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Nozzle-less electrospinning: Nanoencapsulation of ajwain essential oil using chitosan-gelatin nanofibers

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Abstract

The aim of this research was to investigate the efficiency of nozzle-less electrospinning for encapsulation of ajwain essential oil (as a hydrophobic bioactive) using two hydrocolloids (chitosan/gelatin) in order to enhance its antioxidant properties and stability for food applications. Nanofibers were spun using chitosan/gelatin in ratios of 1:6, 1:8 and 1:10 and ajwain concentrations of 20 and 40%. Solution properties (i.e. viscosity and electrical conductivity) were measured. Encapsulation efficiency and loading capacity data illustrated an enhancement with increasing of essential oil concentration. Fibers diameter and morphology were studied by scanning electron microscopy (SEM). The chitosan/gelatin nanofibers with ratio of 1:6 containing 40% essential oil had the highest encapsulation efficiency (99.9%), loading capacity (39.9%) and the smallest diameter (146 nm). Attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) proved that during electrospinning, no any chemical interaction was occurred between ingredients and differential scanning calorimetry (DSC) data showed that essential oil was well encapsulated in nanofibers. Antioxidant properties were analyzed by 2,2-diphenyl-1-picrylhydrazylradical and approved the efficiency of encapsulation for protection of antioxidants.

Keywords: *Ajwain* essential oil; Antioxidant activity; Encapsulation; Nanofibers; Nozzle-less electrospinning.

Introduction

Oxidation reaction has a series of adverse effects on food quality; thus, it is necessary to develop food packaging material incorporated with natural antioxidants. Hence, in recent years many studies have been conducted on investigating the effects of natural antioxidants such as plant essential oils (Eos) as an alternative to chemical preservatives and synthetic antioxidants for extending the shelf life of food products (Wu et al., 2012)

Trachysper ammi, known as ajwain, is an erect annual herb with striate stem which is traditionally used as a medicinal plant for its antiseptic, appetizer and carminative properties. Thymol, the major phenolic compound presents in ajwain's EO, has been reported as an anti-inflammatory, antifungal, antipyretic, antifilarial, analgesic, antinociceptive and antioxidant agent (Tabatabai et al, 2019). However, EOs are water-insoluble, and biologically sensitive to environmental conditions such as light, oxygen,

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humidity enzymes, alkaline pH and high temperature (Trifković et al., 2014). Recently new methods have been introduced to enhance their sustainability and bioavailability such as encapsulation. Nanoencapsulation process involves entrapment of a bioactive matter within a nanometer size carrier which leads to increase stability, solubility and controlled release of the bioactive compound (Cevallos, Buera, & Elizalde, 2010). Among various nanomaterials such as: nanoparticles, nanoplatelets and nanofibers, the latter with a high aspect-ratio, low density, extremely large surface-to-mass ratio, and superior mechanical performance have been shown to possess excellent mechanical, thermal and electrical properties (Naebe et al., 2007). Among the classical methods to produce nanofibers such as phase separation, drawing, template synthesis, self-assembly, and thermal oxidation, electrospinning is a suitable candidate for establishing fibers due to its attractive features to produce fibers in nanoscale at low cost and its ability to be used for a large variety of materials (Rezaei et al., 2015). Nevertheless, the efficiency of a single-needle electrospinning system is too low for industrial scale. Therefore, nozzle-less electrospinning was investigated in order to enhance productivity in large scale with forming many jets from free surface of polymer solutions (Kostakova et al., 2009).

Chitosan and gelatin are two natural biopolymers used in electrospinning because of their biocompatibility and biodegradability (Ebrahimi et al., 2019). Chitosan, a modified carbohydrate polymer with average molecular weight of 100– 500 kDa, is synthesized through the partial deacetylation of chitin. Chitosan is a cationic polymer with a pKa value of 6.3, that is readily soluble in dilute acid solutions with a pH less than 6 (Voron'ko et al., 2016). It had been widely used in food, cosmetic, biomedical, and pharmaceutical applications due to its excellent properties such as biocompatibility and antibacterial activity. Since the electrospinning of pure chitosan proved to be impossible, due to its structure, viscosity, electrical conductivity, therefore chitosan was mixed with other spinnable biopolymers. Gelatin is a natural biopolymer derived from acid or alkaline hydrolysis of animal collagen (Xu et al., 2020). Gelatin is a typical amphoteric biopolymer with isoelectric point (pI≈ 5.3), which contains both positive and negative charges depending on the functional groups (amino and carboxyl groups) present in the molecule (Zhu et al., 2018). The combination of chitosan and gelatin in the acidic pH, can be successfully applied to synthesize nanofibers with good physical properties by electrospinning (Amjadi et al., 2019; Dhandayuthapani et al., 2010; Xu et al., 2020).

The aims of this study were to encapsulate ajwain essential oil in chitosan/gelatin nanofibers by using nozzle-less electrospinning and investigate their antioxidant properties for its potential application as a natural food additive.

