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Co-crystallization of yerba mate extract (*Ilex paraguariensis*) and mineral salts within a sucrose matrix

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Abstract

Calcium lactate, magnesium sulphate and yerba mate (*Ilex paraguariensis*) extracts with antioxidants properties were encapsulated by co-crystallization in a supersaturated sucrose solution. Solubility, hygroscopicity, bulk density, water activity (a_w), particle size distribution and repose angle of co-crystallized products were determined. The surface structure analysis of the co-crystallized products was performed by scanning electron microscopy (SEM). The concentration of mineral components in co-crystallizates was quantified by a volumetric titration method with EDTA (ethylenediaminetetraacetate); Folin–Ciocalteau method was used to determine total polyphenols of yerba extract in co-crystallized products. Size distribution, solubility, density and flow properties strongly depended on sucrose matrix, whereas hygroscopicity and a_w varied with the active component.
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Keywords: Co-crystallization; Sucrose; Encapsulation; Antioxidants; Minerals

1. Introduction

Co-crystallization is an encapsulation process in which a second (active) ingredient is incorporated in supersaturated sucrose syrup to reach simultaneous crystallization of both components (Hartel, 1993). However, Maulny, Beckett, and Mackenzie (2005) working on co-crystallization of honey, glucose and fructose, found that the second ingredient may be in an amorphous state. Crystallization of the active ingredient could also take place during storage depending upon temperature and moisture conditions (Bhandari, Datta, D'Arcy, & Rintoul, 1998).

Granulated sucrose is composed of solid, dense, monoclinic crystals with limited surface. This structure has to be modified to be used as an encapsulation material, changing from perfect crystals to irregular, agglomerated and micro sized crystals. The increased void space and surface area provide a porous base for the incorporation of the active compound (Bhandari et al., 1998; Chen, Veiga, & Rizzuto, 1988).

In general, co-crystallization improves solubility, wettability, homogeneity, dispersibility, hydration, anticaking, stability and flowability of the encapsulated materials (Beristain, Vázquez, García, & Vernon-Carter, 1996; Vázquez & Beristain, 1998). Chen et al. (1988) summarized co-crystallization of typical active ingredients: volatile substances, emulsifiers, acids; many of these developments were reported as patents. Basic studies of co-crystallization process to retain flavor compounds of honey, Jamaica granules and orange peel oil, were carried out by Bhandari et al. (1998), Beristain, Mendoza, García, and Vázquez (1994) and Beristain et al. (1996).

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The active compounds studied in the present work were antioxidants extracted from yerba mate (*Ilex paraguariensis*) and salts of calcium and magnesium. Antioxidants, in general, can protect the body against the damage caused by free radicals and degenerative diseases. Synthetic antioxidants, usually employed in industry are effective and stable, but their use is limited in many countries because they are not considered completely safe for human health (Nakatani, 1997). Yerba mate is a nutrient beverage, rich in xanthine and minerals like potassium and magnesium, traditionally drunk in various countries of South America. Mate is prepared as an infusion of the dried minced leaves of *I. paraguariensis*. This infusion is drunk for its claimed diuretic, anti-inflammatory, and mainly for its mild stimulant properties (Schinella, Troiani, Dávila, de Buschiazzo, & Tournier, 2000). Phytochemical investigations of *I. paraguariensis* found many classes of caffeoyl derivatives and flavonoids as chlorogenic acid, caffeic acid, dicaffeoylquinic acids, rutin, quercetin and kaempferol (Filip, López, Giberti, Coussio, & Ferraro, 2001). Once extracted, active compounds are more labile and should be protected.

Calcium plays an important role in a broad number of metabolic processes and variable physiologic requirements manifested during the stage of skeletal development and maintenance (Fishbein, 2003). Magnesium is involved in at least 300 enzymatic steps of intermediate metabolism, so its deficiency could produce biochemical and symptomatic problems to the body (Vormann, 2003). Mineral fortification is complicated due to the taste of salts, and some solutions to this problem have been analyzed. For example, the bitter taste associated with inorganic salts as calcium chloride may be modified when calcium is combined with larger organic ions such as lactate, gluconate or glycerophosphate (Lawless, Rapacki, Horne, & Hayes, 2003). Besides, recent studies in suppressive effects of mixtures showed that sucrose masked the bitterness of $CaCl_2$ in a wide range of concentrations of this salt (Lawless, Rapacki, Horne, Hayes, & Wang, 2004). Thus, co-crystallization with sucrose could improve palatability of mineral salts as well as handling properties of the materials.

