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Canola meal phenolic compounds electrosprayed into capsules to increase the oxidative stability of canola oil

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Abstract

Nano-encapsulation is a developing area of study across several fields, including the food, pharmaceutical, and cosmetic sectors. In this study, nanocapsules containing polyphenols were made from canola meal by electrospraying, and it was determined how the capsules' walls affected their shape, encapsulation efficiency, ζ-potential, and particle size. Furthermore, the impact of nanocapsules on canola oil was examined using the TBA index, oxidative stability, and iodine value. Our findings demonstrated that spherical nanoparticles were produced using electrospraying, and that the amount of wall materials used to create them had an impact on their size. Maltodextrin/β-cyclodextrin at a ratio of 1:1 resulted in the smallest capsule sizes, with an encapsulation efficiency of 68% and an 80% release over 40 days at ambient temperature. The ζ-potential of each particle was negative. With a PDI of 0.074–0.650 and a mean size of 232.3–659.8 nm, the population of electrosprayed nanoparticles was found to be heterogeneous. By increasing nanocapsules of polyphenols to the canola oil, the oil stability and oil quality were increased. Our results showed that 800 ppm of polyphenols can improve the oil stability similarly to TBHQ, and therefore it is possible to use canola meal polyphenols as natural antioxidants in the oil industry.

Keywords Canola oil, Phenolic compounds, Encapsulation, Oxidative stability

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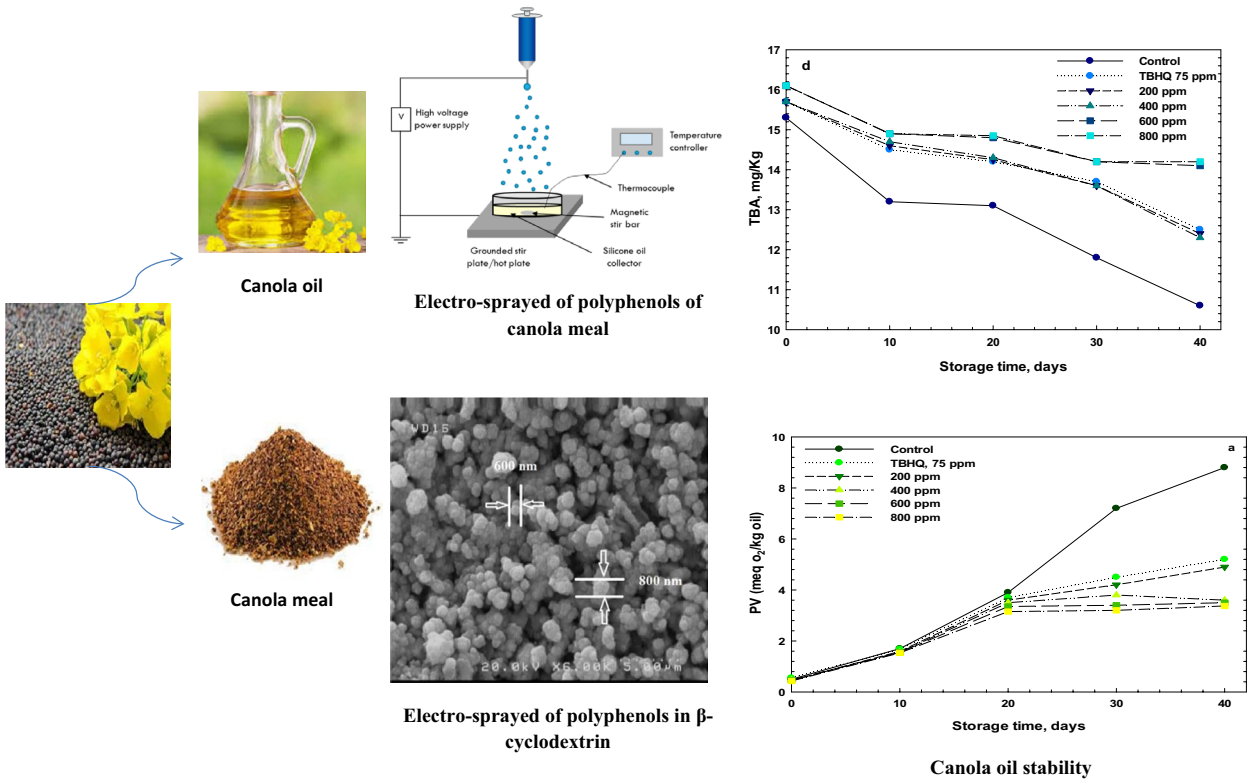
Graphical Abstract

Canola meal phenolic compounds electrosprayed into capsules to increase the oxidative stability of canola oil



Introduction

Canola (*Brassica napus*) seed is one of the most significant oilseed crops in the world, as its production has quickly increased during the last decade. It possesses about 40% oil and produces a meal containing 38 to 43% protein [1]. The primary method in producing canola oil is seed crushing, followed by solvent extraction. However, canola oil mostly consists of triglycerides; it also contains trace amounts of proteins, phenolic acids, phospholipids, free fatty acids, sterols, and coloring pigments [1, 2]. Compared to other oilseeds, canola has a substantially higher phenolic content, which comprises free phenolic and esterified phenolic acids that are mostly retained in the canola meal following oil extraction [3]. The esterified phenolic acids with sinapine being more prevalent in the phenolic chemicals found in canola meal. Defatted canola meal by-product, which might be a significant source of phenolic and antioxidant chemicals, is disposed of annually as part of the oil waste sector in quantities of thousands of metric tons [2, 4]. These natural by-products can be applied as nutraceuticals due to their strong antioxidant behaviors. As a result, many methods of extracting polyphenols from canola meal have been investigated [3, 4].

