Critical Review

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Anthocyanin content and storage stability of spray/freeze drying microencapsulated anthocyanins from berries: a review

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Abstract: A comprehensive literature search for articles published on spray and freeze-dried anthocyanins from a large variety of berries was performed. Out of a total of two-hundred and eight collected values, anthocyanin content in encapsulates had a 120-fold variation depending on the raw material and type of encapsulating agents. Highest observed anthocyanin concentration amounted to about 3500 mg/100 g powder. In most cases increasing the amount of encapsulant agents led to a noticeable reduction in the concentration of anthocyanins, this being attributable to a predominance of the dilution effect. Retention of encapsulated anthocyanins after storage at 25 °C (in darkness) for periods between 90 and 180 days were in the range of 80–67%, as long as the water activity (a_w) was 0.33 or less. Some predicted values of half-time ($t_{1/2}$) from literature must be taken with precaution since in many cases they were derived from experimental measurements taken at storage times smaller than predicted half times. Anthocyanin degradation during storage occurred even below the glass transition temperature (T_g) of the amorphous matrices.

Keywords: anthocyanins; berries; freeze-drying; microencapsulation; spray-drying; storage stability; water activity.

1 Introduction

Colorants for food applications obtained from natural sources are an attractive alternative to consumers [1, 2]. Anthocyanins form a group of pigments responsible for the red, purple, and blue colors and have potential as colorants. They are water-soluble pigments found in many fruits, flowers and leaves and the most abundant anthocyanins are pelargonidin, cyanidin, delphinidin, peonidin, petunidin and malvidin [3]. The interest in the use of natural colorants goes beyond their pigmentation capacity, since these compounds have bioactive properties that may be beneficial for consumers health [4].

It is well known that anthocyanins may undergo degradation during processing and storage; however, their stability may be increased through encapsulation. The encapsulated material is called core material, and the packaging material is called carrier, or encapsulating agent. Encapsulating agents act as protecting coat against factors such as light, humidity and oxygen, and, maltodextrin, Arabic gum, and modified starches are among most used carriers [5]. Several reviews about encapsulation techniques are available in the literature and the reader is referred to them [6–9]. Spray-drying is the most common technique used to encapsulate anthocyanins [9]. Freeze-drying is also an efficient method for anthocyanin encapsulation to produce a porous structure especially useful for temperature-sensitive bioactive products like anthocyanins [10].

One of the important conditions for an encapsulated anthocyanin to be used as a colorant is that it has a relatively high concentration in the powder resulting from spray/freeze-drying. For this, and other factors, it is necessary to minimize the addition of encapsulant to avoid a dilution effect. The amount of encapsulant is associated with the protection of anthocyanins and with maintaining desired flow properties of the powder product (absence of stickiness, caking or collapse) during dehydration and storage. For this reason, an elevated glass transition temperature (T_g) is also required for encapsulants [11].

Anthocyanins are found in various small fruits such as grapes, blueberry, blackberry, strawberry, blackcurrant, and many other berries. In the past two decades a large number of articles on microencapsulation of berries have

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been published. It is the purpose of present review to compile and analyze a huge number of articles with appropriate data on, a) content of total anthocyanins in the dry powders, and b) the storage stability of anthocyanins at 25 °C. The stability of the anthocyanins refers to the observed retention at the end of the storage period and effect of type of encapsulating agents and water activity on length of storage stability is also discussed.

2 Anthocyanin content in powders

2.1 Data collection from the literature

A huge amount of literature data on anthocyanin encapsulation was initially reviewed, but only those papers that showed data on anthocyanin concentration and encapsulant/core ratio, were chosen. Table 1 summarizes literature data compiled on microencapsulation – via spray-drying or freeze-drying – of a wide variety of berries which were obtained from 50 eligible articles with appropriate data. The level of addition of encapsulant/s, and anthocyanin content in the final dry powder (mg anthocyanin/100 g powder) were collected. In the vast majority of cases the anthocyanin concentration is expressed as Cy3-glu equivalent, as usually done in berry fruits [12].

The concentration of anthocyanins in the encapsulates (obtained via spray drying or freeze-drying) depends on various factors; a) the anthocyanin concentration in the raw material, b) the efficiency (i.e., anthocyanin retention) of the encapsulation process and, c) the amount of encapsulant added. Type and amount of encapsulating agent serves to protect anthocyanins and also increase the glass transition temperature (T_g) of encapsulated powder by preventing stickiness, caking and collapse, either during drying or storage [11]. However, the amount of encapsulant also leads to dilution of final anthocyanin concentration.

Two hundred and eight anthocyanin concentration values were obtained from Table 1 corresponding to different raw materials encapsulated under different conditions. It is not easy to say what anthocyanin concentration would be needed to be useful as a natural colorant, but it is reasonable to assume that low values will not be useful from a practical point of view. The compiled literature values of anthocyanin content ranged from about 30 to 3600 mg/100 g powder, depending on raw material, encapsulation method and type and amount of encapsulating agent/s. This range represents a 120-fold variation in anthocyanin content of encapsulated powders.

Figure 1 shows a Pareto chart for anthocyanin concentration in the encapsulates; this chart contains both bars and a line graph, where individual values are represented in descending order by bars, and the cumulative total is represented by the line. Although arbitrarily, anthocyanin concentration values can be ordered in ranges, e.g., low: up to 600 mg/100 g powder; intermediate: 600 to 1500 mg/100 g powder and high: more than 1500 mg/100 g powder. It can be seen (Figure 1) that anthocyanin values up to 600 mg/100 g powder represent 65% of literature values collected.

Several authors have reported anthocyanin concentration data according to whether they have used spray or freeze drying while all other variables (raw material, amount and nature of encapsulants) were kept identical. It is interesting to compare the values obtained by one or the other of these encapsulation methods. Michalska et al. [13] reported anthocyanin content after encapsulation of blackcurrant juice (12.4 °Brix) using maltodextrin, inulin and their mixtures as encapsulants. The mean value of anthocyanin concentration in nine samples encapsulated by freeze-drying was only 20% higher than those corresponding to spray drying. Murali et al. [14] also reported anthocyanin content in black carrot juice (6 °Bx) encapsulated by freeze-drying and spray-drying using identical encapsulants (maltodextrin, Arabic gum and tapioca starch) in the same proportions. The average of anthocyanins values in three samples encapsulated via freeze-drying was 16.6% higher that corresponding to identical samples dried by spray. These results suggest that in some cases spray drying allows obtaining anthocyanin concentrations that are not much lower than those obtained in freeze-drying.

As shown in Table 1, the maximum total anthocyanin concentration values were about 3500 mg/100 g powder and corresponded to Aronia berry extract (ultrasound assisted) spray-dried with maltodextrin [15] and to açai juice spray-dried with maltodextrin [16].

2.2 Effect of addition of encapsulant agents

The glass transition temperature is mainly a function of water content, molecular weight and nature of the dry matter compounds. Berries are rich in low molecular weight sugars (fructose and glucose) and organic acids (citric, malic and tartaric acids). As noted by Das and Jaya [17], these compounds have low glass transition temperatures. Khalloufi et al. [18] reported T_g values for various berries at “zero” (freeze-dried powdered berries

Table 1: Compilation of literature data on anthocyanin concentration after microencapsulation – via spray drying or freeze-drying – for a wide variety of berries and other anthocyanin-rich materials. Q13 Q14

Encapsulation method	Raw material	Encapsulant	% Encapsulating agent (or ratio extract)	Total anthocyanins (mg Cy3-glu/100 g powder)	Reference
Freeze-drying	**Blueberry by-product extract**	MD DE10	30% in 8% concentrate	297.9	Yamashita et al. [46]
		MD DE20	30% in 8% concentrate	265.7	
Spray drying	**Blackcurrant juice, 12.4 °Bx**	Maltodextrin DE20-40	30%	172.6	Michalska et al. [13]
		Maltodextrin DE20-40	35%	139.1	
		Maltodextrin DE20-40	40%	99.0	
		MD DE20-40:Inulin (3:1)	30%	198.1	
		MD DE20-40:Inulin (3:1)	35%	165.8	
		MD DE20-40:Inulin (3:1)	40%	137.0	
		Inulin	30%	190.1	
		Inulin	35%	167.4	
		Inulin	40%	190.1	
Freeze-drying	**Blackcurrant juice, 12.4 °Bx**	Maltodextrin DE20-40	30%	211.0	Michalska et al. [13]
		Maltodextrin DE20-40	35%	180.6	
		Maltodextrin DE20-40	40%	211.0	
		MD DE20-40:Inulin (3:1)	30%	224.7	
		MD DE20-40:Inulin (3:1)	35%	182.8	
		MD DE20-40:Inulin (3:1)	40%	152.3	
		Inulin	30%	233.3	
		Inulin	35%	198.3	
		Inulin	40%	155.6	
Freeze-drying	**Elderberry pulp, 10.7 °Bx**	MD DE10	4%	1059	Baeza et al. [38]
		Capsul™	4%	1200	
		Promitur™	4%	1251	
		k-Carrageenan	2%	1363	
Freeze-drying	**Sour cherry pomace extract**	Soy protein isolate	33%	92	Saponjac et al. [47]
Freeze-drying	**Cherry juice, 18.7% °Bx**	MD10 + A. gum (80:20)	20%	67.5	Sanchez et al. [48]
Freeze-drying	**Maqui berry extract**	MD DE15	10%	1185.7	Romero-González et al. [49]
		MD DE15	20%	662.4	
		MD DE15	30%	419.4	
		Inulin	10%	1021.4	
		Inulin	20%	835.4	
		Inulin	30%	446.2	
		Arabic gum	10%	481.3	
		Arabic gum	20%	309.3	
		Arabic gum	30%	466.0	
		MD DE15 + Inulin (1:1)	10%	1118.1	
		MD DE15 + Inulin (1:1)	20%	773.5	
		MD DE15 + Inulin (1:1)	30%	237.7	
		MD DE15 + A. Gum (1:1)	10%	530.8	
		MD DE15 + A. Gum (1:1)	20%	312.6	
		MD DE15 + A. Gum (1:1)	30%	367.4	
		MD DE15 + A. Gum + Inulin (1:1:1)	10%	476.4	
		MD DE15 + A. Gum + Inulin (1:1:1)	20%	341.3	
		MD DE15 + A. Gum + Inulin (1:1:1)	30%	565.1	
Freeze-drying		MD:Soy protein isolate (2:1)	2.6–10.4%	330	Fredes et al. [50]

