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DETERMINATION OF Cu, Mn AND V ADSORPTION CAPACITY IN DRY MACROPHYTE BIOMASS

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ABSTRACT

The importance of macrophytes in aquatic and wetland environments is of great importance. Among its relevant role are the applications for bioindication, phytoremediation and removal of potentially toxic elements from aquatic media. Aquatic environments have always been exposed to all types of contamination, whether natural or anthropogenic, from volcanic eruptions to the deliberate release of untreated chemical sewage. The importance of research to minimize the harmful effects caused by discharges of pollutants in water bodies is have been raising. The objective of this study was to determine the adsorption capacity of elements considered essential for plant growth at low concentrations, but acting as pollutants at high ones: copper, manganese and vanadium. The methodology used is was the cultivation of plants in an environment free of polluting charges for subsequent adsorption tests at different times and pH concentrations. The methods used to perform the measurements was INAA and GF-AAS. Copper at the concentrations used did not show favorable results for adsorption with the macrophyte biomass *Eichhornia crassipes*, *Egria densa*, *Pistia stratiotes* and *Salvinia auriculata*.

1. INTRODUCTION

Water is essential to life and all living organisms, including man, that depend on it for their survival. It can be found in various forms and states of aggregation necessary for its renewal so that it maintains and develops life. Over the time and the development of human civilizations, the multiple uses of water have produced many problems, such as its degradation and pollution [1]. Its importance for life lies in the fact that no metabolic process occurs without its direct action. Compared to other compounds, water behaves in a totally different way, especially from the physicochemical point of view, and its specific properties also guarantee its unique characteristics [2]. Therefore, aquatic environment NGOs (Non-governmental organizations), research institutions and government agencies have been highlighted the importance of the control and reduction of pollution levels [3] [4].

The scarcity of water free of any potentially contaminating agents is increasingly accentuated due to anthropogenic actions, agriculture, livestock, aquaculture, [1] urban growth and the discharge of domestic and industrial effluents that may be identified as the main launchers. However, these activities may be sources of insertion of potentially toxic elements in watercourses and reservoirs, due to pesticides used incorrectly and indiscriminately, water abstraction from regions subject to erosion, mining areas and large industries capable of dispersing large amounts of these elements into the atmosphere which return to waterways through rainfall and leaching [5] [6]. Environmental, governmental, socioeconomic problems related to the scarcity of drinking water in its various uses, whether industrial, agricultural, psychology, leisure and recreational, ecotourism, domestic, tend to be increased and aggravated by demand.

The availability of drinking water is inversely proportional in regions where the availability of water sources with characteristics of potability and quality are reduced. Given these factors, the economic valuation of water resources has increased considerably [7]. The development of actions and techniques that help in the treatment of water resources becomes urgent and necessary, since there are many sources of contamination and eutrophication of water resources [8] [1].

Stroke and water quality monitoring, water resources management are becoming increasingly necessary so that pollution problems are minimized and compromise is reduced, while ensuring minimum usage characteristics. Reliable and cost-effective monitoring and data systems available to system managers are increasingly needed [7]. Monitoring can be done through equipment or even aquatic plants that can, in a controlled manner, reduce costs and help decision-making by system managers. The water quality parameters indicated by monitoring in state of São Paulo are; temperatures, pH, total filterable and unfilterable residues, dissolved oxygen, total and fecal coliforms, nitrogen, nitrite, nitrate, ammonia, total phosphorus, soluble orthophosphate, total iron, manganese, chloride, surfactant, COD, barium, cadmium, lead , copper, total chromium, nickel, mercury, zinc, and phenol [9] [7] [10].

Iron and manganese values may increase mainly at the bottom of reservoirs, interfering with water quality. When the dissolved oxygen levels required for concentrations to remain at acceptable levels, values up to 200mg/L Fe and 100mg/L Mn can sometimes be achieved and still be considered normal. When these values are exceeded, there are difficulties in the treatment process [11].

