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Kinetics of arsenic absorption by the species *Eichhornia crassipes* and *Lemna valdiviana* under optimized conditions

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HIGHLIGHTS

- Arsenic speciation was studied on phytoremediation with 2 macrophytes.
- As decreased exponentially over the time allowing fit of 1st order kinetic equation.
- Dynamics of As(III) and As(V) influenced the absorption of As by water-hyacinth.
- The absorption of As by lemna showed minor relation to the oxidation dynamics.
- [As] greater than 1 mg L^{-1} implied deleterious effects in both macrophytes.

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ABSTRACT

This work aimed to study the kinetics of arsenic absorption by *Eichhornia crassipes* and *Lemna valdiviana* under pre-established conditions of pH phosphate and nitrate in the nutrient solution. Additional aims were to evaluate the conversion kinetics between As(III) and As(V), and the effect of arsenic concentrations on development of the species. The plants were cultivated in nutrient solutions containing different arsenic concentrations: 0, 0.56, 0.89 and 1.38 mg L^{-1} for the water-hyacinth, and 0, 0.13, 0.48, 0.99 and 1.4 mg L^{-1} for Lemna. Monitoring of arsenic removal by the plants was performed by sampling at intervals of 0, 4, 8, 16, 24, 48, 96, 144, 192 and 240 h for the water hyacinth, and 0, 4, 8, 16, 24, 48, 96, 144 and 168 h for Lemna. The samples were submitted to analysis of total arsenic, As(III), As(V) and phosphorus. The first-order kinetics was fit to the arsenic removal kinetics by the plants, and it was observed that the decay coefficient (k) decreased with the increase of its initial concentration in the nutrient solution. For the, absorption was observed after 96 h of culture, the time coinciding with the greatest As(V) concentrations. For Lemna, the metal was only absorbed by the plant after decay of the phosphate levels of the medium, which occurred at 48 h. Concentrations above 1 mg L^{-1} implied deleterious effects in both plant species and in the phytoremediation process, and the bioaccumulation factor decreased for concentration above this for both *E. crassipes* and *L. valdiviana*.

1. Introduction

Numerous studies have shown the presence of high arsenic concentrations in natural waters, a fact that has generated worldwide concern. The most relevant pollution cases have been reported in countries including China, Taiwan, India, Bangladesh, USA, Canada, Mexico, Chile, Argentina, New Zealand, Poland, Hungary, Croatia, Serbia and Romania (Jovanovic et al., 2011). In Brazil, studies have indicated human exposure to arsenic in surface waters, where the state of Minas Gerais is the most studied due to the mining activities (Litter et al., 2012).

Considering its dissemination in the environment, the removal of As from contaminated waters has been treated as a necessary technology to minimize its impacts on ecosystems. Although different physical, chemical and biological approaches have been

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employed for this purpose, phytoremediation is highlighted as a promising technology in which plants are used to remove contaminants from water (Ali et al., 2013). There are some plants that can accumulate As in their plant biomass, such as *Pteris vittat*a L. (Raj and Singh, 2015), *Wolffia globosa* (Zhang et al., 2009), *Spirodela polyrhiza* L. (Rahman et al., 2008), *Lemna gibba* L. (Duman et al., 2010), *Azolla caroliniana* (Zhang et al., 2008) and *Eichhornia crassipes* (Alvarado et al., 2008).

These plants, when cultivated in media contaminated with heavy metals, present tolerance and accumulate them by means of adjustments and changes of their physiological mechanisms, depending on the type of pollutant, concentration and conditions of the medium and cultivated plant species (Islam et al., 2015). In the case of As, the main pathway of As(V) absorption is through the phosphate carrier and As(III) utilizes aquaglycerporines (Meharg and Jardine, 2003).

The species *Eichhornia crassipe*s (water-hyacinth) and *Lemna* sp. are promising species in this context, since they have the capacity to accumulate expressive quantities of arsenic. Both are rapidly propagating macrophytes in eutrophic environments, known as aquatic weeds, a desirable fact when attempting to remove a contaminant. Additionally, they are species adapted to the tropical climate and easily accessible throughout Brazil.

Given the danger of arsenic and its environmental dissemination, several studies have been conducted to evaluate the physiological aspects of the plant, regarding its potential as a remediator of contaminated media. There are still few factors considered that make this process feasible in real applications, nor studies which obtain engineering parameters for its application.

