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Saffron and beetroot extracts encapsulated in maltodextrin, gum Arabic, modified starch and chitosan: Incorporation in a chewing gum system

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ABSTRACT

Maltodextrin (MD-21DE), gum Arabic (GA), gum Arabic–modified starch (GA–MS), modified starch–chitosan (MS–CH) and modified starch–maltodextrin–chitosan (MS–MD–CH) were used as agents for beetroot and saffron coloring-extracts microencapsulation by freeze drying. The produced powders were evaluated in terms of coloring strength (E) during storage at 40 °C for 10 weeks and a first-order kinetic was applied. Color parameters (L^*, a^*, b^*, C^* and ΔE^*) and water sorption behavior was also studied. Moreover, incorporation of the powders in a chewing gum model system was conducted. The type of encapsulating agent significantly ($P < 0.05$) affected the studied parameters with the order of protection in both extracts being as follows: MD > GA > GA–MS > MS–CH > MS–MD–CH. The water sorption study revealed that MD and GA kept their structural integrity up to water activities of 0.66 and 0.82, respectively. The chewing gum samples produced with coloring extracts encapsulated in GA–MS showed the greatest a^* (for beetroot) and b^* (for saffron) values indicating a better protection.

1. Introduction

Color is one of the most important characteristics of foods, being considered as a quality indicator that determines their acceptance (Azeredo, 2009). Although chemical food additives such as artificial colorants have been widely applied for coloring purposes of food products, their use is still a controversial issue in the food industry due to their toxicological potential on human health (Mizutani, 2009; Reyes, Valim, & Vercesi, 1996). The consumption of artificial colorants has been associated with the development of allergies in children (Inomata, Osuna, Fujita, Ogawa, & Ikezawa, 2006) and the increased risk of cancer (Sasaki et al., 2002). Therefore, legislative actions and consumer concerns have resulted in an increased interest toward replacement of chemical colorants with natural pigments, which are considered not only to be harmless but also to possess functional properties that can exert beneficial effect to human health (Moreira et al., 2012; Rutkowska & Stolyhwo, 2009).

Beetroot and saffron are basic natural sources of pigments which are typically used as colorants in quite a wide range of food products. Beetroot pigments consist of two major water soluble fractions, betacyanins that confer the red-violet color and betaxhantins, a yellow–orange colorant also present in beetroot in lesser proportion than betacyanins (Pitalua, Jimenez, Vernon-Carter, & Beristain, 2010). They are typically used at levels of 4–25 mg/kg in a wide range of dairy and confectionery products as well as in meat substitutes. However, their use in foods is limited due to their poor stability when exposed to heat and light (Serris & Biliaderis, 2001).

On the other hand, saffron pigments include crocins, a group of water soluble carotenoids, which are glycosyl esters of 8,8-diapocarotene-8,8-dioic acid (or crocetin) with biologically activity on human health (Tarantilis, Tsoupras, & Polissiou, 1995). Saffron pigments are typically used at levels of 1–260 ppm in a wide range of culinary, bakery and confectionery preparations as well as in alcoholic and non alcoholic beverages. However, as being highly unsaturated components, they are prone to oxidation and isomerization reactions that lead to losses of coloring strength and nutritive value (Tsimidou & Biliaderis, 1997). Therefore, a protective encapsulation technique is needed for the feasible usage of the afore-mentioned natural pigments in food products.

Among the common encapsulation techniques used are spray (Akhavan, Jafari, Ghorbani, & Assadpoor, 2014) and freeze–drying of the oil-in-water prepared emulsion containing the encapsulating agent and the pigment-core (Lim, Tan, Bakar, & Ng, 2011).

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Microencapsulation by freeze drying leads to products with excellent sensory characteristics and preserved biofunctionality since changes associated with high temperatures are minimized, due to the low temperatures involved in the process (Minemoto, Adachi, & Matsuno, 2001). Moreover, the selection of the encapsulation agent is very crucial for an efficient process and it depends on the final application of the encapsulated pigment. In our previous works, various edible polymers have been examined (plain and in mixtures) in fennel oleoresin (Chranioti & Tzia, 2013, 2014a) and saffron volatile flavor substances (Chranioti, Papoutsakis, Nikoloudaki, & Tzia, 2012) encapsulation. Among the studied encapsulating agents, plain gum Arabic (GA), binary blends of gum Arabic–modified starch (GA–MS) and chitosan-modified starch (MS–CH) as well as a ternary one of modified starch–maltodextrin–chitosan (MS–MD–CH) were selected as they displayed relatively high encapsulation efficiencies while plain maltodextrin (MD) was chosen since it is colorless and provides good protection against oxidation (Chranioti & Tzia, 2014b).

Although there have been some studies on encapsulation of beetroot (Pitalua et al., 2010) and saffron (Cormier, Dufresne, & Dorion, 1995; Dufresne et al., 1999; Khazaei, Jafari, Ghorbani, & Hemmati Kakhki, 2014) extracts, the use of the afore-mentioned mixtures of agents has not been investigated.

Therefore, the aim of this study was to produce natural colorants encapsulated in different mixtures of agents with the use of freeze drying technique and then: (i) to examine the color stability of the obtained encapsulated colorants, (ii) to study their sorption behavior at various relative humidity environments and (iii) to evaluate their incorporation in a chewing gum model system.