What appears in the literature as new is the use of adsorption for water treatment. The definition of adsorption is a process where a substance is accumulated on the threshold of two phases that can be liquid-solid, liquid-liquid and can also occur in gas-liquid. What is called adsorbent is the phase in which the one that accumulates is called adsorbate, occurs on the surface between phases, promoting an increase in the concentration of substances between two phases, due to the behavior of slightly positioned atoms on the surfaces, therefore subject to attracting interactions to a surface. There are two types of adsorption, physics, also called physisorption, usually occurs by the action of low intensity intermolecular forces.

Chemisorption or chemical absorption occurs with the formation of chemical bridges between the adsorbent surface and the adsorbate molecules, according to which [12] it is relatively difficult to characterize one or another form of adsorption due to the phenomenon. occur between physical and chemical adsorption.

The macrophyte biomass for the removal of potentially toxic elements has already been used in studies for Cr, Ni, Cu, Zn, Cd and Pb adsorption [13]. Studies with the use of these materials over time have received terminology from phytoremediators or bio remediators, for their characteristics of removing unwanted elements at high concentrations of the aqueous medium. This occurs through a passive process due to physicochemical interactions between the ions and functional groups present on the surface of the biomass used as adsorbent, can occur relatively quickly and can be reversed, indicating that it can be properly used for removal. of metal ions in solution [14]. The retention of metal ions on the surface of bio sorbents can occur by several types of process, such as chemisorption, complexation, pore adsorption-complexation, ion exchange, microprecipitation, condensation of hydroxides on the biomass surface [15] [16] depending on the chemical functional groups existing in the material [17].

Over time, macrophytes have shown their capacity for use in biomonitoring studies of aquatic environments that undergo anthropogenic changes, either by communities as indicators of impacts suffered, or to act as recovery agents for disturbed water bodies. They can show the degree of impact suffered and, also have their plant matrix used as a source for determining potentially toxic and/or bioaccumulated metal agents [18] [19]. Biomass for adsorption of potentially toxic elements has gained space among alternatives with reduced costs and possibility of reversal [20].

Information on the conditions of the aquatic environment where these plants are inserted can be obtained by the occurrence of their presence, indicating that there is abundant organic matter [21]. The presence of *Eichhornia crassipes, Egeria densa, Pistia stratiotes* and *Salvinias* is a strong indicator of these situations. The use of biomass of these macrophyte species, has advantage over other treatment methods because of the low cost, abundance and easy of being found, in many places are considered invasive species.

The objective of this work is to determine the dry biomass adsorption capacity of four macrophyte species commonly found in São Paulo State reservoirs: *E. densa*, *E. crassipes, P.stratiotes* and *S. auriculata* for copper, manganese, and vanadium adsorption. Plant water content, biomass moisture content, ash content and specific surface area, pH effects, time of contact were evaluated.

2. METTHODOLOGY

2.1. Plant cultivation

For the production of biomass, macrophyte seedlings were purchased from the aqua scaping and aquarium trade, the seedlings were placed in aquariums with water supply and were in an area with natural light reception for development and growth without the use of fertilizers.

2.2. Preparation of dry macrophyte biomass samples

In the laboratory, the obtained plants were washed with deionized water, weighed and placed in a ventilated oven for drying to constant weight, weighed again and ground to a 150µm particle size, stored in polypropylene bags for further analysis. To determine the amount of water in each macrophyte, the samples were weighted before and after the first drying.

2.3. Physical chemical biomass characterization

In the moisture determination, 4 porcelain crucibles were washed, and oven dried at 100°C for 60 minutes, one gram of dry and ground biomass sample from each of the macrophytes were weighed, the crucibles with the biomass were placed in an oven at 110 ± 5°C for drying for 72 hours, cooled in a desiccator and weighed again.

In the ash determination, 4 porcelain crucibles were washed and oven-dried at 450°C for 90 minutes, the crucibles were weighed and 1.000 ± 0.005g of dry and ground biomass each was added. After the macrophytes, the crucibles with the biomass were then placed in an oven at 450 ± 20°C for 4 hours, left in a desiccator for 20 hours for acclimatization and weighed again.

For alkaline chemical activation of the samples the following procedure was applied: 30g of dry biomass of each macrophyte were added to 0.1 Mol.L^{-1} NaOH solution for 24 hours, the liquid phase was removed and the wetted part was dried in a ventilated oven at 60 ± 5 °C to constant weight for new milling and sieving up to 150µm particle size, stored in polypropylene bags for adsorption tests with solutions containing the elements of interest in this work.

