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Review

Encapsulation of betacyanins and polyphenols extracted from leaves and stems of beetroot in Ca(II)-alginate beads: A structural study

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The aim of this work was to use the recovery of antioxidant compounds (betacyanin and polyphenols) derived from beetroot industrial wastes (stems and leaves), and their subsequent encapsulation in Ca(II)-alginate beads containing sugars, providing a detailed structural characterization of these systems determined by SAXS from the molecular (arrange of Ca(II)-alginate dimers) to the supramolecular (interconnection of the rods composing the hydrogel microstructure). Water extract contained significant quantities of betacyanin and polyphenol, which were retained in Ca(II)-alginate beads between 15 and 60%, depending on the formulation, retaining also the antioxidant activity. Both the inclusion of sugars as synthesis additives and beetroot extracts induced main structural changes, which can have counteracting effects. We revealed that, though being overlooked in most alginate encapsulation research, the presence of natural extracts prompts important structural changes in the alginate network, affecting key parameters which define the encapsulation performance in most of industrial and environmental applications.

Contents

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1. Introduction

Beetroot (*Beta vulgaris*) has been cataloged among the ten vegetables with greater antioxidant activity (Halvorsen et al., 2002) and its commercially exploited commodities are growing increasing interest. Recent studies have provided compelling evidence that beetroot ingestion offers beneficial physiological effects that may translate to improved clinical outcomes for several pathologies, such as hypertension, atherosclerosis, type II diabetes and dementia (Clifford et al., 2015). In addition, antioxidants from beetroot are bioavailable for the human organism as they permeate from the alimentary tract to the bloodstream (Netzel et al., 2005). The growing demand in the consumption of this vegetable has generated diverse studies of its health benefits. The bulb (root), being by far the most consumed, has become the main object of study, leaving the leaves and the stems as waste, even if the shoot have also nutritional value and important benefits for human health. Red beets (including root, leaves and stems) contain betalain pigments, one of the most important natural colorants (FDA and EFSA approved) and also one of the earliest natural colorants developed for use in food systems (Francis., 1999), belonging to the group of cation antioxidants (Kanner et al., 2001). Betalains are water-soluble nitrogen compounds, found in the cell sap; they show antioxidant and radical scavenging activities (Pedreño and Escribano, 2000; Gliszczyńska-Świgło et al., 2006; Allegra et al., 2005). Betalains can be divided into two groups: red-violet betacyanins and yellow-orange betaxanthins. Its concentration is decreasing in the following order: peel, crown and flesh (Kujala et al., 2000, 2002). The betacyanin and betaxanthin concentration ratio usually ranges between 1 and 3. It depends on beetroot varieties, part of the plant and applied extraction technology (Nemzer et al., 2011). Polyphenols are naturally occurring compounds largely found in fruits, vegetables, cereals and beverages (Pandey and Rizvi, 2009). Studies suggest that a diet based on rich-polyphenols provides significant protection against the development and progression of many chronic pathological conditions, thus developing great scientific interest from their beneficial effects on human health (Jastrebova et al., 2003; Georgiev et al., 2010; Graf et al., 2005; Arts and Hollman, 2005). Current tendency leads to recover target compounds from what is commonly known as food waste, as an alternative and cheap source of several bioactive compounds with technological and healthy properties. In this scenario, no effort should be spared in developing low-cost methods for recovering these valuable components of food by-products and recycling them inside the food chain (Galanakis, 2012, 2015).

Encapsulation is being used to improve stability and bioavailability of several bioactive compounds due to the interest in developing more efficient and selective methods for their protection and preservation (Aguirre Calvo and Santagapita, 2016; Traffano-Schiffo et al., 2017a, 2017b; Lupo et al., 2014). The incorporation of bioactives into food products provides many advantages in food preservation and contributes to the development of functional foods promoted by the application of emerging technologies (Galanakis, 2013). Thus, in the food industry, encapsulation not only allows adding value to a product food and generating a source of new additives with specific properties (Campañone et al., 2014), but it is also characterized, in addition to scalability, by the ease of operation, cost effectiveness, and broad regulatory acceptance (Abubakr et al., 2010). The study of alginates has generated many research due to their renewability, biodegradability, biocompatibility, and nontoxicity characteristics (Messaoud et al., 2015; Santagapita et al., 2012). In particular, much research is focused on the design and development of encapsulation systems capable of producing beads with the desired characteristics, among them the rapid, reproducible and controlled formation of uniform drops (Traffano-Schiffo et al., 2018; Santagapita et al., 2012; Deladino et al., 2008. Balanč et al., 2015). Studies have shown that interaction of dextran and alginate during the formation of beads improves encapsulation efficiency of bioactive compounds while increasing the stability of the system at typical gastric tract pH conditions (Martins et al., 2007). Sucrose is highly used for the generation of alginate beads and films due to its cryo-protective properties (De Giulio et al., 2005). The advantage of its addition during the external gelation procedure and its ability to modify the crosslinking reaction to generate uniform films without the appearance of localized gelling areas at the surface (Al-Remawi; 2012) are also to be noted.

In order to explore the nanoscale morphology and microstructure of the Ca(II)-alginate, small angle X-ray scattering (SAXS) affords information in the scale 1–100 nm. The most recognized mechanism of Ca^{2+} serving as the cross-linker for alginate through the G-blocks where specific Ca-mediated interactions involve two polymer chains was named the egg-box model, which describes the local cage conformation adopted by adjacent L-guluronate residues involved in coordination to the divalent cations (Wang et al., 1995; Sikorski et al., 2007a,b; Waters et al., 2010). The gelation of Ca(II)-alginate is explained by the cooperative association of these polymer dimers, to form rod like structures and the subsequent ramification of these rods, generating a percolating network (Traffano-Schiffo et al., 2018). Thus, this technique gives insight into different scales, providing information of the cross-sectional radius of gyration of the rods, which allows assessing the “junction zone multiplicity” or the size of the junction zone domains (Stokke et al., 2000), but also at larger scale indicating the degree of ramification of rods, and at a smaller scale, giving information on the polymer dimers formation. Being their functional properties highly dependent on the nano and microstructure, a detailed structural characterization of these systems becomes of great scientific and technological interest.

The aim of this work was to emphasize in the extraction of antioxidant compounds (betacyanins and polyphenols) derived from two industrial wastes (stems and leaves) of beetroot, and their subsequent encapsulation in Ca(II)-alginate beads, providing a