Structural effects of selected hydrocolloids on Ca (II)-alginate beads containing hydrosol from *Rosa damascena* Mill

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Abstract. Alginates are suitable for the encapsulation of a great variety of biomolecules. Recent trends include encapsulation of plant extracts or macromolecules in alginate gel to enhance their health and functional properties when they are applied in food matrix or pharmaceutical products. The rose hydrosol is produced by the distillation of petals of (*Rosa damascena* Mill.). This product is popular in cosmetics also it is used as a food additive in some Eastern country. The aim of this study was to investigate the chemical composition, antioxidant potential of rose hydrosol and to evaluate the influence of different hydrocolloids on the structural-mechanical properties of Ca (II)-alginate beads with rose hydrosol. The alginate microspheres were formed with different amounts of sodium alginate (2-4%), sucrose, rose hydrosol and selected hydrocolloids, as neutral polysaccharides (inulin and guar gum) and anionic heteropolysaccharides (pectin, κ-carrageenan, xanthan). The addition of inulin in the concentration 3% and 6% resulted in the increase of the rupture force by 34% and led to improvement in plasticizing effect. The additional complete characterization of the beads with rose hydrosol was performed by Fourier-transform infrared spectroscopy, assigning the characteristic bands to each individual component. In this study, the obtained information for structure-mechanical properties allows the design of Ca (II)-alginate systems enriched with dietary fibers and rose hydrosol, with an acceptable sensory profile for future application in foods. Key words: alginate microsphere, rose hydrosol, texture profile analysis.

1. Introduction

Hydrocolloids capable of forming strong gels have been used during the last two decades as the most promising approaches for the delivery of therapeutic and bioactive substances. Many scientific studies aim to developed water-insoluble micro-particles with reduced porosity and postpone the release of entrapped substances. Colloidal delivery systems are one of the most convenient methods of
incorporating bioactive substances into food products. This system can improve chemical and biochemical stability, and controlling the stability of active substances in the gastrointestinal tract [1].

Various polysaccharides can be used as delivery matrices of biologically active compounds and agents. The combination of Ca$^{2+}$ alginate with hydrocolloids (inulin, pectin, and others) or biopolymers (carrageenan) may serve as a successful strategy to increase the gel mechanical properties [2].

Algicin acid, also called alginate, is an anionic polysaccharide distributed widely in the cell walls of brown algae. It is capable of absorbing 200-300 times of water and it forms a viscous gum. Alginites have variations in their chemical structure, resulting in different physicochemical properties. Some alginate gives a strong gel. Sodium alginate has been used as a thickening and gelling agent and because it reduces interfacial tension between an oil and water phase and it is used for preparation of emulsion [3]. Due to the properties of its carboxyl groups and as a polyanionic polymer alginate has been widely studied. Alginites have been applied as a delivery system of active compounds, they are biodegradable and non-toxic also masks flavour [2,4]. Alginate has some limitations, such as low stability and a high porosity. In order to improve the structural and mechanical properties of alginate microspheres with encapsulated agents coating is required.

Alginate microspheres have a wide range of applications in the medicinal, pharmaceutical, food technology and biotechnology fields [5,6,7,8].

R. _damascena_ has been traditionally cultivated in Bulgaria and Turkey more than 400 years. This species is also considered as superior in terms of the essential oil quality. Various rose products have a long historical use in the traditional medicine and as a valuable oil bearing plant [9]. Currently the rose extracts are used as a food additive in order to improve the antioxidant capacity and colour stability of some canned fruits [10]. The rose hydrosol (also rose water) is produced by distillation. This product is popular as an additive in the food industry in some Eastern country for specialty foods [11]. Some industrial houses also use rose oil for the preparation of rose hydrosol. Rose hydrosol possesses some clinical properties as relief from toothache, aphthous lesions, and gingival and throat inflammation. It has been used as a remedy for gastrointestinal complications, bacterial infections, gastric and duodenal spasms [12]. In Bulgaria rose hydrosol has mainly cosmetic purposes with the exception of some oriental desserts flavoured with rose.

The aim of this study was to investigate the chemical composition, antioxidant potential of rose hydrosol and the influence of different hydrocolloids on the structural-mechanical properties of Ca(II)-alginate beads with rose hydrosol.

