

Research Article

Comparison Study between Cherry and Arabic Gums in Preparation and Characterization of Orange Peel Extract Nanocapsules

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This study was aimed at determining the potential use of cherry gum (CG) and chitosan (CS) as wall materials, to encapsulate an orange peel extract (PE) via the ionic gelation method and compare its efficiency with that of Arabic gum (AG). Different ratios of chitosan to gum (1:1, 1:2, and 1:3, v/v) and CS to PE (1:0.5, 1:1, and 1:1.5, v/v) were studied to evaluate the nanocapsule properties. The results showed that the capsules entrapping the PE were successfully created with an encapsulation efficiency (EE %) of more than 80% via the ionic gelation method. The ratio of chitosan:gums and CS:PE was affecting both the encapsulation efficiency and capsule size. The capsules' spherical shape and nanometer size were confirmed using an Atomic Force Microscope (AFM). The relative ratios 1:1 of CS:CG and 1:0.5 of CS:PE gave the highest EE% (89.27%) with an average capsule size of 70 nm, whereas the maximum EE% with AG was 97.39% with a mean size of 50 nm at the CS:PE ratio of 1:0.5 and AG:CS ratio of 1:2. The release profile of PE from the CS-CG matrix during 240 min under acidic and alkaline conditions was about 94.45% and 98.53%, respectively, and that from the CS-AG matrix was about 25.54% and 19.49%, respectively. The FTIR spectra confirmed the electrostatic interactions between the protonated amino group of chitosan (-NH_3^+) and carboxylic ions (-COO^-) of the gums. These findings indicated that the CS-CG could be used as an efficient and ecofriendly coating material for nanoencapsulation of PE.

1. Introduction

Throughout history, human beings seek bioactive compounds originating from nature as healthy foods. The phenolic compound group is the interesting bioactive compounds in food and pharmaceutical industry that are commonly found in plant foods. They have higher antioxidant activity, and also, they can be used in the food and other biological formulations as an antiallergenic, anti-inflammatory, and antimicrobial agent [1].

Citrus is Syria's largest fruit crop with a production estimated at 502966 tons in 2020, and orange accounts for about 60.33% of the total production of Syria's citrus [2]. During processing, about 44% of peels are produced as by-

products, which can cause environmental pollution [3]. Orange peel is a good source of phenolic compounds which have important benefits for human health [4]. Generally, phenolic compounds are sensitive to heat and light and have low bioavailability, which decreases their efficiency and health benefits [5]. To prevent degradation, control release, and improve the shelf life, they need to be encapsulated. In this technique, one substance (bioactive compounds) is entrapped within another substance (wall materials) [6].

Nanoencapsulation was widely investigated for drug delivery due to its higher surface areas which resulted in higher efficiency of absorption and uptake [7]. Today, the design of stable nanocapsules using available, safe, and cheap materials

is a challenge. Several nanocapsule preparation methods have been used, and one approach based on polysaccharides is the method of ionic gelation. Chitosan and gums are the major polysaccharides used in this technique. Particles are formed by the electrical attraction between positively charged amine groups of chitosan and negatively charged gum. The encapsulating agent type and core to coating ratio are the most important variable for the polyphenol encapsulation [8]. Razavi and Kenari [9] studied the influence of wall material type and percentage on encapsulation efficiency, the particle size of nanocapsules, and zeta potential.

Chitosan (CS) is a successful encapsulating agent [10]. It is a hydrophilic polymer composed of linear beta-(1-4) linked D-glucosamine and N-acetyl-D-glucosamine. It can easily cross-link with polyanions like gum to control the release of the drug [11].

Polysaccharides of tree gum are natural and flexible green materials that have various functional and structural properties to assemble different nanostructures [12]. Plant gums are produced through a phenomenon called gummosis. These exudates get in place of damage from branches of trees. Natural plant gums can be graded as food additives and are considered safe for human consumption. In addition, they were used in different industries as stabilizers, thickening and gelling agents, crystallization inhibitors, encapsulating agents, etc. [13]. The most popular gum used in nanoencapsulation of bioactive compounds is Arabic gum.

Arabic gum (AG) is a natural arabinogalactan protein obtained from *Acacia senegal* [14]. It is one of the oldest exudate gums and has been shown to have more negative charge sites for interaction with polycationic chitosan [15]. Because of the high price of Arabic gum, scientists are looking for new gum resources with good physical, chemical, and functional properties, such as gum produced by the *Rosaceae* family trees.

Most genera of the *Rosaceae* family produce gum after a microbial attack as a result of disease and mechanical damages [16]. Cherry gum (CG) polysaccharides consist of arabinose, galactose, glucose, rhamnose, and xylose [17]. The physicochemical, structural, and functional properties of *Rosaceae* gum exudates have been studied and characterized [18, 19, 20]. Nowadays, *Rosacea* gums are used in many fields, including encapsulation. Rezaei and Nasirpour [21] employed an almond gum/polyvinyl alcohol (PVA) combination to encapsulate curcumin and improve its solubility using the electrospinning technique. In another study conducted by Mahfoudhi and Hamdi [22], *Prunus dulcis* gum was proposed to offer greater protection β -carotene compared to Arabic gum.

