An integrated approach towards biopolymer aerogels using high pressure solvent exchange

Raman S.P., Pavel Gurikov, Irina Smirnova
1 Technische Universität Hamburg Harburg, Eißendorfer Straße 38, 21073 Hamburg
E-mail corresponding author: raman.subrahmanyam@tuhh.de

ABSTRACT

Aerogels derived from (bio) polymers, e.g. alginate, starch, chitosan, are in the limelight due to biocompatibility, improved mechanical properties and abundant natural sources. Major drawback of the existing process is that gelation of biopolymers takes place in aqueous media. Therefore, hydrogels produced in this way cannot be converted into aerogels directly due to wide immiscibility between water and supercritical carbon dioxide. Thus, solvent exchange to organic solvents is needed prior to supercritical drying.

In this work we present a novel integrated process where the solvent exchange is carried out in pressurized carbon dioxide. Hydrogels is exposed to ethanol/water mixtures saturated with carbon dioxide at pressure in the range of 50 – 150 bar. Ethanol concentration is gradually increased from 0% up to 100% followed by supercritical drying. Applicability of the process to alginate hydrogels and their hybrids is shown. Textural properties of the aerogels are comparable and in some cases superior to reported in the literature. Kinetic study of both the ambient and high pressure solvent exchange processes was performed. It was shown that the solvent exchange kinetics obeys pseudo second-order equation. Solvent exchange rate at high pressure is comparable with ambient conditions. Based upon kinetic data, number of steps and their duration were optimized that allowed to reduce processing time significantly. Influence of the operating conditions (pressure, temperature, gel composition) on aerogel textural properties is also discussed.

INTRODUCTION

Aerogels are ultra light materials consisting of nanosized particles or fibers arranged in a highly porous three-dimensional network. Conventional route toward aerogels is to subject a low molecular weight precursor to hydrolysis and condensation in an organic solvent (e.g. ethanol, acetone). The solvent can be substituted for supercritical fluid within supercritical drying step leaving behind the solid backbone, an aerogel. Aerogels composed of inorganic oxides, mostly silicon oxide are considered as highly attractive candidates to be used as thermal and sound insulators, adsorbents, supports for catalysts and drug delivery systems [1]. However, poor mechanical properties along with lack of biocompatibility limit extensive foray into these potential applications. Aerogels derived from (bio)polymers, e.g. alginate, starch, chitosan, cellulose and lignin are promising alternatives on account of their biocompatibility and immediate natural availability and thereby are in the limelight.

One impediment on the way to turn biopolymers into aerogels is that gelation or cross linking takes place in aqueous media. Hydrogels produced in this way cannot be converted into aerogels directly due to very low solubility of water in supercritical carbon dioxide. Thus, solvent exchange for organic solvents is needed prior to supercritical drying. Factors such as biopolymer concentration, degree of cross-linking, the concentration gradient between the

solvent and the gel, and exchange frequency between the solvents play a pivotal role in the shrinkage behavior of the alcogel [2] and could also influence the final surface characteristics of the aerogel. This work makes an attempt to evaluate the kinetics of solvent exchange process of calcium alginate gels of varying biopolymer concentrations and crosslinking degree at ambient conditions. As supercritical drying with CO_2 is a quintessential step in the production of aerogels, and also any improvement to the solvent exchange kinetics would mark a significant reduction in the overall processing time; solvent exchange study at high pressure was also performed to compare and contrast with ambient pressure solvent exchange kinetics.

MATERIALS AND METHODS

Sodium alginate was purchased from Sigma Aldrich (suitable for immobilization of micro-organisms grade, catalogue no. 71238). Calcium carbonate (light, precipitated powder) was kindly provided by Magnesia GmbH (Germany). Ethanol 99.8 % was obtained from H. Möller GmbH (Germany). Carbon dioxide with a purity > 99.9 % was supplied by AGA Gas GmbH (Hamburg, Germany). All chemicals were used as received. Deionized water was used throughout the study.

Solvent exchange procedure for ambient pressure kinetic study

The solvent exchange was performed at pressure 1 bar and temperature $20 \pm 1\,°C$, i.e. at ambient conditions. The multistep solvent exchange was performed in seven steps as follows: 10, 30, 50, 70, 90, 100 wt% (the last step with pure ethanol was made two times to remove the water completely). Density of the ethanol-water mixture and, thus, its concentration were measured using Density Meter DMA 4500 (Anton Paar Company, Austria). Three samples from each formulation were measured in parallel. Once equilibrium reached, hydrogel was transferred into the next ethanol-water mixture to perform the next solvent exchange step.

