



Pilot plant scale extraction of alginates from *Macrocystis pyrifera* 4. Conversion of alginic acid to sodium alginate, drying and milling

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Abstract

The last three steps of the alginate production process were studied: conversion of alginic acid to sodium alginate, drying, and milling. Three methods were used to follow the conversion reaction: measuring the pH (a) in the ethanol-water liquid of the reaction mixture, (b) after dissolving a sample of the fiber taken from the reaction mixture, (c) after dissolving the dried sodium alginate obtained from the reaction. To obtain a neutral dried sodium alginate, in the first method the pH should be adjusted to 9, and in the second the pH should be adjusted to 8. The best method to control the reaction was to dissolve a sample of the fiber and adjust the pH to 8. The best proportion to reach the critical point, where pH just begins to rise, was 0.25 parts of sodium carbonate to 1 part of alginate in the initial dry algae. A pH above 7 may produce a break down of the molecule, reducing significantly the viscosity of the final alginate. Four different temperatures were used to dry the alginate: 50, 60, 70, and 80 °C. Drying time to reach 12% moisture ranged from 1.5 h at 80 °C to 3 h at 50 °C. The best drying temperature was 60 °C for 2.5 h. The effect of drying temperature on alginate viscosity was dependent on the alginate type. Low and medium viscosity alginates were not significantly affected, but alginate with high viscosity was reduced by 40 to 54% using the temperature range of 60 to 80 °C. A fixed hammer mill was used to reduce the particle size of the dried sodium alginate. Particle size measurements showed that after a first milling the product contained 76% large particles (20–60 mesh) and 24% fine particles (80–120 mesh). After a third milling the product still contained 42.9% large particles. No significant effect was found on alginate viscosity because of the milling steps.

Introduction

Previous papers in this series (Hernández-Carmona et al. 1998, 1999; McHugh et al. 2001) have discussed the scarcity of useful information in the literature on the production of alginates. While many general outlines of the processes have been given, there has been a lack of practical detail, even in the few patents available. Some of the studies most useful to the potential alginate producer were carried out at the former Norwegian Institute of Seaweed Research. Haug (1964) published a detailed summary of the re-

sults of many years of work with colleagues at the Institute. This fundamental work was on a laboratory scale and was probably used in developing pilot plant and full industrial scale extraction by the Norwegian alginate industry but no results have ever been published. This is not surprising, since alginate producers prefer to keep details of their methods confidential. The present studies were undertaken, on a pilot plant scale, in an effort to fill this gap in the alginate literature. While all the work has been on one species only, the results, taken with the laboratory scale work on other species at the Norwegian Institute of Sea-

weed Research, provide an excellent basis for expansion by any potential alginate producer using any species of seaweed. The present paper deals with the final steps in the process: the conversion of alginic acid to sodium alginate followed by the drying and milling of the product.

Materials and methods

Preparation of alginic acid

Alginic acid was prepared using the optimum conditions found in the previous studies. Therefore 10 kg of dried and milled *Macrocystis pyrifera* (L.) C. Agardh collected from Punta Eugenia, Baja California Sur, México, was processed at pilot plant level. The alga was placed in a tank to rehydrate overnight with 90 L of 0.1% formalin solution. The residual solution was drained off and the alga was washed with 100 L hydrochloric acid solution at pH 4 in the same tank for 15 min with constant agitation (Hernández-Carmona et al. 1998). The material was then transferred to an extraction kettle containing 166 L of water, the pH was adjusted to 10 with powdered anhydrous sodium carbonate and heated at 80 °C for 2 h, with constant stirring (Hernández-Carmona et al. 1999). The paste was diluted to 45 mPa s and filtered in a rotary vacuum filter, using diatomaceous earth as filter aid (Hernández-Carmona et al. 1999). During filtration, the filtrate was pumped to the precipitation tank and simultaneously 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 on a metal screen, the calcium alginate fibers were suspended in 150 L of water and bleached with 700 mL of sodium hypochlorite solution (5%). The fibers were suspended in 150 L of water and washed three times with constant agitation, adjusting the pH with hydrochloric acid to 2, 1.8 and 1.8 respectively (McHugh et al. 2001). After each of the three washings, the alginic acid was separated on a metal screen and pressed in a hydraulic press to remove as much water as possible.

