E-ISSN: 2583-9667
Indexed Journal
Peer Reviewed Journal
https://multiresearchjournal.theviews.in/

Received: 07-12-2023
Accepted: 13-01-2024

INTERNATIONAL JOURNAL OF ADVANCE RESEARCH IN MULTIDISCIPLINARY

Volume 2; Issue 1; 2023; Page No. 100-104

Use of natural macroalgae and chemically modified macroalgae for removal of heavy metal cations in aqueous medium

[1]Luana Lins de Andrade, [2]Yvan Jesus Olortiga Asensios and [3]Sidney Fernandes

[1]Degree in Biological Sciences, UNIP Campus Santos, Brazil
[2]Teacher at of Institute of the Sea, UNIFESP Campus Baixada Santista, Brazil
[3]Biologist of Institute of the Sea, UNIFESP Campus Baixada Santista, Brazil

Corresponding Author: Luana Lins de Andrade

Abstract

This study aimed to obtain biosorbents based on seaweed, which can be used to remove heavy metal cations present in aqueous systems. Evaluate the ability to remove cations by natural algae and chemically modified algae. Taxonomic and chemical characterization of these algae was carried out and then two stages of biosorption tests where the first with the purpose of estimating the biosorption potential of the metal Co (II) and the second with the intention of understanding the variables involved in the biosorption process. of the chosen seaweed. The concentration of elements and / or chemical substances in macroalgae will serve as indicators of pollutants and probably new contributions to science, since, to date, no study on the topic has been carried out in the metropolitan region of Baixada Santista. Through this information, one can have subsidies for long-term ecological studies in the sense of local preservation. Among the observations made, it was found that the macroalgae bioaccumulated many substances such as calcium (Ca), chlorine (Cl) and Silicon (Si) in high concentrations as shown in the graphs, but nothing that could harm the fauna, flora and fauna. population that happens to have contact with water, other sampling will be carried out in different places in order to have different results. In addition to serving as bioaccumulators for heavy metals as shown in the graphs, they also served as a shelter for small animals, found several times. It is believed that with the continuation of the project we will have rich information about the importance of macroalgae for the environment, helping the recovery of seas and oceans where anthropic action may have occurred.

Keywords: Biosorption, marine macroalgae, heavy metals

Introduction

Seaweed is used as a raw material for products such as medicines, fuels, cosmetics, paints; and also serve as animal and human food (Teixeira, 2013) [1]. Benthic marine algae can be divided into chlorophyceous (green algae), rhodophyceous (red algae) and pheophyceous (brown algae), among which brown algae have greater efficiency in removing heavy metals [Mehta and Gaur (2005) [2]; Guimarães *et al*. (1982)] [3].

This study aims to obtain biosorbents based on marine algae present on the coast of Baixada Santista, which can be used to remove contaminating heavy metal cations Cd2+ and Pb2+ present in aqueous systems and seek the recovery of aquatic environments through marine macroalgae, making them viable the sustainable use of the surrounding communities and making them viable for fauna and flora. The anthropic changes observed over the years, mainly in the 70s and 80s, where industrial expansion occurred in Cubatão, affected directally the local water bodies, as well as the environment itself. The biota, water and sediments of the estuarine area between the cities of Cubatão and Santos have been considered contaminated mainly by Hg, as a result of the presence of an important industrial hub that encompasses petrochemicals, fertilizer industries, steel mills, among others (Luiz-Silva *et al*., 2002) [4]. This study will allow evaluating the removal capacity of Cd2+ and Pb2+ cations by natural algae and chemically modified algae, collected on the coast of Baixada Santista; modify natural algae by chemical treatment based on acid protonation (HCl); characterize natural and modified algae using different physicochemical techniques. The structural polysaccharides of the algal cell wall are mainly responsible for the affinity that these chemical structures present to adsorb metallic cations in solution. These cations can adsorb coordinately on the surface functional groups of the polysaccharides (Costa & França, 1996) [5]. Seek the recovery of aquatic environments, making them usable for both the local population and the species that need it for drinking water or nesting there. The suppression of aquatic ecosystems in the region and predatory exploitation are concerns, leading us to carry out this project.