Phenolic antioxidants can effectively prevent the lipid oxidation via donation hydrogen to lipid peroxyl radicals, which avoids the initiation or propagation of the primary oxidation [5]. These substances are unstable and sensitive to heat, light, pH, and other extrinsic factors. The stabilization of phenolic compounds can be achieved by microencapsulation technologies, which are suitable to protect polyphenols against degrading environments. By blocking interaction with oral taste receptors, microencapsulation can also lessen the bitterness of phenolic compounds and stop the unpleasant taste sensations [6]. Varying wall materials, mostly proteins and polysaccharides, are used in the encapsulation process [7]. Furthermore, several encapsulation methods, including spray-drying [7, 8], freeze-drying [9], sonication [10], emulsification [11], and co-extrusion [6] have been applied for phenolic compounds. Although these encapsulation techniques are widely used, electrospray has gained increasing attention due to its superior efficiency and safety [12].

Electrospray (ES), in which an electrical force is applied to the surface of a capillary in the direction of gravity force, is a promising new technique for encapsulating nanoparticles loaded with bioactives. The surface of the liquid capillary at a nozzle's outflow is subjected to shear stress by keeping the nozzle at a high electric potential. When the electrostatic force created in the solution is stronger than its surface tension, the fluid droplet at the capillary tube's tip, known as a fluid jet, swiftly moves towards the collecting plate. After coming into touch with adjacent air molecules, the solvent then evaporates. Without the need for high heat, the solvent evaporates, causing the particles to contract and dry [13].

To the best of our knowledge, there is no research on the phenolic compounds from canola meal electrosprayed as nanoparticles or on their antioxidative behavior in food systems. Moreover, canola oil's huge global output and appeal due to its high oleic acid, low saturated fat, and favorable 6:3 ratio make it an appropriate model for unsaturated oil in assessments of oxidative stability [14]. Therefore, characterizing the phenolic nanoparticles electrosprayed from canola meal with diverse wall components, such as maltodextrin, β-cyclodextrin, and inulin, is an intriguing issue. In this work, the chemistry, morphological, and microstructure of the canola meal phenolic-loaded electrosprayed particles were investigated. The inclusion of nanoparticles in canola oil and comparison of their effectiveness to traditional synthetic antioxidants is the other goal.

Materials and methods

Materials

Canola seeds (Hyola cultivar 401) were procured from local markets (Golestan province, Iran), and impurities such as stone, straw, and damage seeds were removed. They were then stored at 4 °C till the experiments. Maltodextrin, β-cyclodextrin and inulin were used as wall materials and purchased from Sigma-Aldrich chemical Co. (Saint Louis, MO, USA). All the other reagents were all analytical grades obtained from Merck (Merck Company, Darmstadt, Germany).

Extraction of phenolic compounds

Canola oil was initially extracted by the solvent extraction technique and the meal was separated. Briefly, the solvent extraction was carried out by a Soxhlet extractor using commercial hexane for 4 h. The solvent was then eliminated using a rotary evaporator (B-480, BUCHI, Switzerland) at a low temperature (60 °C) to eliminate any surplus solvent, the oil was recovered, and the meal was dehydrated overnight in a vacuum oven (Heraeus, VT 6130 M, Germany) at 60 °C and one bar vacuum pressure [15].

Phenolic compounds from canola meal were extracted by the Amarowicz's procedure with some modifications [16]. Briefly, canola meal was completely ground to a size of 1 mm by a lab ultra-centrifugal mill (ZM-200, Retsch, Germany). According to the preliminary experiments, phenolic compounds were extracted from the oil cakes with ethanol 80% (v/v) at a solid-to-solvent ratio 1:10 (canola meal: solvent) and 50 °C for 90 min along with ultrasonication at 60 Hz for 30 min to increase the extraction efficiency. The phenolics in the canola meal were then removed using a solvent extractor (ASE300, Dionex, ThermoFisher Scientific, ON, Canada). The final extract was concentrated using rotary evaporator (BUCHI Rotovapor, R-100, Switzerland) to remove the excess solvents. Phenolic compounds were subsequently stored at − 18 °C prior to the encapsulation.

Determination of total phenolic content

The total phenolic content (TPC) of the canola meal was measured by Folin–Ciocalteu's reagent using a UV/visible spectrophotometer at 765 nm and the outputs were expressed in mg gallic acid per g of extract [8]. In brief, the canola meal extracts (0.5 mL) were incorporated with Folin–Ciocalteu's reagent (2.5 mL) in a conical flask. The mixture was thoroughly agitated to complete the reaction by adding 2 mL of sodium carbonate (7.5%) and it was kept in a dark place for 2 h with intermittent shaking at half an hour intervals. The absorbance of the colored complex was determined by a UV/visible spectrophotometer (Cary 100, Varian, USA) at 765 nm. Standard solutions of gallic acid and ethanol as the blank were prepared to plot the standard curve ($R^2 = 0.99$) and the TPC was calculated in mg gallic acid per g of extract as follows:

$$A = 0.94C + 8.52, \tag{1}$$

where A, and C are absorbance and concentration of gallic acid, respectively.

Nanocapsules preparation

Maltodextrin, β-cyclodextrin, and inulin at different concentrations (2, 4, 6 and 8%) were used as wall materials in an electrospray process to encapsulate phenolic chemicals from the canola meal. Initially, the phenolic compounds were mixed at ratio 1:5 with wall materials (maltodextrin, β-cyclodextrin and inulin) in an ethanol solution, which was then homogenized by using a homogenizer (SR30, MTOPS, Korea) at 10,000 rpm for 30 min. Then, they were kept overnight in a refrigrator to complete the hydration. The solutions were also subjected to a 30-min ultrasonication at 30 kHz in order to minimize the particle size. An electrospray equipment

was used to encapsulate the final solutions (NanoAzma, Iran), which was set up according to the Moghadam's procedure [17]. The operational parameters were as follows: 30 °C temperature, 30 kV applied voltage, 1 mL/h flow rate, 15 cm distance to collector, and nozzle diameter 2 mm.