To the best of our knowledge, no previous research has been done on the use of chitosan (CS) and cherry gum (CG) exudates in the preparation of nanocapsules. This work was aimed at evaluating the efficacy of CG, which is available in Syria, in the encapsulation of the polyphenol orange peel extract (PE) via the ionic gelation method, as well as the feasibility of employing it as a native alternative to imported Arabic gum (AG). The impact of different preparation procedures on particle size and encapsulation efficiency was investigated. The morphology, antioxidant activity, and nanocapsule release have all been studied.

2. Materials and Methods

2.1. Materials. Sweet orange peels (*Citrus sinensis*) were collected from local juice shops (Damascus, Syria) in 2018. The cherry gum (CG) sample was collected from the trunks and branches of cherry trees (*Prunus avium*) from Serghaya in southwestern Syria (August 2017). Arabic gum (AG) was purchased from the local market in Damascus City. Chitosan (CS) low molecular weight (MW = 50,000 – 190,000 Da, degree of deacetylation 75–85%) and all the chemicals and solvents used in this work were obtained from Sigma-Aldrich.

2.2. Extraction and Determination of Total Polyphenols from Orange Peel. Orange peels were cleaned and dried at 40°C for 48 h. Phenolic compounds were extracted by applying previously optimized conditions. The orange peels were mixed with ethanol (50%) at the ratio of 1:10, and the mixture was left to stand in the water bath at 36°C for 2 h. After extraction, the mixture was centrifuged at 4500 rpm for 6 min. The total polyphenolic compounds were determined using the Folin-Ciocalteu reagent according to the method described by Ebrahimzadeh et al. [23]. The standard curve was prepared with different concentrations of gallic acid ranging from 25 to 250 mg/L.

2.3. Preparation and Purification of Gums. Exudate gum purification was performed using a recorded method of Bhushette and Annapure [24] with some modifications. The gums were ground with a hammer mill and sieved. The powdered gum exudate solution (5% w/v) was stirred for 3 h at 50°C and flirted to remove impurities and then concentrated twice at 50°C. Absolute ethanol precipitated the CG exudate (exudate solution:ethanol, 1:3 v/v). The precipitated exudate was separated by centrifugation at 4500 rpm for 3 min and dried in the oven for 48 hours to have a constant weight and placed in an airtight container for further use. The solution of pure AG was dried in the oven until its weight was stable. Dry gums were collected and ground into a soft powder with an electrical mill and kept in an airtight container for further use.

2.4. Preparation of Orange Peel Extract Nanoparticles. Chitosan-gum nanocapsules containing PE were synthesized via an ionic gelation technique between CS positively charged and gums (CG and AG) negatively charged. Initially, CS (0.5%) was dissolved in acetic acid solution 1%. PE with different ratios to chitosan (0.5:1, 1:1, and 1.5:1) was slowly added to the chitosan solution. After that, gum solution (2%) was added dropwise to CS solution containing the orange peel extract using relative ratios of gum:chitosan (1:1, 2:1, and 3:1), and the mixture was stirred (1300 rpm) at room temperature for 2 h. The nanoparticle suspension was centrifuged at 13,000 rpm for 30 min at 4°C [25]. The supernatant was used for the measurement of free phenolic compounds.

2.5. Encapsulation Efficiency (EE). After separation of nanoparticles from the aqueous medium, the amount of free total phenolic compounds in the supernatant was measured by Folin-Ciocalteu methods described by Ebrahimzadeh et al.

[23] using a spectrophotometer at 765 nm, and the encapsulation efficiency was calculated according to the following formulation:

$$\text{EE} (\%) = \frac{(\text{total amount of phenols} - \text{free phenols})}{\text{total amount of phenols}} \times 100. \quad (1)$$

2.6. Nanostructure Characterization. The Atomic Force Microscope (AFM, Nanosurf easyScan2, Switzerland: tapping mode (Tap190 Al-G), NanoSensors™, Neuchatel, Switzerland) was used to determine the morphology and surface topography, particle sizes, and particle size distribution of CS-CG and CS-AG nanocapsules after dilution in water and drying in the open atmosphere at room temperature on a clean glass surface overnight.

2.7. Determination of Morphology, Antioxidant Activity, In Vitro Release, and Fourier Transform Infrared Spectrometry Analysis. The optimum formulations were selected based on the highest encapsulation efficiency to study morphology, antioxidant activity, *in vitro* release, and Fourier transform infrared spectroscopy (FTIR) after the nanocapsules dried in a freeze-drier (Alpha 1-2 LDplus, Germany).

2.7.1. Surface Morphology Analysis. The morphology of the freeze-dried CS-CG nanocapsules and CS-AG nanocapsules was determined using high-resolution scanning electron microscopy (SEM, XMU II-VEAG) at an acceleration voltage of 20 kV.

2.7.2. Determination of Antioxidant Activity. Fifty milligrams of dried nanocapsules was suspended in 50 mL ethanol (50%) and placed in a water bath with ultrasonic for 2 min.

(1) DPPH Free Radical Scavenging Activity. The sample suspension (100 µL) was added to 3.9 mL of DPPH ethanol solution (0.1 mM). After the mixture was incubated for 30 min in the dark at room temperature, the absorbance was read at 517 nm [26]. The radical scavenging activity was calculated using

$$\text{Inhibition} (\%) = \frac{\text{Absorbance of control} - \text{sample Absorbance}}{\text{Absorbance of control sample}} \times 100. \quad (2)$$

(2) Ferric Reducing Antioxidant Power (FRAP) Assays. First, 100 µL of the sample suspension, 250 µL sodium phosphate buffer (pH 6.6), and 250 µL potassium ferricyanide (1%) were mixed and incubated at 50°C for 20 min. After cooling to room temperature, 250 µL of trichloroacetic acid (10%) was added. 250 µL of the mixture was taken and mixed with 100 µL of water and 25 µL of freshly prepared ferric chloride solution (0.1%). The absorbance was measured at 700 nm. The standard curve was prepared from the ascorbic acid solutions at concentrations of 0.5 to 2.5 µg/mL, and the antioxidant activity was expressed as micrograms of ascorbic acid equivalents per 100 g [27].