Materials and Methods

In this study, 2 phases of biosorption tests were carried out. The preliminary test (first phase) was carried out with 6 algae selected and sampled from Cibratel Beach, Itanhaém, Baixada Santista in order to estimate the biosorption potential of the metal Co (II) by each one in its natural form and after chemical treatment, with potassium permanganate.
The second phase of tests was carried out only with the alga *Ulva lactuca*, which had the best performance among the 6 algae in the first phase, with the intention of understanding the variables involved in the biosorption process of this alga (contact time, biosorbent concentration, treatment chemical).

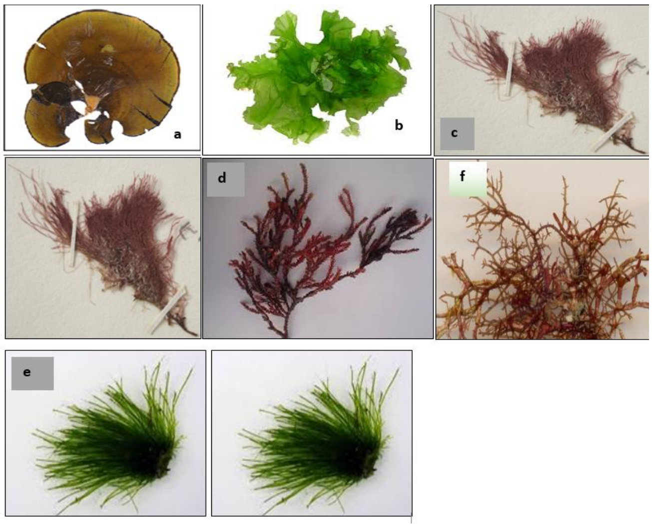

Fig 1: Algae used in this study: a) *Padina gymnospora*; b) *Ulva lactuca*; c) *Centroceras clavulatum*; d) *Bryothamnion seaforthii*; e) *Hypnea spinella*; f) *Chaetomorpha anteninna*.

Biomass Preparation

Initially, the sampled algae were washed with distilled water to remove contaminants that could interfere with the results. They were then taken to an oven at a temperature of 60 °C for 24 hours to dry and subsequently crushed in a Tecnal® knife mill until we obtained a powder.
Part of the biomass resulting from each alga was oxidized following the proportion of 10 g of algae powder to a solution of 10 mM potassium permanganate mixed at 30 ºC for 30 min. in a mixer. The biomass was filtered, washed with distilled water and dried again at 70 ºC for 8 h and stored. Another part was left untreated.

Synthetic Effluent Containing Cobalt (CO II)

An artificial effluent containing 100 ppm of cobalt in distilled water was prepared from salt Cobalt (II)

Nitrate (Co $(NO_3)_2$. 6 H_2O).

First Phase

Biosortion Tests

Biosorption tests were carried out in bottles containing 25 mL of effluent and 0.0250 g of each biosorbent (biosorbent: effluent ratio 1 g/L). This solution was mixed in a GoStirrer® rotational shaker at 500 rpm for 3 h at a temperature of 25 ºC. Subsequently, the solution was filtered using quantitative filter paper and analyzed using ICP-OES (Varian) to quantify metal removal in each condition.

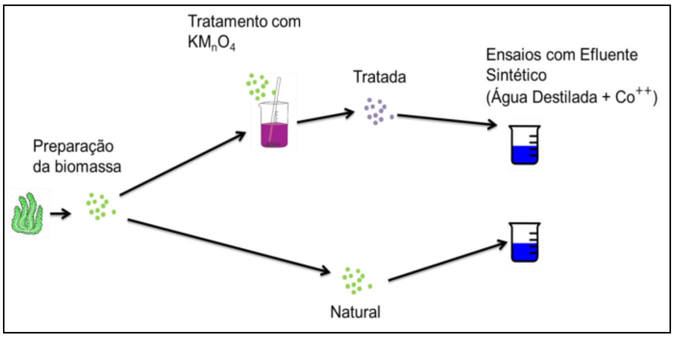

Fig 2: Biosorption assay flowchart.

