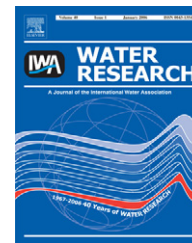


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Biosorption of arsenic (V) with acid-washed crab shells

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ABSTRACT

Highly toxic arsenate occurs naturally in some well water as well as in industrial wastewaters. Removal of arsenate (As(V)) by biosorption with acid-washed crab shells (AWCS) is very sensitive to solution pH. It greatly increased when the solution pH was lowered from 3.44 ± 0.07 to 2.51 ± 0.02 , but it was reduced at pH below 1.99 ± 0.01 . Change of solution pH not only affected the charged functional groups on AWCS but also the speciation of arsenate in solution. Increasing ionic strength of solution negatively affected the arsenic uptake. At ionic strength 0.1 M, arsenic uptake was seriously depressed. Arsenic biosorption with AWCS was mainly through arsenate binding on the amide groups in the AWCS. AWCS has a dense structure and low extent of swelling in aqueous solutions. This might prevent effective arsenate access to the functional groups in AWCS.

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1. Introduction

Arsenic has been known as a notorious toxic substance for centuries (Abernathy et al., 1999). Widespread contamination of drinking water by arsenic has relatively recently come to the forefront of world attention (Abdullah et al., 1995; Abedin et al., 2002; Murugesan et al., 2006; Seki et al., 2005). Estimates put the number of people poisoned by arsenic in regions of Bangladesh and eastern India alone close to 70 million, perhaps the largest poisoning in the world's history (WHO, 2006). Apart from arsenic originating from natural sources, it is also found in certain types of industrial effluents (Hansen et al., 2006). Current treatment methods such as sulfide or hydroxide precipitation create sludge that is difficult to handle. Furthermore, these methods consume considerable amounts of reagents in order to precipitate, coagulate and flocculate the contaminants (Gulledge and O'Connor, 1973; Lee and Rosehart, 1972). Advances in the knowledge of biosorption during the last decades revealed high adsorption capacities, low costs and regenerability of natural biosorption materials (Gavrilescu, 2004; Volesky, 2003). Some efforts have

been made to remove arsenate by biosorption (Hansen et al., 2006; Seki et al., 2005). However, challenges in developing biosorbents with high uptake and low cost as well as in understanding the biosorption mechanism still remain. Earlier results demonstrated that acid-washed crab shells (AWCS) have a promising potential for binding anionic metal species such as gold cyanide, chromate and vanadate (Niu and Volesky, 2003a). In this work, arsenate biosorption with AWCS was further examined. The effect of solution conditions pH and ionic strength on biosorption uptake was evaluated. The mechanism of arsenate biosorption was studied by Fourier transform infrared analysis (FTIR).

2. Materials and methods

2.1. Biosorbent preparation (Niu and Volesky, 2003a)

Raw waste crab shells of *Ucides cordatus* were obtained sundried from a food processing plant in Paraiba, Piaui, and Brazil. Crushing of shells in a grinder and sieving gave

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Nomenclature		q_i^M	arsenic initially loaded on the biosorbent (mmol/g)
BNH	the neutral amide group	v	the working volume of the adsorption sample (L)
BNH_2^+	the positively charged amide group	w	the dry net biosorbent weight (g)
K_a	the conjugated acid dissociation constant of the amide group (mol/L)	<i>Subscript:</i>	
K_1, K_2, K_3	proton dissociation constants in Eqs. (6)–(8), respectively	T	the total amount of amide groups in AWCS or total arsenic in the solution.
$[M]_0$	initial arsenic concentration (mmol/L)	[]	the concentration of species (mol/L or mmol/L in solution or mmol/g on AWCS)
$[M]$	equilibrium arsenic concentration (mM)		
q^M	equilibrium arsenic uptake (mmol/g)		

particles within useful size ranges between 1 and 3.35 mm for biosorption and 0.5–0.85 mm for the FTIR analytical studies. They were washed with 1N HCl (55 g dry shells/L HCl) for 6 h to remove minerals and then rinsed with distilled water until the wash-solution pH stabilized at pH ~4.0. The residual material was dried at 55 °C and represented approximately 23% of the original-sized crushed shells by weight. The AWCS contained 53 ± 4(%) chitin, 43 ± 3(%) protein, 0.2 ± 0.1(%) ash and about 4 ± 0.3(%) of moisture and other matter. The extracted chitin had 78 ± 10(%) *N*-acetylation degree (i.e. the percentage of acetylated amino groups in chitin). The nitrogen of chitin amide was 2.0 ± 0.4 mmol/g AWUS.

