Carbohydrate Polymers 180 (2018) 264–275

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Research paper

Effect of processing parameters on preparation of carrageenan aerogel microparticles

Mohammad Alnaief[a,*], Rana Obaidat[b], Hadeia Mashaqbeh[b]

[a] Department of Pharmaceutical and Chemical Engineering, Faculty of Applied Medical Sciences, German Jordanian University, Jordan
[b] Department of Pharmaceutical Technology, Faculty of Pharmacy, Jordan University of Science and Technology, Jordan

ARTICLE INFO

Keywords:
Carrageenan aerogel
Microparticles
Supercritical CO_2-extraction

ABSTRACT

The aim of this work is to produce aerogel microparticles using a biocompatible polymer. Commercial available carrageenan suitable for gelation was used as a precursor for gel preparation. Microspherical carrageenan gel particles were obtained by applying emulsion technology. The gel was converted to an aerogel using supercritical carbon dioxide extraction process. Several process parameters were investigated for their effect on the final properties of the produced aerogel. The produced aerogel particles were characterized for their textural properties using gas sorption analysis. For complete understanding the following characterization techniques were employed: FTIR, PXD, TGA, SEM, Zeta sizer, particles density and particle size distribution.

In conclusion, biodegradable aerogel micro-spherical particles based on three different commercial available carrageenan were produced. Depending on the process parameters the surface area of the produced aerogel ranged between 33 and 174 m^2/g, the average pore volume and pore sized were 0.35 ± 0.11 cm^3/g and 12.34 ± 3.24 respectively. The produced porous material shows potential characteristic for drug delivery application.

1. Introduction

Polysaccharide based aerogels combined the unique properties of aerogel and the attractive properties of polysaccharides which allows tailoring them to the targeted application. Due to their availability, surface properties, diverse functionality, low toxicity, biocompatibility and biodegradability they have been proposed for wide range of challenging applications. For instance, tissue engineering (Cai et al., 2014; Cardea, Pisanti, & Reverchon, 2010; Duarte et al., 2013), food technology (Mikkonen, Parikka, Ghafar, & Tenkanen, 2013), drug delivery application (García-González, Alnaief, & Smirnova, 2011; Lovskaya, Lebedev, & Menshutina, 2015; Ulker & Erkey, 2014), environmental remediation (Oshima, Sakamoto, Ohe, & Baba, 2014; Wörmeyer, Alnaief, & Smirnova, 2012; Yu et al., 2013), catalysis (Guibal, 2005; Saha, Pal, Kundu, Basu, & Pal, 2010) and many other applications (Malafaya, Silva, & Reis, 2007; Maleki et al., 2016; Martins et al., 2015; Miao et al., 2008).

In general, it is possible to prepare aerogel from any polysaccharide precursor as long as it is possible to prepare a stable gel out of that precursor. Generally, after dissolving the biopolymer in a suitable solvent, a crosslinking step is needed to generate a stable network structure. Depending on the nature of the biopolymer, a chemical or a physical crosslinking can be used to produce the gel (Dumitriu, 2005; Grant, Morris, & Rees, 1973; Walter, 1998). If supercritical carbon dioxide is used for the elimination of the solvent, the hydrogel should be converted to an alcogel by mean of solvent exchange (García-González et al., 2011). Finally, the solvent of the alcogel is transferred to aerogel using supercritical fluid extraction, in which the solvent of the alcogel is replaced by air while maintaining the solid network intact (Leventis, Aegerter, & Koebel, 2010).

