a flow rate of 0.8 mL min^{-1} using a peristaltic pump. In addition to spiked ultrapure water, spiked tap water samples from IZTECH campus were also used. The effluent was collected in 1.0-mL volume intervals.

3 Results and Discussion

3.1 Characterization Studies

The amount of acetyl groups removed from a starting material (chitin) in terms of the degree of deacetylation was determined as 87.3 % by potentiometric titrimetry (Tolaimate et al. 2000). This result is in agreement with the result of the elemental analysis (84.7 %). The elemental compositions of chitosan, pumice, and chitosan-immobilized pumice are summarized in Table 2. The elemental analysis results are not only indicative of deacetylation process but also valuable for determining

Table 1 Summary of the parameters and ranges used throughout the study

| 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 (°C)	25, 50, and 75

Table 2 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

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 accordance with the amount determined gravimetrically after calcination of the chitosan-immobilized pumice (11.3 %).

SEM images of pumice, chitosan, and chitosan-immobilized pumice can be seen in Fig. 1. As shown, pumice is highly porous as compared with 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.

TGA of the sorbents was carried out by flowing N_2 gas from room temperature to 800 °C. It can be seen from Fig. 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 (Fig. 2); yet, at higher temperatures, small changes in the weight were due to the decomposition of chitosan in the composite structure leaving pumice itself.

Original particle size of pumice was in the range of 250–1,000 μm. This wide range of particle size precluded its direct use due to difficulties in getting homogeneous amount of chitosan in final sorbent. Therefore, an average particle size of 143 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 μm.
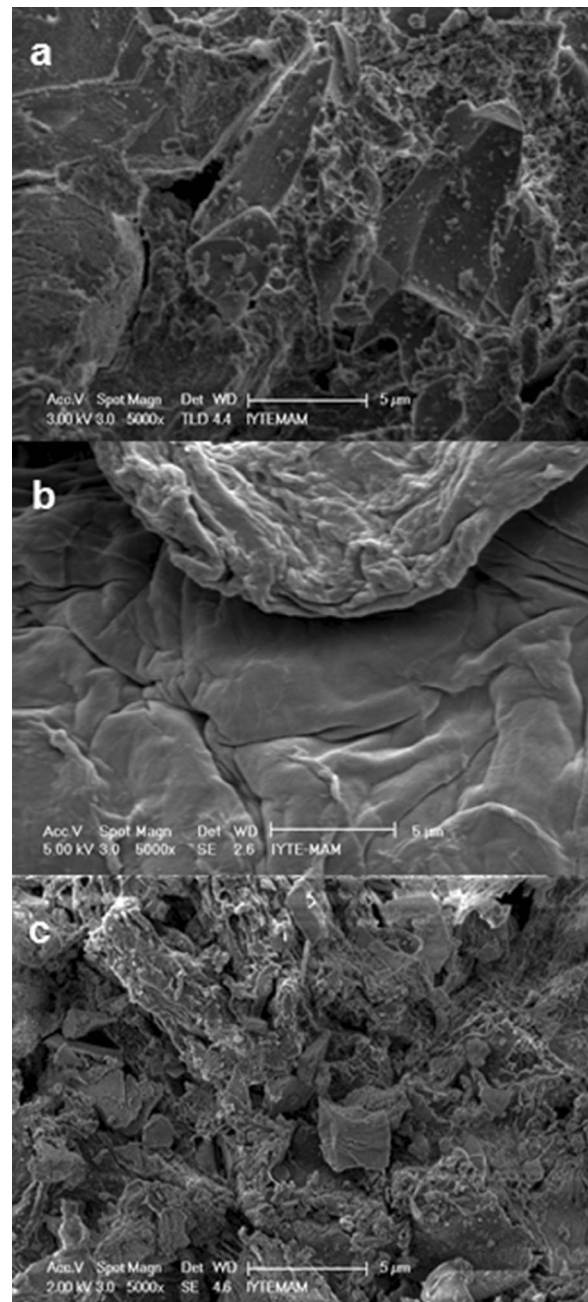
Fig. 1 SEM images of **a** pumice, **b** chitosan, and **c** chitosan-immobilized pumice

PZCs of chitosan-immobilized pumice and pumice were determined by application of potentiometric mass titration as described by Bourikas et al. (2003). After application of the aforementioned method, the PZCs of pumice and chitosan-immobilized pumice were determined to be about 6.8 and 7.4, respectively.

