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Use of Alternative Residues for Adsorption of Chemical Elements from River Sediment

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ABSTRACT

The present study aimed to evaluate the efficiency of pollutant adsorption in river sediment, through the use of agro-industrial residues and a macrophyte plant. Rice husk, due to its characteristics such as low density and very low nutritional value, has been discarded irregularly in the open sky. Therefore, this residue can be used as an adsorbent to remove undesirable substances in the aqueous medium. In addition, malt bagasse (barley) from breweries has been used as an adsorbent of contaminants in wastewater, through biosorption, as it is low cost and has a natural biomass of great relevance to the environment. Some species of aquatic plants, like baroness macrophyte (Eichhornia crassipes), are phytoremediation agents, helping to improve water quality through the remediation, extraction, immobilization, containment and degradation of contaminants. Therefore, an experiment was set up, under laboratory conditions, with a randomized block design, whose treatments were composed by the relation: Sediment(S)/water hyacinth, Sediment/barley, Sediment/rice husk, Sediment/barley + water hyacinth and Sediment/barley + rice husk, equal to 100S/0; 75S/25; 50S/50; 25S/75; 0S/100, with three repetitions. After statistical analysis of the extracts collected and analyzed at seven and 15 days, it was noticed that the results presented demonstrated that the adsorption of calcium, magnesium, sodium and potassium was more effective at eight days of contact of the sediment with the rice husk, water hyacinth and barley.

Keywords: *Rice husk, Barley, Baroness macrophyte, Biosorbent, Sediment.*

INTRODUCTION

One of the most serious problems faced by society is environmental pollution, defined as the action of contaminating water, soil and air. In addition, water pollution is the most serious, as it is the result of human actions, due to the inadequate disposal of domestic, agricultural and industrial waste in rivers.This pollution directly affects the passage of sunlight through the waters, decreasing the natural aquatic photosynthetic activity and simultaneously causing the toxicity of these ecosystems [1].

The constant urban and population growth contributes to this scenario of environmental degradation. Industrial and agricultural effluents are the most aggressive to the environment, as they generate large volumes of solid waste to be accumulated and discarded in dumps and landfills. An example of these residues is the rice husk [2].

According to [2] and [3], the Brazilian rice crop produced an average of 12 million tons of rice in the 2018/2019 harvest. For every 100 kg of rice, around 68 kg of grains, 10 kg of bran and 22 kg of rice husk were obtained; that is, the amount of bark generated in Brazil is approximately 15 million tons per year.

Due to its abrasive morphology, low density, low nutritional value, fibrousness and difficult degradability, its use is limited, corroborating for its disposal in the open-air and in river banks.Although there are some alternatives for the use of rice husks, such as: manufacture of blocks for civil construction, heat generation, animal feed, fertilizer and soil correction, it continues to be discarded in a harmful way; therefore, it can be conveniently used to remove unwanted species in aqueous media, as an adsorbent for ions [2].

According to Law no. 12,305/10, Art. 9, the National Solid Waste Policy establishes guidelines for the management and administration of waste, putting into practice sustainable consumption, specifically the nongeneration of waste, its reduction, reuse, recycling, treatment and, finally, their environmentally correct destination. The volume of solid waste generated daily in industries has been bringing a series of environmental, social, economic and administrative problems, all linked to the increasing difficulty of implementing a system or process for the proper disposal of this waste, as stated in the Law. Brazil is a country that generates immeasurable numbers of residues from industrial waste[4].

The beer industry is one of the most important for the economy; annually, an average of 185 billion liters of beer are consumed worldwide. For every 100 liters of beer produced, 20 kg of dry waste and 85% of the total solid waste from the production process are generated [5, 6].

Brazil produces about 2.6 million tons / year of wet waste (malt bagasse) from the brewery. Along with industrial growth, there is also an increase in the generation of by-products and waste, constituting a problem from the environmental point of view, due to its composition that contains high levels of carbohydrates, proteins, fats and fibers, giving it a chemical oxygen demand (COD) about 100 times greater than that of domestic sewage, acting as a source of contamination in the environment [7, 8].

In view of this scenario, it is necessary to reuse industrial waste, especially solid waste, as in the case of malt bagasse, enabling the reduction or elimination of environmental impacts, caused by their incorrect disposal, adding to the legal requirements regarding destination of such residues produced by the brewing industries. Biosorption has been a more accessible alternative compared to other technologies for water treatment, due to its low cost, because it has a natural biomass and of great relevance to the environment [8, 9].

Phyto remediation of organic compounds is the technology used with plants to remedy, degrade, extract, immobilize or contain soil and water contaminants, as it is a low-cost operation technique. Some species of aquatic plants are used to improve water quality, such as the macrophyte *Eichhornia crassipes* [10].

Macrophytes are plants capable of absorbing nitrogen in the form of ammonium, nitrate and amino acids. *Eichhornia crassipes*, belonging to the Pontederiáceas group, is a floating aquatic herbaceous plant, with dense, feathery and dark roots, measuring 20 to 50 cm in height. It has a fast vegetative reproduction, which occurs through the multiplication of seedlings originated from the stolons that the plant emits. In the Brazilian territory, it presents productivity values of up to 1,000 kg/ha/day, having several nomenclatures: mururé, moreru, baroness, camalote, water lily and water hyacinth [10, 11, 12].

The treatment of wastewater using macrophytes is quite attractive due to low operating costs, where the simplest solution for the final destination of this biomass is the disposal in landfills. However, sustainable alternatives for reusing biomass have been sought, such as: use for biogas generation, composition of animal feed and composting treatment for fertilizer production [13].

This work’s objective was to evaluate the efficiency of adsorption of chemical elements of the river sediment, through the use of agro-industrial residues and macrophyte plant aiming at the use of these residues so that they are not disposed incorrectly and do not pollute the environment.

Materials and Methods

The experiment was conducted at the Analytical Chemistry Laboratory, on the 8th floor of Block D, at the Science and Technology Center of Universidade Católica de Pernambuco, Recife, Pernambuco, Brazil.

