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Original Article

Physicochemical Properties and Stability of Encapsulated *Ferulago angulata subsp. carduchorum* Essential Oil using Polymer Coating

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Abstract

Nowadays, the tendency to use natural preservatives such as essential oils instead of synthetic additives has increased. Due to the volatile compounds of essential oil; encapsulation is an appropriate method to preserve voletile and phenolic compounds, *Ferulago angulata* subsp. *carduchorum* (Boiss. & Hausskn.) D.F.Chamb. is a native medical plant in the west of Iran. The aim of this study was to determine physicochemichal properties of encapsulated *F. angulata* subsp. *carduchorum* essential oil using Maltodextrin 20% and Maltodextrin 20%+Arabic gum 20% and Modified starch 20% + Maltodextrin 20%. The coating process was performed by spray dryer. The efficiency of the coating process was 59-89%. The antioxidant activity was carried out by ABTS method and the highest percentage of free radical scavenging was related to Maltodextrin 20% + Arabic gum 20% containing 3% essential oil and the obtained result was 52.81%. The highest content of total phenolic compounds was 66.88 mg/mL belonged to Maltodextrin 20% + Arabic gum 20% containing 3% essential oil ($P< 0.05$). The microstructure of the encapsulated essential oil was characterized using scanning electron microscopy (SEM) and dynamic light scattering technique (DLS) and the presence of the essential oil in the microencapsules was confirmed by fourier-transform infrared spectroscopy (FTIR). The results of the electron microscopy showed the effective and useful role of modified starch in creating a uniform, crack-free structure. The results of the DLS test indicated that the largest sample in terms of sample size was Maltodextrin 20% + Arabic gum 20% containing 3% essential oil. The most significant change in the spectrum of chemical structure in FTIR test was related to Maltodextrin 20% + Arabic gum 20% microcapsule. Results of density test of microcapsules showed that the lowest density was related to Maltodextrin 20% + Arabic gum 20% containing 3% essential oil (0.25 g /cm^3). The stability of microcapsules in different environments was evaluated by pH test and the results showed that the most stable microcapsules in alkaline conditions were Maltodextrin 20% + Arabic gum 20% containing 3% essential oil. Therefore, the 3% essential oil coated by Maltodextrin and Arabic gum was selected as the best treatment for protection of essential oil compounds.

Keywords: Essentional oil, Encapsulation, Physicochemical, *Ferulago angulata* subsp. *Carduchorum*

Introduction

Ferulago angulata subsp. *carduchorum* (Boiss. & Hausskn.) D.F.Chamb. is known as a native plant that grows in the west of Iran and it was used as a natural preservative to delay meat spoilage [1]. Essential oils are volatile compounds responsible for fragrance and functional properties, which are unstable in the presence of oxygen, moisture and heat [2]. Microencapsulation of these ingredients before adding to the food products is a way to reduce the degradation or loss of flavor and fragrance during storage and processing, as well as controlling their release during consumption. The microencapsulation of fragrance materials preserves the aromatic substance, which is released at a particular time or place [3]. The microencapsulation is a process in

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which solid, liquid, or gas components are encapsulated in a small capsule as its content released at a controlled condition [4]. The core materials such as volatile oils, color-generating materials, enzymes, etc., are surrounded by wall substances, which can be a variety of proteins, carbohydrates, or lipids and are protected against external factors [5]. The main purpose of this method is to increase product life. Some advantages of the microencapsulation include protecting the core substances from adverse effects of biological conditions, such as light, moisture, and oxygen and reducing speed transfer of the core substances to the external environment by modifying the physical properties of the main substances, and optimizing the release of the core substances [6].

The microencapsulation methods are performed in a variety of methods including emulsification, coacervation, spray drying, spray cooling, freeze drying, and encapsulation by fluid bed and extrusion [7]. The spray drying is a dominant method for production of microcapsules. In this continuous process, the spray of emulsions on wall droplet is used with high level exchange for heat and mass transfer as contacting with hot air. The solvent evaporation in this method from the initial droplets is very rapid. The waste of volatile compounds may occur during the early stages of droplet formation and drying prior to the formation of a dry surface layer of molecule preservation. The main factor for the loss of aroma molecule is related to the combination of the wall substances, molecular weight, relative volatility, polarity type, and the aroma/wall ratio. The optimum conditions depend on the spray state and rapid drying of the initial drop compared to the emulsion properties as high total solid content and small size. The nature and quality of the wall substances are important for optimal dosage, and are considered as a good protector against the moisture and oxygen maintenance and for durability. The properties of the wall substances vary with the molecular weight and stability against temperature. The wall substances may be hydrophilic and hydrophobic with emulsifying properties. The main polysaccharides include cellulose, proteins, gums, fats, waxes, ester of glyceride acids, and modified starch alone or in combination [8]. The Arabic gum is regarded as one of the most common wall substances used in the microencapsulation with spray-drying. The polymeric arabic gum contains D-gluconic acid, L-rhamnose, di-galactose and L-arabinose, containing approximately 2% protein, and creating stable emulsion with most oils. Maltodextrin is a hydrolyzed starch obtained by partial hydrolysis of starch with acid or enzyme, which is commonly used as wall substances in the microencapsulation of food combinations. This combination has advantages such as low cost, natural aroma and taste, low viscosity at high concentration and good taste protection against oxidation. However, the greatest limitation of the wall substances is the low emulsification capacity and low residual level of volatile substances [2].

