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Alginate aerogels as adsorbents of polar molecules from liquid hydrocarbons: Hexanol as probe molecule

Rosalia Rodriguez Escudero [1], Mike Robitzer, Francesco Di Renzo *, Françoise Quignard

Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM2-ENSCM-UM1, Matériaux Avancés pour la Catalyse et la Santé, ENSCM, 8 rue Ecole Normale, 34296 Montpellier Cedex 5, France

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ABSTRACT

Ionotropic gels of alginate, a polysaccharide, can be easily converted to aerogels of high surface area. The potential of alginate aerogels as adsorbents for trace polar contaminants in hydrocarbon feedstocks is evaluated, *n*-hexanol being used as a polar probe molecule. The influence of the nature of the gelling cation has been studied by testing Ca-, Ba-, Ni-, Co-, and Cu-alginate aerogels and a gel of alginic acid, formed by proton exchange of Na-alginate. Adsorption capacity can reach 15% hexanol (w/w) without any swelling of the gel. The amount adsorbed in the monolayer allows to evaluate the surface area of the adsorbent and confirms that the immersion in hydrocarbon does not modify the size and the dispersion of the polysaccharide fibrils. The comparison of the surface density of adsorbate with the structure of the surface indicates that hexanol is adsorbed on alginic acid by the formation of hydrogen bonds between the alcohol heads and two hydroxyls of the polymer surface. In the case of alginates gelled by divalent cations, stronger adsorption sites allows completion of a monolayer at lower concentrations of the polar molecule.

1. Introduction

The natural function of polysaccharide hydrogels (hydrocolloids) is to store water in mechanically stable reservoirs to cope with needs as different as the conservation of fruits and grains, the survival of cactaceae in dry environment, or the floatability of seaweed in sea water (Walter, 1998). Gelling polysaccharides are able to store from twenty to one hundred times their weight of water in a network of secondary structures of hydrophilic polymer. The interaction with water depends both on the nature of the surface of the polysaccharide and the size of its secondary structures.

The hydrophilicity of polysaccharides is based on the formation of hydrogen bonds between their hydroxyl groups and water or other polar molecules. Cellulose, the most diffused polysaccharide, presents 18.5 mmol g^{-1} hydroxyls. Natural functionalised polysaccharides also present additional polar sites, namely Brønsted acid or basic sites. For instance, chitosan, the deacetylated form of chitin, the second most diffused natural polysaccharide, presents up to 5.8 mmol g^{-1} amino groups. Alginic acid, a seaweed-extracted polysaccharide, presents up to 5.6 mmol g^{-1} carboxylic groups.

The accessibility of the polar surface depends on the formulation of the hydrocolloids. In a general way, the smallest the secondary structures of the polysaccharide, the largest their surface area. The adsorption of dyes has been used to measure the accessible surface of polysaccharide structures in water (Inglesby & Zeronian, 2002; Goodrich & Winter, 2007). Supercritical drying has been shown to preserve the texture of polysaccharide hydrogels in the dry state (Valentin, Molvinger, Viton, Domard, & Quignard, 2005). Supercritically dried polysaccharide aerogels present macropore volumes as high as 98%. Their surface areas can be as high as 175 $m^2\,g^{-1}$ in the case of chitosan (Di Renzo et al., 2005) and 500 $m^2\,g^{-1}$ in the case of alginate (Valentin, Molvinger, Quignard, & Di Renzo, 2005). FT-IR spectroscopy of probe molecules has shown the functional groups of alginate aerogels to be completely accessible to small molecules from the gas phase (Valentin, Horga et al., 2005, 2006).

Fibres of synthetic hydrophobic polymers are widely used as filtering media to separate oils from emulsions in water (Koltuniewicz, Field, & Arnot, 1995; Tansel, Regula, & Shalewitz, 1995). The use of hydrophilic fibres to separate polar molecules from organic solvents is less widespread, despite the availability of many synthetic and natural hydrophilic polymers. A suitable adsorbent for polar molecules should present a high concentration of adsorption sites, high surface area, and wide pores for good circulation of the solution. Polysaccharide-based hydrocolloids are especially attractive from these points of view. They present the

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* Corresponding author. Tel.: +33 607508148.
E-mail address: direnzo@enscm.fr (F. Di Renzo).

