

# Optimisation of critical parameters during alginate aerogels' production



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## ABSTRACT

A new method – ethanol-induced gelation seems a promising method for preparing gels from various polysaccharides. Anyhow, the characteristics of alginate aerogel, prepared by this method are not the best and the process parameters should thus be optimized. In this research we investigated the effect of process variables, such as the viscosity of alginate, gelation time and type of primary alcohol, on the characteristic properties of prepared materials. Three types of alginic acid were used during the research. The gelation times were set at 1 h and 24 h. Methanol, ethanol, propanol and *n*-butanol were used for the gelation. The best characteristics of alginate aerogels were obtained by the 24 h gelation time and by using high-viscosity alginic acid. Gelation in methanol is the best method as the surface areas of those samples were much higher ( $370 \text{ m}^2 \text{ g}^{-1}$ ) than those prepared in ethanol ( $180 \text{ m}^2 \text{ g}^{-1}$ ). Those samples also provided low thermal conductivity ( $0.042 \text{ W m}^{-1} \text{ K}^{-1}$ ).

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## 1. Introduction

Alginate is a natural polysaccharide, extensively used in pharmaceutical [1–3], biomedical [4,5], food [6,7] and other applications. It is an anionic polysaccharide and a linear copolymer with homo-polymeric blocks of (1–4)-linked  $\beta$ -*D*-mannuronate (M) and its C-5 epimer  $\alpha$ -*L*-guluronate (G), covalently linked together. Alginate is known for its great gelling and stabilising abilities. In most applications it is used in the form of a gel. Today the better known and applied methods for the gelation of alginate are in the presence of divalent ions, usually by the so-called internal setting method, by the diffusion method [8] or by the emulsion method [9,10]. Different divalent ions could be used for the gelation and they provide different mechanical and also textural properties of the final gels [11]. The gel is simply formed by binding the guluronic segments of alginate to cations, and thus creating three-dimensional networks. Depending on the M or G block content, chain-shapes, viscosities, and molecular weights, the obtained gels possess different porosity percentages, pore size, and surface properties.

After producing the wet gel, the drying step should be performed in order to obtain materials for their final applications. Drying may be performed by different routes, one of them is by using supercritical technology. Advantageous materials may be obtained by using a supercritical solvent, mostly carbon dioxide. The outstanding properties include high porosity and large surface area as well as low thermal conductivity [12, 13]. The materials are named aerogels and are among the lowest density materials known today. Aerogels could find their applications in thermal insulations [14,15], food or pharmaceutical industries [16], in medicine etc.

Conventionally, the preparation of alginate aerogels starts with the sol-gel process, using divalent ions. Hydrogels are then dried supercritically, mostly by carbon dioxide as it is considered as a green solvent with a relatively low critical point (304.18 K, 73.8 bar). One additional step should be performed between obtaining the hydrogel and its supercritical drying. Water could not be extracted with supercritical CO<sub>2</sub> and thus the dehydration should be made in organic solvent. Usually the hydrogels are immersed in a series of water-ethanol baths of increasing ethanol contents (10, 30, 50, 70, 90, 100%) and the solvent replaced each hour [17,18]. This process is time-consuming not to mention of high organic solvent consumption. In addition, the conventional sol-gel method with calcium ions should not be used for aerogels that are intended for pharmaceutical or biomedical applications, as it was recently proven that calcium ions cause inflammatory responses in the human body when released from the carrier [19].

Due to the above-mentioned, a novel gelation method has been developed by our research group [20]. The aim was to reduce the processing time. As the dehydration is one of the most time-consuming steps within the whole process, we investigated a process in order to avoid this step. In the literature it was already proven that the addition of ethanol to alginate films improves their mechanical stabilities [21]. In this manner, we have introduced a new method of producing polysaccharide aerogels directly in alcohol (Fig. 1). By the conventional route, alginate aerogels are usually prepared by cross-linking with divalent ions, mostly calcium. First step is the preparation of hydrogels. Since the water in hydrogels could not be eliminated by supercritical carbon dioxide, additionally the dehydration in alcohol is needed. Using the novel method of gelation in alcohol, we were able to eliminate an enormous step (dehydration in alcohol) in the production of polysaccharide aerogels. In the previous research we used ethanol to prepare alginate, pectin, xanthan and guar aerogels [20]. Alginate aerogels prepared by

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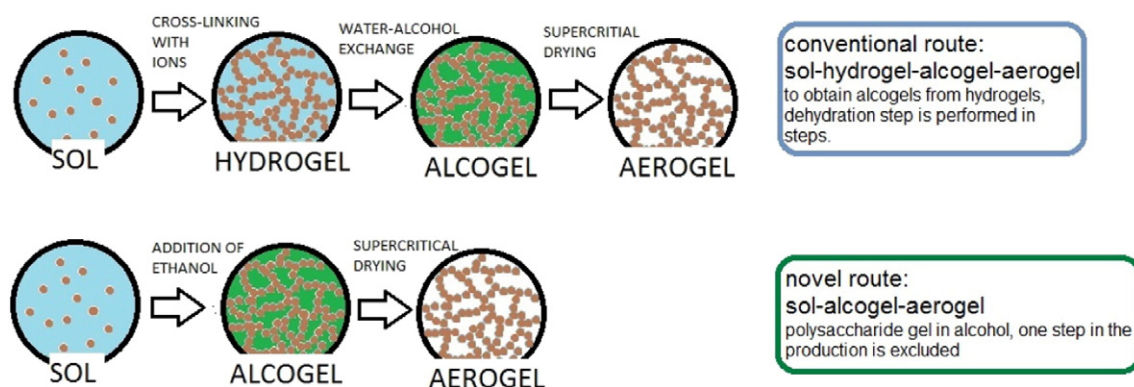


Fig. 1. Alginate aerogels production: comparison of novel route to conventional route.

the novel gelation method using ethanol provided lower surface areas than from other published research [22,23]. Thus this research is focused on optimising the gelation process in order to maximise the surface area and obtain materials with outstanding properties.