Materials Preparation

The sediment subsamples were collected from the Jaboatão River, on Comporta Road, 200, in the municipality of Jaboatão dos Guararapes, Pernambuco, Brazil, in geographic coordinates 1 = 8°11'13.41"S; 34°57'26.12"W; 2 = 8°11'11.80"S; 34°57'28.29"W;and 3 = 8°11'12.35"S; 34°57'26.82"W. These subsamples were mixed to form a composite sample, with the following characteristics: Apparent density, g/cm^3 = 1.05; Real density, g/cm^3 = 2.49; Degree of flocculation, % = 32; Texture class = clay loam; Natural clay, % = 25; Residual humidity, % = 2.75; Humidity 0,33 atm, % = 56.80; Humidity 15 atm, % = 28.14; Available water, % = 28.66; pH (H_2O) = 5.70; Calcium in Ca^{2+} - $cmol_c$ / dm^3 = 4.00; Magnesium in Mg^{2+} - $cmol_c$ / dm^3 = 1.10; Sodiumin Na^+ - $cmol_c$/dm^3= 0.34; Potassiumin K^+ - $cmol_c$/dm^3 = 0.20; Sum of Exchangeable Bases (S) - $cmol_c$ / dm^3 = 5.60; Cation Exchange Capacity (CEC) - $cmol_c$ / dm^3 = 10.3; Base Saturation (V) - % = 55, according to the methodology of the Brazilian Agricultural Research Corporation[14].

The samples of baroness or water hyacinth (*Eichhornia crassipes*) were collected at Apipucos Weir, Apipucos neighborhood, Recife, Pernambuco, Brazil. They were dried in an air-circulating oven at 60 ° C. After bromatological analysis, the following results were obtained: Dry matter - DM, %= 90.77; Mineral matter - MM, % = 36.08; Total nitrogen - TN, % = 2.73; Total protein - TP, % = 17.06; Acid detergent fiber - ADF, % = 49.74; Neutral detergent fiber - NDF, % = 77.14; Non-nitrogen extract - NNE, % = 3.2; Total fiber - TF, % = 42.14; Ethereal extract - EE, % = 1.52; Sodium-Na^+, % = 0.56; Potassium- K^+, % = 0.91; Calcium-Ca^{2+}, % = 2.80; Magnesium-Mg^{2+}, % = 3.10, according to Official Methods of Analysis[15].

The brewery residue (malt or barley bagasse) was acquired in a beer industry located in the municipality of Jaboatão dos Guararapes, Pernambuco, Brazil. It was dried in an oven with air circulation, at 60 ° C, for bromatological analysis, with the following results: Dry matter - DM, %= 78.30; Mineral matter - MM, % = 34.22; Total Nitrogen - TN, % = 3.90; Total protein - TP, % = 24.37; Acid detergent fiber - ADF, % = 28.83; Neutral detergent fiber - NDF, % = 50.30; Non-nitrogen extract - NNE, % = 43.16; Total fiber - TF, % = 24.13; Ethereal extract - EE, % = 4.12; Sodium-Na^+, % = 0.03; Potassium- K^+, % = 0.06; Calcium- Ca^{2+}, % = 3.80; Magnesium- Mg^{2+}, % = 3.00, according to Official Methods of Analysis[15].

The rice husk residue was purchased from a rice processing plant located in the municipality of Cabrobó, Pernambuco, Brazil. The samples were dried in an oven with air circulation, at 60 ° C, and analyzed bromato logically, with the following results: Dry matter - DM, %= 91.28; Mineral matter - MM, % = 15.12; Total Nitrogen - TN, % = 0.56; Total Protein - TP, % = 3.50; Acid detergent fiber - ADF, % = 52.12 Neutral detergent fiber - NDF, % = 85.20; Non-nitrogen extract - NNE, % = 30.28; Total fiber - TF, % = 50.12; Ethereal extract - EE, % = 0.98; Sodium- Na^+, % = 0.14; Potassium - K^+, % = 0.07; Calcium- Ca^{2+}, % = 5.20; Magnesium-Mg^{2+}, % = 4.32, according to Official Methods of Analysis [15].

All samples of baroness, barley and rice husk residues were ground in a forage crusher (Wiley), at the Agronomic Institute of Pernambuco - IPA, Recife, Pernambuco, Brazil, being sieved through 14 mesh sieves to obtain uniform granulometry, according to the Brazilian Association of Technical Standards - NBR 6.923/81[16] and NBR 8.112/83 [17].

Experiment and Statistical Treatment

The experimental design used was that of random blocks, whose treatments were composed by the relation presented in Table 1, with three replications, in a total of 75 experimental units (beakers of two liters of capacity).

Table1. *Treatments used to set up the experiment with alternative residues*

Relation	Treatments				
Sediment/Baroness	100S/0B	75S/25B	50S/50B	25S/75B	0S/100B
Sediment/Barley	100S/0C	75S/25C	50S/50C	25S/75C	0S/100C
Sediment/Rice husk	100S/0A	75S/25A	50S/50A	25S/75A	0S/100ª
Sediment/Barley + Baroness	100S/0CB	75S/25CB	50S/50CB	25S/75CB	0S/100CB
Sediment/Barley + Rice husk	100S/0CA	75S/25CA	50S/50CA	25S/75CA	0S/100CA

One liter of de ionized water was added to each beaker and, after seven and 15 days, extracts were collected, by vacuum filtration, and determined pH and electrical conductivity, using the methods ASTM D1293-12 [18] and ASTM D1125-14 [19] respectively; sodium and potassium by flame emission spectro photometry; calcium and magnesium by complexation titrimetry. The data obtained were submitted to statistical analysis, generating Box Plot type graphics, using the software PAST 10.0.

Results and Discussion

It is worth noting that T0 (sediment without any treatment = control), T1 (sediment after eight days of contact with the residues) and T2 (sediment after 15 days of contact with the residues), will be considered as a relevant point in all the results presented here.

Statistical Data Processing

From the data from the determinations made in the treatments used, it was necessary to statistically validate them before any type of investigation. The first step was to ensure that T1 and T2 presented results with the least possible variation and were statistically relevant. For this, the coefficient of variation (CV) and points outside the curve (outliers) were calculated where the criteria were adopted in accordance with [20]:

CV≤0.1 →excellent data obtained (low dispersion);

0.1< CV ≤ 0.2 → good data obtained (medium dispersion);

0.2< CV ≤ 0.3 →bad data (high dispersion);

CV >0.3 → bad data.

