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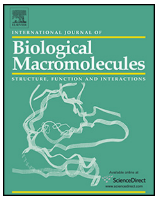

Microencapsulation optimization of natural anthocyanins with maltodextrin, gum Arabic and gelatin

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ABSTRACT

The barberry (*Berberis vulgaris*) extract which is a rich source of anthocyanins was used for spray drying encapsulation with three different wall materials, i.e., combination of maltodextrin and gum Arabic (MD + GA), maltodextrin and gelatin (MD + GE), and maltodextrin (MD). Response Surface Methodology (RSM) was applied for optimization of microencapsulation efficiency and physical properties of encapsulated powders considering wall material type as well as different ratios of core to wall materials as independent variables. Physical characteristics of spray-dried powders were investigated by further analyses of moisture content, hygroscopicity, degree of caking, solubility, bulk and absolute density, porosity, flowability and microstructural evaluation of encapsulated powders. Our results indicated that samples produced with MD + GA as wall materials represented the highest process efficiency and best powder quality; the optimum conditions of microencapsulation process for barberry anthocyanins were found to be the wall material content and anthocyanin load of 24.54% and 13.82%, respectively. Under such conditions, the microencapsulation efficiency (ME) of anthocyanins could be as high as 92.83%.

1. Introduction

There is a worldwide trend toward the use of natural colorants as alternatives to synthetic colors in food applications because of both legislative actions and consumer concerns. Seedless barberry, *Berberis vulgaris*, which is widely cultivated in Iran, is a rich source of anthocyanins and could be used as a good source for producing a brilliant red color for many foods. Anthocyanins (Greek *anthos*, flower and Greek *kyanose*, blue) are generally accepted as the largest and most important group of water-soluble pigments in nature and responsible for color of many fruits, flowers, and other parts of plants [8,23].

The interest in anthocyanin pigments and scientific research have increased in recent years mainly due to their role in nutraceutical and health benefits which is given by natural antioxidants [24]. However, stability of anthocyanins depends on a combination of environment and chemical factors such as pH, metal ions, exposure to light, temperature, oxygen, and enzymatic activities [22,28]. So, due to low stability in environmental conditions during processing and storage, introducing those compounds into foods is challenging [7].

Microencapsulation may be an efficient way to introduce such compounds into those products. Microencapsulation is defined as a process to entrap one substance (active agent) within another substance (wall material) [12,31]. The main objective of encapsulation is to protect the core material from adverse environmental conditions, such as undesirable effects of light, moisture, and oxygen, thereby contributing to an increase in the shelf life of the product, and promoting a controlled liberation of the encapsulate [29,30]. There are many encapsulation techniques; among which some have been successfully applied to anthocyanins [11]. The selection of a microencapsulation method depends upon specific applications and parameters such as required particle size, physicochemical properties of the core and coating materials, release mechanisms, process cost, etc. [26]. Spray-drying is the most commonly used technique, on account of it being a continuous, low cost process that produces dry particles of good quality, and for which the machinery required is readily available. Spray drying encapsulation has been successfully used for a number of anthocyanin rich materials [26].

Different types of wall materials have been used for microencapsulation including polysaccharides (starches, maltodextrins, corn syrups and gum Arabic), lipids (stearic acid, mono- and diglycerides), and proteins (gelatin, casein, milk serum, soy and wheat)

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[9]. The use of different carrier agents for powder production can result in different physicochemical properties, depending on the structure and the characteristics of each agent. Anthocyanins are hydrophilic colorants and specifically compatible with a water-based gel formulation such as gum, or maltodextrin and starches as coating molecules for polar solid matrices [20]. Maltodextrins of different dextrose equivalent (DE) are commonly used as wall material by its high water solubility, low viscosity, low sugar content and their solutions are colorless. These properties make them as the most commonly used carrier or wall materials in the microencapsulation [32]. Gelatin is also a good choice as wall material especially in spray drying due to its good properties of emulsification, film-formation, water-solubility, high stabilizing activity, and a tendency to form a fine dense network, etc. [37]. Gum Arabic, a natural colorless plant polysaccharide exudate of acacia is a well-known effective wall material used for many years and still a good choice because of its stable emulsion formation and good retention of volatiles [18]. According to Fang and Bhandari [11], a single encapsulating matrix does not possess all required characteristics and efforts to improve encapsulation properties have been done by using mixtures of carbohydrates with proteins and polysaccharides at different proportions. The choosing of polymer blends that could result in higher encapsulating efficiency and lower cost than the individual biopolymers has been object of increasing interest [5,10,14,25,32,33,30].

