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Biomass Valorization of Brown Algae residues *Macrocystis pyrifera*: obtaining Alginate

Yésica D. Alvis Hernandez, Wilma Y. Calderón Meza, Carlos Castañeda-Olivera, Eusterio Acosta Suasnabar, Elmer Benites-Alfaro\*

Universidad César Vallejo, Av. Alfredo Mendiola 6232 Lima 15314, Lima – Perú

\*ebenitesa@ucv.edu.pe

The proliferation of *Macrocystis pyrifera* algae, known as brown algae or Pacific giant kelp (giant kep), when abundant can cause environmental problems such as: modification of the marine habitat by providing shelter and food to various species altering the community of species of the place, can compete with native algae in marine ecosystems, can impact water quality by retaining nutrients and sediments, can alter the primary productivity in the marine ecosystem by consuming nutrients and light from other forms of marine life, as well as cause impact on fishing and aquaculture by damaging nets even hindering navigation, also the waste of these algae cause environmental problems on beaches (example: in Central and South America). The objective of the research was to use the biomass of Macrocystis pyrifera algae residues that are stranded on the beaches by the sea, to obtain alginate. The method consisted in performing acid pre-treatment, then an alkaline treatment, followed by precipitation (in two different cases: first with sodium chloride, and second with ethanol), then drying and milling. These two Alginate products obtained were hydrated by measuring the time to obtain gelation and the percentage of water retention. From the tests, 97.2 % and 97.99 % of water retention were obtained at a time of 10 and 7.5 minutes for the two types of alginates obtained.

* 1. Introduction

Marine algae play a fundamental role in the marine ecosystem, they are essential in the production of oxygen such as diatomaceous algae that produce 20 % of oxygen, food production, water filtration, coastal protection and climate change reduction (Lora-Vilchis M.C., López Fuerte F. O., Pérez Rojas C. A., 2020). Brown algae are abundant in the sea in southern Peru, where they are being exploited by artisanal fishermen to market them to the industry to obtain alginate for food, textile and pharmaceutical industry mainly, alginates are salts of alginic acid that constitute the cell walls of the intercellular areas of brown algae, to give strength and flexibility to the algae (Motta L. and Rodriguez F., 2020).

There is also a percentage of algae that wash up on the shores of the sea and that form waste, producing a negative impact by changing the color of the landscape (Rodríguez R. E., Tussenbroek B., 2023), making it impossible to take advantage of the environmental services of the beaches, in some cases the algae produce a bad smell when decomposing, they also affect biodiversity; On the contrary, they can also be used to obtain biofuels (Amaya, et al., 2022), as well as taking advantage of their high composition in nutrients, polysaccharides, fatty acids and amino acids, among others, to use them for food, pharmaceutical products and fertilizers. , as mentioned in a study funded by BBVA in Mexico (Rodriguez R.E, 2023).

Algal waste can be used to improve soils as an amendment, due to its high nutrient content, it can be converted to hydrochar according to the study carried out for agricultural soils (Di Fraia, et al., 2022). In addition, it is also pertinent to improve the methods of extraction or processing of algae for their better use, such as that carried out to obtain bio-oil using the hydrothermal liquefaction method (Costa et al., 2023).

One way to take advantage of brown algae is the possibility of obtaining alginate from its natural structure. Natural alginate has several advantages over chemically obtained alginate, such as being renewable and sustainable, also being a natural product, it has unique properties such as greater water holding capacity ideal in the pharmaceutical, textile, cosmetic and food industry, another advantageous aspect is the characteristic of biodegradability over chemically obtained alginate, making it environmentally friendly (AL-Rawi, et al., 2018).

In this sense, the research aimed to obtain alginate from the biomass of *Marcrocystis pyrifera* algae while determining its fundamental properties. To carry out the research, the biomass of the algae in question was collected from Bahia Independence beach, province of Pisco, Ica region - Peru, where the sea washed them up. This algae biomass is considered waste by the residents of said place, so proposals to give economic value to it are a viable alternative within the concept of circular economy.

* 1. Methodology

The experimental design research process was developed by collecting samples of *Macrocystis pyrifera* algae on the beach of Independencia Bay, Paracas - Ica area, Peru. Two samples were collected which gave rise to two experimental trials to obtain alginate: For the first trial, the sample consisted of 3,258 kg, while for the second trial it was 2,458 kg. The experimental design of the trials followed the stages with the details given in Table 1.

The algal sheets for the experimental work of obtaining alginate from samples of Macrocystis pyrifera algae are shown in Figure 1.



