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Formation, characterization and release behavior of citrus oil-polymer microparticles using particles from gas saturated solutions (PGSS) process

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ABSTRACT

Citrus oil was encapsulated in polyethylene glycol (PEG) using the particles from gas saturated solutions (PGSS) technique. The impact of process conditions, i.e., pressure, temperature, and citrus oil/PEG mixing ratio on the characteristics of formed microparticles has been investigated. The particles with sizes of 190.56–373.32 μm and different shapes were obtained. The efficiency of encapsulation ranged between 43.95% and 83.87%. The oxidative stability and *in vitro* release was significantly changed depending on storage temperature and pH of the incubation medium, respectively, and the oxidative stability was significantly improved by encapsulation using PGSS process.

Introduction

The citrus oils have been used in many applications including food, cosmetics, perfumery, and pharmaceuticals industries, and in agriculture for the preparation of insecticides, painting, and adhesives, as well as textiles and plastics industries [1]. Recently, the use of essential oils from citrus by-products has been increased due to their biological activity since they contain a wide range of bioactive compounds. Especially, the application of the citrus oils as a natural antioxidant and antimicrobial agents has been demonstrated [2–4]. The advances in new applications of citrus oils are bolstered by the fact that the public is increasingly getting concerned about the use of industrial manufactured chemicals as additives in foods and other applications.

Citrus oils can be easily degraded when they are subjected to moderate or high temperatures, the action of oxygen, and light due to their volatile compounds and other non-stable components; hence if they are added to food and/or in other formulation, they can be easily degraded and/or oxidized. In addition, to achieve an efficient bioactivity of the oil or another plant extract, a strict and exact dosing is required [5]. The use of essential oils is difficult due to their insolubility in water, which as a result limits their bioactivity, bioavailability, and their application in food or in other formulations [6]. Therefore, there is a need for the encapsulation of the citrus oils not only to protect those non-stable and volatile bioactive compounds of citrus oils but also to improve their bioavailability and applicability.

Solid forms (micro-composites or microcapsules), semi-liquid forms (liposomes, gels, etc.) and liquid forms (liquid solutions, micelles emulsions, etc.) are among the possible formulations that have been used [7]. Various conventional methods for producing such formulations have been studied, which include coacervation, spray-drying, emulsion techniques, and the use of foam mediums [8]. However, those conventional methods have presented many disadvantages. The disadvantages of those conventional methods include the use of hazardous organic solvents, severe operation conditions and multiple purification steps [9]. Moreover, those methods can cause the thermal or mechanical degradation of the product, poor control of the particle size and morphology, lack of brittleness of some polymers and low encapsulation efficiency [10].

The formation of polymer composites and encapsulation of active ingredients using the supercritical carbon dioxide (SC-CO_2) has shown to be an alternative to those conventional techniques due to its eco-friendliness, operates at mild operational conditions and the ability to get solvent-free and homogenous products. Particularly, the use of the particle from gas saturated solutions (PGSS) process has effectively been used for encapsulating liquid ingredients and other active materials using polymers as wall material. The PGSS

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process involves two major steps: (1) The SC-CO_2 saturation of a mixture (polymer + active material to be encapsulated). (2) The gas-saturated solution expands into an expansion chamber at room pressure via a nozzle. After the expansion of the mixture into a spray chamber, the temperature of the mixture diminishes significantly due to the Joule-Thomson effect, thus causing the polymer solidification [11]. In addition, PGSS has been successfully used to obtain composites or encapsulates, in order to ameliorate the preservation of product and to control the rate of dissolution of some active compounds and their delivery system [12]. So, due to all of those advantages of PGSS process coupled with the desperate need for protecting the unstable and volatile bioactive compounds of citrus oils as well as enhancing their bioavailability and applicability, this work was designed.

The objective of this work was to extract and encapsulate the citrus oil in polyethylene glycol (PEG) by the PGSS technique. To study the influence of PGSS process conditions including the pre-expansion conditions (pressure and temperature) and the citrus oil-to-PEG mixing ratio on the characteristics of formed micro-particles. Moreover, the oxidative stability and release behavior of encapsulated citrus oil were examined.

Materials and methodology

Chemicals

PEG (molecular weight: 8000 g mol^{-1}) was obtained from Yakuri Pure Chemicals Co., Ltd. (Kyoto, Japan). Carbon dioxide (99.99%) was obtained from KOSEM Company (Busan, South Korea). Hexane was bought from SK Chemicals (Busan, South Korea). All the reagents and chemicals were of analytical grade.