The objective of this study was to study the influence of different types of wall materials (MD + GA, MD + GE and MD) as well as different ratio of core to wall materials on encapsulation efficiency and to investigate physiochemical properties of the produced encapsulated powders along with optimization of the process.

2. Materials and methods

Fresh barberry fruits (*B. vulgaris*) were obtained from Birjand located in South Khorasan, Iran and were kept at −18 °C in a freezer till used. Maltodextrin (DE = 18–20) (Foodchem, China), Gum Arabic (Samchon Chemical, Korea), and bovine gelatin with bloom value 240 (Foodchem, China) were used as wall materials. All other chemicals used in this study were of analytical grade and purchased from chemical suppliers.

2.1. Extraction of natural anthocyanins

Extraction method was adopted from Sharifi and Hassani [36] using a reflux system. The barberries were first ground by means of a grinder (Black & Decker, USA). They were put into a solvent flask including acidified ethanol and distilled water (1:3). The flask and the condenser in the water bath were exposed to a temperature of 50 °C for 2 h. Then, the flask was removed from the system and kept in the dark for 2 h. Finally, the obtained solution was filtered in vacuum using Watman filter (grade 1) and the produced extract was concentrated to 15° brix by a rotary evaporator at 40 °C (IKA, Germany). Table 1 presents the physicochemical properties of produced extract.

2.2. Microencapsulation of natural anthocyanins

For encapsulation purposes, MD, MD + GA and MD + GE were evaluated as encapsulating agents (wall materials) and anthocyanin extract as core material. Different proportions of core/wall materials (12, 25, 35 and 50%) were tested. the ratios between MD/GA and MD/GE were selected 3/1 according to the best ratio of these wall materials presented by previous studies [13,19,27,39]. MD and MD + GA solution were dissolved in warm distilled water (70 °C) under constant stirring at 120 rpm for 1 h and were kept overnight at 4 ± 2 °C for rehydration. Gelatin was dissolved in hot distilled water, being stirred, to form an aqueous solution. These wall materials containing different ratios, were combined with the pigment extract (15° Brix) until reaching to 20% final solid content and stirred until all the materials were completely dissolved. The resulting mixtures were subsequently spray dried. 500 mL of feed mixtures were fed into a pilot spray-dryer (Novin industries, Iran) at flow rate 800 mL/h. The inlet and outlet air temperatures were 150 and 100 °C, respectively; these conditions have been established in a previous work [34]. Spray dried powders were packaged to prevent light incidence and stored over silica gel in desiccators at room temperature for further experiments.

Table 1
Physicochemical properties of barberry extract subjected to encapsulation process.

Analysis	Mean values	Method
Moisture content (% wet basis)	82.79 ± 0.02	AOAC (2006)
pH	3.5 ± 0.07	pH meter
Titrable acidity (% citric acid)	0.71 ± 0.03	AOAC (2006)
Total soluble solids (° Brix)	15.5 ± 0.02	Refractometer
Anthocyanin content (mg/100 mL extract)	609.25 ± 2.18	AOAC [4]
Color		Lovibond (100CAM, England)
*L**	59.3	
*a**	76.8	
*b**	31.7	

All data are the mean of triplicate measurements ± standard deviation values.

Table 2
Influence of the core/wall ratio for anthocyanin extract on microencapsulation efficiency.

Core/wall ratio (%)	Wall materials	Microencapsulation efficiency (%)
12	MD + AG	94.291 ± 1.01^{a}
	MD + GE	93.064 ± 0.4^{b}
	MD	89.491 ± 1.0^{c}
25	MD + GA	96.215 ± 1.02^{d}
	MD + GE	94.972 ± 0.2^{a}
	MD	93.087 ± 1.0^{b}
35	MD + GA	94.391 ± 0.02^{a}
	MD + GE	92.972 ± 0.4^{b}
	MD	90.087 ± 0.6^{c}
50	MD + GA	89.091 ± 1.02^{c}
	MD + GE	87.572 ± 0.1^{e}
	MD	86.068 ± 0.7^{f}

Different letters within column indicate significance difference at $P < 0.05$.
GA, gum Arabic; GE, gelatin; MD, maltodextrin.

2.3. Encapsulation efficiency

The encapsulation efficiency is an important indicator for microencapsulated particles and refers to the potential of the wall materials to encapsulate or hold the core material inside the microcapsule. In order to evaluate the effectiveness of microencapsulation, total anthocyanin content (TAC) and surface anthocyanins content (SAC) of the microcapsules were determined according to a modified method from Idham et al. [20]. To obtain the TAC, 100 mg of samples was weighed and about 1 mL distilled water was added and then the samples were ground using pestle and mortar to destroy the microcapsule membrane. Then, 10 mL ethanol was added and the samples were extracted for 5 min and then filtered.