Barbosa-Cánovas, Malave-López, and Peleg (1987) stressed that bulk density, compressibility and flowability of food powders are related physical properties, that are largely influenced by the chemical composition of the powder, particle size and mainly by its relationship with ambient conditions (temperature and moisture). Both physical and chemical characterization determine handling and stability of the food powders during processing and storage.

The objectives of this work were to co-crystallize *I. paraguariensis* extracts; magnesium sulphate and calcium lactate in a sucrose matrix and to characterize these products by evaluating their functional, physical and chemical properties like water sorption isotherms, hygroscopicity, flowability and their microstructure by SEM.

2. Materials and methods

2.1. Materials

Commercial sugar (Ledesma, Argentina) was used as encapsulating material and the active compounds were magnesium sulphate ($MgSO_4 \cdot 7H_2O$) and calcium lactate ($CaC_6H_{10}O_6 \cdot 5H_2O$), both salts of food grade quality (Parafarm, China), and a yerba mate (*I. paraguariensis*) lyophilized aqueous extract obtained in our laboratory (Anbinder, 2004). Among some calcium organic salts, calcium lactate was selected due to its high solubility (Gerstner, 2002).

2.2. Samples preparation

To reach a sucrose syrup of 71.5% w/w, 10 g of total supersaturated solution were obtained by heating 50 g of sucrose in water in a metallic vessel with continuous stirring. When a slight turbidity was detected in the syrup, indicating the beginning of crystallization process from the solution, the second compound was rapidly added to the syrup (Bhandari & Hartel, 2002). Mineral salts (5 g magnesium sulphate and 2 g calcium lactate per 100 g sucrose) were incorporated in powder form or in solution to evaluate the effect of their physical state on the final product, whereas antioxidant extract (0.7 g/100 g sucrose) was added in powder form. At this moment the mixture was placed over a cold surface, with continuous stirring until a solid product was obtained. Crystallized product obtained from 71.5% sucrose syrup without any other component was taken as control.

Co-crystallized products were transferred to a glass vessel and stored for 24 h in a desiccator. After this time, the agglomerates were dried in a vacuum oven at 65 °C during 5 h, then they were passed through 2 mm sieves to determine their size distribution. The agglomerates were grounded with a blade grinding machine (Braun GmbH, Germany).

2.3. Product characterization

Moisture content (H) was determined by drying the grounded samples in a vacuum oven at 65 °C, until constant weight.

a_w of the co-crystallized products was determined after 5 h drying process, using an Aqua Lab Serie 3 TE (USA) equipment. Solubility was determined as the time (min) in which 10 g of powder were dissolved in 100 ml of distilled water with continuous stirring (Beristain et al., 1994).

Powder bulk density (g/cm^3) was evaluated by measuring the volume occupied by a given weight of powder in a graduated cylinder, without compacting. Size distributions of the agglomerates were obtained sieving and weighing the powder retained in each sieve; sieves size varied from 2 to 0.250 mm. Flowability of the powders was deter-

mined with a repose angle chamber (Solids handling study bench, CEN, Armfield, United Kingdom). All measurements were performed at least in triplicates.

2.4. Scanning electron microscopy

Samples were analyzed in a scanning electron microscope (SEM, Jeol JSM-6360, Japan). Co-crystallizates were attached to SEM stubs using a two-sided adhesive tape, then they were coated with a layer of gold (40–50 nm) and examined using an acceleration voltage of 10 kV.

2.5. Water sorption isotherms: measurements and modelling

Water sorption isotherms were obtained equilibrating 1 g of sample in glass flasks at different relative humidities (RH), within the range 33–95%. Saturated salt solutions used were magnesium chloride (RH 33%), potassium carbonate (RH 43%), sodium nitrite (RH 65%), sodium chloride (RH 75%), potassium chloride (RH 85%) and potassium nitrite (RH 93%) (Fennema, 1996). Isotherms of pure yerba mate extract, magnesium sulphate and calcium lactate were also determined.