[1] Present address: Department of Chemical and Environmental Technology, Rey Juan Carlos University, 28933 Móstoles, Madrid, Spain.

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additional advantage of being issued from renewable resources and can be easily shaped as membranes or spheres.

Hydrogels of chitosan have been proposed as selective adsorbents to extract sulphonated contaminants from hydrocarbon feedstocks (Aburto, Mendez-Orozco, & Le Borgne, 2004). The use of a hydrogel implies that polar molecules can be both adsorbed at the surface of the polysaccharide and absorbed in water retained by the polysaccharide scaffold. The use of an aerogel would be more adapted to the study of the direct interactions between polar probe molecules and the polysaccharide surface. It can be expected that the high values of surface area of the aerogels are retained when the aerogels are wetted by liquids with low surface tension, as the hydrocarbons. In the case of aerogels of chitosan immersed in organic solvents, a good accessibility of the amine functional groups to specific probe molecules has been reported (Valentin, Molvinger, Quignard, & Brunel, 2003).

Among polysaccharides, alginate forms strong ionotropic gels which can be easily converted to aerogels of high surface area. Alginate is a block copolymer of (1-4)-linked β-D-mannuronate (M) and α-L-guluronate (G) residues (Fig. 1) and is extracted from brown algae. World production is about 36,000 t per year (McHugh, 2003).

The divalent cations which form electrostatic links between alginate chains can provide additional adsorption sites for polar molecules. The evaluation of the potential of the alginate aerogels as adsorbents for trace polar contaminants in hydrocarbon feedstocks requires to verify the stability of the dispersion of the aerogel in the hydrocarbon. This is the rationale of the present study on the adsorption of a polar probe molecule as *n*-hexanol on alginate aerogels immersed in oil. The influence of the nature of the gelling cation has been studied by testing Ca-, Ba-, Ni-, Co-, and Cu-alginate aerogels and a gel of alginic acid, formed by proton exchange of Na-alginate.

2. Experimental

2.1. Preparation of gel beads

Alginate gel beads were formed from a 1% (w/w) aqueous solution of sodium alginate (Sigma–Aldrich from Macrocystis Pyrifera, 3600 cP viscosity of a 2% solution, mannuronic/guluronic ratio 1.82 by spectroscopic evaluation) (Mackie, 1971). The polymer solution was added drop-wise at room temperature to a stirred cation solution by using a syringe with a 0.8 mm diameter needle. The solutions used were $CaCl_2$ 0.24 M, $CoCl_2$ 0.12 M, $CuCl_2$ 0.24 M, $NiCl_2$ 0.24 M, $BaCl_2$ 0.24 M, and, for the preparation of an alginic acidic gel, HCl 1 M. All reagents were from Aldrich. The hydrogel beads formed were cured in the gelation solution for three hours, filtered and washed twice with distilled water. The exchange ratio of sodium cations by divalent cations was 100% for Ca- and Ba-alginate and for alginic acid, 88% for Co-alginate, 87% for Cu-alginate, 93% for Ni-alginate (Valentin, Horga et al., 2005; Valentin et al., 2006). Virtually no sodium cations were present in the gel samples, the charge balance being assured by protons.

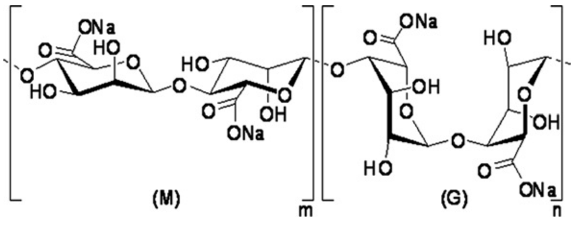

Fig. 1. The blocks of mannuronate (M) and guluronate (G) residues which form the alginate.

The microspheres were afterwards dehydrated by immersion in a series of successive ethanol-water baths of increasing alcohol concentration (10%, 30%, 50%, 70%, 90%, 100%) during 15 min each (Martinsen, Storrø, & Skjåk-Bræk, 1992). Finally, the alcohol was displaced by liquid CO_2 and the gel beads were dried beyond the critical point of CO_2 (74 bar, 31.5 °C) in a Polaron 3100 apparatus.