The extraction of surface anthocyanins from the capsules was carried out by quickly washing with 10 mL ethanol in a vortex for 10 s, followed by centrifugation at 3000 rpm for 3 min at 20 °C. After

Table 3
Physical properties of encapsulated powders containing Barberry anthocyanins with different wall materials.

Wall material	Moisture content (%)	Hygroscopicity (%)	Degree of caking (%)	Solubility (%)	Bulk density (g/cm^3)	Absolute density(g/cm^3)	Porosity (%)	Flowability
MD + GA	3.07 ± 0.2^{a}	19.532 ± 0.9^{a}	21.052 ± 2.1^{a}	91.091 ± 1.02^{a}	0.431 ± 0.1^{a}	0.909 ± 0.2^{a}	52.582 ± 0.1^{a}	1.301 ± 0.5^{a}
MD + GE	4.267 ± 1.0^{b}	21.227 ± 0.8^{b}	20.502 ± 0.3^{a}	90.972 ± 0.2^{a}	0.409 ± 0.1^{b}	0.911 ± 0.6^{a}	55.104 ± 0.3^{b}	1.303 ± 0.5^{a}
MD	3.475 ± 0.7^{a}	20.447 ± 0.5^{a}	20.094 ± 1.14^{a}	90.687 ± 0.6^{a}	0.395 ± 0.2^{b}	0.919 ± 0.7^{a}	57.1 ± 0.4^{b}	1.303 ± 0.1^{a}

Different letters within column indicate significance difference at $P < 0.05$.
GA, gum Arabic; GE, gelatin; MD, maltodextrin.

phase separation, the clear supernatant was collected and filtered through 0.45-μm-sized Millipore membrane.

Quantification was carried out using the pH-differential method described by AOAC [4], using two buffer systems: potassium chloride buffer at pH 1.0 (0.025 M) and sodium acetate buffer at pH 4.5 (0.4 M). An aliquot of the extract was transferred to a 10 mL volumetric flask and made up to 10 mL with corresponding buffer and the absorbance was measured at 520 and 700 nm by a UV–vis spectrophotometer. The reason for measuring the absorbance at 700 nm is to correct for haze. TAC was calculated as cyanindin-3-glucoside according to the following equation:

$$\mathrm{TAC(mg/L)} = \Delta A \varepsilon \times 1 \times M \times 103 \times D \tag{1}$$

where ΔA, (A520 pH 1.0–A700 pH 1.0) − (A520 pH 4.5–A700 pH 4.5); ε (molar extinction coefficient) = 26,900 L/mol/cm for cyanidin-3-glucoside; 1, path length in cm; M (molecular weight) = 448.8 g/mol for cyanidin-3-glucoside; D, dilution factor; 103, conversion from gram to milligram.

Encapsulation efficiency (%EE) was calculated according to Eq. (2) through the results from total (TAC) and surface anthocyanin (SAC) contents.

$$\%\mathrm{EE} = \frac{(\mathrm{TAC} - \mathrm{SAC})}{\mathrm{TAC}} \times 100 \tag{2}$$

2.4. Physical properties of encapsulated powders

After determination of efficiency, samples containing different wall materials with the highest efficiency were analyzed for physical properties. The powder moisture content was determined gravimetrically by drying in a vacuum oven at 70 °C until constant weight [3]. Hygroscopicity was determined according to the modified method of Cai and Corke [6]. Samples of each powder (approximately 1 g) were placed at 25 °C in a container with NaCl saturated solution (75.29% RH), and were weighed until equilibrium was reached. Hygroscopicity was expressed as g of adsorbed moisture per 100 g of dry solids (g/100 g).

