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Preparation and characterization of citrus essential oils loaded in chitosan microcapsules by using different emulsifiers

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ABSTRACT:

Citrus essential oils (CEOs) loaded in chitosan microcapsules (CS-CEOs) were prepared by 6 different emulsifiers (Tween 20, Tween 40, Tween 60, Tween 20/Span 801:1, Tween 20/SDBS1:1, Span 80) with emulsion-ionic gelation technique. Their rheological properties, embedding and release rate as well as microcapsules diameters were analyzed. The results indicated that emulsifier types significantly affected the size and embedding efficiency of microcapsules, obtaining sample groups of Tween 60, Span 80, Tween 20/Span 80 with typical diameters 289.3 nm, 3893.2 nm, 8843.2 nm, respectively. The structures and thermal properties of CEOs microcapsules were analyzed by using fourier transform infrared spectrophotometry (FT-IR), X-ray diffractometry and differential scanning calorimetry (DSC). Results demonstrated that CEOs oil were successfully embedded in the microcapsules and group of Tween 60 has the minimum particle size with the best embedding rate of 68.1%. The strength of the intermolecular interaction as well as exothermic peaks of microcapsules prepared with different emulsifiers were different, Tween 60 holds the lowest temperature value of exothermic peak for smallest internal energy is needed for melting, corresponds with its lowest particle size. Fourier transform infrared spectroscopy (FT-IR) provided profiles on the major functional groups of CS-CEOs. The results proved condition to prepare CS-CEOs microcapsules by using different emulsifiers.

1. Introduction

Citrus essential oils (CEOs) is extracted from citrus peel and it has been widely used in anti-inflammatory (Amorim et al., 2016), anti-anxiety (Namazi et al., 2014), antioxidant and antibacterial fields (Phi et al., 2015). CEOs can be extracted by the methods of liquid-liquid extraction (Gonçalves et al., 2016), vacuum fractional distillation (Perini et al., 2017) and solvent extraction (Lago et al., 2014). CEOs contains a variety of volatile components which provide its unique odor. However, it is not stable and is easily oxidized. To solve the problems, microcapsules technologies have been widely used as transfer vehicle and stabilizers in the field of food, chemistry engineering and drug delivery, etc. Hence, it is a good option to prepare CEOs as the core material into microcapsules, which effectively slow down the volatility of its active ingredients.

Among the cliff materials of microcapsules, chitosan (CS) is an expected one due to its safety, biocompatibility and biodegradability. It has been frequently applied in conserving pH, heat or temperature sensitive compounds (Estevinho et al., 2013), and allows the reformulation of a large quantity of pharmaceutical products and food in order to apply them better or new properties (Patel and Patel, 2010). Furthermore, chitosan was reported as a reliable candidate in preparation and performance of microcapsules embedding essential oils (Javid et al., 2014; Hu et al., 2015; Jiang et al., 2015; Yang et al., 2014; Chung et al., 2013).

Preparation methods of chitosan-based microcapsules include interfacial polymerization, in-situ polymerization, multiple emulsion-solvent evaporation method and emulsion-ionic gelation technique, etc. In the process of emulsion-ionic gelation technique,

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the coagulant is added into the cliff material, then the microcapsules are formed by ion coagulation of the two-phase mixture. When the core material is oil phase, the addition of emulsifier can help to affect the particle distribution in microcapsules-formed emulsion to obtain microcapsules with higher quality (Martins et al., 2010; Petrovic et al., 2010).

Hydrophilic and lipophilic parts both exist in the molecular structure of emulsifiers, which are surface-active amphiphilic molecules. During emulsification, emulsifiers prevented oil droplets from aggregation by forming the oil-water interface (Kralova & Sjöblom, 2009, McClements et al., 2005). The microcapsules-forming emulsions are formulated by mixing oil, solution of wall material and an emulsifier (Salviatrujillo et al., 2017). Essential oils tend to produce emulsions with small droplet sizes because of their low viscosity and interfacial tension. The addition of emulsifier with higher viscosity prior to homogenization could decrease the size of the oil droplets produced by increasing the disruptive shear stresses generated inside the homogenizer (Qian and Mcclements, 2011). The incorporation of those emulsions in the aqueous phase also alters their long-term stability by slowing down gravitational separation and droplet collisions. Oil-in-water (o/w) emulsifier were chose to prepare CS-CEOs microcapsules since the oil phase is used as core material. Emulsifiers can be divided into four categories depending on non-ionic, anionic, cationic and amphoteric ionic properties. Geng et al. (2016) reported that non-ionic additive could contribute to emulsifiability of emulsifier. Non-ionic additive could decrease the critical micelle concentration of emulsifier (Geng et al., 2016). Owing to the preferential adsorption of ions from the water phase, nonionic emulsifiers (eg. polyoxyethylene sorbitan esters of monoglycerides (Tweens); sorbitan monooleate (Span 80)) may cause a charge (Hsu and Nacu, 2003), and they are illustrated as the emulsification agents for stabilizing emulsions and are used as solubilization agents for food products as well as cosmetics (Martins et al., 2010). The effect of Tweens on the preparation of micro-emulsions to make oil in water emulsions was studied and it has been used in production of nano-emulsion (Salvia-Trujillo et al., 2013). Anionic emulsifiers such as sodium dodecyl benzene sulfonate (SDBS) has the effect of stabilizing emulsions. Nonionic surfactants and anionic emulsifiers are often mixed for usage.