2.2. Characterization of materials

Nitrogen adsorption isotherms were recorded in a Micromeritics ASAP 2010 apparatus at −196 °C after outgassing the sample at 50 °C under vacuum until a stable 3×10^{-3} Torr pressure was obtained without pumping. The surface area was determined by the BET equation assuming 0.162 nm^2/molecule as the molecular area of N2. The average size of the alginate fibrils was evaluated from the surface area by the formula $D = 4000/(\rho S)$, where D is the fibril diameter in nm, S the surface area in $m^2\ g^{-1}$, and ρ the density of alginate in $g\ cm^{-3}$. For this calculation, the densities of the ionotropic alginates were calculated from the experimental density of the alginic acids, 1.60 $g\ cm^{-3}$ (Atkins, Nieduszynski, Mackie, Parker, & Smolko, 1973a, 1973b), under the assumption of invariance of the cell parameters with the cation exchange (Mackie, Perez, Rizzo, Taravel, & Vignon, 1983).

The cation content of the ionotropic gels was evaluated by weighting the mineral residue after heating at 900 °C in air flow. The composition of the residue was verified by EDX analysis. The water content of the gels was measured as the loss of weight at 130 °C in thermogravimetric experiments with heating rate 5 $°C\ min^{-1}$ in air flow.

Scanning electron microscopy was performed on a Hitachi S-4500 apparatus after platinum metallisation.

2.3. Adsorption experiments

Adsorption tests in liquid phase were carried out on aerogel samples outgassed in a Schlenk tube at 50 °C under vacuum during three hours. The adsorption of a polar compound (1-hexanol) from dodecane with 0.1% decane as internal standard (all compounds from Aldrich) was tested in a glass microreactor at 25 °C on alginate gel beads (30 mg alginate per ml of hydrocarbon). 1-hexanol was added by doses under stirring. 0.3 µl of the solution were extracted 15 min after the introduction of each dose and analysed in a Varian GC 3900 gaschromatography equipped with a CP SIL-5CB capillary column and a flame ionization detector. The adsorbed 1-hexanol was calculated by the difference between the 1-hexanol added to the sample and the 1-hexanol analysed in the solution. To test the effect of moisture adsorbed by the samples after the supercritical drying, some adsorption experiments were replicated without previous outgassing of the sample. All reported adsorption data are referred to the mass of aerogel dried at 50 °C under vacuum. The adsorption isotherms were evaluated by the Langmuir method.

3. Results and discussion

3.1. Hexanol adsorption, monolayer saturation and surface area

Adsorption of hexanol was carried out on the aerogel samples immersed in dodecane. Typical adsorption isotherms on aerogels of Ca-alginate, Ba-alginate and alginic acid are shown in Fig. 2. All isotherms followed the same pattern, with the adsorbed amount increasing with the concentration in solution with a continuously decreasing slope. It can be remarked, in the case of

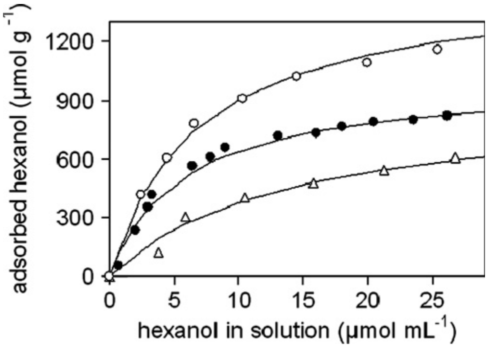

Fig. 2. Adsorption isotherm of 1-hexanol on aerogels of Ca-alginate (empty circles), Ba-alginate (filled circles), and alginic acid (empty triangles). The lines are Langmuir plots of the data.

Ca-alginate aerogel, that more than 600 µmol of hexanol per gram of aerogel (6% w/w) are at the equilibrium with 5 µmol of hexanol per cm^3 of hydrocarbon (about 0.06% w/w), suggesting that the alginate aerogels can be effective adsorbents for polar molecules.