Fig. 2 TGA curves of **a** pumice, **b** chitosan-immobilized pumice, and **c** chitosan
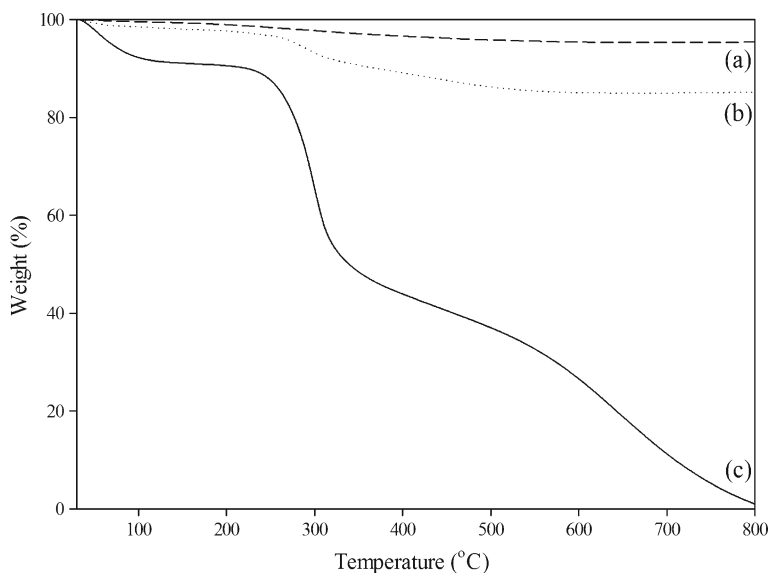
3.2 Sorption Studies

#### 3.2.1 Effect of pH on the Sorption of As(V) and As(III)

A review of the literature has shown that chitosan-immobilized pumice was not subjected to investigation as a sorbent for water treatment previously. In this study, initial experiments were carried out to investigate sorption characteristics of newly prepared 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 Fig. 3. As shown in Fig. 3a, 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 nanoparticles, in addition to hybrid materials and commercial resins, have been employed as sorbents for removal of inorganic arsenic species. In contrast to pumice, chitosan was very effective in the sorption of As(V) only at a specific pH of 3.0, as already been demonstrated in our 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 PZC of chitosan is about 6.3, and under this pH, amine groups of chitosan are protonated. Lowering 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). The use of more acidic conditions is not recommended because of the possibility of dissolution of chitosan flakes.

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 toward As(V) are completely distinctive from chitosan or pumice which suggest a predominant chelation of arsenate between chitosan functional groups and pumice surface active sites. In addition, 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 was capable of removal (<20 %) from solutions under the working conditions (Fig. 3b). 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)