2. Material and methods

2.1. Material

Rose hydrosol (Ikarov, Bulgaria) was purchased from a local drugstore in Plovdiv, Bulgaria and it was used without further pretreatment. Sucrose, sodium alginate, CaCl$_2$ and xanthan were purchased from Sigma (Germany). Inulin with two different degrees of polymerization (DP = 22) and (DP = 9-12) were kindly supplied by Frutafit®TEX with DP 22 were supplied by Sensus (Roosendaal, the Netherlands). Pectin from celery tubers with the low degree of esterification (DE) = 46%, anhydrouronic acid content (AUAC) 70% and average Mm of 912694 g/mol were obtained as previously described [13]. Guar gum and κ-carrageenan was purchased from Orion (Karlovo, Bulgaria).

2.2. Characterization of phytochemical compounds of hydrosol from _R. damascena_

2.2.1 GC-MS analysis

The composition of the rose hydrosol was determined by GC-MS [14]. The hydrosols from _R. damascena_ were extracted by liquid-liquid extraction with diethyl ether in triplicate [15]. The GC-MS analyses were performed on a 7890A gas chromatograph (Agilent Technologies) coupled to a 5975C quadrupole mass spectrometer (Agilent Technologies) (Agilent, Santa Clara, CA, USA). The analytes were separated on a HP-5 MS capillary column (30 mm × 0.25 mm with a phase thickness of 0.25 μm).
The split/splitless injector temperature was set at 250°C and the temperature program was 60°C for 3 min, 6°C min\(^{-1}\) ramp rate to 250°C and held constant for 3 min. The carrier gas was helium (99.999%) at a 1 ml min\(^{-1}\) flow rate. In the solid phase microextraction analysis, splitless injection (3 min) was used at 250°C. The carrier gas was helium (99.999%) at a 1 ml min\(^{-1}\) flow rate. In the solid phase microextraction analysis, splitless injection (3 min) was used at 250°C. The mass spectrometer was operated in the electron-impact mode (EI) at 70 eV. The identified components were arranged according to the retention time and their quantity is given in percentages. The obtained mass spectra were analyzed using 2.64 Automated Mass Spectral Deconvolution and Identification System (AMDIS) (National Institute of Standardization and Technology, NIST, Gaithersburg, MD, USA).

2.2.2. Determination of total polyphenolic content (TPC)
The total phenolic content in the rose hydrosol was determined using the Folin–Ciocalteu’s reagent [16]. The analysis was performed as 0.2 ml hydrosol from \(R.\) \(dama\)scena was mixed with 1 ml Folin–Ciocalteu reagent diluted five times and then 0.8 ml 7.5% \(Na_2CO_3\) was added. After 20 min, the absorption was measured at 765 nm against a blank sample, prepared with distilled water. The results were expressed in \(\mu g\) equivalent of gallic acid (GAE) per ml.

2.2.3. Determination of total flavonoids content
The total flavonoids content was determined by \(Al(NO_3)_3\) reagent. The absorbance was measured at 415 nm. The results were presented as mg equivalents quercetin (QE) per ml according to the calibration curve with quercetin as a standard [17].

2.2.4. The DPPH radical-scavenging ability
Rose hydrosol (0.15 ml) was mixed with 2.85 ml freshly prepared 0.1mM solution of DPPH in methanol. The reduction of absorbance at 517 nm was measured by spectrophotometer in a comparison to the blank containing water. The percent inhibition was also calculated. The results were expressed in \(\mu M\) Trolox® equivalents (TE)/ml [17].

2.2.5. ABTS+ radical scavenging ability
The ABTS+ solution (2.85 ml) was mixed with 0.15 ml rose hydrosol. After 15 min at 37°C in darkness, the absorbance was measured at 734 nm against ethanol. The percent inhibition was also calculated. The results were expressed in \(\mu M\) Trolox® equivalents (TE)/ml [17].

2.2.6. CUPRAC assay
Rose hydrosol (0.1 ml) was mixed with1 ml CuCl\(_2\) \(\times\) 2H\(_2\)O, 1 ml methanol solution of Neocuproine, 1 ml 0.1 M ammonium acetate buffer and 1 ml distilled H\(_2\)O. After 20 min at 50°C in darkness, the samples were cooled to 25°C and the absorbance was measured at 450 nm. The results were expressed in \(\mu M\) Trolox® equivalents (TE)/ml [17].