Materials and methods

Gelatin powder (Type A; Bloom number of 220) from bovine and chitosan (molecular mass of 60000- 120000) were obtained from Merck. Ajwain essenential oil was extracted from *Trachysper ammi* which was collected from eastern Esfahan province, Iran. All reagents were at least of analytical grade.

Preparation of solutions for electrospinning

Solvents and solutions were prepared according to our previous work (Vafania et al., 2019).

Solvents were selected based on solubility of different materials. Chitosan and gelatin were soluble in acetic acid and ajwain essential oil was soluble in ethanol. Therefore the solvent consisted of 50% ethanol, 45% acetic acid and 5% deionized water. Chitosan (2% W/V) and gelatin (9% W/V at 40°C) were stirred separately for 24 h and 30 min, respectively. The two obtained solutions were mixed with different ratios (chitosan to gelatin volume ratio of=1:10, 1:8 and 1:6) and then ajwain essenential oil was added to the biopolymer solution with the ratios of 20 and 40% (V/W of solid biopolymers).

Solution characterization

Important parameters of the solution for electrospinning are viscosity and electrical conductivity which were measured by a viscometer (Brookfield, DV2, USA) using the spindle No. 21 at 50 rpm (shear rate of 46.5 s^{-1}) and an electrical conductometer (Inolab, Germany), respectively. The experiments were performed at 25± 0.5◦C in three replications (Karim et al., 2020).

Nanofiber fabrication

Disk shape nozzle-less electrospinning with 5 disks (Fig. 1) was used to fabricate nanofibers from free surface of chitosan/gelatin solutions containing ajwain essential oil. During the electrospinning process, the voltage was 25 kV, tip to collector distance was 5 cm and rotation speed was 20 rpm. Fibers were collected over an aluminum foil.

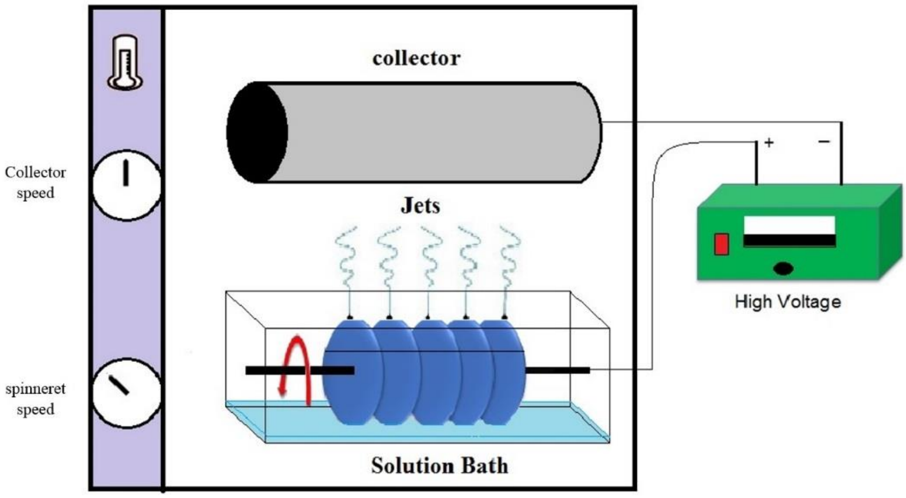


Fig. 1. Schematic of nozzle-less electrospinning.

Scanning electron microscopy (SEM)

The produced fibers were analyzed for their morphologies using a scanning electron microscope (Philips, model X130, Netherlands) after coating with a thin layer of gold. SEM images were used to measure fibers' diameters using ImageJ software (USA).

Determination of encapsulation efficiency and loading capacity

Encapsulation efficiency (EE%) and loading capacity (LC%) were determined by measuring the surface essenential oil. Ethanol was used to extract the surface essential oil from the gelatin/chitosan nanofibers and absorbance was read at 267 nm (T60 UV, England). The EE and LC were determined using following equations (Bashiri et al., 2020; Nahr et al., 2018):

$$\%EE = \frac{\text{Total essence weight} - \text{Free surface essence weight}}{\text{Total essence waight}} \times 100 \quad (1)$$

$$\%LC = \frac{\text{Total essence weight} - \text{Free surface essence weight}}{\text{Total nanofibers weight}} \times 100 \quad (2)$$

Attenuated total reflection Fourier-transform infrared spectroscopy

Attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) is a method to identify functional groups of organic compounds and changes in chemical structure of gelatin, chitosan, ajwain essential oil and nanofibers (chitosan to gelatin ratio of 1:6 with 40% essential oil). The samples were mixed with KBr (with ratio of 1:100) to prepare tablets. The spectra were acquired at wavenumbers of 4000- 500 cm^{-1} with resolution of 4 cm^{-1} (Broker, model Tensor-27, Germany).

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a common method to investigate thermal behavior of materials. Five mg of samples (gelatin, chitosan and nanofibers containing essential oil) were used for analysis by DSC instrument (Bakher, Germany). Samples were placed into aluminum hermetic crucibles, sealed and analyzed for the temperature range of 25ºC to 350ºC at a heating rate of 10ºC/min.

