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Alginate-based polysaccharide beads for cationic contaminant sorption from water

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Abstract Massive amounts of agricultural and industrial water worldwide are polluted by different types of contaminants that harm the environment and impact human health. Removing the contaminants from effluents by adsorbent materials made from abundant, inexpensive polysaccharides is a feasible approach to deal with this problem. In this research, alginate beads combined with two types of cellulose, starch or xylan were synthesized. Their average diameters in air- and freeze-dried conditions were assessed by optical microscopy. Differences in morphology were observed by scanning electron microscopy. Their capacity for water uptake, their sorption capabilities for a model cationic pollutant and their charge density was investigated in relationship to their composition and their surface characteristics. Their interaction with water was evaluated using low-field NMR spectroscopy. It was found that nanocrystalline cellulose added the most to the beads' sorption capacity for cationic contaminants while xylan admixture created the beads with the highest water sorption after lyophilization.

Keywords Alginate · Sorption · Low-field NMR · Contaminant · Polysaccharide

Introduction

Water contamination is a very severe global environmental problem. Although much research has been focused on water purification, many challenges still remain. Agricultural run-off, by-products of pulp and paper, textile and food industries are major contributors to the problem [1]. Heavy metals, nitrates, pesticides, fertilizers

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and other chemicals are among the most persistent hazardous contaminants that demand highly efficient treatment processes. At the same time these measures must be cost-effective and affordable in all countries, especially in those with low economic development [2].

Alginic acid is a naturally abundant polysaccharide extracted from brown algae and soil bacteria. Chemically, it is a linear copolymer composed of two monomers, (1-4)-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues at different ratios and distribution along the chains [3]. Around neutral pH alginate contains a significant amount of negative charges due to deprotonated carboxylic acid groups. These negative charges enable alginate to induce repulsive electrostatic forces and to swell as well as to interact with positively charged ionic groups. Sodium alginate exhibits a sol–gel transition when sodium counter-ions are substituted with divalent cations, such as calcium, zinc, or barium.

Beads made from alginic acid salts have been found to be suitable as a supporting matrix for cell immobilization and drug encapsulation as documented in numerous publications [4–15]. For instance, calcium-crosslinked alginate beads were used as preliminary material for matrices in enzyme immobilization. Zhu et al. [4] encapsulated glucose oxidase in alginate microspheres; Ai et al. [5] incorporated boehmite into alginate, forming hybrid beads for enhanced enzyme loading. Furthermore, some researchers found that fungal biomass could be entrapped in alginate beads which improved the removal of specific metal ions or dyes. For instance, Torres et al. [6] prepared calcium alginate beads to target the removal of gold and silver. Live and heat-inactivated fungal mycelia of *Phanerochaete chrysosporium* were employed to bind mercury, lead, cadmium and other metals [7, 8]. Live and dead *Lentinus sajor-caju* [9] were entrapped into alginate beads for increased Hg(II), Zn(II) and Pb(II) removal from waste water. Biosorption of the metal ions occurred within a short time frame and at an astonishingly high yield.

Besides heavy metals, dyes are a serious problem in waste water treatment, since colorants do not easily decompose. Elzatahry et al. [10] used a dynamic batch process to investigate the efficiency of methylene blue removal from colored effluents by alginate micro-beads. Extensive research has been performed on biosorption of metals and proteins as well as basic dyes from effluent of the leather industry by Aravindhan et al. [11, 12] using different types of sorbents. Sorption isotherms have been determined for the different sorbent/pollutant systems. Chitosan, a positively charged polysaccharide, can be applied as a surface layer on the outside of alginate beads to reinforce the beads' properties and removal capacity of heavy metal ions and dyes.

A number of publications focused on the performance of magnetic alginate beads [13, 14] for use in cationic dye removal. Magnetism and sorption properties were provided through the combination of active carbon and magnetic nanoparticles which made it possible to recover the beads in a magnetic field. Halloysite nanotubes, a well-known material for removal of various organic pollutants and metal ions, were incorporated to create a new kind of bead with high porosity according to the work reported by Liu et al. [15]. However, many natural, abundant and biodegradable polysaccharides such as starch, cellulose and xylan also have potential to improve the capacity of waste water remediation and controlled release

of chemicals, such as plant hormones [16]. They have not yet been investigated in alginate composite beads to a large extent with the exception of alginate–chitosan combinations.