To determine the specific surface area (S) 1.5g of dried and grounded macrophytes biomass samples were added to 50 ml of 0.1 mol L^{-1} HCl solution, then 30 grams of NaCl and ultrapure water were added up to 150mL. The specific surface area was determined for untreated biomass, activated with HCl solution and with NaOH solution. For the titration, the pH was adjusted to 4 with a 2 mol L^{-1} NaOH solution. Titration was performed with a standard 0.1 mol L-1 NaOH solution until the pH changes from 4 to 9 and become stable. The value of S was obtained by using equation 1.

$$\boxed{S=32.V-25} \tag{1}$$

Being:
S: specific area in square meters per gram;
V: volume in milliliters of sodium hydroxide.

2.4 Evaluation of the adsorption parameters

To evaluate the pH effect on the adsorption process, 0.500 ± 0.005 mg of dry biomass of each activated alkaline macrophyte biomass were added to 30 ± 2mL of solutions containing the ions of interest: Cu, Mn, and V. The solutions were prepared by diluting standard solutions (SPEX - Certiprep) with initial concentration of 1000 mg.L^{-1} diluted in ultra-pure water. The pH of each solution was adjusted for testing at pH 2, 4, 6, 8 and 10 and stirred for 30 minutes, then the liquid phase was separated by centrifugation for 20 minutes at 3500 rpm, an aliquot of 1.00 ± 0.02mL from each test was pipetted onto filter paper for drying under infrared light for further irradiation, and the resulting concentration calculated.

The best pH test result was used to test the contact times influence, starting at 5, 15, 30, 60 and 120 minutes of stirring, then the mixtures were centrifuged for 20 minutes at 3500 rpm and the liquid phase separated. An aliquot of 1.00 ± 0.02mL from each test was pipetted onto filter paper for drying under infrared light for further irradiation and the resulting concentration calculated.

The best results in contact time tests were used for the evaluation of initial solution concentration. All tests cited were performed in duplicate.

For the determination of adsorption capacity (qe) equation 2 was used.

$$qe - \frac{(C_f - C_i)V}{m} \tag{2}$$

where:

C_i is the initial concentration of the solution ($mg.L^{-1}$), Ct is the concentration at a given measurement time ($mg.L^{-1}$), V is the volume in liter (L) and m the adsorbent mass in gram (g).

2.5 Sample Activation for determination final concentration (INAA).

The Instrumental Neutron Activation Analysis INAA is a widely used method to identify and measure low concentrations of elements present in multi-element solid and liquid samples, with or without previous treatment [24]. The samples containing the elements Mn and V were analyzed using irradiation in the IEA-R1 Reactor (IPEN-CNEN/SP Nuclear Reactor) for 20 seconds under approximately $1.9 \times 10^{12}\ cm^{-2}\ s^{-1}$ thermal neutron flux. After irradiation, the samples were transferred to an HPGe EG & G detector (Ortec model) and Maestro software was used to obtain the spectra, which was converted into readable data in Microsoft Excel spreadsheet via CAX softwere [23], to calculate final concentrations.

2.6 Graphite Furnace Atomic Absorption Spectrometry (GF-AAS).

Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) is a sensitive method for quantitative determinations from the measurement of the transmitted radiation intensity converted to an analytical signal by a detector [25].

The analysis by GF-AAS technique aims to determine the concentration of the element Cu in samples of non-activated and chemically activated biomass, before and after its use as adsorbent, as well as in the solutions used in adsorption testes. Biomass samples, before and after treatment, were digested in HNO_3 and H_2O_2. Solutions used in the adsorption testes were taken before and after cupper solutions being treated with the biomass. Analysis were done in a Perkin Elmer's model AAnalyst 800 GF AAS equipment at LAN / IPEN-SP Atomic Absorption Laboratory. For this purpose, Cu solutions were prepared from stock solutions of this element in 0.2% (v / v) HNO_3 (Merck), used as diluent, to construct the calibration curve. This equipment is accompanied by the Winlab 32 program for AAS version 6.2.0.0079 (Perkin Elmer). Cu concentrations were determined from the peak absorption area using the linear regression mode for curve fitting. The linearity of the calibration curves can be visually checked at the time of measurement as well as by the linear correlation coefficient of the curves.