The aim of this study was to determine physicochemical and antioxidant properties of encapsulated *F. angulata* subsp. *carduchorum* essential oil which has been extracted from native plant of Iran using different wall substances to increase stability and shelf storage of the essential oil.

Material and Methods

In this section, material preparation include, microencapsulation, maltodexterin, modified starch preparation and the determination of spray dryer efficiency, total phenolic content, mass density of the powders, moisture of the powders, and also characterization analysis and the effect of pH and antioxidant activity will be described.

Materials Preparation

In the present study, chemicals such as Folin Ciocalteau reagent, potassium sulfate, sodium carbonate from Merck Company (Germany) and ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid), and Tween 20 provided by Sigma-Aldrich (Germany) with laboratory purity. Further, Maltodextrin, Arabic gum, and sunflower oil were prepared from domestic brands and modified starch was purchased from Cargill Company (USA). The mini spray dryer B-290 (BUCHI brand) from Germany was used for preparing microcapsules.

Essential oil Preparation

The essential oil was prepared as previously described by Golfakhrabadi *et al*. (2015), the ground aerial parts of *Ferulago angulata* subsp. *carduchorum* (Boiss. & Hausskn.) D.F.Chamb. (150 g) and 1,000 mL distilled water were placed in a Clevenger Apparatus and distilled by hot water [1].

Microencapsulation

The substances used as a wall or cover in microencapsulations with spray-drying should be well-soluble in water. For this reason, substances such as Arabic gum, Maltodextrin, modified starch, and their mixture were used in this method. The microencapsulation with spray drying was considered as the most common method of preserving active and sensitive substances [9]. The operating conditions of the spray dryer after the initial tests and reaching the optimum conditions were set as inlet temperature: 130-135°C, outlet temperature: 80-85 ºC, Nozzle diameter 6-7, dry air flow 700 L/h, Aspirator 90% and pump speed 15%. The solutions were prepared as follows:

Maltodextrin (20 g) was slowly added to distilled water (100 mL) on the stirrer (MTops brand, MS300HS model) at medium speed at ambient temperature until it was thoroughly mixed to prepare a 20% Maltodextrin solution. 20 g of arabic gum was gradually added into the beaker containing 100 mL distilled water on the stirrer (MTops brand) with medium speed at ambient temperature until it was thoroughly blended to obtain 20% arabic gum solution. Modified starch was also prepared as 20% starch solution. The obtained emulsions were kept in the refrigerator for a full day to be hydrated.

The ratio of the composition of the raw material used for each treatment during the spray drying process has been classified to 1-9 items:

1. 100 mL Maltodextrin 20% (MD)
2. 100 mL Maltodextrin 20% + 1mL Essential oil + 4 mL Tween 20 + 5 mL sunflower oil (MD1%)
3. 100 mL Maltodextrin 20% + 3 mL Essential oil + 4 mL Tween 20 + 5 mL sunflower oil (MD3%)
4. 50 mL Maltodextrin 20% + 50 mL Arabic gum 20% (MG)
5. 50 mL Maltodextrin 20% + 50 mL Arabic gum 20% + 1 mL Essential oil + 4 mL Tween 20 + 5 mL sunflower oil (MG1%)
6. 50 mL Maltodextrin 20% + 50 mL Arabic gum 20% + 3 mL Essential oil + 4 mL Tween 20 + 5 mL sunflower oil (MG3%)
7. 50 mL Maltodextrin 20% + 50 mL Modified Starch 20% (MS)
8. 50 mL Maltodextrin 20% + 50 mL Modified Starch 20% +1 mL Essential oil + 4 mL Tween 20 + 5 mL sunflower oil (MS1%)
9. 50 mL Maltodextrin 20% + 50 mL Modified Starch 20% +3 mL Essential oil + 4 mL Tween 20 + 5 mL sunflower oil (MS3%)

Determination of spray dryer efficiency

In order to determine the process efficiency, the weight of the microencapsuls obtained from the spray dryer was gained and the percentage was calculated in relation to the initial amount of solid existing in the solution fed to the dryer device [9].

Determination of Total Phenolic Content

The total phenolic compounds were measured by Folin Ciocalteau colorimetric method. First, 0.1 mL of the free and microencapsulated essential oil solution was mixed with 0.5 mL of Folin reagent and 7 mL of distilled water and was placed at ambient temperature for 8 min. Then, 1.5 mL of 20% sodium carbonate and distilled water was added and after mixing was kept at ambient temperature and away from light for 2 h and then, their absorbance was determined at 765 nm. Gallic acid was used as standard and the total phenolic compounds were calculated based on the equivalent of gram of gallic acid [9].

Determination of Antioxidant Activity

The ABTS method was used in the present study to evaluate the antioxidant capacity of the essential oil of *F. angulata* subsp. *carduchorum* and its microencapsuls. The ABTS radical was obtained by dissolving in water and in exposure to potassium persulfate for 12-16 h. Then, the absorbance was determined at 734 nm with the presence of the samples for 5 min using ELISA Plate Reader [9].