Effect of sodium carbonate on pH during conversion of alginic acid to sodium alginate

The alginic acid obtained by the method described above was weighed to determine the amount of water

in the fibers. To calculate the amount of water, the expected amount of alginate, based on previous analysis of the original alga at laboratory level, was subtracted from the above total weight; this gave the approximate amount of water in the alginic acid. The fibers were placed in a double planetary mixer. Enough ethanol was added to reach an ethanol:water ratio of 50:50 in the fibers. Increasing amounts of anhydrous sodium carbonate were added to neutralize the alginic acid, ranging from 100 g to 450 g. At the end of the experiment, the exact ratio of sodium carbonate to alginate used was calculated, based on the alginate yield obtained in each run. The ratios ranged from 0.07 to 0.32 g sodium carbonate per g of alginate obtained, with increments of approximately 0.01–0.02 g. Sixteen ratios were used in the experiment. The maximum ratio gave a pH of 9.5 in the ethanol-water liquid.

After adding the first experimental amount of sodium carbonate, the paste was mixed for 10 min and three determinations of pH were obtained: a) by measuring the pH of the ethanol-water liquid in the reaction mixture, using a pH indicator paper; b) by taking a sample of the alginate fiber from the mixer, squeezing it to remove the excess ethanol-water, dissolving 5 g of the fiber in a beaker with 50 mL of distilled water and measuring the pH by immersing a pH indicator paper in the alginate solution; c) by taking a sample of the alginate fiber from the mixer, squeezing it to remove the excess ethanol-water and drying the fiber at 50 °C, then a 1% solution of the alginate fiber was prepared and the pH measured with pH indicator paper. After sampling at the first experimental ratio, more sodium carbonate was added, the paste was mixed for another 10 min, samples were taken and tested, and so on.

Effect of sodium carbonate on the alginate viscosity during conversion of alginic acid to sodium alginate

The viscosity of the alginate was measured after each addition of sodium carbonate. To a 1% alginate solution, prepared from the dried reaction product, sodium hexametaphosphate (0.5 g per 100 mL of alginate solution) was added to sequester the calcium ions present. The viscosity was then measured using a Brookfield viscometer at 22 °C.

Effect of temperature and drying time on moisture content

Sodium alginate was produced following the process described above, neutralizing the alginic acid until the fiber, sampled by method (b), reached a pH of 8. The fibers were pressed in a hydraulic press until a moisture between 61 and 69% was obtained. The fibers were distributed on trays with a 40-mesh screen and dried in an oven with a hot air current at temperatures of 50, 60, 70 and 80 °C. During the drying process, samples of alginate were taken every 30 min until the moisture was reduced to 12% (4.5–5.5 h) and the moisture was measured using an infrared thermobalance. To reduce the variation because of different drying rates in different trays, the trays were rotated and samples were obtained combining subsamples from each tray. Two-way ANOVA was carried out to compare the effect of temperature and time. Analysis was calculated for the first 2.5 h since by then most of the samples had dried to the maximum moisture recommended (12%).

Effect of drying temperature on alginate viscosity

The viscosity of alginates, dried for 5.5 h at 50 °C and 4.5 h at 60, 70 and 80 °C, was measured as described above. To avoid interference because of any residual calcium ions in the sample, average viscosity comparisons were carried out using the readings obtained after adding sodium hexametaphosphate. Three types of alginate were used: high viscosity (average 1207 mPa s), medium viscosity (average 219 mPa s), and low viscosity (average 76 mPa s).

Effect of milling on alginate particle size distribution and viscosity

Sodium alginate was obtained following the process described above, drying at 50 °C to 12% moisture. The fibers were milled in a fixed hammers mill (Pulvex) with a screen of 3 mm diameter. The milled sodium alginate was separated by particle size using a sieve shaker with five sieves of 30 (0.594 mm), 60 (0.250 mm), 80 (0.177 mm), 100 (0.149 mm) and 120 (0.125 mm) mesh. Particles greater than 30-mesh were retained on the top of the screen and considered as 20-mesh (0.833 mm). The percentage retained on each sieve was calculated. Then all sieve samples were recombined and milled a second time using a screen of 1 mm diameter. The separation was carried

out again and the percentage retained on each sieve was calculated. All sieve samples were then recombined and the procedure was repeated for a third time using a screen of 0.5 mm diameter. The mill was only warm to touch after each of the first two millings; during the third milling the residence time of the material was longer, the mill became hot and milling was stopped when it was judged to be too hot.