The following models were used to find the best fit of the experimental data of water sorption isotherms (Iglesias & Chirife, 1982; Arévalo-Pinedo, Dos Santos, Salles Arévalo, Zúñiga, & Arévalo Pinedo, 2006):

$$\text{Oswin model} \quad X = B_2[a_w/(1-a_w)]^{B_1} \tag{1}$$

$$\text{Smith model} \quad X = B_2 - B_1 \ln(1-a_w) \tag{2}$$

$$\text{Iglesias and Chirife model} \quad X = B_1[a_w/(1-a_w)] + B_2 \tag{3}$$

$$\text{Halsey model} \quad a_w = \exp[-B_2/X^{B_1}] \tag{4}$$

$$\text{GAB model} \quad X = [((B_2-1)X_m B_1 a_w)/(1+(B_2-1)B_1 a_w)] + [X_m B_1 a_w/(1-B_1 a_w)] \tag{5}$$

where X is the moisture content expressed on dry basis, X_m is GAB monolayer moisture content expressed on dry basis, a_w is the water activity of the saturated salts solutions, B_1 and B_2 are fitting parameters to describe the isotherm.

2.6. Hygroscopicity determination

Hygroscopicity equation from Jaya and Das (2004) was modified to calculate water gain values on dry basis as follows:

$$\text{HG}\% = \frac{b+H}{a-H} \times 100 \tag{6}$$

where b (g) is the weight increase, a (g) is the initial sample weight and H is the initial water content of the powder (g).

2.7. Quantification of active compounds and yield process

Co-crystallized products were dissolved in distilled water and the concentration of the mineral components was quantified by a volumetric titration method with EDTA (Ethylenediaminetetraacetate), a chelating agent of calcium, magnesium and other cations (Kolthoff, Sandell, Meehan, & Bruckenstein, 2004). Similarly, Folin–Ciocalteau method (Schlesier, Harwat, Böhm, & Bitsch, 2002) was used to determine total polyphenols of yerba mate extract; this test is based on the oxidation of phenolic groups with phosphomolybdic and phosphotungstic acids. After oxidation a green–blue complex is measurable at 725 nm.

The process yield (% w/w) was calculated using the mineral concentration (mineral (g)/co-crystallizate (g)) obtained by the titration method and the initial amount of mineral added to the syrup as mineral (g)/(sucrose (g) + mineral (g)).

Similarly, the process yield in polyphenols was calculated with the polyphenols concentration obtained by the Folin–Ciocalteau method (lyophilized extract (g)/co-crystallizate (g)) and the amount of the raw lyophilized extract per gram of total sucrose plus lyophilized extract.

2.8. Statistical analysis

Systat-software (SYSTAT, Inc., Evanston, Ill., USA, 1990) version 5.0 was used for all statistical analysis. Analysis of variance (ANOVA), Fisher LSD (Least Square Difference) mean comparison test and regression analysis were applied with a significance level (α) of 0.05.

3. Results and discussion

Fig. 1a and b shows the surface structure of co-crystallized sucrose control sample. All samples have a similar basic porous structure corresponding to typical cluster-like agglomerates with void spaces and a sucrose crystal size varying between 2 and 30 μm. Co-crystallized magnesium sulphate (Fig. 1e and f) exhibits a well defined crystalline structure with smaller crystals probably due to the added salt. Co-crystallizates of calcium lactate (Fig. 1g–i) and yerba mate extracts (Fig. 1c and d) show different type of surface structure covering the sugar agglomerates; co-crystallized yerba mate has a network with neat edges whereas calcium lactate product shows a rough needle-like structure. Sakata, Shiraishi, and Otsuka (2005) studied the dehydration of this last compound through differential scanning calorimetry (DSC), powder X-rays diffractometry and SEM, finding an endothermic transition at 95.9 °C. During co-crystallization process temperatures higher than 100 °C were achieved, thus dehydration of calcium lactate pentahydrate may have been occurred. Besides, our observations compared well with Sakata et al. (2005) SEM micrographs of the anhydrate, which had a rough surface with high aggregation between particles, while the pentahydrate had a plate-like crystals with a smooth surface.