Where: Cv= $\frac{\sigma}{Xm}$ (Ratio between standard deviation and mean)

Outlier ≤ 2

Where: O=$|\frac{Xi-Xm}{\sigma}|$ (Absolute ratio between the point difference by the mean and the standard deviation)

The criterion adopted was to purge the values that did not meet the statistical standards so that they do not generate inconsistencies in the data analysis, as shown in Table 2 for the CV values at times T1 and T2 of the pH, EC, Ca, Mg, Na and K. The values highlighted in bold will be disregarded in the analysis process.

Table2. *Results of coefficient of variation (CV) for the determinations carried out in treatments T1 (sediment after eight days of contact with the waste) and T2 (sediment after 15 days of contact with the waste). Boldvalueswillbediscarded.*

Treatments	pH		EC		Ca		Mg		Na		K	
	T1	T2	T1	T2	T1	T2	T1	T2	T1	T2	T1	T2
1	0.19	0.03	0.00	0.02	0.00	0.06	0.00	**0.46**	0.07	0.07	0.00	0.00
2	0.03	0.02	0.01	**0.63**	0.00	0.14	0.00	0.15	0.12	0.18	0.00	0.00
3	0.02	0.01	0.00	0.14	0.08	0.03	0.11	**0.83**	0.05	0.10	0.00	0.00
4	0.02	0.01	0.00	0.03	0.04	**0.24**	0.05	**1.01**	**0.41**	**0.43**	0.14	0.13
5	0.04	0.03	0.12	0.17	0.06	**0.53**	0.16	**1.6**	0.19	0.00	0.02	0.29
6	0.17	0.03	0.02	0.03	0.03	**0.44**	0.20	**0.24**	0.05	**2.85**	0.01	0.19
7	0.13	0.02	0.01	0.06	0.13	**0.42**	**0.24**	**0.95**	0.04	0.14	0.00	0.76
8	0.06	0.02	0.05	0.16	0.12	**0.28**	**0.21**	**0.28**	0.05	0.07	0.00	0.00
9	0.02	0.02	0.03	0.05	0.08	0.14	0.12	**0.44**	0.09	0.09	0.00	0.00
10	0.01	0.03	0.01	**0.22**	0.05	0.13	**0.45**	**0.47**	**0.34**	0.00	0.12	0.26
11	0.08	0.04	0.00	0.16	0.00	0.12	0.15	**0.26**	0.08	0.00	0.00	0.25
12	0.05	0.01	0.01	0.02	0.00	0.04	**0.21**	0.04	**0.10**	**0.57**	0.00	0.10
13	0.03	0.02	0.00	0.01	0.00	0.12	0.05	0.16	**0.21**	0.00	0.00	0.09
14	0.03	0.02	0.01	0.04	0.00	0.00	**0.23**	0.05	0.00	0.00	0.00	0.05
15	0.04	0.04	0.00	0.12	0.00	0.08	0.07	0.05	0.00	0.00	0.00	0.38

Where: S = sediment; A = rice (husk); B = baroness/water hyacinth; C = barley. 1= 75S25B; 2 = 50S50B; 3 =25S75B; 4 =75S25C; 5 =50S50C; 6 =25S75C; 7 =75S25CB; 8 =50S50CB; 9 =25S75CB; 10 =75S25CA; 11 =50S50CA; 12 =25S75CA; 13 =75S25A; 14 =50S50A; 15 = 25S75A.

As the treatments vary with time, with high CV values for T1 and / or T2, it makes the next statistical evaluations of them impossible. Therefore, the data obtained in determining the CV factor was:

- pH: all treatments performed well in their variations;
- Electrical Conductivity (EC): treatments 2 (50S50B) and 10 (75S25CA) obtained dispersion above the minimum required, and it is not possible to use these data for the following steps;
- Calcium: treatments 4 (75S25C), 5 (50S50C), 6 (25S75C), 7 (75S25CB) and 8 (50S50CB) obtained dispersion above the minimum required, and it is not possible to use their data for the following steps;
- Magnesium: treatments 2 (50S50B), 13 (75S25A) and 15 (25S75A) obtained dispersion within the expected; therefore, the other treatments will not have the data used for the next steps;
- Sodium: treatments 4 (75S25C), 6 (25S75C), 10 (75S25CA), 12 (25S75CA) and 13 (75S25A) obtained dispersion above the necessary minimum, making it impossible to use the data for the sequence;
- Potassium: all treatments performed well in their variations.

Another relevant point regarding the coefficient of variation (CV) data is that they can be combined disregarding the time differences between the first and the second treatment, in order to increase the amount of data, in order to reduce the variation. However, this effect was not considered favorable from the point of view of the variation of treatments over time. It can be said that in view of these results, the adsorption and decontamination process is directly affected by time T1 and T2 (Tc).Table 3 presents these results together with the values obtained from Outliers (O), where the values in bold will be disregarded in the analysis process.

Table3. *Outlier (O) and coefficient of variation (CV) results for the determinations made in treatments T1 (sediment after eight days of contact with the residues) and T2 (sediment after 15 days of contact with the residues) combined (Tc). Bold values will be discarded.*