Encapsulation efficiency

The efficiency of nanocapsules preparation was determined by the Robert's procedure with some modifications [8]. An aliquot of 200 mg of nanocapsules were mixed with 2 mL of a mixture of ethanol to methanol (ratio 1:1). The solutions were then sonicated at 20 kHz for 20 min to disrupt the coatings and the core was released from the wall materials. Subsequently, it was centrifuged at 5000 rpm for 10 min and the supernatant was collected. The TPC in the supernatant was measured according to the Sect. "Determination of total phenolic content". The surface bioactive compounds (SB) and encapsulation efficiency (EE) of phenolic materials were calculated according to the following equations:

$$\mathrm{SB}(\%) = \frac{\text{Surface TPC}}{\text{Total TPC}} \times 100, \tag{2}$$

$$\mathrm{EE}(\%) = 100 - \mathrm{SB}(\%). \tag{3}$$

Nanocapsules properties

The zeta-potential, particle size, and poly dispersity index (PDI) of nanocapsules were determined using a dynamic light scattering (DLS) method (Malvern instruments, Worcestershire, United Kingdom) [18]. The average surface electrical charge (ζ-potential) of the samples was determined using a Malvern Nano Zetasizer (Malvern Instruments Ltd., United Kingdom) with a U-shaped cuvette. The experiment was carried out using a refractive index of 1.57, and the "fine particle" mode was activated to improve the measurement. The mean diameters of the particles were stated as volume mean diameter (d_{43}) by using the Mie Theory. The measurements were carried out with five repetitions [19]. Fresh samples were measured in 3 replicates at ambient temperature, and the mean values were reported.

Scanning electron microscopy (SEM) analysis

The nanocapsule's structures of phenolic compounds were accomplished by scanning electron microscopy (SEM). The nanocapsules were attached to aluminum stubs using a two-sided adhesive tape and coated with gold/palladium using a sputter coater at 30 mV and argon gas. The images were taken by a Hitachi electron microscopy (S4160, Germany) at 20 kV with 2000 magnifications.

Release properties of phenolic compounds

The release properties of nanocapsules were measured according to the Esmaeilzade et al. [10]. The nanocapsules (5 mg) was added to the 5 ml of phosphate buffer solution (pH 7) and then centrifuged in 4500 rpm at ambient temperature for 90 min. The lower phase of the tube was then collected and the TPC was measured by Folin–Ciocalteu's method. The release amount of phenolic compounds was calculated by the following equation:

$$E(\%) = \left(\frac{T_{\text{total}} - T_{\text{free}}}{T_{\text{total}}}\right) \times 100, \tag{4}$$

where T_{total}, and T_{free} are the amount of phenolic compounds in the electrosprayed nanoparticles and the free phenolic compounds, respectively.

Canola oil fortification by phenolic nanocapsules

Canola oil, free of antioxidant, was combined with nanocapsules containing the phenolic compounds at concentrations of 100, 200, 400, and 800 ppm. To compare with canola oils devoid of antioxidants, the synthetic antioxidant tertiary butyl hydroquinone (TBHQ) at 75 ppm was employed as the control. The oil samples were stored at 30 °C for 60 days and they were analyzed at 15-day intervals.

Antioxidant activity and oxidative stability

The samples of canola oil were tested for their antioxidant activity using the DPPH radical scavenging technique. As previously noted, the positive control was TBHQ.

The Rancimat (Metrohm, 743, Switzerland) was used to calculate the induction period (IP) [20]. In the instrument's reactor tube, the sample was weighed at 3.0 g, the reaction temperature was set at 120 °C, and the flow rate was 20 L/h. After the oil processing, the IP was calculated at the beginning, 10, 20, 30 and 40 days.

Chemical tests of canola oil

The peroxide, iodine, acid value and thiobarbituric acid (TBA) assay of the oils were measured according to the American Oil Chemists' Society (AOCS) method (Cd 8–53), (Cd 1–25), (Cd 3–63), and (Cd 19–90), respectively [21].

Statistical analysis

All the experiments were carried out in triplicates and the mean ± SD were given. The tests were carried out in a completely randomized factorial design. The data were

analyzed by one way analyses of variance (ANOVA); the means were compared by the Duncan's multiple range tests at the 5% level through SPSS version 22 (IBM, USA).

Results and discussion

Canola meal polyphenol characteristics and encapsulation

Total phenolic content

The polyphenols content of the canola meal extracted by solvent extraction method are provided in Table 1. The TPC of canola meal extracted by high pressure was greater than that of solvent extraction. TPC of canola meal was 10–19 mg/g. According to Amarowicz, ethanolic extracts made from rapeseed oil cake that was kept for two weeks before extraction contained between 76 and 78 mg/g of total phenolic components. Total phenolic content varied from 22 to 194 mg/g in the fractions that were extracted from the crude canola extract using Sephadex LH-20 column chromatography [22]. Higher than those in the current study, canola and rapeseed husk crude extract preparations had phenolic contents that varied from 128 to 296 mg/g [16]. They discovered that the amount of total phenolics in canola hull fractions devoid of tannins ranged from 14 to 112 mg/g [16].

Based on the combined oxidation of linoleic acid and β-carotene, all the extracts under investigation showed high antioxidant activity (Table 1). Rapeseed cake extracts have antioxidant effects that were comparable to those of nonpressed seed extract.

