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The Effects of Maltodextrin and Gum Arabic on Encapsulation of Onion Skin Phenolic Compounds

Busra Akdeniz, Gulum Sumnu*, Serpil Sahin

Department of Food Engineering, Middle East Technical University, 06800, Ankara, Turkey
gulum@metu.edu.tr

In this study, the effect of coating material and core to coating ratio on the encapsulation of phenolic compounds extracted from the onion skin was investigated. As coating material maltodextrin and gum arabic at different ratios were chosen (10:0, 6:4 and 8:2). The core to coating ratios were 1:10 and 1:20. The microcapsules were prepared with high speed homogenizer at 10000 rpm for 10 min. The freeze dried microcapsules were analysed in terms of encapsulation efficiency, antioxidant activity and particle size distribution. The encapsulation efficiencies were mostly lower when core to coating ratio was 1:10 as compared to the core to coating ratio of 1:20. There was positive correlation between total phenolic content and antioxidant activity. The ratio of maltodextrin and gum arabic had significant effect on encapsulation efficiency, however antioxidant activity values did not change significantly with different ratios. As core to coating ratio increased, the size of microcapsules were found to be larger. Maltodextrin and gum arabic ratio had also significant effect on particle size distribution.

1. Introduction

In plant metabolism, secondary pathways participate in physiology and cellular metabolism and generate unique compounds like terpenoids, phenolics and alkaloids (Rosa et al. 2010). These compounds generally have aromatic ring carrying one or more hydroxyl group (Robards et al. 1999). Phenolic compounds are the most important group of plant secondary metabolites. Phenolic compounds have powerful antioxidant properties (Balasundram et al. 2006). In addition, phenolic compounds exhibit various physiological properties like anti-microbial, anti-inflammatory, anti-carcinogenic, anti-allergenic, anti-mutagenic and anti-thrombotic effects (Balasundram et al. 2006; Robards et al. 1999). Phenolic substances can be classified into different groups including phenolic acids, lignins, stilbenes and flavonoids with regard to the number of phenol rings and the structural elements binding these rings (Fraga, 2010).

Encapsulation is a process in which one material is entrapped or coated with another material in order to protect the coated material against adverse conditions and the nutritional deterioration. The coated one is named as core or active material and the surrounding one is coating material (Mcnamee et al.1998). In addition to protection, by encapsulation process, controlling the release of core material and masking the undesired properties of core material can be achieved (Dubey et al. 2009).

Coating materials have significant role in stability of the encapsulation process. Different kinds of coating materials are used for encapsulation process such as polysaccharides, proteins and lipids (Mcnamee et al., 1998). Maltodextrin has good solubility in water and low viscosity values even at high concentrations. These properties make maltodextrin useful for coating material. On the other hand, maltodextrins are deficient in terms of emulsification property and surface-active features. For this reason, combining other coating materials with maltodextrin is required to form stable capsules (Rosenberg and Sheu, 1995). Gum arabic (Gum acacia) is composed of branched arrangement of simple sugars like galactose, glucuronic acid, arabinose and rhamnose and small amount of covalently bonded protein. This protein gives functional properties to gum arabic (Mcnamee et al., 1998). It has high water solubility and low viscosity than other gum types (Madene et al. 2006). In addition, it can create a protective film around core material and acts like emulsifier. In other words, it prevents aggregation by forming a thick layer (Zuidam and Nedović, 2010)

Onion (*Allium cepa*) which contains various kinds of health promoting phytochemicals is one of the most consumed vegatable in the world (Albishi et al. 2013). There are flavonoid molecules in onion. In industrial scale, onion has large amount of wastes which are onion skin, roots or damaged bulbs. Flavonoid levels in the onion skin which is about 2-10 g/kg is higher than flavonoid level of edible part. Onion skin contains mostly glycosides of quercetin derivatives like quercetin diglucoside and quercetin acyclone. This components provide antioxidant and radical scavening acitivity. In addition, onion skin contains various kinds of other flavonoids such as; isorhamnetin, kaempferol and myricetin derivatives (Albishi et al. 2013; Suh et al. 1999).
There is no research in literature about encapsulation of phenolic compounds from onion skin. The objective of this study was to encapsulate phenolic compounds extracted from onion skin. Moreover, the effects of core to coating ratio and coating materials with different ratios were investigated in terms of encapsulation efficiency, antioxidant activity and particle size distribution.