Treatments	pH		EC		Ca		Mg		Na		K	
	CVTc	O	CVTc	O	CVTc	O	CVTc	O	CVTc	O	CVTc	O
1	0.13	0.75	**0.68**	0.77	**0.29**	0.77	**0.60**	0.75	0.09	0.75	**0.43**	0.77
2	0.03	0.71	**1.05**	0.77	**0.44**	0.78	**0.85**	0.74	0.16	0.75	**0.43**	0.77
3	0.15	0.72	**0.41**	0.73	**0.76**	0.76	**2.59**	0.77	0.08	0.72	**0.42**	0.77
4	0.05	0.77	**0.80**	0.72	**0.26**	0.72	**0.57**	0.72	**1.75**	0.77	**0.39**	0.75
5	0.07	0.72	**0.70**	0.72	**0.45**	0.77	**2.89**	0.75	**1.39**	0.67	**0.34**	0.72
6	0.12	0.75	**0.80**	0.73	**0.42**	0.70	**0.82**	0.76	**1.11**	0.77	**0.23**	0.68
7	0.15	0.72	**0.85**	0.75	**0.40**	0.69	**14.30**	0.69	**0.27**	0.71	**0.64**	0.77
8	0.09	0.76	**0.78**	0.71	**0.39**	0.77	**0.77**	0.75	**0.27**	0.76	**0.42**	0.00
9	0.05	0.75	**0.89**	0.75	**0.32**	0.76	**0.70**	0.73	0.11	0.75	**0.42**	0.00
10	0.07	0.74	**0.82**	0.77	**0.15**	0.74	**1.60**	0.76	**1.60**	0.71	**0.30**	0.75
11	0.06	0.73	**0.88**	0.74	**0.34**	0.74	**0.45**	0.73	**1.54**	0.77	**0.24**	0.74
12	0.08	0.76	**0.86**	0.70	**0.43**	0.76	**0.86**	0.72	**2.02**	0.77	**0.24**	0.77
13	0.05	0.73	**0.86**	0.73	**0.64**	0.76	0.13	0.74	**4.62**	0.74	0.06	0.77
14	0.02	0.74	**0.86**	0.73	**0.94**	0.82	**4.30**	0.74	**4.35**	0.82	0.03	0.71
15	0.03	0.76	**0.84**	0.74	**0.34**	0.77	**0.20**	0.74	**1.84**	0.82	**0.24**	0.77

Where: *S = sediment; A = rice (husk); B = baroness/water hyacinth; C = barley. 1= 75S25B; 2 = 50S50B; 3 = 25S75B; 4 = 75S25C; 5 = 50S50C; 6 = 25S75C; 7 = 75S25CB; 8 = 50S50CB; 9 = 25S75CB; 10 = 75S25CA; 11 = 50S50CA; 12 = 25S75CA; 13 = 75S25A; 14 = 50S50A; 15 = 25S75A.*

Determinations Made

pH

The determination of the pH in the sediment before going through the treatments is characterized in Fig.1 through the acronym T0 with a result of 5.7, that is, slightly acidic and below the reference value of Conama Resolution n. 357/2005 (6.0 to 9.0).This is in line with the local environmental conditions: fauna, flora, organic load on the river, external contamination. After that, the tests were carried out with eight and 15 days (T1 and T2 respectively), for all the proposed treatments.

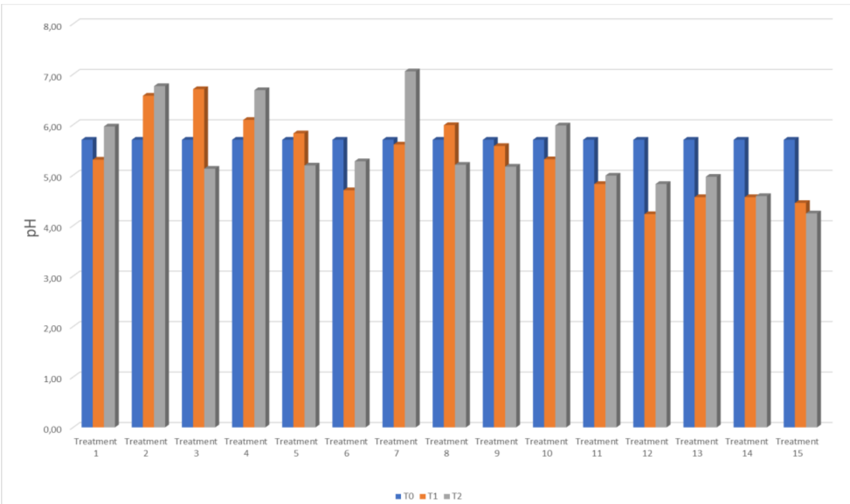

Fig1. *pH variation curve in T1 (sediment after eight days of contact with the residues), T2 (sediment after 15 days of contact with the residues) and T0 (control) for the treatments1= 75S25B; 2 = 50S50B; 3 = 25S75B; 4 = 75S25C; 5 = 50S50C; 6 = 25S75C; 7 = 75S25CB; 8 = 50S50CB; 9 = 25S75CB; 10 = 75S25CA; 11 = 50S50CA; 12 = 25S75CA; 13 = 75S25A; 14 = 50S50A; 15 = 25S75A. Where: S = sediment; A = rice (husk); B = baroness/water hyacinth; C = barley, with a 95% confidence interval.*

Treatments 2 (50S50B) and 4 (75S25C) were the only ones that obtained an increase in the pH value after the first week of treatment (T1) and remained on the rise in this value in the second week of treatment (T2).For the other tests, a reduction in the pH value was observed, occurring in T1 and / or T2. Treatments 3 (25S75B), 5 (50S50C) and 8 (50S50CB) had the behavior of increasing the pH value in T1, and then decreasing their values in T2.Treatments 1 (75S25B), 6 (25S75C), 7 (75S25CB), 10 (75S25CA), 11 (50S50CA), 12 (25S75CA), 13 (75S25A) and 14 (50S50A) obtained a behavior where in T1 the values of pH dropped in relation to T0 and then showed an increase in T2, an increase that came to exceed the value in the initial time T0.

Treatments 9 (25S75CB) and 15 (25S75A) had the behavior of decreasing in the pH value in T1 and T2, comparing with the pH value in T0.

It is important to note that the studies already carried out by [21] indicated that the *Moringa oleifera* seed proved to be efficient in removing water turbidity and removing metals, without causing a change in pH; it proves to be a viable and significant alternative in the treatment of water in places where salt concentrations are present.A possible assumption for these different results may be the fact that, in the present study, the substance tested was waste, which presents considerable levels of salts. [22] obtained results that related low pH values with high levels of MO (greater than 10%) in a state of decomposition, which was not found in the present study.

Electrical Conductivity (EC)

Electrical conductivity is the parameter that determines the concentration of ions that are present in a given medium; for this research, the value of 13.43 µS / cm was obtained in T0. Fig. 2 shows the process of evolution of electrical conductivity results after eight and 15 days of treatment.