2.2. Solution preparation

Arsenate solution was prepared by dissolving solid $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water. Ionic strength of solutions was adjusted by adding NaCl. 0.1 M or 0.5 M HCl and NaOH were used for pH adjustment. All chemicals used in this work were of analytical grade (Sigma-Aldrich Corp.).

2.3. Equilibrium sorption experiments

Approximately 40 ± 2 mg of dried AWCS material was mixed with 20 ± 0.2 mL of solution containing arsenic in 30 mL Nalgene bottles. The pH of the solutions before and during the sorption experiments was controlled with HCl or NaOH. The suspension was mixed on an orbital shaker at 200 rpm for 24 h (experimental convenience) that was confirmed to be more than adequate time for establishing sorption equilibrium at room temperature. Sorption samples were run in triplicates, with a blank undergoing the same treatment, and the data presented are the average values. Uptake of arsenic was determined from the difference in arsenic concentrations in the solutions before and after the sorption contact using the following mass balance:

$$q^M = q_i^M + ([M]_0 - [M]) (v/w) \quad (1)$$

where q^M is the equilibrium arsenic uptake (mmol/g), and q_i^M the arsenic initially loaded on the biosorbent (mmol/g). As neither of the selected acid-washed biosorbents in this study initially contained arsenic, $q_i^M = 0$. $[M]_0$ is the initial arsenic concentration (mmol/L), $[M]$ the equilibrium arsenic concentration (mmol/L), w the dry net biosorbent weight (g), and v the working volume of the adsorption sample (L).

2.4. Swelling experiments

Swelling experiments were conducted in order to analyze the extent of the AWCS swelling. In these experiments, 0.25 g of crab shell biomass particles and 8 mL of distilled water at pH 2–3 were equilibrated for 24 h. AWCS biomass was weighted after separation from the solution and oven dried at 55 °C. The water uptake (mL/g dry AWCS) was calculated by the weight difference.

2.5. Analyses

The total arsenic concentration in solution was determined with an sequential inductively coupled plasma atomic emission spectrometer (ICP-AES) (Thermo Jarrell Ash, Trace Scan).

Arsenate (As(V)) was determined using ion chromatography (IC; Dionex, DX100) with a Dionex AS12A column. The retention time for arsenate was 10 min and 20 s.

FTIR was used to investigate the main functional groups involved in arsenic biosorption. The arsenic-loaded biosorbent samples were prepared by contacting of 40 mg batches of biosorbent particles (0.5–0.85 mm) with 20 mL of solution containing 7 mmol/L arsenic at the optimum pH (2.51 ± 0.02) for maximum arsenic uptake (0.11 ± 0.02 mmol/g). The arsenic-loaded biosorbent particles were then collected by filtration, washed with distilled water and finally freeze dried. The blank biomaterials were treated in the same way except for the absence of arsenic. Disks of 100 mg KBr containing 1% of finely ground powder of each sample were prepared less than 24 h before analyzing. Infrared spectra of samples were recorded on a Michelson 100 FTIR spectrophotometer.

3. Results and discussion

3.1. pH effect

Fig. 1 shows the adsorption isotherms obtained for arsenic on AWCS at equilibrium pH values of 1.99 ± 0.01, 2.51 ± 0.02, 3.01 ± 0.03 and 3.44 ± 0.07. This pH range was chosen based on the optimum application conditions for anion biosorption with AWCS whereby the major chemical functional groups on chitin of AWCS are amide groups (Niu and Volesky, 2003b). With the logarithm of the proton dissociation constant of the positively charged protonated amide being 3.5 (Roberts,

1992a), the pH below the value of 3.5 assures the protonation of the amide groups for effective binding of negatively charged anions. The data points are experimental results and the error bars represent 95% confidence interval. As pH decreased from 3.44 ± 0.07 to 2.51 ± 0.02 , arsenic uptake increased. However, further lowering of pH to 1.99 resulted in a decreased arsenic uptake. Among the tested pH values, pH 2.51 ± 0.02 is the optimum for arsenic uptake at the equilibrium arsenic concentration of 1.5–7 mmol/L.