2. Materials and Methods

2.1 Materials

Onion skin was taken from the local market in Ankara. Maltodextrin whose Dextrose Equivalent (DE) value was 4.0-7.0, and gum arabic were the coating materials and purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). The reagents used in the experiments, which were acetic acid, ethanol, methanol, gallic acid, sodium carbonate, DPPH˙ (2,2-diphenyl-1-picrylhydrazyl), Folin-Ciocalteau's phenol reagent were all bought from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA).

2.2 Extraction of phenolic compounds and phenolic powder preparation

The extraction was done in shaking water bath (GFL 1086, Burgwedel, Germany) at 40 °C and 70 rpm for 4 hours using 20 g of grounded onion skin and 400 ml of ethanol water (50:50 v/v) mixture. Then the extract was vacuum filtered using micro filter paper (Whatman 4, GE Healthcare UK Limited). The filtered extract was concentrated at 35°C by means of rotary vacuum evaporator (Heidolph Laborota 4000 efficient, Schwabach, Germany). Then, samples were dried by freeze dryer (Christ, Alpha 1-2 LD plus, Osterode, Germany) below 0.1 mPa for 48 hours. At the end of drying, onion skin phenolic powder was stored at freezer at -18°C until it was used.

2.3 Preparation of coating materials for microcapsules

Maltodextrin solutions with 10%, 12% and 16% (w/w) concentrations were prepared with high speed homogenizer at 7000 rpm for 3 min. In addition, 4% and 8% (w/w) gum arabic solutions were prepared with again high speed homogenizer at 6000 rpm for 4 min. Coating solutions were prepared 1 day before the encapsulation process to obtain full hydration and they were stored in refrigerator at 4°C.

2.4 Encapsulation

Phenolic powder of onion skin of 2 g and 1 g were separately weighed for encapsulation with 1:10 and 1:20 core to coating ratio, respectively. Then, 20 g of required coating material was added into it. In order to get capsules, the mixtures were homogenised by a high-speed homogenizer (IKA T25 digital Ultra-Turrax, Selangor, Malaysia) at 10000 rpm for 10 min. Then, capsules were freeze dried for 48 hours.

2.5 Encapsulation efficiency

The encapsulation efficiency (EE) was calculated using Eq (1);.

$$EE(\%) = \frac{EPC}{TPC} \times 100 = \frac{TPC - SPC}{TPC} \times 100 \quad (1)$$

where EPC was the encapsulated phenolic content which was calculated by substracting total phenolic content (TPC) from surface phenolic content (SPC). The TPC and SPC were determined by Folin-Ciocalteau method (Cilek et al. 2012).

2.6 Antioxidant activity

For determining total antioxidant activity (AA), DPPH˙ (2,2-Diphenyl-1-picrylhydrazyl) method was used (Yen and Duht, 1994). 100 mg of dry microcapsule was weighed and mixed with 1 mL ethanol:acetic acid:water mixture (50:8:42 v/v).Then the mixture was filtered through a filter whose pore size is 0.45 µm (Gema Medical Filter, Spain). Then, samples were diluted with ethanol:acetic acid:water mixture (50:8:42 v/v). Pure methanol was used as a blank. 100 µl methanol and 3.9 ml of 25 ppm DPPH˙ solution was mixed and absorbance was measured by UV/VIS spectrophotometer T 70 (PG Instruments LTD, UK) at 517 nm and was recorded as A_1.

