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Capacity of Absorption and Removal of Heavy Metals from *Scirpus californicus* and Its Potential Use in the Remediation of Polluted Aquatic Environment

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Abstract

The research aimed to evaluate the absorption and removal capacity of Cu, Pb, Fe and Zn from *Scirpus californicus* for potential use in the remediation of polluted aquatic environments. Initially, *Scirpus californicus* plants were conditioned in 1.5 liters of 10 ppm Cu solution at a pH of 2.3 as well as Pb, Fe and Zn. Subsequently, the concentration of heavy metals in the root-rhizome, submerged stem and aerial stem was determined; the solution and pH were also analyzed. The greatest capacity of absorption and accumulation occurred in the root-rhizome reaching values for Cu of 491.84, Pb of 739.43, Zn of 830.71 and Fe of 2624.72 mg/kg dry followed by the submerged stem and low values for the aerial stem. The removal efficiency of Cu from the solution was 52.10%, Pb 53.50%, Fe 48.00% and Zn 50.20%. It is concluded that the contact time has a significant effect on the absorption and removal capacity of the metals under study.

Keywords

Phytoremediation, Absorption and Accumulation, Heavy Metals, *Scirpus californicus*

1. Introduction

Environmental pollution by heavy metals is one of the main problems of society in the 21st century, as it affects not only the physical environment but also the functioning of ecosystems. Once released into the environment, heavy metals circulate between biotic and abiotic cycles, accumulate in different compartments of the food chain and can reach toxic concentrations for animals, plants, microorganisms and even man [1]. Nowadays, heavy metals have a great significance as indicators of the ecological quality of any aquatic ecosystem due to their toxicity and especially to the bioaccumulative behavior they possess.

Water pollution by heavy metals is a major environmental problem in modern society. Pollutants enter aquatic ecosystems through the discharge of wastewater from industrial, urban and agricultural runoff. Compared to organic pollutants, natural decomposition processes do not remove heavy metals. In contrast, they can accumulate in aquatic biota and become organic complexes, which can potentially become more toxic [2] and cause irreversible damage to human health. The removal of toxic metals from wastewater is essential for the control of environmental pollution.

Today, there are a variety of technologies to reduce water pollution, but they are expensive. An interesting alternative approach is phytoremediation, in which plants are used to stabilize or even remove metals from water through mechanisms of phytoaccumulation, phytodegradation and phytostabilization [3].

Aquatic macrophytes are the predominant organisms in lake ecosystems, which in comparison with other plant species can absorb metals through their roots and rhizomes, as well as through their leaves [4]. However, the accumulation of metals by macrophytes is affected by concentrations of metals in water and sediments and the speciation of metals such as free ions and humic complexes [5]. The emerging aquatic macrophyte *Scirpus californicus*, known as totora, is one of the most common plants living in the high Andean wetlands, able to withstand extreme environmental conditions, including the presence of toxic pollutants. The objective of this study was to evaluate the absorption and removal capacity of Cu, Pb, Fe and Zn of *Scirpus californicus* for its potential use in the remediation of polluted aquatic environments.

2. Material and Methods

2.1. Breeding of Plants of *Scirpus californicus*

S. californicus plants were collected from the community of Pomachaca-Tarma, in the Junín region, forming 64 experimental units; they were transferred in 10 liter capacity containers with water from their medium (**Figure 1**). Each of the experimental units consisted of 4 plants placed in 1.5 liters of distilled water. Of the total number of experimental units, 16 were placed in solutions of copper,

Figure 1. Selection of plants *Scirpus californicus*.

lead, zinc and iron at a concentration of 10 ppm. Then, from each experimental unit and after contact times in each metal (θ_1, θ_2, θ_3, θ_4, θ_5, θ_6, θ_7 and θ_8), the plants were extracted and divided into root-rhizome, aerial stem and submerged stem. Each of the parts was washed with drinking water and finally with distilled water and then proceeded to its analysis. We also collected 500 ml of the solutions from the experimental units for the pH and concentration analyses of Cu, Pb, Fe and Zn.