Encapsulation efficiency (EE) and release of polyphenols within electrosprayed

The effect of different coating materials on the microcapsule size of the phenolic compounds which isolated from canola meal was evaluated. The results obtained from the encapsulation of polyphenols using inulin, maltodextrin and β-cyclodextrin are provided in Fig. 1. The encapsulation efficacy at different treatments for polyphenols varies from 58.43 to 55.17%. It is feasible to see the percentage of phenolic compounds and flavonoids conserved inside the matrix as well as the antioxidant activity of the samples after encapsulation when the antioxidant activity of the samples is compared to the original values discovered in the extract. The findings showed that the matrix's ability to retain antioxidant phenolic chemicals was significantly influenced by the coating utilized for encapsulation. The greatest outcomes came from employing wall materials made entirely of maltodextrin. Under these conditions, the amount of phenolic compounds and flavonoids retained in the encapsulated sample corresponded to 62% and 73%, respectively. These results are in agreement with the previous work, where the highest content of phenolic compounds was attained when the compounds were subjected to freeze-drying and 100% maltodextrin was used as wall material [23]. Independent of the drying method used, inulin maintained the least phenolic chemicals. This phenomenon may be explained by the fact that the coating material employed and the encapsulated chemicals have a significant impact on encapsulation efficiency [24]. Due to the decreased concentration of phenolic and flavonoid components in the encapsulated sample, the antioxidant activity was predicted to be lower compared to the extract's original antioxidant capacity. Furthermore, the quantity of phenolic compounds maintained showed a clear relationship with the percentage of TAA values reduced for the matrices containing 100% maltodextrin and 100% gum Arabic, regardless of the drying method (linear correlation, $R^2 = 0.99$). The lowest TAA values, however, were seen when maltodextrin and β-cylcodextrin were combined, showing a negative impact on the antioxidant activity of mixing the two matrices.

The drying procedure was shown to be crucial to the encapsulation efficacy, with freeze-drying being a more successful method for encapsulating phenolic chemicals and flavonoids. The behavior may in part be attributable to the morphological modifications brought on by drying. In comparison to the microspheres produced by the spray-drying process, which have larger surface areas for the same amount of materials due to their smaller sizes, the lyophilization process's sawdust-like shape results

Table 1 Polyphenols content of the canola meal

Temperature (°C)	TPC (mg gallic acid/g)	TFC (µmol QE/g)	DPPH (%)	FRAP (µmol TE/g)
Control	15.45 ± 1.63^{b}	1.58 ± 0.33^{c}	45.47 ± 1.82^{d}	378.32 ± 0.03^{c}
30	10.26 ± 1.87^{d}	1.95 ± 0.30^{a}	47.43 ± 1.55^{a}	102.99 ± 0.04^{d}
40	12.86 ± 1.52^{c}	1.47 ± 0.28^{d}	46.22 ± 1.38^{b}	382.50 ± 0.01^{b}
50	19.06 ± 2.16^{a}	1.85 ± 0.34^{b}	45.13 ± 1.72^{c}	925.44 ± 0.06^{a}

All the experiments were performed in triplicates and reported as mean ± standard deviations

[a] TPC, total phenolic content: results expressed as mg gallic acid per g of dry matter

[b] TFC, total flavonoid content: results expressed as µmol quercetin equivalents per g of dry matter

[c] DPPH, the radical activity in %

[d] FRAP, ferric antioxidant power assay: results expressed as µmol Trolox equivalents per g of dry matter

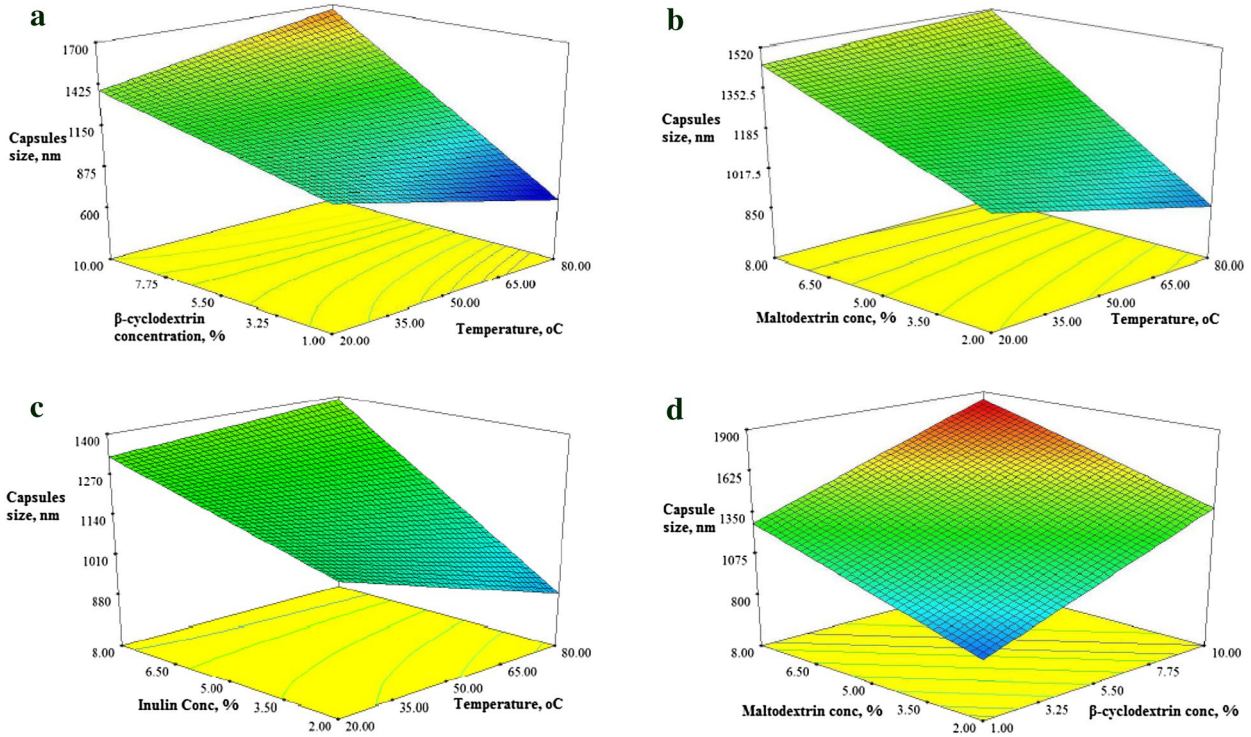


Fig. 1 3D graphic response-surface optimization of **a** incorporation efficiency as capsules size (nm) vs. β-cyclodextrin concentration (% w/w), **b** incorporation efficiency (nm) vs. maltodextrin concentration (% w/w), **c** incorporation efficiency as capsules size (nm) vs inulin concentration (% w/w), and **d** effect of the β-cyclodextrin and maltodextrin concentration on the capsules size (nm)

in a lower surface area/volume ratio, which promotes the degradation of the surface's phenolic and flavonoid compounds.

