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Encapsulation of Antioxidants from Spent Coffee Ground Extracts by Spray Drying

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Spent coffee grounds (SCG) represent a good raw material for the recovery of bioactive compounds. Indeed, SCG extracts are rich in antioxidants, particularly in chlorogenic acid (5-caffeoylquinic acid) (CGA) and melanoidins, which are able to prevent serious neurodegenerative and cardiovascular diseases. In order to preserve the activity of these compounds, encapsulation by spray drying can be used. In this study, an extract rich in phenolic compounds from spent coffee grounds was obtained by microwave-assisted extraction, using a mixture of ethanol:water 54:46 (v/v) as solvent, operative temperature of 150 °C, and extraction time of 90 min. Encapsulation process, using inulin and maltodextrin as coating agents, was studied by means of an experimental design and the response surface methodology was used for data treatments. Inulin:maltodextrin ratio and sample flow rate effects on encapsulation yield, efficiency and product features was evaluated. Results demonstrated that high encapsulation efficiency (63%) can be reached using inulin as the carrier, leading to the production of microencapsulated dried powders rich in polyphenols that can have potential industrial applications in food and cosmetic areas.

1. Introduction

Spent coffee grounds (SCG) is one of the most abundant wastes produced worldwide by food industry. This exhausted matrix is still rich of bioactive molecules and is a good raw material for antioxidant extraction processes. Several studies show the possibility of using different extraction techniques and solvents (Mussatto et al., 2011; Ludwig et al., 2012; Bravo et al., 2013; Panusa et al., 2013; Ranic et al., 2014), in order to obtain extracts that exhibit high antiradical power. This can be traced back to chlorogenic acids, its derivatives, and melanoidins (Kučera et al., 2016). These antioxidant molecules have a great interest in medical and biomedical fields because of their ability to prevent and hinder some chronic and degenerative diseases (Wadhawan & Anand, 2016; Campos-Vega et al., 2015). In addition, antioxidant compounds find many applications in food and cosmetic areas. On the other hand, phenolic compounds are unstable and easily degradable if exposed to light, heat and oxygen. Thus, in order to extend extract shelf life and to prevent their activity loss, stabilization methods should be applied. Encapsulation by spray drying is a well-known technique able to produce dried microparticles from a liquid extract, trapping the bioactive molecules in a coating agent. Particularly, spray drying is one of the most widely used methods for this purpose, being easy, cheap and suitable for thermosensitive products such as polyphenols (Okos et al., 2006). Particle dimension is generally around 10 μm with a large size distribution due to the different size of the drops during atomization. The most influent parameters on particle dimensions are nozzle geometry and the initial viscosity of the inlet suspension (Okos et al., 2006). If these variables are related to the particular device and the raw materials, other parameters can be changed in order to optimize the process. Air inlet temperature influences evaporation velocity, the moisture of the product as well as air outlet temperature (Fazaeli et al., 2012), but Paini et al. (2015) found that the yield of microencapsulation of phenolic compounds from olive pomace has not been prejudiced by this operative parameter. Solid content of feed suspension and the surface tension play an important role on the atomization step (Okos et al., 2006), while feed suspension temperature and flow rate have a strong effect on the solvent evaporation: a decrease of feed temperature and an increase of its flow rate lead to a less efficient removal of the solvent and to a higher powder moisture (Fazaeli et al., 2012; Paini et al., 2015). In spray drying applications several carrier materials has been tested in order to obtain good

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product recovery and stability. Gum arabic is the most common coating agent because of its high solubility and low viscosity in aqueous solution, however the fluctuating trend of its supply and cost led to move the attention toward the use of other wall materials (Carneiro et al., 2013). Maltodextrins (MD) are widely used in spray drying processes, either alone either combined with other materials, for polyphenols encapsulation (Paini et al., 2015; Medina-torres et al., 2016; Tolun et al., 2016). The selection of the dextrose equivalent (DE) of maltodextrins is critical for microencapsulation spray drying process. When DE increases a higher moisture of the product was reported because of the greater amount of hydrophilic groups in smaller molecules. In addition, DE influences also the glass transition temperature (Tg) of the powder and consequently powder structure and stability (Fazaeli et al., 2012). Bakowska-Barczak & Kolodziejczyk (2011) did not report any DE effects on the black currant polyphenols encapsulation ability of maltodextrin. Nevertheless, maltodextrins alone lack the required interfacial properties to obtain high microencapsulation efficiencies, thus they are often used together with other wall materials, such as gum arabic (Gharsallaoui & Chambin 2007). Inulin (I) is an interesting coating agent for food applications being a dietary fibre that exhibits prebiotic effects, suitable also for diabetic food (Bakowska-Barczak and Kolodziejczyk, 2011; Fernandes et al., 2014). Indeed, the current trend is to consuming compounds with functional activity, so replacing conventional coating agents, such as modified starch or gum arabic, with a healthy compound such as inulin that can add a higher value to the product (Zabot et al., 2016).
The objective of this work was to investigate the effect of feed flow rate and the coating agent composition on encapsulation of antioxidant extracted from spent coffee grounds using spray drying process. For this purpose, different mixtures of maltodextrin and inulin were analysed as wall material. Experimental design and response surface methodology were used to evaluate the effects on the product in terms of moisture, encapsulation yield, encapsulation efficiency and product recovery.