The stability and behavior of hydrates can vary widely, and hydrate formation and dehydration may occur during processing or storage (Sakata et al., 2005). A similar

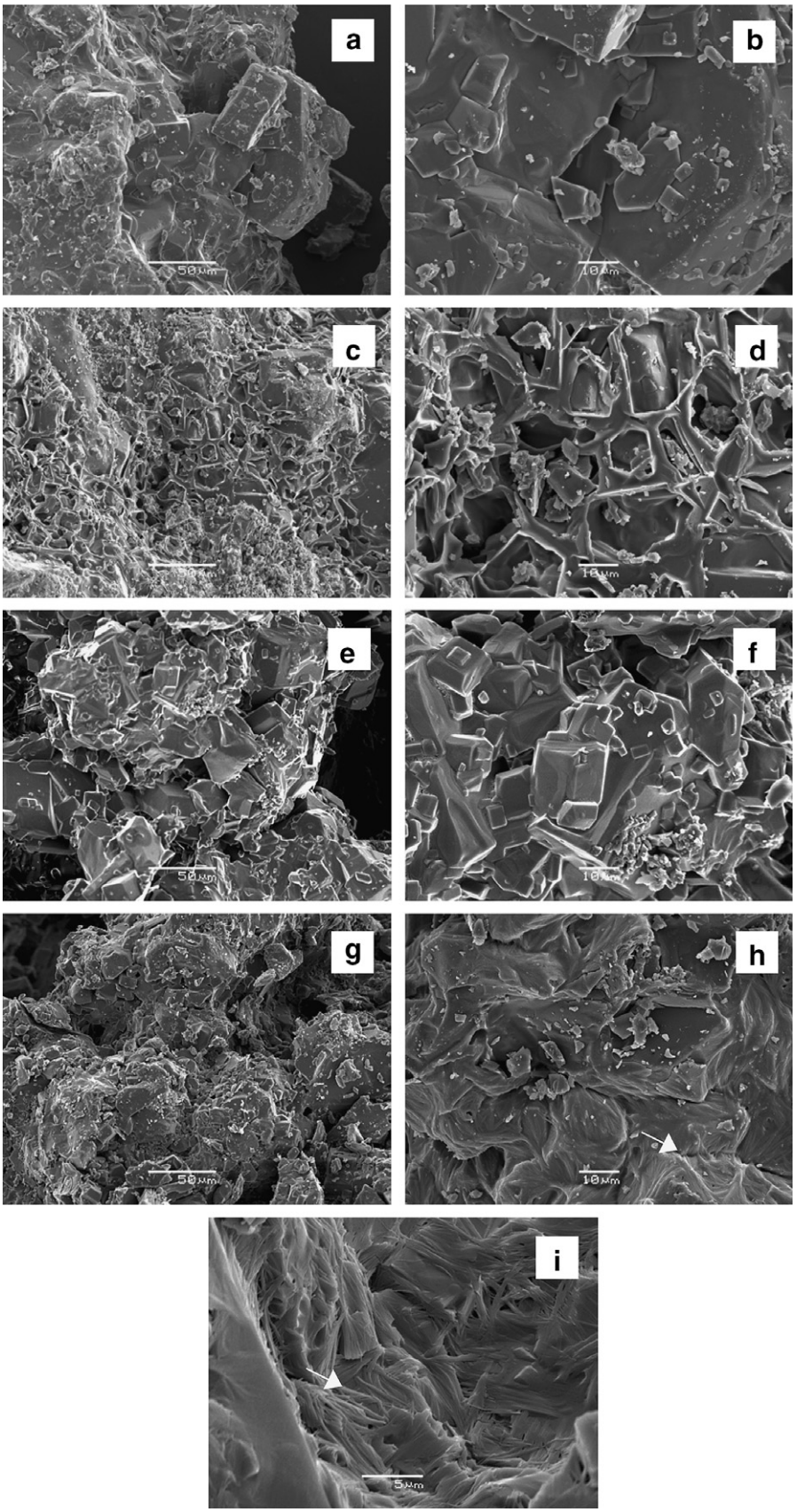

Fig. 1. SEM microphotographs of co-crystallized products: (a) sucrose, scale bar: 50 μm; (b) sucrose, scale bar: 10 μm; (c) yerba mate extract, scale bar: 50 μm; (d) yerba mate extract, scale bar: 10 μm; (e) magnesium sulphate, scale bar: 50 μm; (f) magnesium sulphate, scale bar: 10 μm; (g) calcium lactate, scale bar: 50 μm; (h) calcium lactate, scale bar: 10 μm; (i) calcium lactate, scale bar: 5 μm.

behavior to that of calcium lactate was also observed for magnesium salt. a_w of magnesium co-crystallizates ranged between 0.38 and 0.33 (Table 1), similar to the values found in dried magnesium sulphate. The measured a_w value of pure magnesium salt ($MgSO_4 \cdot 7H_2O$) was 0.83, whereas for dried magnesium sulphate a_w was 0.37. Magnesium co-crystallizates could have changed to an anhydrous or other hydrate form during co-crystallization process. Several hydrates forms of magnesium sulphate can be obtained depending on the processing conditions. Paulik, Paulik, and Arnold (1981) when performing calorimetric studies, even found intermediate forms corresponding to mixtures of two or more hydrates. Significant differences ($p < 0.05$) in a_w values were detected for co-crystallized products. As shown in Table 1, the final water activity of the co-crystallizates was dependent on the active component incorporated. In general, values of a_w were equal or lower than 0.47 denoting the microbiological safety of these products.