2.7.3. In Vitro Release Study. The study was carried out according to the method of Yadav et al. [28] with some modifications. The release of PE from the matrix-complex was tested in two release solutions: 0.2 M phosphate buffer solution (pH = 7.2) and 0.1 N HCl (pH = 1.2). About 0.03 g of the freeze-dried nanoparticles was suspended in glass bottles with 1 mL of the release solution and incubated at 37°C in a shaking water bath. A sample was withdrawn after regular periods of 0, 15, 30, 60, 90, 120, 150, 180, 210, and 240 min, and the amount of phenols released was determined by the method in Section 2.2.

2.7.4. Infrared Spectrum Analysis. FTIR spectra of chitosan, two gums, and their nanoparticles are used to check the interaction of chemical bonds between phenolic compounds and polymers. They were recorded on an FTIR-4200 Jasco spectrometer in the wavelength range of 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹, using the KBr disc method.

3. Statistical Analysis

All analyses were performed in triplicate for each treatment, and the results are expressed as mean ± standard deviation. Data were subjected to analysis of two-way analysis of variance (ANOVA) followed by Fisher's least significant difference (LSD) test to determine the significant difference between treatments at the 5% level using Genstat software 12.

4. Results and Discussion

4.1. Topographical Properties. The surface detailed topology of CS-CG and CS-AG nanocapsules (which were measured using AFM and are illustrated in Table 1 and Figure 1 (proved that chitosan and gums were able to successfully form capsules in nanometer dimensions via the ionic gelation method. AFM images showed uniformly distributed structure and nearly spherical shape. The particle size distribution histogram of CS-CG and CS-AG nanocapsules infers that the particles are distributed in a very narrow range (Figure 1).

The mean size dimensions of CS-CG nanocapsules which are presented in Table 1 showed that they ranged from 40.5 to 70 nm, except that CS-CG ratios of 1:2 and 1:3 did not form any capsules when the CS:PE ratio was 1:0.5. The nonformulation of the capsules may be due to an increase in the viscosity of the CG solution at its higher ratios, which may result in a limited reduction in the functional groups [29] and a blocking of the interaction between the gum hydroxyl groups and CS amine group. On the other hand, CS-AG also produced nanometer-sized particles ranging from 30 to 77.5 nm. M. Hasani and S. Hasani [10] recorded that the mean size of nanocapsules of thyme essential oil prepared with CS-AG via the ionic gelation method ranged from 385.2 to 756.1 nm, which is larger than that of the capsules obtained in this study. The difference between our findings and the results of previous studies could be attributed to the variations in the size and molecular weight of the bioactive compounds, core material concentration and the ratio of the wall materials, and molecular weight which

TABLE 1: The size of chitosan-gum nanoparticles loaded with PE.

Size (nm)*	CS : PE ratio	CS : CG ratio			CS : AG ratio	
		1 : 1	1 : 2	1 : 3	1 : 1	1 : 2
1 : 0.5		70 ± 1.41 ^{b,c}	NF	NF	37 ± 1.83 ^{cd}	30 ± 4.25 ^e
1 : 1		52.5 ± 3.53 ^b	40 ± 1.71 ^d	41 ± 1.41 ^d	46 ± 1.42 ^{bc}	50 ± 7.07 ^b
1 : 1.5		46 ± 1.41 ^c	60 ± 1.42 ^a	52.5 ± 3.53 ^b	75 ± 2.83 ^a	77.5 ± 4.24 ^a
						39.5 ± 4.95 ^{cd}

*Mean ± SD values of triplicate samples. Different letters in the results of each gum studied indicate a significant difference ($P < 0.05$). NF: not formed.

are the factors affecting the size of nanocapsule formed by ionic gelation of biopolymers [30].

The analysis of variance (ANOVA) in Table 2 showed that the particle size was significantly affected by the individual factors and their interactions ($P < 0.05$).

As shown in Table 2, the different ratios of wall materials (CS-CG and CS-AG) had a significant effect on the size of the nanoparticles ($P < 0.05$), and the size of the capsules decreased as the ratio of the gums (CG or AG) increased. This can be attributed to the greater interaction between the negative charge of the gums and the positive charge of chitosan which is reflected in the small size of the nanocapsule [15]. These results are consistent with those obtained by Rajabi et al. [31] for encapsulation of saffron by CS and AG.

The findings of the statistical analysis in Table 2 also showed that the addition ratios of CG had a lower effect on the size of the particles ($P = 0.042$) than the Arabic gum ($P < 0.001$). This may be due to the fact that AG has more functional sites (hydroxyl group) than cherry gum [32] which makes it have a greater impact on particle sizes.