To calculate degree of caking, after determination of hygroscopicity, the wet sample was placed in a vacuum oven at 102 °C ± 2 °C for 1 h. After cooling, the dried sample was weighed and transferred into a sieve of 500 μm size. The sieve was then shaken for 5 min in a shaking apparatus. The weight of the powder remaining on the sieve was measured. The degree of caking was calculated as Eq. (3), where b is initial amount of powder and a is the amount of powder left on the sieve [16].

$$\%\mathrm{Degree\ of\ caking} = \frac{b}{a} \times 100 \tag{3}$$

The water solubility index (WSI) of the powders was measured using the method described by Anderson et al. [2]. 12.5 g of the power was mixed thoroughly for 5 min in 30 mL distilled water in a 50-mL centrifuge tube. The centrifuge tube was incubated at 37 °C in a water bath for 35 min. The solution was then centrifuged at 17,640 × g for 20 min at 4 °C. The supernatant was collected in a pre-weighed 80-mL beaker and vacuum dried in an oven at 105 °C for 2 h [38]. The bulk density (ρ_{bulk}) of the powders was measured by weighing 1 g of sample and placing it in a 10 mL graduated cylinder. The cylinder was tapped by hand and the bulk density was calculated as the ratio between the mass of powder contained in the cylinder and the volume occupied [13]. The absolute density (ρ_{abs}) was determined in a pycnometer, using 99% ethanol as the immiscible liquid. Porosity (ε) was calculated as follows [38]:

$$\varepsilon = 1 - \frac{\rho_{\mathrm{b}}}{\rho_{\mathrm{a}}} \tag{4}$$

Flowability of the powders was determined according to the Hausner ratio which is a number that is correlated to the flowability of a powder or granular material (Hausner, 1967). 10 g of powders was placed in a 25 mL graduated cylinder. After observing the initial volume (V_{b}), the cylinder was mechanically tapped, and volume was recorded until reached to a constant volume (V_{f}). Flowability was calculated by the following formula.

$$\mathrm{Hausnerratio\,(HR)} = \frac{V_{\mathrm{b}}}{V_{\mathrm{f}}} \times 100 \tag{5}$$

Difference ranges for HR in defining the flowability is as below:

(i) $1.0 < \mathrm{HR} < 1.1$, free flowing powder;
(ii) $1.1 < \mathrm{HR} < 1.25$, medium flowing powder;
(iii) $1.25 < \mathrm{HR} < 1.4$, difficult flowing powder; and
(iv) $\mathrm{HR} > 1.4$, very difficult flowing powder.

A scanning electron microscope (Philips XL, FEI Co., Eindhoven, the Netherlands) was used for the morphological study of the encapsulated powders (optimum concentration) which operated at an accelerating voltage of 20 kV. After mounting the powder samples directly onto the aluminum sample stub, a thin (200 nm) coating of gold was applied under vacuum using SPI Sputter coating unit (SPI supplies, division of structure probe Inc., USA) to assess their microstructural morphology.

2.5. Statistical analysis

In this research, Response Surface Methodology and central composite design with three independent variables, including concentration of anthocyanin (%), concentration of wall material (%), and type of wall material (MD, MD + GA, and MD + GE, at three levels) were used to study the influence of different concentrations for the core materials and wall types on improvement of the responses (probability level of 0.05). The dependent variables (responses) were microencapsulation efficiency and physical properties of final powders. Design-Expert® 6.0.8 (StatEase, Inc., Minneapolis, MN) was used for regression analysis, optimisation procedure and to determine the best fitting models. All data are reported as mean ± standard deviation of three replicates. Duncan's multiple range tests and SPSS Statistics Software (Version 20.0, IBM SPSS Inc, Armonk, NY, USA) were applied to detect differences among mean values of responses.

3. Results and discussion

3.1. Encapsulation efficiency of anthocyanin powders

A successful encapsulation method relies on achieving high retention of the core materials and minimum amounts of the core

Table 4
Best fitted models of microencapsulation efficiency and physical characteristics for anthocyanin encapsulated powders with different wall materials (in terms of actual factors).