3. RESULTS AND DISCUSSION

Table 1 shows the values of water content and percent of ash in each type of live macrophyte. All species presented high values of water content giving a yield in biomass varying from 3.4 to 7.8%. The ash content as well as the moisture content, calculated in the basis of dry mass, were very similar for the four plants.

Table 1: Water content in each type of macrophyte.

Macrophyte	% water	% ash	% moisture
E. crassipes	92.2	12.7	1.4
E. densa	95.6	10.7	1.5
P. stratiotes	95.3	10.2	1.4
S.auriculata	96.6	11.7	1.7

Results for the specific surface area are shown in table 2. The analysis of the obtained values indicates higher values do S when treated with alkaline solution than with acid one. For this reason, all the samples were alkaline treated for the adsorption studies.

Table 2: Results for specific surface area in $m^2.g^{-1}$ of the evaluated biomass.

Macrophyte	No treatment		Activated w/ HCl		Activated w/NaOH	
	Mean	DP	mean	SD	mean	SD
E. crassipes	257	4	277	10	292	0
E. densa	267	4	264	3	378	54
P. stratiotes	333	5	340	68	369	14
S. auriculata	484	3	479	10	503	14

During the adsorption tests, it was observed that the addition of biomass to the solution caused an increase in its pH. Due to this fact the pH of the solutions was adjusted before and after the addiction of the biomass.

Figures 1, 2, 3 and for shows the results obtained for the effect of pH and the time contact for Mn adsorption in the four studied macrophytes. Results shows that Mn adsorption in all the biomass is pH dependent and it is favored in pH values of 4, the characteristics can be observed for all biomasses, except for E. densa. Adsorption capacity (qe) and percentage removal were higher at the initial times between 5 and 15 minutes and the percentage of removal decreases over time indicating that Mn adsorption changes also depends on contact time. The biomass obtained from E. densa was not efficient in manganese adsorption and the opposite occurred the solution after the adsorption test presented higher concentrations than before, indicating that desorption of Mn from the sample could be occurred. The highest values of adsorption capacity were obtained with S. auriculata biomass with more than 95% of removal from the solution.

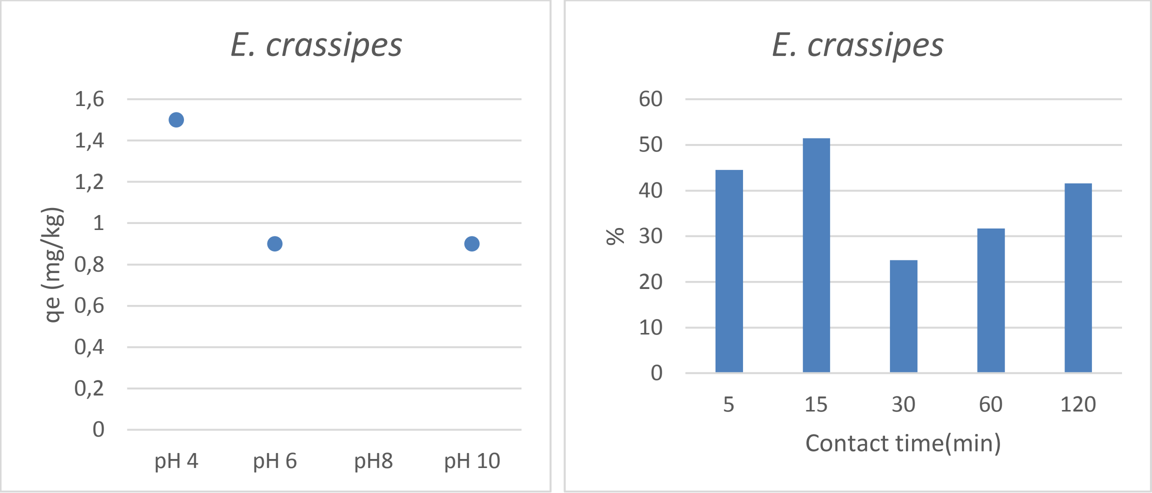

Figure 1 - Adsorption capacity (qe, mg/kg) and removal efficiency (%) as a function of pH for manganese ion in *E. crassipesa*, biomass.