Antioxidant activity

The antioxidant capacities of ajwain essential oil and nanofiber containing ajwain essential oil were analyzed by 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging assay. DPPH method is regarded as a fast and extensive approach to assess antioxidant activity and power of combining with free radicals or donating hydrogen in food materials. DPPH radical is a stable free radical with the central atom of nitrogen. DPPH changes from purple to yellow with reduction reaction through capturing hydrogen or electron. To this end, a 0.2 mmol/L DPPH solution was prepared with 1 mg/ml (effective concentrations of EOs in samples) of sample solution prepared in 70 ml/100 ml aqueous ethanol after continuous incubation in a dark space at 4°C. The DPPH radical scavenging activities of the samples were evaluated by measuring absorbance at 517 nm against 70 ml/100 ml aqueous ethanol as a blank. The experiments were performed for different storage periods (1, 6, 12 and 18 days). The antioxidant activity of free essential oils and nanofibers were determined by the following equation (Piran et al., 2012):

$$\text{Antioxidant activity } (\%) = \frac{\text{Control absorbance} - \text{Sample absorbance}}{\text{Control absorbance}} \times 100 \quad (3)$$

Results and discussions

Properties of solutions

Solution viscosity plays an essential role in spinnability of biopolymers. Increasing the concentration of the polymeric solution will lead to an increase in the viscosity, which then increases the chain entanglement among the polymer chains. These chain entanglements overcome the surface tension and ultimately results in uniform bead-less electrospun nanofibers. This viscosity is called critical viscosity at lower which the polymer chains are less involved together and cannot overcome the repulsion forces that leads to formation of particles, instead of fibers. Nevertheless, when the viscosity of solution is too high, electrical field cannot overcome the internal foresees and fibers are not formed again. Hence, it can be concluded that determination of the critical value of the viscosity is essential to obtain bead-less nanofibers (Kurd et al., 2017).

Electrical conductivity of a solution depends upon the type of polymer, solvent and the presenential oil of ions. Increasing the conductivity of the solution to a critical value will not only increase the charge over the surface of the droplet to form Taylor cone but also cause decrease in the fiber diameter (Haider et al., 2018).

Nine series of polymer solutions with different ratios of chitosan to gelatin (1:6, 1:8 and 1:10) with (20% and 40%) and without ajwain essenential oil were prepared and their viscosities and electrical conductivities were measured (Table 1). According to the results a shear thinning behavior was observed in all cases. In fact, an increase in shear rate leads to higher ordering of the polymer chains, which tend to orientate toward the applied stress (Bertolo et al., 2020; Rodrigues et al., 2021). By increasing chitosan volume ratio, electrical conductivity increased as viscosity of the polymer solutions decreased ($P<0.05$). Actually, total concentration of the polymer solution could be dominant with increasing the ratio of chitosan which played a significant role in decreasing viscosity. On the other hand, the electrical conductivity dramatically increased by increasing chitosan volume ratio because of the fact that electrical conductivity of chitosan solution was higher than gelatin. Liu et al. (2020) indicated that unlike viscosity, the electrical conductivity of the gelatin/chitosan (6:1) solution was higher than that of the gelatin/chitosan (8:1) solution.

Park et al. (2004) reported the same results for silk fibroin/chitosan solutions and indicated that by increasing chitosan ratio, the electrical conductivity of the polymer solution increased and diameter of nanofibers decreased.

On the other hand, the results indicated that viscosity and electrical conductivity of the solutions decreased due to increase of percentage of essential oil ($p<0.05$). According to observation of Moomand and Lim (2015), increasing amount of fish oil in polymer solution caused a reduction in electrical conductivity.

Table 1- Viscosity and electrical conductivity (mean± SD) of solutions for different chitosan to gelatin volume ratios (1:6, 1:8 and 1:10) and amount of ajwain essence (0, 20 and 40%).

Sample number	Chitosan to gelatin ratio	Amount of ajwain essence (%)	Viscosity (cp)	Electrical Conductivity (µS/cm)
1	1:10	0	117±1.41^{a}	480± 5^{f}
2	1:8	0	95± 2.8^{b}	547± 7^{c}
3	1:6	0	66.5± 2.1^{d}	883± 5^{a}
4	1:10	20	89.5± 3.5^{c}	411± 5^{h}
5	1:8	20	60.5± 2.1^{d}	490± 8^{ef}
6	1:6	20	50.0± 2.8^{e}	519± 10^{d}
7	1:10	40	82.5± 4.9^{c}	445± 10^{g}
8	1:8	40	63.0± 7.1^{d}	504± 6de
9	1:6	40	41.5± 4.9^{e}	670± 11^{b}

* Values with different superscript letters in the same column were statistically significant ($p<0.05$).