The effect of milling on alginate viscosity was determined by taking samples of each of the six mesh size particles after each milling and measuring the viscosity as described above. Three types of alginate were used according to their viscosity after the first milling: high viscosity (average 1365 mPa s), medium viscosity (average 417 mPa s), and low viscosity (average 103 mPa s).

Experiments were run at pilot plant level with 3 to 5 replicates. The mean and standard error were calculated for each experiment. ANOVA was used to detect significant differences among treatments ($p < 0.05$) and the Tukey test was used to find significant differences between means (Zar 1984; StatSoft, Inc. 1995).

Results

Effect of sodium carbonate on pH during conversion of alginic acid to sodium alginate

The results are shown in Figure 1 for the three methods used to determine pH. The third method, using a 1% solution of the dried sodium alginate, gives the true pH of the final product. The results for the other two, more practical, methods of checking pH during reaction, show the relationships to the pH of the final product. Significant differences were obtained for the three pH determinations. Tukey analysis showed that pH determinations in ethanol-water liquid and in the dissolved fiber were not significantly different when the ratio varied from 0.07 to 0.27:1, while pH determinations of 1% solutions were significantly different for the ratio 0.28:1 and above. This ratio (0.28:1) corresponded to the use of about 400 g of sodium carbonate in a sample of 10 kg of alga, with a 14.3% yield of alginate.

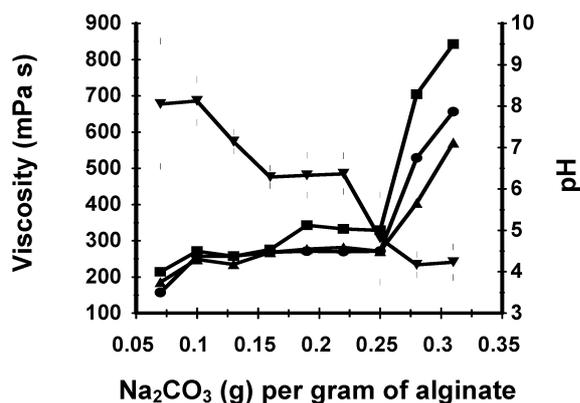


Figure 1. Effect of the amount of sodium carbonate on the alginate pH and viscosity during the conversion of alginic acid to sodium alginate. Determinations of pH: (■) ethanolic solution; (●) fiber sampled and dissolved in water; (▲) 1% alginate solution. (▼) Alginate viscosity. Vertical bars represent \pm SE.

Effect of sodium carbonate on the alginate viscosity during conversion of alginic acid to sodium alginate

The results are shown in Figure 1. Significant differences were obtained in the viscosity using ratios of sodium carbonate:alginate above 0.22:1.

Effect of temperature and drying time on moisture content

The results for drying temperature versus drying time are shown in Figure 2. Significant differences were found when comparing the four experimental temperatures. Tukey analysis showed that 80 °C produced a significantly faster drying, compared with other temperatures. Comparison of moisture at different times, showed significant differences, except for comparison of times 1 vs 1.5 h, 1.5 vs 2 h and 2.0 vs 2.5 h.

Effect of drying temperature on alginate viscosity

The results for drying temperature versus alginate viscosity are shown in Figure 3. No significant difference was found at any temperature for low and medium viscosity alginates. For high viscosity alginate the decrease in viscosity was significant only for samples dried at 70 and 80 °C.

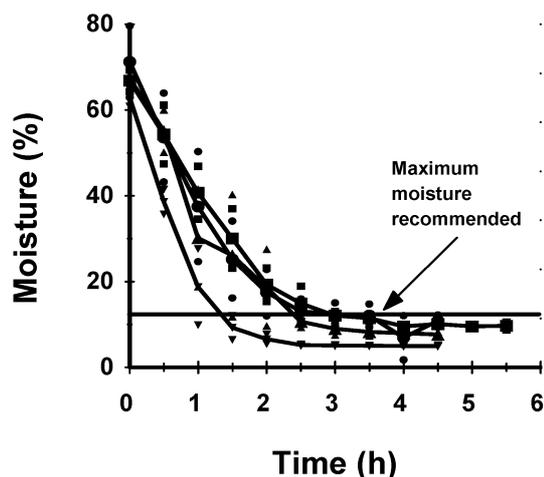


Figure 2. Effect of drying time and temperature on moisture content (%) of the alginate: (■) 50 °C; (●) 60 °C; (▲) 70 °C; (▼) 80 °C. Small symbols represent \pm SE.