Table 1: (continued)

Encapsulation method	Raw material	Encapsulant	% Encapsulating agent (or ratio extract)	Total anthocyanins (mg Cy3-glu/100 g powder)	Reference
Spray drying	**Maqui juice, concentrated, 65 °Bx**	MD:Soy protein isolate (2:1)	2.6–10.4	330	
Freeze-drying	**Blueberry pulp, 9 °Bx**	MD DE10:A. Gum (80:20)	20%	74.3	Busso Casati et al. [51]
	Elderberry pulp, 11.8 °Bx	MD DE10:A. Gum (80:20)	20%	171.8	
	Maqui berry pulp, 14.8 °Bx	MD DE10:A. Gum (80:20)	20%	421.8	
	Blackcurrant pulp, 13.0 °Bx	MD DE10:A. Gum (80:20)	20%	254.6	
Freeze-drying	**Jauboticaba by-product extract**	MD10	NR	273	Rodríguez et al. [52]
		MD10:Guar Guam (0.95:0.05)	NR	265	
Spray drying	**Chokeberry extract, 15 °Bx**	MD DE18-20 + Arabic gum	1.2 g carrier/1 g chokeberry extract	1940.2	Pieczykolan and Kurek [53]
		MD DE18-20 + Inulin	1.2 g carrier/1 g chokeberry extract	2730.8	
		MD DE18-20 + B-Glucan	1.2 g carrier/1 g chokeberry extract	3055.6	
		MD DE18-20 + Pectin	1.2 g carrier/1 g chokeberry extract	2853.8	
		MD18-20 + Guar Gum	1.2 g carrier/1 g chokeberry extract	2319.8	
Spray drying	**Blackcurrant extract from waste**	Maltodextrin DE12	40%	63.0	Archaina et al. [54]
Spray drying (120/80 °C)	**Aronia berry extract (ultrasound-assisted)**	Maltodextrin 5.9	20%	3200	Vidović et al. [15]
		Maltodextrin 5.9	40%	2977	
		Maltodextrin 5.9	60%	2764	
		Maltodextrin 13.1	20%	3313	
		Maltodextrin 13.1	40%	2828	
		Maltodextrin 13.1	60%	2785	
		Maltodextrin 19.7	20%	3511	
		Maltodextrin 19.7	40%	3119	
		Maltodextrin 19.7	60%	2747	
Spray drying	**Black carrots extract, 6 °Bx**	Maltodextrin DE 28-31	to 20%	480	Ersus and Yurgadel [44]
		Maltodextrin DE 20-23	to 20%	630	
		Maltodextrin DE 10	to 20%	500	
Spray drying	**Elderberry, ss. 2.9%**	MD DE12	20%	125	Gagneten et al. [55]
	Blackcurrant, ss. 3.1%	MD DE12	20%	100	
	Raspberry, ss. 2.23%	MD DE12	20%	50	
Spray drying	**Acai juice**	MD DE 10	6%	3436.9^{b}	Tonon et al. [16]
		MD DE 20	6%	3402.3^{b}	
		Arabic gum	6%	3416^{b}	
		Tapioca starch	6%	3247.2^{b}	
Spray drying	**Blackberry pulp, 6.43% sugars**	Maltodextrin	7%	666.0	Ferrari et al. [42]
		Arabic gum	7%	545.1	
		Maltodextrin:A. Gum (1:1)	7%	637.3	

Table 1: (continued)

Encapsulation method	Raw material	Encapsulant	% Encapsulating agent (or ratio extract)	Total anthocyanins (mg Cy3-glu/100 g powder)	Reference
Spray drying	**Chokeberry juice, 12 °Bx**	Maltodextrin DE10	Juice (db):Carrier (2:3)	2002	Bednarska and Janiszewska-Turak [56]
		Maltodextrin DE15	Idem	1830	
		A.Gum:MD10 (1:3)	Idem	2028	
		A.Gum:MD10 (1:1)	Idem	1878	
		A.Gum:MD10 (3:1)	Idem	1889	
		A.Gum:MD15 (1:3)	Idem	1927	
		A.Gum:MD15 (1:1)	Idem	1844	
		A. Gum:MD15 (3:1)	1dem	1488	
		Arabic gum	Idem	1936	
Spray drying	**Blackberries residues extract, 8.6 °Bx**	Polyvinylpyrrolidone	PVP:Dry extract mass ratio of 5:2	136	Da Fonseca Machado et al. [57]
Spray drying	**Jucara fruit pulp**	MD DE18:Arabic gum (1:1)	Pulp:Carrier (2:3)	151.7	Mazuco et al. [58]
Freeze-drying		MD DE18:Arabic gum (1:1)	Pulp:Carrier (2:1)	116.9	
		MD DE18:Arabic gum (1:1)	Pulp:Carrier (2:3)	150.8	
Spray drying	**Blackberry extract**	Arabic gum	10%	1280	Rigon and Zapata Noreña [59]
		Arabic gum	15%	1260	
		Polydextrose	10%	922	
		Polydextrose	15%	905	
Spray drying	**Blackcurrant extract, 12 °Bx**	Maltodextrin 11	to 35 °Bx	452.8	Bakowska-Barczaka and Kolodziejczy [60]
		Maltodextrin 18	to 35 °Bx	451.3	
		Maltodextrin 21	to 35 °Bx	430.4	
		Inulin	to 35 °Bx	398.9	
Spray drying	**Bayberry juice, 11 °Bx**	Maltodextrin DE10	1:1 (juice:MD at 11 °Bx)	56.4	Fang and Bhandari [29]
Spray drying	**Mao fruit juice**	Maltodextrin DE10-12	25%	334	Suravanichnirachorn et al. [61]
		Maltodextrin DE10-12	30%	271	
		Maltodextrin DE10-12	35%	263	
		Arabic gum	25%	347	
		Arabic gum	30%	286	
		Arabic gum	35%	234	
Spray drying	**Blueberry juice**	MD18/Whey Prot. Isolate = 0.4	10%	434	Darniadi et al. [62]
		MD18/Whey Prot. Isolate = 1.0	10%	484	
		MD18/Whey Prot. Isolate = 1.6	10%	513	
		MD18/Whey Prot. Isolate = 2.3	10%	529	
		MD18/Whey Prot. Isolate = 3.2	10%	538	
Foam-mat freeze-drying	**Blueberry juice**	MD18/Whey Prot. Isolate = 0.4	5%	711	Darniadi et al. [62]
		MD18/Whey Prot. Isolate = 1.0	5%	726	
		MD18/Whey Prot. Isolate = 1.6	5%	728	

Table 1: (continued)

Encapsulation method	Raw material	Encapsulant	% Encapsulating agent (or ratio extract)	Total anthocyanins (mg Cy3-glu/100 g powder)	Reference
		MD18/Whey Prot. Isolate = 2.3	5%	785	
		MD18/Whey Prot. Isolate = 3.2	5%	809	
Spray drying	**Corozo fruit extracts (a) & (b)**	Maltodextrin 18	Extract (a)/MD = 1:1	118	Osorio et al. [63]
		Maltodextrin 18	Extract (b)/MD = 1:1	131	
Spray drying	**Maqui juice + extract**	MD19:A. Gum (1:1)	10%	1938	Bastías-Montes et al. [64]
Spray drying	**Andes berry 9 °Bx**	MD20	Aq. extract:Carrier (1:1)	54.5	Villacrez et al. [65]
		Corn starch	Aq. extract:Carrier (1:1)	30.2	
		Yucca starch	Aq. extract:Carrier (1:1)	38.7	
		Capsul® TA	Aq. extract:Carrier (1:1)	46.0	
		Hi-CapTM 100	Aq. extract:Carrier (1:1)	59.4	
		MD DE 20/Yucca starch (1:1)	Aq. extract:Carrier (1:1)	58.1	
Spray drying	**Blueberry conc. extract, 35% ss**	Mesquite gum 17%	M. Gum 17%:Extract 35% (67:33)	1495	Jimenez-Aguilar et al. [28]
Spray drying	**Bayberry syrup (crushed)**	Maltodextrin DE10 (13%)	MD:Syrup (1:1)	80	Cheng et al. [66]
Freeze-drying		**Maltodextrin DE10 (13%)**	**MD:Syrup (1.1)**	121	
Spray drying	**Black carrot extract**	Starch, Soy protein, emulsifier	NR	3000	Mishra et al. [33]
		Starch, Soy protein, emulsifier	NR	2750	
Spray drying	**Cranberry juice, 15% ss**	MD DE11	15%	79.5	Zhang et al. [67]
		MD DE18	15%	74.9	
		Arabic gum	15%	86.4	
		A. Gum:MD DE11 (1:1)	15%	102.8	
Spray drying	**Chokeberry pulp juice**	HP-B-cyclodextrin	15%	307	Wilkowska et al. [25]
		Maltodextrin DE14-17	15%	427	
		A. Gum:MD DE14-17 (1:1)	15%	366	
Spray drying	**Pomegranate juice, 16 °Bx**	MD DE16	20.1%	74[a]	Robert et al. [68]
		Soy protein isolate	7.5%	69[a]	
Spray drying	**Red raspberry puree**	Arabic gum	10%	485[c]	Syamaladevi et al. [69]
Spray drying	**Barberry juice, 14 °Bx**	MD12	15%	360	Sharifi et al. [70]
		MD DE12:A. Gum (1:1)	15%	380	
		MD DE12:A. Gum (3:1)	15%	360	
		Arabic gum	15%	350	
		MD DE12:A. Gum (1:3)	15%	355	
Freeze-drying	**Blackberry pulp, 9 °Bx**	Starch:Arabic gum (1:1)	1:1.78 (pulp solids/ encap.	126	Nogueira et al. [71]
Spray drying		Starch:Arabic gum (1:1)	Idem	86.4	
Freeze-drying	**Blackberry juice, 5.4%**	MD DE12	Juice:Matrix 80:20	162	Franceschinis et al. [72]
		MD DE12:Trehalose (1:1)	Juice:Matrix 80:20	112	
Spray drying	**Blackberry juice, 5.4%**	MD DE12	Juice:Matrix 60:40	70	
		MD DE12:Trehalose (1:1)	Juice:Matrix 60:40	61	

