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The kinetics of the swelling process and the release mechanisms of *Coriandrum sativum* L. essential oil from chitosan/alginate/inulin microcapsules

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ABSTRACT

The encapsulation by spray drying method of coriander essential oil (CEO) in various materials (chitosan, alginate, chitosan/alginate, chitosan/inulin) was studied. The viscoelastic properties of the oil-in-water (O/W) emulsions and the characteristics of CEO-loaded microcapsules like morphology, moisture, wettability, solubility, flowability properties, swelling and release mechanisms were investigated. The chitosan microcapsules had a brain-like structure while the alginate and chitosan/alginate microcapsules are spherical with a smooth surface.

The Compressibility Index (CI = 29.09–32.25%) and Hausner Ratio (HR = 1.38–1.44) values showed that all the microcapsules prepared correspond to the "poor" flowability powders group. The chitosan microcapsules exhibited the maximum release rate at pH 2.5 while the alginate microcapsules exhibited the maximum release rate at pH 6.5. Kinetics and mechanism of CEO release were studied using various mathematical models such as, zero order, first order, Higuchi model and Peppas model. The diffusional exponent (n) values of Peppas equation explains a non Fickian transport mechanism and diffusion or diffusion-swelling controlled process.

1. Introduction

In the last few years, the requirements regarding the production and consumption of food have been considerably changed. Consumers nowadays are aware that foods, beyond the role of satisfying the sensation of hunger, are also responsible for the pleasure of eating and for their health.

In this context, food manufacturers were focused on innovative products obtaining, that are able to satisfy consumers' requirements regarding both taste and health.

Nowadays, the vegetal extracts are highly used in food production either as sources of biocomponents or as alternative to the synthetic additives with proven high toxicity risk. From the vegetal extracts used in the food production, an important role is assigned to essential oils, extracted from aromatic herbs (Burdock & Carabin, 2009).

The essential oils are used in a wide variety of applications in pharmaceutical, cosmetics and food industries due to their antiinflammatory, antibacterial, antifungal, analgesic, sedative, spasmolytic, antioxidant and flavouring properties (Calo, Crandall, O'Bryan, & Ricke, 2015; Pesavento et al., 2015; Raut & Karuppayil, 2014).

One of the most studied and used essential oils due to its complex bioactive properties is coriander one (Burdock & Carabin, 2009).

The essential oils are complex mixture of chemical compounds sensitive to oxygen, light and high temperature. These factors contribute to the degradation of essential oils and subsequently to the decrease of their biological potential.

Therefore, the encapsulation of essential oils in different matrices is required in order to prevent these inconvenience. The data in the literature reflect the worldwide interest regarding the improvement of the encapsulation methods of essential oils (Beirão-da-Costa et al., 2013; Dima, Cotârlet, Alexe, & Dima, 2014; Fernandes, Borgesa, & Botrel, 2014; Hosseini, Zandi, Rezaei, & Farahmandghavi, 2013). The microencapsulation of essential oils assures: the stability of the volatile compounds during thermic processing, the transformation of essential oils from liquid state

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into free flowing powder and a slow and controlled release of volatile compounds (Asbahani et al., 2015).

Various techniques are used for the encapsulation of essential oils, like: emulsification, coacervation, gelation, extrusion, spray drying, spray cooling etc. (Asbahani et al., 2015; Dima et al., 2014; Martins, Barreiro, Coelho, & Rodrigues, 2014).

The spray drying method is one of the most used encapsulation method of flavour compounds.

The most important factors that influence the efficiency of encapsulation and the quality of the microcapsules obtained by spray-drying method are: the nature of the encapsulating material, the viscosity of the O/W emulsions, oil: solid content ratio, the spray-drying parameters (gas-flow rate, liquid flow rate, air inlet and outlet temperature), (Estevinho, Rocha, Santos, & Alves, 2013; Turchiuli, Jimenez Munguia, Hernandez Sanchez, Cortes Ferre, & Dumoulin, 2014).

For the encapsulation of the essential oils were used different materials such as: arabic gum, gelatin, starch, soy proteins, whey proteins, karrageenans, alginates, chitosan etc. (Fernandes, Marques, Borges, & Botrela, 2014; Martínez et al., 2015). In this work it were obtained microcapsules loaded with CEO extracted from *Coriandrum sativum* L. seeds using supercritical CO_2. Spray drying method was used and chitosan, sodium alginate and inulin were used as encapsulating materials.

In comparison with arabic gums and proteins, the literature makes less reference to studies regarding the use of the aforementioned substances as encapsulating materials for the spray-drying method.

The chitosan is a linear polysaccharide formed from glucosamine and N-acetylated glucosamine units. It is a non-toxic polymer, biocompatible and biodegradable, with bioadhesive and antibacterial properties, obtained through alcaline deacetylation of chitin. Its properties depend on the deacetylation degree. It is soluble for a low pH values, when the amino groups are protonated and they can react with polyanions (alginates, acacia gum, carrageenans, tripolyphosphate) forming complex coacervate hydrogels (Dima et al., 2014; Dutta, Tripathi, Mehrotra, & Dutta, 2009; Zou, Zhao, Ye, Wang, & Li, 2015).

Alginates are linear biopolymers formed from β-D-manuronic acid (M) and α L-guluronic acid (G). The quality of the alginate microcapsules depends on the G/M ratio. In the presence of divalent ions (Ca^{2+}, Mg^{2+}, Ba^{2+} etc.) the sodium alginate forms hydrogels and in the presence of some polycations (chitosan, proteins) it forms complex coacervates (Paques, van der Linden, van Rijn, & Sagis, 2014).

Inulin is a branched polysaccharide containing units of β-(2-1) fructosyl fructose.

Due to its low hydrolysis capacity, inulin is used as dietary fibres and also in the preparation of microcapsules resistant at the pH variation in the gastrointestinal tract, allowing the release of biocomponents in the colon. Inulin acts as a good prebiotic as it ensures the development of the bifidobacteria present in the human gut (Roberfroid, 2007).

In food industry, the encapsulation and the controlled release of biocomponents ensure the maintenance of the nutritive and sensorial characteristics of foods and prolonges the period of storage.

The release mechanisms depend on many factors such as: the encapsulating material, the encapsulated substance, the geometry and morphology of the capsule, the release conditions (solvent, pH, ionic strength, temperature) and the preparation method of capsules (Maderuelo, Zarzuelo, & Lanao, 2011).

