Ecological Engineering 106 (2017) 431–435

Contents lists available at ScienceDirect

Ecological Engineering

journal homepage: www.elsevier.com/locate/ecoleng

Determination of inorganic arsenic in natural waters after selective extraction using *Moringa oleífera* seeds

Vanessa N. Alves[a,*], Taís S. Neri[b], Simone S.O. Borges[b], Dayene C. Carvalho[b], Nívia M.M. Coelho[b]

[a] Department of Chemistry, University of Goiás, Av. Dr. Lamartine Pinto de Avelar, 1120 Setor Universitário, CEP 75704-020 Catalão, GO, Brazil
[b] Institute of Chemistry, University of Uberlândia, Av. João Naves de Ávila 2121, CEP 38400-902, Uberlândia, MG, Brazil

ARTICLE INFO

Article history:
Received 5 May 2016
Received in revised form 1 June 2017
Accepted 2 June 2017
Available online 15 June 2017

Keywords:
Inorganic arsenic
Selective extraction
Moringa oleifera
GF AAS

ABSTRACT

Moringa oleifera seeds were used as a biosorbent for the selective extraction of inorganic arsenic in water and detection by furnace graphite atomic absorption spectrometry. The behavior of the As(III) and As(V) adsorption onto the biosorbent was evaluated at pH 1.0–9.0 in batch studies. The results indicated that As(III) was adsorbed at pH 7.0 while As(V) was poorly retained. So much, in a sample contained As(III) and As(V), the As(III) is going to be retained while most pentavalent species remained free in solution, allowing their determination by GF AAS. The operational variables of the separation method were optimized, the adsorbent mass of 1.0 g was found to be sufficient to retain the As(III) present in the solutions with a stirring time of 1 h. The limit of detection for As(V) determination is 6.3 $\mu g\,L^{-1}$ and the precision was below 1.23%. Results for recovery tests using different water samples were higher than 92% As(V). The accuracy of the method was proven through the analysis of a certified water sample (APS 1071).

1. Introduction

Arsenic (As) is an element that is known to be toxic to humans, but the degree of toxicity is dependent on whether the chemical species are inorganic or organic (Hughes, 2002). In this regard, knowledge of the speciation of arsenic in natural water is important because the bioavailability and the physiological and toxicological effects of arsenic vary according to its chemical form (Munoz and Palmero, 2005).

High performance liquid chromatography with inductively coupled mass spectrometry (HPLC-ICP-MS) and atomic spectrometry with graphite furnace (GF AAS) are the most common techniques used for arsenic analysis but it has a limitation: it relies on an extraction step that can be incomplete or alter the arsenic compounds (Gonzalvez et al., 2009).

To enhance sample throughput and reduce costs, non-chromatographic approaches have been developed. These methods require less manipulation of the sample, thereby decreasing the risk of cross-species conversion and contamination. In this regard, solid phase adsorption appears to be a promising method (Podder and Majumder, 2016).

The use of solid phase extraction (SPE) techniques has been frequently proposed for speciation analysis. SPE offers the advantages of high sensitivity, due to the possibility of performing a simultaneous enrichment step, and versatility, since different substrates interact with distinct metal species (Podder and Majumder, 2016).

Many new materials are being exploited as novel sorbent media for the solid phase extraction of target analytes. Cheng et al. (2016) investigated 22 adsorbents for cadmium adsorption and the peanut husk biochar (PHB) was the best sorbent (99.9% of Cd adsorption). Saqib et al. (2013) investigated the use of different wastes such as blue Pine wood shavings, walnut shell and chick pea testa in arsenic removal from aqueous solutions. Walnut shell pieces also showed good biosorption (88%).

Considerable attention has been focused on the application of biomaterials as sorbent media for performing sample pretreatment. Modified egg-shell membrane (MESM) was used by Chen et al. (2013) in arsenic speciation studies. At pH 6, 100% sorption of As(V) onto MESM was achieved, while virtually no adsorption of As(III) was observed. Total inorganic arsenic extraction was achieved by converting As(III) to As(V) and following the same sorption process.

* Corresponding author.
E-mail address: vanessanalves@gmail.com (V.N. Alves).

http://dx.doi.org/10.1016/j.ecoleng.2017.06.007
0925-8574/

Table 1
Temperature program optimized for determination of As by GF AAS using iridium as a permanent modifier.

Step	Temperature (°C)	Time (s)	Argon Flow ($L\,min^{-1}$)
Drying 1	85	5.0	0.3
Drying 2	95	40.0	0.3
Drying 3	120	10.0	0.3
Pyrolysis	1148	8.0	0.3
Atomization	2155	2.6	0.0
Cleaning	2600	2.0	0.3

In this context, the *Moringa oleifera* seeds have shown good potential, offering a low cost material and high adsorption capacity, and they have been applied in selective procedures for the preconcentration and extraction of various metal ions (Alves et al., 2010; Alves and Coelho, 2013). However, to date, there appears to have been no reports in the literature proposing the use of *M. oleifera* seeds in order to differentiate between the two species of arsenic for analytical applications.