Table 1: (continued)

Encapsulation method	Raw material	Encapsulant	% Encapsulating agent (or ratio extract)	Total anthocyanins (mg Cy3-glu/100 g powder)	Reference
Spray drying	**Barberry juice, 16 °Bx**	MD DE6	4%	1110	Emam-Djomeh et al. [73]
		MD DE6	6%	1060	
		MD DE6	8%	1070	
Spray drying	**Mulberry juice**	MD:A. Gum:MCC (21:9:0)	30%	468	Do and Nguyen [74]
		MD:A. Gum:MCC (21:8.5:0.5)	30%	341	
		MD:A. Gum:MCC (21:8:1)	30%	356	
		MD:A. Gum:MCC (21:7.5:1.5)	30%	330	
		MD:A. Gum:MCC (21:7:2)	30%	319	
Spray drying	**Red grape marc extract, s.s. 2.97%**	Maltodextrin DE18	Encapsulant:Extract 1:1	210	Moreno et al. [75]
		Maltodextrin DE18	Encapsulant:Extract 0.8:1	280	
		Maltodextrin DE18	Encapsulant:Extract 0.5:1	340	
		Maltodextrin DE18	Encapsulant:Extract 0.25:1	350	
		Maltodextrin DE18	Encapsulant:Extract 0.1:1	400	
		Whey protein isolate	Encapsulant:Extract 1:1	120	
		Whey protein isolate	Encapsulant:Extract 0.5:1	260	
		Whey protein isolate	Encapsulant:Extract 0.25:1	350	
		Whey protein isolate	Encapsulant:Extract 0.1:1	410	
		Pea protein isolate	Encapsulant:Extract 1:1	250	
		Pea protein isolate	Encapsulant:Extract 0.5:1	270	
		Pea protein isolate	Encapsulant:Extract 0.25:1	420	
		Pea protein isolate	Encapsulant:Extract 0.1:1	480	
Spray drying	**Black carrots juice, 6 °Bx**	Maltodextrin DE20	to obtain 20 °Bx in mixture	1461.2	Murali et al. [14]
		Tapioca starch	to obtain 20 °Bx in mixture	1085.8	
		Arabic gum	to obtain 20 °Bx in mixture	1381.5	
Freeze-drying		Maltodextrin DE20	to obtain 20 °Bx in mixture	1650	
		Tapioca starch	to obtain 20 °Bx in mixture	1353.5	
		Arabic gum	to obtain 20 °Bx in mixture	1577.3	
Spray drying	**Blackcurrant extract 12 °Brix**	MD10	to obtain 35 °Bx in mixture	452.8	Bakowska-Barczaka and Kolodziejczyk [60]
		MD18	to obtain 35 °Bx in mixture	451.3	
		MD21	to obtain 35 °Bx in mixture	430.4	
		Inulin	to obtain 35 °Bx in mixture	398.9	

Table 1: (continued)

Encapsulation method	Raw material	Encapsulant	% Encapsulating agent (or ratio extract)	Total anthocyanins (mg Cy3-glu/100 g powder)	Reference
Spray drying	***Garcinia indica* Choisy fruit extract, hhh6 °Bx**	Maltodextrin DE6	5%	325.3	Nayak and Rastogi [7]
		Maltodextrin DE19	5%	365	
		Maltodextrin DE21	5%	430.3	
		Maltodextrin DE33	5%	399.0	
Spray drying	**Bordo grape skin extract**	Gum Arabic:Polydextrose (1:1)	10%	1718[a]	Kuck and Noreña [76]
		Arabic gum	10%	1841[a]	
		Partially hydrolyzed gum guar (PHGG)	10%	2084[a]	
		PHGG:Polydextrose	10%	2105[a]	
Freeze-drying		Gum Arabic:Polydextrose (1:1)	10%	1838[a]	
		Arabic gum	10%	1727[a]	
		PHGG	10%	1825[a]	
		PHGG:Arabic gum (1:1)	10%	1707[a]	
Spray drying	**Maqui berry extract, 10.1 °Bx**	SiO_2	Soluble solids:SiO_2 (1:0.5)	1514 (average)	Garrido Makinistian et al. [77]
Spray drying	**Blackberry extract, 13.4 °Bx**	Maltodextrin DE10	22.5 g Encap:7.5 g solids juice	87.2	Diaz et al. [78]
		Arabic gum	Idem	106.9	
		Whey protein concentrate	Idem	34.1	
Spray drying	**Pomegranate juice, 16.5 °Bx**	Modified starch Capsul™	16.50%	75.8	De Araujo Santiago et al. [79]
		Maltodextrin DE6	16.5%	56.4	
		Gum Arabic	16.5%	94.8	
		Capsul + Maltodextrin	16.5%	70.4	
		Arabic gum + Capsul	16.5%	111.5	
		Arabic gum + maltodextrin	16.5%	84.5	
Spray drying	**Grape juice, 14 °Bx**	Soy protein-maltodextrin	1.25 g encap./g sol. Solids	717[d]	Moser et al. [80]
		Soy protein-Maltodextrin	1.0 g encap/g soluble solids	677	
		Whey protein-Maltodextrin	0.75 g encaps./g sol. Solids	815	
		Whey protein maltodextrin	0.85 g encap./g sol. Solids	776	
Spray drying	**Blueberry waste extracts**	Sodium alginate	2%	1954	Waterhouse et al. [26]
		Inulin	2%	1821	

[a]Total anthocyanins expressed as mg malvidin-3-glucoside.[b]Total anthocyanins expressed as mg cyanidin-3-rutinoside/100 g powder.[c]Total anthocyanins expressed as mg cy-3-soph-5-glu/100 g powder.[d]Total anthocyanins expressed as mg malvidin-3,5-diglucoside/100 g powder.

dehydrated to almost “zero” moisture by keeping them in desiccators under vacuum and over desiccant at least for a week) or very low moisture values (3–4%). Reported T_g values were relatively low since for all berries having a moisture content of 0% the they ranged between 26 and 45 °C, while for berries having around 3% moisture T_g values did not exceed 20 °C. Similar low values were also reported by Staniszewska et al. [19], Syamaladevi et al. [20] and Moraga et al. [21] for low moisture cranberry, raspberry and strawberry. This justifies the need of addition of high T_g encapsulants (i.e., maltodextrins, Arabic gum and the like). Saavedra-Leos et al. [22] determined

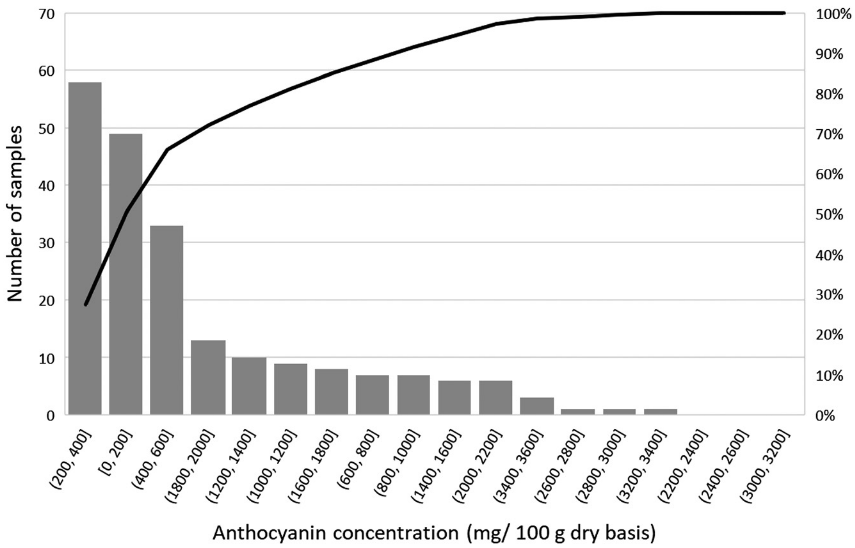

Figure 1: Pareto chart for frequency of anthocyanin concentrations in powders.

the glass transition temperature of a large number of ternary and binary mixtures of glucose, fructose and sucrose having different mass fractions mixtures resembling berries and obtained T_g values relatively close to those showed here.

Twenty eligible articles (from Table 1) had appropriate data to calculate the relation *r* defined as: g encapsulate/g of soluble solids in the juice (or extract). The values of *r* varied widely ranging from <1 to 22; the majority (69%) of them were in the range <1 to 4 and 17% in the range 8 to 22. It is well known in literature [23] that compatible blends of amorphous solids show a single T_g that is intermediate to the T_g values of the solids and is related to the mixture composition. When the additive raises the T_g it is to have an anti-plasticizing effect, and this the case when a biopolymer (i.e., maltodextrin) is used for encapsulation of a berry product. The relationship of T_{gmix} to the mixture composition is known as Gordon and Taylor equation (Eq. (1)),

$$T_{gmix} = \left[\frac{w_1 T_{g1} + K w_2 T_{g2}}{w_1 + K w_2}\right] \tag{1}$$

where w_1 and w_2 are mass fractions, T_{g1} and T_{g2} are individual T_g of components, and K is a constant. In some cases, Eq. (1) can be written as the Fox equation [24],

$$1/T_{gmix} = (w_1/T_{g1}) + (w_2/T_{g2}) \tag{2}$$

which is a very crude approximation to predict T_{gmix} only knowing the weight fraction and T_g of each component. Nevertheless Eq. (2) is useful to illustrate that increasing the mass fraction of encapsulant will increase the T_g of material to be encapsulated.