2. Materials and methods

2.1 Chemicals and reagents

Methanol, ethanol, acetic acid, sodium carbonate, Folin-Ciocalteau's phenol reagent, inulin, maltodextrins (DE 16.5-19.5), caffeic acid standard were purchased from Sigma-Aldrich (St. Louis, MO, USA). Caffeic acid solutions were prepared with methanol and stored in dark bottles at -20 °C. All chemicals were of reagent grade and used without further purification.

2.2 Antioxidant recovery by microwave-assisted extraction and inlet suspension preparation

The liquid extract used for spray drying tests was obtained from dried spent coffee grounds collected from common vending coffee machines and a mixture of ethanol:water (54:46 v/v) as solvent. The extraction was carried out in a professional multimode oven operating at 2.45 GHz (MicroSYNTH, Milestone, Italy) at 150°C, utilizing a solvent solid ratio (L/S) of 10 mL/g for 90 minutes. The extract was centrifuged at 6000xg for 10 min (ALC PK131, Alberta, Canada) and filtered through at 0.45 μm filter. Then the extract was diluted with deionized water (1:2 v/v) and stored at -18±1°C for further operations.
Feed suspension for each spray drying test was prepared adding 5.0 g ±0.1 of coating agent to 50 mL of the diluted extract; the composition of the coating agent in each test is reported in **Table 1** as percentage of inulin (I%). The suspension was left for 10 min at 50°C under stirring in order to promote coating agent dissolution.

Table 1.Value of the two input variables at the corresponding design level

Variable	Level -1	Central point	Level +1
I (%, wt)	*20*	*50*	*80*
Flow rate (mL/min)	*5*	*7.5*	*10*

2.3 Experimental Design and spray drying tests

Spray drying of spent coffee grounds extract was performed using a Büchi Mini Spray Dryer B-290 (BÜCHI Labortechnik AG, Flawil, Switzerland). In order to investigate the effects of coating agent composition (I%) and of the inlet flow rate (FR) the tests were planned by means of the software Design Expert. The two variables were coded into 3 levels (-1,0,+1) and the corresponding value are reported in **Table 1.**

The number of the experiments and the corresponding value of the input variables for each test were established by the 3-level factorial logic, chosen among the response surface methodologies allowed by the program. The other operating conditions were always maintained at the following values: air flow rate 30 m^3/h; inlet air temperature 160°C; coating agent concentration 100 g/L. Response surface methodology was employed for data treatment and the influence of the parameters was assessed by analysis of variance (ANOVA). Four response variables were chosen to evaluate the input variables effect: encapsulation yield (EY), expressed as milligrams of equivalent caffeic acid per gram of dried powder (mg_{CAE}/g_{DP}); powder moisture (%), product recovery (%), expressed as grams of dried powder per grams of dried solids (g_{DP}/g_{DS}) and encapsulation efficiency (%).

2.4 Analytical methods

Moisture (%) was determined after drying powder samples in an oven at 110 °C until a constant weight. The moisture content of microparticles was calculated based on the loss in weight between powders before and after drying.
Encapsulation yield (EY, mg_{CAE}/g_{DP}), shown in Eq.(1), was determined as difference between the total phenolic compounds (TPC, $mg_{CAE}/g_{\text{WET POWDER}}$) and surface phenolic compounds (SPC, $mg_{CAE}/g_{\text{WET POWDER}}$), extracted from the powder by the methods described by Robert et al. (2010).