High solubility values of co-crystallized products were observed and they were not significantly different ($p > 0.05$) from sucrose control (Table 1). Comparing the solubility of co-crystallized products with raw active compounds, in general, it was not hardly modified. Additionally it can be pointed out that when the lyophilized yerba extract is not protected against ambient conditions, it becomes a sticky material; thus, co-crystallization process helped improve its dispersibility without altering the high solubility of the dry extract. Bulk density values ranged between 0.65 and 0.72 g/cm^3; these values were similar to those obtained by Beristain et al. (1996) who found values between 0.67 and 0.75 g/cm^3 in co-crystallized orange peel oil. Although solubility and density of the products were not significantly different, the following increasing trend was observed: control $\leqslant$ yerba $<$ calcium lactate $<$ magnesium sulphate (Table 1). Samples with higher densities showed lower solubility, this fact could be attributed to the facilitated solute–solvent interaction in low density products. A low water content and a low hygroscopicity characterize a high stability product during storage. Water contents of the co-crystallizates products (Table 1) were below those found by Bhandari et al. (1998), who reported values of 6.8 and 8.2 g/kg for honey–sucrose co-crystallizates. Size distribution of grounded samples was similar to original ones (without grinding). Thus, former data are shown. Active components did not significantly ($p > 0.05$) modify size distribution of control sucrose systems (Fig. 2). Approximately 30% of total weight of all products

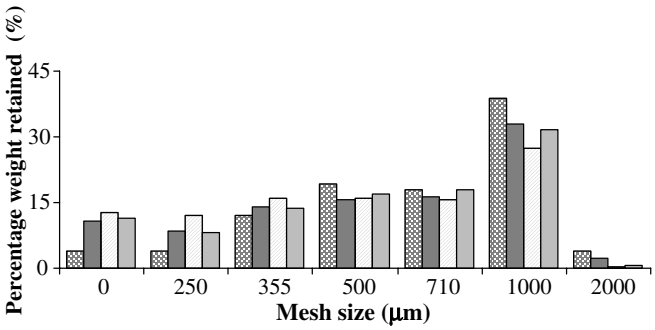

Fig. 2. Size distribution of grounded co-crystallized products, magnesium sulphate (▨), yerba mate extract (■) calcium lactate (▨) and sugar (□).

was retained in the 1 mm sieve, whereas agglomerates smaller than 0.250 mm represented only 12% of the total weight. This is an important factor in powder handling since, according to Mathlouthi and Rogé (2003), the flow of sugar becomes difficult with sizes below 0.250 mm. Both, small particles and high hygroscopicity, contribute to reduce flowability. Besides, fines particles have a higher tendency to absorb moisture (Barbosa-Cánovas et al., 1987). Flow properties are useful to predict powder handling during production and caking characteristics during storage. Different active components and the physical state of the added salts did not significantly ($p < 0.05$) modify flow properties of sucrose matrix as determined by repose angle measurements (Table 2). Similar values were obtained by Bhandari et al. (1998), working with different ratios of sucrose–honey mixtures. According to Peleg (1977), powders with repose angles lower than 40° are non-cohesive and powders with repose angles above 50° or more cause flow problems. Compared to the original materials, raw $MgSO_4 \cdot 7H_2O$ flowability was not affected by the process, showing a repose angle of 40.7°. In the case

Table 2
Repose angle of untreated and co-crystallized products

Type of product	Repose angle (°)
Sucrose	41.9 ± 2.56
Lyophilized yerba mate extract	Not determined
Co-crystallized yerba mate extract	39.7 ± 1.29
Raw magnesium sulphate	40.7 ± 0.84
Co-crystallized magnesium sulphate	40.9 ± 0.95
Raw calcium lactate	65.9 ± 3.87
Co-crystallized calcium lactate	40.4 ± 1.19