Higher EE values were produced as a result of increase in maltodextrin content in polyphenol constant levels. In general, when compared to other maltodextrin contents, maltodextrin 8 percent carriers loaded with 500 and 1000 ppm phenolics had the highest EE ($P<0.05$). Our findings (Fig. 1) showed that as maltodextrin content was increased; smaller particle sizes were generated, leading to a greater EE. Using electrosprayed WPC, Pérez-Masiá demonstrated that the EE of folic acid was 80%, which is similar with the findings of our study [25]. Their findings showed that the EE of folic acid within capsules generated by spray dryer and electrospraying did not differ significantly, and that WPC had a higher EE than resistant starch. The excessive rise in core material concentration in other polymeric matrices has resulted in a decrease in the EE [26].

Table 2 Characterization of electrospraying polyphenols from canola meal loaded with different wall materials

Coatings	Concentration, %	Particle size, nm	PDI	Z-potential, mV
Inulin	2	410.03 ± 0.57	0.60 ± 0.12	− 64.7 ± 1.31
	4	559.81 ± 0.15	0.39 ± 0.09	− 67.5 ± 0.31
	6	656.21 ± 0.74	0.74 ± 0.12	− 65.7 ± 2.11
Maltodextrin	2	317.84 ± 0.15	0.51 ± 0.10	− 61.2 ± 1.11
	4	356.16 ± 0.60	0.65 ± 0.13	− 60.2 ± 0.30
	6	242.07 ± 0.57	0.07 ± 0.04	− 64.91 ± 1.59
β-Cyclodextrin	2	232.32 ± 0.15	0.59 ± 0.09	− 68.8 ± 0.96
	4	232.24 ± 0.64	0.74 ± 0.12	− 71.7 ± 0.85
	6	410.03 ± 0.57	0.60 ± 0.12	− 64.7 ± 1.31

Among all samples, β-cyclodextrin (83.66%) and inulin (36.66%) particles had the greatest and lowest EE, respectively. According to reports, decreasing EE was caused by adding more oil during the encapsulation of flaxseed oil using zein [27]. Maltodextrin was used to encapsulate polyphenols, resulting in EE values of 73% (based on TPC) [28]. Increasing the wall material concentration resulted in a larger level of bioactive chemicals being trapped inside the created carriers. It has been reported that by increasing the extract concentration in the particles, the protein–protein and protein–polyphenol interactions may be weakened, causing more extract and protein to be ingested and wasted into the transparent liquid rather than being encapsulated and contributing to the formation of particles [29]. In general, the encapsulated chemicals and the covering material are crucial to EE [24]. Another study used spray-drying to encapsulate polyphenols with chitosan, and the EE ranged from 27 to 44 percent in terms of TPC [30].

Characterization of electrosprayed phenolic compounds

Some described properties of the generated nanocapsules loaded with polyphenols are shown in Table 1. Among the most crucial properties of nanocarrier systems are particle size and PDI. With a mean particle size in the range of 232.3–659.8 nm and a PDI of 0.074–0.650, the nanocapsules created in the current work by varying the ratios of the encapsulating wall materials clearly reflect a heterogeneous population. These results show that the particle size and population distribution may be impacted by varying concentrations. While the particle size of the inulin and maltodextrin samples increased with increasing coating levels in the fixed polyphenol concentrations, it decreased for the carriers of β-cyclodextrin.

Smaller electrosprayed particles were produced by the biopolymer solutions with lower surface tension; the electrical conductivity of feed solutions (Table 2) may possibly be a significant influence on the particle size. The region of stable cone-jet mode will shrink as conductivity rises, producing droplets with a multimodal