$$EY = \frac{(TPC-SPC)}{(1-Moisture)} \tag{1}$$

The amount of polyphenols (TP) in both cases was measured through a colorimetric method using the Folin–Ciocalteau assay **(**Swain & Hillis, 1959). The calibration curve was made with standard solutions of caffeic acid and measures were carried out at 725 nm using a UV–Vis spectrophotometer (model Lambda 25, Perkin Elmer, Wellesley, MA, USA). The same assay was used for the calculation of TP of the spent coffee grounds extract (EPC) before spray drying. In this case, TP yield was expressed as milligrams of equivalent caffeic acid per gram of dried biomass (mg_{CAE}/g_{DB}). The method response was described with a linear equation (Absorbance at 725 nm=0.0023×Concentration) using standard methanolic solutions of caffeic acid (10-1000 µg/mL), with a R^2 of 0.9993.
Product recovery was calculated as reported in Eq.(2):

$$\text{Product recovery} = \frac{\text{mass of dried powder}}{\text{mass of coating agent+dried extract residue}} \tag{2}$$

Where dried extract residue was obtained drying 2 mL of the diluted extract at 110°C until constant weight.
Encapsulation efficiency has been evaluated according to Eq.(3):

$$\text{Encapsulation efficiency} = \frac{\text{mass of encapsulated polyphenols}}{\text{mass of polyphenols in the feed}} \tag{3}$$

3. Results and discussion

Folin-Ciocalteau's assay on the diluted extract revealed an amount of total polyphenols content of 30±0.9 mg_{CAE}/g_{DB}, while the dried extract residue resulted of 9.97±0.22 mg/mL.
Experimental Design led to 11 tests, among them central point was repeated 3 times. Response surface methodology showed that a polynomial fitting of the response variables resulted not to be significant for what concerns the responses moisture and product recovery. Although statistical design demonstrated that the data could be fitted for the variables EY (*p*-value 0.0442) and encapsulation efficiency (*p*-value 0.0394) according to the fitting models Eq.(4) and Eq.(5), respectively, no terms of both the equations resulted significant and the R^2 (0.72 for Eq.(4), 0.71 for Eq.(5)) highlighted low accuracy.

$$EY= -0.11 \cdot I +2.9 \cdot \text{Flow rate} +1.4 \cdot 10^{-3} \cdot I^2 -0.19 \cdot \text{Flow rate}^2 \tag{4}$$

$$\text{Encapsulation efficiency} =-5.5 \cdot 10^{-3} \cdot I+0.16 \cdot \text{Flow rate}+ 7.37 \cdot 10^{-5} \cdot I^2- 0.01 \cdot \text{Flow rate}^2 \tag{5}$$

Then, it is possible to assess that the range of value of the variables and the polynomial fitting of data did not allow a good description of experimental data.
Figure 1 shows the moisture as a function of the input variables. It can be observed that the values ranged between 5.3 % and 7.0 %, and then it is quite constant in the considered design space.

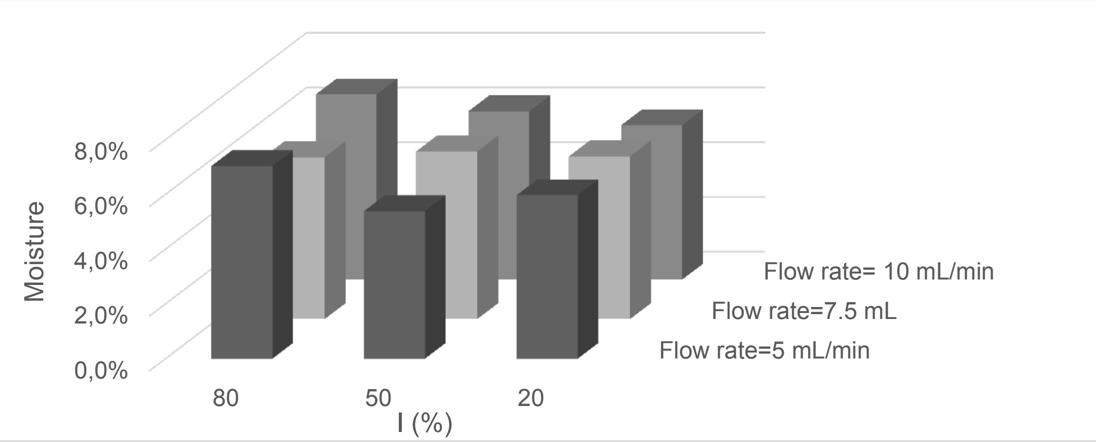

Figure 1: Spray-dried powder moisture as a function of the composition of the wall material, expressed as percentage of Inulin (% wt) and as a function of the inlet suspension flow rate (mL/min).