In terms of mass fraction, the mass fraction of encapsulating agents (i.e., g encapsulate/g soluble solids) can be calculated from the *r* values shown above, the most common values of encapsulant mass fraction ranged from 0.29 to 0.80, but some values were as high as 0.90 or 0.956.

It is to note that a high mass fraction of encapsulant would not be compatible with the use as a potential natural colorant.

Figures 2 and 3 were constructed using data from Table 1 and show the effect of the amount of encapsulating agent (maltodextrin, Arabic gum or inulin) on anthocyanin content after encapsulation (spray drying or freeze drying) of different raw materials, namely, Aronia berry extract, maqui berry extract, mao fruit juice, red grape marc extract and blackcurrant juice. As observed, increasing encapsulant addition decreases anthocyanin concentration in the encapsulated material. Freeze-dried maqui berry (Figure 2a), shows the largest relative decrease in total anthocyanin content with increasing encapsulant addition. This can be attributed to the fact that freeze-drying "per se" is a beneficial process for temperature-sensitive products, so that the increase in addition of solutes favors dilution rather than protection during lyophilization. Thus, the least amount of encapsulant compatible with the desired anthocyanin protection and flow properties (absence of stickiness, caking or collapse) should be used to maximize anthocyanin concentration in the encapsulating powder.

3 Storage stability of microencapsulated anthocyanins

3.1 Compilation of literature data on storage stability

Table 2 summarizes literature data compiled on measured storage stability at 25 °C of encapsulated anthocyanins. The

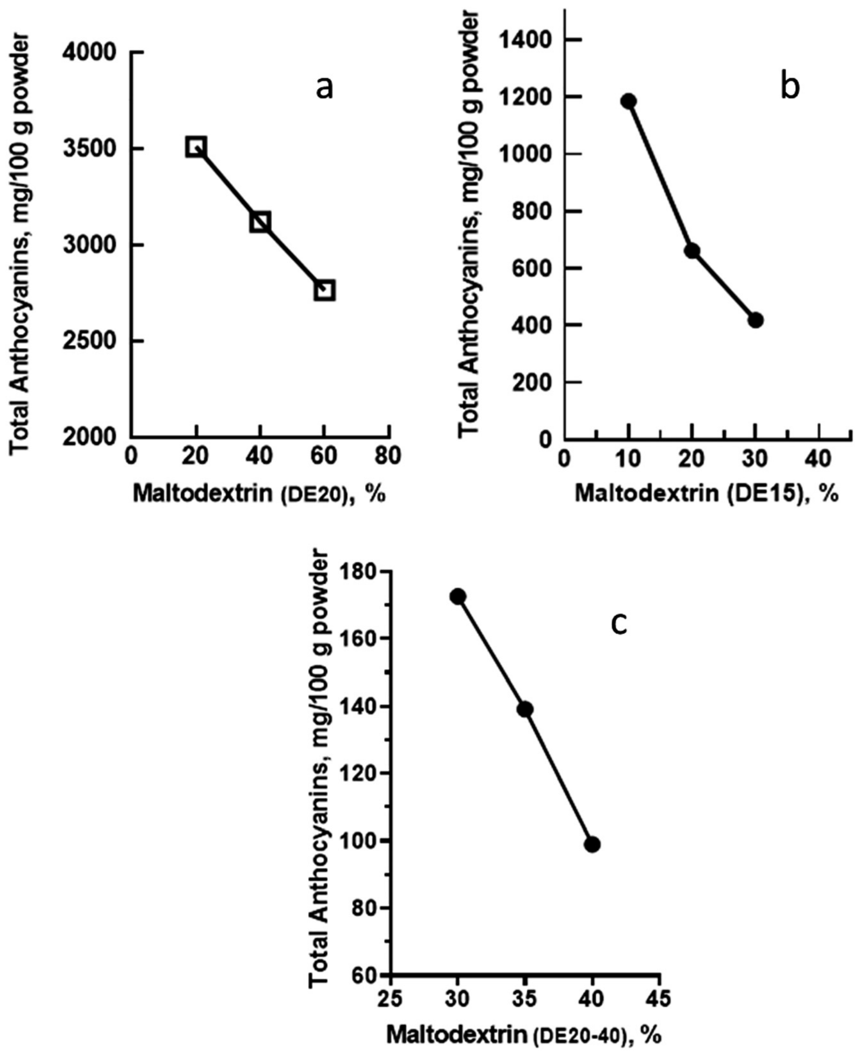

Figure 2: Effect of encapsulant addition on anthocyanin content of powders.
a. Aronia berry extract spray-drying encapsulated in maltodextrin (from data of Vidovic et al. [15]) – The standard deviation bars were 0.3–2% of the data shown in the figure. **b.** Maqui berry extract freeze-drying encapsulated in maltodextrin (from data of Romero-González et al. [49]) – The error bars were 0.4–4.4% of the data shown in the figure. **c.** Blackcurrant juice spray-drying encapsulated in maltodextrin (from data of Michalska et al. [13]) – The error bars were 1.6–4.2% of the data shown in the figure.

sources of anthocyanins comprised a large variety of berries which were obtained from eligible articles from literature reporting appropriate storage stability data. The anthocyanin stability is indicated by the calculated retention $C_t/C_0 \times 100$, where C_0 is the initial anthocyanin concentration and C_t is the concentration at the end of studied storage period. Type of encapsulating agents, storage temperature and water activity (a_w) or moisture content, are also indicated. Only works which stored the samples at least for 90 days were chosen for this survey.

Several observations can be made about the data shown in Table 2. Storage times studied vary widely from author to author, ranging from 90 to 360 days. Tonon et al. [16] reported that after 120 days at 25 °C and a_w = 0.328, the retention of acai anthocyanin encapsulated in maltodextrin DE10, maltodextrin DE20 or Arabic gum was very similar, namely 87, 80 and 83.5%, respectively. Wilkowska et al. [25] reported the storage stability of chokeberry anthocyanin encapsulated in maltodextrin, maltodextrin + Arabic gum or HP-β-cyclodextrin at 25 °C during 360 days at 3% moisture content. Observed retentions of anthocyanin were more or less similar, namely 72.6, 70.6 and 78.8%, respectively.

Nayak and Rastogi [7] encapsulated *Garcinia indica* Choisy in five different encapsulants with moisture content from 4.4 to 5.8% at 25 °C. Encapsulants were, Maltodextrin DE6, DE19, DE21, DE33 and maltodextrin DE21 + gum acacia. After 98 days they observed anthocyanin retentions of 70, 72.4, 72.9, 72.7 and 80%, respectively indicating that

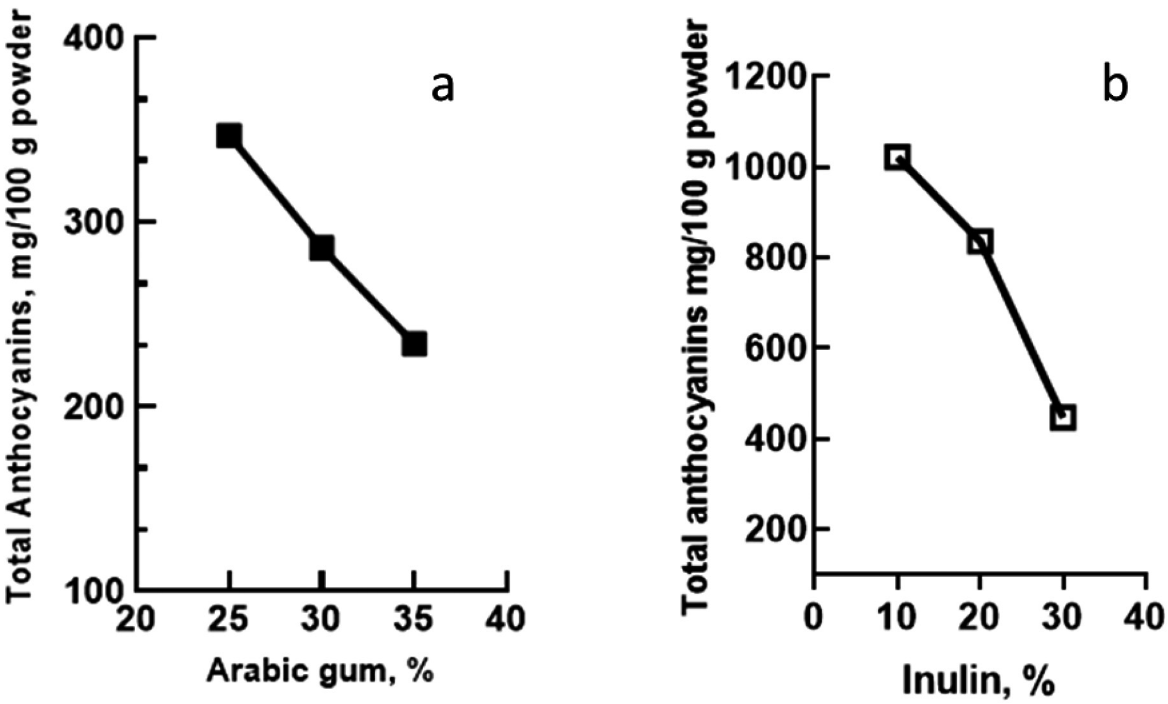

Figure 3: Effect of encapsulant addition on anthocyanin content of powders.
a. Mao fruit juice spray-drying encapsulated in Arabic gum (from data of Suravanichnirachorn et al. [61]) – The standard deviation bars were 7.0–9.0% of the data shown in the figure.
b. Maqui berry extract freeze-dried encapsulated in inulin (from data of Romero-González et al. [49]) – The error bars were 1.0–4.5% of the data shown in the figure.