Diluted sample of 100 µl and 3.9 ml of 25 ppm $DPPH^{\cdot}$ solution were mixed and kept in dark for 1 hour at 25°C. After 1 hour, the absorption values were recorded as A_2 . A_1 and A_2 values can be converted to concentrations of C_1 and C_2 by calibration curve. The antioxidant activity was calculated with Eq (2);

$$AA \text{ (mg } DPPH^{\cdot}\text{/ g dry weight)} = \frac{(C_1 - C_2)}{W} \times D \times V \quad (2)$$

where V is the volume of extract in mL, D is the dilution rate, W is the amount of dry sample in g.

2.7 Particle size analysis

Particle size analysis of emulsions were performed by using particle size analyser (Mastersizer 2000, Malvern Instruments, Worcestershire, UK). Sauter mean diameter D32 in µm Eq (3), span Eq (4) and specific surface area in m^2/g values were calculated by the instrument (McClements, 2005).

$$D32 = \frac{\sum n_i \, d_i^3}{\sum n_i \, d_i^2} \quad (3)$$

$$Span = \frac{[d(v,90) - d(v,10)]}{d(v,50)} \quad (4)$$

where, d_i is the diameter and n_i is the number of particles in each size and d(v,90), d(v,50), d(v,10) are the diameter values at 90%, 50% and 10% of the cumulative volume, respectively.

2.8 Statistical analysis

The analysis of variance (ANOVA) was applied by MINITAB (Version 16) in order to determine if there is significant difference between coating material types and ratios. Tukey's Multiple Comparison Test was used for comparisons ($p \leq 0.05$). All results were replicated twice for each variable.

3. Results and discussion

3.1 Encapsulation efficiency

As can be seen in Figure 1, the efficiency value was higher in capsules with core to coating ratio of 1:20 and maltodextrin gum arabic ratio of 10:0 and 6:4. Since the concentration of phenolic powder without coating was higher in capsules with core to coating ratio of 1:10, coating material was not enough to envelop the core material as compared to capsules with core to coating ratio of 1:20. As core to coating ratio increased, the encapsulation efficiency decreased in literature (Cilek et al. 2012; Turasan et al. 2015). Coating material type had a significant effect on encapsulation efficiency.

The highest efficiency values were found when only maltodextrin was used as a coating material in the case of both core to coating ratios. In 1:10 core to coating ratio, efficiency values increase with decreasing gum arabic concentration, the reverse condition was found in 1:20 ratio capsules. The optimum maltodextrin gum arabic ratio differed in two different core to coating ratio. Gum arabic had emulsifying and stabilizing ability on encapsulation procedure. Moreover, it could form strong protective matrix around the core material, this resulted in higher encapsulation efficiency values with increasing gum arabic concentration in coating material (Madene et al. 2006; Mcnamee et al. 1998). In microcapsules with 1:10 core to coating ratio, the opposite behaviour of encapsulation efficiency was explained with the inefficient mixing due to highly viscous solution.

3.2 Antioxidant activity

Total phenolic content and antioxidant activity results were correlated with correlation coefficient of 0.795 ($p=0.002$). The correlation between phenolic compounds and antioxidant activity have been observed by other researchers also (Cordenunsi et al. 2005; Nile and Park, 2016; Somawathi et al. 2014).

As expected, microcapsules with 1:10 core to coating ratio had higher antioxidant activity than the ones prepared with 1:20 core to coating ratio. As seen in Figure 2, maltodextrin gum arabic ratio had no significant effect on antioxidant activity values.