A similar trend is reported in Figure 2 for what concerns product recovery: the responses at the input variables resulted not statistically significant (p>0.05) and all the values are around 0.79 g_{DP}/g_{DS}.. Then, only the 20% of the total load solids was lost during spray drying.

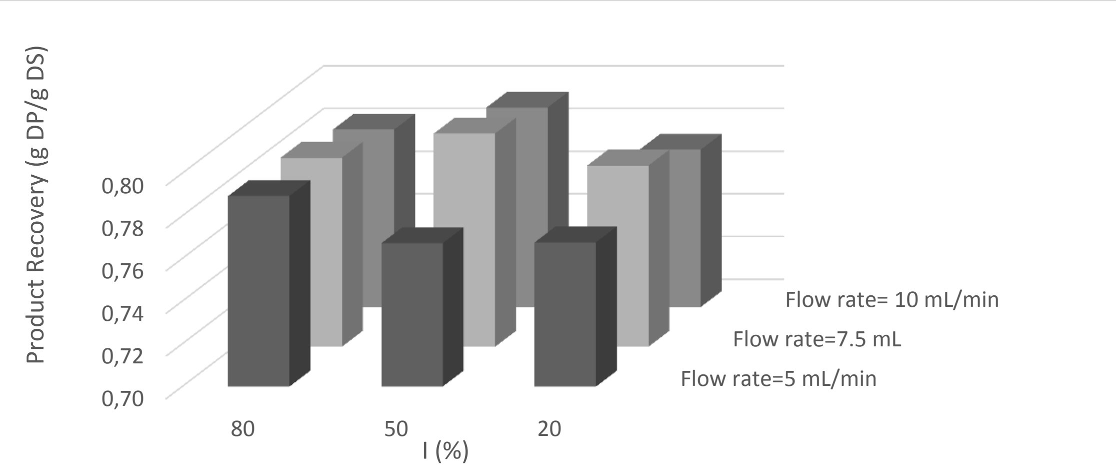

Figure 2: Product recovery as a function of the composition of the wall material, expressed as percentage of Inulin (%, wt) and as a function of the inlet suspension flow rate (mL/min).

Encapsulation yield is reported in Figure 3. Its values range from 7.2 to 10.8 mg_{CAE}/g_{DP}. In this fraction the amount of superficial polyphenols was not taken into account, but only the aliquot trapped inside the particles. Total polyphenols found in the powder was from 8.5 to 13.3 mg_{CAE}/g_{DP} and the highest values belong to the powder built with the 80% of Inulin and the 20% in weight of MD. Obviously, also the highest encapsulation efficiencies (62%, 63%, 58%) correspond to the same wall material composition, but no dependence on flow rate was observed (Figure 4). Fernandes et al. (2014) encapsulated rosemary essential oil using spray dryer. They reported that the increase of the ratio inulin/gum arabic in the carrier led to a lower encapsulation efficiency. Also from the study of Bakowska-Barczak & Kolodziejczyk (2011) the inulin was less effective in encapsulation of black currant polyphenols than maltodextrin. The difference can be due to the nature of the fed extract and particularly to the presence of ethanol in the loaded suspension of this study, in addition to the dissimilar operating conditions used during spray drying. Total efficiencies, which include also superficial polyphenols, for tests with Inulin 80% wt were 72, 73 and 68%. This means that about 30% of the polyphenols loaded with the suspension was lost in the device (product loss is about 20%) and because of the thermal treatment.