2. Experimental

2.1. Instrumentation

A Varian AA 240Z atomic absorption spectrophotometer equipped with deuterium lamp background correction and a GTA 120 graphite furnace atomizer system was used for the determination of arsenic. Graphite tubes with pyrolytic coating and a L'vov platform inserted were used as electro-atomizers. The total volume of sample injected into the graphite tube was 20 μL in all experiments. All measurements were performed using integrated absorbance (peak area). An arsenic hollow cathode lamp operating at 193.8 nm was used as the radiation source. The operating conditions were those recommended by the manufacturer. The temperature program used is shown in Table 1.

2.2. Standard solutions and reagents

All solutions were prepared with analytical grade reagents and high purity deionized water obtained from a Milli-Q® system (Millipore, Bedford, MA, USA). The glassware and recipients for storage of the solutions were washed with neutral detergent, immersed in 10% (v/v) nitric acid and rinsed with deionized water before use. A standard stock solution of 1000 mg L^{-1} As(III) was prepared by dissolving 1.3203 g of As_2O_3 (Vetec, Rio de Janeiro) in 25 mL of 20% (m/v) potassium hydroxide followed by neutralization with 20% (v/v) sulfuric acid and further dilution to 1000 mL with H_2SO_4 1% (v/v). A standard stock solution of 1000 mg L^{-1} As(V) was prepared by dissolving 4.1645 g of $Na_2HAsO_4{\cdot}7H_2O$ (Vetec) and further dilution to 1.00 L with deionized water.

2.3. Preparation Moringa oleifera seeds

The *M. oleifera* seeds were obtained from trees which were cultivated in the city of Ituiutaba (Minas Gerais, Brazil). The seeds were separated from the pods, crushed in a household blender (Black & Decker, São Paulo, Brazil) and strained through 500–75 μm sieves. After obtaining the material, the seeds were washed twice with deionized water and dried in air for 8 h.

2.4. Optimization for the selective extraction of arsenic

The pH is a critical variable that directly affects the arsenic adsorption. The effect of pH on the As(III) and As(V) separation using the proposed biosorbent was investigated by varying the pH from 1–9. The pH was adjusted by adding HCl or NaOH 0.1 mol L^{-1}. Aliquots of solutions (100 mL) containing one of the arsenic species were kept under stirring with 1.0 g of biosorbent for 60 min and after filtration the supernatants were diluted and the concentration of arsenic species was measured by GF AAS. The amount of arsenic retained in the biosorbent was calculated from the difference between the initial and final arsenic concentrations.

In order to obtain the optimum conditions for the As(III) adsorption, the following variables were studied: extraction time (5, 20, 30, 40 and 120 min) and sorbent mass (0.05, 0.1, 0.5, 1.0, and 2.0 g).

General procedure for As(V) determination and analytical features for As(V) determination.

An aqueous solution containing As(III) and As(V) species was prepared and the pH 7.0 was adjusted using HCl or NaOH 0.1 mol L^{-1}. An aliquot (100 mL) was mixed with 1.0 g of *M. oleifera* seeds and the As(III) was retained on the adsorbent while the As(V) remained free allowing its determination by GF AAS. The concentration of total inorganic As in the remainder of the sample which was not placed in contact with the seeds was determined directly by GF AAS. Applying the optimized adsorption conditions, the method was evaluated through the main analytical features. The detection limit was calculated as three times the standard deviation of 15 independent measurements of a blank sample divide by the slope of the calibration curve (Analytical Methods Committee, 1987).

The repeatability was assessed by performing seven consecutive extraction step at a concentration level of 20 mg L^{-1} As(V) and expressing the result in terms of relative standard deviation.

2.5. Application of the method and recovery tests

The proposed method was applied to water samples (mineral water, tap water and river water). In order to assess the analyte recovery, all samples were spiked at concentration levels of 0.2–10 mg L^{-1} of As(V) in solution in the presence of 5 mg L^{-1} of As(III) solution. Analytical curves were constructed in order to compare the slopes.

Moreover, the accuracy was also checked by using water certified sample (APS 1071) – Drinking Water. This certified material contains As, Ba, Cd, Cr, Pb, Hg and Se in the concentrations 100, 50, 50, 100, 100, 20, 50 and 100 μg mL^{-1}, respectively.

3. Results and discussion

3.1. Optimization of arsenic speciation experiment

The mechanisms associated with metal ion adsorption by biomass are still not clear, however, it is important to note that this process is not based on a single mechanism. Metal sequestration occurs through complex mechanisms, including ion-exchange and complexation and it is quite possible that at least some of these mechanisms act simultaneously to varying degrees depending on the biomass composition, the metal ion and the solution environment (Araújo et al., 2013).

The seeds can act as adsorbent cations and anions depending on the electrical charge of the surface, the initial pH of the solution is the determining factor in the separation process of inorganic arsenic species. The effect of the solution pH on the As(III) and As(V) adsorption using the biosorbent was investigated by varying the pH from 1 to 9. The influence of pH on the adsorption of the inorganic arsenic species is shown in Fig. 1.

In acidic media, As(III) is almost entirely present in the uncharged form as H_3AsO_3, inhibiting electrostatic interaction with the adsorbent. The adsorption behavior can be explained by Lewis acid-base interactions and complexation mechanisms[27]. In basic medium, As(III) is predominantly present in the $H_2AsO_3^-$ form