Fig. 3 Effect of pH on the sorption of 100.0 $\mu g \ L^{-1}$ of **a** As(V) and **b** As(III). The *circles*, *triangles*, and *squares* denote chitosan-immobilized pumice, pumice, and chitosan, respectively (reaction time 4 h, sorbent amount 200.0 mg, sample volume 20.0 mL, sorption temperature 25 °C, $n=3$)
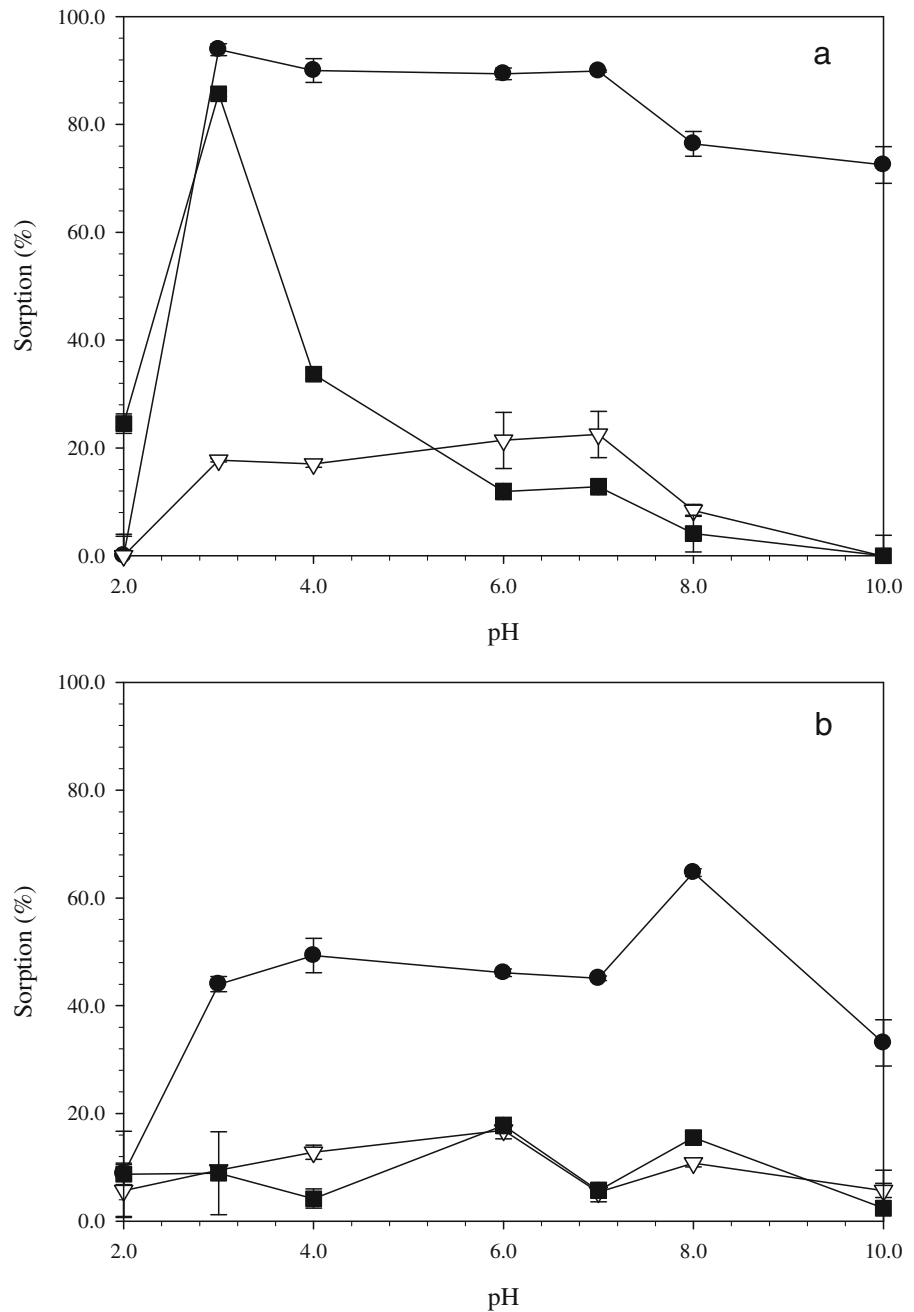
is in the form of $H_2AsO_3^-$, and the sorption decreased below 40 % at pH 10.0. At any particular point in the studied pH range, the arsenite species cannot display electrostatic interaction with the sorbent. However, some hydroxyl groups present in the biosorbent may be involved in the coordination 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).

As can be followed from the previous discussion, the high efficiency (greater than 90 % sorption) of the novel sorbent toward 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.

3.2.2 Effect of the Sorbent Amount on the Sorption of As(V)

The effect of the sorbent amount on As(V) sorption is demonstrated in Fig. 4. It was found that as the amount of sorbent increased, the sorption also increased. The maximum sorption was reached at the investigated highest amount of 250.0 mg; however, increasing the amount from 75.0 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 probable application of the

novel sorbent for municipal water treatment since pumice has the advantage of being a low-cost and naturally abundant material.