The study of the release mechanisms is carried out on some mathematic models which explain the four types of transport of bioactive molecules through the wall of the microcapsules: type I transport or Fickian diffusion, when the release rate is controlled by the diffusion process; type II transport which corresponds to the case when the release of the bioactive is controlled by the swelling process of the polymer; anomalous transport or non-Fickian transport that corresponds to the case in which the release rate depends simultaneously on the swelling and diffusion processes and last but not least, the "supra II" type for which the release rate is controlled by the erosion/dissolution process of the polymer under the action of the dissolution medium (Siepmann & Peppas, 2001; Zou et al., 2015).

The aim of this paper was to characterise the microcapsules, loaded with CEO, prepared by the spray drying method using chitosan, alginate and inulin as wall materials. In order to investigate the kinetics and the CEO release mechanism from alginate, chitosan, chitosan/alginate and chitosan/inulin microcapsules were applied various mathematical models such as, zero order, first order, Higuchi model and Peppas model, in different conditions of pH.

2. Materials and methods

2.1. Materials

Sodium alginate (CAS 9005-38-3) extracted from the *Laminiaria Hyperborea* brown algae having an average molecular weight M_w = 189 kg/mol (60% manuronic acid and 40% guluronic acid) was purchased from AppliChem. The average molecular weight of sodium alginate was calculated using the Mark-Houwink equation: $[\eta]_{20^\circ C} = 4.85 \cdot 10^{-3} M_W^{0.97}$ (0.1 M NaCl), (Davidovich-Pinhas & Bianco-Peled, 2010). The chitosan (CAS 9012-76-4) was acquired from Sigma Aldrich, Germany, and was characterised by a deacetylation degree of (DDA) 75% and the average molecular weight M_w = 387 kg/mol, determined through the viscosimetric method using the following equation $[\eta]_{25^\circ C} = 1.81 \cdot 10^{-3} M_W^{0.93}$ (0.1 M CH_3COONa), (Gupta & Jabrail, 2010).

Inulin (CAS 9005-80-5) extracted from chicory root (*Cichorium intybus* L.,) with a polymerisation degree PD = 10 and M_w = 5000 g/mol was purchased from Sigma Aldrich, Germany. Soybean lecithin (CAS 8002-43-5), type II-S, 14–23% choline basis was purchased from Sigma Aldrich, Germany.

The COE was extracted from mature *Coriander sativum* L. seeds using supercritical CO_2. The seeds were purchased from Supremia SRL, Romania. The extraction of CEO with supercritical CO_2 was realised on a pilot plant, manufactured by Natex Proyesstechnologie GembH (Ternitz, Austria). Ten compounds, among which linalool (70.20%), were identified through GC analysis (Dima, Ifrim, Coman, Alexe, & Dima, 2015). Only ultrapure water was used in the preparation process of solutions (Milly Q, conductivity < 0.1 μS cm^{-1}). For the preparation of phosphate buffers solutions (PBS) were used citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$; M_w = 210.14) and sodium hydrogen phosphate (Na_2HPO_4; M_w = 141.98), purchased from Sigma Aldrich, Germany. All the other chemicals and solvents used were of analytical grade.

2.2. Biopolymer stock solution preparation

The chitosan solution (4% w/v) was prepared through electromagnetic stirring of a chitosan suspension in an aqueous solution of acetic acid 1% (v/v) at room temperature for 6 h.

The sodium alginate solution (4% w/v) was prepared through electromagnetic stirring of a sodium alginate solution in ultrapure water, at room temperature for 4 h. In order to eliminate the gas bubbles, the solutions of biopolymers were ultrasonated for 3 min and were kept overnight.

The inulin solution (15% w/v) was prepared through electromagnetic stirring of an inulin suspension in ultrapure water at 70 °C for 30 min.

2.3. Preparation of emulsions

The solutions of biopolymers were mixed with the coriander essential oil in a weight ratio of solid content: essential oil 4:1 (w/w), in the presence of soy lecithin (0.1% w/w from the content of the emulsion). The blend was homogenised (Ultra-Turax T25 Basic, IKA, Germany) at a speed of 5000 rpm for 10 min on ice bath. The primary oil-in-water emulsion was ultrasonated on ice bath at a frequency of 30 kHz and an amplitude of 40% for 5 min (SonoPlus, Bandelin, Germany) which led to fine emulsions stable for more than 60 days. These emulsions contained 20% (w/w) solid wall material, 5% (w/w) CEO and 75% (w/w) water.

The spray drying process was carried out 6 h after the preparation of the emulsions. The codes of emulsions (E) and microcapsules (M) and the blending reports of components are available in Table 1.

2.4. Emulsions rheology

The rheologic measurements were realised with a strain control AR-2000ex rheometer (TA Instruments, DE, USA).

A cone plate geometry system was used with the cone diameter of 40 mm and the cone angle of 2° with a closing gap of 1000 μm.

For measuring the viscoelastic properties of emulsions first a frequency sweep test was applied in the domain of 0.1–10 Hz. The temperature was set to 10 °C controlled with the Peltier system. The test was performed at a constant strain of 0.1% determined to be in the linear viscoelastic region. Through oscillatory tests were determined the elastic (storage) modulus (G'), the loss modulus (G'') and the shift angle (δ).

For studying of the flowing behaviour of samples was used at shear ramp test by increasing shear rate from 0.1 to 100 s^{-1} at a constant temperature of 10 °C.

The viscosity was determined as the ratio of the shear stress (τ) to shear rate ($\dot{\gamma}$).

2.5. Microencapsulation by spray drying

The spray-drying process was performed with the Büchi minispraydryer (Model B-191, Büchi Laboratoriums-Technik, Germany) in the following conditions: atomizing gas flow rate 360 L h^{-1}, drying gas flow rate 30 L h^{-1}, inlet air temperature 120 °C and outlet air temperature 70 °C. The powders obtained were weighed and kept in airtight polypropylene bags at 4 °C in the dark. The yield of microencapsulation was calculated using the Eq. (1):

$$YE = \frac{W_2}{W_1} \cdot 100 \quad (1)$$

where YE is the yield (%), W_2 is the weight (g) of the powder in the collection bottle and W_1 is the dry weight (g) of the feed mass calculated as the total weight of the CEO and the polymer used for each bath (Bustos-Garza, Yáñez-Fernández, & Barragán-Huerta, 2013). Each determination was carried out in triplicate.

The adhered powder to the drying chamber wall was not considered in the yield assessment.

2.6. Characterisation of the microcapsules

2.6.1. Moisture content

The moisture content of CEO-loaded microcapsules was determined gravimetrically by oven-drying at 105 °C up to constant weight (AOAC, 2007; Fernandes, Borgesa, et al., 2014). It was used one gram of powder and the moisture was expressed in terms of percentage dry basis.

2.6.2. Wettability and solubility of microcapsules

The wettability and solubility of CEO-loaded microcapsules were measured using the method described by Fernandes, Borgesa, et al. (2014).