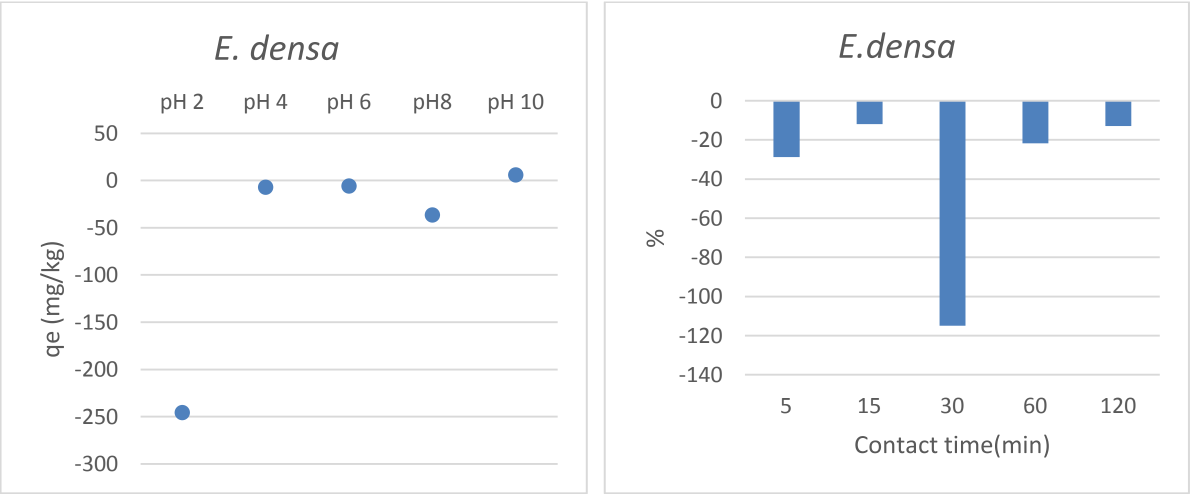

Figure 2 - Adsorption capacity (qe, mg/kg) and removal efficiency (%) as a function of pH for manganese ion in *E. densa* biomass.

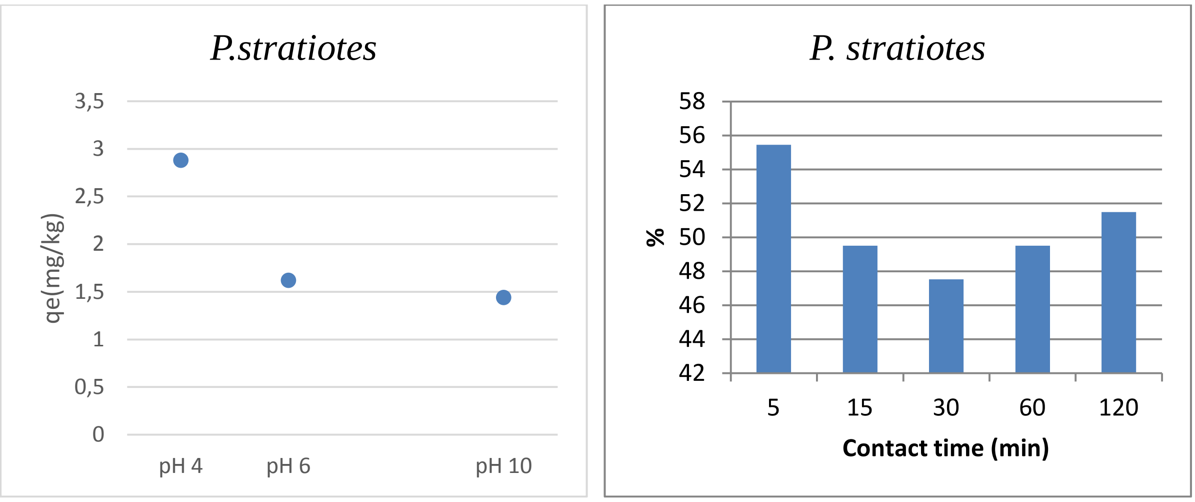

Figure 3 - Adsorption capacity (qe, mg/kg) and removal efficiency (%) as a function of pH for manganese ion in *P. stratiotes* biomass.

