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# Biosorption of arsenic from groundwater using *Vallisneria gigantea* plants. Kinetics, equilibrium and photophysical considerations

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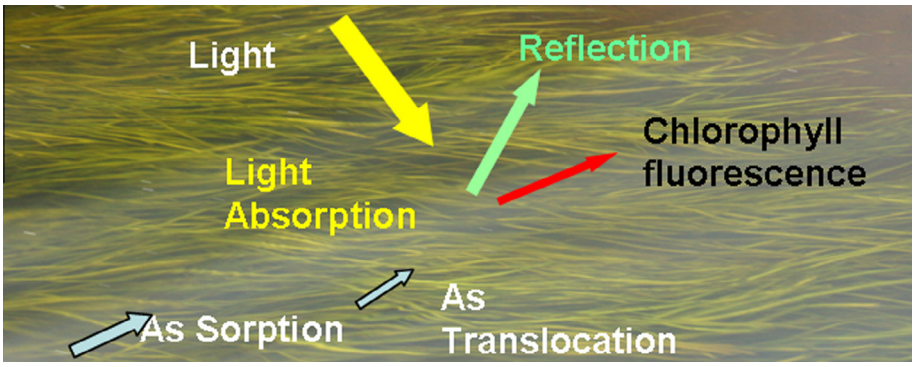
## HIGHLIGHTS

- *Vallisneria gigantea* plants were able to remove 1 mg of As (V) during a week.
- Changes in optical properties were related to arsenic concentration in solution.
- Plants translocated As from roots to fronds.
- As uptake followed a first-order kinetic law.
- Adsorption isotherm models described experimental data from arsenic uptake.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Arsenic (V) uptake from groundwater by using *Vallisneria gigantea* plants was studied using batch experiments. Reflectance and fluorescence of intact plants were investigated and changes in photophysical properties following arsenic absorption were reported. Good correlations have been found between arsenic concentration in groundwater and parameters derived from reflectance and fluorescence measurements. This system reached its equilibrium after seven days when the removal quantities were strongly dependent on the initial arsenic concentration. Interestingly, *Vallisneria* plants were able to accumulate from 100 to 600 mg As $kg^{-1}$ in roots and fronds although the translocation factors were low (0.6–1.6). Kinetic data for biosorption process followed a first-order law. At low arsenic concentrations the uptake in plants was governed by diffusion aspects. Langmuir, Freundlich and Dubinin–Radushkevich models were applied and results demonstrated that arsenic uptake was better described by the Langmuir model. As a final remark we concluded that a plant of this species should be able to remove 1 mg As per week.

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## 1. Introduction

Arsenic is naturally found worldwide in rocks and sediments as a soil constituent. As a result of erosion, arsenic species are dissolved in water and released in groundwater (Bhattacharya et al., 2002; Smedley and Kinniburgh, 2002) becoming a pollutant leading to serious health risks. In addition, anthropogenic activities like mining accelerate the release of arsenic in the environment (Bundschuh et al., 2012a,b). Agricultural activities and calcination of wood treated with preservatives are other sources of arsenic drainage in the environment (Ancelet et al., 2012). The risk related

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to arsenic presence is not only associated with its concentration but with its availability and speciation, being inorganic forms more dangerous than organic ones (Bundschuh et al., 2012a,b; Kar et al., 2010). Because of its toxicity, it is important to determine the speciation of arsenic in environmental matrices (Tuzen et al., 2009a).

Even so, drinking water containing arsenic probably posses the greatest threat to human health due to its daily intake, even in low concentration. It is associated with illnesses such as cancer (Morales et al., 2000; Sinha et al., 2007), skin pigmentation changes, keratosis, hyperkeratosis (Kazi et al., 2009), gastric complications, liver fibrosis, peripheral neuropathy (Sayeed et al., 2013) and diabetes (Tseng et al., 2000) which have been previously reported in literature.

Therefore many efforts have been done to remove As from drinking water by using classical technologies such as membrane filtering, adsorption (Mohan and Pittman, 2007) coagulation/co-precipitation and ionic exchange (Ahmed, 2001; Choong et al., 2007). Although these procedures work very well in some cases, they have several disadvantages such as high cost, the requirement of specialized supervision and in some cases the difficulty of transfer to small population like those dispersed in rural areas. In this regard, a number of emerging technologies have been developed in the last years (Litter et al., 2012) among which phytoremediation appears as an interesting proposal from the economic and sustainable point of view (Salido et al., 2003). In this context, studies performed on physicochemical aspects of arsenic removal are decisive to assess the optimal parameters of this process (Sari and Tuzen, 2009, 2010; Tuzen et al., 2009b; Sari et al., 2011).