In order to determine the wettability, one gram of powder was spreaded over the surface of 100 mL water contained into a glass vessel with the diameter of 5 mm without stirring at room temperature (23–25 °C).

The wettability of microcapsules loaded with CEO was done by the time the microcapsules leave the water surface and sink.

The solubility of microcapsules was calculated by adding 25 mL ultrapure water over one gram of powder, gently stirring for 30 min at room temperature. The resulting suspension was centrifuged using the Sigma-2–16KC (Germany) laboratory centrifuge for 10 min at 9000 rpm. The supernatant was transferred into a separatory funnel over which 5 mL *n*-hexane was added in order to extract the traces of released oil. The aqueous phase was then separated and placed on a pre-weighed Petri dish with the mass (m_1) and then inserted in an oven at 105 °C. The drying regime was maintained up to the constant weight of the sample (m_2). The solubility of microcapsules (S%) was calculated as a percentage of dry matter (from the supernantant) compared to the initial powder mass (m_0) and thus the following Eq. (2) was done:

$$S = \frac{m_2}{m_0} \cdot 100 \quad (2)$$

2.6.3. Powder flowability experiments

The flowability properties of powders are presented as a function of the poured bulk density (D_p), the tapped density (D_T), the Compressibility Index (CI) and the Hausner Ratio (HR).

For the assessment of the poured bulk density (D_p) it was used the method described by Jinapong, Suphantharika, and Jamnong (2008). A determined quantity of microcapsules (M) was slowly poured into a graduated cylinder.

The poured bulk density was calculated as follows Eq. (3):

Table 1
Formulation (w/w) and properties of CEO emulsions and CEO microcapsules.

CEO emulsions						CEO microcapsules				
Code	Composition of emulsions (g/100 g)				Droplet size (μm)	Code	Size (μm)	Yield (%)	Surface oil (g/100 g microcapsules)	EE (%)
	Ch	Alg	In	CEO						
E_{Ch}	20	–	–	5	1.12 ± 0.08	M_{Ch}	9.87 ± 0.76	58.89 ± 2.78	14.38 ± 0.62	54 ± 2.15
E_{Alg}	–	20	–	5	1.86 ± 0.05	M_{Alg}	9.36 ± 0.21	69.34 ± 1.65	8.74 ± 0.36	63 ± 3.63
E_{Ch-Alg}	10	10	–	5	1.32 ± 0.01	M_{Ch-Alg}	10.28 ± 0.47	67.12 ± 2.59	10.76 ± 0.47	59 ± 1.73
E_{Ch-In}	10	–	10	5	1.67 ± 0.02	M_{Ch-In}	14.86 ± 0.64	63.56 ± 3.42	11.63 ± 0.52	51 ± 3.12

Ch – chitosan; Alg – alginate; In – inulin; CEO – coriander essential oil. Values are the means ± standard deviation of three replicate experiments.

$$D_P = \frac{M}{V_P} \quad (3)$$

where V_P (cm^3) is the poured bulk volume of microcapsules read directly on the graduated cylinder.

The same mass (M) of poured bulk microcapsules, still in the same graduated cylinder, was subjected to consolidation using a mechanical tapping device until a negligible difference in volume between successive measurements was observed. The tapped bulk density (D_T) was calculated using the following Eq. (4):

$$D_T = \frac{M}{V_T} \quad (4)$$

where V_T (cm^3) is the tapped bulk volume of microcapsules.

The Compressibility Index, also known as the Carr index (CI) and the Hausner Ratio (HR) were calculated using the following Eqs. (5) and (6):

$$CI = \frac{D_T - D_p}{D_T} \cdot 100 \quad (5)$$

$$HR = \frac{D_T}{D_p} \quad (6)$$

2.7. Particle size and morphology of microcapsules

The size of the particles was measured by laser light diffraction using a Mastersize 2000 MU (Malvern Instrument, Malvern, UK). The samples were suspended in isobutyl alcohol and the volume-weighted mean diameter ($d_{4,3}$) was measured. The microstructure of CEO-loaded microcapsules was analysed with a Scanning Electron Microscope (SEM) Quanta 200 FEI, operating at 15 kV and with an electron beam current of 110 μA using a secondary electron detector. The samples were fixed directly on aluminium stubs using electrically conductive double adhesive tape (Agar Scientific, Christine Gröpl Austria). Afterwards they were sputtered with a thin gold layer in SPI-Sputter Coater with Etch Mode (West Chester, Pennsylvania, USA) for 40 s, with a current of 18 mA and thickness of 50 Å. After metallization, the samples were analysed using magnification between 400 and 24,000×.

2.8. Swelling studies

The swelling degree of microcapsules was assessed using a modified method described by Dima et al. (2014). A quantity of 0.5 g of microcapsules were introduced into 15 mL phosphate buffer solution at different pH values (2.5 and 6.5) and different temperatures (37 °C and 65 °C). The swollen microcapsules were removed from the solution, dried with filter paper and then weighed.

For each sample three measurements were performed. The swelling degree (SW%) was calculated using Eq. (7).

$$SW = \frac{W_t - W_0}{W_0} \cdot 100 \quad (7)$$

where W_t is the mass of the swelled microcapsules weighed at different time intervals, and W_0 is the initial mass of dried microcapsules.

2.9. Encapsulation efficiency and loading capacity

2.9.1. Surface oil content

The CEO on the surface of microcapsules was determined by Jafari, Assadpoor, He, and Bhandari (2008) adjusted method. A quantity of 5 g of microcapsules were dispersed in 10 mL *n*-hexane followed by 10 min stirring. The suspension was filtered and the residue was washed three times with 5 mL petroleum ether.

The obtained powder was dried in an oven at 90 °C until the weighed mass was constant (W). The quantity of CEO on the surface of microcapsules ($W_{Surface\ CEO}$) was determined calculating the difference between the initial microcapsules mass and the powder mass obtained after drying (W).

2.9.2. Total oil content

The total content of CEO represents the content of CEO inside microcapsules and the content of oil at the surface of microcapsules. A suspension formed through the dispersion of 5 g of microcapsules into 180 mL petroleum ether was sonicated on ice bath for 5 min at an amplitude of 50% and a frequence of 30 kHz (Rodea-González et al., 2012). The CEO was extracted using a Soxhlet (VLP-SER 148/6) system, with an extraction time of 6 h. After extraction the powder was dried until constant mass ($W_{Soxhlet}$). The total content of CEO ($W_{Total\ CEO}$) was calculated as the difference between the initial mass of microcapsules and the powder mass obtained after extraction with Soxhlet ($W_{Soxhlet}$).