The phenolic extract ratio showed a significant impact on the size of the capsules produced by CS-CG and CS-AG (Table 2). In addition, the size of the particles increased by increasing the ratios of CS:PE. These results confirm the findings of Akdeniz et al. [33] who reported that since core material ratios increased, the coating material was inadequate to encapsulate it and this resulted in the coalescence of particles and larger droplet size. Similarly, Lee et al. [34] reported that as the concentration of the phenolic extract increased, the size of nanoparticles increased.

4.2. Encapsulation Efficiency (EE). The efficacy of encapsulation is an important parameter used to calculate the efficacy of active compound encapsulation. The higher value of the encapsulation efficiency means that the coating material is more capable of protecting the core material [35].

The results in Table 3 showed that the CS-CG encapsulation efficiency ranged from 63.94 to 89.27%, whereas the encapsulation efficiency of CS-AG ranged from 45.21 to 97.39%. The difference in EE% between AG and CG can be attributed to the differences in functional and physico-chemical properties of the gums, which, depending on molecular weight, chemical composition, monosaccharide sequence, and glycosidic bond position [36], cause differences in the interaction with CS.

The statistical results in Table 4 indicated that the ratio of PE had a significant effect on the EE% ($P < 0.05$) and

the efficiency decreased when the PE ratio was increased. This result may explain that at low ratios of PE, the formation of hydrogen bonds between OH-polyphenol groups and OH-chitosan groups was at the maximum, while as the PE increased, the solution density increased and the cross-linking between the matrix and phenolic extract was lost. Our result agreed with Rajabi et al. [31] who revealed that the EE% of saffron nanoparticles had decreased by increasing the ratio of the core (saffron) because the wall materials (CS and AG) were limited to entrap them.

On the other hand, the ratio of gum to chitosan had a significant effect on EE% ($P < 0.05$). The statistical analysis showed that the EE% improved significantly ($P < 0.05$) with an increase in the ratio of chitosan:gum. This can be explained by the fact that encapsulation materials are insufficient to produce a strong structural matrix and protective layer at a low ratio [37], while a thicker and stronger wall layer is formed around nanocapsules at the higher ratios of chitosan:gums, resulting in a higher EE%.

The correlation coefficient (r) between the mean sizes and EE% of CS-CG and CS-AG was found to be -0.36 and -0.60, respectively, indicating that the EE% was increased by decreasing the size of the capsules. This may be clarified by the fact that the reduction in the size of the particles has increased in surface area value which provides availability of the sites of the phenolic extract leading to higher EE%.

4.3. Scanning Electron Microscopy (SEM) Images. The samples with the highest encapsulation efficiency formulation were selected to investigate the morphology (size and shape) of the synthesized nanocapsules by SEM microscopy. Figure 2 shows SEM micrographs of the freeze-dried samples of CS-CG nanocapsules (Figures 2(a)-2(c)) and CS-AG nanocapsules (Figures 2(d)-2(e)). It is shown that irregular sponge-like nanoparticles with pores are highly interconnected and this morphology is in agreement with the literature of M. Hasani and S. Hasani [10]. The spongy pore structure of the particles is due to the formation and sublimation of ice crystals during the freeze-drying process [38]. Kuck and Noreña [39] reported a porous structure and irregular shape when the grape skin extract was encapsulated with gums.

As shown in Figure 2, CS-AG capsules have a tiny and more dense/compact porosity compared to CS-CG capsules, which allows an efficient entrapment of the PE within the CS-AG structure. These results agree with the study of the efficacy of encapsulation.