There are a lot of studies that analyze the behavior of several species of plants, in contact with solutions of trace elements, where the removal percentage is calculated. However, considerations about the kinetics and the maximum uptake capacity by live plants are scarce in literature. Nevertheless, this information is crucial to select the best way to process the groundwater or wastewater.

Additionally, plants exhibit properties linked with their physiological state that can be modified in arsenic presence due to its toxic effect. Indeed, several authors reported the synthesis of reactive oxygen species in photosystems as an answer to arsenic presence (Mascher et al., 2002; Hartley-Whitaker et al., 2001). In addition, some authors stated that plants develop mechanisms to rapidly detoxify themselves or use them to activate defence strategies depending on circumstances (Apel and Hirt, 2004; Laloi et al., 2004).

In a previous work we have studied reflectance and fluorescence of *Vallisneria gigantea*, *Azolla filiculoides* and *Lemna minor* in contact with solutions containing 2 mg $kg^{-1}$ of As (V) and we have found several changes in their photophysical properties which were strongly species-dependent (Iriel et al., 2015). In that work, *Vallisneria* plants have removed the highest amount of arsenic. Though, the authors have not performed detailed studies concerning the kinetics and the capacity of As removal. The present work studies the performance of *V. gigantea* plants in arsenic uptake from groundwater where we expect kinetic and equilibrium models which are normally applied in inert systems, could be applicable in live plants, too.

## 2. Materials and methods

### 2.1. Plants

*V. gigantea* plants were obtained from a local store and were cleaned with HClO (Baker, USA) 5% to remove traces of organic matter and rinsed with distilled water. They were acclimated to laboratory conditions during ten days before starting the experiments.

### 2.2. Arsenic solutions

A stock solution of As (V) was prepared by dissolving $Na_3AsO_4{\cdot}7H_2O$ (Biopack, Argentina) in milliQ water. Working solutions were obtained by dilution of the stock solution in groundwater from a 70 m-depth well (geographical coordinates 34°32′8851″ S58°6′16,086″W) to reach a final concentration ranging from 0.075 to 3.413 mg $kg^{-1}$ As. Physicochemical parameters of the well water used in this work was previously described in Iriel et al. (2015).

### 2.3. Experimental procedure

#### 2.3.1. Batch experiments

Plants were weighed, around 20 g of them were put in plastic containers and were immersed in working solutions during 10 days in a ratio of 10 g of plant for each liter of arsenic solutions (2 L). Containers were covered with a plastic film to avoid water evaporation during the experiment and the plants were illuminated by using artificial light. Illuminating cycles were of 16 h light and 8 h dark. Light was emitted at a photosynthetic photon flux density of 200 μmol $m^{-2}$ $s^{-1}$. The photosynthetically active radiation (PAR) was measured by using a sensor provided by Cavadevices SA (Argentina). Plants were kept at room temperature during the whole experiment (about 20 °C). Water samples were obtained daily to determine quantitatively As concentration in solution. For this, around 5 mL of solution were taken out and were filtered with a cellulose nitrate filter (0.45 μm). Then, it was acidified to 0.5% with $HNO_3$ (Merck, Suprapur®, Germany) and was stored at 4 °C until measurements. Plants immersed in water without additional aggregates were used as controls. The pH values were already constant around 7.4 ± 0.2 during the experiences (Hanna Instruments, Model HI 255, Romania).

#### 2.3.2. Arsenic quantification

After ten days of treatment all the plants were removed, cleaned with distilled water, rinsed with MilliQ water and the roots and leaves were separated and dried at 65 °C in an oven (San Jor, Argentina) until constant weight. After that, the whole plant material was pulverized by using a commercial mill at 3000 rpm (Ultracomb, Argentina). Around 10 mL of concentrated $HNO_3$ (Merck, Suprapur®, Germany) were added to weighed quantities of separately powdered roots and leaves and the mixtures were heated to 65–70 °C in a sand bathroom until the solution was clear. Solutions were filtered by using a cellulose nitrate membrane filters (0.45 μm) and refrigerated until measurements. Arsenic concentrations in plants digested solutions and water samples taken during the experiment, were determined by ICP-OES (Perkin Elmer, Optima DV 2000, USA). From these data arsenic uptake ($q_e$) by the plant was calculated as:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where $C_0$ and $C_e$, (mg $L^{-1}$) are the initial and equilibrium arsenic concentrations in the bulk phase, respectively, $V$ is the volume of the groundwater used in liter and m is the weight of the entire plant expressed in grams.

