# New greener routes to mesoporous materials from marine polysaccharides

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#### Introduction

Mesoporous materials are widely used in liquidphase applications as catalysts, adsorbents and chromatographic supports.<sup>1</sup> Due to the resource and energy intensive nature of sacrificial structuredirecting templating approaches there is interest in the use of abundant materials.<sup>2</sup>

Researchers have successfully produced mesoporous materials from extracted alginic acid and alginates, chitosan and carrageenan as well as other polysaccharides.<sup>3</sup> However, the materials produced are sensitive to the presence of the menisci of high surface-tension liquids, resulting in the need for  $scCO_2$  drying to prevent pore collapse. This work presents three alternative approaches for the production of mesoporous materials by direct drying of fresh macroalgae, freeze-drying of alginic acid and hydrothermal carbonisation of chitosan.

#### **Results and Discussion**

An innovative route to the direct formation of mesoporous materials from fresh biomass is demonstrated of three brown seaweeds from the UK are demonstrated.<sup>4</sup> Uniquely, little variation in the surface area, mesoporous volume or average pore diameter are observed upon drying the solvent-exchanged expanded seaweed samples by vacuum drying compared to using scCO<sub>2</sub> (Figure 1), offering a major advantage over the use of extracted polysaccharides.



Figure 1 Textural properties of macroalgae samples a) N<sub>2</sub> isotherms and pore size distributions for *Laminaria digitata* during expansion and b) pore volumes of five expanded seaweed species.

Alternatively, a unique and innovative route to polysaccharide aerogels with controllable meso- and macropore ratios is demonstrated using freeze *38<sup>a</sup> Reunião Anual da Sociedade Brasileira de Química* 

acid, chitosan, green chemistry, freeze-drying drying of aqueous TBA mixtures from alginic acid gels (Figure 2). The meso- to macro pore ratio is shown to be dependent on the TBA/water phase diagram with maximum mesopore volumes around the eutectic points. As freeze drying technology is accessible, scalable and widely used in applications, great potential exists for the industrial production of polysaccharide aerogels with clear green credentials



**Figure 2.** BJH pore volumes of alginic acid aerogels prepared by a) TBA addition method b) direct gelation

A final approach enables the direct formation of mesoporous carbonaceous materials from chitosan via hydrothermal treatment, producing a porous nitrogen-doped material ideal for electronic applications.

### Conclusions

This work demonstrates a wide variety of greener routes to high-value mesoporous materials which opens new lower cost applications for catalysis, adsorption and water purification.

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1. Budarin, V.; Clark. J. H.; Deswarte, F. E. I.; Hardy, J. E.; Hunt, A. J. and Kerton, F. M. *Chem. Commun.*, **2005**, *23*, 2903-2905.

2. Dodson, J. R.; Cooper, E. C.; Hunt, A. J.; Matharu, A.; Cole, J.; Minihan, A.; Clark, J. H. and Macquarrie, D. J. *Green Chem.*, **2013**, *15*, 1203-1210.

3. Budarin, V.; Clark. J. H.; Hardy, J. E.; Luque, R.; Milkowski, K.; Tavener, S. J. and Wilson, A. J. *Angew. Chem.-Int. Edit.*, **2006**, *45*, 3782-3786.

4. Dodson, J. R.; Budarin, V. L; Hunt, A. J.; Shuttleworth, P. S. and Clark, J. H. J. Mater. Chem. A, **2013**, *1*, 5203-5207.