the type of encapsulant did not influence the stability too much. The sample of maltodextrin DE21 + gum acacia which had the highest retention (80%) also had the lowest moisture content (4.4%) and this may have contributed to a somewhat higher retention than the other samples having higher moisture contents (5.0 and 5.8%). Waterhouse et al. [26] stored blueberry waste extract encapsulated with sodium alginate or inulin at 20 °C and a_w = 0.25–0.31 for 90 days and calculated anthocyanin retentions were 94.5 and 89%, respectively. Pavón-García et al. [27] measured anthocyanin content during storage at 20 and 30 °C of muitle (*Justicia spicigera*) encapsulated in mixtures of mesquite gum, maltodextrin DE10 and Arabic gum having a_w between 0.555 and 0.592. Little difference was observed in anthocyanin content after 120 days of storage and the calculated retention values were between 84.7 and 89.2% again suggesting that the type of encapsulant also played a minor role in observed storage stability. Jimenez-Aguilar et al. [28] reported that encapsulated (mesquite gum) blueberry extract stored at 4 and 25 °C had a higher stability at the lower temperature. Fang and Bhandari [29] studied the storage stability at 5 and 25 °C of encapsulated (maltodextrin DE10) of various water activities. After 3 months storage at a_w = 0.33 calculated anthocyanin retention at 5 °C was 90%, while at 25 °C it was 86%. After 6 months at 5 °C, retention was 86% while at 25 °C it was 81.7%. Mahdavi et al. [30] reported that encapsulated barberry extract using spray-drying and three different carriers: a combination of Arabic gum + maltodextrin, maltodextrin + gelatin and maltodextrin. The spray-dried encapsulated samples were stored at several temperatures for 90 days and they reported that the half-life (time for 50% retention) was significantly different between 4 and 25 °C. Q6

3.2 Effect of exposure to light

It is known that native anthocyanins had poor stability to light and when exposed to natural light the retention of anthocyanins decrease rapidly [31]. Even with encapsulated anthocyanins, exposure to light during storage must be avoided since several authors reported that encapsulated anthocyanins stored in darkness (or amber-colored vials) were more stable than exposed to light. Wilkowska et al. [25] reported that black chokeberry encapsulated in maltodextrin and other encapsulants, were more stable stored in darkness than exposed to light. Patel et al. [32] encapsulated black carrots juice with starch, soy protein, whey protein and emulsifier, and found that samples were more stable stored

Table 2: Retention (%) of total microencapsulated anthocyanins observed after storage at 25 °C.

Anthocyanin source	Encapsulant/s and encapsulation method	Storage temperature, °C	Water activity (a_w) or moisture content (%)	Total anthocyanin retention (%) at the end of storage period (indicated)	Reference
Açai (*Euterpe oleracea* Mart.)	Maltodextrin DE10- (spray drying)	25	$a_w = 0.328$	87% at 120 days	Tonon et al. [16]
		25	$a_w = 0.529$	81.9% at 120 days	Tonon et al. [16]
	Gum arabic (spray-drying)	25	$a_w = 0.328$	83.5% at 120 days	Tonon et al. [16]
	Gum arabic (spray-drying)	25	$a_w = 0.529$	75.8% at 120 days	Tonon et al. [16]
	Maltodextrin DE20	25	$a_w = 0.328$	80% at 120 days	Tonon et al. [16]
	Maltodextrin DE20	25	$a_w = 0.529$	74.0% at 120 days	Tonon et al. [16]
Chokeberry (*Aronia melanocarpa*) juice	Maltodextrin (spray-drying)	25	3.2%	72.6% at 360 days	Wilkowska et al. [25]
	Maltodextrin + Arabic gum (spray-drying)	25	3.5%	70.6% at 360 days	Wilkowska et al. [25]
	HP-β-cyclodextrin (spray-drying)	25	2.9%	78.8% at 360 days	Wilkowska et al. [25]
Bayberry juice	Maltodextrin DE10 (spray drying)	25	$a_w = 0.33$	81.6% at 180 days	Fang and Bhandari [29]
	Maltodextrin DE10 (spray drying)	25	$a_w = 0.22$	86.7% at 180 days	Fang and Bhandari [29]
Blackcurrant extract	Maltodextrin DE11 (spray-drying)	25	3.6%	79.8% at 360 days	Bakowska-Barczaka and Kolodziejczyk [59]
	Maltodextrin DE18 (spray-drying)	25	3.9%	63.9% at 360 days	Bakowska-Barczaka and Kolodziejczyk [59]
	Maltodextrin DE 21 (spray-drying)	25	3.1%	70.7% at 360 days	Bakowska-Barczaka and Kolodziejczyk [59]
	Inulin (spray-drying)	25	3.8%	82.7% at 360 days	Bakowska-Barczaka and Kolodziejczyk [59]
Blueberry waste extract	Sodium alginate (spray-drying)	20	$a_w = 0.25$	94.5% at 90 days	Waterhouse et al. [26]
	Inulin (spray-drying)	20	$a_w = 0.31$	89% at 90 days	Waterhouse et al. [26]
Garcinia indica Choisy	Maltodextrin DE6 (spray drying)	25	5.8%	69.8% at 98 days	Nayak and Rastogi [7]
	Maltodextrin DE19 (spray drying)	25	5.7%	72.4% at 98 days	Nayak and Rastogi [7]
	Maltodextrin DE 21 (spray drying)	25	5.0%	72.9% at 98 days	Nayak and Rastogi [7]
	Maltodextrin DE33 (spray drying)	25	5.6%	72.7% at 98 days	Nayak and Rastogi [7]
	Maltodextrin DE21 + gum acacia and TCP (spray drying)	25	4.4%	80% at 98 days	Nayak and Rastogi [7]
Hibiscus sabdariffa extract	Maltodextrin DE11-15 + Arabic gum (spray drying)	25	as it comes out of dryer	65.7% at 104 days	Idham et al. [81]
Pomegranate juice	Arabic gum/Capsul (spray drying)	25	as it comes out of dryer	60% at 120 days	De Araujo Santiago et al. [79]
Muitle (*Justicia spicigera*) aqueous extract	Mesquite gum/Maltodextrin DE10 (1:1), spray-drying	20	$a_w = 0.581$	89.2% at 120 days	Pavón-García et al. [27]
	Maltodextrin DE10/Arabic gum (1:1), spray drying	20	$a_w = 0.555$	84.7% at 120 days	
Blueberry juice	Maltodextrin DE5-7, spray drying	22	$a_w = 0.328$	41% at 90 days	Turan et al. [82]
	Maltodextrin DE 5–7 + Arabic gum, spray drying	22	$a_w = 0.328$	76% at 90 days	
Bordo grape wine-making pomace extract	Maltodextrin DE9-12, spray drying, 10%[a]	25	$a_w = 0.328$	73.3 at 120 days	Souza et al. [45]
	Maltodextrin DE9-12, spray drying, 20%[a]	25	$a_w = 0.328$	81.2% at 120 days	
	Maltodextrin DE9-12, spray drying, 30%[a]	25	$a_w = 0.328$	81.4% at 120 days	

[a]Average of 3 inlet air temperatures between 130 and 170 °C.

in amber-colored vials tan transparent ones. Jimenez-Aguilar et al. [28] also reported that spray-dried blueberry extract encapsulated with mesquite gum and stored in presence of light increased the rate of anthocyanins degradation. Patel et al. [32] studied the degradation kinetics of encapsulated anthocyanin during storage in transparent as well as amber-colored vials at 37 °C. They found that the rate of degradation of anthocyanin was significantly higher in the microcapsules stored in transparent vials compared to those stored in amber-colored ones. Mishra et al. [33] encapsulated (starch/soy protein/whey protein) black carrot anthocyanins powder in amber colored bottles and transparent bottles and placed at 25 °C. After 63 days anthocyanin retention was 50% in amber colored bottles, but decreased to 35% in transparent bottles.

3.3 Water activity effects

As noted by several authors storage equilibrium relative humidity plays an important role on anthocyanin degradation of powders. The effect of water activity of powders can be explained by the fact that the degradation reaction of anthocyanins is controlled by the mobility of the reactants [16, 34]. The higher the water content (or water activity), the higher is the molecular mobility, which facilitates reactions of degradation. Selim et al. [35]. evaluated degradation kinetics of Roselle encapsulated anthocyanin under a_w of 0.43, 0.54, 0.64 and 0.75 and observed that the lowest degradation rate was observed at a_w = 0.43 and increased when a_w was increased. Lavelli et al. [36] determined the kinetics of degradation of individual anthocyanin compounds in encapsulated extract of grape stored at 30 °C and different water activities and calculated corresponding half-times ($t_{1/2}$). Four selected anthocyanins from their data were plotted in Figure 4 as a function of a_w. It can be seen that increasing a_w from 0.22 to 0.75, decreased half-times dramatically (i.e., less stability). Figueiredo et al. [37] reported that storage stability of camu-camu anthocyanins encapsulated in maltodextrin, inulin or oligosaccharide was drastically reduced when water activity was increased from 0.22 to 0.75. Figure 5 is a plot of their half-times (time to decrease anthocyanin to 50%) showing that half-times decrease (or stability is increased) when a_w is increased.

Fang and Bhandari [29] indicated that best condition to minimize degradation of encapsulated bayberry anthocyanin was an a_w below 0.33. Baeza et al. [38] found that decreasing a_w from 0.43 to 0.12–0.20 decreased the rate of anthocyanin degradation in freeze-drying encapsulated elderberry pulp.

