

EXAFS And XANES STUDIES OF IRON AND ARSENIC RETENTION BY *L. SATIVA*

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RESUMO

A biossorção consiste na retenção de íons metálicos em solução em material de origem biológica. O presente trabalho tem como objetivo entender os mecanismos de sorção de arsênio em biomassa constituída de folhas secas de alface (*L.sativa*). Para tentar compreender como o arsênio é retido na presença do ferro, foram coletados, no Laboratório Nacional de Luz Síncrotron, espectros de Absorção de Raios-X das amostras de folhas de alface carregadas apenas com ferro e carregadas com ferro e arsênio. Analisando-se os espectros na região de XANES confirmou-se que o estado de oxidação do ferro dentro da biomassa é sempre Fe(III), e concluímos que o estado de oxidação do arsênio dentro da biomassa é sempre As(V), independentemente de se ter As(III) ou As(V) nas soluções. Na região de EXAFS, observou-se que o primeiro vizinho do Fe(III) é o mesmo em todas as amostras, inclusive nas que continham ferro e arsênio. Podemos então dizer que o arsênio não é o primeiro vizinho do ferro. Dando continuidade à pesquisa do grupo, pretende-se propor um mecanismo de sorção do arsênio e estudar a melhor forma de aplicação da biomassa.

PALAVRAS-CHAVE: Biossorção; Folhas de alface; Celulose; Ferro; Arsênio; XANES; EXAFS.

ABSTRACT

Biosorption is the property of biomasses to retain metallic ions from solutions. The aim of this work is to understand the mechanism of arsenic sorption by dried lettuce leaves (*L.sativa*). In order to understand the mechanism of arsenic uptake by Fe-loaded biomass, X-ray absorption spectra of the Fe-loaded and As-Fe-loaded biomass samples have been collected at the *Laboratório Nacional de Luz Síncrotron* (LNLS). The analysis of XANES spectra confirmed that Fe ions were incorporated as Fe(III) inside the biomass and showed that arsenic is incorporated as As(V), regardless sorption was carried out with As(III) or As(V) solutions. The features of EXAFS spectra suggest that the nearest neighboring atoms of iron ions are the same in all the samples, even in the As-Fe loaded ones. These results allowed us to conclude that As ions are not the nearest iron neighbors. The following stages of this investigation are intended to propose a mechanism for arsenic sorption on dried Fe-loaded lettuce leaves and, based on that, to develop novel applications for the biomass.

KEY-WORDS: Biosorption; Lettuce leaves; Cellulose; Iron; Arsenic; XANES; EXAFS.

1. INTRODUCTION

Arsenic has been considered one of the most important global environmental pollutants. Its occurrence in water systems is a result of natural processes and anthropogenic activities. In view of their high toxicity and the consequent health problems associated with human exposure to contaminated waters, there is an increasing interest in the identification of new adsorbent materials for both the removal and fixation of arsenic species. The environmentally important arsenic species are the pentavalent arsenate (H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} and AsO_4^{3-}) and the trivalent arsenite (H_3AsO_3 , H_2AsO_3^- , HAsO_3^{2-} and AsO_3^{3-}) species. The trivalent and neutral arsenic species is the most toxic, the most mobile in the environment and the most difficult species to be effectively removed from aqueous systems (Smedley and Kinniburgh, 2002).

Although many different methods have been applied to arsenic removal, the adsorption is the basis for many treatment techniques applied to aqueous systems (Jong and Parry, 2004). Many types of adsorbents have been used, especially Fe(III)-bearing materials because of the Fe(III) affinity towards inorganic arsenic species and the consequent selectivity of the adsorption process (Raven *et al.*, 1998; Deschamps *et al.*, 2003; Ladeira and Ciminelli, 2004; Zhang *et al.*, 2004). The conventional water treatment processes generate a significant quantity of sludge, which has to be subsequently disposed off as hazardous wastes. Biosorption appears as an attractive alternative to these conventional treatment systems due to the low costs and the possibility of regeneration of the biosorbents (Volesky and Naja, 2005). Also, reusing biomasses coming from food, pharmaceutical or wastewater treatments is a way to reduce the impact of worthless wastes (Teixeira and Ciminelli, 2005).

Lettuce leaves are a waste material from the food industry. Dried lettuce leaves have already been investigated for copper and iron uptake (Carvalho *et al.*, 2003, 2005). The present work investigates the removal of arsenic ions from aqueous solutions using dried lettuce leaves (*L. sativa*), both *in natura* and previously loaded with Fe(III). It stands out as specific purposes the determination of the oxidation states and neighbors of the absorbed species, which will help to establish the sorption mechanism of arsenic by the biomass.

