Mössbauer and EXAFS spectroscopy investigation of iron and arsenic adsorption to lettuce leaves

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Abstract The accumulation of iron and arsenic from aqueous solution by lettuce leaves biomass was investigated using Mössbauer and EXAFS spectroscopic techniques. Mössbauer spectroscopy results show that iron is oxidized during sorption while EXAFS results indicate that iron is coordinated by approximately 6 oxygen and 2 carbon atoms while arsenic is coordinated by approximately 4 oxygen atoms with iron as a second neighbor.

Keywords Mössbauer spectroscopy · EXAFS · Arsenic

1 Introduction

Environment contamination by chemical and radioactive wastes has attracted considerable attention as a consequence of ever increasing mining and industrial activities. Arsenic is one of the most important pollutant metalloid and is naturally found in the environment. It is present in gold and other base-metals ores and large amounts are mobilized in the process of extraction of these metals. Mostly all of arsenic complexes are considered toxic and cause several diseases [1]. Investigations focusing on metal accumulation in vegetables grown in mine waste areas found that lettuce leaves tend to accumulate a larger amount of metal than other vegetable species, such as beans and tomatoes [2]. This accumulation pattern suggests that lettuce leaves have potential active sites for arsenic and metalloid complexation. It has been shown [3, 4] that iron plays an important role on arsenic retention by biomass.

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However, detailed information about interaction amongst iron, arsenic, and biomass is still lacking. In this contribution we present Mössbauer and X-ray absorption fine structure spectroscopy results and analysis on iron and arsenic adsorption on dried lettuce leaves with the aim to contribute to the investigation of the arsenic retention mechanisms including the important role of iron on arsenic accumulation.

2 Experimental methods

After dried and ground, lettuce leaves were washed with an aqueous solution at pH 4.0, filtered, and dried. Further treatment was performed like in [5, 6]. For the adsorption experiments, the washed biomass was brought together with solutions of Fe(III) as $FeCl_3.6H_2O$ or Fe(II) as $FeSO_4.7H_2O$. For arsenic sorption, Fe(III)-loaded biomass was brought together with a solution of As(V) as $AsHNa_2O_4.7H_2O$. Values of pH were selected so as to avoid iron precipitation and maximize arsenic loadings. Details of the adsorption process will be published elsewhere and show that arsenic is sorbed only when the biomass has been previously loaded with iron.

Extended X-ray Absorption Fine Structure (EXAFS) measurements on biomass samples loaded with iron and arsenic were performed at Laboratório Nacional de Luz Sínchroton (LNLS) in Campinas, Brazil. Fe and As K-edges (7112 eV and 11868 eV) EXAFS data were collected at the XAFS1 workstation in transmission geometry with a Si(111) channel-cut monochromator and ion chamber detectors. The data were analyzed using FEFF8 [7] and ATHENA/ARTEMIS [8] software packages. Analysis of the data was carried out as described in [9]. Mössbauer spectra of iron-loaded samples were recorded using a conventional constant acceleration Mössbauer spectrometer in transmission mode with a ^{57}Co (Rh) source. The data were evaluated with discrete subspectra using a least-square fitting routine provided by the Normos software package. All isomer shift values (δ) quoted are relative to α-Fe.

3 Results and discussion

Figure 1 shows the Mössbauer spectra for samples of biomass loaded with (a) Fe(II) and (b) Fe(III)+As(V) (see Table 1 for hyperfine parameters). It can be observed that the oxidation state of iron inside the biomass is mainly +3, even when the biomass is in contact with a Fe(II) solution, indicating that Fe(II) is oxidized to Fe(III). Previous studies have reported that iron oxidation does not occur in solution [10] but do not offer an explanation for the observed oxidation. It is, thus, assumed that a constituent of the biomass is capable of promoting iron oxidation. Values of quadrupole splitting (Q.S.) indicate that Fe(III) is in an octahedral coordination. While Fe(II) is oxidizing to Fe(III), the opposite likely does not occur, as the attempt to fit the data for the Fe(III)+As(V)-loaded biomass with a model that includes an Fe(II) component yields a negligible (within the uncertainty of the measurement) contribution of this Fe(II) subspectrum (see Fig. 1b).

Figure 2a shows the real part of Fourier transformed EXAFS data (and fit) obtained from the Fe(II)-loaded biomass sample. The fitting model is based on the experimental evidence that iron is mainly complexed to carboxyl groups inside the
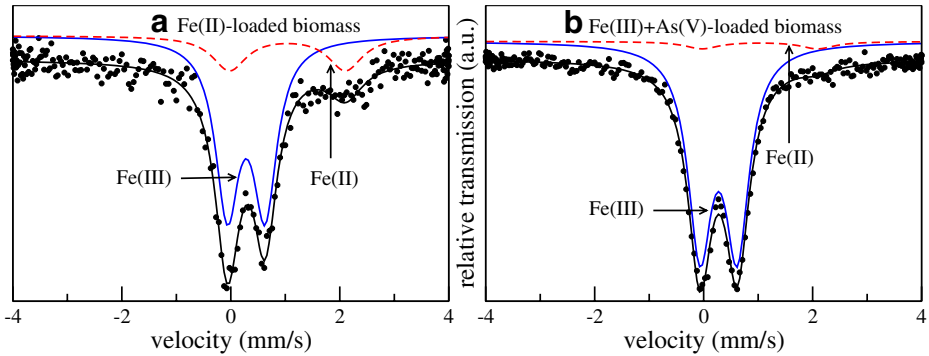
Fig. 1 (color online) Mössbauer spectra of iron-loaded biomass samples: **a** Fe(II)-loaded biomass; **b** Fe(III)+As(V)-loaded biomass