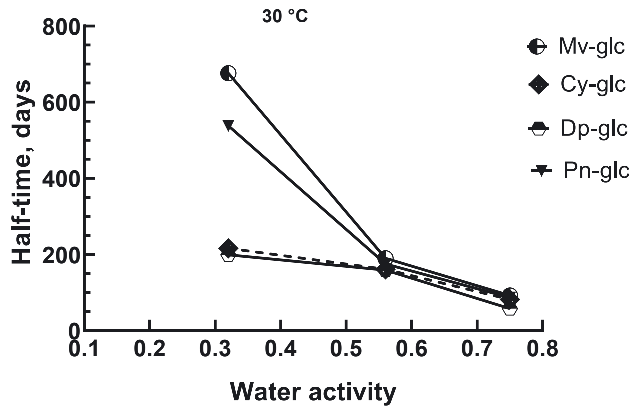

Figure 4: Effect of water activity on half-time (days) for degradation of individual anthocyanin compounds in encapsulated (maltodextrin DE12) grape skin extract. (From data of Lavelli et al. [36]) – Mv-glc: malvidin 3-O glucoside; Cy-glc: cyanidin 3-O-glucoside; Pn-glc: peonidin 3-O-glucoside; Dp-glc: delphinidin 3-O-glucoside – Standard deviation bars for first-order rate constants (from which half-times were derived) were 1.2–4.0% of their values, with the exception of two data for which the standard deviation reached 10%.

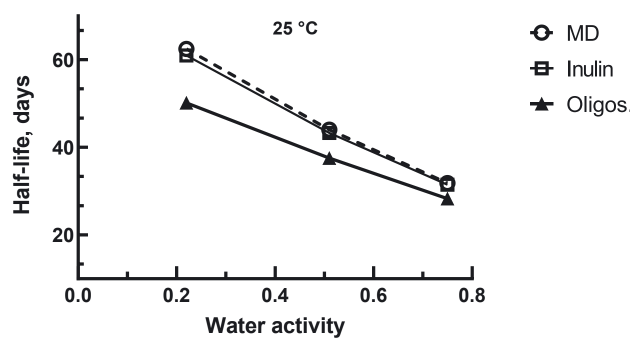

Figure 5: Effect of water activity on half-life of anthocyanin degradation in encapsulated camu-camu extract (from data reported by Figueiredo et al. [37]) – MD: maltodextrin; Oligos: oligosaccharide – Authors did not provide error bars for their half-times.

Gradinarua et al. [39] reported kinetic studies of anthocyanins stability from *Hibiscus sabdariffa L.* (roselle) co-lyophilized with an amorphous polysaccharide (pullulan) stored in different relative humidity environments (water activities 0.33, 0.53, 0.75 and 0.84) at 40 °C. The rate constants for degradation were obtained from first-order reaction kinetic plots and the degradation rate constants increased with the water activity, particularly above 0.53.

3.4 Effect of glass transition (T_g)

The glass transition theory has been also used to explain the effect of moisture on storage stability. According to theory, when a material is in the glassy state, the high viscosity of the matrix does not allow the occurrence of diffusion-controlled reactions [40]. However, some authors have demonstrated that some diffusion-controlled reactions, may occur, even at the glassy state [41]. Tonon et al. [16] reported that anthocyanin loss did occur in the glassy state of encapsulated acai. Ferrari et al. [42] reported that anthocyanin loss did occur in the glassy state of encapsulated acai or blackberry. Gradinarua et al. [39] measured the degradation kinetics of anthocyanins encapsulated by freeze-drying in pullulan and did not find any dependence on the molecular mobility of the system, as it relates to the glass–rubber transition. As they noted anthocyanin degradation occurred, even at sub-T_g temperatures of the amorphous matrices, whereas no changes in the rate constants were observed in the vicinity of the glass transition.

This contradicts the theory of Slade and Levine [40], according to which the storage at a temperature inferior to the glass transition temperature (T_g) assures product stability. The diffusion of oxygen may cause pigment degradation in the stored powders. According to Schebor et al. [43], factors like aging of the glassy material, rotational mobility and diffusion throughout pre-existing holes (pores), due to defects and porosity in the structure can explain the occurrence of chemical reactions in foods, even in the glassy state.

The occurrence of anthocyanin degradation at temperatures below the T_g points to the possibility of some sort of reactant mobility in the glassy state and indicates the insufficiency of using T_g as an absolute threshold of stability.

3.5 Kinetic analysis of anthocyanins during storage

Several authors had analyzed the stability of total anthocyanins in different systems using a kinetic approach, and degradation of encapsulated anthocyanins has been calculated according to the following equations,

$$\ln(C_t/C_0) = -k.t \tag{3}$$

where k is the rate constant, C_0 is the initial anthocyanin content and C_t is the anthocyanin content after storage time t. The degradation constant (k) for the anthocyanin content was determined from slope of a plot of the natural log of anthocyanins retention (C_t/C_0) versus time. The half-time ($t_{1/2}$) (at a specific temperature) is determined as per the following equation:

$$t_{1/2} = \ln 2/k \tag{4}$$

Knowledge of half-time is a simple way to compare the kinetics of anthocyanin degradation in different systems.

Time required for bioactive compounds to degrade to 50% of their original values (half-life) is an easy way to compare the storage stability of encapsulated anthocyanins and has been utilized by several workers. Table 3 shows a literature compilation of time required for encapsulated anthocyanins to degrade to 50% of their original value at 25 °C and specified water activity (or moisture content). Tonon et al. [16] found that anthocyanin degradation during storage of encapsulated acai exhibited two first-order kinetics with two values of k and $t_{1/2}$. Since half-life is determined as the time at which the anthocyanin content was reduced by 50% with respect to the zero-time, uncertainty appears in this case. It is to be noted that when the storage period studied cover a period of time much shorter than the predicted mean time, the risk of a failed extrapolation is important.

Ersus and Yurgadel [44] determined that the half-time at 25 °C of black carrot juice encapsulated with maltodextrin DE29 or Glucodry were identical (400 days) but when maltodextrin DE10 was used as encapsulant, the half-time was slightly reduced (360 days). The half-time for *Garcinia indica* Choisy encapsulated with maltodextrin of different dextrose equivalent, DE6, DE19, DE21 and DE33 [7] were 420, 450, 450 and 420 days respectively indicating that the encapsulant used did not change half-time too much. Similar behavior was reported by Madhavi et al. [30] for half-life times of barberry juice extract encapsulated in maltodextrin DE19, maltodextrin DE19 + Arabic gum, and maltodextrin DE19 + Gelatin. Souza et al. [45] indicated that increasing the added amount of maltodextrin DE10 increased the half-times for encapsulated anthocyanins extracted from red grape residues extract. Data obtained by Pavón-García et al. [27] indicated that half-life of anthocyanins in a mixture of mesquite gum/maltodextrin was significantly higher than for a mixture of Arabic gum/maltodextrin.

4 Conclusions

Amount of encapsulants added, and content of total anthocyanins in the encapsulated dry powders, were analyzed in relation to potential of powders as natural food dyes. Over a total of two-hundred and eight values surveyed, anthocyanin encapsulates exhibited a 120-fold variation in their anthocyanin content, depending on the raw material and type and amount of encapsulating agents. The highest observed anthocyanin concentration amounted to about 3500 mg/100 g powder, corresponding to Aronia berry extract (ultrasound-assisted) and acai juice both spray-dried with maltodextrin.

Table 3: Literature predicted half-life for anthocyanin degradation in several encapsulates at near 25 °C and $a_w \leq$.

Anthocyanins source	Encapsulant/s	a_w	Temp. (°C)	$t_{1/2}$, days	Reference
Blackberry	MD DE20	0.259	25	**374**	Ferrari et al. [42]
	Arabic gum	0.314	25	**297**	
	MD DE20 + GA	0.278	25	**348**	
Black carrot juice	Maltodextrin DE29	As it comes out from dryer	25	**400**	Ersus and Yurdagel [44]
	Glucodry DE 20-23	As it comes out from dryer	25	**400**	
Roselle (*Hibiscus sabdariffa*)	Maltodextrin	As it comes out from dryer	25	**159**	Idham et al. [81]
	Maltodextrin + A. gum	As it comes out from dryer	25	**162**	
	Arabic gum	As it comes out from dryer	25	**141**	
	Soluble starch	As it comes out from dryer	25	**120**	
Barberry extract	Maltodextrin DE19 + A. gum	As it comes out from dryer	25	**150**	Madhavi et al. [30]
	Maltodextrin DE19 + Gelatin	As it comes out from dryer	25	**141**	
	Maltodextrin DE 19	As it comes out from dryer	25	**141**	
Bordo grape winemaking pomace extract	Maltodextrin DE10 (10%), spray drying[a]	a_w = 0.328	25	**271**	Souza et al. [45]
	Maltodextrin DE10 (20%), spray drying[a]	a_w = 0.328	25	**403.2**	
	Maltodextrin DE10 (30%), spray drying[a]	a_w = 0.328	25	**380**	
Blueberry juice	Maltodextrin DE 4–7, spray drying	a_w = 0.328	22	**69.3**	Turan et al. [82]
	Maltodextrin DE 4–7, spray drying	a_w = 0.328	22	**231**	

[a]Average of 3 inlet air temperatures between 130 and 170 °C.

In most cases increasing the amount of encapsulant/s led to a noticeable reduction in the concentration of anthocyanins, this being attributable to a predominance of the dilution effect. Consequently, the least amount of encapsulant compatible with the desired anthocyanin protection and flow properties of powders (absence of stickiness, caking or collapse) should be used to maximize anthocyanin concentration since high mass fractions of encapsulants would not be compatible with the use of encapsulated anthocyanins as a colorant.

Several identical samples (raw material, type and quantity of encapsulant) encapsulated by spray drying or by freeze-drying showed a difference of only 17–20% (in favor of freeze-drying) in the amount of anthocyanins in the final powder.