Morphology and size of nanofibers

The SEM morphologies of electrospun fibers from the different ratio of chitosan/gelatin containing various concentrations of essenential oil are shown in Fig 2. The results showed that increasing of the chitosan volume ratio had a significant effect on reducing the diameter of the nanofibers due to its low viscosity and higher electrical conductivity. Therefore, the ratio of 1:6 chitosan/gelatin possessed the smallest diameter, with smooth bead-free surface. Similar results were reported for chitosan/gelatin solution by (Ebrahimi et al., 2019). On the other hand, thinner diameters of nanofibers with higher ratio of chitosan were obtained because of its higher electrical conductivity values. Liu et al. (2020) have proved that chitosan has high electric charge density, and the extra charge can lead to the repulsion of the polymer jet, as a result reduced diameters of nanofibers when the ratios of chitosan were increased. Haider et al. (2010) studied electrospinning of biopolymer and reported that by increasing chitosan ratio, the diameter of fibers decreased. On the other hand, increasing the percentage of essential oil had a significant effect ($P<0.05$) on increasing the diameter of nanofiber, which were related to the reduction of electrical conductivity that reduced the elongation of polymer jet through the applied voltage (Charernsriwilaiwat et al., 2013). In our previous report, entrapment of thyme essential oil within the fibers caused an increase of diameter (Vafania et al., 2019). Shao et al. (2018) demonstrated that the incorporation of tea polyphenols can increase the diameter of pullulan-CMC nanofiber.

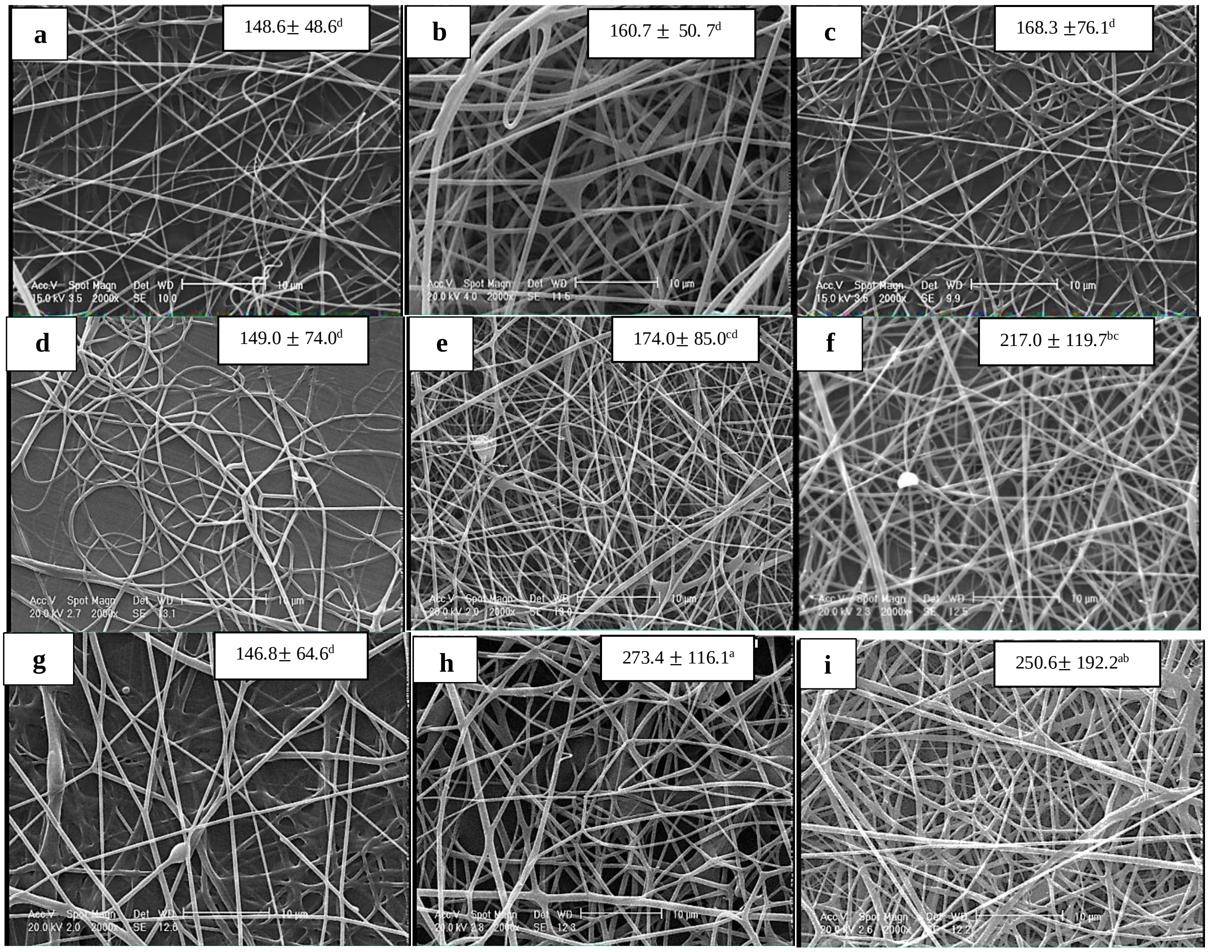


Fig. 2. SEM images of electrospun chitosan/gelatin with different volume ratios (1:6, 1:8 and 1:10) containing ajwain essential oil (%20 and %40): (a) chitosan/gelatin nanofibers in ratio of 1:6 without essential oil (b) chitosan/gelatin nanofibers in ratio of 1:8 without essential oil (c) chitosan/gelatin nanofibers in ratio of 1:10 without essential oil (d) chitosan/gelatin nanofibers in ratio of 1:6 containing 20% essential oil. (e) chitosan/gelatin nanofibers in ratio of 1:8 containing 20% essential oil (f) chitosan/gelatin nanofibers in ratio of 1:10 containing 20% essential oil (g) chitosan/gelatin nanofibers in ratio of 1:6 containing 40% essential oil (h) chitosan/gelatin nanofibers in ratio of 1:8 containing 40% essential oil (i) chitosan/gelatin nanofibers in ratio of 1:10 containing 40% essential oil.