In the AWCS, chitin takes up to 53% of the dry weight. Chitin is a natural polysaccharide consisting of (1,4) 2-acetamide-2-deoxy-D-glucose units, some of which are deacetylated (chitosan) (Roberts, 1992b). The structure of chitin is shown in Fig. 2, and that of chitosan is in Fig. 3. While the names “chitin” and “chitosan” are widely used in the literature, neither term represents a unique chemical structure. The terms chitin and chitosan describe a continuum polymorphic form of copolymers of N-acetyl-D-glucosamine and D-glucosamine residues. The N-acetylation degree, i.e. the percentage of acetylated amine called amide over all the amino groups of the AWCS in this work was 78% (Niu and Volesky, 2003a), which determined the amide group to be the predominant form of amino groups. Similar to the conventional amine family, the N atom of the chitin amide group is able to donate and share the lone electron pair with the empty orbit of other cations, featuring thus with weak-base

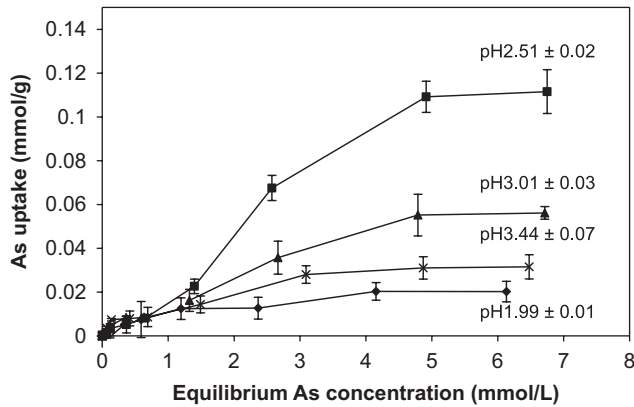


Fig. 1 – Effect of pH on As uptake. Room temperature, 24 h, 20 ± 0.2 mL solution, 40 ± 2 mg AWCS, no NaCl addition.

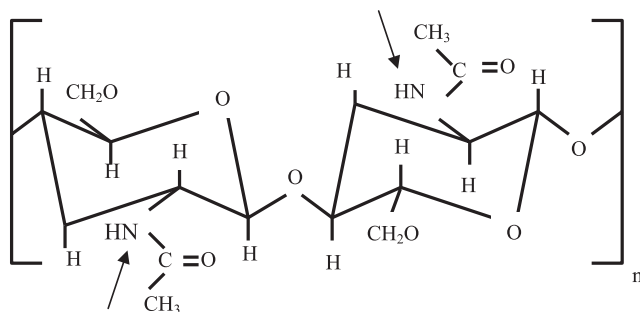


Fig. 2 – The structure of Chitin.

characteristics. The conjugated acid dissociation constant pK_a of the chitin amide group is lower than 3.5 (Roberts, 1992a). Therefore, only when the solution pH is lower than the corresponding pK_a , the amide sites could be effectively protonated with a positive charge, and an anion could thus be bound, which is illustrated in Fig. 4.

Under ideal conditions, the percentage of positively charged amide groups can be determined by the following equations:

$$BNH_2^+ = BNH + H^+, \tag{2}$$

$$K_a = \frac{[H^+][BNH]}{[BNH_2^+]}, \tag{3}$$

and amide group mass balance is

$$[BNH]_T = [BNH_2^+] + [BNH]. \tag{4}$$

From Eqs. (3) and (4), the percentage of positively charged amide can be obtained:

$$\frac{[BNH_2^+]}{[BNH]_T} = \frac{1}{1 + K_a/[H^+]}, \tag{5}$$

where BNH represents the neutral amide group and BNH_2^+ the positively charged amide group, the subscript T represents the total amide group in AWCS. K_a is the conjugated acid dissociation constant of the amide group (mol/L). The pK_a value was reported to be about 3.5 by Roberts (1992a). [] represents the concentration (mol/L).

The percentage of positively charged amide calculated by Eq. (5) is plotted against pH in Fig. 5 and it can be seen that the percentage of positively charged amide increased from 54% to 91% when pH decreased from 3.44 ± 0.07 to 2.51 ± 0.02 . This favors the binding of anionic arsenate species.

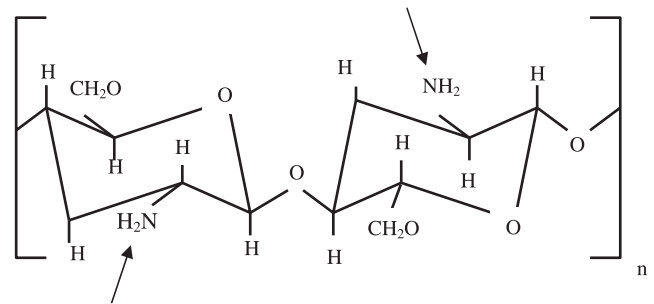


Fig. 3 – The structure of Chitosan.