The work described here is concerned with preparing a series of polysaccharide blended beads composed of alginate and an additional polysaccharide (starch, xylan, cellulose powder and nanocrystalline cellulose) with the goal of influencing internal and external surface properties and swelling/sorption behavior. The average size and size distribution in air/freeze dry state, the swelling ratios, and the morphologies of the resulting beads were studied. The maximum charge density that the beads can acquire and the amount of bound and free water at different moisture contents using low-field NMR spectroscopy were also investigated. In addition, the sorption capacity for a cationic model dye—methylene blue—was assessed and was found to be affected by several factors, including drying methods and pH of crosslinking at the bead formation stage. The admixture of the additional polysaccharide component proved to be a key factor affecting morphology, porosity and sorption sites of the beads for cationic compounds.

Experimental

Materials

Alginic acid sodium salt from brown algae (medium viscosity, M_w 80,000–120,000, M/G ratio of 1.56), cellulose (Avicel powder, ~20 micron), xylan from beechwood (M_w ~21,000), and methylene blue (MB) were purchased from Sigma Aldrich. Nanocrystalline cellulose (CNC) was provided by the US Department of Agriculture, Forest Products Laboratory, Madison, WI. Unmodified regular food grade corn starch (M_w 10^6–10^7; approx. 27 % amylose), sodium hydroxide solution (0.0498–0.0502 N), hydrochloric acid (0.1 N) and potassium chloride were obtained from Thermo Fisher, and calcium chloride from Merck. All materials were used as received.

Preparation of polysaccharide beads

A series of homogenous aqueous suspensions were prepared by mixing 2 % w/v aqueous sodium alginate with corn starch, cellulose powder, nanocrystalline cellulose, or xylan (all in powder form) with stirring at room temperature. Concentrations of corn starch and cellulose powder were 1, 3, 5 or 10 % w/v, while the concentrations of xylan were 1 and 3 %, and nanocrystalline cellulose 1 % w/v. The suspensions were added to 0.2 M calcium chloride solution as the crosslinking agent through a 10-mL syringe with a needle size of 18G × $1^1/_2$ to form spherical beads at a rate of 4 mL/min. The beads were allowed to crosslink for additional 30 min with gentle stirring. Finally, they were rinsed with distilled water and dried (air-drying or freeze-drying) or used freshly made without drying in the case of methylene blue sorption experiments.

Size measurement of beads

Optical microscopy was used to measure the sizes of both air-dried and freeze-dried beads. 20 beads within each sample and three diameters for each bead (maximum, minimum and diagonal) were measured and the average diameter was recorded.

Swelling ratios of beads

Defined amounts of wet beads obtained directly from synthesis were dried to equilibrium by either air-drying or freeze-drying. The average weight of the dried beads was determined and the beads immersed in distilled water for 48 h. The swelling ratio was calculated based on the formula shown in Eq. 1.

$$\text{Swelling ratio } \% = \frac{W_s - W_d}{W_d} \times 100\ \% \tag{1}$$

where W_s is the weight of the water-swollen beads, and W_d the weight of the dried beads.

NMR measurements

Low-field, nuclear magnetic resonance experiments were done using a Bruker mq20 NMR Analyzer with a 0.7 T magnet, operating at 20 MHz and 40 °C. The CPMG (Carr–Purcell–Meiboom–Gill) pulse sequence was used with a pulse separation of 5 ms, the collection of 1000 echoes, 64 scans, and a 5-s recycle delay. T2 distributions were determined using Contin [17]. Samples were prepared by saturating $\sim$1 g of air-dried and freeze-dried beads overnight in 3 mL of deionized water.

Scanning electron microscopic (SEM) analysis of beads

The surface morphologies of air-dried and freeze-dried beads as well as morphologies of their cross sections were observed by scanning electron microscopy (SEM) at a 20 kV accelerating voltage and working distance 8.5–17 mm, using a Zeiss EVO 50 Variable Pressure SEM. The samples were sputter-coated with gold in an EMS 550X Auto Sputter Coating Device.

Charge density of suspensions with different compositions

The charge density of suspensions in meq g^{-1} of alginate of different compositions was determined according to published procedures for direct potentiometric titration of natural organic matter (NOM) [18]. A homogenous mixture was prepared by adding 0.1 M KCl solution into 20 mL of a suspension composed of 2 % w/v alginic acid sodium salt solution containing 1 % of corn starch, nanocrystalline cellulose and cellulose powder, respectively. These solutions were titrated starting at pH 7.4 (initial pH of suspension). 2 % w/v alginic acid sodium salt with 1 %

xylan had an initial pH of 5.4. Therefore, a second alginate control solution was adjusted to pH 5.4 by adding 0.03 N hydrochloric acid. The mixture was titrated with 0.02 N NaOH solution. NaOH solution was added in 0.2 mL increments or its integral multiple; the pH was recorded after each addition of titrant. All samples were titrated up to approximately pH 11. The titrations were performed four times and the values averaged. The charge density of alginate was calculated based on pH measurements and the charge balance of solution calculated as shown in Eq. 2:

$$\text{Charge density (meq g}^{-1}\text{alginate)} = \frac{[H^+] + [Na^+] - [OH^-]}{C_{alginate}} \quad (2)$$