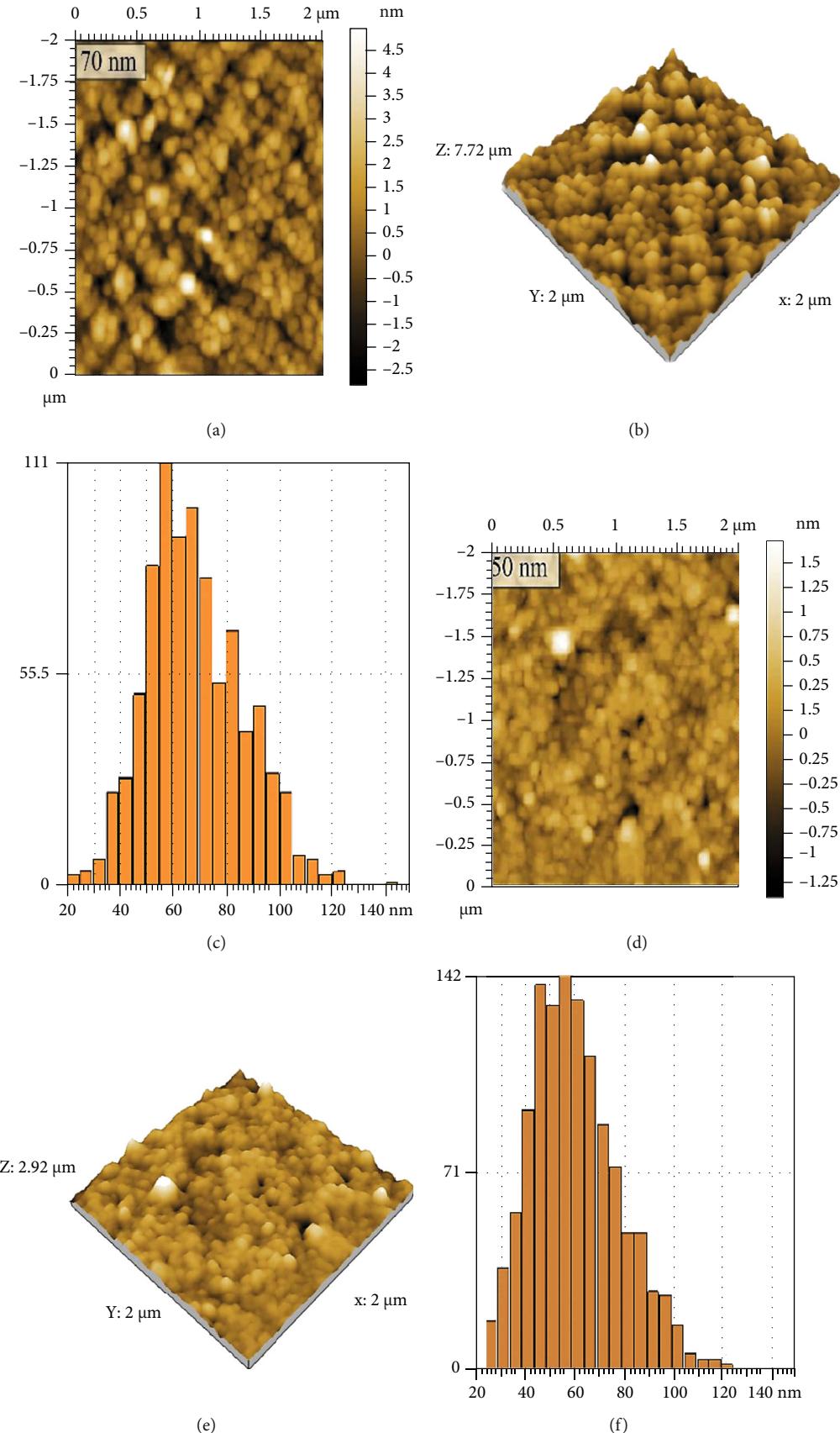


FIGURE 1: $2 \times 2 \mu\text{m}^2$ (2D and 3D) AFM images and particle size distribution of nanocapsules entrapping PE: (a-c) CS-CG nanoparticles (1:1 CS-CG and 1:0.5 CS:PE) and (d-f) CS-AG nanoparticle (1:2 CS:AG and 1:0.5 CS:PE).

TABLE 2: Analysis of variance of chitosan-gum nanoparticle sizes.

Source of variation	d.f	CS-CG			CS-AG			F
		S.S	M.S.	F	d.f	S.S	M.S.	
Gum ratio	2	32.667	16.333	0.042	2	1308.78	654.39	<0.001
Phenolic extract ratio*	1	216.750	216.750	<0.001	2	2855.44	1427.72	<0.001
Gum × phenolic extract	2	378.000	189.000	<0.001	4	1046.56	261.64	<0.001

*The ratio of the phenolic extract (1 : 0.5) which did not form any capsules was excluded from the statistical analysis of CS-CG nanocapsule size.

TABLE 3: The encapsulation efficiency of chitosan-gum nanoparticles loaded with PE.

Encapsulation efficiency (EE) (%) [*]	CS : CG ratio			CS : AG ratio			F
	CS : PE ratio	1 : 1	1 : 2	1 : 3	1 : 1	1 : 2	1 : 3
1 : 0.5	89.27 ± 0.39 ^a	—	—	—	88.99 ± 0.01 ^c	±97.390.12 ^a	94.96 ± 2.49 ^b
1 : 1	74.40 ± 0.39 ^c	82.11 ± 1.17 ^b	86.23 ± 1.56 ^a	69.71 ± 1.56 ^g	84.67 ± 0.12 ^d	79.63 ± 0.78 ^e	
1 : 1.5	63.94 ± 0.39 ^e	71.92 ± 2.34 ^c	68.61 ± 0.78 ^d	±45.210.39 ^h	73.79 ± 0.11 ^f	74.12 ± 1.56 ^f	

*Mean values ± SD values. Different letters indicate a significant difference ($P < 0.05$) between the results of each of the gum studied.

TABLE 4: Analysis of variance for the encapsulation efficiency of chitosan-gum nanoparticles.

Source of variation	d.f	CS-CG			CS-AG			F
		S.S	M.S.	F	d.f	S.S	M.S.	
Gum ratio	2	173.143	86.571	<0.001	2	1039.276	519.638	<0.001
Phenolic extract ratio*	1	488.198	488.198	<0.001	2	2610.783	1305.392	<0.001
Gum × phenolic extract	2	35.514	17.757	0.021	4	349.547	87.387	<0.001

*The ratio of the phenolic extract (1 : 0.5) which did not form any capsules was excluded from the statistical analysis of CS-CG nanocapsules.

4.4. Antioxidant Activity. The antioxidant activity of PE was investigated before and after encapsulation using chitosan and gums and is shown in Table 5. The values of scavenging activity of the orange peel extract, CS-CG nanocapsules, and CS-AG nanocapsules were 63.58, 20.4, and 45.56%, respectively. On the other hand, the antioxidant activity, according to the reducing power method of the orange peel extract, CS-CG nanocapsules, and CS-AG nanocapsules, was 5.38, 3.94, and 4.9 mg/100 g, respectively (Table 5). The results of antioxidant activity confirmed that the PE was trapped and preserved by the wall capsule materials (chitosan and gums) and the antioxidant activity of nanoparticles was ascribed to the low concentration of phenolic compounds on the surface of the capsules. These results were consistent with those reported by Sari et al. [40] who found that the encapsulation not only preserves the bioactive compound degradation but can also protect its action against antioxidants. The difference between the antioxidant activity of CS-CG and CS-AG is due to the difference in EE%, and the capsules with the highest EE% illustrated the highest antioxidant activity. Shaygannia et al. [41] observed similar results when Arabic, Persian, and basil seed gums were used as the wall materials for encapsulating a lemon waste extract.