From values of arsenic concentration, bioconcentration factor in roots, BCF, and the translocation factor, TF, were calculated using Eqs. (2) and (3).

$$\mathrm{BCF} = \frac{\text{mg kg}^{-1}\ \text{As root (dw)}}{\text{mg kg}^{-1}\ \text{As in solution}} \quad (2)$$

$$TF = \frac{\text{mg kg}^{-1}\ \text{As frond (dw)}}{\text{mg kg}^{-1}\ \text{As root (dw)}} \quad (3)$$

where dw indicates that the concentration is obtained on a dry basis of the material. The concentration in the solution to be used in Eq. (2) corresponds to the last day of the experiment.

*2.3.2.1. Quality assurance.* Perkin Elmer NIST® traceable quality control standard (N9300211) was used as the stock standard to prepare working solutions. The sample introduction unit consisted of a Scott chamber and a flow GemCone™ nebulizer. The water samples were analyzed by triplicate (standard deviation less than 4%). Furthermore, each sample of dried plant was divided into three parts. These were digested separately as has been mentioned before and analyzed in triplicate by ICP-OES. A blank was run to correct the all measurements (for water and plants digested). The water used throughout the present study was obtained from a Milli-Q water purification system (Millipore GmbH, France) with a resistivity of 18.2 MΩ cm. Pro-analysis reagents were used throughout the study. For both water and digested plant samples, in every ten of them, blank and a spike sample, involving all reagents, were run to check any interference and cross-contamination. Reported results have been corrected for the blanks evaluated in relation to the quality-assurance samples worked up at the same time. The detection limits for water samples (LOD) in $\mu g\ L^{-1}$ based on three times the standard deviation of the blank signal was 10 for As and the quantification limits (LOQ) in $\mu g\ L^{-1}$ based on the lowest calibration point was 25.

*2.3.3. Spectral measurements*

From each plant, full developed leaves were detached and thick layers (null transmittance) of them were placed in the sample holder for both reflectance and fluorimetric recorder. These measurements were performed by triplicate and the final spectrum was calculated as an average.

*2.3.3.1. Diffuse reflectance.* Reflectance measurements were performed using a spectrophotometer (Shimadzu 3100, Japan) equipped with an integrating sphere where barium sulfate was used as a standard of 100% reflectance. Thick layers of detached leaves were placed in the sample holder and reflectance spectra were recorded between 400 and 800 nm. The first derivative from the reflectance spectrum was obtained from these data as the ratio $\Delta R/\Delta\lambda$, where $R$ is the diffuse reflectance and $\lambda$ the wavelength. From the first derivative spectra, areas under major peaks were calculated.

*2.3.3.2. Non-variable fluorescence.* Fluorescence spectra from intact leaves were carried out on a spectrofluorometer (PTI, model QM-1, USA) under low photon flux conditions. Previous to the measurements the samples were kept in darkness during 15 min to deactivate variable fluorescence from chlorophyll. Samples were excited at 460 nm and chlorophyll spectra were recorded between 500 and 800 nm using front face geometry.

Experimental fluorescence spectra were corrected as usual using a correction function provided by the manufacturer in order to avoid distortions due to the photomultiplier detector response. Additionally, a second correction was performed to eliminate effects related to light reabsorption processes that occur into the plant material. For this, a previous model developed for leaves, was used to correct experimental fluorescence spectra. True emission spectra were obtained dividing experimental spectra by a function $\gamma_{\lambda,\lambda_0}$ (Eq. (4)) according to Ramos and Lagorio (2004):

$$\gamma_{\lambda,\lambda_0} = \frac{1}{1+\sqrt{\frac{F(R)_\lambda}{F(R)_\lambda+2}}} \cdot \frac{1}{1+\sqrt{\frac{F(R)_\lambda[F(R)_\lambda+2]}{F(R)_{\lambda_0}[F(R)_{\lambda_0}+2]}}} \quad (4)$$

where $F(R)$ is the remission function, representing the sample absorption. The subscripts $\lambda$ and $\lambda_0$, stand for emission and excitation wavelengths respectively. It was calculated from reflectance data as $F(R) = (1-R_\lambda)^2/(2R_\lambda)$. Function $\gamma$ can be interpreted as the fraction of the luminescence emitted at wavelength $\lambda$ that escapes from the optically thick sample excited at wavelength $\lambda$. The method employed here was developed by our working group and has been successfully applied to correct fluorescence spectra of leaves (Ramos and Lagorio, 2004; Cordon and Lagorio, 2006) and fruits (Novo et al., 2012). From these data a ratio $F_{red}/F_{far\text{-}red}$ between maxima emission bands of chlorophyll located at about 685 nm and about 735 nm was calculated for the whole set of spectra.