2. MATERIALS AND METHODS

X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) analyses of dried biomass samples loaded with iron (Fe(II) and Fe(III) - pH 2.0) and arsenic (As(III) and As(V) - pH 3.0), and *in natura* biomass samples were performed using the synchrotron facilities at the *Laboratório Nacional de Luz Síncrotron* (LNLS) in Campinas, Brazil. The samples loaded with As were previously loaded with Fe(III). The sorption experiments were carried out batchwise using 0.1g of biomass and 50mL of solution at a concentration of 250mg/L. XANES and EXAFS data from the iron (7112eV) and the arsenic (11868eV) K-edges were obtained at XAS workstation. The spectra were recorded at room temperature using a Si (111) double crystal monochromator with an upstream vertical aperture of 0.3 mm and calibrated with Fe K-edge (7112eV) for iron measurements and Au L1-edge (11918 eV) for arsenic measurements. The solid samples were fixed onto acrylic holders, sealed with Kapton tape film. The measurements were carried out in the transmission mode for iron and in the fluorescence mode for arsenic. The detectors were low-pressure air-filled ionization chambers (transmission mode) and 15-element Ge (fluorescence mode). XANES and EXAFS spectra were analysed by using Athena and Artemis softwares.

3. RESULTS AND DISCUSSION

Fig. 1 shows the Fe K XANES spectra of the iron-loaded and *in natura* biomasses. It also shows the XANES spectra of Fe_2O_3 (Fe(III)) and FeO (Fe(II)) standard samples. Spectra were normalized and only their shapes are to be compared. By comparing the absorption edge of our samples and Fe(III) and Fe(II) standards, one can conclude that the oxidation state of iron inside the biomass is +3, even when the biomass is contacted with a solution containing Fe(II) ions only. Although in a relatively smaller concentration (approximately 100 times lesser than in the Fe(III)-loaded biomass), Fe(III) is also present in the *in natura* biomass. The presence of Fe(III) in the *in natura* biomass agrees with the previous results of Carvalho *et al.* (2005).

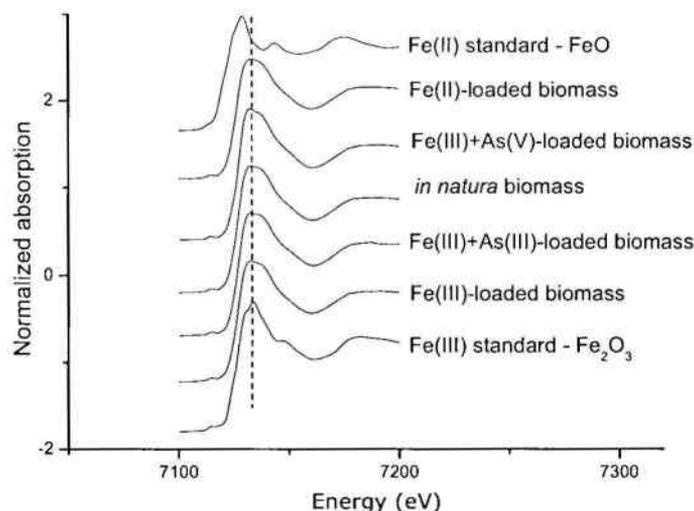


Fig. 1: Normalized Fe K XANES spectra of Fe(II) and Fe(III) sorbed by dried lettuce leaves and of Fe₂O₃ and FeO standard samples.

Fig. 2 shows the Fourier transforms of Fe K EXAFS spectra of iron-loaded biomasses. One can observe the oscillations in the absorbed radiation intensity caused by the scattering from the atoms in the neighboring coordination shells. The first peaks are the ones that correspond to the first coordination shell. Fig. 3 shows the isolated first-shell EXAFS oscillations. The fit results shown in Table I indicate similar iron coordination environments with oxygen being the element found in the first coordination shell. The dominant chemical species of Fe in water at pH=2 is the hydrolyzed form of Fe(III), Fe(H₂O)₅OH²⁺. Therefore, the sorbed Fe is expected to be coordinated with hydroxyl ions and water molecules as well as with oxygen present in the biomass structure.