4.5. In Vitro Release of PE. The release of phenolic compounds was performed to monitor the ability of encapsulation agents to retain the phenolic compounds [30]. The highest EE treatments with CS-CG and CS-AG were chosen to examine the release mechanism under acidic and alkaline conditions.

Under acidic conditions, the polymer matrix swells due to the high solubility of chitosan. In an acidic medium, the release of phenolic compounds from capsules was increased with the time of incubation increased. After 240 min, 94.45% and 25.54% of phenolic compounds were released from CS-CG and CS-AG nanocapsules, respectively (Figure 3). Tan et al. [42] achieved 16% of the curcumin which was released after 3 h, but Rajabi et al. [31] reported rapid release (about 80%) of the saffron extract from chitosan-Arabic gum nanocapsules during 240 min in acidic solutions.

In the media with pH values above 6.5, the chains of gums tend to swell and disrupt the structure of nanoparticles, resulting in greater porosity in the structure of nanoparticles and greater release [15]. At pH = 7.2, the maximum PE release was about 98.53% from CS-CS, while CS-AG showed a 19.49% release during 240 minutes (Figure 4).

The results of the release study were consistent with the SEM images, and we can observe that CS/AG nanocapsules

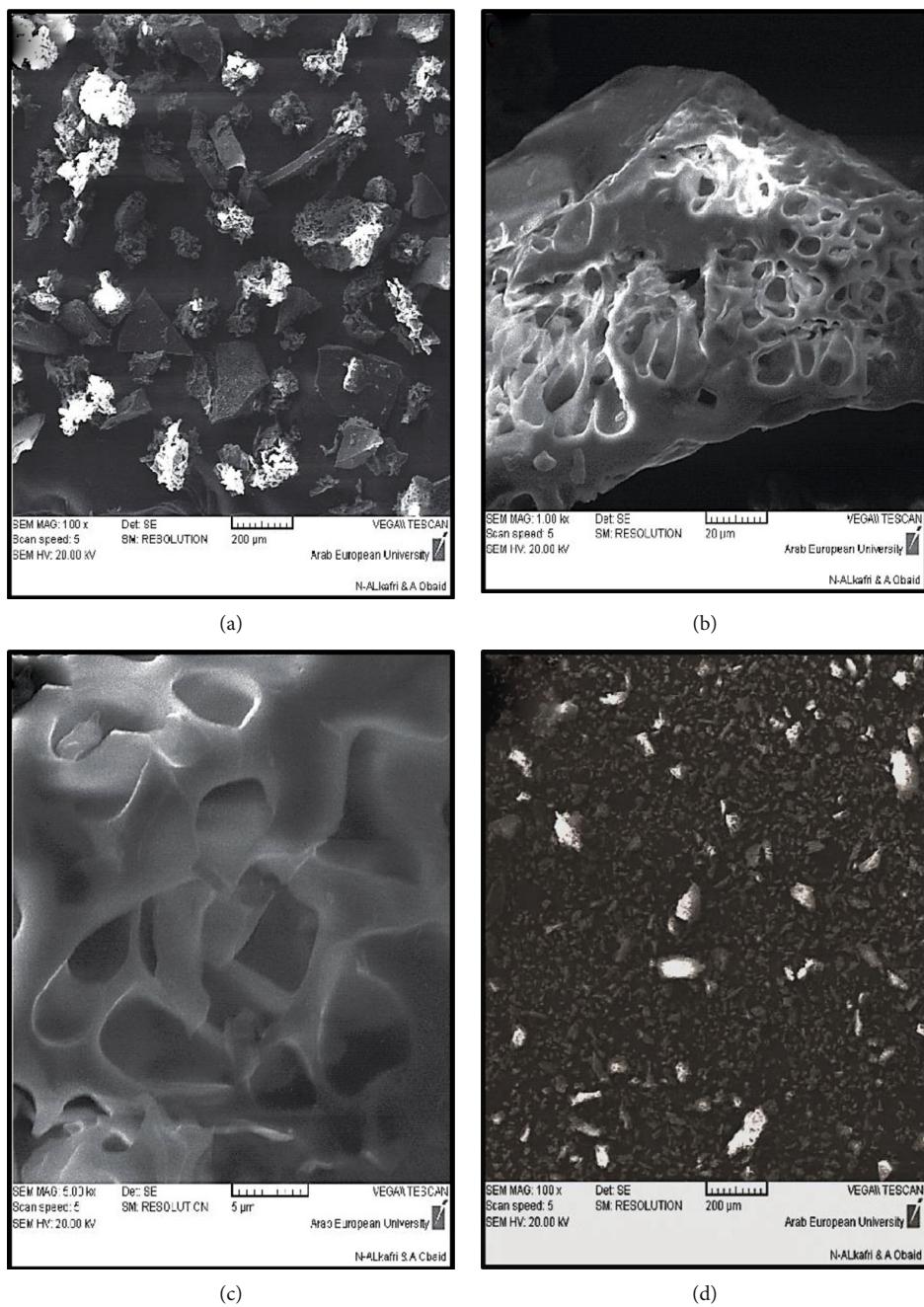


FIGURE 2: Continued.