The concentrations of H^+, Na^+ and OH^- are recorded in meq mL^{-1} and $C_{alginate}$ in g mL^{-1}. Potassium and chloride were not taken into account in the charge balance as they were opposite in charge and equal in concentration.

Capacity of beads to adsorb methylene blue (MB) in aqueous solution

The sorption capacity of the beads for a cationic compound (MB) was investigated with two types of freshly made wet beads (10 g wet weight; crosslinked with $CaCl_2$ solutions at pH 9 and at pH 11, respectively). The beads were added to 50 mL aqueous MB solution of an initial concentration of 5 mg L^{-1}. Additionally, two types of dried beads were investigated: 0.5 g air-dried and 0.5 g freeze-dried beads, respectively, were placed into 30 mL MB solution each (2 mg L^{-1}). In order to determine unknown concentrations of MB solutions, a calibration curve was created by UV–Vis measurements from a standard MB solution series with known concentrations. Readings were taken at intervals of 15 min until equilibrium was reached. The formula used to calculate the sorption capacity is given in Eq. 3.

$$\text{Sorption Capacity } q = \frac{(C_0 - C) \times V}{m} \quad (3)$$

V signifies the volume of MB solution in mL; C_0 the initial MB concentration in mg L^{-1}; C the MB concentration at intervals of 15 min (mg L^{-1}); and m the weight of the dried beads in g.

Results and discussion

Size and size distribution of beads

The average diameter of air-dried beads formed with alginate and alginate blends is shown in Fig. 1a. As can be seen, the average size of blended polysaccharide beads only slightly differed from alginate alone at low admixture concentrations. Within the same series, beads were noticeably larger for higher percentages (5 and 10 % starch and cellulose powder, respectively). CNC could not be homogenously distributed in alginate at concentrations above 1 % and xylan above 3 %. Therefore, experiments were limited to lower admixture concentrations of CNC and xylan.

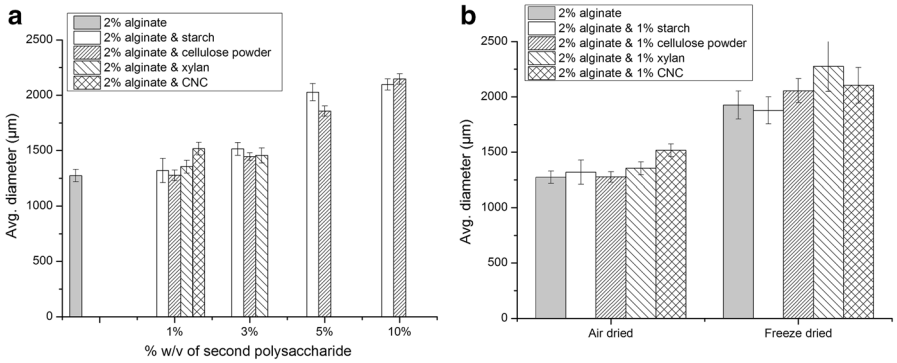

Fig. 1 Average diameters of **a** air-dried alginate beads of different compositions, **b** beads treated by different drying methods

Corn starch at room temperature has a granular structure and remains in granular form under the applied conditions. Starch granules were the largest sized particles of the fillers investigated in this study. Beads composed of alginate with a higher concentration of starch were thus larger in size than beads made from alginate with cellulose powder. It is possible that the granules had a stabilizing effect and to a certain degree prevented the collapse of the internal structure of the beads during drying.

The drying method had a considerable effect on the size and swelling behavior of the beads. As shown in Fig. 1b, larger sizes were observed for the freeze-dried samples. During lyophilization enclosed water was quickly removed from the beads without major collapse of the pores which might more or less reflect the state in which they were under wet conditions. All freeze-dried samples showed a highly porous structure as can be seen from their cross sections (discussed below, Fig. 4f). A homogenous filler distribution in alginate and a relatively strong interaction between the polysaccharide components and alginate might have resulted in the less compact, but still mechanically stable bead structure with large pores as observed by SEM.