Plant material and sample preparation

The citrus fruits (*Citrus junos*), Common name: Yuzu, Origin: Namhae-gu, Gyeongsangnam-do province, South Korea, Season: November–January (2017) were used. The fruits were washed, peeled off and the peels and seeds were collected separately. The citrus peels (CP) were freeze-dried (−50 °C for 4 days) while the citrus seeds (CS) were oven dried at 103 °C and then crushed, sieved (with 710 μm metal sieve) to get powder for extraction.

Oil extraction

The extraction setup and procedure were the same as those reported in our previous works [13,14]. The SC-CO_2 extraction conditions were the pressure of 20 MPa, the temperature of 45 °C, and flow rate of 35 g min^{-1}. The extraction time was 2 h and the samples were CP, CS, and a mixture (MX) of CP and CS (mixing ratio was 6:4, for peels and seeds, respectively). This mixing ratio (6:4) was chosen based on our preliminary experiments since it was shown that the optimum mixing ratio (CP to CS ratio) which can give the higher level of the bioactive compounds and bioactivity is 6:4, for peels and seeds, respectively.

Encapsulation process

The encapsulation of citrus oil was performed using the PGSS apparatus shown in Fig. 1. Experiments were carried out at the pressure of 20–40 MPa, temperature of 40 °C and 50 °C and mixing ratio (citrus oil-to-PEG ratio) of 0.2–0.4 g oil g^{-1} PEG (Table 1). The MX oil was chosen to be used in this process due to its high bioactive compounds and bioactivities compared with CP oil and CS oil as was demonstrated by our preliminary experiments. The PGSS process started by pumping the CO_2 from the cylinder into the reactor (carrying the mixture of PEG-8000 + citrus oil (MX oil)) until the required pressure was attained. The size of the nozzle was 300 μm and the mixture was stirred at 400 rpm. After 1 h of reaction, the depressurization was done by suddenly opening the needle valve and the particles were collected in the precipitation chamber which was kept at room temperature and pressure.

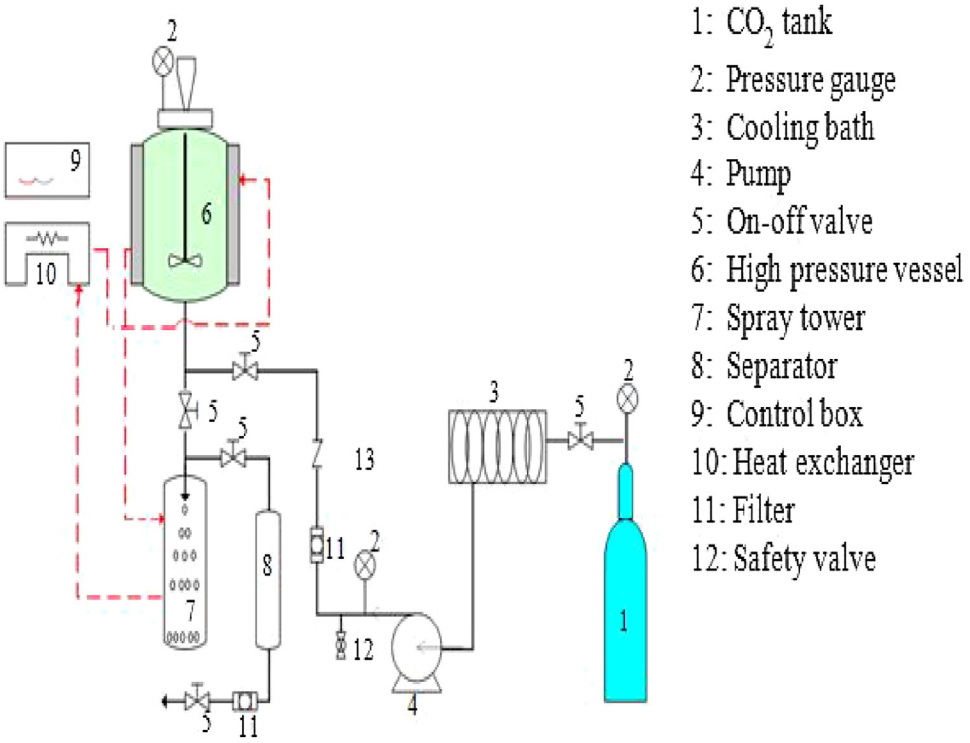

Fig. 1. Schematic diagram of PGSS process used for encapsulation of citrus oils.

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