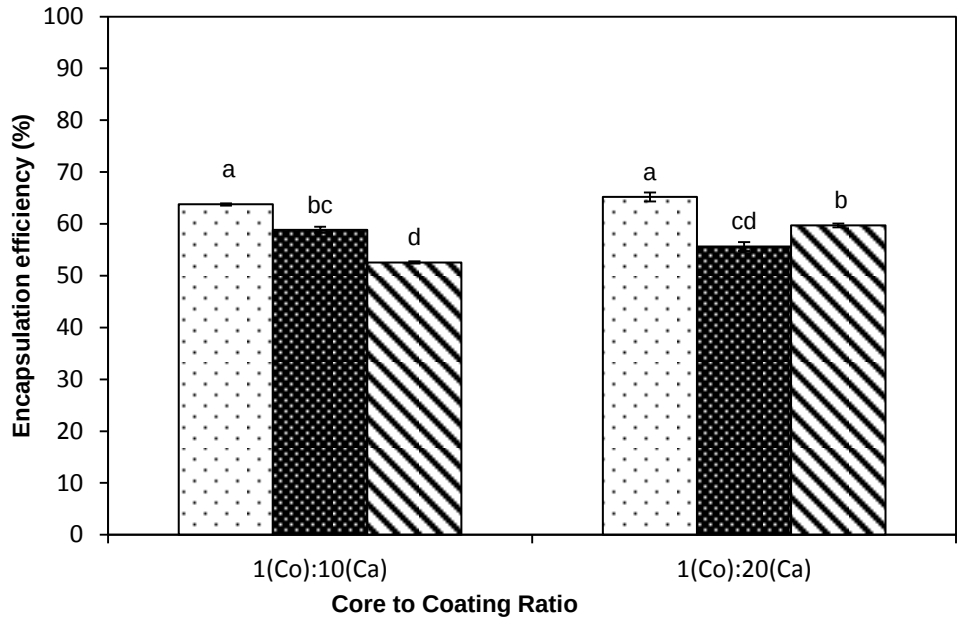

Figure 1: The encapsulation efficiency values of microcapsules with core to coating ratio of 1:10 and 1:20 and coating with different MD: Gum arabic ratios ; 10:0 ( ), 8:2 ( ) and 6:4 ( ) Different letters shows significant difference (p ≤ 0.05)

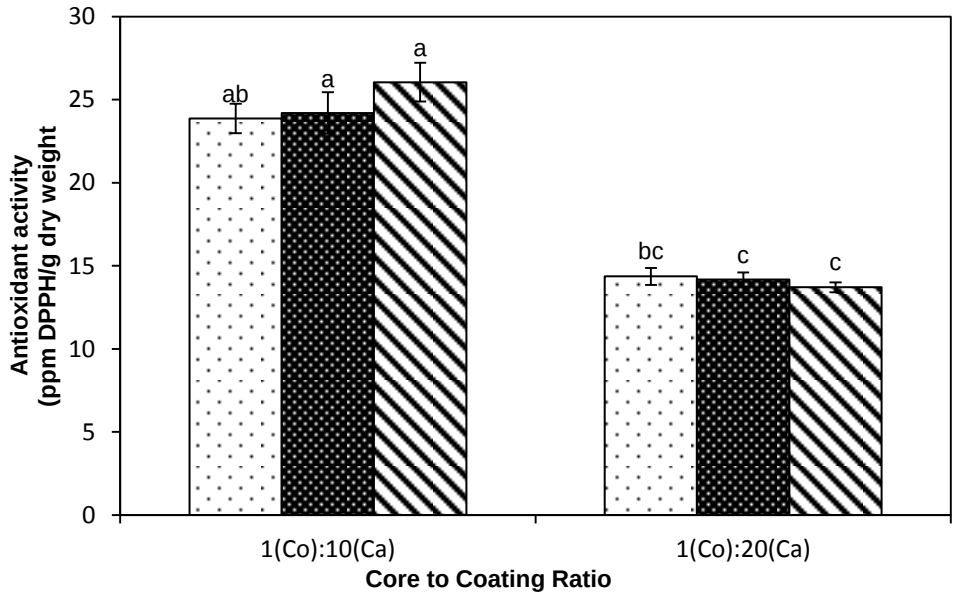

Figure 2: The antioxidant activity values of microcapsules with core to coating ratio of 1:10 and 1:20 and coating with different MD: Gum arabic ratios ; 10:0 (8:2 ( ) and 6:4 ( ). Different letters shows significant difference (p ≤ 0.05)

3.3 Particle size analysis

Capsules with 1:20 core to coating ratio had smaller Sauter mean diameter (D32) value than those with 1:10 core to coating ratio. It was shown that average particle size value increased with increasing core:coating ratio

in literature (Hogan et al. 2001). Since core material concentration increased, the coating material was insufficient to encapsulate it and this resulted in coalescence of particles and larger droplet size.