Encapsulation efficiency (EE) was calculated by the Eq. (8)

$$EE = \frac{W_{Total\ CEO} - W_{Surface\ CEO}}{W_{Total\ CEO}} \cdot 100 \quad (8)$$

2.10. In vitro release study

The study of the *in vitro* release of CEO was carried out using a method described by Hosseini et al. (2013).

The CEO-loaded microcapsules (250 mg) were added in an Erlenmeyer flask containing 60 mL phosphate buffer solution (PBS) at pH values of 2.5 and 6.5 and ethanol in a 3:2 ratio (v/v). The suspension was slowly stirred at constant temperature (37 °C and 65 °C).

At regular time intervals, samples of 2 mL were withdrawn from the suspension and being immediately replaced with an equivalent volume of fresh media. The sink conditions were maintained at all time. The samples were filtered using 0.45 μm MF – Millipore membrane filter (Millipore Corporation, Bedford, USA). The CEO concentration was determined spectrophotometrically at a wavelength of 273 nm using the UV–VIS spectrophotometer (Model Jasco 560, Germany). The blank sample was a PBS/ethanol 3:2 (v/v) solution. The CEO concentration in the release medium at sampling time intervals was calculated using a calibration curve of free CEO in PBS/ethanol 3:2 (v/v) solution (Absorbance = 4.736·Conc.(mg/mL) + 0.1359 ; R^2 = 0.9973).

The cumulative percentage of CEO release (Q_t%) was calculated with Eq. (9).

$$Q = \sum_{t=0}^{t} \frac{M_t}{M_0} \cdot 100 \quad (9)$$

where Q is the cumulative release percentage, M_t is the cumulative amount of CEO released at each sampling time and M_0 is the initial mass of CEO loaded in the sample (Hosseini et al., 2013).

2.11. Statistical analysis

The experiments were carried out in triplicate and the results are reported as means ± standard deviation (SD). The analysis of the results was performed using the ANOVA method and they were related to those obtained by Tukey test. A value of $p < 0.05$ was considered to be statistically significant (Sigma Plot, 2008, Systal Software Inc., USA).

3. Results and discussion

3.1. Droplet size and rheology of CEO emulsions

The emulsions quality represents one of the main factors which influence oil retention during spray drying. The stable O/W emulsions were prepared in a two-step process involving the preparation of the coarse emulsions followed by ultrasonication. Table 1 presents the values of the droplet size of fine emulsions, measured two hours after preparation. After a period of ten days storage, the droplet size of the CEO emulsions has not registered significant changes ($p > 0.05$). All emulsions showed a great stability, with no phase separation.

The rheological properties of the O/W emulsions were previously reported to influence the droplet size, the transport of infeed materials, the morphology and the loading capacity of the microcapsules obtained by spray drying technique (Estevinho et al., 2013).

Fig. 1a shows the viscosity evolution under increasing shear rate for the four emulsions prepared. For each emulsion a viscosity decrease with increasing shear rate was observed. Therefore, it could be concluded that the prepared emulsions behaved as shear thinning fluids. The profile of viscosity curves varied depending on the encapsulating material. A significant decrease of viscosity was observed for the emulsions prepared with the following mixtures of polymers: Ch–Alg and Ch–In ($p < 0.05$). Thus, for an increase of the share rate varying between 0.1 s^{-1} to 100 s^{-1} the E_{Ch-Alg} displayed the highest decrease of viscosity from 85.95 ± 0.87 Pa s to 1.38 ± 0.13 Pa s, while the viscosity of the E_{Ch-In} emulsion decreases from 8.94 ± 0.25 Pa s to 0.829 ± 0.11 Pa s. The high value of the E_{Ch-Alg} emulsion is the result of complex structures formation due to the electrostatic interactions between the protonated amino groups of chitosan and the carboxylic groups of sodium alginate. The increase of the shear rate leads to the destruction of the complex structures and boosts the chains flexibility of the two polymers. The viscosity of polymers solutions was stated to be also influenced by the intramolecular interactions which modify the conformation of polymeric chains (Khong, Aarstad, Skjĺk-Brćk, Drage, & Vĺrum, 2013).

The results from the oscillatory rheological tests (Fig. 1b–d) explain the viscoelastic properties of the studied emulsions. It was noticed, for all emulsions, an increase of the dynamic moduli (G', G'') and a decrease of the shift angle as a function of increasing frequency. Storage modulus values resulted appretiable higher than loss modulus in the case of E_{Ch-Alg} emulsion, which together with the shift angle values under 45° denoted a solid like behaviour. Thus it could be stated that analysed emulsion behaved as a soft solid. Similar results were stated by other researchers too, for chitosan/alginate emulsions (Saha & Bhattacharya, 2010), chitosan/glycerophosphate gel (Cho, Heuzey, Bégin, & Carreau, 2006) and sodium alginate/pea proteins gel (Mession et al., 2013). As regarding the other formulations, a liquid like behaviour was observed, with G'' values prevailing G'.

3.2. Particle size and morphology of microcapsules

The type of biopolymer, the rheological properties of emulsions, the atomization method and the drying conditions were found to influence the form and morphology of the microcapsules obtained by spray drying method as reported by Gharsallaoui, Roudaut, Chambin, Voilley, and Saurel (2007) and Jafari et al. (2008). The size of M_{Ch-Alg} microcapsules was greater than the size of M_{Alg} microcapsules ($p < 0.05$), because of the high viscosity of E_{Ch-Alg} emulsion. The presence of inulin in the encapsulating material determines the growth of the microcapsules size.

These results are in accordance with those reported by Beirão-da-Costa et al. (2013) for the preparation of inulin microcapsules loaded with oregano essential oil and Fernandes, Borgesa, et al. (2014) for gum arabic, starch, maltodextrins and inulin microcapsules loaded with rosemary essential oil.

The form and morphology of microcapsules influence properties such as: bulk density, mechanical resistance, swelling degree, protection and release of the encapsulated biocomponents (Martínez et al., 2015). All types of microcapsules loaded with CEO and obtained by spray drying technique, did not display cracks and presented a wall thickness of about 2–3 μm.

Fig. 2 presents the SEM images of the microcapsules prepared with different encapsulating material.