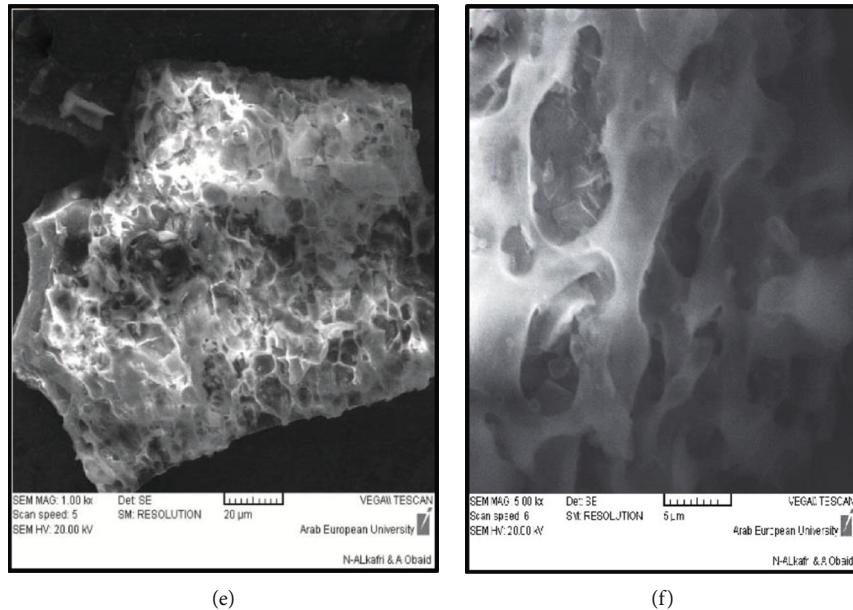


FIGURE 2: SEM images of nanocapsules entrapping PE: (a-c) CS-CG nanoparticles and (d-f) CS-AG nanocapsules at different magnification scales.

TABLE 5: Antioxidant activity of free and encapsulated PE.

Sample	% free radical scavenging activities*	Reducing power (mg/100 g)*
Orange peel extract	63.58 ± 0.21 ^a	5.38 ± 0.01 ^a
CS-CG nanocapsules	20.4 ± 1.6 ^c	3.94 ± 0.12 ^c
CS-AG nanocapsules	45.56 ± 0.08 ^b	4.9 ± 0.05 ^b

*Mean ± SD values. Different letters in the same column indicate significant difference ($P < 0.05$) between the results.

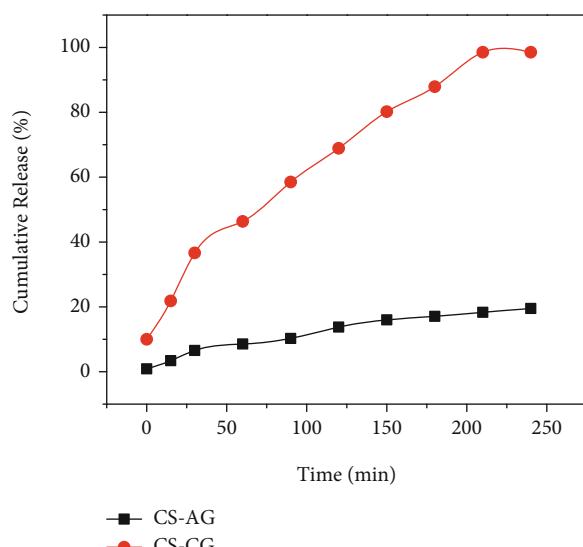


FIGURE 3: The cumulative release of PE from CS/AG and CS/CG nanocapsules in acidic medium.

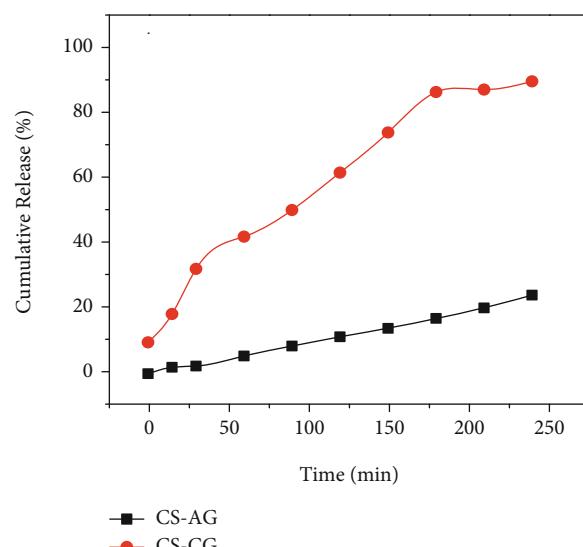


FIGURE 4: The cumulative release of PE from CS/AG and CS/CG nanocapsules in alkaline medium.