Factor	The best fitted models for samples encapsulated with			R^2	Prob > F
	MD	MD + GA	MD + GE		
ME	$-0.61(A) - 0.21(W) + 0.02(A)(W)$	$-0.64(A) - 0.17(W) + 0.02(A)(W)$	$-0.69(A) - 0.15(W) + 0.02(A)(W)$	70.62	<0.0001
MC	$-0.16(A) + 0.07(W) + 0.01(A)^2 - 0.001(W)^2$	$-0.16(A) + 0.08(W) + 0.01(A)^2 - 0.001(W)^2$	$-0.18(\mathrm{i}) + 0.08(W) + 0.01(A)^2 - 0.001(W)^2$	97.03	<0.0001
WSI	$-0.18(A) - 0.05(W) + 0.01(A)^2 - 0.005(A)(W)$	$-0.11(A) - 0.005(W) + 0.01(A)^2 - 0.005(A)(W)$	$-0.22(A) - 0.04(W) + 0.01(A)^2 - 0.005(A)(W)$	97.57	<0.0001
ρ_{bulk}	$-0.003(A) + 0.001(W) + 0.0001(A)^2$	$-0.003(A) + 0.001(W) + 0.0001(A)^2$	$-0.003(A) + 0.001(W) + 0.0001(A)^2$	97.93	<0.0001
ρ_{abs}	$+0.0001(A) + 0.002(W) - 0.0001(A)(W)$	$+0.001(A) + 0.002(W) - 0.0001(A)(W)$	$+0.001(A) + 0.002(W) - 0.0001(A)(W)$	86.52	<0.0001
ε	$+0.39(A) - 0.01(A)^2 - 0.005(A)(W)$	$+0.42(A) - 0.01(A)^2 - 0.005(A)(W)$	$+0.47(A) - 0.01(A)^2 - 0.005(A)(W)$	93.72	<0.0001
HYG	$+0.11(A) - 0.07(W) - 0.003(A)^2 + 0.001(W)^2$	$+0.10(A) - 0.07(W) - 003(A)^2 + 0.001(W)^2$	$+0.11(A) - 0.07(W) - 003(A)^2 + 0.001(W)^2$	98.78	<0.0001
DC	$+0.12(A) - 0.04(W) - 0.004(\mathrm{A})^2 + 0.001(W)^2$	$+0.11(A) - 0.004(W) - 004(A)^2 + 0.001(W)^2$	$+0.13(A) - 0.04(W) - 004(A)^2 + 0.001(W)^2$	96.25	<0.0001
L^*	$+0.05(A) - 0.01(W)$	$-0.003(A) + 0.004(W)$	$-0.30(A) + 0.13(W)$	98.34	<0.0001
a^*	$+0.28(A)$	$-0.21(A)$	$-0.20(A)$	99.04	<0.0001
b^*	$-0.04(A)$	$-0.03(A)$	$-0.06(A)$	99.66	<0.0001

$P < 0.05$.
A = anthocyanin level; W = wall level.

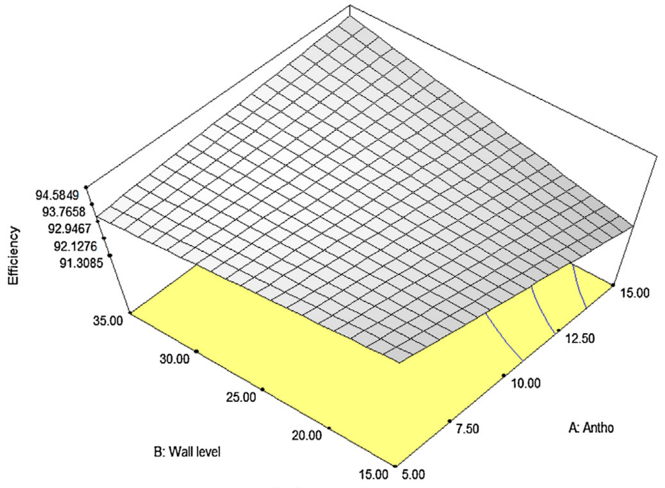
materials on the surface of powder particles. According to Jafari et al. [21], properties of the wall and core materials as well as the emulsion characteristics and drying parameters (especially conditions of the spray-drying such as inlet and outlet temperatures, feed flow rate, air flow and humidity, powder particle size, etc.) are the factors that can affect the efficiency of encapsulation. Table 2 shows the encapsulation efficiencies after the drying process. Our results indicated that microencapsulation efficiency was largely dependent on type of wall material as well as the core/wall ratio. The encapsulation efficiency varied from 89.06 to 96.21%. The results showed that core/wall ratio of 25% (1/4) increased the encapsulation efficiency of anthocyanins significantly ($P < 0.05$), whereas the ratios of 12 and 35% did not show a significant difference. Also, core/wall 50% (1/1) showed the lowest efficiency at a 5% level of significance. These results confirmed the findings of Shu et al. [37] who reported that core/wall = 1/4 was the optimal choice for effective lycopene encapsulation. According to these authors, the reason may be associated with the instability of prepared emulsions when core/wall increased or decreased from 1/4. In addition, Hogan et al. [17] also reported that the core/wall material ratio had a greater effect on the properties of powders such as microencapsulation efficiency.