The asymptotical rise of the isotherms suggests that they can be described by the Langmuir model, which describes a monolayer adsorption mechanism. It is not unexpected that the adsorption of 1-hexanol from a hydrocarbon solution on a polar surface follows a Langmuir mechanism, as the molecule is oriented on the surface: the adsorption of the polar end of the molecule directs the hydrocarbon end of the molecule towards the solvent and forms a non-polar layer which renders further adsorption less favourable, with the so-called autophobic effect (Barto, Durham, Baston, & Wade, 1966) A best-fitting procedure of the experimental data provides the parameters of the Langmuir equation [1]

$$Q_{\mathrm{ads}} = \frac{Q_{\max} C}{K + C} \tag{1}$$

where Q_{ads} is the amount adsorbed at the equilibrium with a solution of concentration C, $Q_{\max}$ is the amount adsorbed at complete coverage of the surface, and K the half-saturation concentration value, measured when the adsorbed amount is $Q_{\max}/2$.

The good fitting of the experimental isotherms of hexanol on Ca-alginate by the Langmuir model is evident from Fig. 2. The lower amount of hexanol adsorbed on the not-outgassed sample suggests that some atmospheric water has been adsorbed by the aerogel after the supercritical drying and competes with hexanol for the adsorption sites (see further).

The force constant K and the asymptotic amount $Q_{\max}$ of the Langmuir fitting of the adsorption data are reported in Table 1, together with their standard errors and the standard deviation of the residuals. A successful application of the Langmuir model requires a good homogeneity of the adsorbent surface and the absence of adsorbate–adsorbate interactions. The good agreement between experimental data and Langmuir modelisation suggests that these conditions are fullfilled for the aerogels of Ca- and Ba-alginate and alginic acid.

A different situation is observed for the outgassed aerogels of alginate gelified in the presence of transition metals: Ni, Co, and Cu. For these samples, the standard deviation of the residuals is higher than 2% of the complete coverage. Fig. 3 shows the experimental 1-hexanol adsorption isotherm over Co-Alg with the best-fitting Langmuir plot (thick line). The Langmuir plot has a systematic bias and underestimates the amount adsorbed at the lowest and highest concentrations. In this case, a bisite Langmuir model provides a better fit of the experimental data.

Table 1
Parameters of the Langmuir fitting of the adsorption data

Sample	$Q_{\max}$ (µmol/g)	K (µmol/l)	Sy.x (µmol/g)
Ca-alginate	1495 ± 23	6.6 ± 0.4	25
Ba-alginate	970 ± 12	4.8 ± 0.2	17
Co-alginate	1076 ± 26	2.0 ± 0.2	45
Cu-alginate	1538 ± 23	4.3 ± 0.2	32
Ni-alginate	1024 ± 25	2.0 ± 0.2	55
Alginic acid	900 ± 29	13.8 ± 1.4	27

The hypothesis of the bisite Langmuir model is that adsorption takes place simultaneously on two kinds of adsorption sites with different adsorption energy (Eq. (2)).

$$Q_{\mathrm{ads}} = \frac{Q1_{\max} C}{K1 + C} + \frac{Q2_{\max} C}{K2 + C} \tag{2}$$

This model significantly improved the fitting for the outgassed aerogels of transition-metal alginates, as evidenced in Fig. 3. The parameters of the model are reported in Table 2, and indicates that the isotherm can be represented by the adsorption on two families of sites, the high-energy one being half-saturated at very low concentration (less than 2.5 µmol L^{-1}) and the low-energy one being half-saturated at higher concentration (more than 10 µmol L^{-1}). The total adsorbed hexanol at the equilibrium is obtained adding the values of $Q1_{\max}$ and $Q2_{\max}$, which are reported in Table 2. The standard deviations reported in Table 2 are much lower than the standard deviations for the single-site Langmuir model, reported in Table 1. On the contrary, for the aerogels of Ca- and Ba-alginate and alginic acid, the bisite Langmuir model did not improve the fitting of the experimental data by the single-site Langmuir model.

The Langmuir constants K are related to the free enthalpy of the adsorption, the adsorption being stronger for lower values of K. The strongest adsorption sites correspond to the very low $K1$ constants of transition metal-gelled alginates. The adsorption on Ca- and Ba-alginate is slightly less energetic. The highest constants are the $K2$ constants of the low-energy adsorption sites of the transition metal-gelled alginates and the K constant of the alginic acid aerogel. This order of adsorption strengths suggests the attribution of the high-energy sites of transition-metal alginates to dehydrated metal cations, the sites of Ca- and Ba-alginate to a surface with incompletely dehydrated cations, and the low-energy sites of transition-metal alginates and alginic acid to hydrogen bonds between the polysaccharide and the hexanol molecule.