2.2. Equipment and Reagents

The equipment used was from the Laboratory of Analytical and Environmental Chemistry of the Faculty of Applied Sciences of the National University of the Center, such as: atomic absorption spectrophotometer Varian AA240, stove-Memmert, analytical balance OHAUS, iron, water distiller, pH meter HANNA instruments HI 3220. Merck branded chemically pure reagents were used such as copper nitrate [$Cu(NO_3)_2$], lead nitrate [$Pb(NO_3)_2$], zinc nitrate [$Zn(NO_3)_2$], iron nitrate [$Fe(NO_3)_3$], nitric acid [HNO_3], hydrochloric acid [HCl], perchloric acid [$HClO_4$], distilled water, 1000 ppm standards of Cu, Pb, Fe and Zn.

2.3. Analysis of Samples

This experiment was conducted to evaluate the ability of *S. californicus* to remove Cu, Pb, Fe and Zn from a synthetic water sample by exposure to different concentrations and contact times (**Figure 2**). Samples of each contact time were analyzed for metal concentration and pH according to standard methods [6].

a. Extraction: *S. californicus* was extracted from the community of Pomachaca-Tarma, taking care that its roots-rhizomes, aerial stem and submerged stem are not mistreated.

b. Selection: The selection of the plant went through a visual inspection, taking into account that the plant has the size and good physical and mature condition of the plant.

c. Washing 1: This washing allowed the elimination of impurities that accompany the plant such as soil, stones, etc., until the water is clear and free of solids.

d. Washing 2: The second washing was done with distilled water to eliminate impurities that can precipitate metals (Cu, Pb, Fe and Zn).

e. Conditioning: The plants were conditioned in plastic containers with 1.5 L of solution of 10 ppm of copper, lead, zinc and iron, individually and 2.30 pH. Sixteen experimental units were then prepared for each test.

f. Sampling: Sampling was conducted in duplicate for each proposed contact time. The samples were divided into parts; aerial stem, submerged stem and root-rhizome, then washed four times with potable water and twice with distilled water to remove impurities from the plant surface, the solution is completed at 1.5 L with distilled water, homogenized and sampled for metal concentration and pH analysis.

