Dry Biomass of the Amazonian Macrophyte Paspalun Repens for Evaluation as Adsorbent Material of Heavy Metals Zn and Cu

Solenise Pinto Rodrigues Kimura[a]*, Rosimary Rodrigues dos Santos[a],

João Christian Paixão Fonseca[a], Joyce Alves da Silva[a], Raimundo Nonato Alves da Silva[a],

José Costa de Macêdo Neto[a], João Evangelista Neto[a], Bruno Mello de Freitas[a], Domitila Pascoaloto[b]

[a]*Departamento de Engenharia de Materiais, Universidade do Estado do Amazonas, Av. Darcy Vargas, 1200, 69065-020, Manaus, AM, Brazil*
[b]*Instituto Nacional de Pesquisas da Amazônia, Av. André Araújo, 2936, Manaus, AM, Brazil*

The present work aims at the preliminary evaluation of the *Paspalun repens* macrophyte dry biomass adsorbent material of zinc (Zn) and copper (Cu) metals from water. The diversity of Species is due to the extensive aquatic environment where it is inserted. The *Paspalun repens* species comes from the Buiuçu lake located in the region of Parintins-Amazonas- Brazil. The macrophyte was dried in a mill and then a digestion through biomass microwaves was done before and after its exposure to the solutions containing different concentrations of zinc and copper (1.00, 1.50, 2.00, 3.00 mg mL^{-1} of metals) for a period of 48 hours. As a source of the metals, zinc sulfate ($ZnSO_4$ $7H_2O$) for zinc, and copper sulfate ($CuSO_4$ $5H_2O$) for copper were used as the source. As a result, the efficiency of *Paspalun repens* was observed in the metals removal, the highest removal percentage, of 29.67 and 37.07% in the leaves, whereas in the root it was 25.25 and 32.84% (at the concentration 1.0 and 2.0 mg/mL consequently), was of zinc, therefore the dry biomass of this species can be considered as a low cost alternative material in the removal of these heavy metals, contributing to the improvement of water quality.

Keywords: *aquatic macrophyte, heavy metals, dry biomass*

1. Introduction

The indiscriminate use of natural resources has caused serious problems of contamination of the ecosystem, mainly due to the chemical pollution of organic and inorganic origin. Wastes with high concentrations of heavy metals require special attention due to their level of danger and the possibility of contamination of groundwater and water courses, making them often unfit for ingestion or costly in relation to abstraction, transport, treatment and distribution. The need to remove these pollutants from liquid effluents is fundamental so that metallic ions are not released into the receiving bodies in concentrations above the standards allowed by the current environmental legislation[1]. This situation has aroused in the authorities a great environmental concern and the need to elaborate effective measures to minimize it[2]. In this way, environmental legislation becomes increasingly restrictive in relation to the maximum limits allowed for the release of pollutants into the environment[3].

The diversified use over adsorbents which contemplate for efficiency in adsorption processes demonstrates a wide variant in conventional treatment methods for the removal of heavy metals from the liquid effluent. Chemical processes such as chemical oxidation, chemical precipitation and chemical reduction, membrane technologies, ion exchange (columns or resins), processes of physical separation such as filtration and sedimentation, electrochemical and sorption processes are highlighted[2]. Considering that these methods are not always efficient, it is interesting to look for alternative and technically more viable technologies when compared to conventional techniques.

The adsorption phenomenon is described as a separation process where constituents present in a fluid stream (adsorbate) are retained on the surface of a porous solid (adsorbent). Studies show that, among the existing adsorbent materials, biomasses, and in particular aquatic macrophytes, present great ability in the removal of pollutants, being well studied for the treatment of domestic and industrial effluents[3,1].

The biomasses, active and dead of macrophytes, are characterized by having functional groups in their structures that attribute them a great affinity with metallic ions. The selective affinity that metals have with the groups belonging to the surface of the biomass permits the metal/biomass interactions, which can reduce the costs of the process.

Considering the toxic effect of metals, zinc is capable of forming complexes with many organic and inorganic binders[4]. Under anaerobic conditions, and in the presence of

*e-mail: solenisekimura@yahoo.com.br

sulphides, the precipitation of zinc limits its mobility. The mobility of zinc in soil is determined by the same factors that influence its transport in the aquatic environment, that is, the solubility of its compounds, pH and salinity[5].

For humans, copper is one of the least toxic metals, and can be considered non-toxic in several exposure situations, due to its amphoteric character[6]. The excessive copper absorption by man can result in Wilson's disease, in which copper excess is deposited in the brain, pancreas, bones, myocardium, and liver[7].