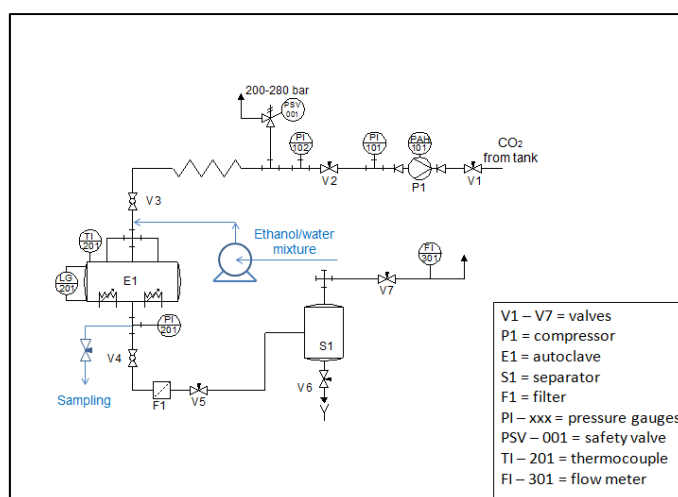*Solvent exchange procedure for high pressure kinetic study*

Fig.1 Autoclave setup for high pressure solvent exchange and supercritical drying

Supercritical drying set-up was equipped with a HPLC pump K-1001 (Knauer GmbH, Germany) and an additional line for sampling (Fig. 1). These changes allow to perform both

SC drying and high pressure solvent exchange in the same autoclave. The solvent exchange was performed at 50 bar and ambient temperature. The multistep solvent exchange was performed in seven steps as follows: 10, 30, 50, 70, 90, 100 wt% similar to the ambient pressure kinetic study. Initial gel mass to solvent ratio was also maintained similar. After solvent exchange, the samples were drying using supercritical CO2 at 120 bar and 45°C.

RESULTS

It was observed from experimental data that the water to ethanol solvent exchange kinetics for calcium alginate based hydrogels follows pseudo second-order equation (similar to first order sorption kinetics initially proposed by Lagergren) as shown in Fig 2. In all the solvent exchange cases the model fit the experimental data very well with R^2 of > 0.995. A similar analysis of the swelling of alginate hydrogels (in terms of water uptake) was successfully described by pseudo second-order kinetic equation by Davidovich-Pinhas et al. (2010) [3].
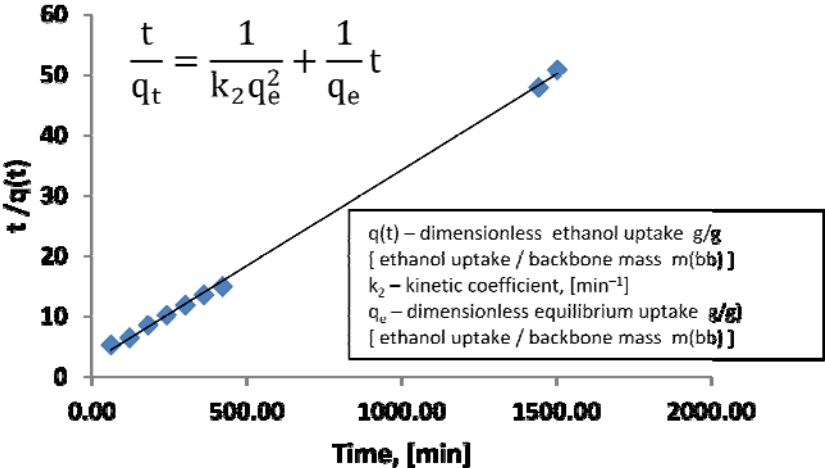

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

q(t) – dimensionless ethanol uptake g/g
[ethanol uptake / backbone mass m(bb)]
k_2 – kinetic coefficient, [min^{-1}]
q_e – dimensionless equilibrium uptake g/g
[ethanol uptake / backbone mass m(bb)]