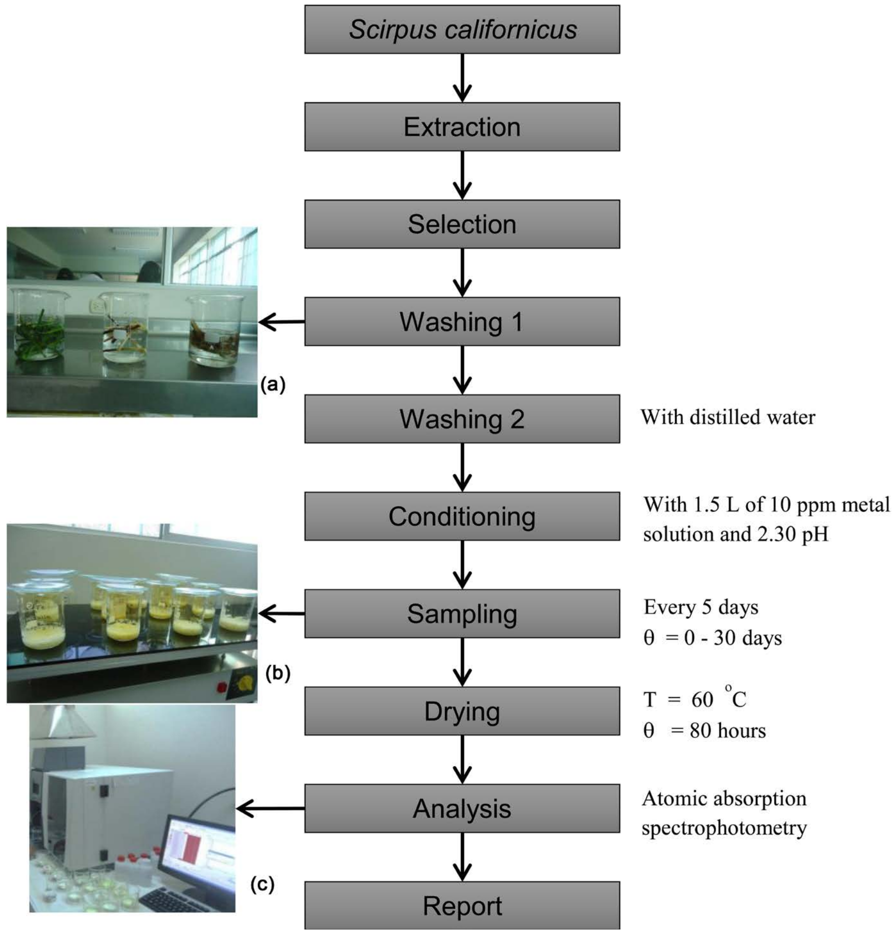

Figure 2. Flowchart to evaluate the *Scirpus californicus* plant. (a) Elimination of impurities, (b) digestion of the sample, (c) Analysis by atomic absorption.

g. Drying: Samples washed with distilled water were conditioned in meshes and dried at 60˚C for 80 hours.

h. Analysis: Analyses were performed using the standardised method by atomic absorption.

i. Report: For plant parts in mg/kg dry and for solution in mg/L (ppm).

2.4. Research Design

S. californicus plants (aerial stem, submerged stem and root-rhizome) were evaluated with concentration solutions of 10 ppm Cu, 10 ppm Pb, 10 ppm Zn and 10 ppm Fe, independently and contact times (θ_1, θ_2, θ_3, θ_4, θ_5, θ_6 and θ_8). The design was applied completely at random, in order to adequately control the variables as detailed in Table 1.

The removal of copper, lead, zinc or iron was determined by applying the material balance formula:

$$\%\text{Removal} = \left(\frac{Y_i - Y_f}{Y_i}\right) \times 100$$

where:

Table 1. Experimental design to be developed in research.

Evaluation days	*Scirpus californicus*					
	Aerial stem		Submerged stem		Root-Rhizome	
	R_1	R_2	R_1	R_2	R_1	R_2
θ_1	A_{11}	A_{21}	A_{11}	A_{21}	A_{11}	A_{21}
θ_2	A_{12}	A_{22}	A_{12}	A_{22}	A_{12}	A_{22}
θ_3	A_{13}	A_{23}	A_{13}	A_{23}	A_{13}	A_{23}
θ_4	A_{14}	A_{24}	A_{14}	A_{24}	A_{14}	A_{24}
θ_5	A_{15}	A_{25}	A_{15}	A_{25}	A_{15}	A_{25}
θ_6	A_{16}	A_{26}	A_{16}	A_{26}	A_{16}	A_{26}
θ_7	A_{17}	A_{27}	A_{17}	A_{27}	A_{17}	A_{27}
θ_8	A_{18}	A_{28}	A_{18}	A_{28}	A_{18}	A_{28}

A_{11} … A_{28} = Concentrations of copper, lead, zinc and iron individually in the *Scirpus californicus* plant (aerial stem, submerged stem and root-rhizome), in solution and pH. θ_1, θ_2, θ_3, θ_4, θ_5, θ_6, θ_7 and θ_8 = Contact times a 0, 2, 5, 10, 15, 20, 25 and 30 days.

Y_i = Initial metal concentration (Cu, Pb, Fe and Zn).

Y_f = Final metal concentration.

2.5. Data Analysis

In order to evaluate the native *S. californicus* plant in the removal of copper, lead, zinc and iron, data were organized and the design was used entirely at random. When the difference between the treatments was found, the Tukey [7] mean comparison test was used at a significance level of 0.05 with the following linear additive model:

$$Y_{ij} = \mu + \Gamma_i + \mathcal{E}_{ij},\ \ i = 1,2,3,\cdots,t;\ j = 1,2,3,\cdots,b$$

where:

i: level of the factor parts of *S. californicus*.

b: level of the factor days of evaluation of the removal and/or absorption of metals.

Y_{ij}: value observed on the *j*-th day of evaluation of metal removal and/or absorption for the *i*th parts of the native plant *Scirpus californicus*.

μ : is the overall mean, estimated by the mean of the experiment: $\overline{x}$.

Γ_i : measures the effect of treatment *i*, estimated by experiment.

$\mathcal{E}_{ij}$: is the random error associated with the answer Y_{ij}.

