Algal Research 34 (2018) 191–197

Contents lists available at ScienceDirect

Algal Research

journal homepage: www.elsevier.com/locate/algal

Hydroxyl radical pretreatment for low-viscosity sodium alginate production from brown seaweed

Feng Gao[a], Xiumin Liu[b], Wuxi Chen[a], Wei Guo[a], Limei Chen[a], Demao Li[a,*]

[a] Tianjin Key Laboratory for Industrial Biological Systems and Bioprocessing Engineering, Tianjin Institute of Industrial Biotechnology, Chinese Academy of Sciences, Tianjin, China
[b] Hebei Jiaotong Vocational and Technical College, Shijiazhuang, Hebei, China

ARTICLE INFO

Keywords:
Alginate extraction
Low-viscosity sodium alginate
Macroalgae
Pre-extraction
Hydroxyl radicals
Fenton reaction

ABSTRACT

Formalin pollution and water wastage are two of the main problems in the alginate industry. A novel pre-extraction treatment method based on the Fenton and electro-Fenton reactions is proposed to disrupt the cell wall of *Macrocystis pyrifera* and reduce the alginate filtrate viscosity, as an environmentally friendly process for alginate extraction. Under optimum Fenton (7.4 mM $FeSO_4$ 90 min) and electro-Fenton (EF-Fere 9 V, 90 min at pH 3, stirring) pre-extraction treatment conditions, the filtrate viscosity decreased by 83.99% and 97.79%, respectively. The filtrate viscosity decreased significantly as compared to the traditional approach under suitable operating conditions. Using of electro-Fenton for pre-extraction reduced water consumption by 60% in the filtration step and eliminated the use of formaldehyde during the process, reducing production costs and environmental pollution. Moreover, the yield and the quality of the alginate extracted after the pre-extraction improved.

1. Introduction

Alginates are constituents of the cell wall in brown seaweed, such as *Macrocystis pyrifera*. The function of alginate is to give strength and flexibility to the algal tissue, and its industrial applications are linked to its ability to retain water and its gelling, viscosifying, and stabilising properties [1]. Alginate is a linear anionic [2] water-soluble polysaccharide [3] consisting of monomeric units of 1–4-linked α-L-guluronate (G) and β-D-mannuronate (M) that are arranged as linear blocks [4]. The chemical composition and the sequence of the M and G units depend on the biological source, growth, and stationary conditions [5]. These polysaccharides have three types of dyad sequences, the MM and GG blocks, which are known as homopolymeric blocks, and the MG blocks, which are heteropolymeric blocks [6,7].

In general, companies offer three main categories of alginate (although there are many other categories), namely high-viscosity (above 800 mPa s), medium-viscosity (400–800 mPa s), and low-viscosity (below 400 mPa s) alginate [8]. In some companies, super high viscosity and super low viscosity are subdivided as separate categories. The low-viscosity and super-low-viscosity alginates occupy important positions in the global alginate industry and account for 30%–40% of the total demand. Alginates are used as thickeners owing to their ability to increase the viscosity of aqueous solutions. Medium- to high-viscosity alginates are used in the beverage and textile printing industries as immobilised biocatalysts (carrying enzymes), release agents, and paper; they also have pharmaceutical and medical uses [2,9,10]. In textile printing, relatively thin pastes with a long flow are required for fine-patterned prints. A less shear-sensitive paste can be made using high concentrations of a relatively low-viscosity alginate.

Commercial alginates are mainly produced from *Laminaria hyperborea*, *M. pyrifera*, *L. digitata*, *Ascophyllum nodosum*, *L. japonica*, *Ecklonia maxima*, *L. berteroana*, *L. spicata*, *Durvillaea antarctica*, and *Sargassum* sp., and the most commercially exploited species for alginate production are *L. hyperborea*, *M. pyrifera*, *A. nodosum*, and the *Lessonia* species [11–13]. Although the alginate industry has a history of more than a hundred years, manufacturers still use the traditional production process. For the extraction of alginate from brown seaweeds, formaldehyde-based pre-extraction treatment has been used as an essential step [14–16] because the resulting product has less colour. After the alkaline extraction, the dissolved sodium alginate must be separated from the alkali-insoluble seaweed tissue. The extract is diluted with a considerable amount of water to produce a suitable viscosity for filtration. One ton of alginate consumes approximately 1000 tons of fresh water [17], and the water is obtained mainly from coastal areas where

* Corresponding author at: Tianjin Key Laboratory for Industrial BioSystems and Bioprocessing Engineering, Tianjin Institute of Industrial Biotechnology, Chinese Academy of Sciences, No. 32 Xiqi Road, Tianjin Airport Economic Park, Tianjin 300308, China.
E-mail address: li_dm@tib.cas.cn (D. Li).

https://doi.org/10.1016/j.algal.2018.07.017
Received 29 September 2017; Received in revised form 8 June 2018; Accepted 26 July 2018
2211-9264/

lack of fresh water. Therefore, it is not a sustainable industry because of the formaldehyde utilization and large amount of water consumed.

There are various forms of alginate, and among these, alginic acid is the most unstable. Its molecules decompose easily at high temperatures, therefore, high-temperature degradation of alginic acid is the main method used for the production of low-viscosity alginate. However, high temperature means high energy consumption and cost. Thus, low-energy-requirement methods, such as hydroxyl radical attachment, have attracted considerable attention recently. In solution, H_2O_2 can react with Fe^{2+} ions, initiating the so-called Fenton radical reaction chain, which leads to the production of reactive oxygen species [18]. The reactive oxygen species, given their high reactivity, are capable of attacking and effectively degrading organic compounds, such as polysaccharides, cellulose, glycoproteins and phospholipids, in the algal cell wall [19]. In our previous research, Fenton's radical reaction was used in the bioconversion of brown macroalgae, *M. pyrifera* which achieved a high rate of cellulose saccharification [18].