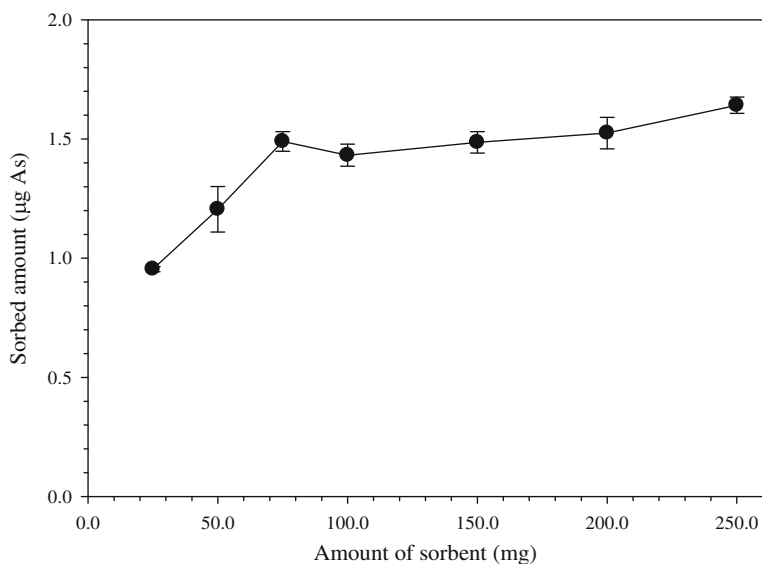### 3.2.3 Effect of the Reaction Time on the Sorption of As(V)

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 Fig. 5, 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 sorption time.

3.2.4 Effect of the Temperature on the Sorption of As(V) and Sorption Isotherm

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).
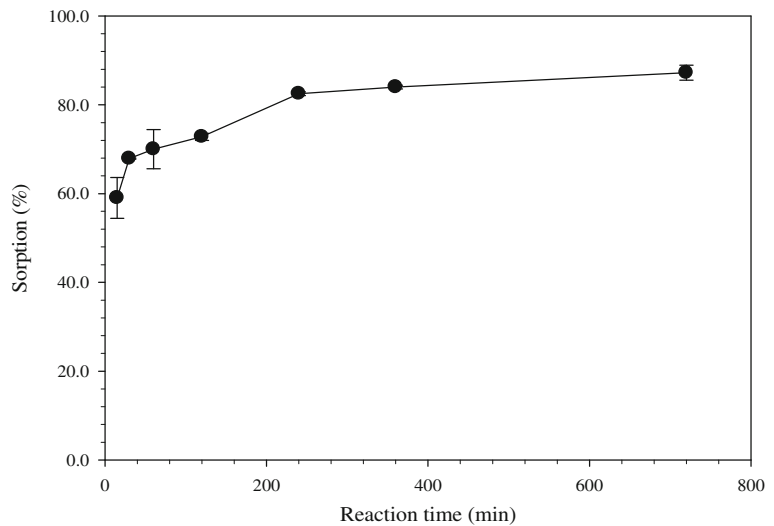
Thermodynamic parameters of sorption ($\Delta G°$, $\Delta S°$, and $\Delta H°$) were calculated using the well-known equations (Atkins and de Paula 2002) for standard Gibbs free energy change (Eq. (1)), standard enthalpy change (Eq. (2)), and standard entropy change (Eq. (3)) for the reaction. Where, R_d (mL g^{-1}) is the ratio of arsenate ions distributed at equilibrium between sorbent (mg g^{-1}) and aqueous

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

Fig. 5 Effect of reaction time on sorption of 100.0 µg L^{-1} As(V) (sorbent amount 200.0 mg, sample pH 7.0, sample volume 20.0 mL, sorption temperature 25 °C, $n=3$)

solution of arsenate (mg L^{-1}) which is in contact with the sorbent (Eq. (4)).

$$\Delta G^{\circ} = -RT \ln R_d \qquad (1)$$

$$\Delta H^{\circ} = R \ln \frac{R_{d(T_2)}}{R_{d(T_1)}} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^{-1} \qquad (2)$$

$$\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T} \qquad (3)$$

$$R_d = \frac{C_{sorbent}}{C_{sample solution}} \qquad (4)$$

According to the thermodynamic parameters given in Table 3, 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 ΔH° value. On the other hand, any significant effects for As(III) sorption with respect to temperature change were not observed.

For further clarification of arsenic sorption by proposed sorbent, Dubinin-Radushkevich (D-R) isotherm model was used. The details of the isotherm model were explained in our previous study (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 mg As per gram sorbent (initial concentration of As 100.0 µg L^{-1}, solution volume 20.0 mL, and sorbent amount 250.0 mg) and according to the maximum sorption capacity (0.3697 mg As per gram 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 kJ mol^{-1}) is indicative of physisorption.