3. Results and Discussion

The *S. californicus* plant, like any living being, has the capacity to absorb or adsorb substances such as copper, lead, zinc and iron. However, many of them are beneficial for their subsistence, while others are detrimental to their physiological processes. In this investigation it is shown values found in the treatments and repetitions, which increase in direct relation to the amount of metals applied in each treatment to *S. californicus*.

Figure 3 shows the absorption of copper during the experimental period for *S. californicus*. The greatest absorption occurred in the root-rhizome, followed by the submerged stem that after 15 to 30 days remains constant and in smaller quantity in the aerial stem that from 2 to 30 days remains constant.

Initially, the removal rates of heavy metals in the experiments were relatively slow in the first two days; this is because plants need a certain amount of time to adapt to a new environment [8]. Figure 4 shows the results of the efficiency of removing copper from the solution at a given pH. During the 30 days the removal was from 10.0 mg/L to 4.79 mg/L. Similar results were observed for emerging species and free floating species [9]. A higher accumulation of metals in aquatic plant roots compared to leaf accumulation is a widely proven fact. However, in exposures of *S. californicus* samples to elevated metal concentrations a significant translocation to the aerial stem was observed. However, they did not exceed the concentrations determined in the root-rhizome system.

Figure 5 shows that the greatest absorption of lead occurred in the root-rhizome, followed by the submerged stem and in lesser quantity in the aerial stem, which remains constant for 10 to 30 days. In Figure 6, the results of the removal of lead from the solution at a determined pH are presented; which reveals that the removal during the 30 days varied from 10.0 mg/L to 4.65 mg/L.

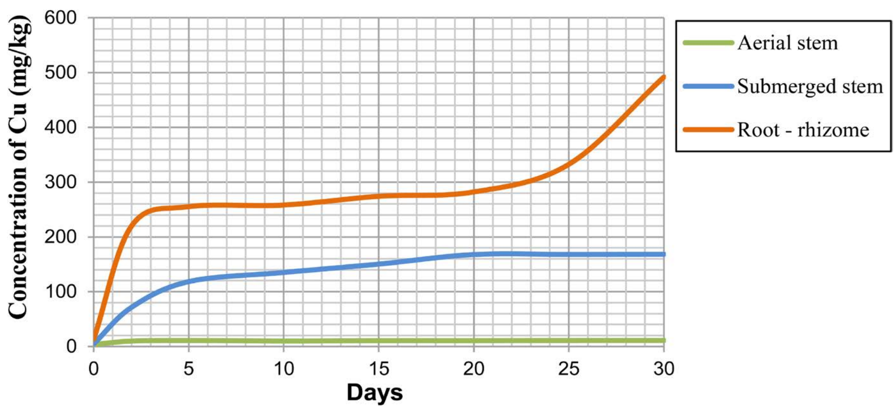

Figure 3. Copper absorption in the aerial stem, submerged stem and root—*Scirpus californicus* rhizome.

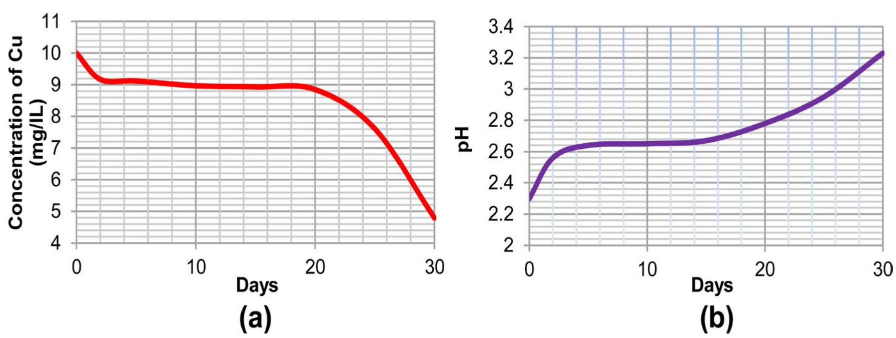

Figure 4. Concentration of Cu of the solution versus time (a). Behavior of pH versus time in copper solution (b).