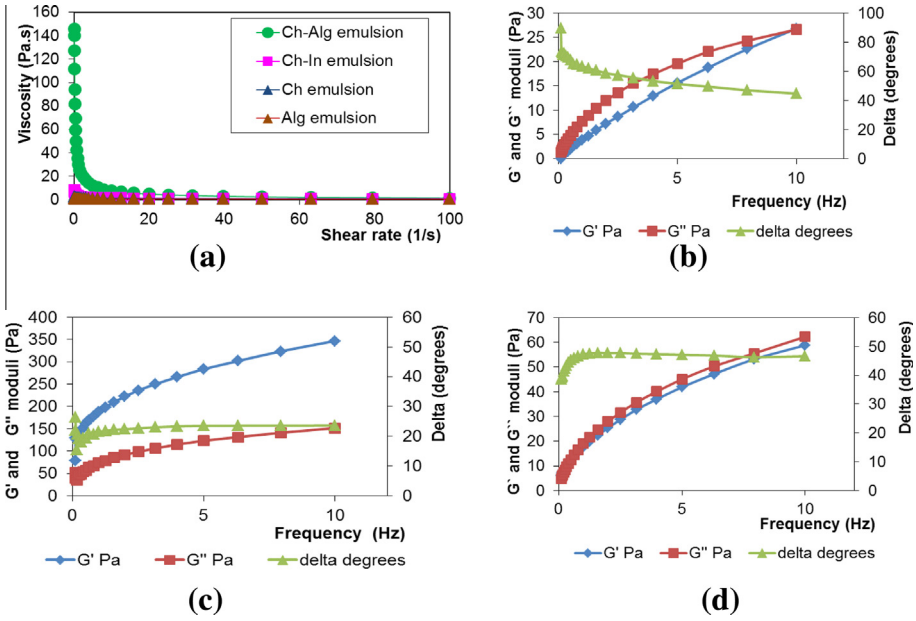

Fig. 1. Rheological diagrams of CEO emulsions (O/W). (a) Flow curves for CEO emulsions (O/W); variations with frequency of the shear modulus (G' and G'') and shift angle (δ) of CEO microcapsules with different polymers: (b) Ch emulsion; (c) Ch–Alg emulsion; (d) Ch–In emulsion.

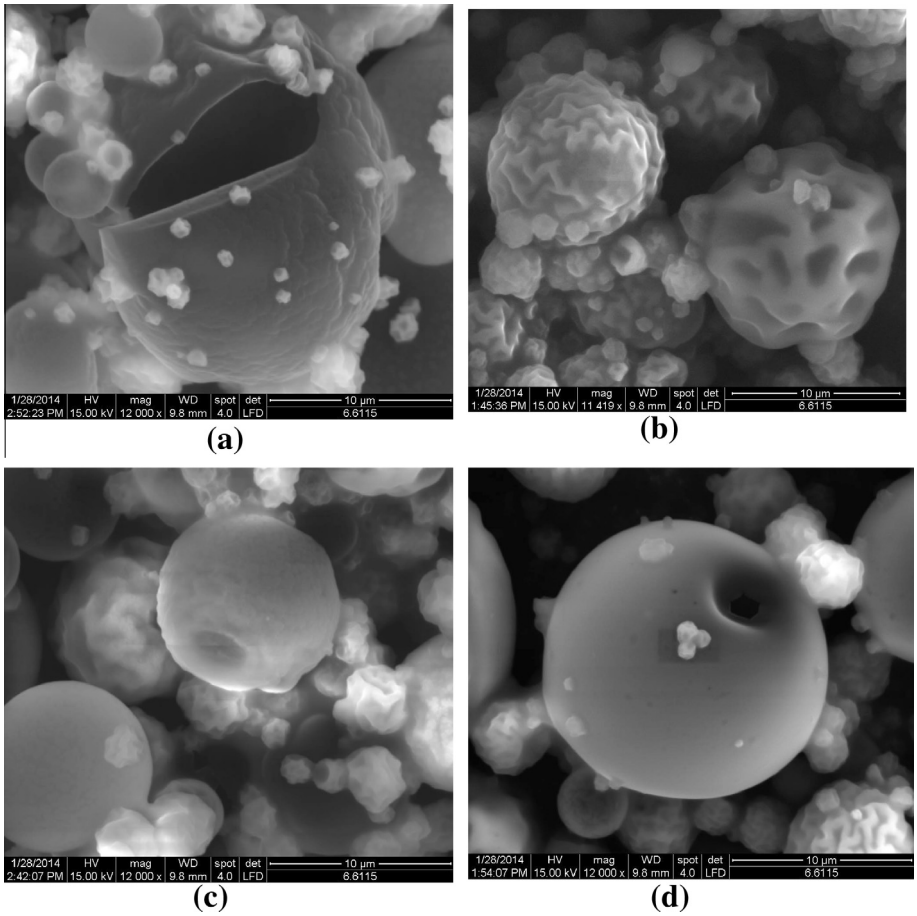

Fig. 2. SEM-micrographs of CEO-loaded microcapsules with different wall material: (a) alginate; (b) chitosan; (c) chitosan/alginate; (d) chitosan/inulin.

The M_{Ch} microcapsules (Fig. 2b) had a brain-like structure, resembling the structure of chitosan microcapsules obtained by spray drying method by Tokárová, Kašpar, Knejzlík, Ulbrich, and Štěpánek (2013), while the M_{Alg} and M_{Ch-Alg} microcapsules were spherical with a smooth surface, in accordance with the viscoelastic properties of corresponding emulsions (Fig. 2a, c and d).

3.3. Characterisation of CEO microcapsules

Table 2 displays the characteristics of the microcapsules prepared through spray drying.

The moisture of the microcapsules loaded with CEO varied between 1.12% and 2.48% depending on the encapsulating material. Thus, the M_{Ch-In} microcapsules presented higher moisture content than other microcapsules ($p < 0.05$) which was thought to be due to the presence of inulin which favoured the adsorption of water at the surface of microcapsule. Similar results were reported by Fernandes, Marques, et al. (2014) for the preparation of microcapsules loaded with rosemary essential oil.

Wettability expresses the capacity of microcapsules to interact with water molecules (Fernandes, Borgesa, et al., 2014) and it was expressed as the time necessary for the submergence of microcapsules in water. This time period varied between 112 s for the M_{Ch-In} microcapsules and 332 s for the M_{Ch} microcapsules. The M_{Ch-In} microcapsules adsorbed water faster due to the high number of hydrophilic groups (–OH) of inulin which increased the adherence capacity of water molecules on the surface of microcapsules. The M_{Ch} microcapsules displayed the lowest wettability capacity due to the macromolecular chain of chitosan which contains fewer hydrophilic groups. The results showed that the wettability increases with decreasing of microcapsules size. Similar results were reported by Fernandes, Borgesa, et al. (2014) for the preparation of microcapsules containing rosemary essential oil, using as encapsulating material inulin blended with arabic gum and maltodextrins.

The results mentioned in Table 2 reveal that the M_{Alg} microcapsules had the highest water solubility at room temperature (18.21 ± 0.09%) in comparison to the M_{Ch} microcapsules which displayed poor water solubility ($p < 0.05$). Likewise, the M_{Ch-Alg} microcapsules manifest poor solubility (6.13 ± 0.16%) due to formation of complex coacervates (Khong et al., 2013).