Swelling ratios

After the beads were prepared via crosslinking in $CaCl_2$ solution they were air- or freeze-dried. Their average moisture loss (freshly made-to-dry) was within the range of 92–95.5 % when air-dried and 94–95.5 % when freeze-dried, thus the original drying method did only little influence the moisture loss.

The dried beads were then exposed to distilled water and their swelling ratios determined. Figure 2 shows a comparison of swelling ratios of air-dried and freeze-dried beads. Air-dried beads clearly had a more compact structure upon crosslinking than freeze-dried ones. Their average swelling ratios were around 50–65 % with alginate–CNC beads showing a somewhat higher water uptake (approximately 85 %) than alginate alone or any of the beads containing the other fillers. Using air-

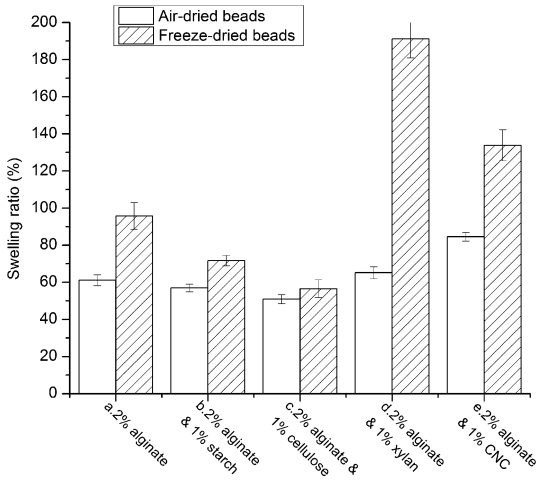

Fig. 2 Swelling ratios of air-/freeze-dried beads

drying, CNC obviously assisted the water uptake the most, while xylan admixture affected the swelling of the freeze-dried beads the most. Freeze-dried alginate–xylan beads reached 190 %, while alginate–CNC showed an average swelling ratio of 135 %. For all other blended beads and alginate alone the difference between freeze-drying and air-drying was much less pronounced. Especially cellulose powder and starch (columns b and c in Fig. 2) seem to have little impact on the water uptake. These beads were obviously comparably compact regardless which drying method was used. The interaction of the beads was further investigated by low-field NMR.

Interaction of water with the beads

Relaxation time distributions from low-field NMR indicated that all the samples exhibited three peaks at 20–40 ms (T2(1)), 450–725 ms (T2(2)) and 800–1700 ms (T2(3)) assigned to bound water, free water and unadsorbed surface water, respectively [19, 20]. For the purposes of the current paper, bound water and free water are defined as chemisorbed water on surfaces, and liquid water in pores, respectively. The former, in which water interacts strongly with the surface, accounts for its short relaxation time, while the latter, due to compartmentalization in small openings will have relaxation times shorter than surface water. In related work on alginate films, bimodal distributions of relaxation times were observed, perhaps indicative of bound and free water, but without a surface water peak probably due to differences in sample preparation and structure [19].

Table 1 shows relaxation times of beads made with different compositions. In general the freeze-dried samples had longer relaxation times than air-dried and for T2(1) and T2(2) the results largely parallel each other. The longer relaxation times associated with the freeze-dried samples are indicative of less interaction between the water and the constituents of the beads. The longest relaxation times (T2(3), Table 1), assigned to unadsorbed surface water, were very similar for all

Table 1 Relaxation times related to air-/freeze-dried beads

Beads components	T2(1) (ms)		T2(2) (ms)		T2(3) (ms)	
	Air-dried	Freeze-dried	Air-dried	Freeze-dried	Air-dried	Freeze-dried
2 % alginate	23	32	520	542	1420	1570
2 % alginate and 1 % cellulose powder	25	33	660	700	1675	1680
2 % alginate and 1 % CNC	23	29	505	600	1670	1600
2 % alginate and 1 % starch	31	34	620	720	1640	1700
2 % alginate and 1 % xylan	30	40	600	450	955	830

formulations except for the beads containing xylan, which was much shorter. Given the hydrophilicity of xylan and its solubility in alginate at low concentrations, this might be interpreted in terms of increased interaction between the water and xylan on accessible surfaces of the beads.

While relaxation times can give an indication of the interaction between a compound and water, it is difficult to make a clear distinction between these interactions and the porosity or pore sizes/geometries of the sample. Both factors strongly govern the swelling behavior and both will influence relaxation times. T2(1) relaxation times of the different polysaccharide–alginate samples in this study did not show an apparent relationship with the swelling ratio. The reason could be that the amount of water bound to polysaccharide by physico-chemical interaction only played an insignificant role for the total uptake of water in swollen beads.