Figure 1: Macrocystis pyrifera algae leaf sample

2.1 Test procedure 1 and test procedure 2

The procedures (1 and 2) are presented in detail for obtaining the alginate in Table 1.

Table 1: Experimental process to obtain alginate from algae biomass Macrocystis pyrifera using calcium chloride (trial 1) and *with ethanol (Trial 2)*

|  |  |  |
| --- | --- | --- |
|  | Test 1Trial 1: Sample 1 | Test 2Trial 2: Sample 2 |
| Sample pretreatment | -Washing of the *Macrocystis pyrifera* sample.- Separation of the leaves from the algae (for testing).- Drying at 50 °C for 12 hours- Moisture calculation: 69.9 %.- Grinding of the dry sample- Sieved at 2 mesh: 110.88 g | - Washing of the *Macrocystis pyrifera* sample.- Separation of the leaves from the algae (for testing).- Drying at 50 °C for 12 hours- Moisture calculation: 70.9 %.- Grinding of the dry sample- Sieved at 2 mesh: 69.54 g |
| Acid Extraction | - 10 g of dry ground biomass is weighed.- A leaching process is carried out with HCl to transform the alginates into alginic acid with the following reaction: MAlg + HCl → HAlg + MCl.- Added 150 mL of distilled water.- Adjusted pH to 4 by adding 1N HCl with stirring.* - The precipitate was filtered and washed (2 times).
 | * 10 g of dry ground biomass is weighed.

- A leaching process is carried out with HCl to transform the alginates into alginic acid with the following reaction:  MAlg + HCl → HAlg + MHcl.- Added 200 mL of distilled water.- Adjusted pH to 4 by adding 1N HCl with stirring.- The precipitate was filtered and washed (2 times) |
| Alkaline extraction | - The filtrate of the previous stage is added 250 mL of distilled water.- The pH is adjusted to 10 by adding a solution of sodium carbonate (NaCO3) to 10 %.- With agitation it is heated to 80 °C for 2 hours.- The precipitate is separated. | * The filtrate of the previous stage is added 300 mL of distilled water.
* The pH is adjusted to 10 by adding a solution of sodium carbonate (Na CO3) to 10 % (1:1).
* With agitation it is heated to 80 °C for 2 hours.

The precipitate is separated. |
| Dilution | - The precipitate of the previous stage is diluted with 3 times the volume of hot water.- It is left to cool for 30 min in refrigerator.- It is filtered separating the solution from the solid part. | * The precipitate of the previous step is diluted with hot water (50 °C) 3 times the volume of hot water.
* It is left to cool for 30 min in refrigerator.

It is filtered separating the solution from the solid part. |
| Precipitation of Alginate | * To the solution is added with agitation 150 mL of calcium chloride at 10 % neutralizing the alginic acid and to obtain the Alginate. The reaction that is presented is:

 2NaAlg + CaCl2 → CaAlg + 2 NaCl* The precipitate (alginate fibres) is filtered.
 | * Ethanol (1:1) is added to the solution with agitation until condensed alginate fibres are obtained on the walls of the stirring rod.
* The precipitate (alginate fibres) is filtered.
 |
| Drying | * The precipitate is dried at 60 °C in an oven for 48 hours.
 | * The precipitate is dried at 60 °C in an oven for 48 hours.
 |
| Grinding | * It is ground and sieved to obtain a uniform sample of sodium alginate (salts).
 | * It is ground and sieved to obtain a uniform sample of sodium alginate (salts).
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The results obtained by different extraction methods of alginate from Macrocystis pyrifera are compared in terms of quality, considering parameters such as storage stability, rheological properties, nutritional, anti-nutritional and microbiological profiles of the extracted alginate. The quality of the alginate should be evaluated based on its chemical composition, physical properties and its performance in various industrial, pharmaceutical or food applications. In addition, characteristics such as gelling capacity, viscosity, formation of complexes with metal ions and other relevant aspects are analyzed to determine the suitability and effectiveness of the alginate extracted in each specific method (Reyes-Tisnado, 2001). This research focused on evaluating the efficiency of obtaining alginate and determining the fundamental characteristics of water retention capacity and gelation time.