Hydrophilic-lipophilic balance (HLB) is a widely used indicator of the relative affinity of an emulsifier for the water and oil phases, which describes the ratio of hydrophilic to lipophilic groups on a molecule. Emulsifiers with HLB numbers larger than 10 have a higher affinity for water (hydrophilic), whereas those with HLB numbers less than 10 have a higher relative affinity for oil (lipophilic) (Hasenhuettl and Hartel, 2008).

Several researches has done on the factors affecting the preparation of emulsion such as emulsifying time, emulsifying temperature, stirring speed and dosage of emulsifiers and nanostructures (Chatzidaki et al., 2016; Mandal et al., 2016; Kavita et al., 2016). But few studies has done on the effect of emulsifiers type on the embedding rate and particle size of microcapsules. The aim of this study was to prepare citrus essential oils loaded microcapsules based on chitosan (CS-CEOs) by emulsion-ionic gelation technique as a promising novel biological fresh-keeping material which is environmental-friendly and non-toxic. The effect of adding different emulsifiers (Tween 20, Tween 40, Tween 60, Span 80, Tween 20/Span 801:1, Tween 20/SDBS1:1) during the preparation on the characteristics of microcapsules was investigated as well. Among those emulsifiers, Tween 20, Tween 40 and Tween 60 are hydrophilic emulsifiers with different HLB, Span 80 is a lipophilic emulsifier, while Tween 20/Span 80 (HLB 10.5) and Tween 20/SDBS (HLB 7.5) are compounded emulsifiers of hydrophilic and lipophilic, respectively. The quality of microcapsules was evaluated by embedding rate, release rate, particle size and film forming property, etc. The molecular structure and thermal stability of CS-CEOs were also analyzed.

2. Material and methods

2.1. Materials

Chitosan (1.86 × 105 Da molecular weight, 95% deacetylation) was purchased from the Qingdao Yunzhou Biochemistry Co., LTD., China. Citrus essential oil was provided by Shanghai Florihana Co., LTD., China. Tween 20, Tween 40, Tween 60, Span 80, SDBS were purchased fromSigma-Aldrich (St. Louis, MO, USA). Acetic acid, TPP and other analytical grade chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., China.

2.2. Chemical composition of citrus essential oils (CEOs)

GC-MS (7890/5975, Agilent Technologies, Palo Alto, USA) was carried out to analyze the chemical composite of CEOs. The electron impact ionization mode mass spectrometer operated in was at a voltage of 70 eV. The mass scan range was 40−400 amu. The flow rate of the helium carrier gas on HP-5 column (30 m × 0.25 mm) was 1 mL/min. The chromatographic column is a fused silica capillary column HP-5 (30 m 0.25 mm). The analysis performed in the splitless mode and injector temperature was 250 °C. The column was held at 40 °C for 1 min, and then increased from 40 °C to 220 °C at 3 °C/min, held at 220 °C for 25 min, and finally increased to 280 °C at a rate of 20 °C/min, then held for 3 min. The identification of the individual compounds was based on the comparison of their relative retention times with those of authentic samples on the capillary column and by matching their mass spectra of peaks with available Wiley and NIST. The relative content of each component was calculated by area normalization method.

2.3. Preparation and rheological properties of the microcapsule-forming solutions (MFS)

The microcapsule-forming solutions (MFS) were prepared by the emulsion-ionic gelation technique. CS (1%, w/v) was dissolved in an acetic acid (1% (v/v)) for 4 h under magnetic stirring. An emulsifier (Tween 20, Tween 40, Tween 60, Span 80, Tween 20/Span 80, SDBS/Span 80 (0.5% v/v)) was then added drop wise to the CS solution with constant stirring for 2 h to obtain a homogeneous solution. The CEOs (0.1%) were subsequently added into the CS solution by homogenizing (2000 rad/s) for 10 min to obtain the emulsion. Encapsulated microcapsules were not added with CEOs. Sodium tripolyphosphate (TPP, 3 mg.ml-1 (w/v)) was gradually dropped into the above emulsion with agitating and then the mixture were homogenizd at 2000 rad/s for 10 min. The MFS was obtained after stirring 24 h under 20 °C. The control group was prepared using the same method with the emulsifier not added. The rheological properties of the MFS was valued by the method of Chunhua Wu et al. (2016).

2.4. Preparation of CS-CEOs microcapsules and assay of CEOs embedding rate

The microcapsule-forming solutions were centrifugating at 7155 g for 20 min at 4 °C and vacuum freezing dried with a freeze dryer (Labconco, Beijing Light Ace HK Limited, China) for 2 days to obtain CS-CEOs microcapsules. Those microcapsules were designated as T20, T40, T60, S80, T20/S80, SDBS/S80, respectively. The microcapsules were stored in a desiccator before further use.

Ɒ-limonene is one of the main components in the CEOs, thus the

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