## 2. Experimental

### 2.1. Materials

Alginic acid sodium salts were purchased from Sigma&Aldrich. Three different types were used: A1 – Alginic acid sodium salt (Viscosity 15–20 cP); A2 – Alginic acid sodium salt from brown algae (Viscosity 100–300 cP); A3 – Alginic acid sodium salt from brown algae (Viscosity >2000 cP). CO<sub>2</sub> (Messer) was used for supercritical drying. *N*-butanol, propanol and methanol were purchased from Merck and the absolute ethanol from Sigma&Aldrich. The methanol standard (99.9%) for headspace analysis was purchased from Sigma&Aldrich.

### 2.2. Methods

#### 2.2.1. Varying process parameters in alginate aerogel production

**2.2.1.1. Viscosity of alginate.** Three different alginic acid sodium salts were used during this research. Firstly, the alginate was mixed with water to form 4% aqueous solution. Then the solution was transferred to a mould and sunk into absolute ethanol. The gelation was performed for 24 h. Thereafter the gels were transferred to an autoclave and dried with supercritical carbon dioxide at 40 °C and 120 bar for 5 h.

**2.2.1.2. Gelation time.** In order to investigate the impact of the gelation time, we used 4% alginate solution (alginate viscosity 100–200 cP) to prepare a gel. The aim was to investigate the effect of 1 h vs. 24 h gelation times on the morphological properties of the final materials. 4% aqueous solution of alginate was prepared and transferred to a mould. The solution was left in absolute ethanol for 24 h to form a gel. Next day, another 4% aqueous solution of the same alginate was prepared and the gelation time in absolute ethanol was 1 h. Then all wet gels were dried with supercritical carbon dioxide at 40 °C and 120 bar.

**2.2.1.3. Alcohol.** It has been published that ethanol induces the gelation of alginate but however the material's characteristics were not really promising [20]. The effect of different primary alcohols on the gelation of alginate was therefore investigated. Alginate (viscosity >2000) solution was prepared as already described. Instead of ethanol the mould was then sunk either in methanol, propanol or *n*-butanol. Supercritical drying was then the same as for ethanol-induced gelation. Table 1 summarises the samples prepared during this research.

#### 2.2.2. Characterisation of dry aerogels

Nitrogen adsorption was performed to investigate the material's surface areas, pores' volumes and pores' size distributions. Prior to the measurements all the samples had been degassed under reduced pressure (<1 mPa) at 70 °C for 10 h. The specific surface area was then determined by the BET method. Pore volume was determined by filling the pores completely with liquid nitrogen at  $P/P_0 = 0.99$  and average pore size distribution was determined by the BJH desorption method.

Scanning electron micrographs of the prepared aerogel samples were obtained using a HRSEM, Helios Nanolab FEI 650. The samples were fractioned and then sputter-coated with gold particles (JEOL-JCF-1100E) and scanned at an accelerating voltage of 5 kV.

Bulk densities of aerogels were determined as the ratio of mass to volume. The mass of the aerogel was determined by five-digit analytical balance and the volume was determined by measuring the diameter and the height of aerogel of cylindrical shape by digital caliper. The bulk density was then determined as the ratio of 5 samples.

Polysaccharide aerogels are highly sophisticated materials, which were recently investigated for their pharmaceutical applications [24–26]. Consequently, their preparation procedure was strict in accordance with the US Pharmacopoeia prescriptions. It is well-known that organic solvents are constantly present during the pharmaceutical production processes. However, for toxicological reasons the amount of organic solvents has to be minimised or kept under a certain level as specified by the Pharmacopoeia. The organic solvents used during this research were primary alcohols: methanol, ethanol, propanol and butanol. All of them, except methanol, are classified as Class 3, meaning the permission of the daily exposure for those solvents is 50 mg or less. Methanol then belongs to Class 2 and its daily exposure is limited to 20 mg [27].

The organic solvents usually cannot be completely eliminated from the product by the drying process and some small amounts of solvents may remain in the final product. Therefore, we performed Headspace GC analysis in order to quantify the amount of methanol in the dry aerogels. The analysis was performed on a Shimadzu GC-2010Plus, Flame ionization detector (FID):290 °C + Headspace HS-20 system. Samples were accurately weighted and placed into the analyser.

**Table 1**  
Process parameters used in the research.

Sample	Gelation time	Viscosity (cP)	Alcohol
A <sub>1</sub> E-24	24 h	Low (15–20)	Ethanol
A <sub>2</sub> E-24	24 h	Middle (100–200)	Ethanol
A <sub>2</sub> E-1	1 h	Middle (100–200)	Ethanol
A <sub>3</sub> E-24	24 h	High (>2000)	Ethanol
A <sub>3</sub> B-24	24 h	High (>2000)	1-Butanol
A <sub>3</sub> M-24	24 h	High (>2000)	Methanol
A <sub>3</sub> P-24	24 h	High (>2000)	Propanol

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