Figures 2, 3 and 4 show the final process for obtaining the alginate detailed in Table 1, using ethanol in the precipitate process. It is this product that is subjected to fundamental tests characteristic of alginate*.*

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| Figure 2: Ethanol precipitate | Figure 3: Filtration to obtain the alginate fibers | Figure 4: Drying of the alginate obtained |

* 1. Results and discussion

3.1 Performance in obtaining Alginate from *Macrocystis pyrifera* algae

The yield level of the *Macrocystis pyrifera* algae biomass to obtain alginate in dry phase was determined to be 3.59 g (35.9 %) for trial 1 and 1.74 g (17.4 %) for trial 2; that is, the use of ethanol in the alginate precipitation was less efficient than in the case of using calcium chloride (CaCl2), as shown in Table 2. These results are within the margin indicated by the scientific literature which indicates that brown algae including *Macrocystis pyrifera* contain approximately 25 % of alginate and the brown algae *Laminaria digitata* contain approximately 15 % of alginate, there are even species that can contain up to 40 %, this content can be affected by several factors, such as the species, growth conditions and extraction method (Al-Jumaily, et al., 2017).

Likewise, the efficiency in obtaining can be in the process of dilution of the algal biomass, in some cases the maturation of arginine for generation of alginate in algae (Vinueza and León (2017). Temperature, the presence of nutrients in the area, among other aspects, also have an influence (Hernández, 1985).

Table 2: Alginate production yield (dry basis)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Trial | Precipitant | Dry sample weight (g) | Weight of alginate obtained (g) | Yield (%) |
| Trial 1 | Calcium Chloride | 10 | 3. 59 | 35.9  |
| Trial 2 | Alcohol | 10 | 1.74 | 17.4 |

3.2 Hydrogen potential, water retention of alginate

The hydrogen potential (pH) is an essential parameter in obtaining alginate, this is done at a basic pH. The alginate product obtained in both tests had a pH around neutral as shown in Table 3.

The water retention test of alginate showed that for the sample of test 1 had a retention percentage of 97.2 % and for the other sample of test 2 the water retention percentage was 97.99 %, very close values with more efficiency for the second case (Table 3), these results are relatively better than those obtained from volva algae biomass which had a retention of 20 % (Estrada et al (2011). The absorption capacity of alginate depends on several factors among which the chemical structure of alginate (formed by alginic acid chains which are polysaccharides of high molecular weight), the temperature (the higher the temperature the higher the absorption capacity) and the presence of other compounds (calcium ions when binding with alginate reduce absorption capacity), from all this in general, the absorption capacity is between 20 to 40 times its weight (Al-Jumaily et al., 2017).

Table 3: Hydrogen potential and water retention of alginate

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Trial | Precipitant | pH | Dry weight (g) | Wet weight (g) | Water retention (%) |
| Trial 1 | Calcium Chloride | 7.84 | 0.11 | 3.93 | 97.2 |
| Trial 2 | Alcohol | 7.87 | 0.11 | 5.46 | 97.99 |

3.3 Alginate gelation time as hydrogel

For the test, samples of alginate obtained in tests 1 and 2 were taken in the amount of 0.11 g and 10 mL of water was added. The result is shown in Table 4, that the hydrogel with alginate obtained in trial 1 took 10 minutes to absorb water, on the other hand the alginate obtained in trial 2 took 7.5 minutes to absorb 10 mL of water, therefore, the latter result the most efficient in gelation time.

*Table 4: Alginate gelling delay time*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Trial | Precipitant | Weight (g) | Volume of water (mL) | Time (min) |
| Trial 1 | Calcium Chloride | 0.11 | 10 | 10 |
| Trial 2 | Alcohol | 0.11 | 10 | 7.5 |

3.4 Advantages of obtaining alginate from *Macrocytis pyrifera* algae

Obtaining alginate from *Macrocystis pyrifera* algae has several specific advantages, including obtaining a biopolymer with unique and versatile properties, with the ability to form gels, emulsions and coatings, making it useful in various industrial and food applications (Ore et al., 2020); In addition, alginate derived from this alga is biodegradable and biocompatible, which makes it safe for use in pharmaceutical and biomedical products (Hernandez-Carmona, 2012); Another important advantage is the ability to form complexes with metal ions, which makes it an effective chelating agent in environmental remediation applications and in the food industry (Reyes-Tisnado, et al., 2004).

* 1. Conclusion

*Macrocystis Pyrifera* algae are ideal for obtaining the gelatizing compound Alginate with good characteristics as a hydrogel of around 97% for water retention, the importance of the product is its nature of being eminently natural, a fact that gives it characteristics of a renewable product and environmental sustainability with unique advantages over chemically obtained hydrogel products. This natural biodegradable characteristic allows it to have great potential for use in food, pharmaceutical and other industries; It is highlighted that this biopolymer has a significant use in the printing of dental materials in medical activity; Likewise, the use of these algae considered waste in these beach areas allows for economic benefits, within the principle of circular economy.

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