Encapsulation efficiency and loading capacity

The results showed that with increasing percentage of essential oil, encapsulation efficiency and loading capacity increased. These results were in agreement with those found by Rezaei et al. (2016) who claimed with increasing the concentration of vanillin from 1% to 3% (w/w) encapsulation efficiency increased from 68% to 75%. Zhang et al., (2020) studied chitosan-gelatin based edible coating incorporated with nanoencapsulated tarragon essential oils (TEO) and their results about encapsulation efficiency and loading capacity showed that the EE values tended to increase with the increase of the initial content of encapsulated TEO. Also these results were in agreement with the findings of Keawchaoon and Yoksan (2011) reporting on the encapsulation of carvacrol in chitosan nanoparticles and showed that LC% increased by increasing EOs content.

However increasing ratio of chitosan/gelatin did not have significant effect on EE and LC (Fig. 3 A and B). The chitosan/gelatin solution with ratio of 1:6 containing 40% essenential oil had the highest EE (99.9%), LC (39.9%) and the smallest diameter (146 nm), so were selected to be the optimum formulae for the remaining study.

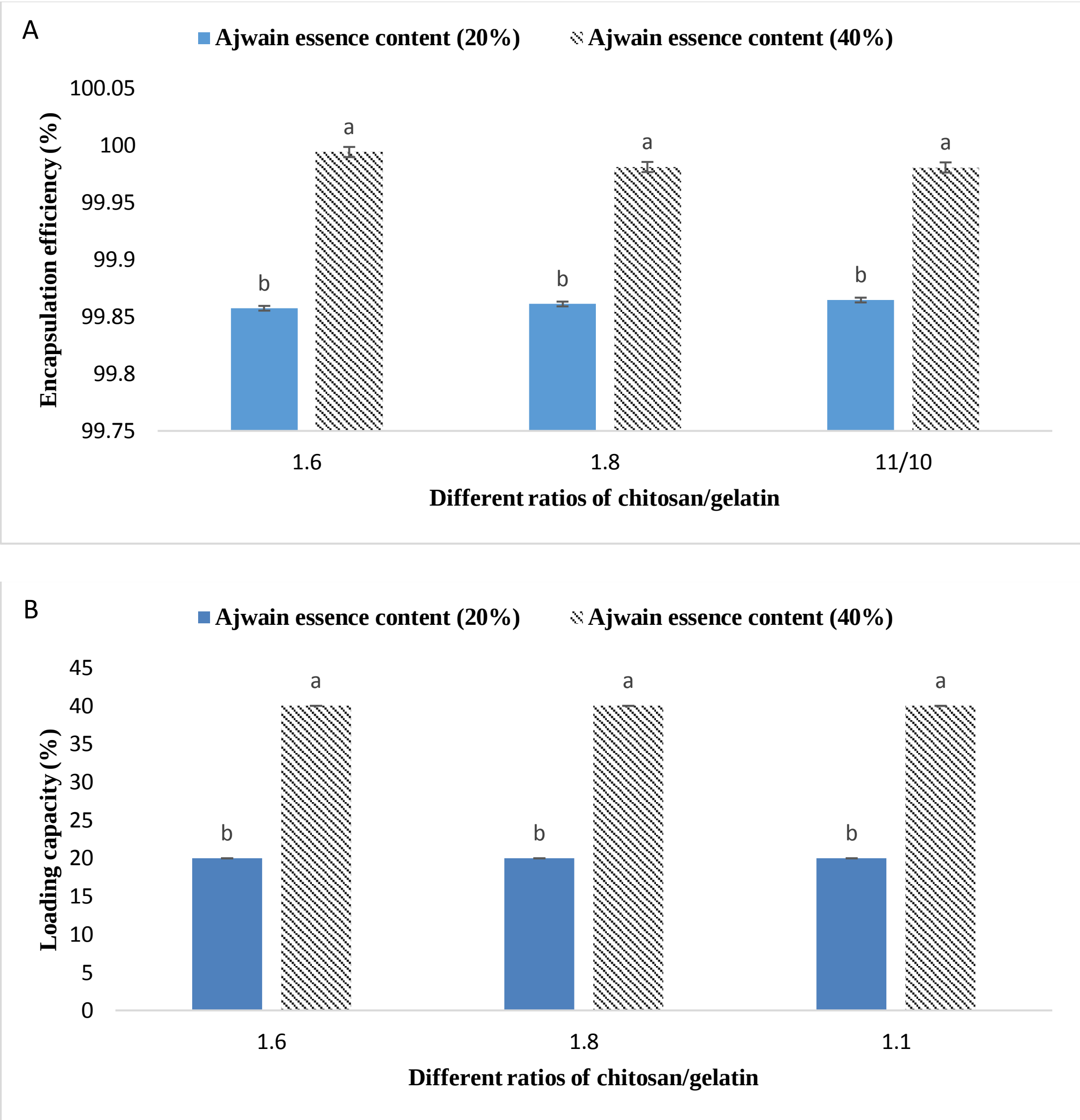


Fig. 3. Encapsulation efficiency (A) and loading capacity (B) of nanofibers (chitosan to gelatin volume ratios of 1:6, 1:8 and 1:10) containing 20 and 40% ajwain essential oil.