3.2.5 Effect of Interfering Ions on the Sorption of As(V)

Effect of the possible interfering ions to sorption of As(V) was studied and shown in Table 4. The sorption percentages for As(V) in the presence of interfering ions

Table 3 Thermodynamic parameters of chitosan-immobilized pumice

	ΔG (kJ mol^{-1})		ΔH (kJ mol^{-1})	ΔS (J mol^{-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 µg L^{-1}, reaction time 4 h, sorbent amount 200.0 mg, sample pH 7.0, sample volume 20.0 mL, $n=3$

Table 4 Effects of interfering ions on As(V) adsorption

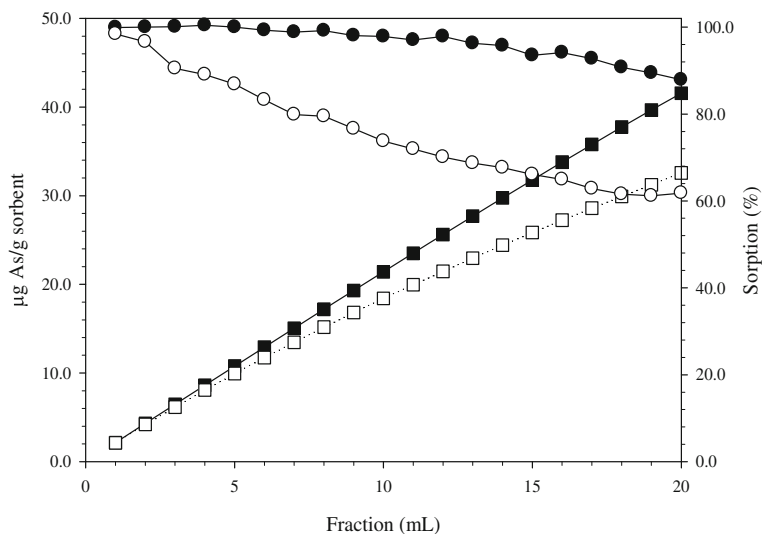|	0.1 mg L^{-1} As(V)		
Interfering ion	0.1 mg L^{-1}	1 mg L^{-1}	10 mg L^{-1}
Mg^{2+}	N	N	N
Ca^{2+}	N	N	N
Fe^{3+}	N	N	N
NO_3^-	I	I	I
PO_4^{3-}	I	I	I

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

N no interference, *I* interference

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 a criterion for 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 noninterfering effects for this ion (Sect. 3.3). 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).

3.3 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 ultrapure, 89.0 (±1.0) for the bottled drinking, and 80.9 (±1.3) for the tap water samples. The small 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 (results are not given) where no significant effect was observed in the sorption characteristics of chitosan-immobilized pumice even after the addition of 0.01 M NaCl. This is especially important for the application of the novel sorbent to the natural waters that have variable ionic concentrations.

3.4 Column Application

In addition to the batch equilibration studies, the potential use of the chitosan-immobilized pumice was also tried in column equilibration. The sorption was studied with both ultrapure and tap water after spiking with As(V). Each milliliter of the effluent collected off the column was analyzed for its As(V) concentration (Fig. 6). As can be seen from the figure, there was a gradual decrease in the sorption of As(V) from the ultrapure 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 fraction. 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

Fig. 6 Microcolumn sorption of 100.0 μg L^{-1} As(V). Sorption (%) scale: tap water (*black circles*) and ultrapure water (*white circles*); μg As g^{-1} sorbent scale: tap water (*black squares*) and ultrapure water (*white squares*) (flow rate 0.8 mL min^{-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)

with 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 (4 h) 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 indicates a potential for simpler water treatment systems.

In addition, a preliminary desorption study was carried out with 1 % (*m/v*) L-cysteine solution in order to evaluate regeneratibility of the novel sorbent. L-Cysteine is a well-known reducing agent that can reduce the adsorbed As(V) to As(III). Thus, in the presence of L-cysteine, retained As(V) is converted to weakly adsorbed As(III). As a consequence, 80 % desorption was obtained which is promising for reusability of the sorbent. However, no further evaluation was performed since the sorbent is designed for single use.

4 Conclusions

It has been shown that chitosan-immobilized pumice can be applied in quantitative (>90 %) sorption of As(V) from the waters at neutral pHs. In addition, 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 the 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 °C, and reaction time of 4 h. Sorption of As(V) decreased with the increase in solution temperature which indicates the exothermic nature of the sorption. Use of the novel sorbent in the column mode has demonstrated its potential for use in water treatment.

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