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Influence of the extraction–purification conditions on final properties of alginates obtained from brown algae (*Macrocystis pyrifera*)

César G. Gomez[a], María V. Pérez Lambrecht[a], Jorge E. Lozano[a], Marguerite Rinaudo[b], Marcelo A. Villar[a,*]

[a] Planta Piloto de Ingeniería Química, PLAPIQUI (UNS-CONICET), Camino "La Carrindanga" Km 7, (8000) Bahía Blanca, Buenos Aires, Argentina
[b] Centre de Recherches sur les Macromolécules Végétales (CNRS), Université Joseph Fourier de Grenoble, BP 53, 38041 Grenoble cedex, France

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ABSTRACT

In this work, three methods (ethanol, HCl, and $CaCl_2$ routes) of sodium alginate extraction–purification from brown seaweeds (*Macrocystis pyrifera*) were used in order to study the influence of process conditions on final properties of the polymer. In the $CaCl_2$ route, was found that the precipitation step in presence of calcium ions followed by proton-exchange in acid medium clearly gives alginates with the lowest molecular weight and poor mechanical properties. It is well known that the acid treatment degrade the ether bonds on the polymeric chain. Ethanol route displayed the best performance, where the highest yield and rheological properties were attained with the lowest number of steps. Although the polymer I.1 showed a molar mass and polydispersity index (M_w/M_n) similar to those of commercial sample, its mechanical properties were lower. This performance is related to the higher content of guluronic acid in the commercial alginate, which promotes a more successful calcium chelation. Moreover, the employment of pH 4 in the acid pre-treatment improved the yield of the ethanol route, avoiding the ether linkage hydrolysis. Therefore, samples I.2 and I.3 displayed a higher M_w and a narrower distribution of molecular weights than commercial sample, which gave a higher viscosity and better viscoelastic properties.

1. Introduction

Although the early state of biosynthesis of carbohydrates in seaweeds is similar than in plants, some of the polysaccharides finally synthesized are found only in seaweeds. These biopolymers are present principally in the cell wall, giving mechanical resistance to algae. Properties such as flexibility and softness in water to support currents are more important than rigidity. Therefore, the polysaccharides that prevail in seaweed are those that possess properties of gels and mucilage, being cellulose also present in a lower amount [1–6].

There are three principal groups of seaweeds classified by their colour: brown, red and green seaweeds. Each of them possesses the predominance of a typical polysaccharide [7], being alginate the most abundant in marine brown seaweed. Although there are different species of brown seaweed that contain alginates, these are no sufficiently abundant and suitably located for commercial production. The species of brown seaweed most commercially exploited are: *Laminaria hyperborea, Macrocystis pyrifera and Ascophyllum nodosum*. These species are mainly manufactured in countries such as USA, Japan, China, France, and Norway [8].

In natural environments, alginates exist in the cell wall as a mixture of calcium, potassium and sodium salts of alginic acid [9]. They constitute a family of linear copolymers of (1 → 4) β-D-mannuronic acid (M) and (1 → 4) α-L-guluronic acid (G) units. The chemical composition and sequence of M and G units depend on the biological source, growth, and stationary conditions. These polysaccharides have three types of diad sequences, i.e. MM, GG and MG blocks [10–12]. Sodium alginate is a water-soluble polymer, which gives highly viscous solutions. It can be used as a stabilizer of suspensions and as thickener in food industries among other applications [9]. Another characteristic property of the sodium alginate solutions is the ability of gel formation in the presence of polyvalent cations, such as Ca^{2+} [13]. Generally, the extraction and purification processes of alginates are based on the conversion from the insoluble form in the plant cell walls to the soluble one, normally the sodium salt, followed by successive dissolutions and precipitations to eliminate impurities [14,15]. Alginates extraction from brown seaweed has been studied during several decades in order to develop economic systems, obtaining high yields and a controlled molecular weight for different applications [16–18]. In some South American countries such as Argentina, there is no industry producing alginates despite the large amount of brown seaweed such as *M. pyrifera* along of its seacoast [19]. In this work we present a comparative analysis of three routes of sodium alginate purification in order to have a product with controlled molar mass and degree of

* Corresponding author. Tel.: +54 291 486 1700; fax: +54 291 486 1600.
E-mail address: mvillar@plapiqui.edu.ar (M.A. Villar).

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purity. Samples of brown seaweeds were collected from Patagonian Argentine coast and used as raw material to carry out this study. Extracted alginate was characterized by SEC, ^{1}H NMR, rheological studies, ability to gel formation and swelling degree. On the other hand, the characteristic properties of extracted sodium alginates were studied and compared with those of a commercial sample.