Determination of Mass Density of the Powders

The mass density of the powders, defined as the weight of a specific volume of powder, was described based on the hitting method. Approximately 0.5 g of powder was placed in a scaled cylinder. Then, the cylinder was hit by hand on a flat surface until it reached a fixed volume. The volumetric density was determined by following formula:

(1) $P=M/V$

Where P represents mass density, M displays the sample mass, and V indicates the mass volume of sample [10].

Determination of Mass Moisture of Powders

For this purpose, 1 g of microcapsules obtained from the microencapsulation process was situated in oven at 70 °C for one day. After drying the samples at ambient temperature in the desiccator, the moisture rate was determined using the following equation [11].

(2) $\text{Moisture percentage} = \frac{\text{Moisture weight}}{\text{Raw sample weight}} \times 100$

The encapsulation efficiency (EE) is calculated by the quotient of the mass of prepared microcapsules to the total mass of solids before microencapsulation [12].

(3) $\text{EE} = \frac{\text{Encapsulated amount of essential oil}}{\text{Initial amount of essential oil}} \times 100$

Particle size and morphology of micro-capsules

Scanning electron microscopy (SEM) was used to observe the microstructure of the prepared microcapsules. A small amount of the sample was placed on aluminum acetate using silver glue and then situated in covering device by a thin layer of gold for 6 min to be conductive. The samples were transferred to a vacuum module. Radiuses of 20 kV accelerating electrons were emitted to the samples and the image was obtained based on the electron radius returned from the samples [13].

Fourier Transform Infrared Spectrum (FTIR)

The infrared spectrometer was used by spectrophotometer to analyze the chemical structure of the microcapsules. The wavelength range was 4,000 -500 cm^{-1} [13].

Differential Scanning Calorimetry (DSC) Analysis

Thermal analysis of the samples was performed by differential scanning calorimetry. An amount of 4 - 8 mg of each sample was placed in an aluminum plate and the

device was heated at a constant speed of 10 °C / min in a range of 30 - 400 °C under a nitrogen atmosphere with a flow of 20 mL / min [13].

Determining the Particle Size Using Dynamic Light Scattering (DLS)

Dynamic light scattering was used to study the size of the produced capsules [14]. The concentrations obtained from samples were prepared and the device conditions were set at 532 nm laser wavelength, temperature of 25 ˚C for took 10 min and samples were repeated three times as shown in Fig. 1.

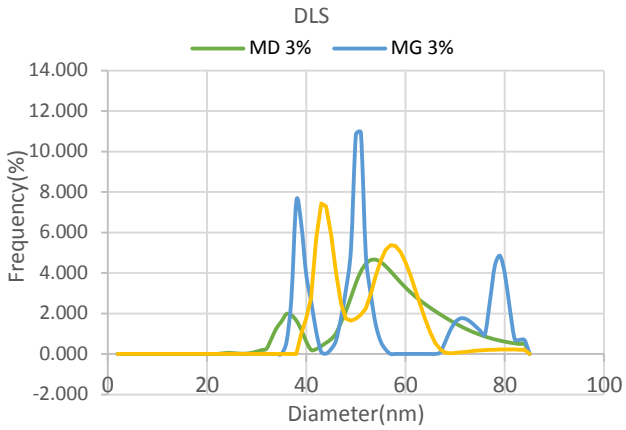

Fig. 1 Dynamic light scattering (DLS) spectrum of microcapsules containing essential oils.

The Effect of pH on Microencapsulations of Essential Oils of *F. angulata subsp. carduchorum*

An appropriate amount of essential oil (254.8 mg) was dissolved in ethanol to determine the effect of different pH on the microencapsulated essential oil. The spectrophotometer device was zeroed by the ethanol solvent prior to placing the sample and then, the maximum absorbance wavelength (λ_m) of the essential oil was obtained by the device. In the next step, solutions (50 mg) were prepared from microencapsulations containing essential oils and their pH was reached 1, 3, 5, 7 and 9. After their centrifugation, the absorbance amount was read at 5 min intervals and after 24 h at the obtained maximum absorbance wavelength.

Statistical Analysis

The data were analyzed using ANOVA and means were compared using Duncan's mean comparison. The SPSS Statistics, Version22 was used for analysis and the results were reported as S.E. ± mean of data obtained from three times repetition with confidence level of 0.05.

Results and Discussion

In this section, the results of the research are shown and argued.

Spray Dryer Efficiency

The microencapsulation efficiency means determining the amount of essential oil encapsulated successfully and calculated from the values of obtained powder and the amount of dry raw material. The microencapsulation efficiency is considered as one of the important factors in determining the stability of encapsulated compounds, as it indicates the ability of walls in preventing the extraction of internal essential oils. In recent years, the microencapsulations of oils, extracts, and edible flavorings have emphasized the enhancement of microencapsulation efficiency, preventing the loss of volatiles, and increasing the product's durability [15]. The performance range of the device is between 55-85%. The lowest microencapsulation efficiency was observed in the sample of *Ferulago angulata* subsp. *carduchorum* (Boiss. & Hausskn.) D.F.Chamb. essential oil microencapsulated with Maltodextrin + Arabic gum + 1% essential oil with a value of 59.7%. Based on the early studies, the type of wall and core, emulsion properties, and drying parameters all influence the microencapsulation efficiency [9,15,16].