Table 1
Physic properties of co-crystallized products

Type of product	Solubility (min)	Density (g/cm^3)	a_w	Water content (% w/w)
Sucrose	1.37 ± 0.29	0.651 ± 0.079	0.473 ± 0.006	0.079 ± 0.002
Yerba mate extract	1.33 ± 0.38	0.697 ± 0.094	0.460 ± 0.006	0.055 ± 0.001
Calcium lactate	1.52 ± 0.26	0.694 ± 0.038	0.442 ± 0.009	0.127 ± 0.004
Magnesium sulphate (in powder)	1.75 ± 0.12	0.723 ± 0.043	0.377 ± 0.012	0.482 ± 0.019
Magnesium sulphate (in solution)	1.68 ± 0.79	0.713 ± 0.069	0.329 ± 0.005	0.487 ± 0.020

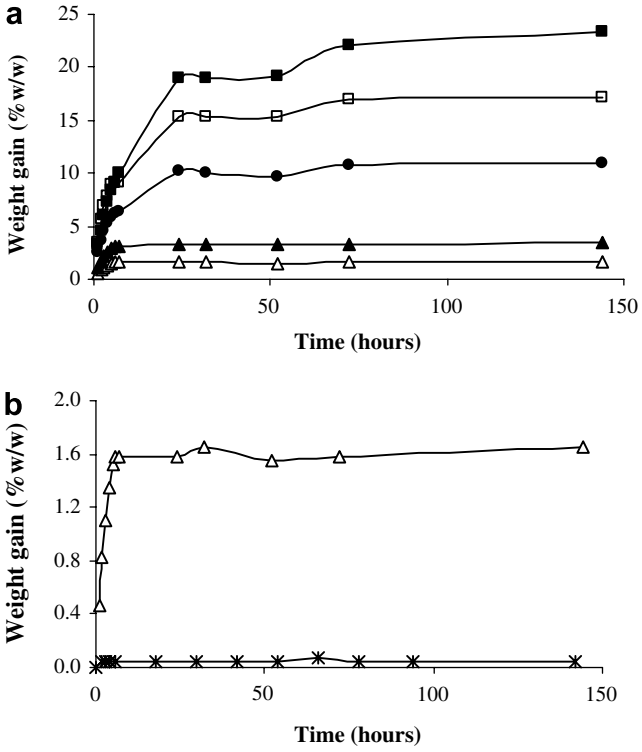

Fig. 3. Water gain of lyophilized yerba mate extract. (a) At different relative humidity: 85% HR (■), 75% HR (□), 65% HR (●), 43% HR (▲), 33% HR (△). (b) At 33% HR: (△) lyophilized and (✱) co-crystallized yerba mate extract.

of calcium salt, the flowability was improved decreasing the repose angle from 66° in raw salt, to approximately 40° in co-crystallized product. This change in the repose angle could be attributed to the transformation of calcium lactate pentahydrate to the anhydrous agglomerates, occurred during the co-crystallization process. A salt and its hydrates may show different physicochemical properties that affect their macroscopic characteristics. Lyophilized yerba mate extract above 75% RH is a sticky powder, thus the repose angle could not be determined. Co-crystallization process also improved the flow properties of this active compound (Table 2).

Sorption curves of yerba mate extract (Fig. 3a) also showed the marked hygroscopic behavior that influences the flowability properties of this product. At high relative humidity (85% RH) the water gain was about 25% w/w for yerba mate extract; even at low values as 33% RH, the water gain was higher than 1.5% w/w. Co-crystallization process was highly effective to reduce water gain in yerba mate extract, as shown in Fig. 3b.

For co-crystallized products (Fig. 4) the water gain was lower than 1% at low values of relative humidity RH (33% and 65%). At 85% RH, a high increase in water content and differences between the co-crystallized products were detected, mainly for magnesium co-crystallizates. Curves of water gain as a function of time were used to calculate percentage of hygroscopicity (Table 3) and sorption isotherms (Fig. 5). Yerba mate lyophilized extract gave hygroscopicity values ranging between 41% and 65% HG and the corresponding co-crystallizates between 0.18% and 0.84% HG, from a_w 0.33 to 0.85, respectively. Raw salts did not show differences in hygroscopicity as compared with co-crystallized products. The physical state (in solution or in powder), in which calcium salt was added during co-crystallization, was not a significant factor in water gain, thus