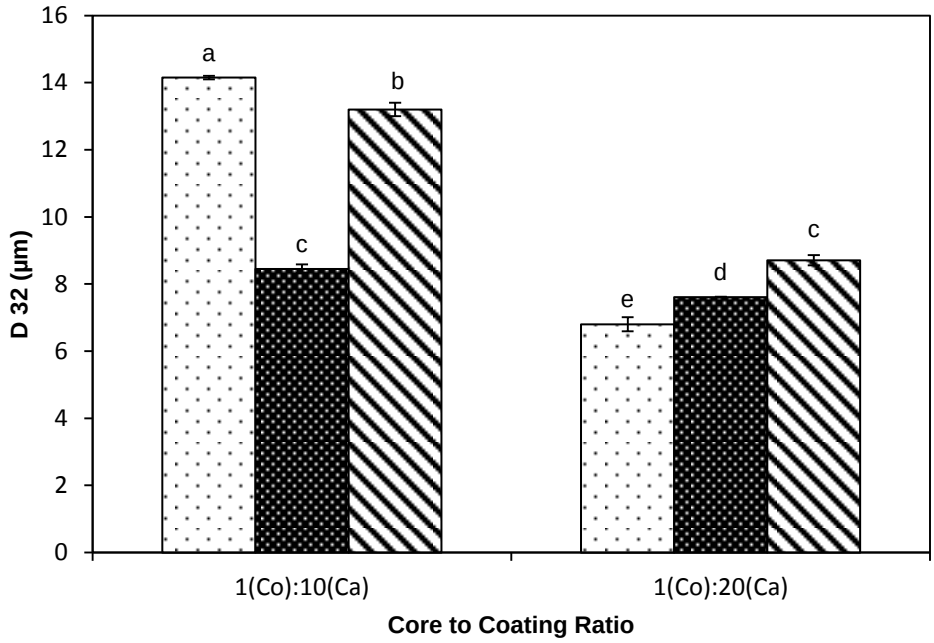

Figure 3: Sauter mean diameter of microcapsules with core to coating ratio of 1:10 and 1:20 and coating with different MD:Gum Arabic ratios; 10:0 ( ), 8:2 ( ) and 6:4 ( ). Different letters shows significant difference (p ≤ 0.05)

Table 1 showed that the span and specific surface area values. As can be seen from Table 1, specific surface area and span values of 1:10 core to coating capsules were lower than capsules having 1:20 core to coating. The increasing particle size resulted a decrease in specific surface area value.

Table 1: Particle size analysis of capsules having different maltodextrin:gum arabic ratio and core to coating ratio

Core to coating ratio	Maltodextrin: Gum Arabic ratio	Span	Specific surface area(m^2/g)
1:10	10:0	$1.52\pm0.05^{c*}$	$0.42\pm0.002^{d*}$
1:10	8:2	3.76 ± 0.05^{ab}	0.71 ± 0.010^{c}
1:10	6:4	3.09 ± 0.39^{ab}	0.46 ± 0.007^{d}
1:20	10:0	2.40 ± 0.02^{bc}	0.92 ± 0.009^{a}
1:20	8:2	4.40 ± 0.17^{a}	0.79 ± 0.001^{b}
1:20	6:4	3.47 ± 0.01^{abc}	0.81 ± 0.006^{b}

*Different letters within the same column shows significant difference (p ≤ 0.05)

4. Conclusion

In this study, in order to get the best encapsulation formulation, onion skin phenolic powder was coated with different ratios of maltodextrin and gum arabic combinations and different core to coating ratios. Among two different core to coating ratio, 1:20 ratio had the highest encapsulation efficiency values and lower particle size than core to coating ratio of 1:10. By changing the ratio of maltodextrin and gum arabic as a coating material coating material combination ratios, statistically different particle size distribution could be obtained. Usage of gum arabic did not affect antioxidant activity significantly. For the future study, encapsulated phenolic powder can be added to a food material in order to utilise high amount of phenolic compounds of onion skin.

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