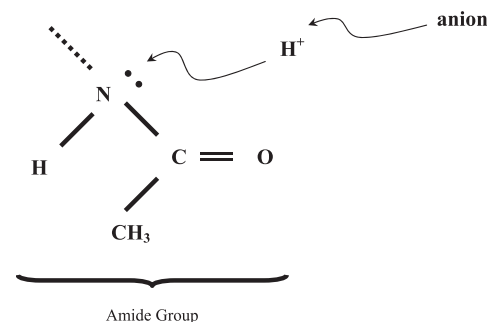
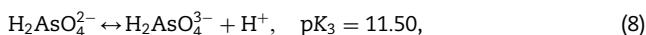
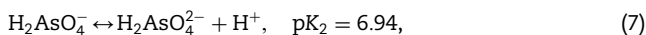
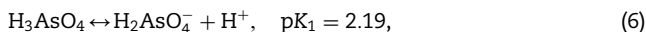


Fig. 4 – Schematics of the anion-sorption mechanism.

However, arsenate biosorption is not only determined by the acid–base properties of functional groups on the biosorbent, but also by the chemical speciation of arsenate in the solution. Arsenate in aqueous solution tends to hydrolyze depending on the solution pH. The following equations control arsenate speciation (Baes and Mesmer, 1976):



where K_1 , K_2 , and K_3 are proton dissociation constants in Eqs. (6)–(8), respectively.

In the experimental pH range of 1.99–3.44, the predominant forms of arsenate are primarily controlled by Eq. (2). Similarly, the arsenate species can be determined by the mass action law

$$K_1 = \frac{[\text{H}^+][\text{H}_2\text{AsO}_4^-]}{[\text{H}_3\text{AsO}_4]}. \quad (9)$$

The total arsenic concentration in the solution $[\text{As}]_T$ equals:

$$[\text{As}]_T = [\text{H}_2\text{AsO}_4^-] + [\text{H}_3\text{AsO}_4]. \quad (10)$$

The percentage of the negatively charged species H_2AsO_4^- which becomes bound onto positively charged amide group BNH_2^+ in AWCS can be determined by Eqs. (6) and (10):

$$\frac{[\text{H}_2\text{AsO}_4^-]}{[\text{As}]_T} = \left(\frac{1}{[\text{H}^+]/K_1 + 1} \right) \quad (11)$$

where K_1 is $10^{-2.19}$ (Baes and Mesmer, 1976).

The percentage of H_2AsO_4^- calculated by Eq. (11) was also plotted versus pH in Fig. 5. When solution pH decreases from 3.44 to 2.51, although the percentage of negatively charged arsenate species H_2AsO_4^- decreases from 95% to 68%, the percentage of positive-charged amide group increases from 53% to 91%. This greatly facilitates the binding of arsenic species onto the positively charged amide groups. As a result, the overall arsenic uptake increased. However, as pH was further decreased from 2.51 to 1.99, the percentage of bound H_2AsO_4^- decreased from the previous 68%–39% and the

neutral species H_3AsO_4 started to predominate. It is unlikely for the neutral species to be bound onto the positively charged amide groups of AWCS and, as a result, the arsenic uptake was lower.

This result is similar to that obtained for biosorption of anionic vanadate, chromate and gold cyanide. This confirming that both the functional group availability and the speciation of the metal in solution can affect the overall metal uptake (Niu and Volesky, 2003b).

3.2. Ionic strength

The effect of ionic strength on the arsenic adsorption by crab shell biomass was studied by adding NaCl to the experimental solutions. The effect of ionic strength is illustrated in Fig. 6.

At pH 2.51 ± 0.02 , increasing the ionic strength strongly reduced the arsenic uptake. Fig. 6 shows that as the concentration of NaCl increased to 0.1M, the uptake of arsenic by AWCS was seriously suppressed. Similar results were observed for chromate and gold cyanide biosorption (Niu and Volesky, 2003a). Changing ionic strength (i.e. the background electrolyte concentration) influences adsorption in at least two ways: first by affecting the interfacial potential and therefore the activity of electrolyte ions and adsorption; second, by affecting the competition of the electrolyte ions and adsorbing anions for available sorption sites (Tien, 1994). In the current study, the added Cl^- could also compete with the H_2AsO_4^- anion for the positively charged binding sites. In the overall result, the arsenic uptake was reduced.