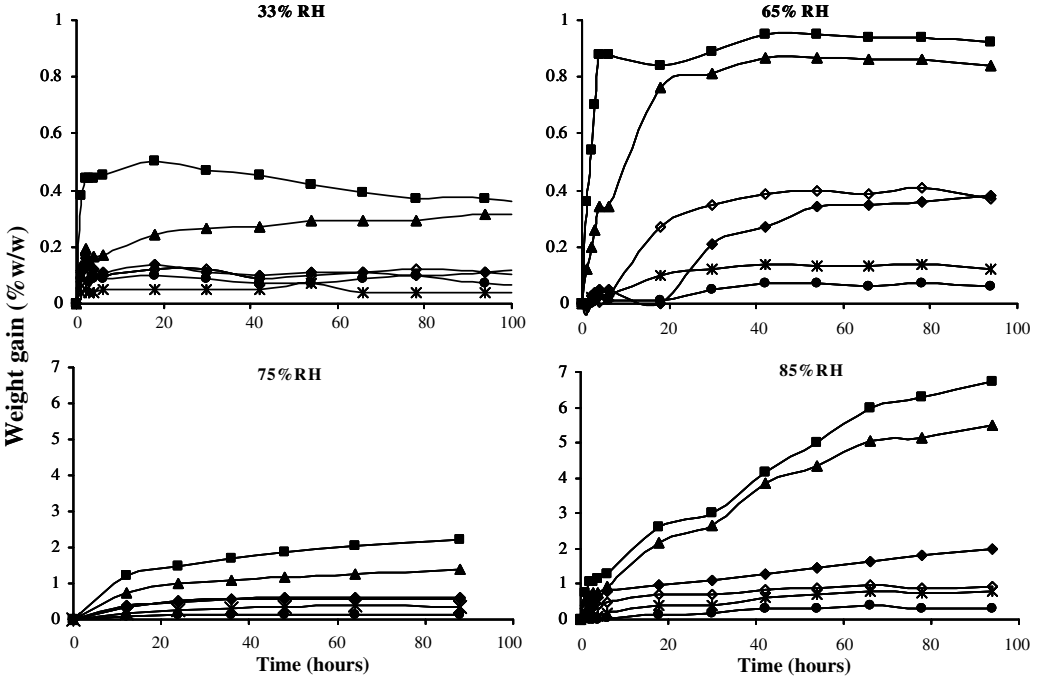

Fig. 4. Water gain at different relative humidity (RH) of co-crystallized products. Sucrose (●), yerba mate extract (✱), calcium lactate in powder (♦), calcium lactate in solution (◊) $MgSO_4$ in powder (▲) and $MgSO_4$ in solution (■).

Table 3
Hygroscopicity (HG%) of co-crystallized products at different % relative humidity

Type of product	HG%				
	93	85	75	65	33
Sucrose	2.042	0.370	0.156	0.100	0.090
Yerba mate extract	2.898	0.844	0.365	0.175	0.185
Calcium lactate	2.331	1.572	0.615	0.503	0.238
Magnesium sulphate (in powder)	12.001	5.994	1.495	1.336	0.807
Magnesium sulphate (in solution)	12.023	7.264	2.329	1.413	0.769

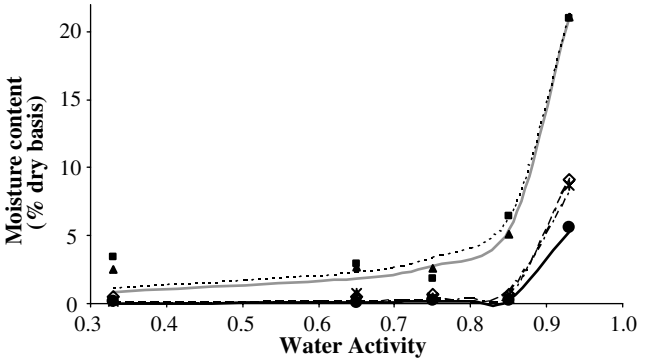

Fig. 5. Comparison of experimental and predicted sorption equilibrium data (Eq. (3)) for co-crystallized products. Experimental data: sucrose (●), yerba mate extract (✱), calcium lactate (◊), $MgSO_4$ in powder (▲) and $MgSO_4$ in solution (■). Predicted data fitted using GAB model: sucrose (—), yerba mate extract (-·-), calcium lactate (- - -), $MgSO_4$ (in powder) (—) and $MgSO_4$ (in solution) (·····).