2.3. Preparation of Ca(II)-alginate beads containing hydrosol from \(R.\) \(damascena\) and hydrocolloids
For the preparation of the alginate beads with rose hydrosol, the sodium salt of alginic acid with M-block 61%, G-block 39% and M/G ratio 1.55 (Sigma Aldrich, France) were used. Sodium alginate (2 g or 4 g) and 3 g sucrose was suspended in 100 ml rose hydrosol followed by heating at 35°C for 3 min and stirring with a laboratory homogenizer Polytron PT45-80 (Kinematica, Switzerland) - 1600 W, max 250.s\(^{-1}\) for 1 min. Nine different samples were prepared as follows: blank samples only with 2% and 4% sodium alginate, samples with the addition of hydrocolloids (0.5% pectin + 2% alginate, 0.5% guar gum +2% alginate; 0.5% \(-\)carrageenan + 2% alginate; 2% alginate + 1% xanthan gum; 2% alginate + 6% inulin, 2% alginate + 3% inulin, and 4% alginate + 6% inulin). The obtained suspension was placed in the fridge for 60 min to remove the air bubbles. The alginate beads were prepared as liquid solutions were transferred into a syringe and dropped into a cold CaCl\(_2\) solution (2% and 4%, respectively) with temperature 7°C. Then the Ca (II)-alginate beads containing rose hydrosol were rinsed with water and used for further analysis.
2.4. Fourier-transform infrared (FT-IR) spectroscopy
The infrared spectra of liophylized Ca (II)-alginate beads with rose hydrosol and hydocolloids were recorded on a Nicolet FT-IR Avatar Nicolet (Thermo Science, USA) spectrometer using KBr pellets, and the absorption was reported in wave numbers (cm\(^{-1}\)) in the frequency range of 4000 – 400 cm\(^{-1}\). Each spectrum was recorded after 120 scans.

2.5. Structural mechanical properties of Ca (II)-alginate beads
The gel strength of the obtained alginate beads was evaluated by the rupture force and the deformation, that were measured by a texture analyzer (TA.XT. plus Stable Micro Systems, England). The mechanical properties were examined in uniaxial extension as a function of deformation. The constant speed of deformation was 0.5 mm by aluminum cylinder with diameter 25 mm. The samples were measured in eighteen replicates for better reproducibility.

3. Results and discussion

3.1. Phytochemical analysis of rose hydrosol
R. damascena is the main rose species in Bulgaria used in the production of aroma products. Its petals and extracts were used in also in food technology, especially in confectionery. Therefore, the chemical composition of the rose hydrosol could bring about flavour and overall acceptance of the final product. The composition of hydrosol from R. damascena was summerized in Table 1. Sixteen compounds were identified in the sample by GC/MS analysis. In comparison with other study for the hydrosol from Bulgarian R. damascena obtained by hydrodissillation, we detected the same compounds without geraniol, farnesol, eicosane, and squalene [14]. The main chemical composition (Table 1) found in our sample of rose hydrosol included phenethyl alcohol (65.34%), \(\alpha\)-terpineol (10.20%), and 3,7-dimethyl-1,7-octanediol (13.25%). Our results were close to Iranian rose hydrosol where, the main components of hydrosol in ethanol as a solvent were phenethyl alcohol (69.7–81.6%), citronellol (1.8–7.2%), and geraniol (0.9–7%) [17]. Similar to some of the commercial rose hydrosol in Iran [18] and in our case geraniol were also not detected. In addition the chemical composition of rose hydrosol depends on different solvents and extraction methods. Ulusoy et al. [19] identified four constituents in hydrosol of R. damascena (obtained from Sebat Ltd., Isparta): geraniol (30.74%), citronellol (29.44%), phenethyl alcohol (23.74%), and nerol (16.12%).

| No. | Compounds                                              | Class of compounds | Retention Time, min | RI     | % from Total Area |
|-----|--------------------------------------------------------|--------------------|---------------------|--------|-------------------|
| 1   | 2,2,6-Trimethyl-6-vinyltetrahydropyran (Linaloyl oxide) | OM                 | 4.30                | 1067   | 0.25              |
| 2   | Eucalyptol                                             | OM                 | 5.52                | 1059   | 0.06              |
| 3   | Benzyl alcohol                                         | PP                 | 5.70                | 1891   | 0.50              |
| 4   | Linalool                                               | OM                 | 6.83                | 1082   | 1.04              |
| 5   | Rose oxide                                             | OM                 | 7.11                | 1114   | 0.10              |
| 6   | Phenethyl alcohol                                      | PP                 | 7.35                | 1136   | 65.34             |
| 7   | (E)-3-Nonen-1-ol                                       | OA                 | 8.65                | 1167   | 0.40              |
| 8   | Terpinen-4-ol                                          | OM                 | 8.95                | 1137   | 0.56              |
| 9   | \(\alpha\)-Terpineol                                   | OM                 | 9.31                | 1143   | 10.20             |
| 10  | Citronellol                                            | OM                 | 9.91                | 1179   | 1.56              |
| No. | Compound                                      | Type     | RI   | Retention index (Kovat’s index) |
|-----|-----------------------------------------------|----------|------|---------------------------------|
| 11  | 6,7-Dihydro-7-hydroxylinalool                 | OA       | 10.01| 1189                            |
| 12  | 2,6-dimethyl-3,7-Octadien-2-ol                | OA       | 12.37| 1041                            |
| 13  | Eugenol                                       | PP       | 13.34| 1392                            |
| 14  | 3,7-Dimethyl-1,7-octanediol                   | OA       | 13.43| 1286                            |
| 15  | Methyleugenol                                 | PP       | 14.51| 1361                            |
| 16  | Nonadecane                                    | AH       | 18.30| 1910                            |