ATR- FTIR spectroscopy

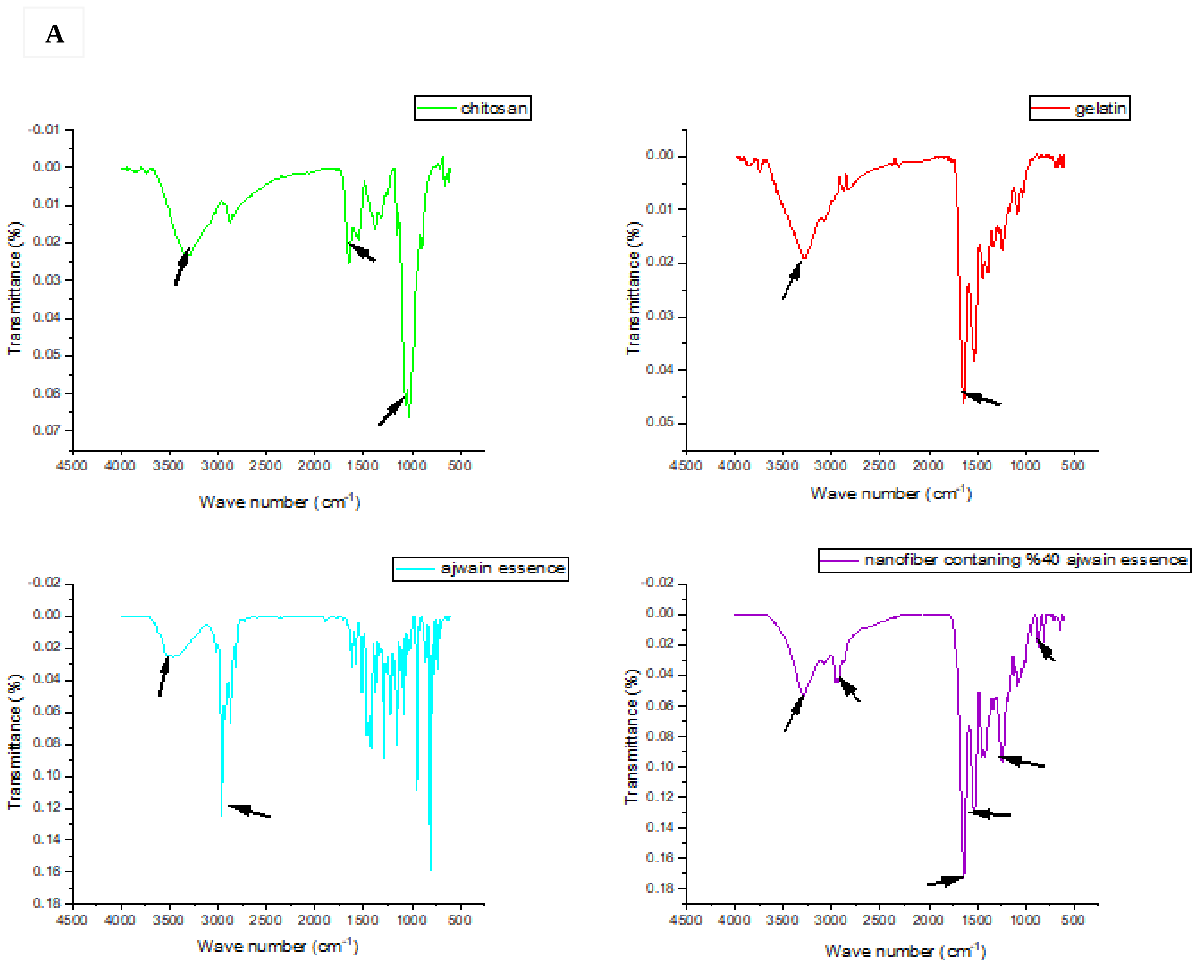
ATR- FTIR analysis was used to identify functional groups and study on any interaction between ingredients (Fig. 4A).