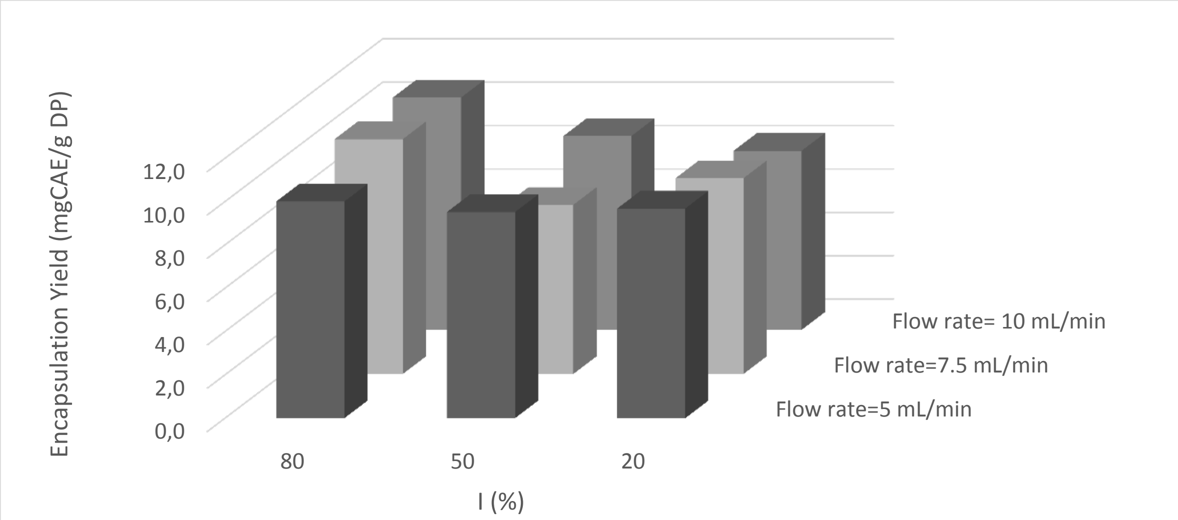

Figure 3: Encapsulation yield (mg$_{CAE}$/g$_{DP}$) obtained from spray drying of spent coffee grounds extract varying inlet suspension flow rate (mL/min) and carrier composition (I, % wt).

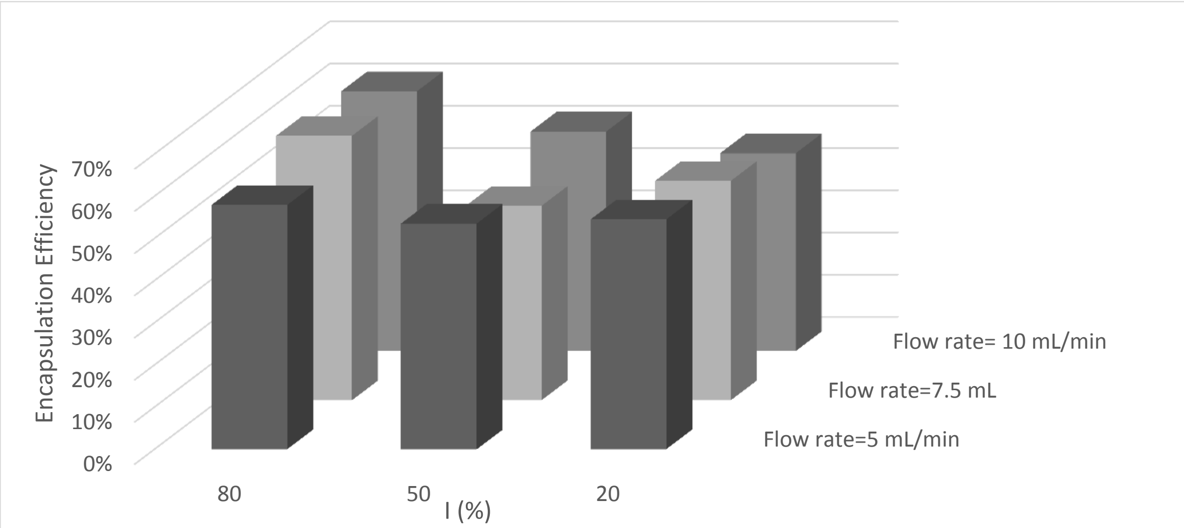

Figure 4: Encapsulation efficiency (mg$_{CAE}$/g$_{DP}$) obtained from spray drying of spent coffee grounds extract varying inlet flow rate (mL/min) and carrier composition (I, % wt).

4. Conclusions

Encapsulation of antioxidants extracted from spent coffee grounds is a necessary technique to preserve the activity of the bioactive compounds during storage. In this work, the effect of the inlet suspension flow rate and wall material composition on spray-dried product was analyzed. Although the response surface methodology resulted not suitable for process optimization in the range of value chosen for the input variables, the study indicated that in the range of flow rate (5-10 mL/min) and varying the composition of the carrier from 20:80 to 80:20 (I:MD wt/wt) no effect are highlighted on the product recovery and product moisture. The presence of inulin, instead, increased the polyphenols encapsulation efficiency, while flow rate seemed to be less influent on the process, in the range of value investigated. Maximum encapsulation efficiencies (63% and 62%) was achieved using a carrier composition of 80% wt of inulin and at the highest inlet flow rates of 7.5 mL/min and 10 mL/min, respectively.

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