Table 1 Hyperfine parameters resulted from fitting of Mössbauer spectra

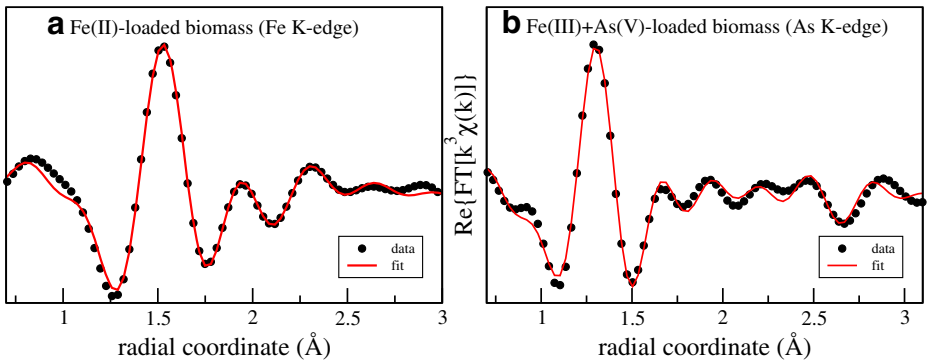| Sample	Site	δ (mm/s)	Q.S. (mm/s)	Area
Fe(II)-loaded biomass	Fe(III)	0.39±0.01	0.69±0.01	77%
	Fe(II)	1.15±0.04	2.13±0.08	23%
Fe(III)+As(V)-loaded biomass	Fe(III)	0.37±0.01	0.72±0.01	

Fig. 2 (color online) Real part of Fourier transformed EXAFS data for ion-loaded biomass samples: **a** Fe(II) at Fe K-edge; **b** Fe(III)+As(V) at As K-edge

biomass. Fe-O and Fe-C scattering paths from a Fe(III) acetate structure were used to fit the data. Table 2 shows the best results for the fitting variables which indicate that iron is bound to 5.4±0.3 oxygen atoms and 3.0±1.0 carbon atoms in the first and second coordination shells. The Fe-O distance of 1.99 Å is consistent with that found in the acetate structure whereas the Fe-C distance of 2.81 Å is shorter than in the acetate group. This can be attributed to Fe bound to carboxyl groups through 2 oxygen atoms, in a bidentate mononuclear geometry, as opposed to the monodentate structure of Fe(III) acetate. The octahedral coordination sphere is completed by two water molecules.

Table 2 Results of fits to
EXAFS data

Sample	Shell	N	R (Å)	σ^2 ($\times 10^{-3}$ Å)
Fe(II)-loaded biomass	Fe-O	5.4±0.3	1.99±0.02	6±2
Fe K-edge	Fe-C	3.0±1.0	2.81±0.04	10±8
Fe(III)+As(V)- loaded biomass	As-O	4.1±0.7	1.71±0.01	3±1
As K-edge	As-Fe	1 (fixed)	2.93±0.03	6±4

Paths from $FeAsO_4.2H_2O$ (scorodite) structure were used to fit the As K-edge
EXAFS spectrum of Fe(III)+As(V)-loaded biomass sample, as can be seen in
Fig. 2b. The first coordination shell (see Table 2 for fit results) is composed of
4.1±0.7 oxygen atoms in agreement with the expected tetrahedral geometry of
aqueous $H_2AsO_4^-$ present in the original solution [11]. The As-O distance of 1.71 Å
found in the fit is consistent with the typical distance for arsenate adsorbed on iron
hydroxides [12]. The structure in the Fourier-transformed data between R = 2.5 Å
and R = 3.0 Å is properly fitted with an As-Fe scattering path. Freely varying the
coordination number of this shell did not yield a stable fit. To circumvent this
problem, several fits were attempted with fixed values of N from 1 to 4. The most
statistically sound fit was achieved with N = 1 which yielded a As-Fe distance of
2.93±0.03 Å. This result was expected in views of the dependence of arsenic sorption
on the presence of iron. The concentration of iron in the biomass samples measured
was about twice as large as that of arsenic which explains no evidence of the
contribution of arsenic to the second coordination shell of iron. These results suggest
that arsenate species are linked to the iron octahedra. The geometry of this complex
has yet to be determined.

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