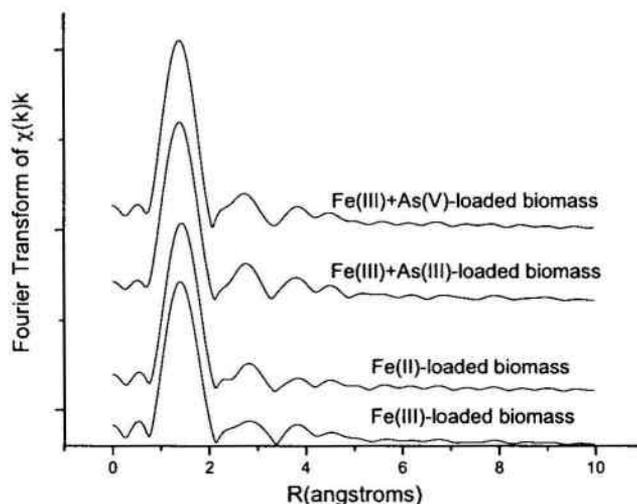


Fig. 2: Fourier transforms of the Fe K EXAFS spectra of iron-loaded dried lettuce leaves.

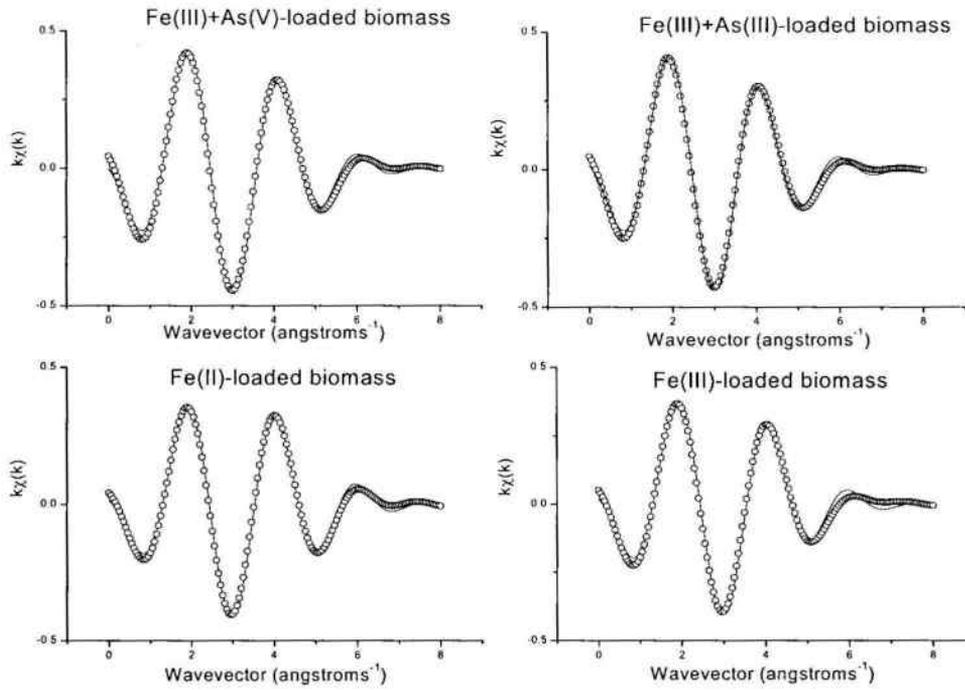


Fig. 3: Isolated first-shell EXAFS oscillations (O) and quick first-shell fits (-) for iron-loaded biomasses.

Table I. EXAFS Results using Artemis Quick-First Shell Theory for Octahedral Fe-O and Tetrahedral As-O

Loading	Fe Coordination Number	Fe-O distance [Angstrom]	As Coordination Number	As-O distance [Angstrom]
Fe(III)+As(V)	4.00 ± 2.00	2.03 ± 0.03	3.40 ± 1.00	1.67 ± 0.04
Fe(III)+As(III)	4.00 ± 2.00	2.04 ± 0.04	3.12 ± 0.90	1.68 ± 0.02
Fe(II)	3.16 ± 1.00	2.05 ± 0.05		
Fe(III)	3.57 ± 1.00	2.05 ± 0.05		

Fig. 4 shows the As K XANES spectra of iron-arsenic-loaded biomasses and of arsenic salts used as standards. The energy of the absorption edges indicates that the oxidation state of arsenic inside the biomass is +5, even when the biomass is contacted with an As(III) solution.