An effort was made to correlate the observed T2(2) relaxation time of the samples with their swelling capacity in water. As the T2(2) relaxation time associated with free water decreased, the swelling ratio of the beads increased. In the case of air-dried samples, alginate–CNC beads clearly showed the best correlation between the gravimetrically determined swelling ratio and the correspondingly shortest T2(2) values. In regard to the freeze-dried samples, alginate–xylan beads had the shortest T2(2) and the highest swelling ratio.

Beads prepared from alginate with starch or cellulose had comparatively low swelling ratios and longest T2(2). Thus, it could be argued that the value of relaxation time T2(2) mostly showed a positive correlation with swelling ratio of different beads under the same drying method.

Overall, both T2(1) and T2(2) of air-dried samples were shorter than those of freeze-dried samples with the same polysaccharide composition. This indicated that air-dried beads had a stronger interaction with both bound and free water, probably caused by a more compact structure, allowing more sorbed water locked inside the beads. The more open, porous structure of freeze-dried samples allowed more surface adsorbed water (as observed with T2(3)). The only exception were alginate/xylan beads in regard to T2(2)). Xylan is the only one of the polysaccharides explored in this study that has some solubility in alginate while the other admixed polysaccharides remained as crystalline or granular fillers.

Morphological analysis

Scanning electron microscopy (SEM, Figs. 3, 4) was used to show the overall shapes and surface morphologies of the 2 % alginate control beads and 2 % alginate beads containing one of the following blended-in polysaccharides: 1 % starch, 1 % cellulose powder, 1 % CNC, or 1 % xylan. The method of drying did not seem to play a major role for the overall shape of the beads. They all were more or less spherical with a somewhat rough surface appearance. However, as it can be expected, the type of admixture impacted the surface morphology.

The differences in appearance may be attributed to the physical form of the polysaccharide and the way the polysaccharide combinations were able to interact. The air-dried beads formed from alginate alone had relatively smooth surfaces (Fig. 3a), while beads containing 1 % starch showed a more granular structure probably because the original granular structure from corn starch was still preserved (Fig. 3b). Blending alginate with 1 % cellulose powder created a coarser surface morphology of the resulting beads (Fig. 3d). The roughest surfaces were observed with xylan and CNC admixtures (Fig. 3c, e).

Unexpectedly the cross sections of the beads did not differ significantly. Figure 3f depicts a cross section through an alginate bead, representative of all other beads. They all had a fairly compact structure with more or less equal-sized pores and some cracks. Freeze-dried samples, on the other hand, showed large open structures of interconnected pores (Fig. 4f).

Compared to the air-dried beads with the same composition, the SEM images of freeze-dried samples (Fig. 4) all showed highly corrugated surfaces with more or less smooth walls (for example, alginate with xylan, Fig. 4c, compared with alginate containing cellulose powder, Fig. 4d). In alginate beads containing starch, the granular structure of starch could still be detected.

pH-dependent charge density changes in polysaccharide suspensions

The charge densities as a function of the pH value of different polysaccharide mixtures are presented in Fig. 5. Alginic acid sodium salt solutions alone and with either starch, CNC, or cellulose powder had an initial pH of 7.4. As mentioned above, these fillers remained in solid form regardless of the pH value. The first point of detectible charge density was at pH 8. Neither cellulose nor starch contain ionizable groups in the neutral and low alkaline range that could contribute to the overall charge density. Granular uncharged fillers might lower detectable charges in the overall solution. Cellulose particles show some swelling at pH values above pH 10 and influence the titration result to a certain extent. Above pH 11 all beads began to disintegrate.

The admixture of xylan lowered the initial pH to 5.4. Therefore, an alginate control sample of the same pH was prepared (termed “acidic 2 % alginate” in Fig. 5) that was measured simultaneously with xylan containing alginate. However, when using a potentiometric method, it has been mentioned in literature that it is difficult to clearly separate the effect of composition of the polymer and its charge density from other parameters such as water content in a swollen polymer or