*2.4. Statistical analysis*

Infostat® statistical software (Di Rienzo et al., 2011) was used in order to perform the statistical analysis. A normal distribution for the whole data set was confirmed using Shapiro–Wilks modified test. Linear regression analyses were performed with Sigma Plot 10.0 (Systat Software Inc., San Jose, CA).

## 3. Results and discussion

*3.1. Arsenic effects on photophysical properties*

The typical distribution of the first derivative of reflectance spectra from *V. gigantea* leaves (data not shown) presented two main minima peaks centered at 520 (green *region*) and 710 nm (red edge) respectively due to the pigment content. Linear correlations were found between the areas of the mentioned peaks and As concentration for *V. gigantea* plants (Fig. 1a). In particular, the effect in the red edge zone was more significant than in the green region. Additionally, there was a red shift in the derivative peak from 706 nm (control plants) to 715 nm (plant treated with arsenic solutions) while in the region of shorter wavelengths no shift was observed (results not shown). It is well documented that changes in derivative reflectance spectra are associated to changes in chlorophyll content (Kochubey and Kazantsev, 2007), however in this work a dependency with chlorophyll concentration has not been found. Actually, variations on chlorophyll content depend not only on the applied As concentration, but also on its speciation, the time of contact, the plant species studied, and others. In literature, an inverse correlation between As concentration and chlorophyll content has been reported for relatively high As concentration ($5\ mg\ kg^{-1}$ in solution and $30\ mg\ kg^{-1}$ in soils) (Azizur Rahman et al., 2007; Stoeva and Bineva, 2003; Stoeva et al., 2005). However, in some cases, an opposite behavior was found (Shaibur and Kawai, 2009; Sánchez-Viveros et al., 2011). In this work, an increase in chlorophyll content with As presence was observed, but no clear correlation between chlorophyll and As concentrations could be inferred. Regarding the bands of the first derivative spectra, a spectroscopic study was previously performed with *Pteris* plants that showed that it was possible to find correlations between arsenic concentration in leaves and bands in first derivative spectra which were not necessarily connected to chlorophyll concentration (Slonecker et al., 2009).

Fig. 1a shows the values for the peak areas of the derivative of reflectance spectra integrated in both regions (520 and 710 nm) as a function of the initial arsenic concentration in solution. Notice that at the lower wavelengths the first derivative poorly correlated with arsenic concentration while the band located

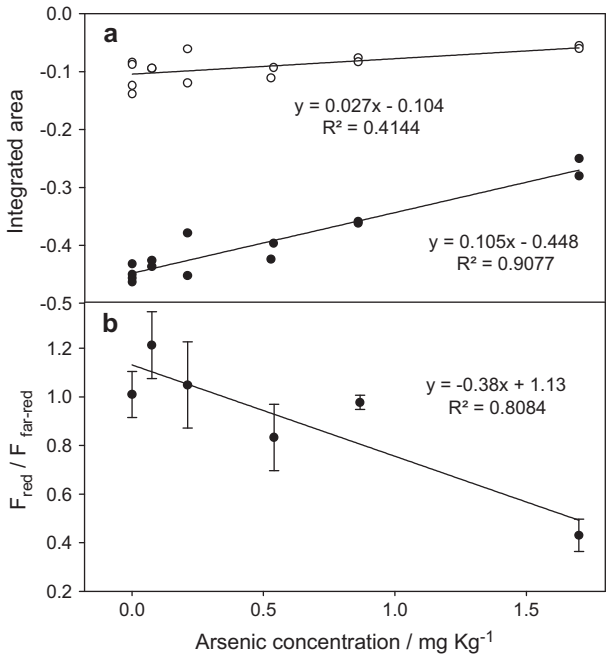


**Fig. 1.** Spectrocopic properties of intact leaves of *Vallisneria gigantea* as a function of the arsenic initial concentration (a) areas under major peaks in the derivative of reflectance spectra recorded between 490–560 nm (○) and 680–760 nm (●) and (b) ratio of chloropyll fluorescence bands at 680 and 730 nm ($F_{red}/F_{far\text{-}red}$).

between 680 and 760 nm was more sensitive. Statistical analysis has shown that there is a linear correlation between these parameters and the arsenic concentration applied.

In fluorescence analysis a diminution of $F_{red}/F_{far\text{-}red}$ ratio was observed in plants exposed to arsenic (V). This behavior has been previously observed by Iriel et al. (2015) where it was connected with a preferential damage in photosystem II due to the potential presence of reactive oxygen species that appeared as a response to the stress situation. In this work, fluorescence response was evaluated at several arsenic concentrations and a linear relation has been found (Fig. 1b).

