

## Natural materials with high surface area. Physisorption methods for the characterization of the texture and surface of polysaccharide aerogels

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### ABSTRACT

Polysaccharide hydrogels are open networks of naturally functionalized hydrocarbon materials. In this study, gels of several polysaccharides (alginate, alginic acid,  $\kappa$ -carrageenan, agar, chitin and chitosan) have been prepared by various gelling methods. Supercritical drying allows to form aerogels with surface areas as high as  $600 \text{ m}^2 \text{ g}^{-1}$  and active sites with acid (alginate or carrageenan) or basic (chitosan) properties, which confer them effective catalytic properties. The macroporous volume of polysaccharide aerogels can reach  $40 \text{ cm}^3 \text{ g}^{-1}$  and provide an excellent accessibility of the active sites. Physisorption of  $\text{N}_2$  at 77 K has allowed to assess a secondary mesoporosity attributed to contacts between polymer fibrils. The enthalpies of physisorption have been analyzed through the BET method and the measurement of isosteric heat of adsorption of Ar. Comparison plots have been drawn on the basis of a reference isotherm exploiting the absence of microporosity of fumed silica and the absence of mesoporosity of Lichrospher. Deviations of the low-pressure part of the comparison plots have been exploited to evaluate a variation of density of the physisorbed monolayers in good correlation with enthalpies of adsorption. The molecular area of adsorbed  $\text{N}_2$  is an inverse function of the energetics of physisorption. The adsorption heat increases with the polarity of the polymer in the order of chitin < chitosan < agar < carrageenan ~ alginic acid ~ alginate, where acetylated chitin is the less polar term and polymers with acidic groups or metal cations are the most polar terms of the series.

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### 1. Introduction

The development of heterogeneous catalytic systems for the synthesis of fine chemical is a major area of research. Recent efforts, driven by the shift from petrochemical-based or inorganic feedstocks toward biological materials, have been directed to the use of biopolymers as supports for catalysis [1–4]. Polysaccharides fulfill most of the properties needed for catalysts or adsorbents: presence of numerous and diverse surface functionalities, insolubility in most of the organic solvents, inherent chirality and for some of them quite a good thermal stability. Moreover, possible conformational effects in relation with the physical structure of the materials are expected [5], the availability of gelling polysaccharides in nature is quite unlimited, industrial processes of extraction already run at large scale [6], and disposal of the organic material at the end of the lifecycle produces less toxic degradation products than equivalent petrochemical-derived resins.

Hydrocolloid-forming polysaccharides are natural polyelectrolytes able to form stable gels which can be easily shaped and are

largely used in food and pharmaceutical industry. Gelling polysaccharides derived from seaweeds or wastes of the seafood industry include polymers with several functional groups: alginates (carboxylic groups), carrageenans (sulphonic groups) and chitosan (amino groups) (see Fig. 1). Their interest as catalysts (basic or acid) or as catalyst supports depends on the presence of appropriate functional groups made easily accessible by the open structure of the gel.

The nature of the polysaccharide defines the method of gelling. Sodium alginate is water soluble. Its solution added dropwise at room temperature to a stirred solution of divalent (or trivalent) cations forms beads of ionotropic gel. The principle of  $\kappa$ -carrageenan bead formation is the thermo- and ionotropic gelation of hot droplets of polymer solution falling into a cold saline (KCl) solution. Aqueous solutions of chitosan are obtained by dissolving chitosan in aqueous acetic acid solution. The polymer solution added dropwise to a NaOH solution forms the gel. In the case of agar, which only brings hydroxyl functional groups, a thermal gel is obtained by cooling down hot solutions.

Polysaccharide hydrogels present a highly open structure but their level of dispersion depends on the presence of the solvent and is hardly retained in the dry state. Evaporative drying brings

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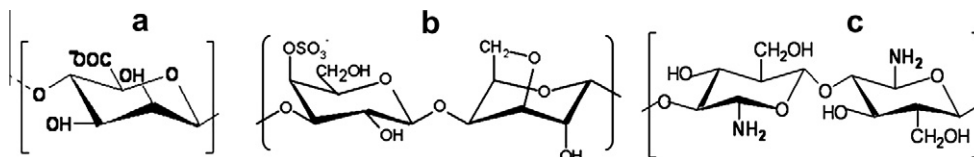


Fig. 1. Building blocks of (a) alginate, (b)  $\kappa$ -carrageenan, (c) chitosan.

about the collapse of the gel structure and does not allow to retain the accessibility of the functional groups. The low surface area of the dried materials generally used, xerogels or lyophilised solids, is a major limit to the use of polysaccharide supports in catalysis. The technique of supercritical drying allows to avoid shrinkage of the gels and improve diffusional properties in dry polysaccharides. The effectiveness of the supercritical drying method depends on the mechanical properties of the polymer but most polysaccharides aerogels maintain the tridimensional network of the parent hydrogel and develop surface areas from 100 to 600 m<sup>2</sup> g<sup>-1</sup> [7].