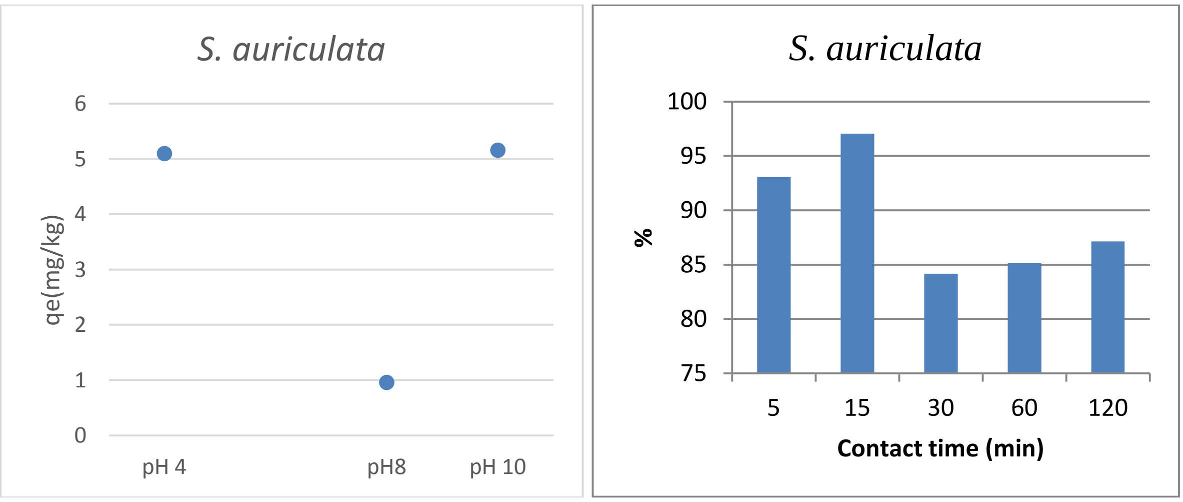

Figure 4 - Removal efficiency (qe, mg / kg) and adsorption capacity (%) of Mn ions as a function of contact time in *S. auriculata* biomass

Figures 5, 6, 7 and 8 shows the results for the effect of pH and the time contact for vanadium adsorption in the four studied macrophytes.

All biomasses have shown promise in the use as adsorbent of this element in solutions where it is present. In the sample of E. crassipes, the removal values occurred in all pH ranges, and pH 6 presented higher values. When observing the percentage of removal as a function of time, it was noted that the highest values were also between 5 and 15 minutes for all macrophytes biomass. For E. densa biomass, the values were all below 60% for all times tested for both removal efficiency and adsorption capacity. The sample of S. *auriculata* biomass showed significant values for adsorption capacity and removal efficiency showing its potential for use in the removal of vanadium in solutions or effluents with this element.