2. Experimental

2.1. Materials and reagents

The raw material from which the alginate was extracted consisted of sheets and stems of brown seaweed (*M. pyrifera*) from Patagonian Argentine coast, which were dried, previously crushed and sifted (10–20 mesh). The following chemicals were also purchased and used in the extraction–purification processes: HCl 37 wt% (Cicarelli, Argentine); NaOH p.a. (Anedra, Argentine); Na_2CO_3 p.a. (Anedra, Argentine); $CaCl_2$ p.a. (Anedra, Argentine); ethanol 96% (Carries, Argentine); diatomaceous earth (Anedra, Argentine); eriochrome black-T p.a. (Fluka, Switzerland). A commercial sample of sodium alginate (N° 71238 Fluka, Switzerland) was employed as a reference. In addition, a solution of eriochrome black-T (5 g per 1 L of ethanol) was prepared, adding then 5 mL of the last one to 5 mL of a 0.5 M NH_4Cl/NH_3 buffer solution at pH 10, in order to obtain the indicator solution used for qualitative detection of calcium ions.

2.2. Extraction of alginates from seaweed

A crushed sample (10 g) of dry seaweed was moistened by addition of distilled water (400 mL) and a 0.1N HCl aqueous solution was added, under high stirring, in order to have a pH 4, following a similar extraction method reported by Arvizu Higuera et al. [16]. This mixture was stirred during 15 min at room temperature

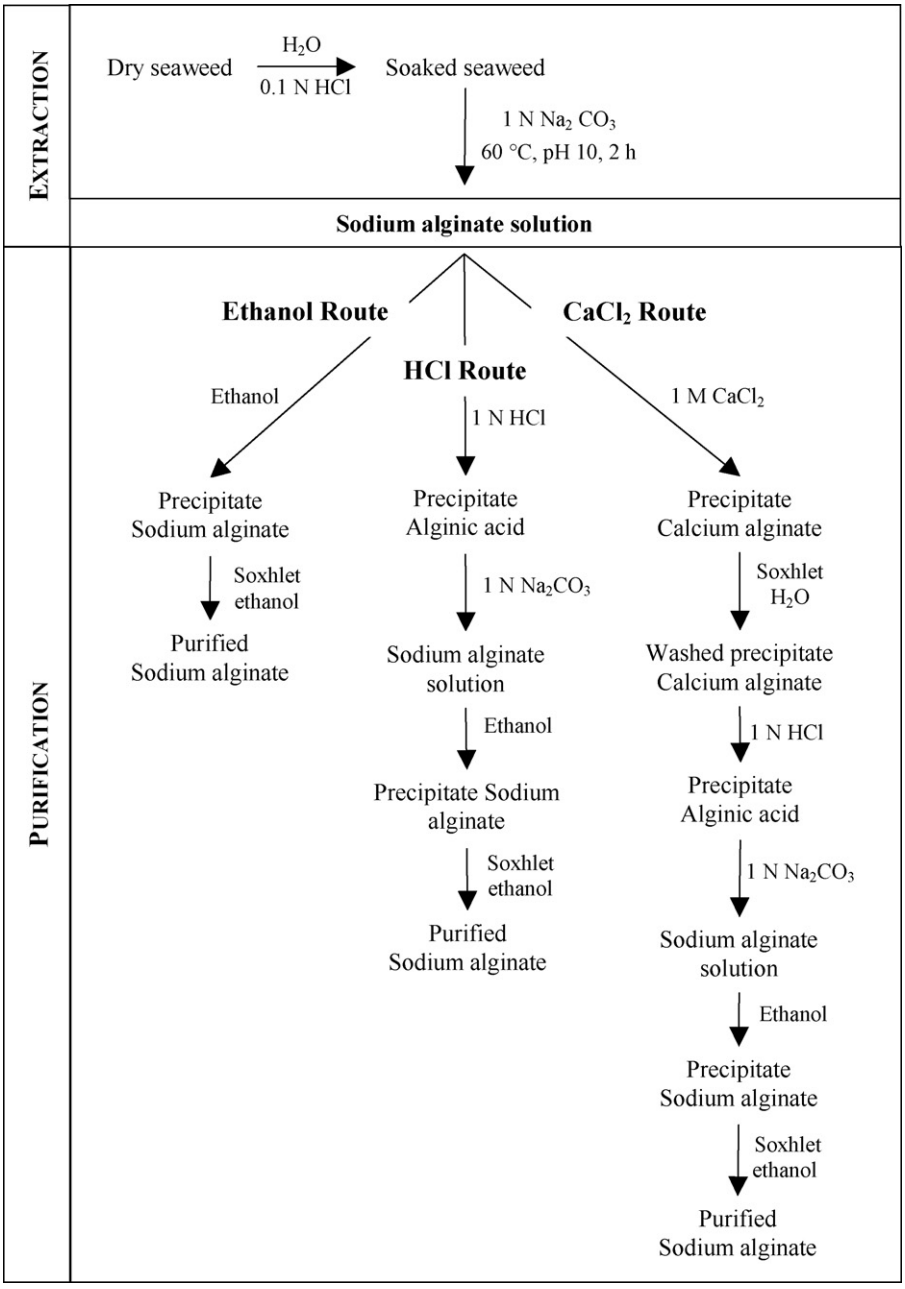

Fig. 1. Scheme corresponding to the three routes of alginate purification.