Characteristic peaks of chitosan were around 3500 cm^{-1} and 3200 cm^{-1} that represented the stretching vibration of O–H and N–H bonds, respectively. The C=O stretching (amide I) peak at 1646 cm^{-1} and N–H bending (amide II) peak at 1580 cm^{-1} showed the existence of N-acetylglucosamine. The peak at 1545 cm^{-1} was allocated to strong vibrations of secondary amide. C–O bonds were indicated in 1030–1160 cm^{-1} region. Furthermore, the peak at 2932 cm^{-1} was attributed to the C–H stretch of CH_2 (Altiok et al., 2010). The spectrum of pure ajwain essenential oil showed several characteristic bands, like peaks from 3250 to 3500 cm^{-1} indicated the presence of hydroxy group. The band from 2900 to 2850 cm^{-1} referred to symmetric methyl group. Dimethyl elements can also be indicated at

1370 cm^{-1}. Peaks at 1750, 1640 and 1460 cm^{-1} were attributed to alcoholic functional group. Characteristic phenolic component peaks were detected at 720, 1030 and 1230 cm^{-1} (Chatterjee et al., 2017). The spectrum of nanofibers containing ajwain essential oil indicated that there was no change in the peak intensities and no shift in the wave numbers of ingredient, therefore all interactions were physical.

Thermal analysis

Thermal profiles of the ingredients and produced nanomaterials are depicted in Fig. 4B. For chitosan powder's diagram, two peaks were noticeable, an endothermic at 83°C due to water evaporation and an exothermic at 300°C which could be attributed to the decomposition of chitosan (Guinesi & Cavalheiro, 2006). Gelatin powder indicated three endothermic peaks at 110, 215 and 280°C corresponding to evaporation of water, melting and decomposition, respectively. For the gelatin/chitosan nanofibers containing 40% ajwain essential oil, endothermic and exothermic peaks were observed at 85°C and 279.4°C, that corresponding to water evaporation and decomposition of nanofibers, respectively. The DSC thermogram showed significant reduction in the melting point of electrospun chitosan/gelatin nanofibers compared to pure chitosan and gelatin powders. The decrease in the melting temperature may be attributed to three phenomenon: (i) high surface to volume ratio of the electrospun fibers, (ii) plasticizing effect of a residual solvent in the nanofiber mats on the polymer chains and (iii) modification of the crystalline structure as a result of rapid solidification of polymer solutions in electrospinning.



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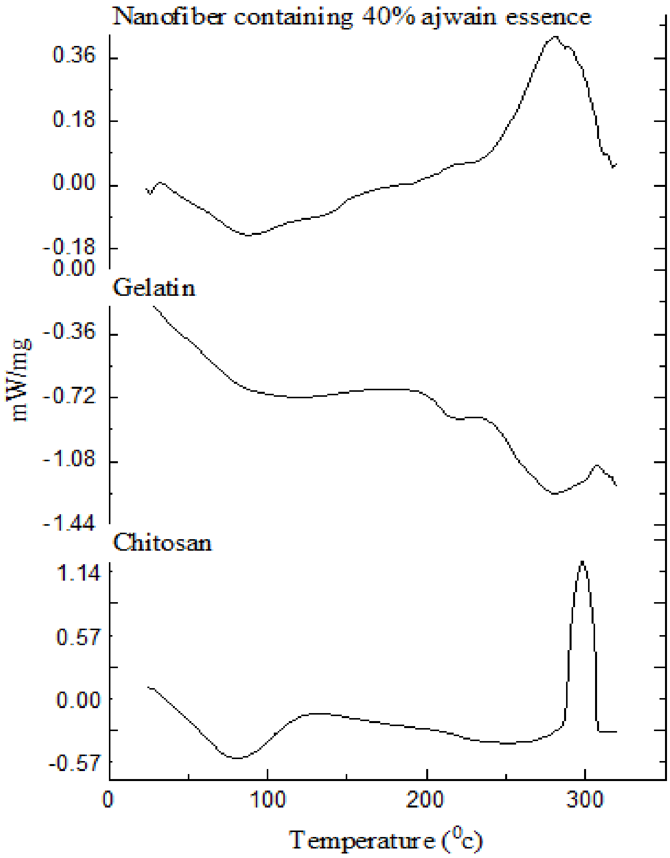

Fig. 4. ATR-FTIR spectrum (A) and DSC thermograms (B) of chitosan/gelatin nanofiber containing ajwain essence and its ingredients.

Antioxidant activity

The radical scavenging activities of the pure essential oil and nanofibers containing essential oil were assessed by the DPPH during 18 days (Fig. 5). For the first day of measurement all the treatments could scavenge free radicals but the pure essential oil showed a higher antioxidant activity than the encapsulated essential oil. This might due to the fact that the phenolic compounds of the pure essential oil were readily available to free radicals. On the other hand, oxidation of some parts of antioxidant compounds during encapsulation could led to lower value of antioxidant activity of encapsulated essenential oil for the first days of storage. During storage both samples showed decrease trends on antioxidant activity. However, after 6th, 12th and 18th days, the encapsulated essential oil exhibited higher antioxidant activity than pure essential oils due to better protecting of phenolic compounds against oxygen and light. The Same results observed in our previous work (Vafania et al., 2019) about encapsulated thyme essential oil. As expected, DPPH radical scavenging activity of the electrospun nanofibers contain thyme essential oil showed the best protecting effect against oxidation than pure one. Gortzi et al., (2008) studied encapsulation of *Myrtus communis* extract in liposomes and reported that its antioxidant as well as its antimicrobial activities were better than pure form.