Characterization of Phenolic Content

The standard curve of gallic acid was obtained with the line equation ($y = 0.0034x - 0.0594$ and $R^2 = 0.9108$). The equivalent concentrations of gallic acid for each sample were obtained based on the standard curve of gallic acid and using the equation. Table 1 shows the equivalent concentration of gallic acid required for microencapsulation containing 1% and 3% essential oil. As shown in Table 1, the highest total phenolic content is for the 3% of microencapsulation essential oil with the microencapsulation of Maltodextrin+Arabic gum which was significantly different from the rest of the treatments. Thereafter, the highest phenolic content was observed in 1% essential oil along with microencapsulation of Maltodextrin + Arabic gum. The lowest amount of phenolic compounds was observed in concentrations of 1 and 3% essential oil encapsulated with maltodextrin. Additionally, the results indicated no significant difference between 1 and 3% of essential oil in maltodextrin and Maltodextrin + modified starch treatments. However, the phenolic content was significantly enhanced by increasing the concentration of essential oil in the Maltodextrin + Arabic gum treatment. The coverage of Maltodextrin+Arabic gum with 3% essential oil had the highest total phenolic content among the other coverages. Accordingly, adding Arabic gum caused this coverage act more potent in protecting the sensitive phenolic compounds of the core.

Table 1 The total phenolic contents (Gallic acid equivalents, mg/mL) of microcapsules containing essential oil (Mean± SE*)

Concentration of microcapsules (mg/mL)	Essential oil	Maltodextrin	Maltodextrin+modified starch	Maltodextrin + gum
0.5	1%	46.290±0.000 aB	49.380±1.030 aB	61.000±1.760 bA
	3%	48.060±1.470 aB	52.320±0.440 aC	66.880±0.880 aA

A statistically significant difference was observed among the means with at least one similar little letter in each column. Further, no statistically significant difference was observed among means with similar capital letter in each row (P >0.05). *SE = Standard Error

Table 2 Inhibitory percentage (%) of ABTS radical at different concentrations of microcapsules containing essential oil (Mean± SE*)

Concentration of microcapsules (mg/mL)	Essential oil	Maltodextrin	Maltodextrin+modified starch	Maltodextrin+gum
0.25	1%	2.070±2.920 bA	0.000 bA	12.580±7.650 bcA
	3%	20.700±2.020 abA	32.170±20.490 aA	0.000 cA
0.5	1%	5.950±0.680 bA	32.640±9.090 aA	33.680±15.120 abA
	3%	37.380±16.710 aA	40.840±2.040 aA	52.810±9.890 aA

A statistically significant difference was observed among the means with at least one similar little letter in each column. Further, no statistically significant difference was observed among means with similar capital letter in each row (P >0.05). *SE = Standard Error

Further, based on the results of the similar studies used Maltodextrin and Arabic gum for microencapsulation of sensitive compounds, the coverage of Maltodextrin and Arabic gum indicated a significant difference in the amount of total phenolic compounds compared to the Maltodextrin coverage, due to the effect of Arabic gum on improving the emulsion stability and decreasing the surface tension [17]. Arabic gum is one of the most common wall substances in spray drying due to its desirable encapsulating properties such as high solubility and desirable emulsifying.

Antioxidant activity

Todays, maintaining food safety and quality during storage has attracted the attention of food industry experts and health authorities of the country. The Food Control and Monitoring Center classified antioxidants as food additives. Most of the studies conducted on antioxidants in food products emphasize the delay in lipid oxidation, resulting from delaying food decomposition and spoilage. Overall, antioxidants have numerous nutritional and medicinal applications [18].

Table 2 shows the ABTS radical inhibition for microcapsules containing 1% and 3% essential oils.

In the present study, the essential oil of *F. angulata subsp. carduchorum* was selected for microencapsulation due to its high antioxidant activity. For this purpose, modified starch, arabic gum and Maltodextrin were used as coverage. The mini spray dryer B-290 (BUCHI brand) from Germany was used. The spray dryer is equipped with a suction pump for inlet emulsion suction for emulsion entry and scattering in the hot chamber. The spray dryer conditions were set after the initial tests and reaching the aforementioned optimum conditions. As shown in Table 2, the highest inhibitory percentage for 0.5 g of capsule was 3% essential oil microencapsulated with Maltodextrin + gum, which is not significantly different from treatments of Maltodextrin and Maltodextrin-starch at the same capsule and starch amount (P <0.05). pH of 3 during 5 min was related to the essential oil sample microencapsulated with Maltodextrin.

Table 3 The mean of the mass density of powders and the results of examining the mass moisture percentage of powders (Mean± SE*)

Sample	Without essential oil		1%		3%	
	Density of Powders	Moisture Powders	Density of Powders	Moisture Powders	Density of Powders	Moisture Powders
MD	0.590±0.035 aA	1.046±0.000 cC	0.420±0.000 bA	1.420±0.000 aC	0.350±0.094 cB	1.290±0.005 bC
MS	0.580±0.017 aA	2.511±0.020 aB	0.400±0.008 bA	1.588±0.000 cB	0.410±0.008 bA	2.014±0.005 bB
MG	0.480±0.023 aB	3.500±0.010 bA	0.360±0.007 bB	3.404±0.005 cA	0.250±0.124 cC	3.772±0.000 aA

A statistically significant difference was observed among the means with at least one similar little letter in each column. Further, no statistically significant difference was observed among means with similar capital letter in each row (P >0.05). *SE = Standard Error (MD=Maltodextrin, MS=Maltodextrin+Modified Starch, MG=Maltodextrin+Arabic gum)

Measuring the Mass density of Powders and Measuring the Moisture Content of Powders

The mean density of the essential oils encapsulated at different concentrations of the essential oil has been shown in Table 3.