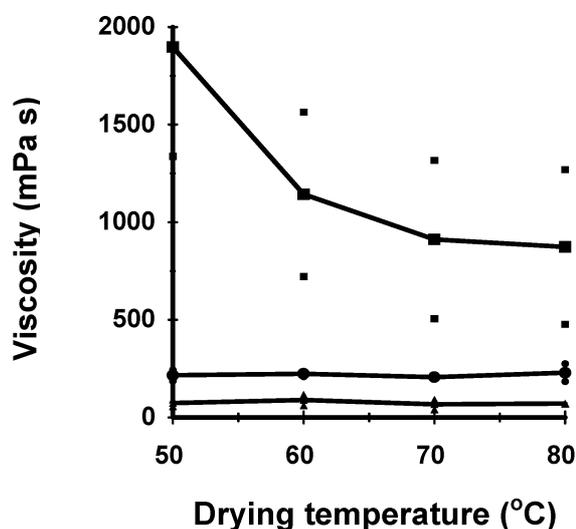


Figure 3. Effect of drying temperature on viscosity of alginate samples with (■) high, (●) medium; (▲) low viscosity. Viscosity was measured using 1% solution of sodium alginate after addition of sodium hexametaphosphate to sequester the residual calcium. Small symbols represent \pm SE.

Effect of milling on alginate particle size distribution and viscosity

The effects of milling on particle size distribution of sodium alginate are shown in Figure 4. The differences after each milling were significant. The effect of milling on alginate viscosity are shown in Figure 5. Analysis of the results showed no significant differences after each milling for any of the mesh sizes.

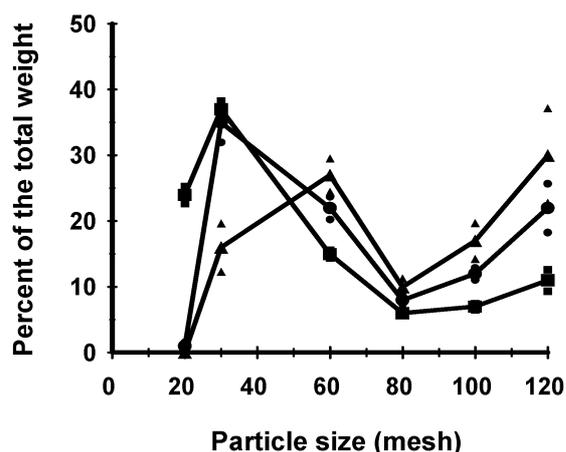


Figure 4. Effect of milling on alginate particle distribution, using a Pulvex fixed hammer mill. Same sample was milled three times: (■) first milling; (●) second milling; (▲) third milling. Small symbols represent \pm SE.

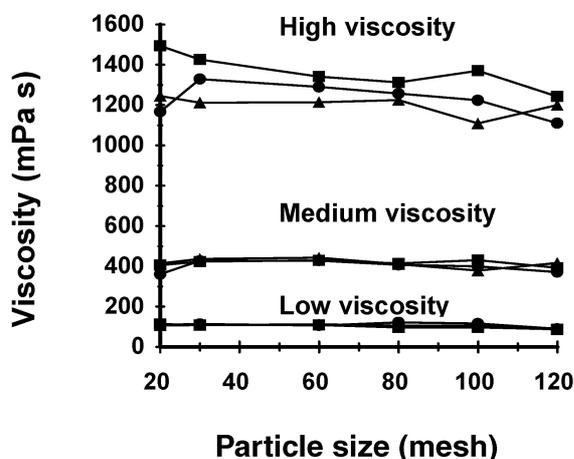


Figure 5. Effect of milling on viscosity of three types of alginate (high, medium, low viscosity), using a Pulvex mill. Same sample was milled three times: (■) first milling; (●) second milling; (▲) third milling. Viscosity obtained after addition of sodium hexametaphosphate to sequester the residual calcium.