mean values between both addition forms are reported. Hygroscopicity values of co-crystallized products were below 2% at 85% RH, except for magnesium co-crystallizates which gave values about 6–7%. The high values observed in the magnesium co-crystallizates were similar to those reported by Jaya and Das (2004) for mango powder at 79.5% RH. When magnesium salts are added at the crystallization point, besides crystals, an amorphous or a partially crystalline layer over the sugar crystals may have been formed leading to a more hygroscopic structure. This behavior can be explained considering the higher water absorption of amorphous structures compared to crystalline ones (Bhandari & Hartel, 2002; Mathlouthi & Rogé, 2003). However, further studies (calorimetric measurements) are needed to confirm this explanation.

Typical isotherms of crystalline state powder were obtained (Fig. 5). Accordingly, Mathlouthi and Rogé (2003) stressed that the crystalline sugar structure is characterized by the crystal/saturated solution equilibrium at a_w around 85–86% of the sorption isotherm. As stated before, sorption curves showed a marked difference between magnesium co-crystallizates and the other products. Fig. 5 shows that all co-crystallized products are stable to ambient humidity below 75%.

Commonly used models of food–water isotherms (Eqs. (1)–(5)) were used to fit water sorption data. The best fitting was obtained with GAB and Oswin's equations, Eqs. (1) and (5) (Table 4). These models gave the lowest LSD and the highest R^2 values. Iglesias and Chirife equation (Eq. (3)) also gave high R^2 values (≅0.90) whereas Eqs. (2) and (4) gave poor fittings. Fig. 5 shows the goodness of fit of GAB model to the experimental data, because in general GAB model gave the lowest LSD and the highest R^2 values.

Final concentration of calcium lactate in the product was 14.6 mg/g of co-crystallized product and the process yield was approximately 103 ± 5.7%. For magnesium sulphate, final concentration was 43.5 mg/g of co-crystallized product and the yield was 93 ± 7.5%. Co-crystallized antioxidants had a final concentration of 2.52 mg of lyophilized extract per gram of co-crystallized product, obtaining an average yield of 72 ± 7.8%. In the case of lyophilized yerba mate extract, the low yield could be attributed to losses of these natural compounds during heating over 120 °C. These results confirm that the yield of co-crystallization technique strongly depends on the second ingredient added. According to Bhandari et al. (1998), the temperature of co-crystallization should be determined by the composition and properties of the second ingredient.

4. Conclusions

The studied technique allowed to obtain different co-crystallized products with a high concentration of the

Table 4
Fitting parameters of Oswin and GAB models obtained with the equilibrium data of the isotherms

Models	Parameters	Sucrose	Yerba mate extract	Calcium lactate	Magnesium sulphate (in powder)	Magnesium sulphate (in solution)
Oswin	B_1	0.001	0.002	0.004	0.507	0.0709
	B_2	3.560	3.181	1.846	1.438	1.308
	R^2	0.998	0.991	0.953	0.983	0.974
	LSD	0.0287	0.2912	0.3865	3.7139	5.8085
GAB	X_m	0.026	0.063	0.087	0.633	0.755
	B_1	1.070	1.067	1.065	1.043	1.037
	B_2	$1.4.10^9$	$6.0.10^8$	$1.7.10^9$	$1.4.10^9$	$3.9.10^8$
	R^2	0.999	0.994	0.996	0.988	0.968
	LSD	0.0130	0.2207	0.1795	2.0528	5.3005

X_m is GAB monolayer moisture content expressed on dry basis, B_1 and B_2 are fitting parameters to describe the isotherm, R^2 is the coefficient of regression and LSD is Fisher least square difference with a significance level (α) of 0.05.

active compound. The resulting powders were free flowing and stable even at high humidity conditions.

Co-crystallized product properties like flowability, solubility, density and size distribution mainly depended on the sucrose matrix. Whereas a_w and hygroscopicity varied with the different active component added. Hygroscopicity of co-crystallizates decreased in the following order: magnesium > calcium > yerba > sugar.

The calcium lactate and yerba mate extracts used in the experiments, after the process, changed from cohesive materials to non-cohesive products. Co-crystallization notably reduced the hygroscopic characteristics of yerba mate extracts without affecting their high solubility. The co-crystallization process resulted in a good alternative to preserve and handle these materials for further applications in food products.

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