After storage times between 90 and 180 days at 25 °C anthocyanin retentions were in the range 87–60% (in darkness) as long as the water activity was 0.33 or lower. In some systems the type of encapsulant played some role in the storage stability, while in others did not. It is noteworthy that some literature predicted values of half-time ($t_{1/2}$) may be taken with precaution, since they were derived from experimental measurements taken at storage times smaller than the predicted half times. Anthocyanin degradation occurred even at sub-T_g temperatures of the amorphous matrices, which confirms the insufficiency of using T_g as an absolute threshold of stability.

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Ethics approval: This manuscript is in compliance with ethical requirements.
Informed consent: All the co-authors are fully aware and agree.r

References

1. Özkan G, Bilek SE. Microencapsulation of natural food colourants. Int J Nutr Food Sci 2014;3:145–56.
2. Albuquerque BR, Oliveira MBPP, Barros L, Ferreira ICFR. Could fruits be a reliable source of food colorants?. Pros and cons of these natural additives. Crit Rev Food Sci Nutr 2020. https://doi.org/10.1080/10408398.2020.1746904.
3. Ngamwonglumlert L, Devahastin S, Chiewchan N. Natural colorants: pigment stability and extraction yield enhancement via utilization of appropriate pretreatment and extraction methods. Crit Rev Food Sci Nutr 2015;57:3243–59.
4. Alvarez-Gaona IJ, Fanzone ML, Sari SE, Assof MV, Perez MD, Chirife J, et al. Spray-dried Ancellotta red wine: natural colorant with potential for food applications. Eur Food Res Technol 2019. https://doi.org/10.1007/s00217-019-03375.
5. De Boer FY, Imhof A, Velikova KP. Encapsulation of colorants by natural polymers for food applications. Color Technol 2019;135: 183–94.
6. Assadpour E, Jafari SM. Advances in spray-drying encapsulation of food bioactive ingredients: from microcapsules to nanocapsules. Annu Rev Food Sci Technol 2019;10:8.1–8.29.
7. Nayak CA, Rastogi NK. Effect of selected additives on microencapsulation of anthocyanin by spray drying. Dry Technol 2010;28:1396–404.
8. Yousuf B, Gul K, Wani AA, Singh P. Health benefits of anthocyanins and their encapsulation for potential use in food systems: a review. Crit Rev Food Sci Nutr 2015;56:2223–30.
9. Mahdavi SA, Jafari SM, Ghorbani M, Assadpoor E. Spray-drying microencapsulation of anthocyanins by natural biopolymers: a review. Dry Technol 2014;32:509–18.
10. Tarone A, Betim Cazarin CB, Marostica C, Junior M. Anthocyanins: new techniques and challenges in microencapsulation. Food Res Int 2020;33:109092.
11. Roos YH. Glass transition temperature and its relevance in food processing. Annu Rev Food Sci Technol 2010;1:469–96.
12. Rios de Souza V, Pimenta Pereira PA, da Silva TL, Oliveira Lima LC, Pio R, Queiroz F. Determination of the bioactive compounds, antioxidant activity and chemical composition of Brazilian blackberry, red raspberry, strawberry, blueberry and sweet cherry fruits. Food Chem 2014;156:362–8.
13. Michalska A, Wojdyło A, Brzezowska J, Majerska J, Ciska E. The influence of inulin on the retention of polyphenolic compounds during the drying of blackcurrant juice. Molecules 2019;24:4167.
14. Murali S, Kar A, Mohapatra D, Kalia P. Encapsulation of black carrot juice using spray and freeze drying. Food Sci Technol Int 2014;21:604–12.
15. Vidovic S, Ramić M, Ambrus R, Vladić J, Szabó-Révész P, Gavarić A. Aronia berry processing by spray drying: from by-product to high quality functional powder. Food Technol Biotechnol 2019;57:1–24.
16. Tonon RV, Brabet C, Hubinger MD. Anthocyanin stability and antioxidant activity of spray-dried açai (Euterpe oleracea Mart.) juice produced with different carrier agents. Food Res Int 2010; 43:907–14.
17. Das H, Jaya S. Glass transition and sticky point temperatures and stability/mobility diagram of fruit powder. Food Bioprocess Technol 2008;2:89–95.
18. Khalloufi S, El-Maslouhi Y, Ratti C. Mathematical model for prediction of glass transition temperature of fruit powders. J Food Sci 2000;65:842–8.
19. Staniszewska I, Dzadz L, Hong-Wei X, Zielinska M. Evaluation of storage stability of dried cranberry powders based on the moisture sorption isotherms and glass transition temperatures. Dry Technol 2020. https://doi.org/10.1080/07373937.2020.1771362.
20. Syamaladevi RM, Sablani SS, Tang J, Powers J, Swanson BG. State diagram and water adsorption isotherm of raspberry (Rubus idaeus). J Food Eng 2009;91:460–7.
21. Moraga G, Martínez-Navarrete N, Chiralt A. Water sorption isotherms and glass transition in strawberries: influence of pretreatment. J Food Eng 2004;62:315–21.
22. Saavedra-Leos MZ, Grajales-Lagunes A, Gonzalez-Garcá R, Toxqui-Teran A, Pérez-Garcá SA, Abud-Archila MA, et al. Glass transition study in model food systems prepared with mixtures of fructose, glucose, and sucrose. J Food Sci 2012;77:E118–26.
23. Hancock BC, Zografi G. The relationship between glass transition temperature and the water content of amorphous pharmaceutical solids. Pharmaceut Res 1994;11:471–7.
24. Newman A, Zografi G. Commentary: considerations in the measurement of glass transition temperatures of pharmaceutical amorphous solids. AAPS PharmSciTech 2020;21:26–39.
25. Wilkowska A, Ambroziak W, Adamiec J, Czyzowska A. Preservation of antioxidant activity and polyphenols in chokeberry juice and wine with the use of microencapsulation. J Food Process Preserv 2016;41: e12924.
26. Waterhouse GIN, Sun-Waterhouse D, Su G, Zhao H, Zhao M. Spray-drying of antioxidant-rich blueberry waste extracts; interplay between waste pretreatments and spray-drying process. Food Bioprocess Technol 2017;10:1074–92.
27. Pavón-García LMA, Pérez-Alonso C, Orozco-Villafuerte J, Pimentel-González DJ, Rodríguez-Huezo ME, Vernon-Carter EJ. Storage stability of the natural colourant from *Justicia spicigera* microencapsulated in protective colloids blends by spray-drying. Int J Food Sci Technol 2011;46:1428–37.
28. Jiménez-Aguilar DM, Ortega-Regules AE, Lozada-Ramırez JE, Pérez-Pérez MCI, Vernon-Carter EJ, Welti-Chanes J. Color and chemical stability of spray-dried blueberry extract using mesquite gum as wall material. J Food Compos Anal 2011;24:889–94.
29. Fang Z, Bhandari B. Effect of spray drying and storage on the stability of bayberry polyphenols. Food Chem 2011;129:1139–47.
30. Mahdavi SA, Jafari SM, Assadpour E, Ghorbani M. Storage stability of encapsulated barberry's anthocyanin and its application in jelly formulation. J Food Eng 2016;181:59–66.
31. Xu Q, Bingjink L, Wang D, Luo L, Liu G, Zhou Y. Microencapsulation and stability analysis of blueberry anthocyanins. In: IOP Conference Series: Earth and Environmental Science; 2019:252 p. https://doi.org/10.1088/1755-1315/252/5/052133.
32. Patel AS, Kar A, Mohapatra D. Development of microencapsulated anthocyanin-rich powder using soy protein isolate, jackfruit seed starch and an emulsifier (NBRE-15) as encapsulating materials. Sci Rep 2020;10:10198.