In this work, the dry biomass of the *Paspalun repens* macrophyte was used as adsorbent, which is an aquatic herb of the poaceae family, of free habit emerged. It presents growth of its branches and rhizomes at great distances into the water, eventually they break off and form islands that continue to grow, reaching large expanses[8]. In another study, the species Paspalum scrobiculatum was studied as an adsorbent in textile dye effluents[9], demonstrating its potential in the removal of other pollutants.

The choice for the adsorbent is due to the fact that macrophytes have a large capacity to remove metallic ions from effluents, besides being renewable and biodegradable[10].

2. Materials and Methods

The study site called Buiuçú Lake is part of the largest river system in the world, the Amazon Basin, known for its great territorial extension, its vast biodiversity and the size of its hydrographic network.

Individuals of the *Paspalun repens* species were collected at Buiuçú Lake, in the region of Parintins/AM, under the geographical coordinates: latitude 2 ° 40'5.20 " and longitude 56 ° 42'7.18 ".

The macrophytes were separated into roots and leaves, oven dried with air circulation for 72 hours at 55 ° C, then passed through a mill with a 1 mm coupled sieve.

For the determination of Cu and Zn metal concentrations, the dry biomass was digested before and after the experiment, and after reading the atomic absorption spectrophotometer, the equipment used was a Perkin Elmer Atomic Absorption Spectrophotometer, Model 1100B, that uses a specific lamp for each metal. The solutions containing the metals were prepared from the analytical reagents zinc sulfate ($ZnSO_4.7H_2O$) and for copper, copper sulphate ($CuSO_4.5H_2O$). Solutions were prepared with the following concentrations: 1.00; 1.50; 2.00; 3.00 mg mL^{-1} of the metals (Cu and Zn).

The solutions containing the metals were packed in polyethylene containers. In each vessel, 1.00L of solution and 10g of the macrophyte dry biomass were placed in bags made of nylon fabric. At time intervals (1, 2, 3, 6, 12, 24, 36 and 48h), aliquots were collected from the aqueous solutions after the installation of the experiment[11]. After 48 hours of the experiment, the biomass was dried in an oven with air circulation for 48h at 65 ° C, comminuted and proceeded

with the digestion in the microwave for the heavy metals reading. Infrared spectroscopy with Fourier transform (FTIR) analysis was performed on a Thermo Scientific brand equipment, model Nicolet 6700, the measurement made in ATR mode using the Smart Omni Sampler accessory, in the region range of 675 to 4000 cm^{-1} and 4 cm^{-1} resolution.

3. Results and Discussion

Tables 1 and 2 show the initial and final concentrations of zinc and copper metals in the solution that remained in contact with the biomass. In all cases it is possible to observe the biomass efficiency in the removal of the metals when compared to different treatments, which is maintained with the addition of the concentrations. The values are presented in terms of removal percentage of the metals in the solution, ranging from 1.0 to 2.00 mg mL^{-1} for solution containing zinc (Table 1) and 1.00 to 3.00 mg mL^{-1} for copper solution (Table 2), demonstrating the efficiency of *Paspalun repens* in the removal of both metals.

Table 1 shows the percentages of zinc removal in the parts of the macrophyte (leaf and root), in which the leaf was the one that most absorbed this metal at all concentrations. It is known the ability of aquatic macrophytes in the removal of metals in solutions, and in most cases these elements are concentrated in the root because the translocation process for the aerial parts is usually slow[12]. However, Papalun repens presented an inverse behavior in this study. The absorbed percentages are higher for the leaves 29.67; 33.33 and 37.07% for treatments with 1.00; 1.50 and 2.00 mg mL^{-1} respectively, while the root removed 25.25; 28.28 and 32.84% at the same concentrations.

In a similar way, copper (Table 2) showed the highest removal in the leaf except for the concentration 3.00 mg mL^{-1}, which had a lower value than that obtained by the root. The accumulation of some metals, among them copper and zinc in the *Typha* and *Persicaria* macrophytes, which showed high concentrations mainly in the root, concluding that these metals were essential for the survival of the species[13]. The accumulation capacity of the metals in the macrophyte is due to the interactions of several factors such as adsorption, absorption, interaction with metabolic sites, etc., and each mechanism has not only the biological characteristics of the macrophyte, but also the conditions of the medium[12].