As clear in Fig. 1a, increasing wall contents at any constant core rates resulted in escalating efficiency degrees for microencapsulation process of anthocyanin with MD + AG; conversely, increasing core rates at any stable wall concentration led to lower efficiency percentages of the process for the same wall and core materials. Interestingly, this pattern was also followed by other wall materials very closely (Fig. 1b,c). Regarding type of wall material, (MD + GA) gave the highest encapsulation efficiencies. This result was in agreement with the fact that a single encapsulating wall material does not possess all required characteristics, so mixtures of carbohydrates with proteins and polysaccharides lead to the highest efficiency [15]. Therefore, the utilization of MD + GA in the formulation had a higher potential to encapsulate the anthocyanins over maltodextrin alone. High efficiency of MD + GA as wall material, confirms the findings of the previous studies such as Burin et al. [5] on grape anthocyanin and Idham et al. [20] on Roselle anthocyanin encapsulation. The higher efficiency of the MD + GA may be related to its structure. Arabic gum is a highly branched heteropolymer of sugars, containing a small amount of protein covalently linked to the carbohydrate chain, acting as an excellent film-forming agent and thus better entrapping the encapsulated molecule. This makes the flavylium cation of anthocyanins less vulnerable to nucleophilic attack by water molecules, increasing the stability of the anthocyanins [5]. In addition, according to Shahidi and Naczk [35], phenolics and flavonols may form complexes with polysaccharides and the affinity of phenolics to polysaccharides depends on the water solubility, molecular size, conformational mobility and shape of polyphenol. Furthermore, the complexity formed when the flavylium cation of the anthocyanins interacted with dextrins prevented their transformation to other less stable forms. MD + GE compared to MD + GA showed more surface anthocyanins so, had a lower efficiency than MD + GA. Using maltodextrin alone as the wall material gave the lowest efficiency probably due to its lack of emulsification and low film-forming capacity.

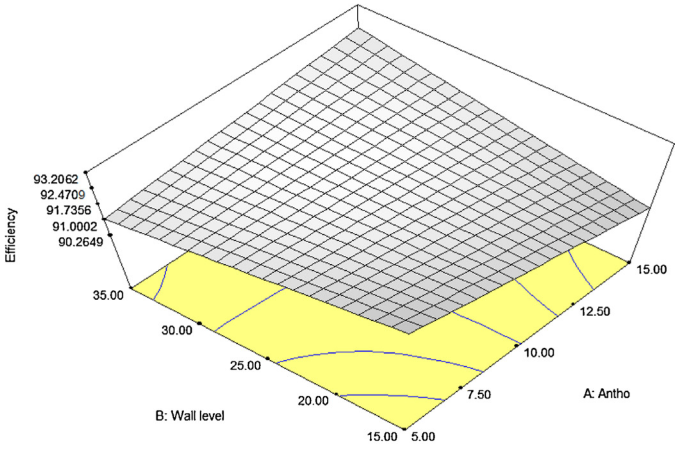
3.2. *Physical characteristics of encapsulated anthocyanins*

3.2.1. *Moisture content*

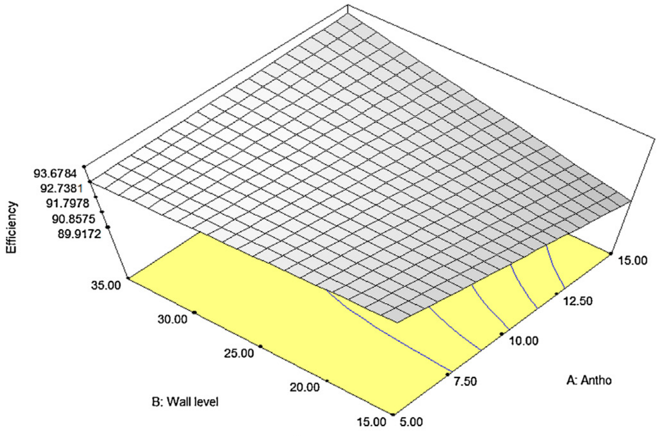
Table 3 shows the effect of different wall materials on the physical characteristics of barberry anthocyanin powders. Moisture content is an important powder property, which is related to the drying efficiency, powder flowability, stickiness, and storage stability due to its effect on glass transition and crystallization behavior. Furthermore, lower moisture content limits the ability of water to



(a) MD+GA



(b) MD



(c) MD+GE

Fig. 1. Microencapsulation efficiency of anthocyanins encapsulated with different wall materials including (a) MD + GA, (b) MD and (c) MD + GE as a function of anthocyanin (Antho) concentration (%) and wall levels (%) GA, gum Arabic; GE, gelatin; MD, maltodextrin.