### 3.2. Effect of contact time and initial concentration

The time required to reach a steady state is of considerable importance in sorption processes because it depends on the system used. So, this point is relevant to analyze the feasibility of the plants to be used in arsenic removal. In order to determine the influence of the initial concentration of As (V) on this aspect, sorption by *Vallisneria* plants was investigated as a function of contact time from 1 to 10 days and at several initial concentrations varying from 0 to 3.4 mg $kg^{-1}$. In fact, arsenic removal was fast at the beginning (first three-five days), increasing slightly afterwards until reaching equilibrium in 7–10 days. This behavior was similar to all the studied concentrations. In addition, the percentage of arsenic removed was strongly dependent on its initial concentration: higher values were found for the lowest concentrations. For concentrations equal or lower than 0.3 mg $kg^{-1}$, removal percentage was around 25% while at 1–2 mg $kg^{-1}$, it decreased to 12–14% for the same contact time (seven days).

### 3.3. Distribution of arsenic in roots and leaves of V. gigantea

In order to evaluate in detail the uptake process of As studied here, it was necessary to determine the concentration values at the different parts of the plant so as to asses if translocation took place. For that, arsenic content in roots and leaves has been determined from the measurements performed on both digested tissues at the end of the biosorption experiments. Fig. 2 shows arsenic concentration in these plant tissues as a function of the initial concentration. These results showed that sorption and translocation from roots to leaves really took place in *V. gigantea*. In fact, both roots and leaves have shown close values when the initial As concentration was low, but above 0.25 mg $kg^{-1}$ differences between them became noticeable. In fact, roots showed a higher ability to retain As.

A similar tendency was observed previously in literature for *A. filiculoides* plants exposed during four days to sodium arsenate in the nutrition solution (Sánchez-Viveros et al., 2011). In that work As concentration diminished after a threshold value in the plant fronds.

Bioconcentration factors in roots (BCF) and the translocation factors (TF) calculated according Eqs. (2) and (3) respectively are presented in Table 1.

Bioconcentration factors are useful to compare the performance of plants to remove pollutants from environmental matrices. However, comparisons with other published values are not so direct and it is easy to make mistakes if the boundary conditions of the experiments are not carefully taken into account. For instance, values of BCF from aquatic plants are normally higher than those from terrestrial plants and they depend on the external concentration (Slonecker et al., 2009; Robinson et al., 2006). In literature they are sometimes calculated on wet basis and on dry basis too (Shaibur and Kawai, 2009).

In this work, *Vallisneria* plants showed that they accumulated As in a moderate level. Our values were in the order of those reported for aquatic plants in Taupo Volcanic Zone (New Zealand) where geothermal activity has resulted in elevated levels of arsenic in lakes and rivers (Robinson et al., 2006) but low translocation factors were found in the present work. To compare, Shaibur and Kawai (2009) observed an accumulation of 90 mg As $kg^{-1}$ in shoots and 4840 mg As $kg^{-1}$ in roots from Japanese mustard spinach grown in hydroponic conditions with 5 mg $kg^{-1}$ of As in the solution (Stoeva et al., 2005). Normally, for hyperaccumulator plants a TF value close to 7–10 is required (Srivastava et al., 2006).

### 3.4. Biosorption kinetics

#### 3.4.1. Reaction order

As a first approach to obtain kinetic data from this system, an analysis of the reaction order as a function of time was performed.

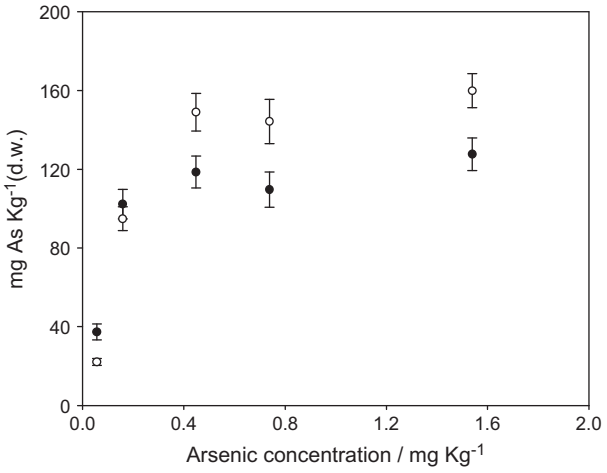


**Fig. 2.** Arsenic concentration in leaves (●) and roots (○) of *Vallisneria gigantea* plants (dry weight) after 10 days of contact with As solutions as a function of the initial concentration.