Results Analysis: Quantification Of Co (II) IONS

Quantification of Co(II) ions from the experiments was performed by ICP-OES. The amounts of metals present in the solution were determined before and after the tests. The percentage of metal removed in the process (X%) was calculated as follows.

$$X\% = ((M0 - Mf) / M0) \times 100;$$

where M0 and Mf are the metal (Co II) concentrations at the beginning and end of each experiment, respectively. In parallel, the algae were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) before and after treatment.

Fig 3: (ICP) - Varian / -720 ES.

Fig 4: (FTIR). Shimadzu®: IRAffinity 1.

Second Phase

The second phase of testing was carried out only with natural *Ulva lactuca* algae and after treatment with potassium permanganate. In this experiment, tests were carried out for different biomass-effluent proportions: 0.5 g/L and 1 g/L. The adsorption process was also evaluated at the following intervals: 5, 15, 30 and 45 min.

Biosortion Tests: In 4 beakers 50 mL, quantities of 0.0125 g of natural *Ulva lactuca* algae (UN) were added and in another 4 beakers the same amount of treated algae (UT) was weighed (biosorbent proportion: effluent 0.5 g/L). In each beaker, 25 mL of effluent containing 100 ppm of Co(II) was added. The test was carried out at room temperature in a rotational shaker at 500 rpm. At each time interval (5, 15, 30 and 45 min.) an aliquot of 1 mL of each assay was removed (from the beaker with natural biomass and another from the beaker with treated biomass). These aliquots were sent for spectroscopic analysis to quantify Co II ions. The same test was repeated for a biomass concentration of 0.0250 g (biosorbent: effluent ratio 1 g/L).

Quantification Of Co (Ii) Ions By Spectroscopy

Quantification of Co II ions was carried out by quantitative spectroscopy of the complex: Co (II) ions with potassium thiocyanate (KSCN), through the construction of a calibration curve at the following concentrations: 10, 25, 50, 75 and 100 ppm of Co(II). For the quantification of samples from the biosorption assays, an aliquot of 250 µL was used from each assay. To these aliquots, 0.2 mL of 6M HCl, 5 mL of KSCN (50%), 1.2 mL of commercial acetone and 0.6 mL of deionized water were added. After homogenization of the sample and development of the blue color, the samples were read at λ=600nm on a spectrophotometer (EppendorfBioPhotometer® D30).

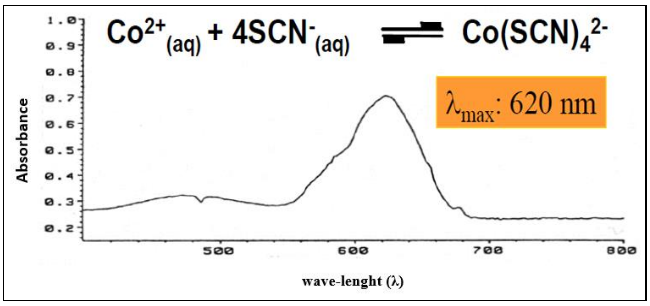

Fig 5: Formation of the complex of Co (II) ions with potassium thiocyanate showing maximum absorption at λ = 620 nm.

Analysis of Results

In the analysis of the experiments carried out by spectroscopy, the amount of metal present in the solution was determined at intervals of 5, 15, 30 and 45 minutes. The percentage of metal removed at each interval (X%) was calculated as follows:

X% = M0 – M(t)/M0 x 100;

where, M0 and M(t) are the metal (Co II) concentrations at the beginning and in the time interval, respectively.

Results

Through a first analysis of the dry material, the concentrations described in the graphs below were obtained. The concentration of elements and/or chemical substances in macroalgae will serve as indicators of pollutants and probably new contributions to science, since to date, no studies on the subject have been carried out in the metropolitan region of Baixada Santista. Through this information, it will be possible to have subsidies for long-term ecological studies towards local preservation.