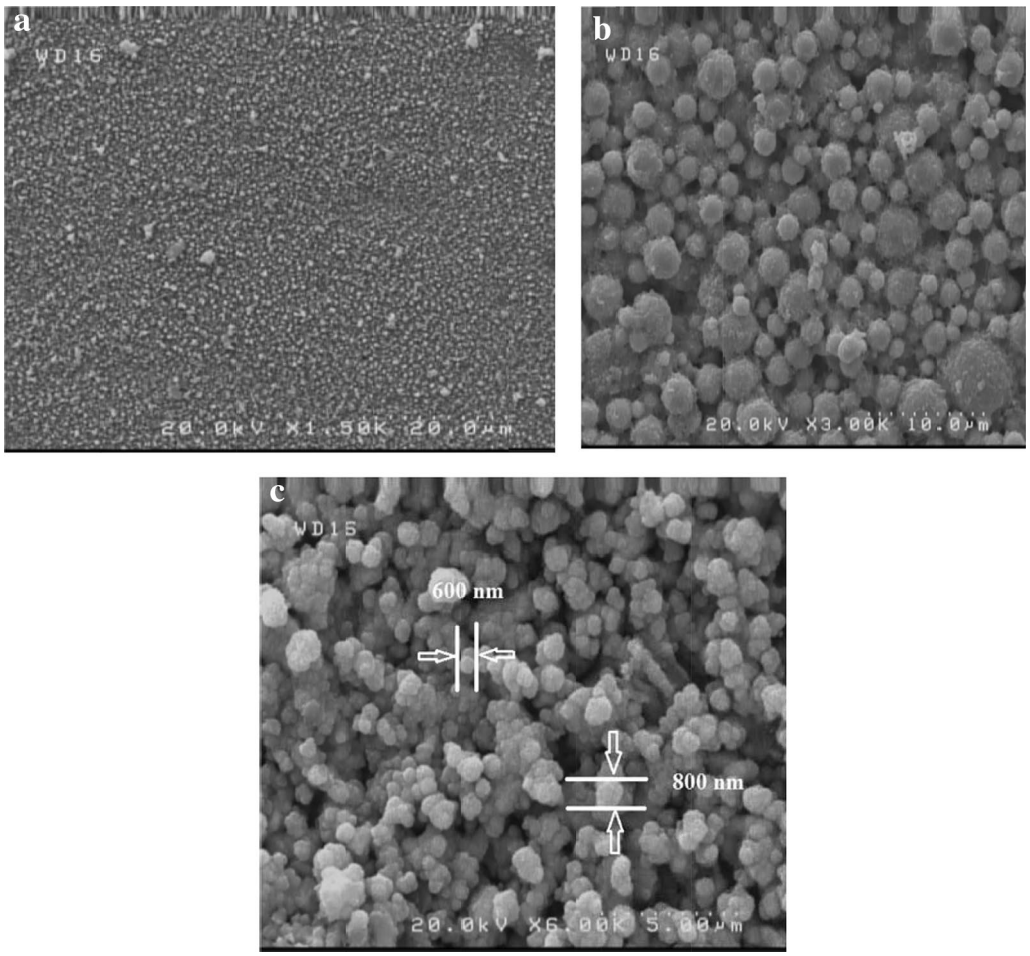


Fig. 2 SEM micrographs of inulin (**a**), maltodextrin (**b**), and β-cyclodextrin (**c**) as wall materials in polyphenolic core

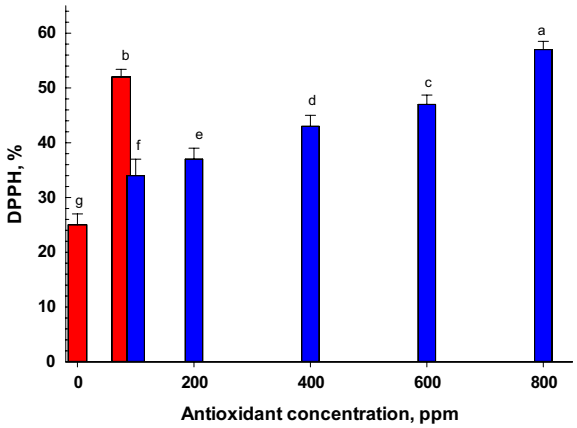


Fig. 3 Effect of polyphenols nanocapsules enrichment in canola oil on its stability (red color = canola oil with TBHQ and blue color = polyphenols nanocapsules). Alphabetic numbers shows the statistical significance difference among the samples ($P < 0.05$)

size distribution. Additionally, high conductivity of the samples causes a high charge density in the Taylor cone, which causes the jet to fragment into a polydispersed spray. As a result, it is possible to identify the samples' ideal conductivity range in accordance with the shape of electrosprayed particles in the stable cone-jet mode [12]. In the electrospray experiments, surface tension is overcome and tiny droplets are formed by the application of an electric force. However, increased surface tension causes the creation of bigger particles on the tip of the needle while the electric field is maintained constant since it will be challenging for them to disintegrate and break down into little particles.

Inulin 8% was the system that generated the largest particle size. This could be because there was not enough inulin to lower the surface tension and because the carrier exposed a lot of phenolics, which resulted to the largest particles consistent with earlier studies [31]. The inulin sample's bimodal size distribution also indicated that there was particle flocculation, making it less stable than samples made with greater inulin concentrations. Due to their high inulin concentration and low phenolic content, inulin carriers were found to have the smallest particle size distribution, suggesting greater homogeneity, less aggregation, and stability of the particles. Particle size increased and the distribution curve became monomodal as inulin concentration rose from 2 to 6 percent, indicating there was enough inulin present to lower surface tension and entrap the polyphenols. A smaller particle size distribution is indicated by a lower PDI. The most homogenous system in terms of particle size was shown by the maltodextrin sample, which had the lowest PDI (0.074).

Another significant characteristic that might show if nanoparticles are stable is their zeta-potential. According to Freitas and Müller, electrostatic repulsions between particles increase with increasing zeta-potential, resulting in less particle aggregation [32]. Additionally, a larger surface charge enhances the interaction of nanoparticles with cells, improving the transport of bioactive substances. Table 2 shows that all electrosprayed particles had negative ζ-potential due to the presence of carboxylate groups, which are the most highly charged functional groups. The majority of the time, when all the particles have a significant positive/negative surface charge (> + 30 mV and − 30 mV) [33].

Our findings demonstrated that electrosprayed samples made with 2, 4, and 6% maltodextrin exhibited for non-encapsulated particles ζ-potentials of − 46.8 mV, − 44.7 mV, and − 48.3 mV, respectively. But intriguingly, a higher negatively charged ζ-potential was seen when polyphenols were added to maltodextrin carriers (Table 2). For instance, we discovered that the ζ-potential for maltodextrin samples loaded with 500 and 1000 ppm phenolics, respectively, was − 64.7 mV and − 67.5 mV, whereas it was − 46.8 mV for unloaded equivalents. This may be caused by the negative surface charge of phenolic compounds on the particles' non-encapsulated surfaces or by a larger exposure of maltodextrin's negative functional groups when they interact with the phenolics they have integrated. This is supported by a higher ζ-potential [34]. Maltodextrin sample, in general, had the lowest negative ζ-potential (− 60.2 mV). Maltodextrin and β-cyclodextrin samples' ζ-potentials did not differ significantly ($P > 0.05$). However, a rise in zeta-potential ($P < 0.05$) was seen from 20 to 30%. Our data supported the earlier findings [31, 33].

Morphological properties

Figure 2a–c presents SEM photographs of microcapsules with wall materials including inulin, maltodextrin and β-cyclodextrin, respectively. Due to the particles' shrinking during the drying process, the morphology of microcapsules made with both encapsulating agents was irregularly spherical in form and had a heavily dented surface. Different DE MDs in microcapsules with the same shape have been observed in the literature [35]. It is possible to neutralize the repellent charges of carboxylate groups by interactions between sodium alginate and Ca^{2+} ions from $CaCl_2$ solution. This facilitates the crosslinking of alginate chains to create an encapsulating gel network [5]. Numerous factors, such as the vibration frequency, nozzle size, flow rate, and physical characteristics of alginate, affect the size of co-extruded beads. Good oil loading efficiency (68 ± 1%) and low bead breakage (2 ± 0.5% and 4 ± 0.5% for before and after freeze-drying,

respectively) were achieved under the present encapsulation circumstances.