**Table 1**
Bioconcentration and translocation factors of As (V) uptake by *Vallisneria gigantea* plants.

| As (mg kg$^{-1}$) | BCF | TF |
|---|---|---|
| 0.056 | 397 | 1.61 |
| 0.158 | 605 | 1.08 |
| 0.448 | 335 | 0.80 |
| 0.738 | 195 | 0.76 |
| 1.540 | 104 | 0.82 |

Using the method of initial rates, we calculated the order as the slope of the straight line resulting when the logarithm of the initial rate ($v_i$) is represented as a function of the logarithm of the initial As concentration $c_0$ (Eq. (5)).

$$\log v_i = \log k + n \log c_0 \quad (5)$$

In Fig. 3 we represent these graphs for changes occurred at the first day and for the changes between the first and third day respectively. The resulting order was close to 1 in the first case and decreased as the considered time augmented.

### 3.4.2. Diffusion intra particle approach

The limiting step of a sorption process can be evaluated by using the diffusion intra particle approach developed by Weber and Morris (1963). This model assumes three consecutive steps that take place during adsorption process: (i) diffusion of sorbate from the solution to the outer surface of the sorbent, (ii) transport of the sorbate from the external surface to the interior sites and (iii) the sorption from the active sites into the interior surfaces.

In this case, an increase in the sorption capacity, $q_t$, of arsenic with the contact time with the roots allows to obtain valuable information about the rate-limiting steps during arsenic removal by *Vallisneria* plants. For this, intra-particle diffusion model is represented by the following equation:

$$q_t = k_{id} t^{1/2} \quad (6)$$

where $k_{id}$ is the internal diffusion coefficient and $q_t$ the quantity sorbed at time $t$. Considering this model, plots of $q_t$ as a function of $t^{1/2}$ should have a zero intercept indicating that the diffusion intra particle is the rate limiting process.

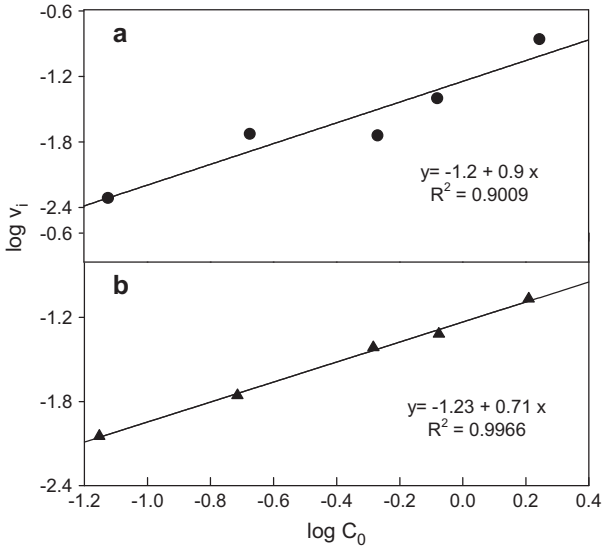


**Fig. 3.** Logarithm of the reaction rate ($v_i$) as a function of the logarithm of the initial As concentration in solution for the first day of treatment (a) and for the period of time between the first and third day of treatment (b).

In the present study, the plot of $q_t$ versus square root time exhibited a linear region followed by a plateau that took place after 13 h (results not shown). In fact, at lower As concentrations, the linear region intercepted the y axis at point zero suggesting that this was a rate-controlling step, but when As concentration increased, the value of the intercept moved away from zero suggesting that although intraparticle diffusion was involved in the arsenic uptake process, it was not the rate controlling step. The values for $k_{id}$ were obtained from the slopes of the linear portions and are presented in Table 2.

As it may be observed from Table 2, a strong deviation from Eq. (6) was present at the highest As concentration tested. A similar tendency was found for cationic adsorption of Cu, Zn, Cd and Pb onto *Gymnogongrus torulosus*. These authors stated that the first part of the curve is assigned to surface adsorption where the diffusion intra particle is the rate-controlling step (Areco and dos Santos Afonso, 2010).

### 3.5. Sorption models

Arsenic uptake is an isothermal process. In this context, sorption isotherms can help to describe interactions of As (V) in solution with the studied plants by classical models such as Langmuir, Freundlich and Dubinin–Radushkevich (D–R). Fittings from the obtained data to these models are presented in the next subsections in order to analyze if the equations involved are able to describe our experimental data. Nevertheless, it should be kept in mind that good fitting to some of these models does not necessarily imply that the basic assumptions of them are fulfilled in plants.