Carrageenan have the ability to form thermos-reversible gel. Upon cooling of the hot aqueous solution of carrageenan, a three dimensional network is formed. The double helix of the polymer form the junction points between polymer chains. Eventually, aggregates of the junction points are formed and subsequently, the gel is formed. The final property of the gel depends mainly on the number and type of theses junction points (Ikeda, Morris, & Nishinari, 2001a; Montoro, Medeiros, & Alves, 2014)

Several groups have reported the production of carrageenan aerogel, which were mainly produced using κ-carrageenan as a precursor. Robitzer et al. reported the production of κ-carrageenan aerogel beads, by adding the κ-carrageenan solution dropwise to KCl solution, the aerogel were 200–230 $m^2\,g^{-1}$ and a mesoporous structure with a pore volume of 0.9–1.4 $m^3\,g^{-1}$ (Robitzer, Tourrette et al., 2011;

* Corresponding author.
E-mail address: mohammad.alnaief@gju.edu.jo (M. Alnaief).

http://dx.doi.org/10.1016/j.carbpol.2017.10.038
Received 15 July 2017; Received in revised form 1 October 2017; Accepted 9 October 2017
Available online 10 October 2017
0144-8617/

Robitzer, Renzo, & Quignard, 2011). Gansen and Ratke reported the production of monolith κ-carrageenan aerogel by heating the carrageenan solution to about 90 °C and dripping KSCN solution as a cross linker, the produced aerogel were white monoliths with fibrillar structure and a specific surface area of 230 m^2g^{-1} (Ganesan & Ratke, 2014). Raman et al. prepared a hybrid aerogel monoliths based on alginate and λ-carrageenan, the gelation was induced using pressurized CO_2 at 50 bar and room temperature. The gelation was achieved due to the ionotropic gelation of alginate. The monoliths have a surface area of 446 $m^2 g^{-1}$ and a pore volume of 2.38 $m^3 g^{-1}$ (Raman, Gurikov, & Smirnova, 2015). Emulsion gelation method was used to prepare hybrid alginate – κ-carrageenan aerogel, the gelation of alginate was induced using internal setting method while the κ-carrageenan co-gelled with alginate. The effect of surfactant concentration on particle size distribution were investigated, microparticles hybrid aerogel were produced with a size range of (1–1000) μm and large surface area (370–417) $m^2 g^{-1}$ and 3.1–3.7 $m^3 g^{-1}$ as a pore volume (Gonçalves et al., 2016). Manzocco et al. reported the production of cylindrical monoliths of κ-carrageenan aerogel by dripping κ-carrageenan solution into KCl solution at 90 °C and cooling the resultant suspension over one day at 4 °C, the produced aerogel were used for oil adsorption and delivery application (Manzocco et al., 2017)

In this work, the production of carrageenan based aerogel from different commercial available precursor as micro particles is reported. Spherical particles were produced with the aid of emulsion gelation technique. Several processing parameters were investigated. A complete physicochemical characterization was employed to evaluate the influence of process parameters on the final aerogel properties. To the best of our knowledge, the preparation of carrageenan aerogel microparticles using emulsion gelation technique still unexplored.

2. Materials and methods

2.1. Materials

Kappa-carrageenan, Carrageenan suitable for gel preparation, Carrageenan type I, Span® 80 and Span® 85 were purchased from Sigma Aldrich. Absolute ethanol was supplied by Solvochem, Holland. Carbon dioxide (CO_2) was provided by the Jordanian Gas Co., Jordan. Water (HPLC grade) was purchased from LabChem, USA. Potassium chloride, extra pure, BP, USP was enquire from AZ Chem For chemicals. Potassium carbonate pure USP food grade was purchased from AppliChem GmbH. Potassium Iodide–pure was packed by J.C.L.E. Calcium chloride anhydruous, granulated extra pure enquire from BBC Chemicals for lab. Aluminum chloride hydrated, was obtained from S.D. fine chem limited. Paraffin oil was enquire from AZ CHEM, India.

All chemicals were used as supplied without any further modification.

2.2. Preparation of carrageenan aerogel microparticles

Table 1 shows the prepared samples in this work. Several process parameters were investigated. Some of them failed to give a proper gel or aerogel and they were discarded from further analysis. The investigated process parameters were: carrageenan type, biopolymer concentration, crosslinker type and concentration and preparation temperature.

A detail description of the gel to aerogel preparation is described in the following sections.