Table 2
The moisture content, wettability, solubility and flow properties of CEO microcapsules.

Microcapsules	Moisture (%)	Wettability (s)	Solubility (%)	Poured bulk density (D_p) (g/cm^3)	Tapped density (D_T) (g/cm^3)	HR	CI (%)
M_{Ch}	2.17 ± 0.11	332 ± 21	0.73 ± 0.04	0.39 ± 0.02	0.55 ± 0.01	1.43 ± 0.04	29.09 ± 0.04
M_{Alg}	2.89 ± 0.48	128 ± 6	18.21% ± 0.09	0.42 ± 0.01	0.60 ± 0.06	1.42 ± 0.01	32.25 ± 0.12
$M_{Ch/Alg}$	2.34 ± 0.26	321 ± 11	6.13% ± 0.16	0.35 ± 0.07	0.50 ± 0.02	1.44 ± 0.01	30.00 ± 0.03
$M_{Ch/In}$	4.38 ± 0.31	112 ± 9	14.52 ± 0.88	0.35 ± 0.02	0.48 ± 0.01	1.38 ± 0.02	31.37 ± 0.08

The study of flowability properties of food powders is carried out in order to understand their behaviour during food processing operations. The food powder flowability is influenced by the size, form and morphology of particles, bulk density, infeed properties, and by the presence of oil at the surface of microcapsules.

According to the data from Table 2 the values of the bulk density (D_p) range between 0.35 g/cm^3 and 0.42 g/cm^3 and the tapped bulk density values varied between 0.50 g/cm^3 and 0.62 g/cm^3. The Compressibility Index also known as the Carr Index (CI) and the Hausner Ratio (HR) were computed using the Eqs. (5) and (6) and with the help of the bulk density values. CI represents the measurement of cohesivity between microcapsules and explains the capacity of microcapsules to agglomerate, while HR expresses the friction force between particles. The powders with CI < 10 or HR < 1.11 display an "excellent" flowability while the powders with CI > 38 sau HR > 1.6 are considered to have a "very very poor" flowability. The intermediate values of CI and HR allow the following classification of powders: "good" flowability powders (CI = 11–15; HR = 1.12–1.18), "fair" flowability powders (CI = 16–20 ; HR = 1.19–1.25), "passable flow powders" (CI = 21–25 ; HR = 1.35–1.45), "poor" flowability powders (CI = 26–31; HR = 1.35–1.45), "very poor" flowability powders (CI = 32–37 ; HR = 1.46–1.59) (Shah, Tawakkul, & Khan, 2008). According to the CI and HR values in Table 2 all the microcapsules prepared for the present study corresponded to the "poor" flowability powders group due to their tendency to agglomerate.

The yield of CEO-loaded microcapsules obtained by spray drying method is presented in Table 1 and it is ranging between 58.89 ± 2.78% and 69.34 ± 1.65%, for M_{Ch} microcapsules and for M_{Alg} microcapsules respectively. The poor values of the yield are caused by the powder adherence on the interior surface of the drying chamber, especially in the case of chitosan which displayed important adhesive properties.

The oil surface influences both the encapsulation efficiency and the release kinetics (Rodea-González et al., 2012). Thus, it was noticed a higher quantity of oil at the surface of M_{Ch} microcapsules, due to their surface striations which enable the easy capture of oil drops, than in the case of other smooth surface microcapsules (Table 1). Furthermore, it could be noticed an increase of the oil surface which was correlated with the decrease of the oil droplets size in the prepared emulsions. The results obtained within the study are in accordance with the results reported by Rodea-González et al. (2012).

The efficiency of CEO encapsulation (EE) represents an important parameter that influences the quality of microcapsules. Significant differences were obtained between the EE of M_{Ch} and M_{Alg} microcapsules ($p < 0.05$). Thus, the highest EE value was obtained for M_{Alg} microcapsules (63 ± 3.63%) and the lowest EE value was obtained for M_{Ch} microcapsules (Table 1). The results reported by other researchers demonstrate that EE is influenced by the wall material: oil ratio and by the type of the encapsulating material (Porras-Saavedra et al., 2015; Turchiuli et al., 2014). Hosseini et al. (2013), using the spray drying method, prepared microcapsules loaded with oregano essential oil with a masic ratio chitosan:oil of 5:1, obtaining an EE of 39.94%.

3.4. Swelling studies

The swelling studies revealed that the penetration of water inside the microcapsule was strongly influenced by the nature of the encapsulating material and also by the conditions of the swelling medium (pH, ionic strength and temperature). According to Fig. 3, for a pH value of 2.5, the lowest capacity of swelling was displayed by the M_{Alg} microcapsules mainly because considering these pH values, the carboxyl groups of uronic acids in the sodium alginate become unionised and thus a part of the sodium alginate could be transformed into alginic acid with low water solubility (Li & McClements, 2011). The high swelling degree of other microcapsules is determined by the protonation of the amino groups on the chitosan chain which increase the water solubility of microcapsules. The kinetic curves of chitosan microcapsules (M_{Ch}; M_{Ch-Alg} and M_{Ch-In}), for pH 2.5, displayed two different phases. The first phase was represented by an initial period (0–80 min) when the swelling degree was fast after a zero order kinetics followed by a second slow swelling phase where the swelling degree became constant after 180 min.

For increased values of pH corresponding to the constant acidity (pKa) values of the two polyelectrolytes (pKa_{Alg} 3.5; pKa_{Ch} 6.5), the values of the swelling degree of chitosan microcapsules (M_{Ch}; M_{Ch-Alg} and M_{Ch-In}) were significantly lower than the values registered for M_{Alg} microcapsules ($p < 0.05$). In this pH range the carboxyl groups of uronic acids are completely ionised which allows the rapid intrusion of water molecules in the M_{Alg} microcapsules thus leading to extremely high values of the swelling degree (Fig. 3b). After 120 min, was registered a decrease of the swelling degree triggered by the dissolution/erosion process. A similar phenomenon was recorded for the M_{Ch-In} and M_{Ch-Alg} microcapsules as a result of the inulin and alginate, solubilisation.

At a pH value of 6.5 (Fig. 3b) the lowest values of the swelling degree were registered for the M_{Ch-Alg} microcapsules because, for this pH value, the amino groups are still $-NH_3^+$ protonated and therefore interact through electrostatic forces with the ionised carboxyl groups ($-COO^-$) of alginate forming a Ch–Alg complex polyelectrolyte structure which inhibits the intrusion of water molecules into microcapsule. Similar results were reported by other researchers (Li et al., 2011; Čalija et al., 2013).