In Fig. 4 the isotherm representing arsenic uptake by *V. gigantea* sorption as a function of the equilibrium concentration of As in solution reached at the end of the experiment is shown.

Unfortunately collected data are insufficient to study the entire adsorption curve because the plateau region was not reached in the concentrations used. This obeyed to the fact that plants showed symptoms of strong injury at As concentrations (in solution) higher than 3 mg kg$^{-1}$ (as browning of plant leaves). Such behavior has been previously well documented for *Vallisneria* where arsenic occurrence affects the photosynthetic apparatus (Iriel et al., 2015). Nevertheless, from Fig. 4 a maximum uptake value of 0.053 mg As g$^{-1}$ can be estimated. Additionally, if we consider an average weight for a medium plant (around 20 g), we can affirm that a plant of this species should be able to remove 1 mg As per week.

Quantities of arsenic removal from *V. gigantea* plants were lower in relation to other sorbents reported in literature. For instance, in a previous work Sari et al. (2011) reported that dried algae (*Maugeotia genuflexa*) had a sorption capacity of 58.48 mg g$^{-1}$. A similar result was found in macrofungus (*Inonotus hispidus*) where a sorption capacity around 48 mg g$^{-1}$ was reported for As (III) and As (V) (Sari and Tuzen, 2009).

### 3.5.1. Langmuir adsorption isotherm

This model describes quantitatively the formation of a monolayer of adsorbate onto the adsorbent surface which contains a

**Table 2**
Slopes ($K_{id}$) and intercepts values obtained from the linear portion of representing $q_t$ as a function of time.

| [As] (mg kg$^{-1}$)[a] | 0.0752 | 0.2117 | 0.5383 | 0.8600 | 1.7573 |
|---|---|---|---|---|---|
| $K_{id}$ (mg g$^{-1}$ h$^{-1/2}$) | 0.0002 | 0.0004 | 0.0009 | 0.0013 | 0.0024 |
| Intercept | −0.0003 | −0.0002 | −0.0023 | 0.0041 | 0.6331 |
| $R^2$ | 0.952 | 0.9955 | 0.9893 | 0.9991 | 0.111 |

[a] Arsenic initial concentration in the solution.

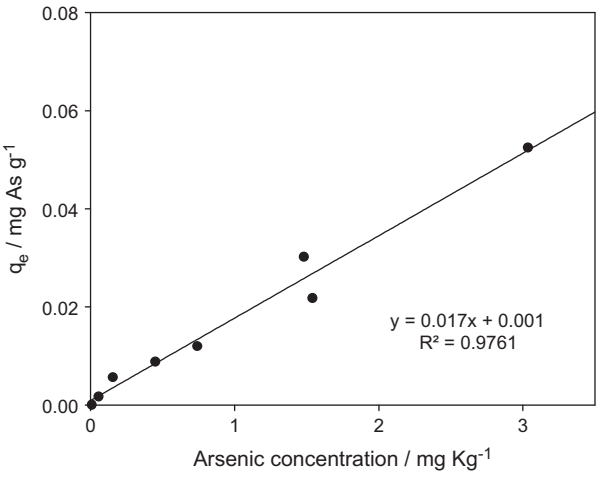


**Fig. 4.** Biosorption isotherm at pH 7.5 and temperature 20 °C for As (V) on *Vallisneria gigantea*, representing the As uptake as a function of the equilibrium concentration of As.

finite number of identical sites. Furthermore, it assumes that energy of adsorption is the same onto the surface and there is no migration of adsorbed species. Based on these assumptions Langmuir equation can be written in a linear form:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e} \tag{7}$$

where the constants $Q_0$ and $K_L$ represent the maximum capacity coverage for a monolayer (mg $g^{-1}$) when saturation is obtained and the constant related to the adsorption process (L $mg^{-1}$) respectively. $C_e$ and $q_e$ were previously defined in this text. The affinity between the sorbent and the sorbate is represented by $K_L$.

Parameters of the Langmuir model were obtained from the slope and intercept in Eq. (7) (data not shown) and are given in Table 3 with the corresponding correlation coefficient.

### 3.5.2. Freundlich adsorption isotherm

The most important multi-site adsorption model is based on the Freundlich isotherm that is commonly used to describe the adsorption characteristics for a heterogeneous surface of energy distribution. The linear form of the exponential equation describing the isotherm is given by Eq. (8):

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \tag{8}$$

where $k_F$ and $1/n$ are dimensionless constants representing the adsorption capacity (a measure of the surface area of the adsorbent) and the adsorption intensity respectively.