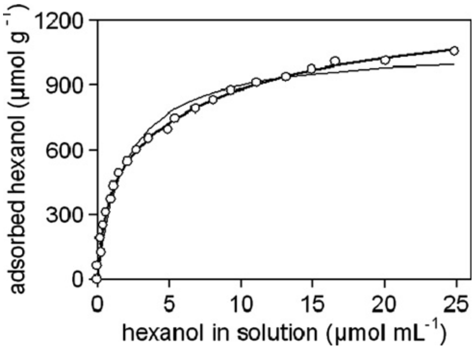

Fig. 3. Adsorption isotherms of hexanol on aerogel of Co-alginate, fitted by single-site (thin line) and bisite (thick line) Langmuir models.

Table 2
Parameters of the fitting of the adsorption data by a bisite Langmuir model

Sample	$Q1_{\max}$ (µmol/g)	$Q2_{\max}$ (µmol/g)	$Q1_{\max}$+$Q2_{\max}$ (µmol/g)	$K1$ (µmol/l)	$K2$ (µmol/l)	Sy.x (µmol/g)
Co-alginate	535 ± 118	777 ± 71	1312 ± 94	0.63 ± 0.20	10.7 ± 5.0	24
Cu-alginate	852 ± 358	863 ± 278	1715 ± 318	2.20 ± 0.79	14.2 ± 9.4	16
Ni-alginate	494 ± 55	769 ± 38	1263 ± 46	0.43 ± 0.10	13.5 ± 3.6	19

The asymptotic adsorbed amounts evaluated by the different Langmuir models correspond to a monolayer coverage, and as such they can be used to evaluate the surface area of the samples in the hydrocarbon environment. If it is assumed that each adsorbed hexanol molecule covers a surface with a given area (the molecular area), the total surface area can be easily evaluated as the product of the monolayer coverage by the molecular area. This approach is commonly used, for instance in the BET method to evaluate the N_2 adsorption data, albeit the nature of the surface and the strength of the interactions between adsorbent and adsorbate largely affect the area covered by an adsorbed molecule (Jelinek & Kováts, 1994). The molecular area of hexanol adsorbed from the vapour phase on silicate glass has been measured at 0.40 nm^2 (Nonaka, 2000). In the case of adsorption on amorphous silica from solutions of organic solvents, the molecular area of hexanol has been evaluated at 0.42 ± 0.09 nm^2 (Goworek, Kusak, & Stefaniak, 1993; Zhao, Zhang, & Lin, 1994; Okunev & Aristov, 1999).

If the immersion in hydrocarbon has not altered the dispersion on the aerogel, the product of the Langmuir monolayer coverages (Q_{max} for the single-site model and $Q1_{max} + Q2_{max}$ for the bisite model) by the molecular area of hexanol (0.42 nm^2) should correspond to the values of surface area measured by N_2 adsorption. The surface areas evaluated by N_2 adsorption and by the hexanol Langmuir monolayer are reported in Table 3. The average difference between the two sets of data corresponds to a few percent points, indicating that the surface area of the aerogel has not been significantly altered by the immersion in hydrocarbon.

The surface areas of the aerogels are quite high and correspond to a good accessibility of the secondary structures of the polysaccharide. A scanning electron micrograph of a cross-section of a Ca-aerogel bead (Fig. 4) shows that the material is formed by a spiderweb network of fibrils. Under the assumption of a circular section of the fibrils, their average diameter D (nm) can be evaluated from the surface area S_{BET} ($m^2\,g^{-1}$) by the correlation $D = 4000/(S_{BET}{}^{*}\,\rho)$, where ρ is the density of Ca-alginate from crystallographic data. The calculated diameter of the fibrils is reported in Table 3.