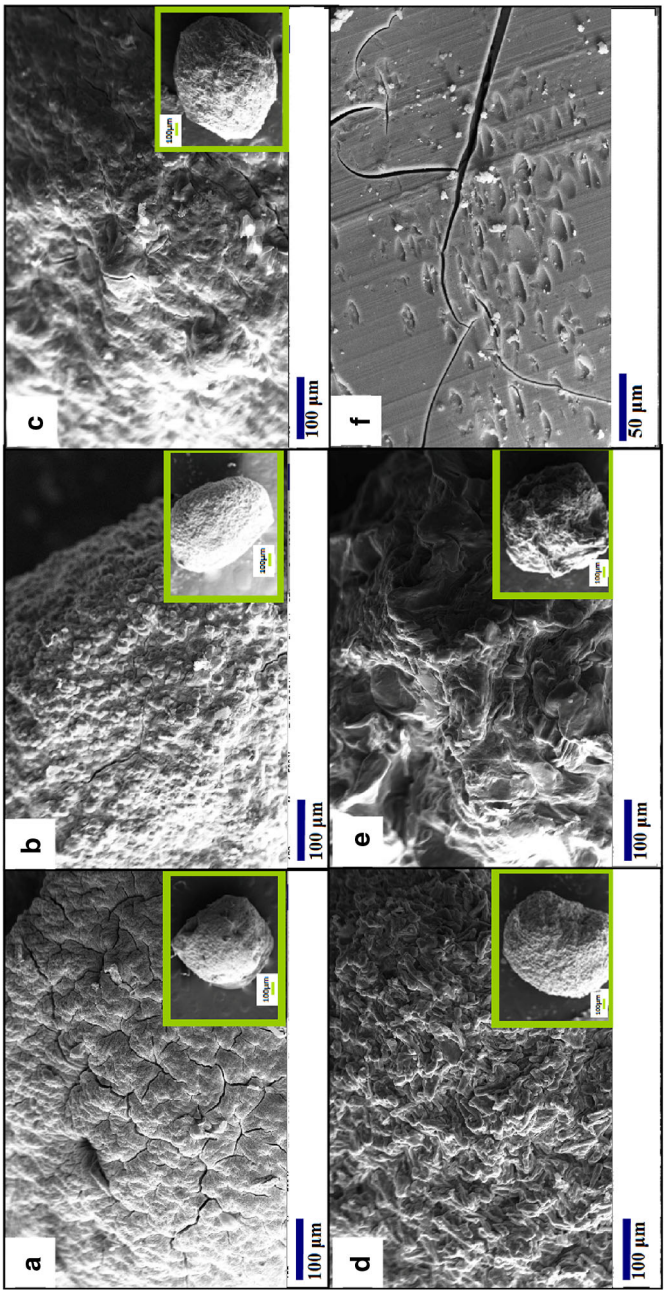

Fig. 3 Surface morphologies and bead shapes of different air-dried polysaccharide beads: **a** alginate only, **b** 2 % alginate with 1 % starch, **c** 2 % alginate with 1 % xylan, **d** 2 % alginate with 1 % cellulose powder, **e** 2 % alginate with 1 % CNC, **f** cross section of an alginate-only bead, representative of all other beads