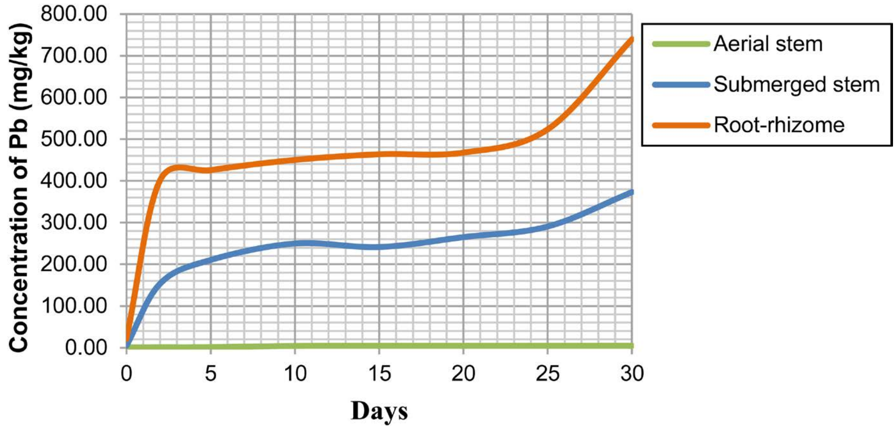

Figure 5. Absorption of lead in the aerial stem, submerged stem and root-rhizome of the plant *Scirpus californicus*.

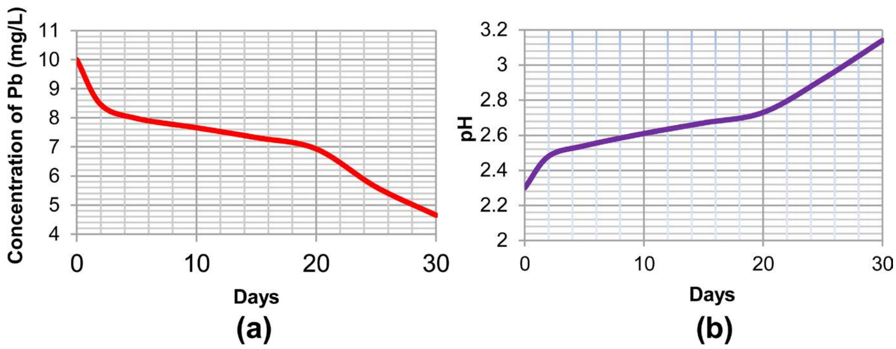

Figure 6. Concentration of lead in the solution versus time (a). Behaviour of pH versus time in lead solution (b).

Lead is the most toxic metal than other metals and immobile because of its strong bond to organic matter and other plant components [10] [11]. The results obtained are supported by Zevallos *et al.* [12], who refer that the accumulation of Pb^{2+} in plants is regulated by physicochemical parameters such as the pH of the medium, presence of exudates, the cation exchange capacity of its surface, etc. Vascular plants absorb and accumulate Pb^{2+} mainly in the roots and only a small part is translocated to the aerial part [13]. It is interesting to note that in similar work using other floating aquatic plants and under analogous experimental conditions, it is reported that most of the Pb^{2+} removed from an aqueous solution (57% - 77.5%) was left in the roots of *Eicchornia crassipes* when exposed to various concentrations in the range of 15 - 200 mg Pb^{2+}/L after 14 days. The retention of Pb^{2+} in the roots is due to its binding to certain cell wall molecules, ion exchange sites and extracellular precipitation, mainly in the form of carbonates.

The *S. californicus* plant showed the ability to tolerate significantly high concentrations of zinc. Figure 7 shows that the highest zinc absorption occurred after 20 days of contact at the root-rhizome, followed by the submerged stem which at 20 to 30 days remains constant and in lesser quantity at the aerial stem which at 15 to 30 days also remains constant. This result is due to the greater capacity of plants to absorb micronutrients compared to non-essential or toxic elements, for which plants can generate tolerance strategies [14]. A range of zinc concentrations between 0.070 and 0.40 mg/g could be considered toxic to plants, while the level of toxic zinc in plant tissue is 0.023 mg/g [14] [15]. In addition, several studies report that zinc binds to organic matter through electrostatic forces, indicating that a significant fraction of the metal bound to organic matter is determined in the interchangeable fraction [16].

In **Figure 8**, the results of the efficiency of zinc removal from the solution at a certain pH are shown, observing that during the 30 days the removal varied from 10.0 mg/L to 7.74 mg/L.