Table 3
Textural properties of alginate aerogel beads

Sample	S(Langmuir) (m^2/g) hexanol 50 °C	S_{BET} (m2/g) N_2 −196 °C	Fibril diameter (nm)
Ca-alginate	383	387	5.8
Ba-alginate	253	251	7.4
Co-alginate	331	327	6.6
Cu-alginate	438	481	4.4
Ni-alginate	323	350	6.0
Alginic acid	228	220	11.4

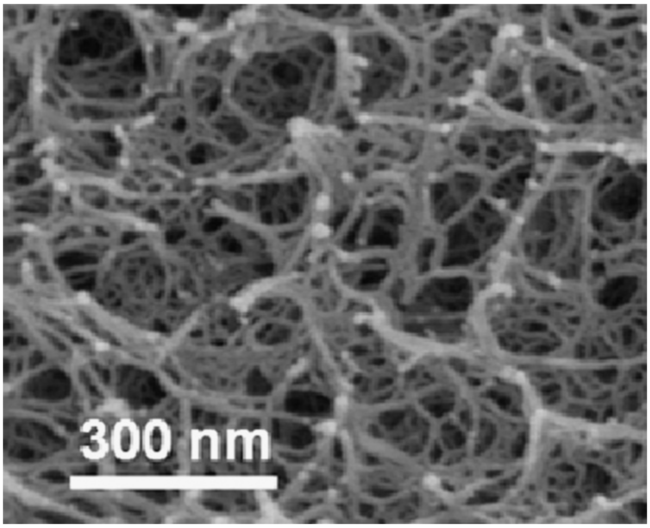

Fig. 4. Scanning electron micrograph of the cross-section of a Ca-alginate aerogel bead.

3.2. Surface density of adsorbed molecules

Small differences among the adsorption behaviors of the samples can be highlighted by an alternative approach to the evaluation of the adsorption data. The assumption, just proved valid, that the surface area measured by N_2 adsorption is an acceptable standard for the surface area of the aerogels immersed in dodecane, allows to calculate the average surface density of the adsorbed hexanol molecules as the Langmuir monolayer coverage Q_{max} normalised by the BET surface area. In the case of the outgassed aerogels of alginates gelled with transition metal cations, the amounts adsorbed on stronger and weaker adsorption sites can be differentiated by using the asymptotic amounts $Q1_{max}$ and $Q2_{max}$.

The calculated values are reported in Table 4 and indicate that the surface density of hexanol molecules adsorbed on ionotropic alginates is quite constant, at a value of 2.31 ± 0.12 nm^{-2}. It is clear that most differences in adsorbed amount among the samples (Tables 1 and 2) have to be attributed to differences in surface area (Table 3) and that the surfaces of all alginate aerogels are nearly equivalent from the point of view of their maximum coverage.

The surface density of adsorbed hexanol can be compared with the surface density of the uronic monomers on the side surface of a fibril. This value, evaluated by X-ray crystallography on oriented crystalline fibrils, is 2.38 ± 0.01 nm^{-2} (Atkins, Mackie, & Smolko, 1970). The close proximity between this value and the surface density of adsorbed hexanol could suggest that the adsorption takes place on specific sites of the polysaccharide, with the interaction of one alcohol polar head per uronic monomer.

A similar mechanism of localised adsorption has been proposed in the case of another polar molecule, water, adsorbed on another hydrophilic adsorbent, silica. It was observed that a water molecule is preferentially adsorbed on the silica surface by two hydrogen bonds with two silanols, one acting as a hydrogen donor and the other as an acceptor (Bolis, Fubini, Marchese, Martra, & Costa, 1991; Fubini, Bolis, Cavenago, & Ugliengo, 1992; Cauvel, Brunel, Di Renzo, Fubini, & Garrone, 1997). The stability of the two hydrogen bonds is a function of the distance between the oxygens of the surface silanols and the energetic optimum was calculated at an O–O distance of 0.49 nm (Fubini, Bolis, Cavenago, Garrone, & Ugliengo, 1993).