Physicochemical properties of fortified canola oil

Antioxidant properties

Effect of polyphenols nanocapsules from canola meal on the stability of canola oil is provided in Fig. 3. The average of the radical scavenging DPPH of different canola oil is given in Fig. 3. As it can be seen the lowest antioxidant behavior was observed for the control (free of antioxidant). However, by increasing the amount of the encapsulated polyphenols antioxidants from canola meal, the antioxidative properties and DPPH level were statistically increased ($P<0.05$). The radical scavenging of canola oil containing 800 ppm nanocapsules of polyphenols was 61.84 which was higher than the canola oil with TBHQ as a synthetic antioxidant (58.40). Canola meal contains various phenolic compounds that exhibit pragmatic activity. The most common polyphenols in canola are hydroxycinnamic acids and flavonoids (flavonols) and important anthocyanin's are canola flavones including quercetin, isorhamnetin, and kaempferol. Caffeic acids and parahydroxybenzoic salicylic have also been found in canola seeds and meal. Phenolic acids and their derivatives and soluble and insoluble tannins are major phenolic compounds reported in canola. Antioxidant activity of extracted phenolic extracts reported less olive and sesame meal than TBHQ. By increasing the concentration of polyphenolic compounds in the extracts, their antioxidant activity and inhibition also intensified [36]; Therefore, increasing the concentration of the extract was directly related to its antioxidant activity. It has also been reported the rise of antioxidative activity of nano-encapsulated extract of nettles by increasing its concentration and stated 2500 ppm of nano-encapsulated extract of nettles has the same antioxidative activity like as TBHQ [10]. It had free radical scavenging activity similar to the synthetic antioxidant TBHQ [10]. The antioxidant activity of sunflower oil containing phenolic compounds extracted from meal was also increased [37].

Oxidative properties

Peroxide value (PV) is the primary product of oxidation of fat substances and in general, the susceptibility of oils and fats to oxidation was increased when unsaturated fatty acids increased. PV is one of the qualitative parameter and indicator related to chemical spoilage of oils and measuring the concentration of peroxides and hydroperoxides during storage time. The results of the PV changes during the oil storage for 40 days are displayed in Fig. 4a. It can be easily found that the oil peroxides has increased for all the samples over time period which are in agreement with previous works on sage seed gum [10] and rosemary extract [38]. However, the difference in PV of the samples was not initially significant ($P>0.05$), by increasing the periods the change in PV was appeared. The maximum increase in PV was seen in the control sample, which was statistically significant on different days of storage and followed by the oil encompassing the TBHQ antioxidant. The amount of PV in the oil containing TBHQ was higher than in soybean oil with rosemary [38] and sage seed gum [10] which are in line with our results. The low PV was observed for the samples contain no nanocapsules of polyphenols. At the end of the storage, the least amount of peroxides was found for the samples containing 800 ppm of polyphenols nanocapsules. In all free and polyphenols nanocapsules, the PV decreased by increasing the polyphenols from 200 to 800 nm but the difference were not statistically significant ($P>0.05$) which may be related to the pro-oxidant activity of polyphenols at high level of concentration. In overall, the highest antioxidant activity during 40 days of storage was observed for the canola oil enriched with 800 ppm of nanocapsules of polyphenols which have the lower PV than that of canola oil with TBHQ as a synthetic antioxidant ($P<0.05$).

The effect of nanocapsules of polyphenols on the oil oxidative is provided in Fig. 4b. It can be seen the oil stability of control was significantly lower than all of the samples ($P<0.05$). By increasing the polyphenols from 200 to 800 ppm, the stability was increased and the highest stability of oil was achieved for the sample with 800 ppm of nanocapsules of polyphenols. The oil stability of canola oil with 800 ppm of polyphenols at days 40 was 12.9 h which was significantly higher than the positive control sample containing TBHQ (12.67).

Iodine value and TBA index

Effect of polyphenols nanocapsules from canola meal on the iodine value and TBA of canola oil is provided in Fig. 4c, d. However, the average of the saturation rate of different canola oil were decreased by storage time, the reduction rate of saturation was much higher in control sample in comparison with the other samples. As can be seen, the lowest iodine value was observed for the control. However, by increasing the amount of the encapsulated polyphenols, the iodine value level was statistically increased ($P<0.05$). The iodine value of canola oil containing 800 ppm nanocapsules of polyphenols was higher than the canola oil with TBHQ as a synthetic antioxidant. The same behavior was also observed for the TBA value.

During the storage period, the iodine number of different oil samples gradually decreased, but the intensity Changes in samples enriched with nano-encapsulated extract and synthetic antioxidants were less than controls