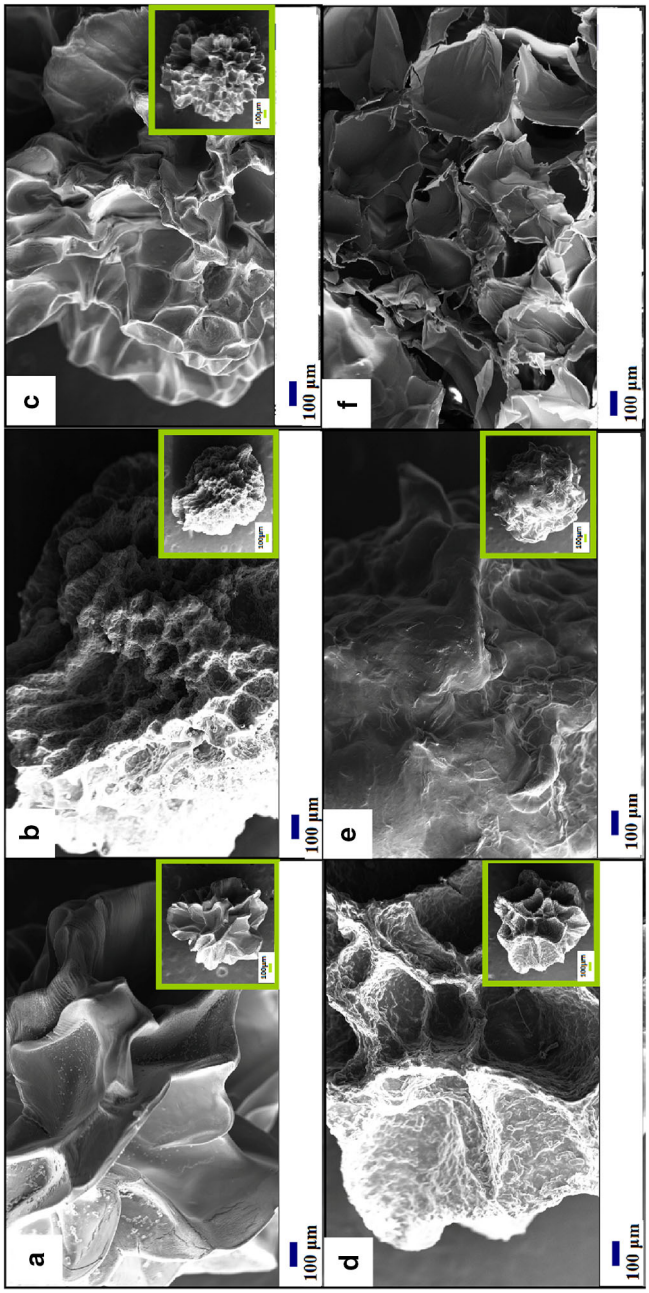

Fig. 4 Surface morphologies of different freeze-dried polysaccharide beads: **a** alginate alone, **b** 2 % alginate with 1 % starch, **c** 2 % alginate with 1 % xylan, **d** 2 % alginate with 1 % cellulose powder, **e** 2 % alginate with 1 % CNC, **f** cross section morphology of alginate bead without additional polysaccharide

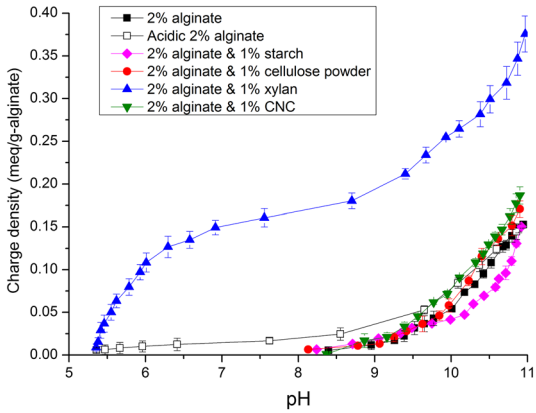

Fig. 5 Charge density of blended polysaccharide suspensions with different compositions

differing porosity when solid surfaces are involved [18]. Therefore, only the difference between two comparable samples rather than absolute values might give an indication of available charges. In the case of xylan–alginate beads the higher charge density at any given pH value must be attributed to additional carboxylic acid groups from xylan that dissociated at a lower pH together with additional dissociated carboxylic acid groups of alginate. These results suggest that beads containing xylan could be expected to be most effective in terms of binding cationic compounds (e.g., MB) if formed at a pH close to 11.

Methylene blue sorption

It was assumed that beads prepared with alginate still contain a certain amount of dissociated carboxylic acid groups after crosslinking. These negative charges could then form electrostatic interactions with positively charged groups in MB. Besides negative charges, the porous structure of the beads was expected to enhance the sorption of the dye. Experiments were performed to investigate whether the incorporation of fillers into alginate would have a measurable effect on its cation sorption capabilities. It was assumed that the driving force was both the formation of electrostatic interactions and sorption phenomena. A series of samples of air-dried (Fig. 6a) and freeze-dried beads (Fig. 6b) prepared with $CaCl_2$ solution at pH 9 were exposed to aqueous MB solutions and the capacity for the dye pick-up measured. Additionally, wet (never-dried) beads prepared in a $CaCl_2$ solution at pH 9 and at higher alkalinity (pH 11) were studied to evaluate the effect of changes in charge density on MB uptake (Fig. 7a, b, respectively). As mentioned above, wet beads became instable above pH 11.

Figure 6 illustrates that air-drying and freeze-drying of the beads did not lead to major differences in MB sorption of the resulting beads that could be associated with the drying method. Within the air-dried series, beads containing cellulose powder initially showed slightly higher MB sorption than the other samples, while the addition of NC to alginate had increased MB sorption in the case of freeze-drying. Although very small, the higher sorption of cationic MB could indicate the