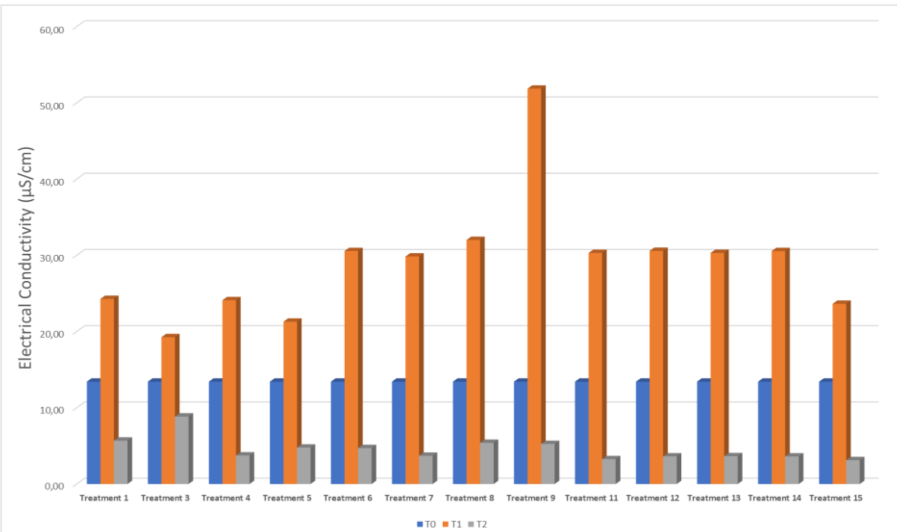

Fig2. *Electric Conductivity variation curve (µS / cm) in T1 (sediment after eight days of contact with the residues), T2 (sediment after 15 days of contact with the residues) and T0 (control) for the treatments1= 75S25B; 2 = 50S50B; 3 = 25S75B; 4 = 75S25C; 5 = 50S50C; 6 = 25S75C; 7 = 75S25CB; 8 = 50S50CB; 9 = 25S75CB; 10 = 75S25CA; 11 = 50S50CA; 12 = 25S75CA; 13 = 75S25A; 14 = 50S50A; 15 = 25S75A.Where: S = sediment; A = rice (husk); B = baroness/water hyacinth; C = barley,with 95% confidence interval.*

It is possible to show the same behavior of conductivity in all treatments. After the two weeks of treatment (T1 and T2) the values reached a peak in the conductivity value and, subsequently, a decrease, being below the conductivity value in T0.The highlights were the treatments 9 (25S75CB), the highest peak with EC of 51.86 µS / cm, and 15 (25S75A), which registered the largest decrease in EC with a value of 3.13 µS / cm.

According to studies by [23] for samples highly contaminated by sewage, conductivity can vary from 100 to 10,000 µS / cm.Therefore, having a maximum limit of 100 µS / cm for good quality water,it can be said that in the collected section the water is in an acceptable condition.

Calcium (Ca2+)

For calcium, in percentage terms, the treatments that most contributed to adsorption were 14 (50S50A) with 97% in T1 (sediment after eight days of contact with the waste) and 60% in T2 (sediment after 15 days of contact) with residues) compared to T0 (control) whose concentration was 801.6 mg/ l.In other words, the calcium desorption process, for treatment 14 (50S50A), had a relevant performance after eight days of contact of 50% of the sediment with 50% of rice husk.

Evaluating the specific performance of calcium in T2 (sediment after 15 days of contact with the residues), treatments 11 (50S50CA) and 15

(25S75A) stand out, for adsorption of 92.1% and 92.8% respectively of their initial fraction (T0 = 801.6 mg/l).These two treatments also stand out not only for keeping the adsorbed calcium for another eight days, but for reducing the values even further when compared to T0 as mentioned above.

Fig. 3 shows the adsorption of calcium in T1 (sediment after eight days of contact with the residues), T2 (sediment after 15 days of contact with the residues) and T0 (control) for accepted treatments: 1= 75S25B; 2 = 50S50B; 3 = 25S75B; 9 = 25S75CB; 10 = 75S25CA; 11 = 50S50CA; 12 = 25S75CA; 13 = 75S25A; 14 = 50S50A; 15 = 25S75A.

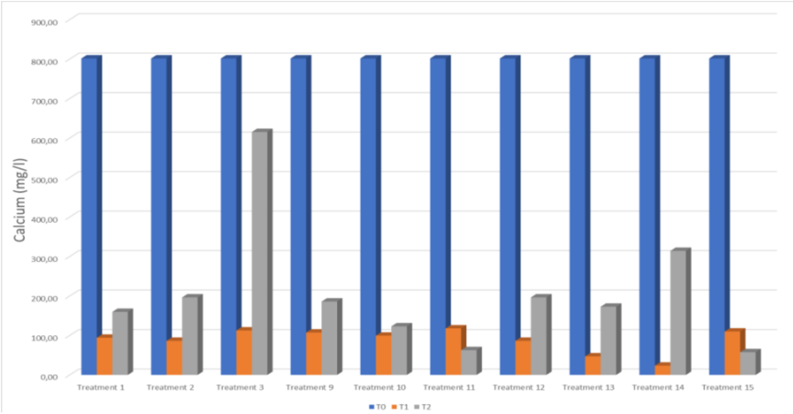

Fig3. *Calcium concentration curve (mg / l) in T1 (sediment after eight days of contact with the residues), T2 (sediment after 15 days of contact with the residues) and T0 (control) for the treatments 1= 75S25B; 2 = 50S50B; 3 = 25S75B; 9 = 25S75CB; 10 = 75S25CA; 11 = 50S50CA; 12 = 25S75CA; 13 = 75S25A; 14 = 50S50A; 15 = 25S75A. Where: S = sediment; A = rice (husk); B = baroness/water hyacinth; C = barley.*

It can be concluded that treatments 11 (50S50CA) and 15 (25S75A) demonstrate a greater capacity over time to keep calcium adsorbed in their structures, but in terms of greater reduction in less time, the treatment stands out 14 (50S50A).Also noteworthy is treatment 3 (25S75B) which, at the end of every experiment, obtained the smallest difference in T0 and T2 in relation to the desorption process, that is, almost all the calcium retained in its structure was returned to the medium.This phenomenon of desorption is also highlighted in Fig. 4, where the average percentage of adsorption was analyzed considering the conditions evaluated in T1 and T2.

Fig. 4 shows the values of the percentage of calcium adsorption as a function of T1 (sediment after eight days of contact with the residues), T2 (sediment after 15 days of contact with the residues) and T0 (control) with 95% confidence interval.