The comparison of the mass density of the samples demonstrated a difference among the samples with different degrees of the materials used such as covering combination for creating powder. The higher volume density is defined by the higher molecular weight of the powder. Heavier materials easily move among the particle spaces and consequently, with less space increase the volumetric mass. Accordingly, as shown in Table 3, the highest density was associated with the sample containing Maltodextrin with 0.59 g/cm^3 and the lowest density was related to the 3% essential oil sample encapsulated with Maltodextrin + Arabic gum with 0.25 g/cm^3. The comparison between the coverages with and without essential oil indicated no significant difference between the samples containing the 1% microencapsulated essential oil and these coverages had the highest density rate compared to the coverages with 3% essential oil. The lowest amount of density was related to the microencapsulation of 3% essential oil + Maltodextrin + Arabic gum.

Table 3 represents the mean moisture of powders for microencapsulated essential oil. Based on the obtained results, the type and concentration of the wall substance significantly affect the final moisture amount of produced powders. Among the coverages containing essential oil the highest amount of moisture (3.77%) was related to the 3% essential oil sample microencapsulated with Maltodextrin+ Arabic gum and the lowest moisture content (1.29%) was associated with the 3% essential oil sample microencapsulated with 3% Maltodextrin.

Efficiency of encapsulating *F. angulata* subsp. *carduchorum* essential oil

As shown in Table 4, the best microencapsulation efficiency (3%) is related to the covering of Maltodextrin and Arabic gum and the lowest efficiency (1%) is concerned with covering Maltodextrin.

Table 4 The efficiency of encapsulating essential oil (Mean± SE*)

Type of coverage	Microencapsulation efficiency (EE%)
MD 1%	74.620 ±0.000 c
MS 1%	79.600± 2.340 bc
MG 1%	91.300 ±2.020 a
MD 3%	75.727± 3.260 c
MS 3%	81.940±0.980 b
MG 3%	98.330±4.020 a

A statistically significant difference was observed among the means with at least one similar little letter in each column (P >0.05). *SE = Standard Error. (MD 1%= Maltodextrin+ 1% essential oil, MS 1% = Maltodextrin+Modified starch+1% essential oil, MG 1%= Maltodextrin+Arabic gum+1% essential oil, MD 3%= Maltodextrin+ 3% essential oil, MS 3%= Maltodextrin+Modified starch+3% essential oil, MG 3%= Maltodextrin+ Arabic gum+ 3% essential oil).

Evaluating the Particle size of Powders

Table 5 indicates the mean particle size obtained for each sample.

Table 5 The mean particle size (micrometer) (Mean± SE*)

Sample	SD ± mean
	Particle size by dynamic light (DLS) (µm)
MD 3%	0.659±91.000 b
MS 3%	0.316 ±5.740 d
MG 3%	1.163±50.590 a
MD	0.266±4.400 f
MS	0.411±3.500 c
MG	0.280±13.100 e

*A statistically significant difference was observed among the means with at least one similar little letter in each column (P >0.05). (SE = Standard Error). (MD3%= Maltodextrin+3% essential oil, MS 3%= Maltodextrin + Modified starch+3% essential oil, MG3%= Maltodextrin+Arabic gum+3% essential oil, MD= Maltodextrin, MS= Maltodextrin+Modified starch, MG= Maltodextrin+Arabic gum) (P<0.05).

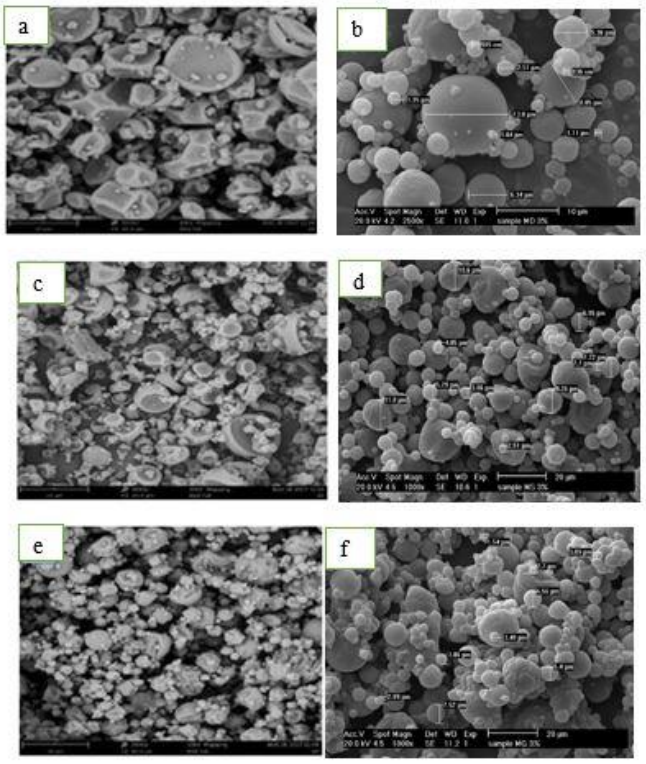

Fig. 2 The micro-structure of microcapsules prepared by scanning electron microscopy **a**. Maltodextrin20%, **b**. Maltodextrin20% + essential oil, **c**. Maltodextrin20% + modified starch20%, **d**. Maltodextrin20% + starch20% + essential oil, **e.** Maltodextrin20% + Arabic gum20%, **f.** Maltodextrin20% + gum20% + essential oil