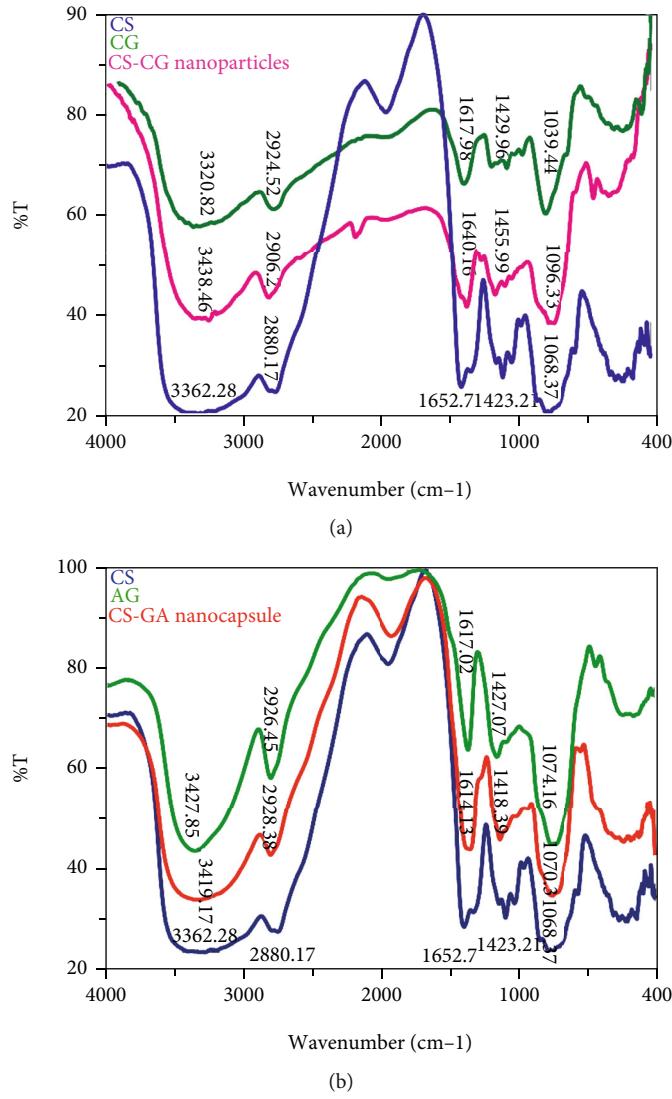


FIGURE 5: FTIR spectra: (a) CS, CG, and CS-CG nanocapsules and (b) CS, AG, and CS-AG nanocapsules.

had strongly retained the loaded polyphenols in different pH media than CS/CG because CS-AG capsules had tiny pores according to the SEM images. Also, AG containing multiple active sites (hydroxyl groups) [32] created stronger interactions with chitosan amino groups.

4.6. FTIR Spectroscopy. The FTIR spectra of chitosan, gums, and the final nanoparticles are shown in Figure 5. The curves of chitosan showed a wide peak at 3362.28 cm^{-1} which is due to hydrogen-bonded O-H stretching vibration and the peak of N-H stretching frequency from primary amine and secondary type amide overlapped in the same region. The weak band at 2880.17 cm^{-1} corresponds to stretching vibrations of C-H bonds in CH_2 and CH_3 groups. Chitosan has the peak at 1652.7 cm^{-1} , a characteristic amide I band attributed to $\text{C}\ddot{\text{O}}$ vibration of the acetylated units ($-\text{CONH}_2$ groups). The signal at 1423.21 cm^{-1} is related to the C-N stretching vibration of type I amine. The strong bands at 1068.37 cm^{-1} are due to the stretching of the C-O bond [42].

In cherry and Arabic gum spectra, the peaks at 3320.82 and 3427.85 cm^{-1} , respectively, are due to the vibration of the O-H bond, and another typical peak was detected at 2880.17 and 2926.45 cm^{-1} , respectively, due to the stretching vibration of the C-H bond. The asymmetric and symmetric stretching vibration of carboxyl was obtained at 1617.98 and 1429.96 cm^{-1} in cherry gum, while in Arabic gum, it was obtained at 1617.02 and 1427.04 cm^{-1} . The bands 1039.44 cm^{-1} and 1074.07 cm^{-1} are due to the stretching of the C-O bond at cherry gum and Arabic gum, respectively [43].

In nanoencapsulation spectra, there was a change in the carbonyl-amide region. The peaks at 1617.98 and 1652.7 cm^{-1} shifted to 1640.16 and 1640.16 cm^{-1} , respectively. Also, the peaks of 1429.96 and 1427.04 cm^{-1} shifted to 1455.90 and 1418.39 cm^{-1} in the spectrum of CS-CG and CS-AG nanocapsules, respectively. The changes in the FTIR spectra confirm the electrostatic interaction between the negative functional groups of the gums and the positive ones of chitosan [42].

5. Conclusion

The capacity of cherry gum (*Prunus avium*) exudates to encapsulate PE was compared to that of AG in this study. The results showed that the PE can be encapsulated using the ionic gelation method with CS-CG as a wall material, but with less encapsulation efficiency and larger capsule size compared to CS-AG. The FTIR analysis verified that the carboxylic ions ($-COO^-$) of the gums and protonated amino group ($-NH_3^+$) of CS were linked in the nanocapsules. The findings of the in vitro release study revealed that the release of PE is different as the wall of the capsule is different, with CS-CG releasing PE faster than CS-AG over time. Based on the results of this study, the CS-CG can be used as an effective natural wall material for encapsulation of PE and can deliver it into the gastrointestinal system.

Future research will focus on the application of PE-loaded CS-CG nanocapsules as a natural antioxidant to extend the shelf life of food products and compare it with synthetic antioxidants.

Data Availability

The datasets used and/or analyzed during the current study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare no conflict of interest.

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