Discussion

The last reaction of the process to produce sodium alginate is the conversion of alginic acid to sodium alginate and this reaction can be controlled by measuring the pH in different ways. Of the three methods used here, the third measures the true pH of the final product but it is too slow to use as a routine test in process control. The other two methods, (a) and (b), are faster and more convenient; they gave higher pH values, two units and one unit respectively, than the

true pH value of the final product but can be used if this is taken into account.

Figure 1 shows that the pH values do not start to rise until after a ratio of 0.25:1 is reached. The approximate amount of powdered sodium carbonate to be used in the reaction can be estimated using this result. The alginate content of the dry alga being processed must have been previously measured. It is recommended to add a ratio of 0.25 parts of anhydrous sodium carbonate per 1 part of alginate in the dry alga and then, as more alkali is added, the pH should be monitored frequently until the required pH is reached, using one of the two methods, (a) and (b), described above. The true pH of the final product is usually 6 to 7.

During neutralization of the alginic acid, the viscosity of samples of the reaction mixture gradually decreased as the pH increased (Figure 1). In the early stages, the reaction mixture contained mainly alginic acid and some sodium alginate so that the $-\text{COO}^-$ ions in the alginate chain were mostly protonated to $-\text{COOH}$. The electrostatic repulsion between chains was reduced and therefore they were able to come closer and form hydrogen bonds, producing a gel type mass (King 1983). As the reaction progressed more $-\text{COO}^-$ ions form, fewer chains retain hydrogen bonding and so the viscosity decreased. Viscosities were high and not significantly different until the ratio of 0.28:1 (sodium carbonate:alginate) was reached where it was reduced to 234 mPa s and remained the same after further addition of sodium carbonate, up to pH 8 using method (b) for viscosity measurement (Figure 1). Excessive alkalinity, especially above pH 10, may produce a breakdown by a β -elimination (Haug et al. 1963; Haug 1964) and reduce significantly the viscosity of the final product.

Drying time and temperature are important factors to consider during alginate production, since the best combination will reduce the costs. The maximum recommended moisture is 12%. The results showed that 50 °C is too slow (3 h) whereas 60 °C and 70 °C were faster (2.5 h) and were not significantly different (Figure 2). Drying at 80 °C was significantly faster (1.5 h) but it had negative effects on the viscosity of some alginates.

The effect of drying temperature on the alginate viscosity was dependent on the type of alginate. Alginates with low and medium viscosity showed no significant difference at any experimental temperature; however, alginates with high viscosity showed significant differences of viscosity depending on the

temperature (Figure 3). The viscosity of high viscosity alginate dried at 50 °C was not significantly different from that dried at 60 °C, but the samples showed a significant decrease when dried at 70 and 80 °C. The reduction of viscosity during the drying step may change with the use of other types of dryer, but the important conclusion is that significant reduction of viscosity should be expected if the temperature used is higher than 60 °C. For large scale drying of alginate a pneumatic dryer is better but this was not possible in the pilot plant. In this type of dryer, heated air carries the product through the drying zone and into a separating section. Utilizing this approach, very intimate contact between the product and the drying air is attained, and if the exposure time is kept to a minimum, product quality may be maintained.

Most applications of alginates require a particle size of 60 mesh or smaller. The results obtained here, using a fixed hammer mill, demonstrate the difficulty of milling a soft, fibrous product. Even after three passes through the mill, with successively smaller screens fitted, the alginate still contained an appreciable quantity (16%) of 30 mesh particles (Figure 4). The expectation after three millings would be for the removal of most particles larger than about 80 mesh yet these still accounted for 43% of the material. One solution to this problem would be to change the solvent used in the alginic acid to sodium alginate conversion step. The use of 50:50 ethanol:water does not allow complete solution of the reactant and product, so, much of the fibrous nature of the original alginic acid is retained in the product. Others (Zvered et al. 1969; Baranov et al. 1967) have instead washed the alginic acid with water until a pH of 4 was obtained and then added dry sodium carbonate until a pH of 7 was reached in the resulting paste. Using water as solvent allows the sodium alginate to dissolve and lose its fibrous texture in the resulting paste. The paste can then be pelletized and dried. Such a product is more readily milled.

As expected, the viscosity of the sodium alginate (Figure 5) was unaffected by the milling process although care is needed to avoid overheating in the mill.

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