Table 5 demonstrates the mean particle size of the powders obtained from dynamic light for essential oil microencapsulated with various biopolymers. Based on the results, in the state of empty cover without essential oil, the smallest size was related to Maltodextrin and the largest size belonged to the Maltodextrin + modified starch. Further, when the essential oil was added to the coatings, the highest amount of particle size by dynamic light was related to the combination of Maltodextrin along with Arabic gum and the smallest particle size was associated with the essential oil microencapsulated with the Maltodextrin + modified starch. The mean particle size range was 0.6593 - 1.1632 µm. The results indicated a significant difference in particle size among all six samples with and without essential oil containing the coating of Maltodextrin, Maltodextrin + modified starch, and Maltodextrin + Arabic gum.

The surface morphology of the samples was examined by scanning electron microscopy. Fig. 2 displays the electron microscope images for each microcapsule.

Generally, produced micro-capsules containing essential oil had spherical shapes and smooth surfaces and some samples had wrinkles or openings. The microcapsules prepared by Maltodextrin had a smoother surface and less ruggedness compared to the other treatments. However, the difference in the type of covering failed to affect the spherical shape of the microcapsules significantly. Additionally, the smallest microencapsulationes were related to the covering of the Maltodextrin + modified starch.

In the present study, the particle size was more uniform and the particle surface was more smooth and wrinkle and crack were less in the microencapsulationes of Maltodextrin and Maltodextrin + modified starch compared to the microencapsulationes of Maltodextrin + Arabic gum, due to the presence of modified starch, acting as covering the surface of the microencapsulation. Using microcapsulated herbal essential oils is considered as an appropriate solution for producing a new, beneficial, and desirable product, as well as improving the nutritional quality of consumers. However, further studies are needed to industrialize these products.

Evaluating the Infrared Spectroscopy

Fig. 3 demonstrates the FTIR spectrum of the microencapsulationes of Maltodextrin, Maltodextrin+starch, and Maltodextrin + Arabic gum.

Infrared spectroscopy is done based on the absorption of radiation and the investigation of the vibrational mutations of molecules and multi-atomic ions. This method is applied as a powerful and extended method for determining the structure and measurement of chemical species [19].

In the present study, infrared spectrum was used to determine the functional groups of polymers and microcapsules, and evaluate the interaction of the polymers with each other and with essential oil, done by the absorbance measurement in the wave number range of 400-4000 cm^{-1}. As indicated in the test, the micrenocapsulation of Maltodextrin demonstrates the index peaks. As displayed in Table 6, the index absorption bands of this microcapsul included 3369.7569 cm^{-1} (tensile vibration of hydroxyl group), 2928.04 cm^{-1} (tensile vibration of CH group), 1645.33 cm^{-1} (asymmetric tensile vibration of carboxyl group) 1417.73 cm^{-1} (symmetric tensile vibration of carboxyl group and tensile).

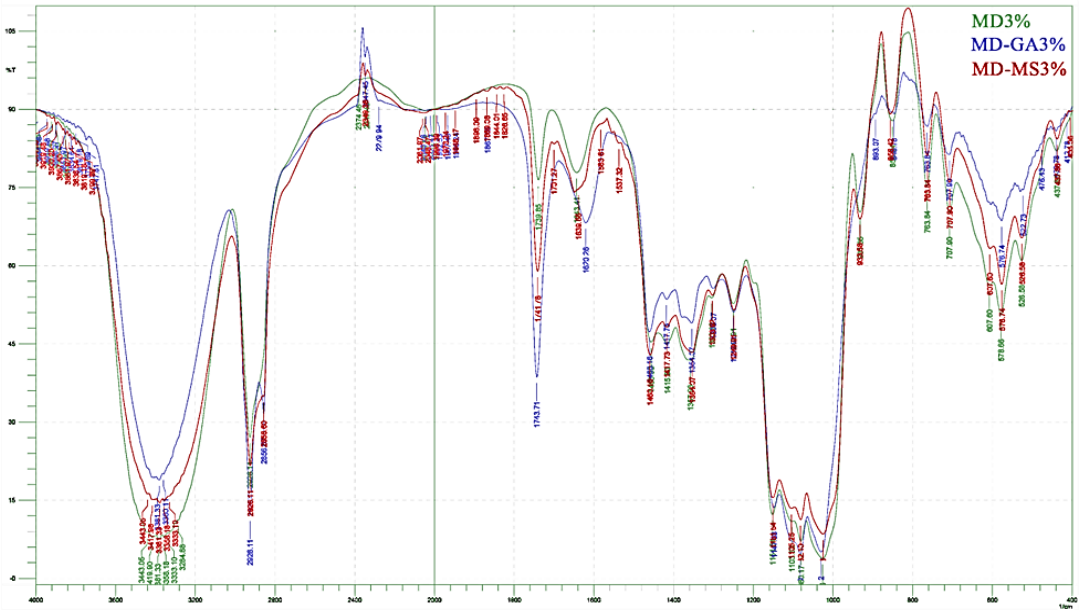

Fig. 3 The FTIR spectrum of the microencapsulationes containing essential oil

Table 6 Infrared spectral index peaks with the Fourier-transform infrared spectroscopy (FTIR) of the samples