3.5. In vitro release studies

The studies of the *in vitro* release of CEO loaded microcapsules were performed under pH and temperature values that simulate the processing conditions of food products inside the gastrointestinal tract. Thus, it was studied the release of CEO from obtained microcapsules in buffers at a pH of 2.5 and pH of 6.5, specific of the gastrointestinal tract and food processing conditions. The two temperatures selected for the study were 37 °C (human body characteristic temperature) and 65 °C (food processing temperature). In order to explain the release mechanisms were used the kinetic equations corresponding to the mathematical models in Table 3. The type of CEO transport through the wall of the microcapsule was explained with the parameters in Peppas equation, Eq. (10):

$$Q = k \cdot t^n \tag{10}$$

where Q is the cumulative percent of essential oil released at time t; k is a constant related to structural and geometric characteristics of the matrix, and n is the diffusional exponent that indicates the mechanism of the essential oil release.

In microspheres/microcapsules, the values of n indicate the following release mechanisms: for $n \leqslant 0.43$, the dominant release mechanism is the Fickian diffusion (case I transport); $0.43 \leqslant n < 0.85$ indicates the diffusion and the swelling release mechanism (non Fickian or anomalous transport) and $n \geqslant 0.85$ corresponds to zero order release kinetics (case II transport) (Maderuelo et al., 2011; Siepmann & Peppas, 2001).

As Fig. 3c shows, the kinetic curve of CEO release from M_{Ch} microcapsules in PSB solution for pH 2.5 and 37 °C displayed two sectors with different slopes. The first segment corresponds to the rapid release phase (burst effect) when after 60 min more than half from the encapsulated CEO quantity was released (57.78 ± 1.78%), followed by a slow growth of the release rate up to constant value achieved after 120 min. The burst effect was reported to be the result of a high oil content on the surface of

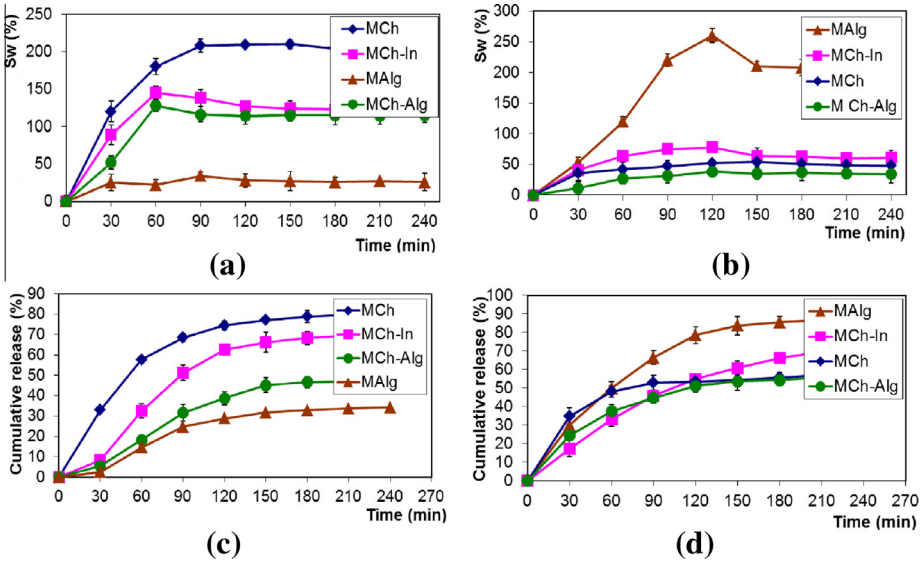

Fig. 3. Swelling kinetics and cumulative release profiles of M_{Ch}; M_{Alg}; M_{Ch-Alg} and M_{Ch-In} microcapsules loaded with CEO at 37 °C: (a) swelling pH 2.5; (b) swelling pH 6.5; (c) cumulative release pH 2.5; (d) cumulative release pH 6.5.

Table 3
Kinetic release parameters of CEO-loaded microcapsules in various media.

Mathematical model	M_{Ch}	M_{Alg}	M_{Ch-Alg}	M_{Ch-In}
pH 2.5				
Zero order	$Q = 11.294t + 43.315$ ($R^2 = 0.7195$); $p = 0.0612$*	$Q = 8.2264t + 6.8643$ ($R^2 = 0.7914$); $p = 0.0723$	$Q = 11.68t + 8.8064$ ($R^2 = 0.8321$); $p = 0.0596$	$Q = 15.955t + 17.628$ ($R^2 = 0.7697$)
First order	$\ln(100 - Q) = -0.0054t + 4.075$ ($R^2 = 0.8383$); $p = 0.0568$	$\ln(100 - Q) = -0.0018t + 4.5397$ ($R^2 = 0.8247$); $p = 0.0559$	$\ln(100 - Q) = -0.0032t + 4.5691$ ($R^2 = 0.8838$); $p = 0.0509$	$\ln(100 - Q) = -0.0052t + 4.459$ ($R^2 = 0.8512$)
Higuchi	$Q = 33.475t^{1/2} + 20.481$ ($R^2 = 0.8320$); $p = 0.0634$	$Q = 24.046t^{1/2} - 9.2825$ ($R^2 = 0.8900$); $p = 0.0501$	$Q = 33.821t^{1/2} - 13.656$ ($R^2 = 0.9183$); $p = 0.0487$	$Q = 46.838t^{1/2} - 13.982$ ($R^2 = 0.8731$)
Peppas	$\ln Q = 3.941 + 0.4032\ln t$ ($R^2 = 0.8703$; $n = 0.4032$); $p = 0.0497$	$\ln Q = 2.8491 + 0.5377\ln t$ ($R^2 = 0.8578$; $n = 0.5377$) $p = 0.0521$	$\ln Q = 3.0822 + 0.6631\ln t$ ($R^2 = 0.8747$; $n = 0.6631$) $p = 0.0504$	$\ln Q = 3.6347 + 0.5229\ln t$ ($R^2 = 0.8428$; $n = 0.5229$)
pH 6.5				
Zero order	$Q = 5.1436t + 40.2060$ ($R^2 = 0.7035$); $p = 0.0741$	$Q = 15.493t + 36.1510$ ($R^2 = 0.8101$); $p = 0.0618$	$Q = 8.2557t + 28.6451$ ($R^2 = 0.8084$); $p = 0.0597$	$Q = 15.1182t + 18.49$ ($R^2 = 0.9196$)
First order	$\ln(100 - Q) = -0.0017t + 4.092$ ($R^2 = 0.7558$); $p = 0.0739$	$\ln(100 - Q) = -0.0085t + 4.319$ ($R^2 = 0.9200$); $p = 0.0442$	$\ln(100 - Q) = -0.0025t + 4.2822$ ($R^2 = 0.8592$); $p = 0.0528$	$\ln(100 - Q) = -0.0052t + 4.4982$ ($R^2 = 0.9806$)
Higuchi	$Q = 15.203t^{1/2} + 29.868$ ($R^2 = 0.8091$); $p = 0.0627$	$Q = 45.095t^{1/2} + 6.0174$ ($R^2 = 0.9034$); $p = 0.0410$	$Q = 24.052t^{1/2} + 12.556$ ($R^2 = 0.9031$); $p = 0.0436$	$Q = 42.96t^{1/2} - 9.4089$ ($R^2 = 0.9774$)
Peppas	$\ln Q = 3.7964 + 0.2208\ln t$ ($R^2 = 0.8667$; $n = 0.2208$) $p = 0.0454$	$\ln Q = 3.8791 + 0.5222\ln t$ ($R^2 = 0.9325$; $n = 0.5222$) $p = 0.0382$	$\ln Q = 3.5713 + 0.3976\ln t$ ($R^2 = 0.9348$; $n = 0.3976$) $p = 0.0325$	$\ln Q = 3.4432 + 0.6833\ln t$ ($R^2 = 0.9680$; $n = 0.6833$)