In **Figure 9**, it is shown that iron absorption was greater in root-rhizome, that from 20 to 30 days remains constant, followed by the submerged stem that from 25 to 30 days remains constant and in lesser quantity in the aerial stem that from 5 to 30 days remains constant. **Figure 10** shows the results of the efficiency of removing iron from the solution at a given pH during the 30 days, which ranged from 10.0 mg/L to 5.20 mg/L. In all cases the tendency to the neutral aqueous medium is observed. Similar to that obtained by Serrano where initial pH was of 5 and increase to 6.5.

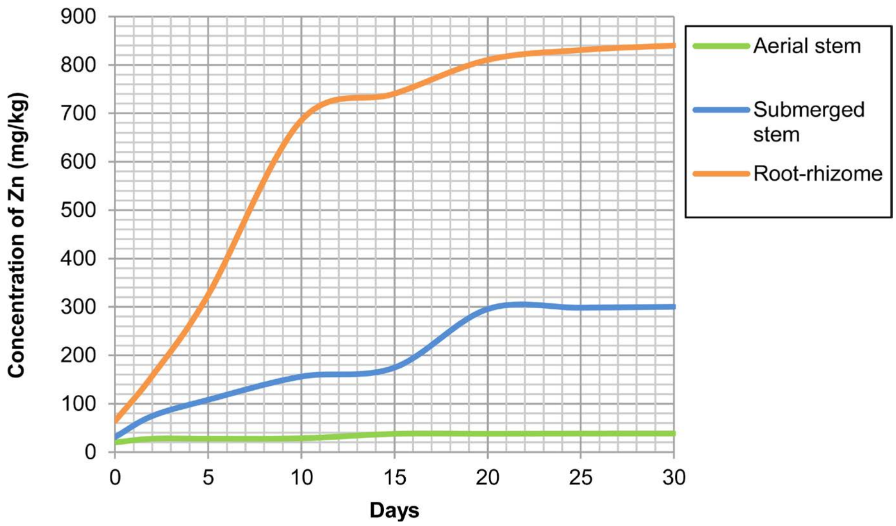

Figure 7. Absorption of zinc in the aerial stem, submerged stem and root-rhizome of the plant *Scirpus californicus*.

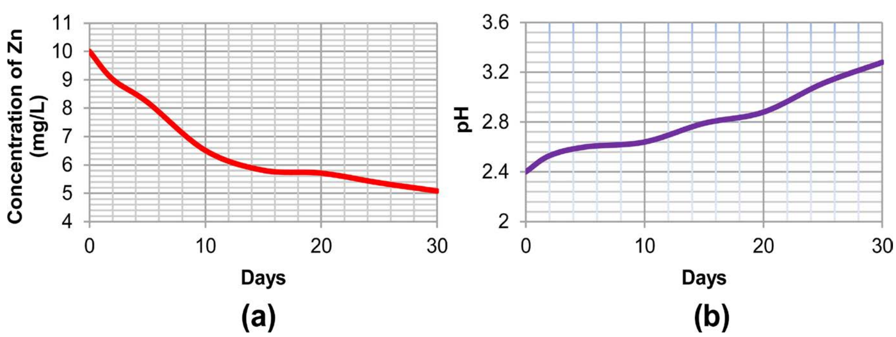

Figure 8. Concentration of Zinc in the solution versus time (a). Behaviour of pH versus time in zinc solution (b).

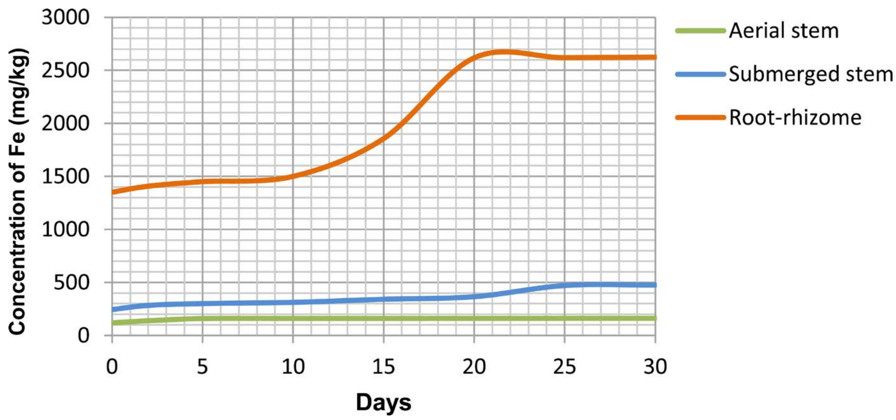

Figure 9. Absorption of iron in the aerial stem, submerged stem and root-rhizome of the plant *Scirpus californicus* against time.