2.2.1. Preparation of the microparticles gel

Emulsion gelation method were used to prepare the carrageenan microparticles, the method was based on previous work and modified to meet the requirement of gelation for carrageenan polymer (Alnaief, Alzaitoun, García-González, & Smirnova, 2011). Initially, carrageenan polymer was dissolved in water to make an overall weight of 85 g and the mixture was heated to 90 °C under stirring for 30 min to insure complete hydration. Meanwhile, the crosslinker was dissolved in 15 g of water to make 100 ml of biopolymer solution. Three different concentrations were prepared, namely: 2, 3 and 4 wt.% carrageenan solution. After that, the polymer solution was poured into a preheated paraffin oil phase, containing a certain amount of surfactant, under stirring (3000 rpm) for 10 min. At this moment, the crosslinker solution was added dropwise and the emulsion was mixed further for 15 min. Finally, the produced dispersion was transferred to a magnetic stirrer mixer and stirred for 30 min at 200 rpm.

Table 1
Samples IDs and preparation conditions in this work.

Sample ID	type	Conc. wt%	cross-link wt%	Temp °C	Surfactant wt%
S1	suitable	4%	2.00% KCl	90	1% Span® 80
S2	suitable	3%	1.50% KCl	90	1% Span® 80
S3	suitable	2%	1.00% KCl	90	1% Span® 80
S4	suitable	4%	0.25% KCl	90	1% Span® 80
S5	suitable	4%	0.50% KCl	90	1% Span® 80
S6	suitable	4%	1.00% KCl	90	1% Span® 80
S7	suitable	4%	4.45% KI	90	1% Span® 80
S8	suitable	4%	1.85% K_2CO_3 (1.85%)	90	1% Span® 80
S11	suitable	2%	1.00% KCl	90	2% Span® 80
S12	suitable	4%	No cross linker	90	1% Span® 80
I1	type I	2%	1.00% KCl	65	2% Span® 80
I2	type I	2%	2.00% KCl	65	2% Span® 80
I3	type I	2%	3.00% KCl	65	2% Span® 80
I4	type I	2%	1.00% KCl	75	2% Span® 80
I5	type I	2%	1.00% KCl	90	2% Span® 80
I6	type I	2%	$CaCl_2$(eq to 1% KCl)	65	2% Span® 80
I7	type I	2%	$AlCl_3$(eq to 1% KCl)	65	1% Span® 80
I8	type I	4%	No cross linker	90	2% Span® 80
K1	kappa	2%	1.00% KCl	90	1% Span® 80
K2	kappa	4%	No cross linker	90	2% Span® 80

2.2.2. Solvent exchange (hydrogel to alcogel)

To replace the water in the prepared hydrogel with alcohol, a stepwise solvent exchange was employed. The prepared dispersion/oil phase was centrifuged at 4000 rpm for 15 min. As a result, the oil phase was decanted. Then the process was repeated after washing the solid gel particles with pure water. At this stage most of paraffin oil was removed and a series of successive solvent exchange was performed. The solvent exchange steps were 20%, 40%, 60%, 80% ethanol:water and two times 100% ethanol. Each step was allowed to mix for 60 min.

2.2.3. Supercritical CO_2 extraction (alcogel to aerogel)

In order to dry the alcogel particles, a supercritical extraction unit was used. The wet gel was placed in a preheated 500 ml stainless steel vessel. The supercritical CO_2 was introduced continuously from the bottom of the vessel at a constant flow of 100 g/min using a double piston pump. The vessel pressure was controlled using a back pressure regulator and was kept constant at 100 bar. The solvent-CO_2 phase was driven to a separation vessel. The condition of the separation vessel was kept at 60 bar and 40 °C. The solvent was collected from the bottom while the solvent lean CO_2 was recycled to the extraction process. The extraction process was performed for four hours. To insure sufficient extraction, fresh CO_2 was introduced several times to the extraction cycle. The small traces of paraffin oil remained from the solvent exchange process was removed at this stage.

2.3. Physicochemical characterizations of the prepared carriers

2.3.1. Scanning electron microscopy (SEM)

The surface morphology of the samples was obtained using Quanta FEG 450, SEM (FEI, US). Before performing SEM analysis, the samples