Fig.2 Pseudo second order model for water-ethanol solvent exchange kinetics

Using this equation, the kinetic coefficients k_2 were calculated at different concentrations of ethanol/water mixtures (method section). k_2 indicates the speed of the mass transfer (see Fig. 4). A similar set of experiments were also carried out under high pressure CO_2 (50 bar). The concentration profiles are compared in Fig. 3.
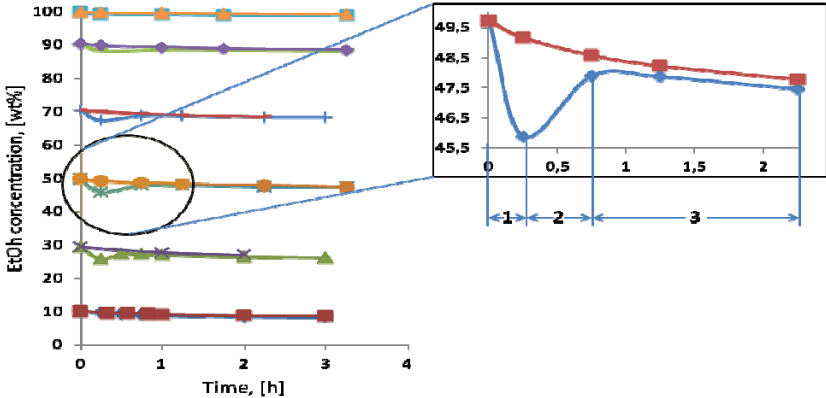

Fig.3 Comparison of concentration profiles for ambient (■) and high pressure (♦) solvent exchange

Two notable observations were made. Firstly, it was observed that the concentration drops were much faster than those observed for ambient pressure. This is also indicated by the higher kinetic coefficients for high pressure solvent exchange at different solvent exchange steps (Fig. 3). Secondly, in the initial stages of the high pressure solvent exchange, there was a steep drop in the concentration which later stabilized. It could be due to any or a combination of the following points. (1) CO_2 participates actively in the ethanol transport inside the gel; (2) The shrinkage behaviour during the solvent exchange steps causes water to be squeezed out and (3) There is some extent of additional ethanol adsorption on the gel body. However the exact reasons are not fully understood and thereby open to further investigation.
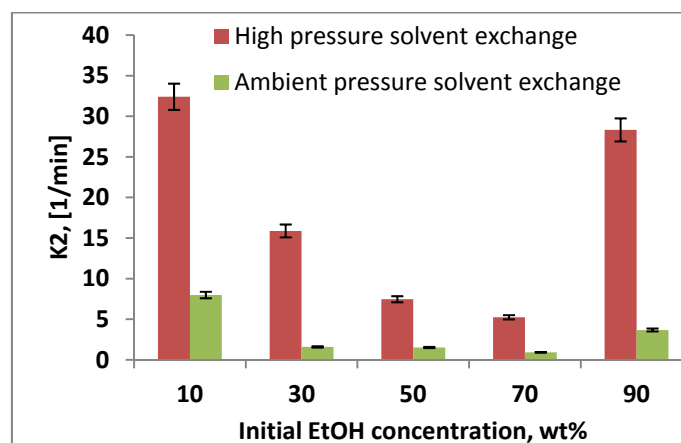

Fig.4 Comparison of kinetic coefficients for ambient and high pressure solvent exchange

CONCLUSION

It was observed that the water to ethanol solvent exchange kinetics follow pseudo second order relation. In addition, during high pressure CO_2 solvent exchange, it was observed that the concentration drop is much faster compared to ambient pressure conditions and is also indicated by the mass transfer coefficients k2 calculated from the pseudo second order equation. However, the reasons for the high mass transfer rate are not fully understood and still need to be further evaluated.

REFERENCES

[1] Leventis, N., Aegerter, M., and Koebel, M. (2011). Aerogels handbook. New York, NY: Springer.
[2] García-González, C.A., Alnaief, M., and Smirnova, I. (2011). Polysaccharide-based aerogels — Promising biodegradable carriers for drug delivery systems. Carbohydrate Polymers 86, 1425–1438
[3] Davidovich-Pinhas, Maya; Bianco-Peled, Havazelet (2010): A quantitative analysis of alginate swelling. In Carbohydrate Polymers 79 (4), pp. 1020–1027. DOI: 10.1016/j.carbpol.2009.10.036.
[4] Ho, Y. (2006): Review of second-order models for adsorption systems. In *Journal of Hazardous Materials* 136 (3), pp. 681–689. DOI: 10.1016/j.jhazmat.2005.12.043.