* Mathematical model is considered to be statistically significant for $p < 0.05$.

microcapsules and of their swelling degree. At the contact with the solution from the environment, water penetrates the microcapsule wall and the polymer passes from a glassy to a rubbery state. During the swelling stage, inside the polymer coexist the inside glassy state and outside the rubbery state (Maderuelo et al., 2011). In these conditions the release rate depends simultaneously by the swelling and the diffusion processes specific to a non Fickian transport mechanism. Such results are sustained by the use mathematic models. Thus, the release kinetics of CEO from M_{Ch} microcapsules at 2.5 pH was best described by the first order equation ($R^2 = 0.8383$) and by the Peppas equation (0.8703) (Table 3). The value of the diffusional exponent $n = 0.4032$ from Peppas equation explains the non-Fickian transport mechanism. For the other microcapsules the release process was slower in the first 30 min and afterwards, increased directly with time (Higuchi equation). The values of the diffusional exponent (n) of Peppas equation also displayed a non Fickian transport mechanism. Significant differences ($p < 0.05$) are observed between the percents of cumulative release of CEO from M_{Ch} and M_{Alg} microcapsules. Thus, after 120 min the release percentage of CEO from M_{Ch} microcapsules is of 74.50 ± 2.21% while the release percentage of CEO from M_{Alg} microcapsules is of 28.78 ± 1.82%. The small percentage of CEO release from M_{Alg} microcapsules could be explained by low swelling degree of microcapsules and by the rigid polymeric chains which do not permitted the CEO diffusion.

The pH growth of the fluid in which the release took place modified essentially the kinetic curves (Fig. 3d). Thus, for pH 6.5 and 37 °C the release process of CEO from M_{Alg} microcapsules was modelled to follow the first-order kinetics ($R^2 = 0.9200$). After 60 min, the difference between the release percents of CEO from M_{Alg} and M_{Ch} microcapsules was insignificant ($p > 0.05$) as compared with the following period when the values of CEO release percents from the two types of microcapsules were statistically significant ($p < 0.05$). It must be emphasised that for both pH values (6.5 and 2.5) the release process of CEO from M_{Ch} microcapsules displayed the burst effect after 30 min due to the surface oil. At pH 6.5 the diffusional exponents of Peppas equation had different values. Thus, for M_{Ch} microcapsules and M_{Ch-Alg}

microcapsules the diffusional exponent values were $n < 0.43$ which explains a diffusion-controlled release process caused by the poor swelling degree and by the presence of oil drops at the surface or in the exterior layer of microcapsules. For the other types of microcapsules the following values are registered $0.43 < n < 0.85$, which demonstrate that the CEO release is a diffusion-swelling controlles process that could be caused by the poor swelling degree and by the presence of oil drops at the surface or in the exterior layer of microcapsules. For the other types of microcapsules registered values of $0.43 < n < 0.85$ demonstrate that the CEO release followed a diffusion-swelling controlled process. Similar results were registered for other systems: alginate/oligochitosan/eudragit microparticles (Čalija et al., 2013), chitosan-alginate matrix tablets (Li et al., 2013) and inulin microparticles (Beirão-da-Costa et al., 2013).

The variation of temperature changed the release rate of CEO from the obtained microcapsules without influencing the release mechanisms. The release rate of CEO increased together with temperature for both pH values 2.5 and 6.5. For a temperature of 65 °C and a pH of 6.5 the release percentage after 6 h exceeded 80% for all microcapsules. Under these circumstances it could be observed that M_{Ch-In} microcapsules suffered advanced erosion, presenting a release percentage of 98 ± 3.7% due to inulin solubilisation.

4. Conclusions

The aim of this paper was the obtaining of microcapsules loaded with coriander essential oil using chitosan, alginate and inulin as encapsulating material by spray drying method. The rheological studies showed that the fine emulsions with coriander essential oil prepared through ultrasonication displayed a pseudo plastic behaviour and the emulsion for which the aqueous phase was the chitosan-alginate system manifested viscoelastic properties as a result of the electrostatic interactions between the two polyelectrolytes with different electric charges. The addition of inulin increased the wettability and solubility of microcapsules and decreased the efficiency of the encapsulation process. The flowing properties of powders were characterised with the Compressibility Index and the Hausner Ratio. The results showed that all the powders obtained belong to the "poor flowability powder" group and manifested agglomeration tendency. The experimental studies and the kinetic modelling based on Peppas, Higuchi, first-order and zero-order equations revealed that the release of the coriander essential oil followed a swelling-diffusion controlled process. The value of the diffusion exponent from the Peppas equation was $0.43 \leqslant n < 0.85$, so the diffusion process could be considered as an "anomalous diffusion". Considering the swelling process, the water penetrated the polymeric matrix and the release rate was determined by the glass-to-rubbery process. The microcapsules swelling and the release of the coriander essential oil were found to be influenced by temperature and pH variations. As a result of the different acid-base character of the two polyelectrolytes, the microcapsules with chitosan had the highest swelling degree and the highest release rate at pH 2.5, while the microcapsules with alginate presented the maximum values of the swelling degree and release rate at pH 6.5. Inulin facilitated the swelling of microcapsules due to its hydrophilicity and a 6.5 pH value ensured a higher release rate than considering the case of chitosan microcapsules.

The results presented in this study proved that the CEO-loaded microcapsules prepared by, spray drying method, using chitosan, alginate, chitosan/alginate and chitosan/inulin as wall materials, are resistant to pH and temperature variations and can ensure a slow release of CEO. Therefore, they could be used both in food and pharmaceutical industry.

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