Links	Wave number (cm^{-1})					
	Microencapsulation along with essential oil			Microencapsulation		
	Maltodextrin	Maltodextrin+ starch	Maltodextrin +gum	Maltodextrin	Maltodextrin+ starch	Maltodextrin + gum
OH tensile	3381.330	3381.330	3381.330	3389.680	3317.670	
CH stretch	2926.110	2926.110	2926.110	2928.040	2929.970	
COO^- Asymmetric tensile	1739.850	1714.780	1743.710	1647.260	1608.690	
COO-Symmetrical tensile	1103.320	1105.260	1147.680	1417.730	1417.730	

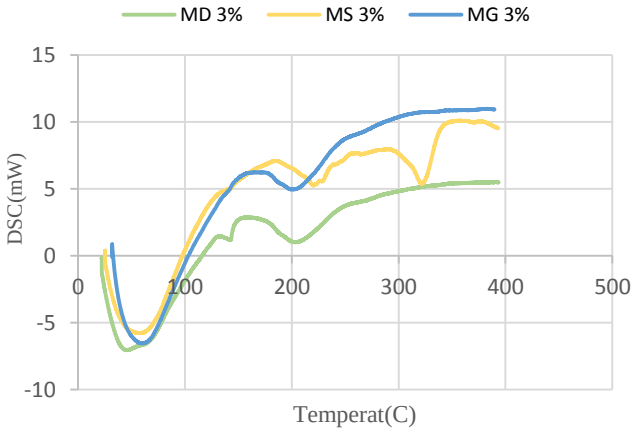

Fig. 4 The thermograms of the differential scanning calorimetry

Table 6 represents the index peaks for each spectrum. Combining Maltodextrin with Arabic gum biopolymers and modified starch changed the peak location of the hydroxyl group from 3369 cm^{-1} to 3389 cm^{-1} and reached 3317 cm^{-1} in the Arabic gum. These changes are related to the hydrogen bond formed between Maltodextrin with modified starch and Arabic gum.

Evaluating the Differential Scanning Calorimetry

Fig. 4 indicates the results of differential scanning calorimetry for the essential oil microencapsulated with Maltodextrin, Maltodextrin + starch, and Maltodextrin + gum. Fig. 4 displays thermograms of the differential scanning calorimetry (DSC) in relation to microencapsulationes of Maltodextrin, Maltodextrin + starch, and Maltodextrin + gum containing essential oil in the temperature range of 30-400 °C.

Further, Fig. 3 indicates the endothermic peaks associated with water loss of samples and exothermic peaks related to the analysis of the samples. As indicated in Table 7, the temperature decreased when the microencapsulation was used with the essential oil.

The differential scanning calorimetry test was used to determine the thermal properties of the manufactured micrenocapsulationes. Further, DSC thermograms were used to evaluate the structural changes of the materials alone or in combination with the essential oil during heating range of 22 - 400 °C. Fig. 5 demonstrates the thermograms of the microencapsulationes containing the essential oil. In general, two endotherm phenomena were observed in all microencapsulationes. The first endotherm peak was observed at room temperature up to 185 °C, varied depending on the type of micrenocapsulation. This endotherm peak is related to the water loss of the hydrophilic groups existing in the structure of polymers, somehow returning to the dehydration process. The second endotherm peak, extended in the range of 200 - 240 °C, is related to the melting point and possibly to the analysis of the microencapsulationes as a result of depolymerization reactions, mainly involving decarboxylation of the carboxyl groups.

Table 7 The endometric and exometric peaks

Temperature	Temperature (°C)					
	Microencapsulation along with essential oil			Microencapsulation		
	Maltodextrin	Maltodextrin + starch	Maltodextrin + gum	Maltodextrin	Maltodextrin + starch	Maltodextrin + gum
First peak (minimum)	45.600	59.000	59.600	70.600	72.900	69.200
Second peak (minimum)	159.500	183.300	166.700	172.800	178.800	184.100
Third peak (minimum)	204.200	220.000	201.460	241.800	222.100	220.600

Table 8 The mean of concentrations equivalent to the essential oil (mg / mL) among different pH (Mean± SE*)

pH	Maltodextrin		Maltodextrin + modified starch		Maltodextrin + Arabic gum	
	5 min	24 h	5 min	24 h	5 min	24 h
1	34.910±0.280 cD	29.910±2.830 eE	27.560±2.260 dE	39.910±0.850 bC	114.620±2.550 aB	287.560±8.910 aA
3	29.320±4.530 dD	35.210±1.560 dC	31.970±4.670 dCD	31.090±0.570 cCD	49.320±3.250 eB	66.970±2.690 eA
5	34.620±0.990 cE	67.850±3.540 cC	62.260±6.790 cD	34.620±4.530 cE	82.560±0.990 cB	88.740±12.020 cA
7	41.090±1.840 bE	90.790±2.830 bB	166.680±4.530 aA	40.210±4.100 bE	66.970±2.970 dD	74.910±3.820 dC
9	75.210±3.680 aE	139.910±1.270 aA	117.850±6.510 bB	45.210±5.660 aF	89.620±3.820 bD	100.500±5.370 bC

* There was no a statistically significant difference among the means with at least one similar little letter in each column. Additionally, statistically meaningful difference was not found among means with similar capital letter in each row (P >0.05). (*SE = Standard Error).