3.3. Comparison of arsenic uptakes

The arsenic uptake by AWCS determined in this work was 0.11 ± 0.02 mmol/g (8.25 ± 0.15 mg/g) at pH 2.51 ± 0.02 . For a comparison, the arsenic uptake by AWCS and other sorbents is summarized in Table 1.

Arsenic uptake determined in this work was higher than that of activated carbon (Bunnaul et al., 1999), hematite (Zhang et al., 2004), and methylated yeast biomass (Seki et al.,

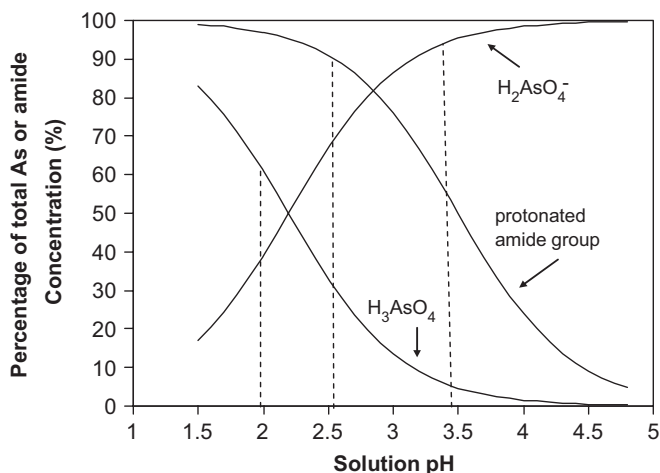


Fig. 5 – As solution speciation versus solution pH (Baes and Mesmer, 1976; Roberts, 1992a,b).

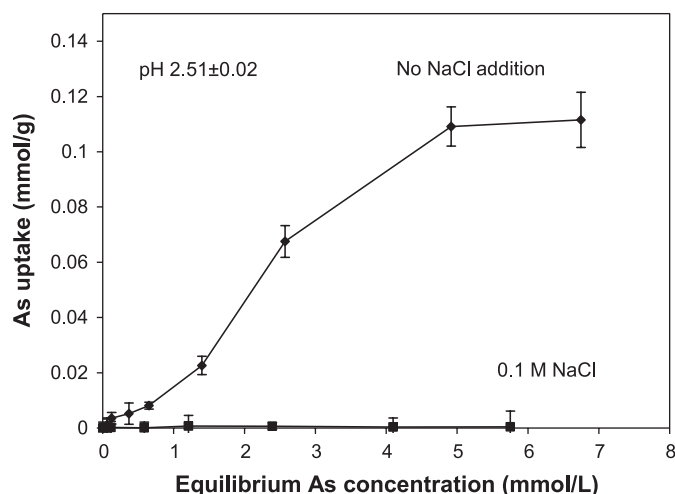


Fig. 6 – Effect of ionic strength on the As uptake. Room temperature, 24 h, 20 ± 0.2 mL solution, 40 ± 2 mg AWCS, pH 2.5 ± 0.02 .

2005), but lower than that reported for *Lessonia nigrescens* biomass (Hansen et al., 2006) and Iron(III) oxide/silica (Zeng, 2004). Considering that the amount of chitin amide nitrogen is 2.0 ± 0.4 mmol/g in AWCS, the arsenic uptake observed in this work was much smaller. This indicates that there is high percentage of amide groups that is not available for arsenic binding. This is because amino-containing chitin and protein are complexed with each other at their interface in crab shells making the shell structure very dense (Roberts, 1992b). This was also confirmed by the experimental results concerning AWCS swelling. In the pH range of 2–3, the water uptake of AWCS was less than 0.1 mL/g dry AWCS which was much lower than that observed for *Sargassum* biomass (1.4 mL/g) (Schiewer, 1996). Apart from that, there was no obvious swelling of AWCS and, as a result, some amino groups in the material may not be available for arsenic binding. However, on the other hand, this also indicates that there is a possibility of further improvement of the AWCS uptake capacity by perhaps quite simple modification of its structure.