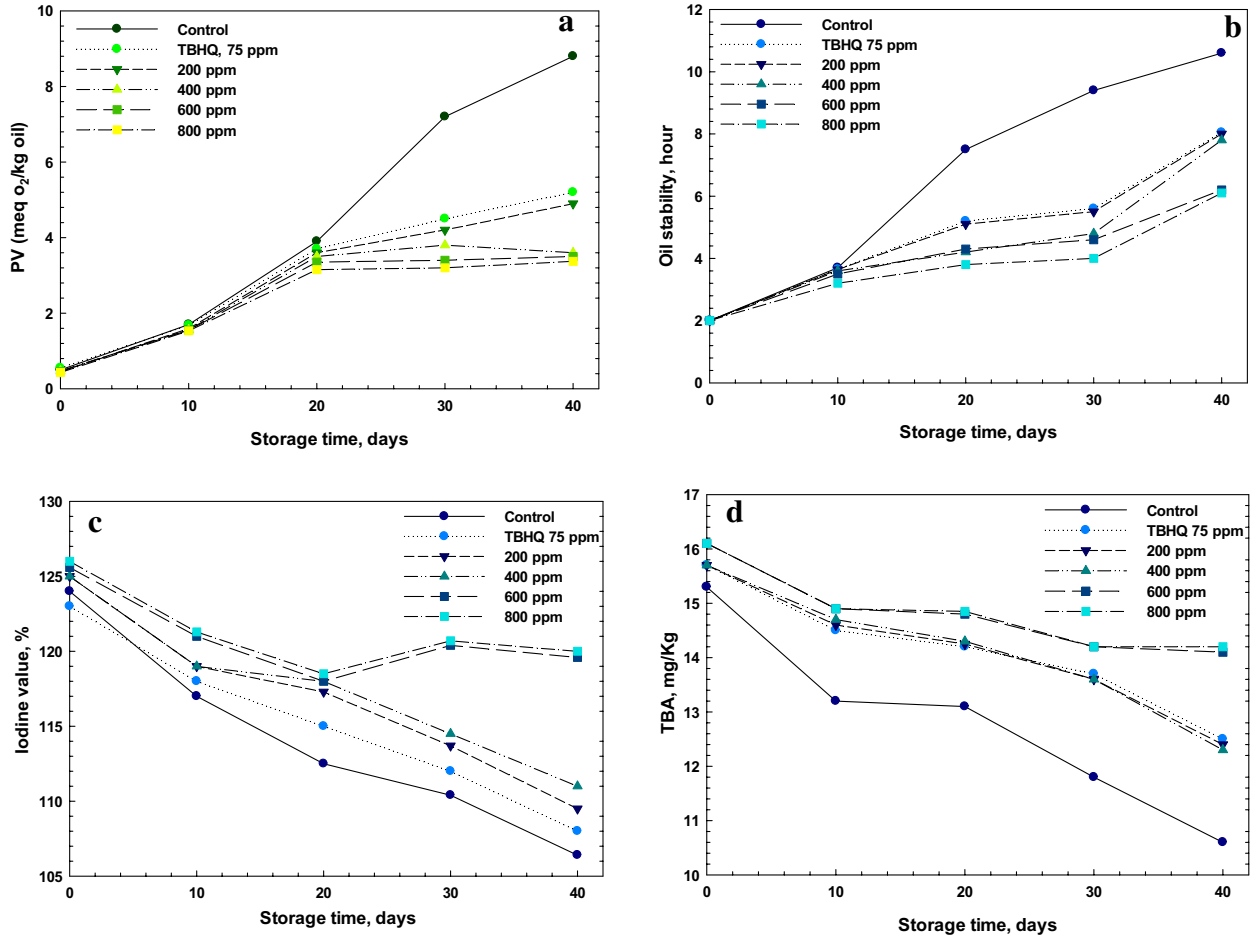


Fig. 4 The changes of physicochemical properties of canola oil as affected by various amounts of antioxidants during storage: **a** peroxide value, **b** oil stability, **c** iodine value, and **d** TBA value

and with increasing the concentration of nano-encapsulated extract, these changes also decreased. As mentioned before, the iodine number indicates the amount of unsaturated fatty acids in the oils and since the use of the extract Active can reduce the hydrolysis of triglycerides and thus reduce the level of fatty acids be released; therefore, it can reduce the severity of iodine index decrease in oil samples during storage Give. Therefore, it can be concluded that canola meal extract is able to reduce hydrolytic residue.

The results of a research on the impact of various concentrations of olive meal extract on the stabilization of sunflower oil's oxidation showed that during the heating period, the iodine number of the sample oil levels significantly decreased, and the intensity of this reduction was greater in the control oil samples than in the oil samples that contained meal extracts. It has also investigated the effect of plant extracts on oxidation of edible oils, which achieved similar results [39]. The iodine content of sunflower oil samples decreased over the heating period, but the addition of the synthetic antioxidant BHT and leek extract in the oil was able to reduce the iodine number during this much shorter duration than the control.

Conclusion

The findings of this work demonstrate the feasibility of isolating polyphenolic chemicals from canola meal, confirming their antioxidant activity and enabling nano-encapsulation. In order to attain higher efficiency, the size of the capsules was decreased through utilizing cutting-edge machinery like an electrospray device. The present study's findings support the idea that encapsulation might enhance the effectiveness of polyphenolic extracts. The shelf life of canola oil was also examined in this study, as were the benefits of adding polyphenolic nanocapsules as natural antioxidants. Fortified canola oil samples were compared to control oil samples and oil samples that included TBHQ over the

course of 40 days. The antioxidant activity of oil samples considerably increased with increasing concentrations of canola meal extract, reaching levels greater than the synthetic antioxidant TBHQ for oil containing 800 ppm of the extract. As the concentration of canola meal extract in oil samples increased, the rate of change of these oxidation parameters decreased significantly. The control sample had the highest oxidation, and the oxidation was reduced in oil samples containing 800 ppm nanocapsules of polyphenolic extract and TBHQ, respectively. During the storage period, the values of oxidation indices of peroxide number and TBA increased and the oxidation stability and iodine number decreased. Over a 40-day period, the rate of sedimentation in several canola oil samples containing nanocapsules was also tested, but no sedimentation was found in any of the samples. Overall, the research findings clearly explain the feasibility of phenolic compounds from canola meal as a potent antioxidant in preserving the canola oil for storage in the stakeholders.

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Author contributions
KZ-K: data curation; investigation; methodology; writing—original draft. VF: conceptualization; supervision; validation; writing—review and editing, MF: conceptualization; supervision; validation; visualization; writing—review and editing. All authors read and approved the final manuscript.

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All data are presented in the manuscript.

Declarations

Ethics approval and consent to participate
The authors will follow the Ethical Responsibilities of Authors and COPE rules. On behalf of all co-authors, I believe the participants are giving informed consent to participate in this study.

Consent for publication
I, Kobra Zadbash-Khansheer give my consent for the submitted manuscript to be published in the Chemical and Biological Technologies in Agriculture. II, Vajiheh Fadaei give my consent for the submitted manuscript to be published in the Chemical and Biological Technologies in Agriculture.

Competing interests
The authors declare that they have no competing interests.

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