The crystal structures of the uronic acids, which constitute the blocks of alginic acid, can provide some hints about the atomic distances in the polymer. The distance between O(2) and O(3) atoms of consecutive monomers on a polymer chain is especially interesting, as it measures 0.47 nm in the case of mannuronic acid and 0.50 nm in the case of guluronic acid (16,17). The geometry of this potential adsorption site is represented in Fig. 5 in the case of man-

Table 4
Surface density of adsorbed hexanol molecules at monolayer saturation

Sample	Strong adsorption sites (nm^{-2})	Weak adsorption sites (nm^{-2})	Complete coverage (nm^{-2})
Ca-alginate			2.38
Ba-alginate			2.32
Co-alginate	1.01	1.47	2.48
Cu-alginate	1.12	1.08	2.20
Ni-alginate	0.86	1.33	2.19
alginic acid			2.52

nuronic acid. The alcohol head of hexanol can be connected to the hydroxyl groups O(2) and O(3) by two hydrogen bonds 0.189 nm long. The strength of the adsorption can be further enhanced by interaction of the adsorbed hexanol with the carboxylic group. The carboxylic group can easily rotate and bring the O(6) at 0.46 nm from the O(2) of the same mannuronic monomer. In this configuration, a third hydrogen bond 0.22 nm long can be established between the oxygen of the hexanol and the carboxylic acid.

Localised adsorption phenomena correspond to interaction energies much higher than the dispersion forces between the adsorbate and the surface. A high adsorption energy is at the basis of the selectivity of separation of polar molecules from a non-polar solvent. However, it brings about the trade-off of a reduced monolayer capacity, as the alcohol heads are widely spaced on the surface and the non-polar chain of the hexanol molecule is replied on the surface by the adsorption site. If a monolayer of straight molecules of fatty alcohol were formed by non-specific adsorption, the surface density of hexanol would be as high as 5 molecules nm^{-2} (Rouquerol, Rouquerol, & Sing, 1999). Localised adsorption also accounts for the lower-than-expected monolayer coverage of hexanol measured on amorphous silica, around 2.38 molecules nm^{-2}. This value, in the assumption of adsorption of one alcohol molecule per two surface silanols, is in good agreement with the usual silanol density of amorphous silica dehydrated at less than 200 °C, namely 4.9 silanols nm^{-2} (Zhuravlev, 1987).

3.3. Influence of pre-adsorbed water

The presence of moisture adsorbed by the aerogel after the supercritical drying treatment can affect the adsorption of hexanol, if pre-adsorbed water is not removed by outgassing at 50 °C in vacuum. The isotherms of hexanol adsorption on outgassed and not-outgassed samples of Ni-alginate aerogel are shown in Fig. 6. The isotherm on the not-outgassed sample presents a lesser slope at low concentrations but tends toward a higher asymptotic adsorbed amount.

All the samples tested without outgassing were similarly affected by pre-adsorbed water and all their isotherms were best-fitted by single-site Langmuir models, also in the case of the transition metal-gelled alginates. The parameters of the Langmuir model are reported in Table 5.

The disappearance of the high-energy adsorption phenomena on the transition metal-gelled alginates suggests that the presence of water completely shields the divalent cations and the corresponding strong adsorption sites. In this way, the strongest adsorption sites observed for the outgassed aerogels with transition-metal cations can be attributed to the cations present in the gel. The average surface density of these strong adsorption sites is $1.00 \pm 0.13\ nm^{-2}$ (Table 4). Crystallographic data indicate that the maximum surface density of divalent cations is 1.19 nm^{-2} (Atkins et al., 1973a, Atkins, Nieduszynski, Mackie, Parker, & Smolko, 1973b). This suggests that most surface cations are accessible to polar molecules from the hydrocarbon solution, in the same way as they are accessible to small probe molecules from the gas phase (Valentin, Horga et al., 2005, 2006).

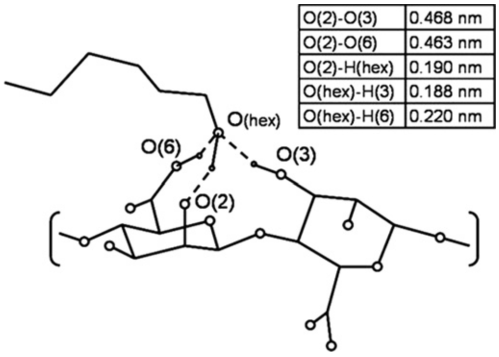

Fig. 5. Preferential site for localised adsorption of hexanol on mannuronic acid. Hydrogen bonds are formed with oxygens of two adjacent monomers.