Parameters $k_F$ and $1/n$ were calculated from the slope and intercept in Eq. (8) and are shown in Table 3.

### 3.5.3. Dubinin–Radushkevich isotherm

This model is useful in order to discriminate if the sorption takes place by a chemical or physical process. D–R equation is more general than Langmuir model and successfully describes experimental results onto macroporous, mesoporous, microporous and nonporous solids and in high and intermediate solute concentrations. It is described in the linear form in the following equation:

$$\ln q_e = \ln q_{max} - \beta\varepsilon^2 \tag{9}$$

where $q_{max}$ is the theoretical isotherm saturation capacity (mg $g^{-1}$), $\beta$ is the activity coefficient related to the mean free energy of biosorption ($mol^2/J^2$) and ε is the Polanyi sorption potential calculated as:

$$\varepsilon = RT \ln\left(1 + \frac{1}{M_{eq}}\right) \tag{10}$$

where $R$ is the constant gas (8.314 J $mol^{-1}$ $K^{-1}$), $T$ is the temperature in Kelvin units an $M_{eq}$ is the concentration of bulk solution at equilibrium time expressed in mmol $L^{-1}$. Polanyi adsorption assumes a fix adsorption volume and an adsorption potential that only depends on the adsorbate and sorbate nature. $\beta$ and $q_{max}$ values were obtained from the slope and intercept of Eq. (9) (data not shown).

In addition, the necessary energy ($E$) to move a mol of sorbate from the infinitum into the solution to the sorbent surface can be calculated as:

$$E = (2\beta)^{-1/2} \tag{11}$$

The low value obtained for $E$ (5.89 kJ $mol^{-1}$) indicates that arsenic uptake is a physical process.

To summarize the obtained fittings of our data to the different models, isotherms parameters and their correlation coefficients $R^2$ are presented in Table 3 to compare.

There is a good correlation between our data and Langmuir, Freundlich and Dubinin–Radushkevich models.

The value for $Q_0$ obtained from the Langmuir isotherm is in concordance with the observed tendency in batch experiments (see Fig. 4). Regarding Freundlich model, the value for $n$ = 1.2 suggested that in arsenic uptake this model is also able to explain the experimental data. In the same way, $R^2$ values from Langmuir and Freundlich linear models are acceptable, 0.9842 and 0.9694 respectively. In addition, Dubinin–Raduskevich fit has reached also a good correlation factor ($R^2$ = 0.9790). However, using this model the $q_{max}$ value resulted twice the Langmuir one. In this case it is difficult to state the correct value because the sorption curve (Fig. 4) did not include the plateau region. Anyway, in arsenic uptake using live plants the useful region of the sorption curve involves having a good physiological state of plants and consequently getting concentrations higher than 3.5 mg $kg^{-1}$ for *V. gigantea* did not make any sense.

## 4. Conclusions

In this study, the removal of arsenic dissolved in groundwater using intact plants of *V. gigantea* was analyzed in terms of physicochemical parameters including photophysical, kinetics and equilibrium considerations. Good correlations have been found between arsenic concentration in groundwater and parameters derived from reflectance and fluorescence spectroscopies. Particularly, the area of derivative spectra peak at the red edge zone and the fluorescence peaks ratio of the principal bands of

**Table 3**
Isotherm models parameters and correlation coefficients for sorption of As (V) by *Vallisneria gigantea* plants from groundwater solutions.

| Isotherm model | Parameters | | $R^2$ |
|---|---|---|---|
| Langmuir | $Q_0$ (mg $g^{-1}$) = 0.05 ± 0.04 | $K_L$ (g $mg^{-1}$) = 0.59 ± 0.03 | 0.9842 |
| Feundlich | $n$ = 1.2 ± 0.1 | $K_F \times 10^{-2}$ = 1.87 ± 0.02 | 0.9694 |
| Dubinin–Radushkevich | $Q_{max}$ (mg $g^{-1}$) = 0.11 ± 0.02 | $\beta \times 10^{-8}$ ($mol^2$ K $j^{-2}$) = 1.44 ± 0.08 | 0.9790 |

chlorophyll are the most sensitive parameters to detect arsenic presence. Regarding kinetic experiments, arsenic removal presented a first order law. Moreover, at lower arsenic concentrations, the uptake in plants is a process governed by diffusion aspects. In addition, several adsorption isotherm models were able to explain the observed results, despite the fact that the adsorption curve is not complete due to the toxicity of arsenic in plants at higher concentrations. This work constitutes a starting point to address the physicochemical study of As removal in living plants which lets a comparison between the performance of different plants species in the sorption process.

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