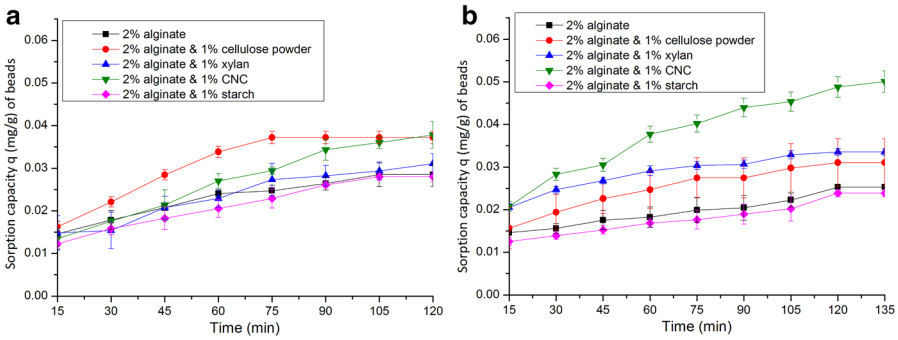

Fig. 6 MB sorption capacity of **a** air-dried beads, **b** freeze-dried beads

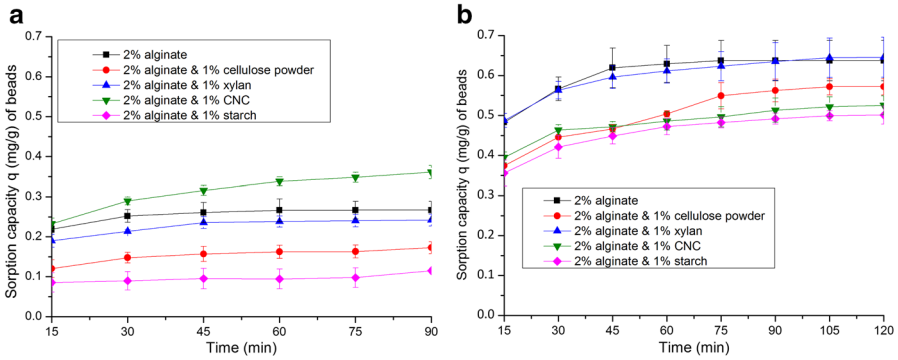

Fig. 7 Sorption capacity for MB of wet (never-dried) beads crosslinked at **a** pH 9 and **b** pH 11

presence of a few negatively charged sulfate groups left in CNC from its production by acid hydrolysis from cellulose and thus might have been available for MB binding. These groups, however, did not show as a measurable difference in regard to the pH-dependent charge density (Fig. 5). The overall lowest MB sorption for all types of beads was observed with starch as the admixture. It is possible that starch acted as a simple filler, reducing the accessible internal surface area for positively charged groups.

It was further observed that freshly made, wet (never-dried) beads had a 5–10 times higher overall MB sorption capacity than dried beads (Fig. 7a), which could be due to a higher accessibility of internal surfaces and charged groups within the beads. Upon drying, some pores might have collapsed and possibly remained unavailable during subsequent exposure to aqueous dye solution. As could be expected, in this series CNC–alginate samples again showed the highest MB uptake capacity as it had been the case with freeze-dried samples. Pure alginate and xylan–alginate beads showed very similar sorption behavior and starch–alginate beads were the samples with the lowest sorption capacity for MB.

If the crosslinking pH was changed from 9 to 11 (Fig. 7b), MB uptake essentially doubled for all samples. At pH 11, pure alginate and xylan–alginate MB sorption

capacity was basically indistinguishable, but clearly higher than in the case of all other samples. CNC and cellulose powder addition did not result in a major difference which matches the results of charge density at this pH (Fig. 5). It should, however, be stressed that for all samples charge density increase cannot be the only factor responsible for MB sorption but also the morphology and porosity of the beads.

Conclusions

A series of polysaccharide beads were prepared from alginate and either one of two types of cellulose (nanocrystalline or powder), starch or xylan and crosslinked with calcium ions. It was found that different bead sizes, swelling properties and surface morphologies resulted due to the nature and concentration of the admixed polysaccharide. The method of drying (air-drying or lyophilization) also showed a significant effect. As could be expected, freeze-dried beads were more porous and adsorbed more water. However, it was surprising that not all freeze-dried samples also adsorbed more cationic contaminants (as exemplified by methylene blue as a model cation) than air-dried beads. Low-field NMR spectroscopy was used to attempt differentiation between tightly bound non-freezing water, free water and surface water. The results indicated that air-dried samples had a stronger interaction with water than freeze-dried due to their denser structure. Overall, beads containing xylan showed the highest interaction with water. These beads also had the highest charge density at pH values below 7. In regard to the adsorption of cations, such as the model dye methylene blue, freshly made beads containing xylan adsorbed most if the beads were prepared at a more alkaline pH 11, while when made at a pH of 9, the ones containing CNC adsorbed slightly more. Thus, for the removal of cationic contaminants from water CNC might be the most effective additive to alginate, while xylan might be preferred if higher water sorption is the goal.

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