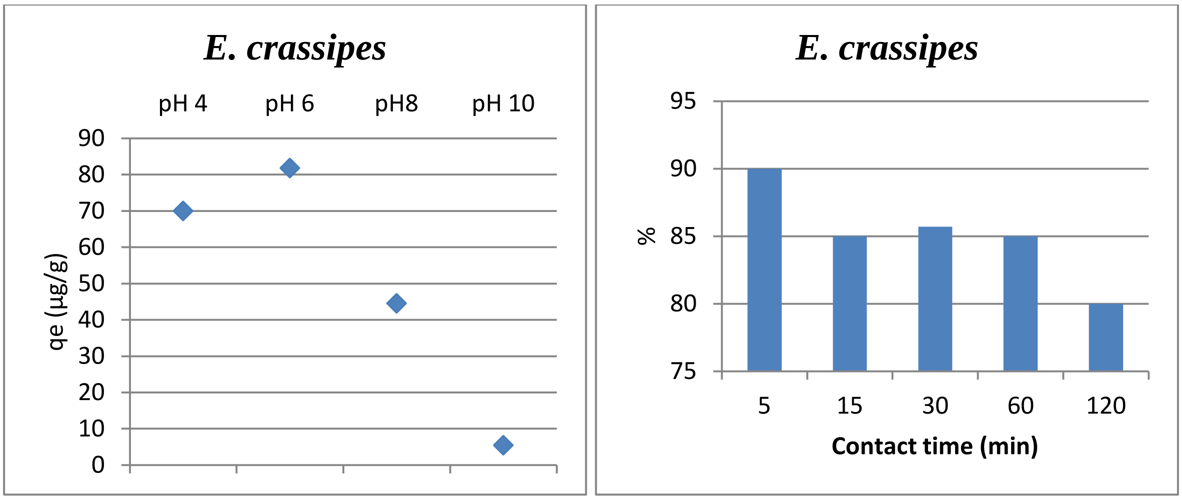

Figure 5 - Removal efficiency (qe, mg / kg) and adsorption capacity (%) of vanadium ions as a function of contact time in *E. crassipes* biomass.

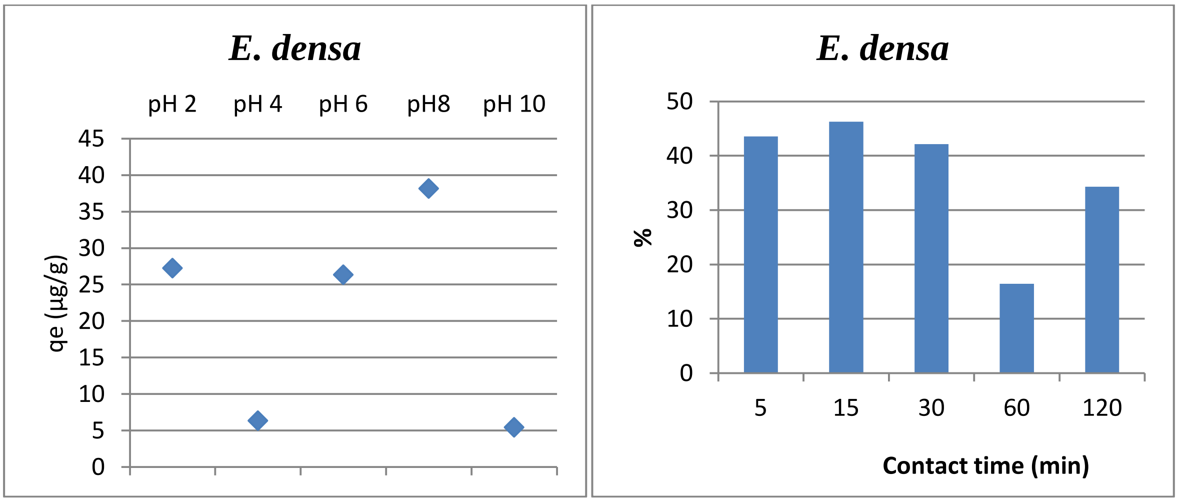

Figure 6 - Removal efficiency (qe, mg / kg) and adsorption capacity (%) of vanadium ions as a function of contact time in biomass of *E. densa*.