Can polysaccharide aerogels compete with existing catalyst supports and adsorbents? Ion exchange resins can be considered as a valid cost benchmark, as they operate in the field of thermal stability of polysaccharides and present similar chemical functions. The cost of anionic resins has steadily rose after a historical minimum around 4 \$ per kg in 2000 with oil price at 25 \$ per barrel [8]. At the current oil price above 70 \$ per barrel, the cost of seaweed-derived refined hydrocolloids, near 10 \$ per kg [6], is in the same range as the cost of synthetic exchange resins. The cost of a supercritically-dried stabilised polysaccharide hydrogel is obviously expected to be higher than the cost of the raw material, but such is also the case for high-surface synthetic resins for specific applications. The costs of CO<sub>2</sub> supercritical treatments, essential for the retention of the hydrogel dispersion in the dry materials, are extremely dependent on the scale and technology of the process. In a mature industrial environment, supercritical treatment costs are expected to represent only a fraction of the cost of the raw material and are reported in the range of 0.30–0.70 € per kg for large extraction plants in the pulp-and-paper industry [9].

The world production of petroleum-derived resins is of the order of 200 Mt y<sup>-1</sup>. The seaweed production in the world is of the order of 8 Mt y<sup>-1</sup>. The replacement of any fraction of the resin market would represent a significant boost for the polysaccharide industry, which expectedly has a significant potential for expansion. If the expansion of non-food uses of most renewable sources of biomass is severely limited by competition with the use of agricultural land for food production, this is not the case for the derivatives of seaweeds, which are acknowledged as the source of biomass in lowest competition with food markets [10]. Moreover, the production of hydrocolloids is not energy-intensive. In the case of the production of seaweed, the energy input is between 10 and 20 kJ kg<sup>-1</sup>, from one to two orders of magnitude lower than the energy input for agricultural sources of biomass [10].

The purpose of this communication is to discuss characterisation methods for the texture of polysaccharide aerogels. Dry materials with high surface area can be easily characterized by the physisorption methods typical of materials science. However, the methods currently used to evaluate the surface area from physisorption isotherms, like the BET method or the comparison plots, are affected by the chemical nature of the surface, whereas the methods used to evaluate mesopore size are unreliable for pores with diameter larger than about 50 nm, the upper limit of mesoporosity. The availability of a series of materials with diverse surface functionalities and a porosity at the borderline between mesoporosity and macroporosity provides an opportunity to finely

tune physisorption methods and approach the limits of their domain of reliability.

## 2. Materials and methods

### 2.1. Preparation of the samples

Agar hydrogel beads were prepared from a 2% (w/w) agarose (D5 Hispanagar) solution rapidly heated at the boiling point in a microwave oven. The polymer solution was transferred to a syringe thermostated at 50 °C and added dropwise to a cooled water bath.

Alginate hydrogel beads were prepared from several Na-alginate with different guluronic content: Protanal FMC Biopolymer (20% guluronic), Sigma-Aldrich (35% guluronic), Cegalum S500 Sanofi (45% guluronic), Satialgine SG 800 Systems Bio-Industries (76% guluronic). Sodium alginate was dissolved in distilled water at a concentration of 2% (w/w). The polymer solution was added dropwise at room temperature to a stirred 0.24 M MCl<sub>2</sub> (Aldrich, M being Ca<sup>2+</sup>, Ba<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup> or Cu<sup>2+</sup>) solution to form alginate gels or to a molar HCl solution to form alginic acid gels. The microspheres were cured in the gelation solution for 15 h.

Carrageenan hydrogel beads were prepared by dissolving 2.5% (w/w)  $\kappa$ -carrageenan (*Eucheuma cottonii*, Sigma, 90%) in deionized water at 80 °C. The solution thermostated at 80 °C was dropped into a 0.6 M KCl solution at 5 °C under stirring. The gel beads were aged for 12 h in this solution at 5 °C without stirring and hence washed with cold water [11].

Hydrogel beads were formed from two different kinds of chitosan, obtained by deacetylation of crab-shell  $\alpha$ -chitin or obtained from squid-pen  $\beta$ -chitin. In the case of chitosan from  $\alpha$ -chitin, a 2.5% aqueous solution of purified Aldrich chitosan (degree of acetylation of 10% as measured by IR spectroscopy,  $M_w = 700\,000$  g mol<sup>-1</sup> determined by viscosimetry) was formed by stirring 2 h at room temperature in the presence of the stoichiometric amount of acetic acid with respect to the glucosamino groups. Gelation was obtained by dropping the chitosan solution into a 4 M NaOH solution through a 0.8 mm gauge syringe needle. The chitosan beads were left in the alkaline solution for 2 h, filtered and washed with demineralised water. In the case of chitosan from  $\beta$ -chitin (Mahtani PVT, degree of acetylation lower than 5%, as measured by NMR spectroscopy, weight-average molecular weight  $M_w = 200,000$  g mol<sup>-1</sup>, measured by light scattering), 1 g of polymer was dissolved in 100 mL of a 55 mM solution of acetic acid. This solution was added dropwise to a 4 M NaOH solution. The chitosan beads were stored in the alkaline solution for 2 h, then filtered and washed with deionized water.

$\beta$ -chitin hydrogel was obtained by complete reacetylation of squid-pen chitosan according to a published procedure [12]. One-hundred grams aqueous acetic acid (0.5% w/w) solution of chitosan (1% w/w) were mixed with 50 mL ethanol and the solution was left to stand overnight for outgassing. A freshly prepared acetylating solution (6.85 mL ethanol, 0.65 mL acetic anhydride) was slowly added to 20 g of the hydroalcoholic chitosan solution. The mixture was then stirred for 30 s and transferred to a cylindrical mould, in which the polymer gelled as soon as acetylation was completed. The gel was aged 4 h and washed twice with ethanol.

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