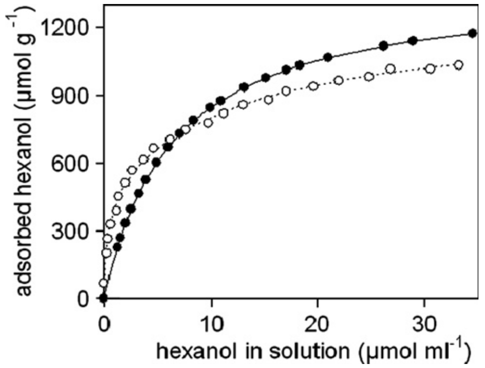

Fig. 6. Adsorption isotherm of hexanol on Ni-alginate aerogel outgassed (empty circles) or not-outgassed (filled circles) before the experiment. The lines are Langmuir plots of the data (single-site for not-outgassed sample and bisite model for the outgassed sample).

For Ca-alginate and alginic acid aerogels, the same single-site Langmuir model applies in the outgassed and not-outgassed state, but the *K* constant is higher in the presence of pre-adsorbed water. This decrease of the energy of interaction is a logical consequence of the competition for the adsorption sites between alcohol groups and pre-adsorbed water molecules. The comparison of the amounts adsorbed in the monolayer of outgassed (Tables 1 and 2) and not-outgassed samples (Table 5) shows that the presence of pre-adsorbed water allows from 7% to 10% more hexanol to be adsorbed. The contribution of water to the retention of polar molecules has been reported in the case of other polysaccharide gels. A water–acetonitrile phase in a chitosan hydrogel contributes to the adsorption of sulfurated molecules from hydrocarbon feedstock (Aburto et al., 2004). In a similar way, the presence of some adsorbed water on the alginate aerogel can increase the amount of hexanol retained, with a mechanism at the borderline between adsorption of the polysaccharide surface and absorption in the surface water.

4. Conclusions

Most polymeric systems used for separation processes operate in the presence of two liquid phases and are based on adsorbate–adsorbate interactions. For instance, hydrophobic polymers favour the coalescence of oil droplets from a polar solvent, while hydrophilic hydrogels favour the adsorption of polar molecules in a supported polar phase. A different case occurs for the adsorption of polar molecules on alginate aerogels. The supercritical drying of the aerogels prevents the presence of a polar liquid phase and

Table 5
Parameters of the Langmuir fitting of the adsorption data on not-outgassed samples and corresponding surface density of hexanol at monolayer coverage

Sample	Q_{max} (μmol/g)	*K* (μmol/l)	*σ* (μmol/g)	Monolayer coverage (molecules nm-2)
Ca-alginate	1598	7.8	28	2.02
Co-alginate	1436	7.0	30	1.98
Ni-alginate	1396	6.5	30	1.86
Alginic acid	960	19.6	23	2.40

the hexanol molecules are directly adsorbed from the hydrocarbon solvent to form a monolayer at the surface of the polysaccharide.

The formation of an adsorbed monolayer is an ideal method to evaluate the surface area of the adsorbent and allows to state that the immersion in hydrocarbon does not modify the size and the dispersion of the polysaccharide fibrils of the aerogel. The monolayer coverage depends on the size of the fibril alone and is virtually independent of the nature of the cation present. The amount adsorbed corresponds to the expected value for the formation of a monolayer of hexanol molecules on a polar surface. This indicates that, on the timescale of the experiment, hexanol molecules do not penetrate into the alginate and the fibrils are not swollen. A slightly higher adsorbed amount on not-outgassed samples corresponds to the interaction of hexanol with moisture adsorbed after the supercritical drying.

The comparison of the surface density of adsorbate with the structure of the surface suggests that hexanol is adsorbed on alginic acid by the formation of hydrogen bonds between the alcohol heads and two surface hydroxyls. The energetics of adsorption are affected by the presence of divalent cations, which increase the strength of the adsorbate–adsorbent interaction. The concentration effects vary with the energy of interaction, and the concentrations of adsorbate in the solid at half monolayer coverage are from 30 to 100 times the concentrations in solution.

Moreover, these results highlight the use of polysaccharides and especially of alginate as host for polar molecules. This property can be used in the aim of making biodegradable materials for detection and trapping of liquid or gas species.

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