Investigating the Effect of pH on Microencapsulationes Containing Essential Oil

The appropriate wavelength was first found to obtain the essential oil absorption rate at different concentrations. For this purpose, a concentration of essential oil was prepared and maximum wavelength was obtained by a spectrophotometer. The essential oil absorption of other samples is determined by specifying the maximum wavelength. This number was 697 nm for the *F. angulata* subsp. *carduchorum* essential oil.

The *F. angulata* subsp. *carduchorum* essential oil absorption at different concentrations was determined by spectrophotometer at the obtained maximum wavelength. Fig. 5 displays the results.

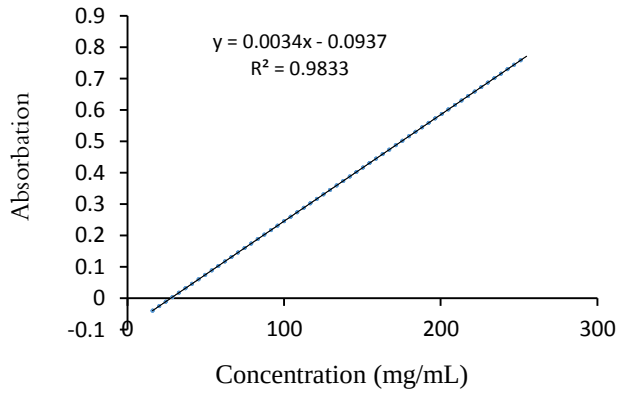

Fig. 5 The *Ferulago angulata* subsp. *carduchorum* (Boiss. & Hausskn.) D.F.Chamb. essential oil absorption at different concentrations

Figure 5 indicates the essential oil absorbance rate at different concentrations with the line equation of y = 0.0034x - 0.0937 and R^2 = 0.9833. Therefore, the absorption rate was enhanced by increasing the concentration of essential oil. The above equation represents the relationship between the concentration and absorption of essential oil at the wavelength of 697 nm.

The different concentrations of microencapsulations were prepared to study the effect of pH on them. The pH of each sample was then adjusted to 1, 3, 5, 7 and 9. After adjusting the pH, the samples were kept once for 5 min and then for 24 h. After this time, the samples were centrifuged for 15 min at a speed of 3000 rpm and their absorbance rate was obtained at wavelength of 697 nm by spectrophotometer.

Fig. 5 displays the absorption rate of essential oil at different concentrations. As shown, the mean of concentrations equivalent to the essential oil was obtained for each sample by inserting the absorption rate of each sample into the afore-mentioned line equation. Table 8. Shows the average concentration of the essential oil equivalent at different pHs.

Table 8 displays the concentrations equivalent to the essential oil for each sample.

In this regard, the highest essential oil release rate (287.56 mg/mL) was obtained in the essential oil sample microencapsulated with Maltodextrin + Arabic gum at pH of 1 and after 24 hours. Further, the lowest essential oil release (29.32 mg / mL).

Conclusion

Based on the results of the present study, *F. angulata* subsp. *carduchorum* essential oil was microencapsulated in coverages of Maltodextrin, Maltodextrin + Arabic gum, and Maltodextrin + modified starch by spray-drying method. The presence of essential oil in the microencapsulations was confirmed by SEM and FTIR tests. Further, the type of coverage is effective in emulsifying, protecting phenolic compounds, and particle size. The highest drying efficiency belongs to the microencapsulation of Maltodextrin containing 3% essential oil. It is worth mentioning that the microencapsulation of Maltodextrin + Arabic gum had the highest percentage of free radical inhibition in the ABTS antioxidant activity test. The highest phenolic content belonged to the Maltodextrin + Arabic gum + 3% essential oil. The lowest density and the highest moisture were associated with the sample of Maltodextrin + Arabic gum + 3% essential oil. The highest microencapsulation efficiency was related to the sample of Maltodextrin + Arabic gum + 3% essential oil. The results of electron microscopy indicated the effective and useful role of modified starch in creating a

uniform and crack-free structure. The results of the DLS test demonstrated that the largest sample in terms of size was the sample of Maltodextrin + Arabic gum + 3% essential oil. The highest change in the spectrum of chemical structure in FTIR test and the most heat resistant sample in DSC test was related to the microencapsulation of Maltodextrin + Arabic gum. The results of pH test demonstrated the stability of the microencapsulationes containing essential oil in alkaline conditions and environment and the best and most stable covering belongs to the Maltodextrin at pH = 1 and after passing 24 hours. Overall, the Maltodextrin + Arabic gum + 3% essential oil was selected as the best treatment among the treatments.

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