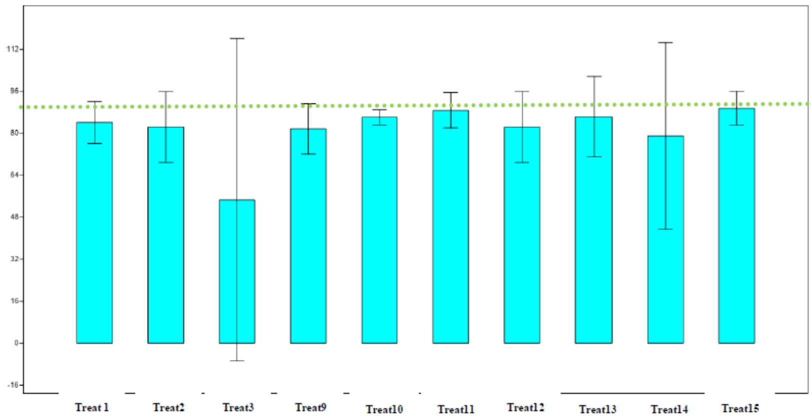

Fig4. *Calcium adsorption curve (mg / l) at T1 (sediment after eight days of contact with the residues), T2 (sediment after 15 days of contact with the residues) and T0 (control) for the treatments (treat)1= 75S25B; 2 = 50S50B; 3 = 25S75B; 9 = 25S75CB; 10 = 75S25CA; 11 = 50S50CA; 12 = 25S75CA; 13 = 75S25A; 14 = 50S50A; 15 = 25S75A. Where: S = sediment; A = rice (husk); B = baroness/water hyacinth; C = barley,with 95% de confidence interval.*

Therefore, it can be seen in Fig.4 that treatments 11 (50S50CA) and 15 (25S75A), independent of T1 and T2, showed greater adsorption of calcium from the sediment with 88.7% and

89.5% respectively. Through laboratorytests [24] realized that the seeds with crushed or ground *Moringa oleifera* bark are equally effective in adsorption of calcium from 1.005.0 mg / l to 894.6 mg / l (11%), with 60 minutes of contact with desalination reject.

Magnesium (Mg^{2+})

The results obtained in the adsorption of magnesium according to Fig. 5, obtained two distinct characteristics: two treatments (13 = 75S25A and 15 = 25S75A) managed to retain the magnesium molecules in T1 (54.67 and 39.32 mg / l respectively) and still resisted to T2 with slight desorption; treatment 2 = 50S50B had a sharp decrease in magnesium concentration in T1 (18.41 mg / l) compared with T0 (133.72) but had high desorption, returning practically 100% of the magnesium concentration present in the T0 sample.

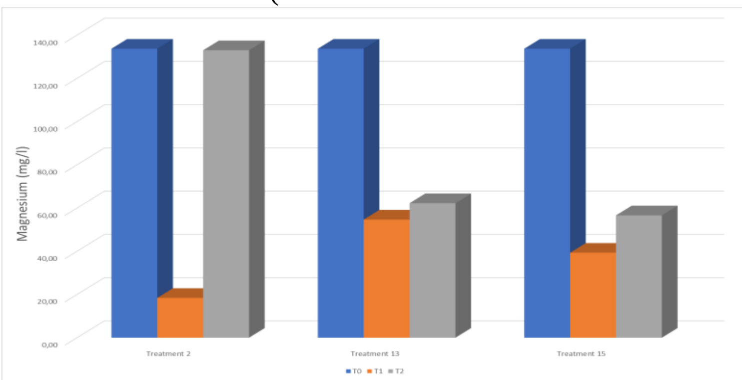

Fig5. *Curve of magnesium concentration (mg / l) in T1 (sediment after eight days of contact with the residues), T2 (sediment after 15 days of contact with the residues) and T0 (control) for treatments2 = 50S50B; 13 = 75S25A; 15 = 25S75A. Where: S = sediment; A = rice (husk); B = baroness/water hyacinth; C = barley.*

When the adsorption capacity is taken into account over time, the treatments are able to decrease the magnesium concentration, especially treatment 15 (25S75A) with the capacity of approximately 60% magnesium adsorption. Treatment 13 (75S25A) is still below the previous treatment even considering the maximum peak of the 95% confidence interval. It was also evident in Fig. 6, through the statistical data of the confidence interval, that treatment 2 (50S50B) has a great adsorption capacity, but also releases Magnesium into the medium in practically the same proportions.

A study carried out by [25], reached the same result: the researcher proved that the powder of *Moringa oleifera*seeds in contact with the organic material of the well water reduces the hardness value in the period of 24 hours.

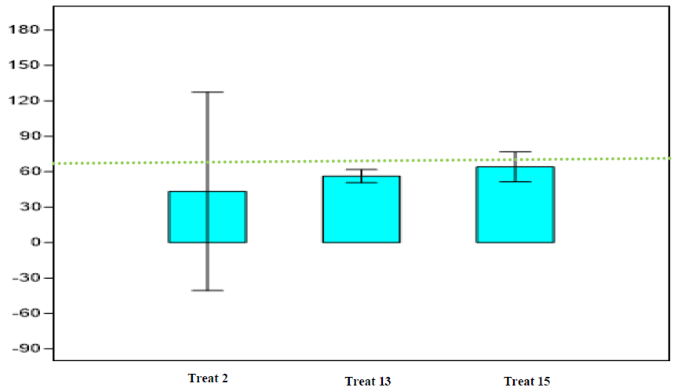

Fig6. *Magnesium adsorption curve (mg / l) in T1 (sediment after eight days of contact with the residues), T2 (sediment after 15 days of contact with the residues) and T0 (control) for the treatments (treat) 2 = 50S50B; 13 = 75S25A; 15 = 25S75A. Where: S = sediment; A = rice (husk); B = baroness/water hyacinth; C = barley,with 95% confidence interval.*

Sodium (Na^{+})

In Figs. 7 and 8 it can be seen that treatments 1 = 75S25B, 7 = 75S25CB, 8 = 50S50CB and 9 = 25S75CB showed higher sodium adsorption at time T1 (sediment after eight days of contact with the residues) compared to time T2 (sediment after 15 days of contact with the residues).Treatments 2 = 50S50B and 3 = 25S75B showed higher sodium adsorption at time T2 (sediment after 15 days of contact with the residues). Such behaviors were sufficient to show values above the T0 sample (control).