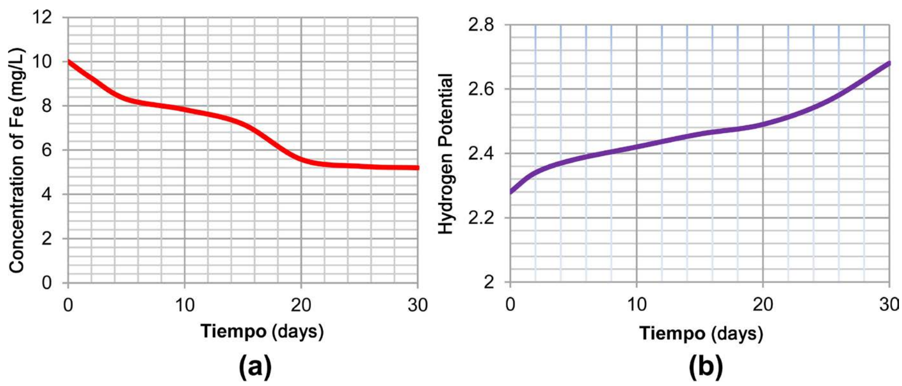

Figure 10. Concentration of iron in the solution versus time (a). Behaviour of the pH against time in the iron solution (b).

Similar studies support the results, stating that the root of *Scirpus californicus* accumulates lead, copper, chromium, nickel and arsenic [17]. In addition, the upward trend in accordance with the concentrations applied allows us to assume that the plant possibly has the capacity to tolerate concentrations greater than 2 ppm; therefore, we can infer that in new experiences we will find values higher than those found.

In general, the tolerance of plants to high concentrations of heavy metals is a function of various internal and external factors, such as phenology, vigour, growth, speciation of elements and water chemistry [18]. However, the compartmentalization of metals in the study made it possible to demonstrate the different patterns of mobility in the plant studied, considerations that must be taken into account in the remediation processes of polluted aquatic environments.

4. Conclusions

The native *S. californicus* plant showed an overall ability to significantly tolerate levels of copper, lead, zinc and iron. The absorption of copper by the root-rhizome of the native plant reached its maximum value at 30 days with 491.84 mg/kg dry, followed by the submerged stem that at 15 to 30 days remains constant with

168.45 mg/kg dry and to a lesser extent in the aerial stem that from 2 to 30 days remains constant with 11.01 mg/kg dry.

The greatest absorption of lead occurred after 30 days in the root-rhizome with 739.43 mg/kg dry, followed by the submerged stem which at 30 days was 373.01 mg/kg dry and in lesser quantity in the aerial stems which from 10 to 30 days remains constant with 4.71 mg/kg dry. Zinc absorption was higher in the root-rhizome with 830.71 mg/kg dry on average at 20 days, and then remains constant, followed by submerged stem with 295.45 mg/kg at 20 days and less in the aerial stem with 37.72 mg/kg dry at 15 days. The greatest absorption of iron occurred in the root-rhizome at 20 and 30 days remains constant with 2624.72 mg/kg dry, followed by the submerged stem that at 25 to 30 days remains constant with 475.07 mg/kg dry and less in the aerial stem that from 5 to 30 days remains constant with 162.12 mg/kg dry.

The efficiency of removing copper from the solution during the 30 days was 52.10%, for lead 53.5%, zinc 50.20% and iron 48.00%. The behavior of the hydrogen potential of the individual tests of removal of copper, lead, zinc and iron was at the beginning of 2.30 on average, which indicates that the aqueous medium is acid during the 30 days evolved in ascending form until the order of 3.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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