Total identified compounds (%) = 98.96
Total oxygenated monoterpenes = 13.76
Total benzenoid compounds = 68.45
Total oxygenated aliphatic hydrocarbons = 15.99

RI – Retention index (Kovat’s index), OM: Oxygenated monoterpenes, PP: Phenyl propanoids, AH: Aliphatic hydrocarbons, OA: Oxygenated aliphatic hydrocarbons

The phenolic content and antioxidant activity of rose hydrosols were determined (Figure 1). It was found that the level of TPC was 20 μg/ml, however the presence of total flavonoids were not detected in the investigated sample. Abidi et al. [20] also detected the absence of flavonoids in some rose water samples. Ulusoy et al. [19] reported for *R. damascena* hydrosol much lower value of 5.2 ± 0.3 μg GAE/ml. However, our data were consistent with Georgieva et al. [15], who found in the hydrosol from *R. damascene* - 32.52 μg GAE/ml. In comparison with rose oil (839.5 ± 59.5 μg GAE/ml) and absolute (2134.3 ± 91.4 μg GAE/ml), the lower level of polyphenols in hydrosol is probably due to their low water solubility.

![Figure 1. Total polyphenols and antioxidant activity of hydrosol from *R. damascena*.

The antioxidant activity of the used rose hydrosol was evaluated by three antioxidant methods based on different mechanisms (Figure 1). The investigated sample in our study demonstrated better metal-chelating activity (CUPRAC assay), than radical scavenging ability (DPPH). The rose hydrosol demonstrated inhibition 15% inhibition by DPPH and 33% inhibition by ABTS assay. The highest antioxidant activity was evaluated by CUPRAC assay - 270 μM TE/ml (Figure 1). In addition, Abidi et
al. [20] demonstrated high value of the ferric reducing power of rose water for evaluation of the antioxidant activity.

The FTIR spectra of Ca (II) alginate beads with rose hydrosol and different hydrocolloids revealed the presence and stability of many functional groups of bioactive carbohydrates and lipid compounds in matrices. The broad bands at 3476 cm\(^{-1}\) typical for the stretching vibrations of OH groups in all polysaccharides were clearly observed in all FTIR spectra (Figure 2).

3.2. **FTIR spectroscopy**

![Figure 2. FTIR spectra of Ca (II) alginate beads with rose hydrosol and different hydrocolloids, where a) with 0.5% pectin, b) with sodium alginate, c) with 0.5% guar gum, d) with 3% inulin and e) with 1% xanthan.](image)