act as a plasticizer and to reduce the glass transition temperature [27]. Our results revealed that the types of wall material affects the moisture content; the particles produced with maltodextrin and gum Arabic did not exhibit significant differences between each other in terms of moisture content, but the moisture of particles produced from maltodextrin and gelatin was significantly higher. This variation in moisture contents could be attributed to the chemical structure of gum Arabic and maltodextrin, which have a high number of ramifications with hydrophilic groups containing shorter chains and more hydrophilic groups, and thus can easily bind to water molecules from the ambient air during powder handling after drying and the ability of gelatin to form a sponge-like structure when submitted to mechanical agitation and subsequent drying may lead to higher moisture content. Abadio et al. [1] and Goula and Adamopoulos [16] observed a similar behavior, studying the spray drying of pineapple juice with maltodextrin and concentrated tomato pulp, respectively.

3.2.2. *Hygroscopicity*

The samples produced with MD + GA was the least hygroscopic, followed by the one produced with maltodextrin and MD + GE. This difference in water adsorption may be attributed to the molecular weight of the particles produced with each one of the agents. Since the glass transition temperature increases with increase in molecular weight [6], so maltodextrin (mean value of 1800 g/mol) and gum Arabic (47,000–3,000,000 g/mol), due to their high molecular weight, are less hygroscopic. On the other hand, according to Tonon et al. [39], hygroscopicity values were inversely increased with moisture content such that lower powder moisture content indicated higher hygroscopicity. According to these authors, powders containing a lower moisture content had a greater capacity to absorb ambient moisture, which is related to the higher water concentration gradient between the product and the surrounding air, consequently: the higher hygroscopicity of spray-dried powders were due to lower moisture content.

3.2.3. *Degree of caking and solubility*

There was no significant difference between degrees of caking for encapsulated powders. Generally, low moisture values are necessary to ensure the stability of atomized powders because they prevent caking, which begins with the agglomeration of wet particles and reduces the retention of the active principle, thereby hindering the powder flow and dispersion (Chen and Özkan, 2007).

Solubility is an important instant property (wettability, dispersability, solubility) for encapsulated powders because it may be subjected to rehydration when used as a food ingredient [38]. With respect to solubility, using different wall materials did not show significant difference. The spray dried powders could be reconstituted instantly with water at room temperature.

3.2.4. *Encapsulated powder density, porosity, and flowability*

According to Tonon et al. [39], bulk density of powders is related to molecular weight of wall materials. The heavier the material, more easily it accommodates into the spaces between the particles, occupying less space and resulting in higher bulk density values. Chegini & Ghobadian, (2005) reported that spray dried powders with higher moisture content tend to have a higher bulking weight, because of the presence of water, which is considerably denser than the dry solid. This behavior can be associated with the results observed in our study, because powders produced with MD + GE and MD showed higher moisture contents.

Absolute density corresponds to the real solid density and does not consider the spaces between the particles, in contrast to the bulk density, which takes into account all these spaces. With respect to absolute density, all the samples showed similar values, not significantly differing between each other. Porosity is also related to the bulk density, because this property measures the fraction of the total volume which is occupied by the air. The porosity of encapsulated powder was attributed to its bulk and apparent density (Eq. (3)) and ranged between 52.5 to 57.1%.

The Hausner values ranged from 1.299 to 1.304. A Hausner ratio greater than 1.25 is considered to be an indication of poor