The present study sought to study the kinetics of arsenic absorption by both species. The objective was to evaluate the conversion kinetics of As(III) and As(V), and the effect of different As concentrations on development of the species.

2. Material and methods

2.1. Acquisition and acclimatization of the plants

Aquatic plants of the species *Eichhornia crassipes* (Mart.) Solms (water-hyacinth) and *Lemna valdiviana* were collected from the botanical garden of the Federal University of Viçosa, sanitized and acclimatized for two months in polyethylene containers ($0.30 \times 0.30 \times 0.22$ m), containing 2 L of nutrient solution Clark (1975), pH 6.5 (Leão et al., 2014). The plants were maintained in a grow room, under controlled temperature (25 ± 2 °C) and luminosity with photoperiod of 16 h, where the nutrient solution was changed every seven days.

2.2. Experimental design: removal kinetics

The species *E. crassipes* and *L. valdiviana* were cultivated in duplicate under different arsenic concentrations, which were 0, 0.56, 0.89 and 1.38 mg L^{-1} for the common water-hyacinth, and 0, 0.13, 0.48, 0.99 and 1.4 mg L^{-1} for Lemna. Arsenic was added in the form of sodium arsenite ($NaAsO_2$). The conditions of the medium with respect to pH, $P-PO_4$ and $N-NO_3$ levels were adjusted according to the conditions obtained in previous studies (Souza, 2016), as shown in Table 1. The other micronutrients were balanced with Clark (1975) nutrient solution.

Table 1
Levels utilized for the assay of As removal kinetics by the plant species.

Plant species	pH	$P-PO_4$ (mmol L^{-1})	$N-NO_3$ (mmol L^{-1})
E. crassipes	7.5	0.0	0.0887
L. valdiviana	6.7	0.0488	7.93

The monitoring of arsenic removal by the species was performed by collecting water samples (10 mL) from all the assays at the time intervals of 0, 4, 8, 16, 24, 48, 96, 144, 192 and 240 h for the common water-hyacinth, and 0, 4, 8, 16, 24, 48, 96, 144 and 168 h for Lemna. In the plant tissue the contents of total arsenic, As(III), As(V) and phosphorus were analyzed. For Lemna, the plant was analyzed in its entirety due to its morphological characteristics. For the common water-hyacinth, quantification of the roots and shoots were performed separately.

The representative curves of the arsenic removal kinetics were obtained by correlating time and efficiency for the different concentrations in the nutrient solutions.

During this period the parameters of pH and oxidation potential (Eh) were monitored daily, as well as the electrical conductivity of the water. At the end of the growing period the evapotranspiration was calculated based on the difference between the initial and final volume of solution in the vessel.

With respect to *Lemna valdiviana*, 4 g of fresh plant mass were conditioned in 2 L vessels containing the nutrient solution contaminated with As. In relation to the common water-hyacinth, plants of similar size were selected, being weighed at the beginning of the experiment and also grown in vessels containing 2 L of nutrient solution contaminated with As.

2.3. Determination of the total arsenic, total phosphorus and the As species (As(III) and As(V))

The concentrations of total arsenic and phosphorus were determined in the nutrient solution contaminated with As, at the abovementioned intervals, and in the macrophytes as a whole (leaves + roots) for Lemna and separately in the leaves and roots for the common water-hyacinth. The plant tissue was subjected to acid digestion, performed by the addition of 10 mL of a mixture containing one part nitric acid and three parts perchloric acid, at a temperature of 100 °C until the samples were clarified. The low temperatures used in digestion of the samples were to prevent As losses by volatilization. The elements were analyzed in the ICP-EOS Plasma Emission Spectrometer.

For quantification of the As(III) and As(V) species, the samples were filtered through 0.45 μm membranes and stored at low temperature (<4 °C). Chemical speciation was performed using a hydride generation atomic fluorescence spectrometer (HG-AFS), coupled to a high performance liquid chromatography column (HPLC).

2.4. Evaluation of performance, bioaccumulation factor and translocation in the plant

To evaluate plant performance after the experimental period, the relative growth rate (RGR) and its tolerance index (TI) to As were calculated. To obtain the RGR, at the end of the assays the plants were abundantly washed with deionized water and placed in a forced ventilation oven at 65 °C until reaching constant mass. The initial dry mass was obtained from an estimate of the water content in the plants, under the same conditions used in the experimental assay, obtaining the ratio between fresh and dry mass.

The RGR was calculated using the equation (Eq. (1)) proposed by Fisher (1921), in which the dry mass of the plants is the independent variable: