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Hydrophilic food compounds encapsulation by ionic gelation

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Among the several methods for encapsulating active compounds, ionic gelation is an interesting technique, because it can be considered as low cost and does not require specialized equipment, high temperature and organic solvents. However, this method is more adequate for encapsulating hydrophobic materials. The current challenge for hydrophilic compounds is to increase encapsulation efficiency and enhance controlled release properties. This review focuses in some ways to encapsulate hydrophilic materials by ionic gelation. Using polymer filler into particle matrix, coating particles to create a barrier external layer, emulsification and internal ionic gelation or applying inverted solidification are some alternatives reported in the literature to contour the drawback of ionic gelation for hydrophilic compounds.

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Introduction

Hydrocolloids gel particles or hydrogel beads are used for encapsulation of bioactive compounds or texture control in food, pharmaceutical, probiotic, medical and cosmetic products [3]. They are formed by ionic polymerization or polyelectrolyte ionic bounding. The process, so-called ionic gelation or ionotropic gelation, begins with an aqueous polymeric solution, with ions of low molecular mass that interact with polyelectrolytes of opposite charges, reacting and forming an insoluble gel [1••,2]. The principle of encapsulation consists in simply entrap an active substance and to further release it via gel phase changes, in response to external stimuli [3]. Different triggering mechanisms are used to release the encapsulated active as pH changes, mechanical attrition, enzymes, osmotic forces [4], and actives are released via diffusion.

Ionic gelation can be conducted by atomization processes, extrusion and coextrusion or electrostatic deposition [4]. Usually, a polymeric or hydrocolloid solution is dripped or atomized into an ionic solution, under constant agitation. The active compound to be encapsulated is dissolved in the polymeric solution. The drops that reach the ionic solution immediately form spherical gel structures, which contain the active dispersed in the whole polysaccharide matrix [5–8]. It is a simple and easy procedure, does not require specialized equipment, high temperature or organic solvent and can be considered low cost [2,7,9]. However, one of its disadvantages is the occurrence of heterogeneous gelation of gel particles due to the diffusion mechanism, as surface gelation often occurs before to core gelation, which in this case becomes a soft core [1••].

Alginate, low metoxilation pectin, chitin, chitosan are normally used as coating agents and the ion Ca^{+2} is the most used reticulation agent. They can be considered a very good encapsulation system for food compounds and controlled release, as they are atoxic, highly biocompatible and mechanically strong [3,7,8].

Capsules produced by ionic gelation are widely used for hydrophobic materials [10–15]. As the shell is made of alginate, gelatin, agar, low metoxilation pectin, or gellan gum, that are hydrophilic, the technique is usually applied for hydrophobic materials or those ones with very low solubility. Hydrophilic actives are more challenging to encapsulate than hydrophobic ones. Hydrocolloids are very helpful for the majority of the actives, but as they are miscible with the hydrophilic cores, it is very difficult to get a good phase separation between core and shell. Furthermore, since hydrogel bead is porous, encapsulation of hydrophilic compounds results in lower encapsulation efficiency and poor controlled release properties [3,8].

This manuscript reviews current works related to the formation and application of hydrocolloids gel particles with hydrophilic compounds. The challenges reported in the literature for encapsulating hydrophilic compounds will be exposed. In addition, some possible ways to contour the drawbacks of hydrophilic compounds encapsulation by ionic gelation will be discussed in the following sections: (a) addition of other polymers to change structure of hydrogel beads or to interact with bioactive

compound; (b) encapsulation by internal gelation; (c) encapsulation by absorption method, (d) use of the called inverted solidification processes [16].

Addition of polymers in hydrogel beads

In order to limit active compound losses during particle preparation by ionic gelation, some authors have studied the influence of addition of other polymers on encapsulation efficiency. These works will be discussed in this section. In general, an improvement on entrapment of bioactive agents in hydrogels was demonstrated for different polymers due to changes in microstructure of beads or interaction between bioactive compound and polymers.