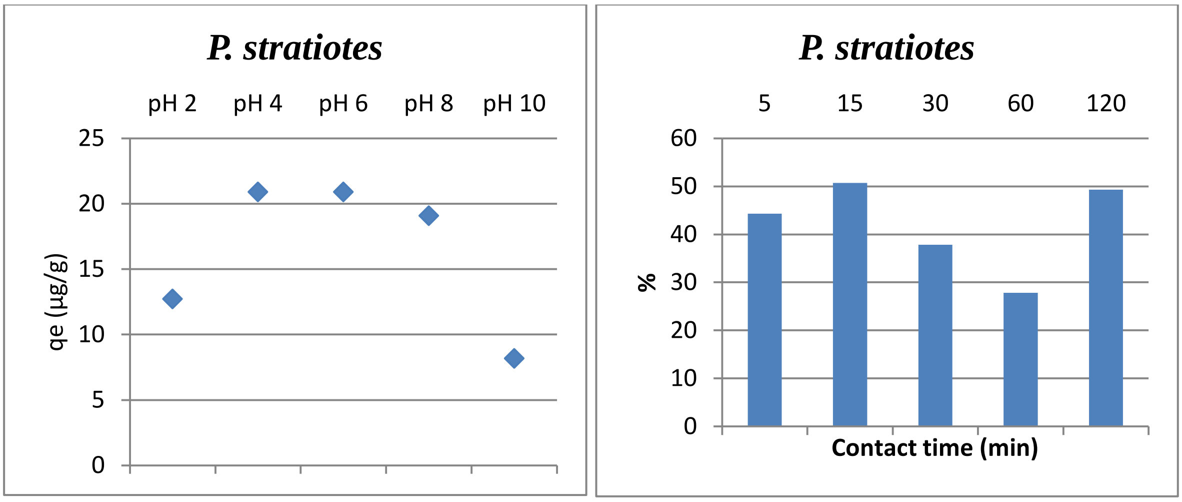

Figure 7 - Removal efficiency (qe, mg / kg) and adsorption capacity (%) of vanadium ions as a function of contact time in biomass of *P.streatiotes*

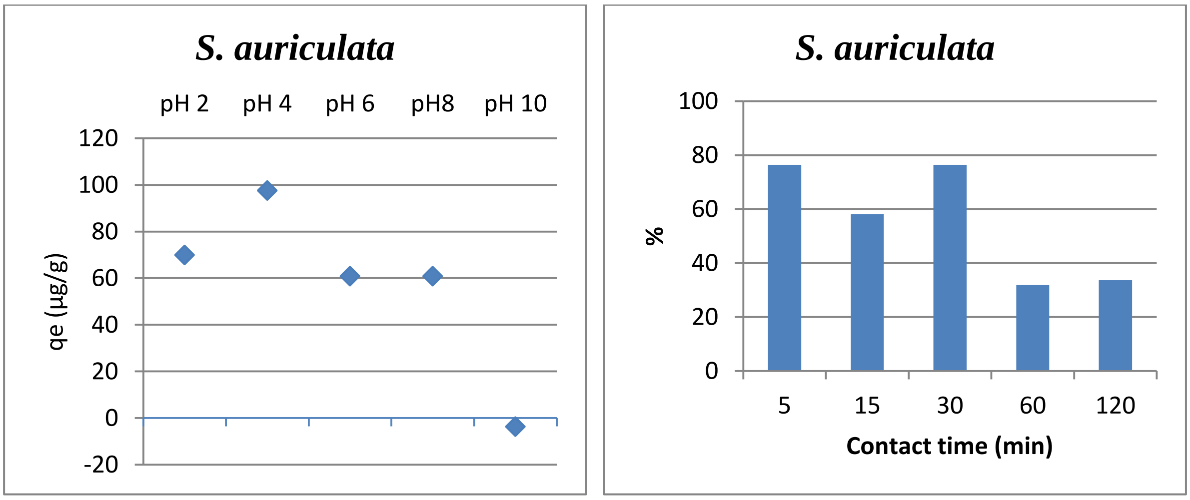

Figure 8 – Removal efficiency (qe, mg / kg) and adsorption capacity (%) of vanadium ions as a function of contact time in biomass of *S. auriculata*.

In the conditions in which the adsorption experiments were conducted, no one of the macrophytes biomass showed satisfactory results for Cu removal from solution.

3. CONCLUSIONS

In this study, it was used the macrophyte biomass of *Eichhornia crassipes, Egeria densa, Pistia stratiotes* and *Salvinia auriculate* grown in controlled environment to test their adsorption capacity for the ions of Cu, Mn and V. Measurement of ash content indicated that after calcination 13% less of the original mass remains. The determination of moisture in dry biomass indicated a low water content in the obtained product. Specific surface area measurements indicated that biomass treated with 0.1 mol.L^{-1} NaOH was higher than the biomass acid treated. It was observed that the pH of the initial solution is changed by the addition of biomass. The influence of contact time and pH involved in the adsorption process of copper, manganese and vanadium ions from aqueous solution was also verified. The favorable contact time for manganese and vanadium removal from solution ranged from 5 to 15 minutes in pH 4 using the *S. auriculata* biomass. No favorable response to the use of macrophyte biomass adsorption was obtained for cupper in the conditions that this study was performed. Nevertheless, the results obtained showed that *S. auriculata* biomass can be used as a low-cost alternative, easily obtained adsorbate.

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