33. Mishra BB, Patel AS, Kar A. Storage stability of encapsulated anthocyanin-rich extract from black carrot (Daucus carota ssp. Sativus) using different coating materials. Curr Agric Res J 2019;7: 53–61.
34. Galmarini MV, Maury C, Mehinagic E, Sanchez VE, Baeza RI, Mignot S, et al. Stability of individual phenolic compounds and antioxidant activity during storage of a red wine powder. Food Bioprocess Technol 2013;6:3585–95.
35. Selim KA, Khalil KE, Abdel-Bary MS, Abdel-Azeim NA. Extraction, encapsulation and utilization of red pigments from Roselle (Hibiscus sabdariffa L.) as natural food colourants. Alex J Fd Sci Technol, Special Volume Conference 2008:7–20.
36. Lavelli V, Pedapati SC, Harsha S, Laureati M, Pagliarini E. Degradation kinetics of encapsulated grape skin phenolics and micronized grape skins in various water activity environments to improve wide-ranging and tailor-made food applications. Innov Food Sci Emerg Technol 2016;39:156–64.
37. Figueiredo JA, Lago AMT, Mar JM, Silva LS, Sanches EA, Souza TP, et al. Stability of camu-camu encapsulated with different prebiotic biopolymers. J Sci Food Agric 2020;100:3471–80.
38. Baeza R, Sanchez V, Salierno G, Molinari F, Lopez P, Chirife J. Storage stability of anthocyanins in freeze-dried elderberry pulp using low proportions of encapsulating agents. Food Sci Technol Int 2020. https://doi.org/10.1177/1082013220937867.
39. Gradinarua G, Biliaderisb CG, Kallithrakac S, Kefalasa P, Garcia-Viguera C. Thermal stability of Hibiscus sabdariffa L. anthocyanins in solution and in solid state: effects of copigmentation and glass transition. Food Chem 2003;83: 423–36.
40. Slade L, Levine H. Beyond water activity: recent advances based on an alternative approach to the assessment of food quality and safety. Crit Rev Food Sci Nutr 1991;30:115–360.
41. Miao S, Roos YH. Nonenzymatic browning kinetics of carbohydrate based low-moisture food systems at temperatures applied to spray drying. J Agric Food Chem 2004;52:5250–7.
42. Ferrari CC, Marconi Germe SP, Dutra Alvim I, de Aguirre JM. Storage stability of spray-dried blackberry powder produced with maltodextrin or gum arabic. Dry Technol 2013;31:470–8.
43. Schebor C, Buera MDP, Karel M, Chirife J. Color formation due to non-enzymatic browning in amorphous, glassy, anhydrous, model systems. Food Chem 1999;65:427–32.
44. Ersus S, Yurdagel U. Microencapsulation of anthocyanins pigments of black carrot (Daucus carota L.) by spray drier. J Food Eng 2007;80:805–12.
45. Souza VB, Fujita A, Thomazini M, Silva ER, Lucon JF Jr., Genovese MI, et al. Functional properties and stability of spray- dried pigments from Bordeaux grape (Vitis labrusca) winemaking pomace. Food Chem 2014;164:380–6.
46. Yamashita C, Song Chung MM, dos Santos C, Mayer CRM, Freitas Moraes IC, Branco IG. Microencapsulation of an anthocyanin-rich blackberry (Rubus spp.) by-product extract by freeze-drying. LWT Food Sci Technol 2017;84:256–62.
47. Saponjac VT, Cetkovic J, Canadanovic-Brunet J, Dilas S, Pajin B, Petrovic J, et al. Encapsulation of sour cherry pomace extract by freeze drying: characterization and storage stability. Acta Chim Slov 2017;64:283–9.
48. Sanchez V, Baeza R, Chirife J. Comparison of monomeric anthocyanins and colour stability of fresh, concentrate and freeze-dried encapsulated cherry juice stored at 38 °C. J Berry Res 2015;5:243–51.
49. Romero-González J, Ah-Henb KS, Lemus-Mondacac R, Muñoz-Fariña O. Total phenolics, anthocyanin profile and antioxidant activity of maqui, Aristotelia chilensis (Mol.) Stuntz, berries extract in freeze-dried polysaccharides microcapsules. Food Chem 2020;313:126115.
50. Fredes C, Becerra C, Parada J, Robert P. The microencapsulation of maqui (Aristotelia chilensis (Mol.) Stuntz) juice by spray-drying and freeze-drying produces powders with similar anthocyanin stability and bioaccessibility. Molecules 2018;23:1–15.
51. Busso Casati C, Baeza R, Sanchez V. Physicochemical properties and bioactive compounds content in encapsulated freeze-dried powders obtained from blueberry, elderberry, blackcurrant and maqui berry. J Berry Res 2019;9:1–17.
52. Rodrigues LM, Januário JGB, dos Santos SS, Bergamasco R, Madronam GS. Microcapsules of ‘jabuticaba’ byproduct: storage stability and application in gelatin. Rev Bras Eng Agríc Ambient 2018;22:424–9.
53. Pieczykolan E, Kurek AM. Use of guar gum, gum arabic, pectin, beta-glucan and inulin for microencapsulation of anthocyanins from chokeberry. Int J Biol Macromol 2019;129:665–71.
54. Archaina D, Leiva G, Salvatori D, Schebor C. Physical and functional properties of spray-dried powders from blackcurrant juice and extracts obtained from the waste of juice processing. Food Sci Technol Int 2017;24:78–86.
55. Gagneten M, Corfield R, Gómez Mattson M, Sozz A, Leiva G, Salvatori D, et al. Spray-dried powders from berries extracts obtained upon several processing steps to improve the bioactive components content. Powder Technol 2019;342:1008–15.
56. Bednarska MA, Janiszewska-Turak E. The influence of spray drying parameters and carrier material on the physico-chemical properties and quality of chokeberry juice powder. J Food Sci Technol 2020;57:564–77.
57. Da Fonseca AP, Machado CA, Tarso Vieira P, Martínez RJ. Encapsulation of anthocyanin-rich extract from blackberry residues by spray-drying, freeze-drying and supercritical antisolvent. Powder Technol 2018;340:553–62.
58. Mazuco RA, Martins Cardoso PM, Bindaco ES, Scherer R, Oliveira Castilho R, Gomes Faraco AA, et al. Maltodextrin and gum arabic-based microencapsulation methods for anthocyanin preservation in juçara palm (Euterpe edulis Martius) fruit pulp. Plant Foods Hum Nutr 2018;73:209–15.
59. Rigon RT, Zapata Noreña CP. Microencapsulation by spray-drying of bioactive compounds extracted from blackberry (*rubus fruticosus*). J Food Sci Technol 2016;53:1515–24.
60. Bakowska-Barczaka AM, Kolodziejczyk PP. Black currant polyphenols: their storage stability and microencapsulation. Ind Crop Prod 2011;34:1301–9.
61. Suravanichnirachorn W, Haruthaithanasan V, Suwonsichon S, Sukatta U, Maneeboon T, Chantrapornchaia W. Effect of carrier type and concentration on the properties, anthocyanins and antioxidant activity of freeze-dried mao [Antidesma bunius (L.) Spreng] powders. Agric Nat Resour 2018;52:354–60.
62. Darniadi S, Idolo I, Ho P, Murray BS. Evaluation of total monomeric anthocyanin, total phenolic content and individual anthocyanins of foam-mat freeze-dried and spray-dried blueberry powder. J Food Meas Charact 2019;13:1599–606.
63. Osorio C, Baudilio A, Hillebrand C, Carriazo S, Winterhalter P, Morales AL. Microencapsulation by spray-drying of anthocyanin pigments from Corozo (Bactris guineensis) fruit. J Agric Food Chem 2010;58:6977–85.

64. Bastías-Montes JM, Choque-Chávez MC, Alarcón-Enos J, Quevedo-León R, Muñoz-Fariña O, Vidal-San Martín C. Effect of spray drying at 150, 160, and 170 °C on the physical and chemical properties of maqui extract (Aristotelia chilensis (Molina) Stuntz). Chil J Agric Res 2019;79:144–52.
65. Villacrez JL, Carriazo JG, Osorio C. Microencapsulation of Andes berry (Rubus glaucus Benth.) aqueous extract by spray drying. Food Bioprocess Technol 2013;7:1445–56.
66. Cheng A-W, Xie H-X, Qi Y, Liu C, Guo X, Sun J-Y, et al. Effects of storage time and temperature on polyphenolic content and qualitative characteristics of freeze dried and spray-dried bayberry powder. LWT Food Sci Technol 2017;53:8706–13.
67. Zhang J, Zhang C, Chen X, Quek SY. Effect of spray drying on phenolic compounds of cranberry juice and their stability during storage. J Food Eng 2019;269:109744.
68. Robert P, Gorena T, Romero N, Sepulveda E, Chavez J, Saenz C. Encapsulation of polyphenols and anthocyanins from pomegranate (Punica granatum) by spray drying. Int J Food Sci Technol 2010;45:1386–94.
69. Syamaladevi M, Insan SK, Dhawan K, Andrews P, Sablani SS. Physicochemical properties of encapsulated red raspberry (Rubus idaeus) powder: influence of high-pressure homogenization. Dry Technol 2012;30:484–93.
70. Sharifi A, Niakousari M, Maskooki A, Mortazavi S. Effect of spray drying conditions on the physicochemical properties of barberry (Berberis vulgaris) extract powder. Int Food Res J 2015;22: 2364–70.
71. Nogueira GF, Fakhouri FM, Oliveira RA. Blackberry pulp microencapsulation with arrowroot starch and gum arabic mixture by spray drying and freeze drying. In: IDS'2018 – 21st International Drying Symposium Valencia, Spain, 18-21 September 2018; 2018.
72. Franceschinis L, Salvatori DM, Sosa N, Schebor C. Physical and functional properties of blackberry freeze- and spray-dried powders. Dry Technol 2014;32:197–207.
73. Emam-Djomeh Z, Seddighi A, Askari G. Influence of process conditions on the functional properties of spray-dried seedless black barberry (berberis vulgaris) juice powder. J Food Process Preserv 2016;41:e12934.
74. Do HTT, Nguyen HVH. Effects of spray-drying temperatures and ratios of gum arabic to microcrystalline cellulose on antioxidant and physical properties of mulberry juice powder. Beverages 2018;4:101.
75. Moreno T, de Paz E, Navarro I, Rodríguez-Rojo S, Matías A, Duarte C, et al. Spray drying formulation of polyphenols-rich grape marc extract: evaluation of operating conditions and different natural carriers. Food Bioprocess Technol 2017;9:2046–58.
76. Kuck LS, Zapata Noreña CP. Microencapsulation of grape (Vitis labrusca var. Bordo) skin phenolic extract using gum arabic, polydextrose, and partially hydrolyzed guar gum as encapsulating agents. Food Chem 2016;194:569–76.
77. Garrido Makinistian F, Gallo L, Sette P, Salvatori D, Bucalá V. Nutraceutical tablets from maqui berry (Aristotelia chilensis) spray-dried powders with high antioxidant level. Dry Technol 2020;38:1231–42.
78. Díaz DI, Beristain CI, Azuara E, Luna G, Jimenez M. Effect of wall material on the antioxidant activity and physicochemical properties of *Rubus fruticosus* juice microcapsules. J Microencapsul 2015;32:247–54.
79. De Araujo Santiago MCP, Nogueira RI, Falcao Paim DRS, Senna Gouvea ACM, De Oliveira Godoy RL, Peixoto FM, et al. Effects of encapsulating agents on anthocyanin retention in pomegranate powder obtained by the spray drying process. LWT Food Sci Technol 2016;73:551–6.
80. Moser P, Benatti Gallo TC, Cirelli Zuanon LA, Pereira JE, Nicoletti VR. Water sorption and stickiness of spray-dried grape juice and anthocyanins stability. J Food Process Preserv 2018;42:e13830.
81. Idham Z, Muhamad I, Sarmidi MR. Degradation kinetics and color stability of spray-dried encapsulated anthocyanins from hibiscus sabdariffa. J Food Process Eng 2012;35:522–42.
82. Turan FT, Cengiz A, Sandıkçı D, Dervisoglua M, Kahyaoglua T. Influence of an ultrasonic nozzle in spray-drying and storage on the properties of blueberry powder and microcapsules. J Sci Food Agric 2016;96:4062–76.