In addition, arsenic uptake obtained in this work is also lower than that of gold cyanide and chromium biosorption by the same AWCS biosorbent (Niu and Volesky, 2003a). This is most probably because only 68% of the total arsenate existed as anionic species $H_2AsO_4^-$ under the experimental conditions (pH 2.51 ± 0.02) in this work (Fig. 5). The other 32% existed as a neutral arsenate form that cannot be effectively bound by positively charged amide groups in AWCS.

3.4. Mechanism

In the preceding section, the possible mechanism of arsenic (V) biosorption by AWCS was postulated. In order to confirm the mechanism of arsenate uptake, it was necessary to experimentally understand arsenate species present in solution and on the AWCS.

The first step in this direction was to verify whether there was arsenic reduction–oxidation taking place during biosorption. The arsenic can be present in the form of As(V) and As(III). Theoretically, referring back to Fig. 5, the arsenate

Table 1 – Comparison of arsenic uptake

Sorbent	As uptake (mg/L)	Source
Hematite	0.4	Zhang et al. (2004)
Activated carbon	0.82–1.02	Bunnaul et al. (1999)
Methylated yeast AWCS	7.5 8.25 ± 0.15 (pH 2.51 ± 0.02)	Seki et al. (2005) This work
Iron(III) oxide/silica	11.3	Zeng (2004)
<i>L. nigrescens</i>	45.2 (pH 2.5)	Hansen (2006)

species present in solution at pH 2.51 ± 0.02 is As(V) either as $H_2AsO_4^-$ or H_3AsO_4 . However, it is necessarily to further verify this for the real biosorption system in the presence of AWCS. To that end, IC was used to determine the concentration of arsenate (As(V)) in solution equilibrating with AWCS, while the total concentration of arsenic (As(V) plus As(III)) was determined by ICP–AES. Then the difference between the concentrations of total As and As(V) must be the concentration of As(III). The experimental results showed that the total arsenic concentration in the solution was exactly equal to that of arsenate obtained by IC when the experimental errors were considered, confirming no arsenic reduction–oxidation occurring in the liquid phase of the biosorption system. This result agreed with similar ones observed for gold cyanide and chromate sorption by AWCS (Niu and Volesky, 2003b). However, it is different from the observations reported earlier on chromate biosorption by *Sargassum* biomass (Kratochvil et al., 1998) whereby chromate was reduced by *Sargassum* biosorbent. In order to further determine the form of arsenic bound on the AWCS and the functional group involved in arsenic binding, FTIR analysis was also conducted. Table 2 summarizes the main peak changes in the FTIR spectra of the arsenic-loaded and blank AWCS.

From the data in Table 2, it can be observed that two peaks were present in the spectrum of arsenic-loaded biomass that could not be seen in that of the blank AWCS. These peaks

Table 2 – Summary of FTIR spectral data (cm⁻¹)

Bond vibration	Arsenate(V)	Arsenate(V)	Amide(II)
Blank AWCS	—	—	1547.88
As-loaded AWCS	438.43	822.67	1550.39

As-loaded sample was prepared at pH 2.5 with 20 ml solution initially containing 7 mmol As/L and 0.04 g AWCS for 24 h.

appear at frequencies of 438 and 822 cm⁻¹. According to Gadsden 1975), these two peaks are characteristic of inorganic arsenate compounds. The appearance of these two peaks proves the presence of arsenate in the biomass.

Another important observation for the FTIR analysis was the slight peak shift from 1547 cm⁻¹ in the blank AWCS spectrum to 1550 cm⁻¹ occurring in the arsenic-loaded AWCS spectrum. This slight shift indicates that the amide group (Roberts, 1992b) was being affected by the arsenate molecule attached to the biomass. These results further confirmed that arsenate was bound on the AWCS and the functional groups mainly responsible for arsenate binding were amide groups. The conclusions agree well with the behavior of AWCS during biosorption of gold cyanide and chromate (Niu and Volesky, 2003b).

4. Conclusions

Arsenate biosorption by AWCS was strongly affected by the solution pH. Among the examined pH values, pH 2.51 ± 0.02 represented the optimum for arsenic uptake within the equilibrium concentration range of 1.5–7.0 mmol As/g. The optimum pH was determined by the charge state of both amide groups in AWCS and of the arsenate species. Elevated ionic strength of the solution (0.1 M NaCl) seriously reduced arsenic uptake. The arsenic uptake was mainly due to arsenate bound on the amide groups of AWCS. As the dense structure of AWCS and its low swelling extent prevent arsenic species from accessing all functional groups available in AWCS, further As uptake improvement may be possible by modifying the AWCS structure.

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