This result was also obtained by [26], in surveys carried out with ground seeds of vegetable loofah, pumpkin, almond, moringa, algaroba, umbu, umburana and mulungu. In order to verify which of these seeds would present the highest sodium adsorption.

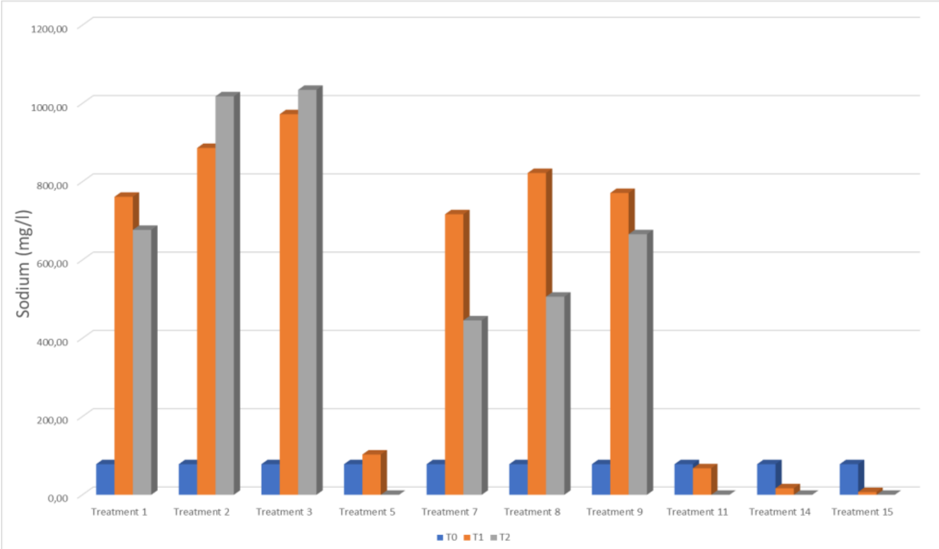

Fig7. *Sodium concentration curve (mg / l) in T1 (sediment after eight days of contact with the residues), T2 (sediment after 15 days of contact with the residues) and T0 (control) for treatments 1= 75S25B; 2 = 50S50B; 3 = 25S75B; 5 = 50S50C; 7 = 75S25CB; 8 = 50S50CB; 9 = 25S75CB; 11 = 50S50CA; 14 = 50S50A; 15 = 25S75A. Where: S = sediment; A = rice (husk); B = baroness/water hyacinth; C = barley.*

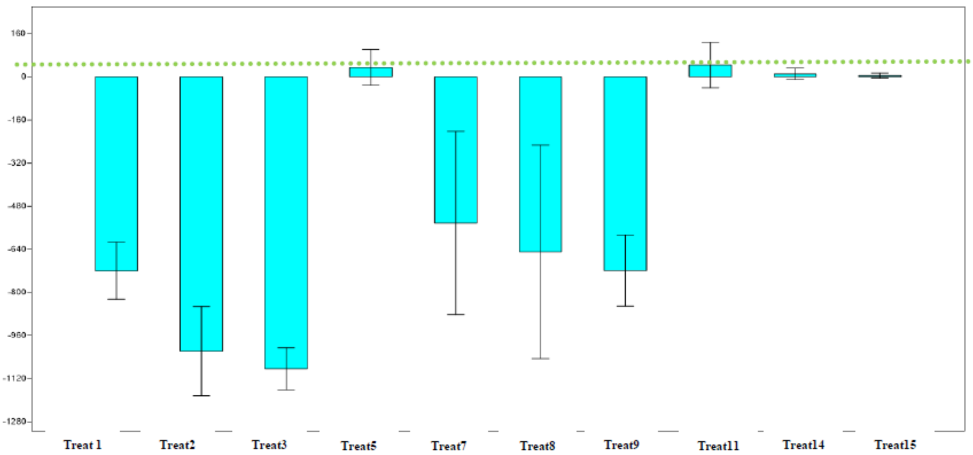

Fig8. *Sodium adsorption curve (mg / l) in T1 (sediment after eight days of contact with the residues), T2 (sediment after 15 days of contact with the residues) and T0 (control) for the treatments (treat)5 = 50S50C; 10 = 75S25CA; 14 = 50S50A; 15 = 25S75A. Where: S = sediment; A = rice (husk); B = baroness/water hyacinth; C = barley, with 95% confidence interval.*

Potassium (K+)

The analyzes related to the potassium adsorption process (Figs. 9 and 10) obtained results distributed in two blocks: the first, with a slight adsorption in T1 (sediment after eight days of contact with the residues), despite being below the values found for T0 (control) for all treatments (1= 75S25B; 2 = 50S50B; 3 = 25S75B; 4 = 75S25C; 5 = 50S50C; 6 = 25S75C; 7 = 75S25CB; 8 = 50S50CB; 9 = 25S75CB; 10 = 75S25CA; 11 = 50S50CA; 12 = 25S75CA; 13 = 75S25A; 14 = 50S50A; 15 = 25S75A); then, the second block where six treatments (1 = 75S25B; 2 = 50S50B; 3 = 25S75B; 7 = 75S25CB; 8 = 50S50CB; 9 = 25S75CB) showed significant potassium adsorption at time T2 (sediment after 15 days of contact with the residues) indicating the fraction of the baroness/water hyacinth present and above the T0 values (control). [27] using the macrophyte *Tripogandradiurética* in an alkali metal adsorption experiment in sediments from the Arroio Araçá microbasin, Canoas, Rio Grande do Sul, observed a good correlation with potassium concentrations, demonstrating to be a reasonable bio accumulator of this element.