2. Materials and methods

2.1. Materials

Dried stigmas of saffron were provided directly from the 'Cooperative of saffron, Krokos Kozanis' while the beetroot vegetable was purchased from a local market. Modified Starch (MS, Cleargum CO-01, an octenyl-succinylated starch), maltodextrin DE-21 (MD, from Waxy Maize) and gum Arabic (GA) were obtained from Chemicotechnica S.A. Chitosan (CH) high molecular weight (viscosity of 800,000 cps, food-grade, water soluble, odorless and tasteless powder as stated by the manufacturer) was obtained from Sigma-Aldrich Chemical Co. Sorbitol and mannitol were purchased from Cargill whereas gum base and lecithin were kindly donated from Kraft Foods and Biotrek—Greece, respectively.

2.2. Preparation of aqueous saffron and beetroot extracts

Saffron (1 g) was extracted with distilled water (50 mL) under continuous shaking in an ultrasound water bath (Elma, S 30H, Elmasonic) at $T = 25\,^{\circ}C$ for 60 min and at fixed-frequency of 30 kHz, while beetroots were washed, peeled and extracted with water in a commercial juice extractor. Both saffron and beetroot aqueous extracts were filtered and kept in the dark at $-30\,^{\circ}C$ until used.

2.3. Microencapsulation of saffron and beetroot extracts by freeze–drying

Plain GA and MD, binary (1:1) blends of GA–MS and MS–CH plus a ternary (1:1:1) one of MS–MD–CH were selected as encapsulating agents. An aliquot of 15 g of GA, MD and MS agent was dispersed individually in distilled water to a final volume of 100 mL, while a 2% chitosan solution (CH) in 1% glacial acetic acid was prepared. A fixed weight ratio (w/w) of 0.33 (extract:agent) was tested (Ahn et al., 2008; Hogan, McNamee, O'Riordan, & O'Sullivan, 2001). The extracts were dissolved into the agents under stirring for 15 min at 600 rpm in a rotor–stator. The resulting solutions were frozen overnight at $-30\,^{\circ}C$ (Shimada, Roos, & Karel, 1991) and lyophilized in a freeze dryer (Christ Alpha 1–4 LD Plus) at $P = 0.017$ mbar and $T = -57\,^{\circ}C$ for 48 h. The freeze-dried encapsulated extracts were converted into powder with help of a pestle and mortar.

2.4. Kinetic studies of beetroot and saffron pigment degradation

Freeze-dried beetroot and saffron powders were stored in brown bottles with a screw cap and kept at $40\,^{\circ}C$ with 20% RH (relatively humidity) as directly measured with a hygrometer for a period of 10 weeks in order to determine the effect of storage temperature on the retention of betacyanins and carotenoids levels, respectively. The degradation of natural pigments was expressed as coloring strength (E) and followed by periodic absorbance measurements of the reconstituted powder (0.2 g) in aqueous solution with distilled water (10 mL, stirring for 10 min and immediate measurement of the absorbance at certain wavelength). The absorbance was measured with a spectrophotometer (DMS 80, Varian Techtron PTY, LTD, Belrose, Australia) at $\lambda_{max} = 537$ nm, the maximum absorption wavelength of betacyanin (Pasch & von Elbe, 1975) and $\lambda_{max} = 440$ nm, the maximum absorption wavelength of crocin (ISO, 1993). The coloring strength, (E), was calculated as follows (Alonso, Varon, Gomez, Navarro, & Salinas, 1990):

$$E^{1\%}_{\lambda max} = \frac{AV}{pdC} \quad (1)$$

where A is the absorbance at the λ_{max}, V is the quantity of solvent added (mL), p is the weight of the sample (g), d is the pathlength of the cell (cm) and C is a constant, the value of which is 100 cm^2/g.

Measurements were carried out in triplicate and reaction rate constants (k) and half-life periods ($t_{1/2}$) were determined by applying a first-order reaction model to the data (Tsimidou & Tsatsaroni, 1993). Powder samples were withdrawn every 2 weeks for a period of 10 weeks for betacyanins and carotenoids degradation kinetic analysis.

2.5. Color change during storage

L^* (lightness), a^* (redness to green), and b^* (yellow to blue) color parameters were measured immediately after freeze–drying (zero time) and after 12 weeks of storage at $40\,^{\circ}C$ and the mean of three replicates was reported. Color measurements were performed directly on the encapsulated powdered products using a colorimeter (Minolta CR 200, Tokyo, Japan). The parameters of chroma (C^*) and total color differences (ΔE^*) were also calculated as follows:

$$C^* = \left[(a^*)^2 + (b^*)^2\right]^{1/2} \quad (2)$$

$$\Delta E^* = \left[\left(L_0^* - L^*\right)^2 + \left(a_0^* - a^*\right)^2 + \left(b_0^* - b^*\right)^2\right]^{1/2} \quad (3)$$

2.6. Water sorption studies

Approximately 0.4 g of freeze dried microencapsulated saffron and beetroot samples was placed in small glass desiccators (10 cm diameter) which contained different saturated salt solutions at ambient temperature ($25\,^{\circ}C$). The prepared saturated solutions of LiCl, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2{\cdot}6H_2O$, KI and KCl provided water activity (a_w) levels of 0.11, 0.31, 0.42, 0.51, 0.66 and 0.82, respectively (Labuza, 1984). The samples were weighed until equilibrium was attained for a period of 15–20 days. The initial moisture content of the samples was measured on a dry weight basis by drying the sample in a vacuum oven at $100\,^{\circ}C$ until constant weight was obtained (AOAC, 2000). The water activity (a_w) was measured using Aqualab 3TE water activity meter (Decagon Devices