In additions, the intense bands in the region from 3400 cm\(^{-1}\) to 3600 cm\(^{-1}\) due to the characteristic stretching vibration of N-H and O-H from polyphenols and amino acids from rose water, as previously described by Abidi et al. [20]. The bands from 2800 cm\(^{-1}\) to 2900 cm\(^{-1}\) were assigned to the C-H symmetric stretching of CH\(_3\) and CH\(_2\) group from carbohydrate and lipids. The bands in the range from 1700 cm\(^{-1}\) to 1850 cm\(^{-1}\) from C=O stretching vibrations indicated the presence of conjugated aldehyde and carbonyl group, typical of volatile compounds from rose hydrosol. In the region 1350-1450 cm\(^{-1}\) aliphatic bending of CH and CH\(_2\) were observed. The bands from 1100 cm\(^{-1}\) to 1200 cm\(^{-1}\) were appeared in the sample from C-O stretching vibration, indicated the presence of OH, ether, carboxylic and anhydrides functional groups. The bands in the region 1200-970 cm\(^{-1}\) common for all polysaccharides were mainly due to C-C and C=O stretching in a pyranosyl ring and to C-O-C stretching vibrations of glycosidic bonds. Moreover, the presence of characteristic bands for carbohydrates was observed and in finger print region. Especially at 817 cm\(^{-1}\) proved the presence and stability of inulin consisted of β-D-fructose residues linked by \(1\rightarrow2\) glycoside bonds (Figure 2 d). The band at 956 cm\(^{-1}\) was considered for characteristic of α-glycosidic linkage and a presence of RG-I of pectin molecule (Figure 2 a) together with the bands at 889 cm\(^{-1}\) and 765 cm\(^{-1}\) typical for α-D-Glep or α-D-Galp in C1 conformation [21]. In the spectrum with guar gum (Figure 2 c) typical bands for galactose and mannose 870-869 cm\(^{-1}\), as well as (1→4), (1→6) linkage of galactose and mannose (930-771 cm\(^{-1}\)) were observed [22]. In FTIR spectra with xanthan gum weak bands at 1400 cm\(^{-1}\) and at 1250 cm\(^{-1}\) due to carboxylate asymmetric stretching and to C=O acetate deformation were observed (Figure 2 e).
3.3. Structural-mechanical properties of alginate microspheres
The role of biopolymers and sugars as additives into Ca (II)-alginate matrices for production of beads with increased loading efficiency of bioactive compounds were reported by many authors [23,24]. The properties that biopolymers impart to Ca (II)-alginate beads (such as mechanical strength or release behaviour) are strongly defined by the structural characteristics.
Experimental data (table 2) suggests that alginate microspheres samples with 3% and 6% inulin with the high degree of polymerization have statistically significant difference of the values of rupturing force. The two-fold increment of the concentration of inulin resulted in 34% increasing the value of the force required for rupturing the alginate microspheres. This additional amount of inulin by 3% leads to the significant changes in viscosity properties of the gel system, as well. The observed data are in accordance with the results obtained by Manev et al. [6], who have proven in their research that the value of the rupture force is always higher than the pure modular system, regardless of the type of added hydrocolloids and their chemical nature.

The high value of rupture force was observed in the samples with 4% alginate – 3.381 N. Increasing the concentration of alginate from 2% to 4% leads to 1.5 higher degree of rupture force. Other authors [2] showed that alginate-pectin blended system has the lowest viscosity than pure alginate system. Our results revealed a similar tendency, the addition of 0.5% pectin in a 2% alginate system impacted on the rupture force reduction by 30%. The following conclusion is warranted, regardless of the nature of the hydrocolloid, when it was added to the alginate system, the rupture force was reduced. Probably, hydrocolloids interfere with the diffusion of calcium ions, this effect influences the gelling properties of the alginate microspheres.

To the best of our knowledge, this is the first report for the encapsulation of rose hydrosol in Ca (II)-alginate systems with hydrocolloids (low methylated pectin). New formulations incorporating guar gum, arabic gum, low methoxyl and high methoxyl pectin are studied in the present work considering that the addition of co-materials such as sugars and hydrocolloids provide additional advantages in Ca (II)-alginate systems. It has been demonstrated that the use of guar gum increases functional properties (such as entrapment of polyphenols and betacyanins), while increasing the microstructural stability of Ca (II)-alginate network [23]. Moreover, the combination of alginate with arabic gum, high methoxyl pectin or low methoxyl pectin improves protection of bioactive compounds [26,27,28].

| №  | Samples                          | Rupture force, (N) | Deformation, (mm) |
|----|---------------------------------|--------------------|------------------|
| 1  | 2% alginate                     | 2.262              | 2.190            |
| 2  | 4% alginate                     | 3.381              | 2.792            |
| 3  | 0.5% pectin + 2% alginate       | 1.653              | 2.691            |
| 4  | 0.5% guar gum + 2% alginate     | 1.555              | 2.645            |
| 5  | 0.5% κ-carrageenan + 2% alginate| 1.970              | 2.394            |
| 6  | 2% alginate + 1% xanthan gum    | 2.199              | 2.808            |
| 7  | 2% alginate + 6% inulin         | 1.431              | 2.439            |
| 8  | 2% alginate + 3% inulin         | 1.066              | 2.689            |
| 9  | 4% alginate +6% inulin          | 2.390              | 4.059            |

4. Conclusion
The encapsulation of biologically active substance from rose hydrosol in Ca (II)-alginate beads with different hydrocolloids (prebiotics and stabilizers) were presented as high reproducibility and low-cost procedure with future application for food purposes. The resulting alginate beads with the addition of
3% inulin demonstrated the best plasticizing effect. Therefore, the described procedure for alginate beads preparation with rose hydrosol revealed the potential application for the design of new foods with desirable and attractive sensory and texture properties, enriched with prebiotics and fibers.

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