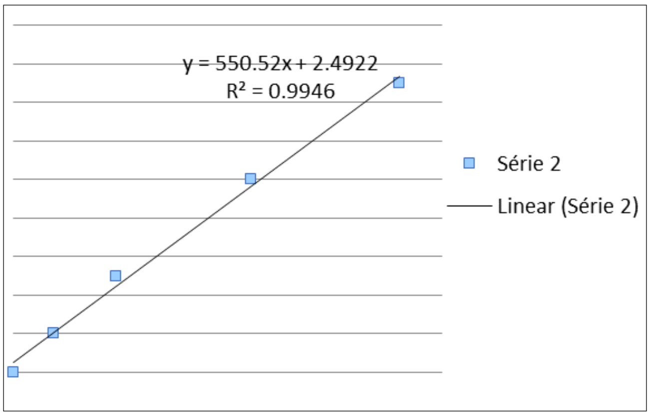

Fig 6: Cobalt II quantification curve.

Table 1: Absorbance relationship with cobalt concentration.

Absorbance (mg.L^{-1})	Concentration Co (II) ppm
0	0
0,014	10
0,036	25
0,083	50
0,135	75
0,308	100

Table 2: Metal concentration in the period of 1-10 min. of treatment. LLD = detection limit. RSD = relative standard deviation

Element	Line	Concent. (mg/L)	Sigma (mg/L)	RSD (%)	LLD (mg/L)	Net area	Backgr.	Chi
Si	K12	722	14	1,9	3	227773	119538	127,53
Cl	K12	1675	28	1,7	1	3221540	193358	3787,49
K	K12	2,76	0,15	5,5	0,22	12637	112640	4,87
Ca	K12	25,29	0,5	2	0,15	172309	115226	106,3
Ti	K12	0,802	0,055	6,9	0,088	9292	115975	2,06
V	K12	0,085	0,036	42,1	0,073	1238	124828	1,51
Cr	K12	0,174	0,031	17,9	0,06	3260	139964	1,51
Fe	K12	4,92	0,11	2,1	0,05	142436	215284	132,05
Cu	K12	2429	39	1,6	0	114858680	1028886	309309,99
Ga	(IS)	K12	0,5	0,017	3,5	0,019	31543	160370
Br	K12	0,54	0,012	2,2	0,004	47481	15011	38,04

Rb	K12	Not det.	Not det.	0,004	12	17831	13,4	621,91
Sr	K12	11,18	0,19	1,7	0,01	1061227	26094	806039,96
Os	L1	3,643	0,08	2,2	0,04	171985	396020	38475,75

Anexos

Fig 7: Pesagem das algas.

Fig 8: Amostras na agitação magnética.

Fig 9: Todas as amostras pós agitação magnética.

Fig 10: Amostras acondicionadas nos tubos para serem utilizadas no TXRF.

Discussion

It is observed that human action, as well as different seasonalities, have not influenced the distribution of macroalgae in Praia do Cibratel, basically maintaining, throughout all sampling periods, high sensitivity to heat, but with the ability to bioaccumulate toxins present in the environment. that the samplings were carried out. Among the observations made, it was found that macroalgae bioaccumulated many substances such as calcium (Ca), chlorine (Cl) and silicon (Si) in high concentrations as shown in the graphs, but nothing that could harm the fauna, flora and population, other samplings may be carried out in different locations, in order to obtain different results.

Concusion

In addition to serving as bioaccumulators of heavy metals as shown in the graphics, they also served as a shelter for small animals, which were encountered several times. It is believed that rich information will be obtained about the importance of macroalgae for the environment, helping the recovery of seas and oceans where anthropogenic action may have occurred.

References

1. Teixeira VL. Revista Virtual de Química. 2013;5:343-362.
2. Mehta SK, Gaur JP. Critical Reviews in Biotechnology. 2005;25:113-152.

3. Guimarães JRD, Lacerda LD, Texeira VL. Revista Brasileira de Biologia. Rio de Janeiro. 1982;42:553-557.
4. Luiz-Silva W, Matos RHR, Kristosch GC. Química Nova. 2002;25:753-756.
5. Costa ACA, França FP. Separation Science and Technology. 1996;31:2373-2393.