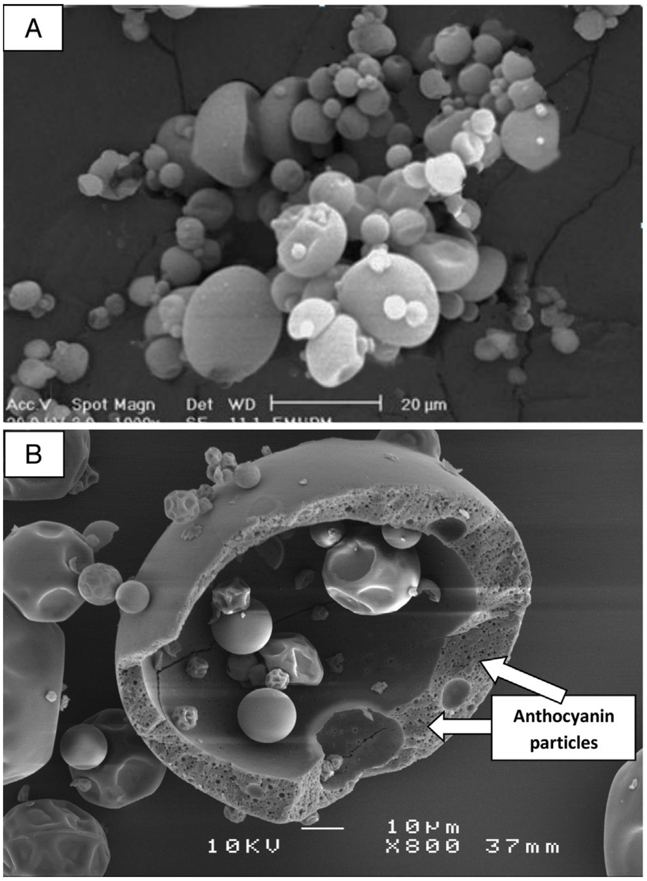


Fig. 2. (A) Scanning electron micrograph of spray-dried encapsulated powder containing anthocyanins by gum Arabic/maltodextrin; (B) cross section of particles showing encapsulated anthocyanins within peripheral region.

flowability (Hausner, 1967), so all the samples showed poor flowing properties.

3.2.5. Microstructural results

Fig. 2 presents SEM photographs of microcapsules for the gum Arabic/maltodextrin encapsulated powders containing anthocyanins. The microcapsules obtained from GA/MD were smooth but not uniform, showing minimum agglomeration and dents on the surface, more porous structure, larger size and were more well-distributed, confirming this blend to be the best encapsulating material. While microcapsules of GE/MD and MD were in broken form, had dents on the surface, showing the shrinkage and more agglomerated indicating the poor encapsulating properties of these wall materials for anthocyanins. No cracks or holes were observed on the surface of any of the samples.

Anthocyanins are hydrophilic colorants and specifically compatible with a water-based gel formulation such as pectin and gum, or maltodextrin and starches as coating molecules for polar solid matrices. After spray drying of their solution, individual spherical particles are formed (as can be seen in SEM results) containing core (pigment) materials within the internal peripheral region of microcapsuls, known as multiple core structure as shown in Fig. 2B. The central part is occupied by a void which is a result of expansion during spray drying.

3.3. Optimization procedure

Table 5
Optimization of microencapsulation efficiency and physical characteristics for anthocyanin pigments encapsulated with different wall materials.

Factor	Goal	Unit	Importance	Optimised values for different wall materials		
				MD + GA	MD + GE	MD
ANT	Maximize	%	3	13.82	9.38	10.16
WL	Minimize	%	3	24.54	21.15	15.00
ME	Maximize	%	3	92.83	92.33	91.69
MC	Minimize	%	1	2.80	4.07	3.19
WSI	Maximize	%	2	95.77	95.05	93.42
ρ_{bulk}	Minimize	g/cm^3	1	0.40	0.42	0.43
ρ_{abs}	Maximize	g/cm^3	1	0.91	0.92	0.93
ε	Minimize	%	1	56.30	54.17	53.33
HYG	Minimize	%	2	19.48	21.22	20.68
DC	Minimize	%	1	21.05	20.66	20.32
L^*	Maximize	–	2	73.27	69.81	66.18
a^*	Minimize	–	1	34.74	30.83	41.74
b^*	Minimize	–	1	-0.14	0.62	2.75
Overall desirability		%		55.10	45.80	35.80

Table 4 lists the best fitted RSM models for different response variables considering three wall materials used in this study. Different levels of core and wall materials and types of wall materials led to diverse optimization rates. Table 5 exhibits how different wall materials, considered for encapsulation purpose, could bring along different optimum desirability for final products. Regarding this Table, MD + GA outperformed MD + GE by nearly 17% improvement in maximum desirability, which surpassed MD with about 22% improvement in the same index; this difference becomes even more important when it comes to higher volumes of final product for bulk usage in industrial scales.

As for MD + GA, the highest desirability of just above 55% was attained at concentrations of 13.82% anthocyanin and 24.53% wall level. Indeed, this type of wall material resulted in better characteristics of powder (compared with other wall materials) in factors with higher importance rates (2 and 3). While higher efficiency, solubility and L^* rates were obtained for MD + GE than for MD, the latter wall type culminated in lower hygroscopicity and moisture contents than for the former.

4. Conclusion

Among the wall materials tested in this study, the combination of maltodextrin and gum Arabic with core/wall ratio of 25% led to the higher efficiency with respect to combination of maltodextrin and gelatin and maltodextrin alone; thus, provided better protection of the anthocyanin pigments. In spite of poor flowability of all samples, all wall materials showed approximately the same physical properties. More studies have to be done to evaluate controlled release from these microocapsules for their use in food applications.

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