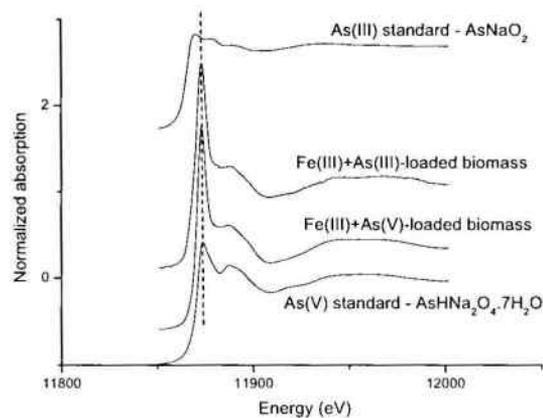


Fig. 4: Normalized As K XANES spectra of As(III) and As(V) sorbed by dried lettuce leaves and of arsenic standards

Fig. 5 shows the Fourier transforms of As K EXAFS spectra of iron-arsenic-loaded biomasses and Fig. 6 shows the isolated first-shell EXAFS oscillations. The results shown in Table I agree with the results found in the literature for As-O distances and coordination numbers (Nico et al., 2004). The dominant aqueous species of arsenate and arsenite in water at pH=3 are $H_2AsO_4^-$ and H_3AsO_3 . Following adsorption, arsenite is oxidized to arsenate.

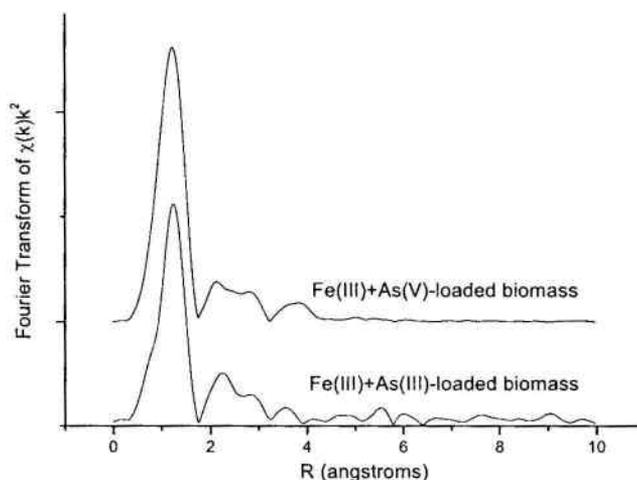


Fig. 5: Fourier transforms of the As K EXAFS spectra of arsenic-loaded dried lettuce leaves.

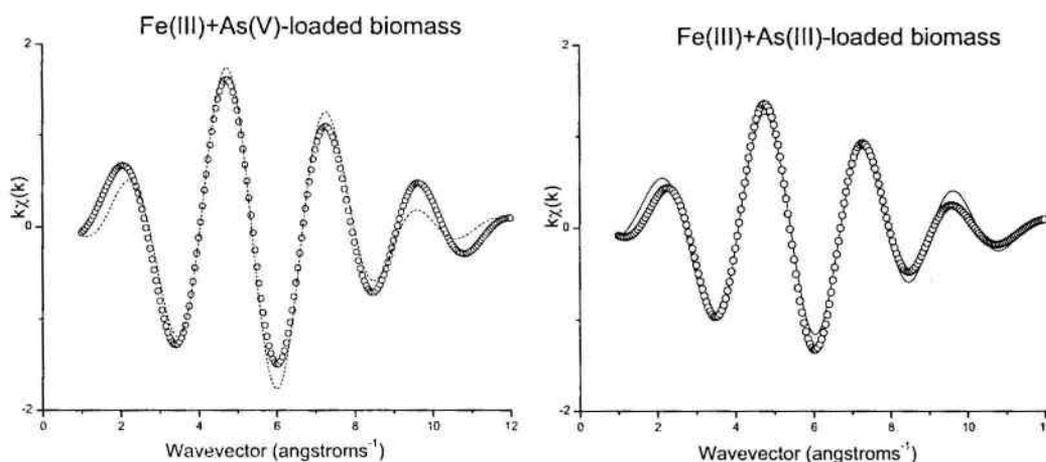


Fig. 6: Isolated first-shell EXAFS oscillations (O) and quick first-shell fits (-) for arsenic-loaded biomasses.

CONCLUSIONS

The uptake of iron and arsenic by lettuce leaves was investigated. XANES results indicated the oxidation of Fe(II) to Fe(III), and As(III) to As(V) inside the biomass. EXAFS results showed that arsenic is not the element found in the iron first coordination shell and that this element is likely to be oxygen.

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