Figure 1 (a) and (b) show the concentration of Zn in the treatments according to the different sampling times of the solution. We can observe graphically that the best absorption time in which the maximum removal of the metals occurred varied in the interval of up to 12 hours for the concentrations 1.5 and 2.0 mg mL, from that period, it is seen a constancy, that can be attributed to saturation of the biomass, demonstrating the efficiency of metal removal in that time interval. For the concentration 1.0 mg mL^{-1} the removal occurred within the first three hours (Figure 1a).

Table 1. Zinc metal removal percentage of the initial and final concentrations of treatments for leaf and root.

Metal	Part	Treatment	Concentration (mg/mL)		
			1.00	1.50	2.00
Zn	Leaf	Initial	0.91	1.53	2.05
		Final	0.64	1.02	1.29
		% R	**29.67**	**33.33**	**37.07**
	Root	Initial	0.99	1.45	2.04
		Final	0.74	1.04	1.37
		% R	**25.25**	**28.28**	**32.84**

%R - percentage removal of metals in solution

Table 2. Metal removal percentage copper concentrations in the initial and final treatments of the leaf and root

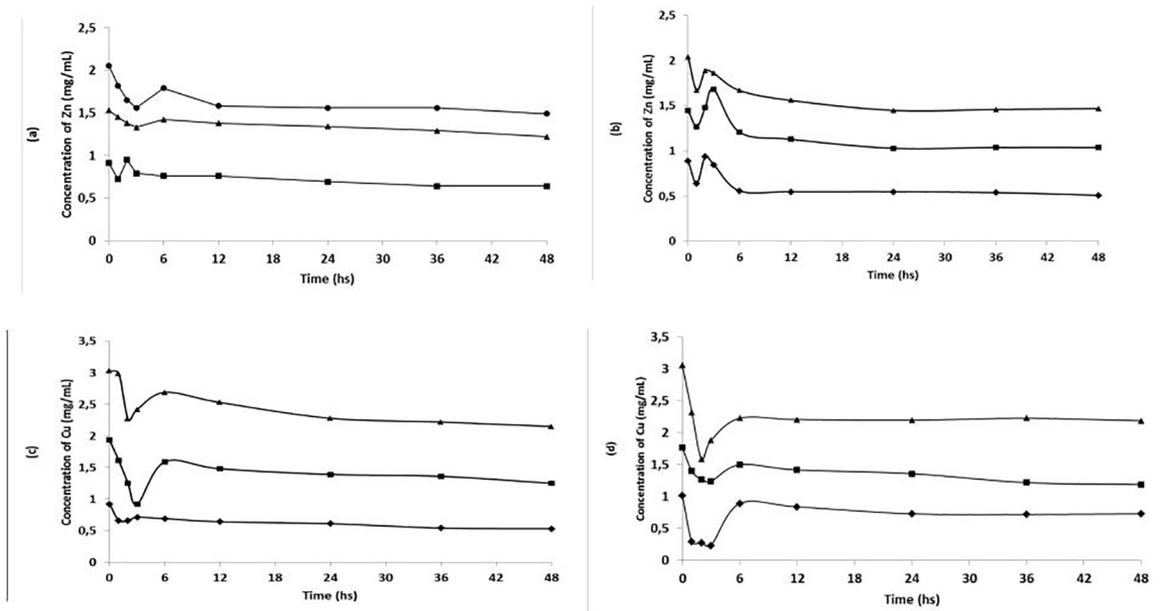| Metal	Part	Treatment	Concentration (mg/mL)		
			1.00	2.00	3.00
Cu	Leaf	Initial	1.02	1.77	3.06
		Final	0.78	1.19	2.09
		% R	**23.53**	**32.77**	**31.70**
	Root	Initial	0.98	1.93	3.03
		Final	0.77	1.36	2.05
		% R	**21.43**	**29.53**	**32.34**