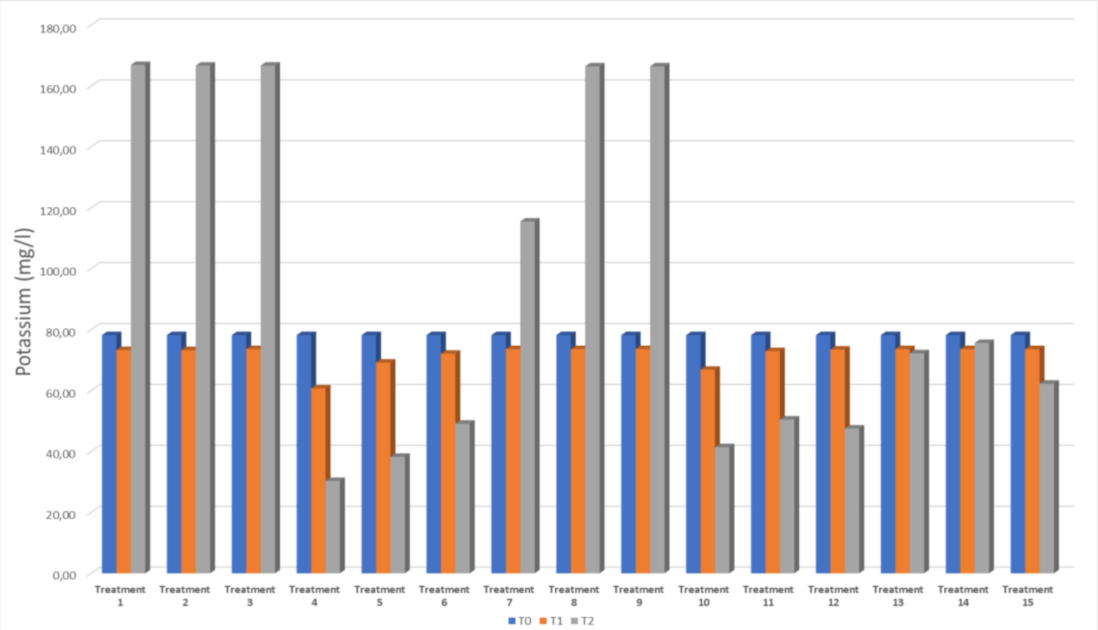

Fig9. *Potassium concentration curve (mg / l) at T1 (sediment after eight days of contact with the residues), T2 (sediment after 15 days of contact with the residues) and T0 (control) for the treatments 1= 75S25B; 2 = 50S50B; 3 = 25S75B; 4 = 75S25C; 5 = 50S50C; 6 = 25S75C; 7 = 75S25CB; 8 = 50S50CB; 9 = 25S75CB; 10 = 75S25CA; 11 = 50S50CA; 12 = 25S75CA; 13 = 75S25A; 14 = 50S50A; 15 = 25S75A.Where: S = sediment; A = rice (husk); B = baroness/water hyacinth; C = barley.*

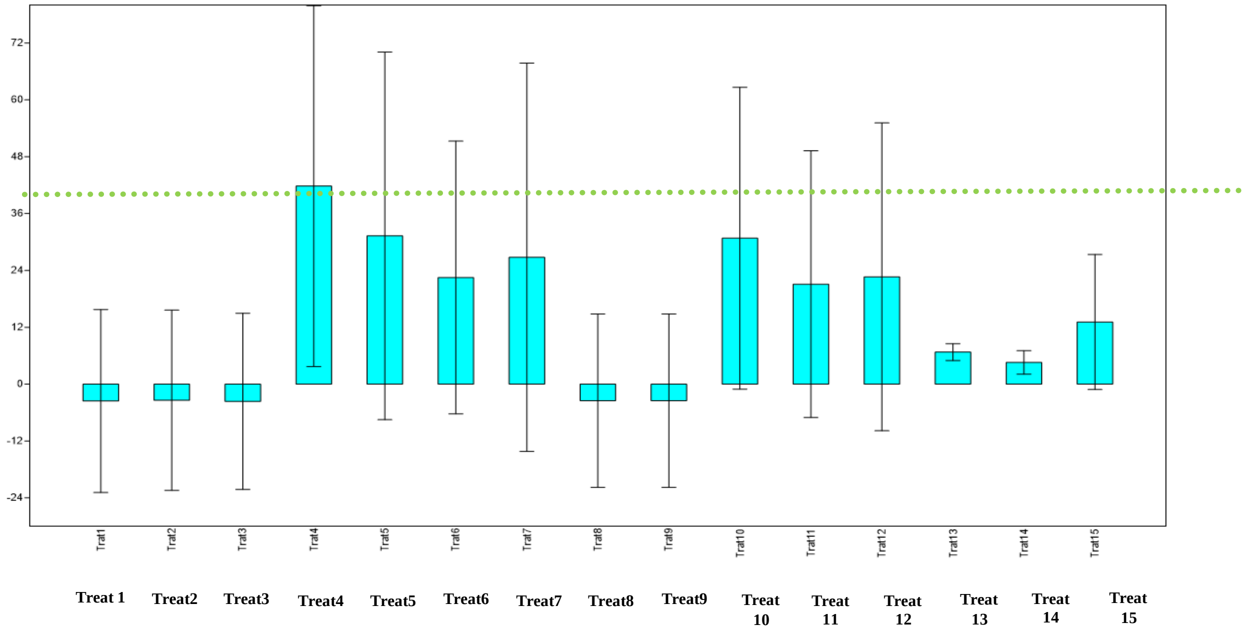

Fig10. *Potassium concentration curve (mg / l) at T1 (sediment after eight days of contact with the residues), T2 (sediment after 15 days of contact with the residues) and T0 (control) for the treatments (treat)1= 75S25B; 2 = 50S50B; 3 = 25S75B; 4 = 75S25C; 5 = 50S50C; 6 = 25S75C; 7 = 75S25CB; 8 = 50S50CB; 9 = 25S75CB; 10 = 75S25CA; 11 = 50S50CA; 12 = 25S75CA; 13 = 75S25A; 14 = 50S50A; 15 = 25S75A.Where: S = sediment; A = rice (husk); B = baroness/water hyacinth; C = barley,with 95% confidence interval.*

CONCLUSION

The studies and research of this work only add more legitimacy to the profitable potential of using alternative waste. However, the profitability of the system must be considered as a point of less relevance, since the important gain is the reduction of the environmental impact caused by the deposition of residues on the soil surface, as well as the uncontrolled reproduction of *Eichhornia crassipes* causing eutrophicity in water bodies

All the results presented showed that the adsorption of calcium, magnesium, sodium and potassium was more effective after eight days of contact (T1) of the sediment with the residues, mainly rice husk (A), baroness/water hyacinth (B) and barley (C) .

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