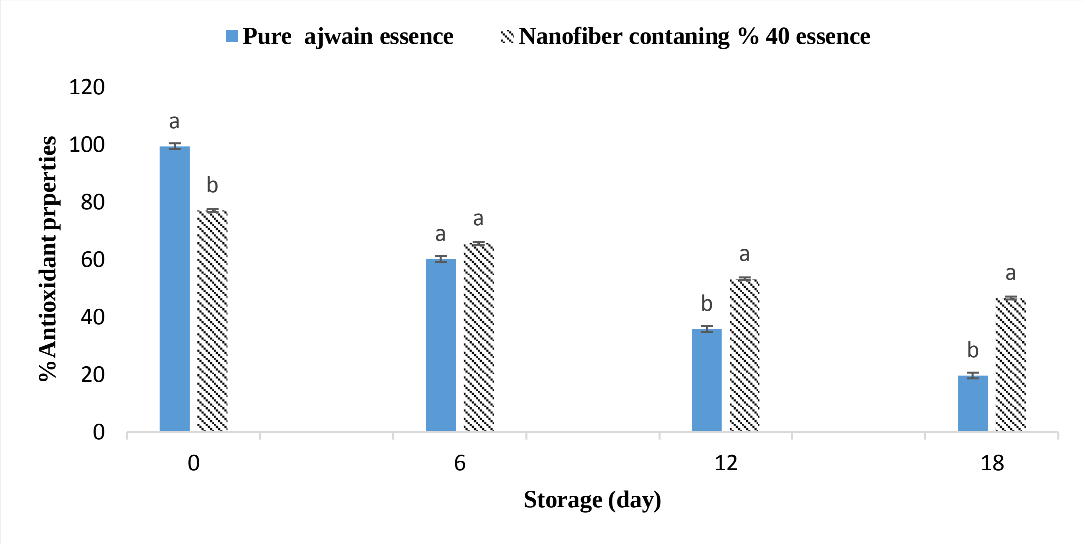

Fig. 5. Antioxidant activity of pure ajwain essence and nanofibers containing 40% ajwain essence during different days of storage.

Conclusion

The extracted ajwain essenential oil was encapsulated in nanofibers of gelatin/chitosan in ratios of 1:6, 1:8 and 1:10 and ajwain concentrations of 20 and 40% using nozzle-less electrospinning. High encapsulation efficiency and loading capacity confirmed the suitability of encapsulation process. The results of SEM, ATR-FTIR and DSC showed that nanofibers of chitosan/gelatin with ratio of 1:6 containing 40% essence had an appropriate diameter and high stability. Antioxidant activities of the pure and encapsulated essential oils were compared. Results from this study supported the use of nanofiber for protection of antioxidants and application of nozzle-less electrospinning technique to facilitate the use of EOs in food preservation.

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الکتروریسی بدون نازل: نانوانکپسولاسیون اسانس زنیان با استفاده از نانوالیاف کیتوزان-ژلاتین

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چکیده

هدف از این تحقیق بررسی کارایی الکتروریسی بدون نازل برای انکپسوله کردن اسانس زنیان (به‌عنوان یک زیست فعال آبگریز) با استفاده از دو هیدروکلوئید (کیتوزان/ژلاتین) به‌منظور افزایش خواص آنتی‌اکسیدانی و پایداری آن برای کاربردهای غذایی بود. نانوالیاف با استفاده از کیتوزان/ژلاتین در نسبت‌های ۱:۶، ۱:۸ و ۱:۱۰ و غلظت‌های ۲۰ و ۴۰ درصد زنیان ریسیده شدند. خواص محلول (ویسکوزیته و هدایت الکتریکی) اندازه‌گیری شد. داده‌های کارایی انکپسولاسیون و ظرفیت بارگذاری مبین بهبود با افزایش غلظت اسانس بود. قطر و مورفولوژی الیاف با میکروسکوپ الکترونی روبشی مورد بررسی قرار گرفت. نانوالیاف کیتوزان/ژلاتین با نسبت ۱:۶ حاوی ۴۰ درصد اسانس دارای بیشترین کارایی انکپسولاسیون (۹۹/۹٪)، ظرفیت بارگذاری (۳۹/۹٪) و کمترین قطر (۱۴۶ nm) بودند. طیف‌سنجی فروسرخ با انعکاس کلی ضعیف شده (ATR-FTIR) ثابت کرد که حین الکتروریسی، هیچ برهمکنش شیمیایی بین مواد تشکیل‌دهنده رخ نداده است و داده‌های کالریمتری روبشی افتراقی (DSC) نشان داد که اسانس به‌خوبی در نانوالیاف محصور شده است. خواص آنتی‌اکسیدانی توسط آزمون DPPH تجزیه و تحلیل شد و کارایی کپسولاسیون برای محافظت از آنتی‌اکسیدان‌ها را تأیید کرد.

واژه‌های کلیدی: اسانس زنیان، فعالیت آنتی‌اکسیدانی، انکپسولاسیون، نانوالیاف، الکتروریسی بدون نازل.

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