Córdoba *et al.* [17] encapsulated yerba mate polyphenols in calcium alginate bead filled with starch and found an improvement on encapsulation efficiency from 55% (control sample, without starch) to 65%. By scanning electronic microscopy, the authors observed that starch granules filled the voids within the calcium alginate matrix, hindering the diffusion of polyphenols into cross-linking solution during ionic gelation. In another work, Córdoba *et al.* [18•] have demonstrated that control samples presented a higher total pore volume than the bead with starch filler. Moreover, starch retarded the total polyphenol release in simulated digestive fluids when compared to the control sample. In order to understand this behavior, Córdoba *et al.* [17] applied the Kopcha model to verify which mechanism was involved in the nutrient release. According to the authors, erosion had significant contribution during the beginning of polyphenol release for control sample. In contrast, the starch granules decreased matrix erosion, being relevant only the diffusion release mechanism.

Hosseini *et al.* [19] also demonstrated that the calcium alginate-starch beads had higher nisin encapsulation efficiency (50.28–59.77%) and loading capacity (19.06–27.08%) than control sample (48.33–54.58% and 16.15–21.15%, respectively). Moreover, the presence of starch delayed nisin release from calcium alginate microspheres. The times required to reach the 50% of initial nisin in the release solution were 96 and 168 h for microspheres without and with starch filler, respectively. Calcium alginate–tapioca starch beads presented higher encapsulation efficiency (96.7%) of chlorogenic acid than particle produced with only alginate (81.7%). This fact was due to the tortuosity produced by tapioca starch in microstructure, reducing diffusional transfer of active compound toward the cross-linking solution [20].

Stojanovic *et al.* [21] observed that the molecular weight of polymers used as fillers might be considered on diffusion of active substances from beads, since low molecular weight substances could not affect the porosity of hydrogel. The incorporation of sucrose, a low molecular weight substance, in calcium-alginate beads did not have any impact on diffusion rate of phenolic compounds of thyme extract. In contrast, when inulin was incorporated to calcium-alginate bead, the phenolic compounds release was extended from 10 to 15 min.

Similarly, the addition of inulin into alginate matrix enhanced encapsulation efficiency of carqueja extract from 49 to 73.8% [22]. The authors proposed that polar fractions of polyphenol molecules interact with the hydroxyl groups of inulin. This positive effect of inulin on encapsulation efficiency was also reported by Stojanovic *et al.* [21] when working with thyme extract, in which there was an increment of about 55% when compared with alginate microbeads without inulin (51% of efficiency).

In order to verify the possible protein-polyphenol interaction, Belščak-Cvitanović *et al.* [23•] evaluated several types of proteins for producing alginate particles with higher retention of green tea polyphenols. The addition of calcium casein ate or whey protein improved encapsulation efficiency of total phenols from 66.1% (without proteins) to 77.2 and 76.5%, respectively. Apart from that, alginate-whey protein particles loaded the highest catechin (19.3 mg/g) and caffeine contents (12.6 mg/g) when compared with alginate (0.2 and 0.8 mg/g, respectively) or other alginate-protein beads. The authors suggested that those proteins interact more intensively with these compounds. For Wichchukit *et al.* [24], whey proteins can decrease diffusion of Ca^{+2} from the hydrogels, leading to lower interaction between alginate molecules with water and, as a consequence, the ability of the gel to swell and suffer erosion. This supposition has been done when the authors observed by magnetic resonance imaging that pure alginate beads showed lower structural stability when immersed in a suspending release solution than beads with whey protein. Moreover, Wichchukit *et al.* [24] observed that pure alginate bead presented rough and cracked surface, allowing higher water penetration into the sample.

Apart from studying the combination of alginate with polymers, several authors have also coated hydrogel beads with an external layer of chitosan to fill or cover the porous alginate matrix, aiming at enhancing encapsulation efficiency or prolonging the release of hydrophilic compounds. Belščak-Cvitanović *et al.* [25] verified an improvement on encapsulation efficiency of raspberry leaf polyphenols encapsulated in alginate beads coated with chitosan. Deladino *et al.* [26] obtained an opposite and unexpected result, in which chitosan-alginate particles entrapped lower yerba mate polyphenols content than the bead without chitosan. According to the authors, significant active compound losses occurred mainly during the immersion in the chitosan solution. Similarly, Bajpai and Tankhiwale [27] obtained higher entrapment of vitamin B_2 in alginate particles than in those coated with chitosan.