%R - percentage removal of metals in solution

Figure 1. Concentration of Zn, (a) leaf, (b) root and Cu (c) leaf, (d) root in different treatments as a function of time counted with biomass.
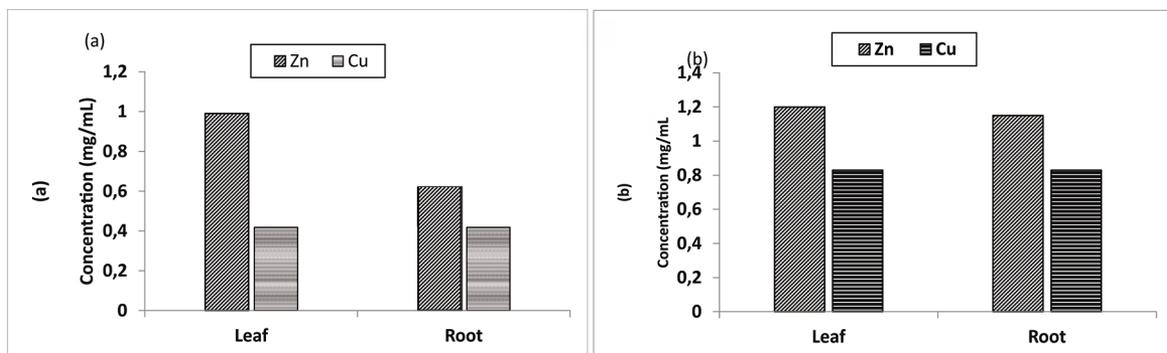
Figure 2. Accumulation of Zn and Cu in the dry biomass at concentrations 1.0mg mL^{-1} (a) and 2.0 mg mL^{-1} (b).
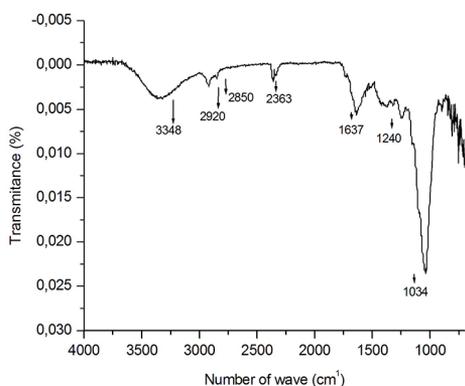

Figure 3. FTIR spectrum of the Paspalun repens leaf before exposure with the solution containing the metals.

For Cu (Figure 1c, d), it is observed that the time that the maximum removal of the metal takes place is of 12h demonstrating more efficiency of the biomass for its absorption, besides having a higher rate of removal, as shown in the Tables 1 and 2, demonstrating that the biomass under study can be efficient due to its bioaccumulative potential.

The dry biomass of the *Paspalun repens* species demonstrated efficiency in the removal of Zn (Figure 2a) accumulating the metals in its tissues mainly in the leaf. In general, it can be seen from the graphs in Figure 2 that after approximately six hours of contact with the solutions containing the metals, the biomass saturates, we can consider that the optimal adsorption time is six hours. The graph also shows that the retention of the metal in the biomass is in agreement with the increase in the concentration in the solution.

3.1 Identification of functional groups - FTIR

In the FTIR analysis (Figure 3), the strong peak 3348 cm^{-1} is attributed to OH stretch vibration, the peak near 2924-2850 cm^{-1} is the asymmetric and symmetrical vibration of the methylene (= CH$_2$), respectively. The presence of the 2363 cm^{-1} band is probably attributed to the (-COO)[14] group, the peak near 1637 cm^{-1} is the absorption range of amide II,

peak 1240 cm^{-1} is attributed to alcohol CO and peak 1034 cm^{-1} is the stretching vibration of COH.

In the aquatic plants, the removal of heavy metals from liquid effluents occurs mainly by ion exchange attributed to the presence of carboxyl groups (R-COO-) that are present on the surface of plants. Of course, these sites are linked to cations (H$^+$, Na$^+$, K$^+$, Ca^{+2}, Mg^{+2}, Fe^{+2}), however, in the presence of metals such as Cu^{+2}, Zn^{+2}, Ni^{+2}, Cd^{+2}, Pb^{+2}, Cr^{+3} there is a tendency for substitution between metals[15,16], which may explain the absorption of the metals in the leaf and root (Figure 2) of *Paspalun repens* macrophyte. FTIR results showed that dry biomass has different functional groups available for binding of heavy metal ions, such as carboxyl, phosphate, amide and hydroxide.

4. Conclusion

Preliminary data show that Paspalun repens has considerable potential for the removal of metallic ions. The results showed higher macrophyte efficiency in the removal of copper. The leaf was the part that presented greater efficiency in the retention of zinc.

The FT-IR results showed the presence of different groups of carboxyl, amide, hydroxide functional groups, these groups are capable of reacting with metal ions in aqueous solution.

Dry biomass can be used as an adsorbent for the treatment of wastewater containing the metals zinc and copper, it is an abundant natural environmental biomass and may be an alternative for more expensive materials, such as activated carbon.

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6. References

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