In the present study, we investigated an improved pre-extraction approach for extracting low-viscosity alginate from *M. pyrifera* by the Fenton reaction. Fenton and electro-Fenton pre-extraction treatments were used to replace formaldehyde fixation and heating in the process of acidification to break the cell wall of the macroalgae and reduce the alginate viscosity. Comparative studies of these methods with traditional treatment methods were also conducted. A new process for low-viscosity alginate production is proposed which will support the sustainable development of the alginate industry (Fig. 1).

2. Materials and methods

2.1. Biomass

M. pyrifera was purchased from Qingdao Bright Moon Seaweed Group (Qingdao, China). The samples were first dried for 24 h at 65 °C and then sifted to an average size on an 80-mesh screen (0.2 mm) using a standard sieve. The sifted material was used directly in the alginate extraction studies.

2.2. Different pre-extraction treatment methods

Five different pre-treatment methods, namely the traditional method, high-temperature acidification, Fenton, EF-Feox, and EF-Fere were conducted.

2.2.1. Alginic acid preparation using the traditional method

For this method, 10 g of dried and milled *M. pyrifera* was processed at the laboratory scale. The algae were placed in a tank to rehydrate overnight with 1 L of a 0.2% formalin solution. The residual solution was drained off, and the algae were washed with a 0.1 mol/L hydrochloric acid solution for 30 min with constant agitation. The material was then transferred to an extraction kettle containing 400 mL of 1.5% anhydrous sodium carbonate and heated to 60 °C for 1 h with constant stirring [20]. The paste was diluted to 600 mL, 800 mL, and 1000 mL, and the viscosity was measured as the diluted viscosity at each dilution step namely filtrate viscosity. The diluent was filtered using a nylon screen, and then, a solution of 10% calcium chloride was added to precipitate the alginate as calcium alginate using a ratio of 2.2 parts of calcium chloride to one part of alginate in the algal raw material. The suspension was filtered using a nylon screen, and the calcium alginate fibres were suspended in 300 mL of a sodium hypochlorite solution (12%). The fibres were suspended in 200 mL of water and washed three times with constant agitation, adjusting the pH to 2 with hydrochloric acid. After each of the three washings, alginic acid was separated using a nylon screen and pressed to remove as much water as possible [21]. The alginic acid fibres were placed in 150 mL of ethanol water (1:1). Then, a sodium carbonate solution (10%) was added until a pH of 8 was obtained. The sample was then stirred for 1 h. Finally, the sodium alginate was filtered and pressed, and the fibres were separated and dried to a constant weight in an oven at 50 °C [21].

2.2.2. High-temperature acidification conditions

High-temperature acidification is similar to the traditional method, but in the acid treatment process, the algae were washed with a 0.1 mol/L hydrochloric acid solution and heated at different temperatures (60, 70, 80, and 90 °C) for 30 min with constant agitation [22].

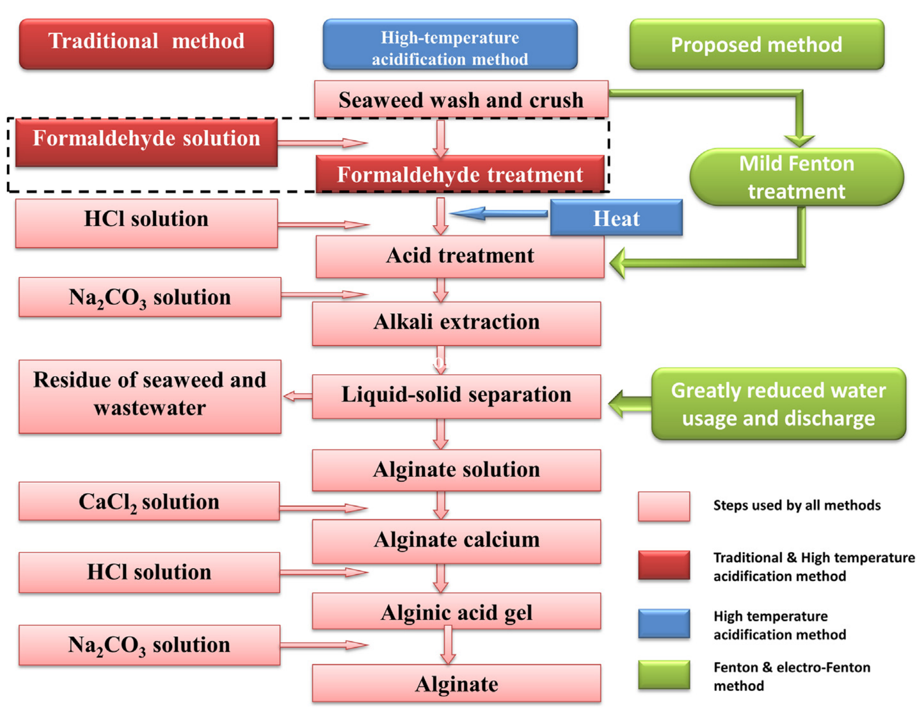

Fig. 1. Schematic representation of different pre-extraction treatment methods.