MORPHOLOGICAL CHARACTERIZATION OF MICROENCAPSULATED GERANIOL OIL

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Abstract. Geraniol oil is one of the essential oils, which can act as an insect repellent, natural pesticides and antimicrobial. It also exhibits a good chemopreventive action, that could represent a new class of cancer treatment agents which opening up new avenues for research. One of the concerns of the Geraniol essential oils is that the essential oils are very volatile. Due to this problem, the current study investigated the formation of microencapsulated Geraniol oil powder to protect them against degradation and evaporation, so that their stabilities are enhanced. In the study, both natural sources of gum Arabic and sodium alginate were used as a wall material to prepare Geraniol oil microcapsules using the spray drying technique since the technique is relatively simple and continuous. The microcapsules were prepared at three different amounts of Geraniol oil which were 0.9 ml, 2.7 ml and 1.8 ml, respectively. From the analysis, the diameter of microcapsules varied which were in the range of 1 to 24.636 µm. Microcapsules produced by 1.8 ml and 2.7 ml concentrations exhibited single discrete particles, whereas microcapsules produced by 0.9 ml had cluster particles. The feasibility to form microcapsules from Geraniol essential oils may offer a potential for further development of the textiles mosquito repellent.

Keywords: Geraniol essential oil, microencapsulation, spray dry, SEM

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Introduction

Essential oils (EOs) and their components are natural compounds obtained from diverse parts of medicinal, culinary, and herbal plants [1]. Due to its pleasant scent, it can be employed as a soothing and pleasant fragrance. EOs are plant secondary metabolic products with strong aromatic components that give them their distinct odour, flavour or fragrance [2]. Some scientific explanations of EOs are also responsible for bettering health [3]. According to a previous study, the presence of phenol and aliphatic components in EOs gives them a strong aroma and flavour [1]. The most efficient component and terpene were discovered to be Geraniol [4]. Geraniol is one kind of derivative compound in EOs. It is plentiful and found in a wide variety of plants, such as Pelargonium Graveolens as shown in Figure 1 [5]. It had been confirmedly registered with the Environmental Protection Agency (EPA) and has been labeled for use on ornamentals and nursery stock [6]. Geraniol is mostly used as a mosquito repellent directly on skin and clothing, which indicates that these compounds are safe among other EOs. In scents, Geraniol has a rose-like odour and a sweet floral rose-like flavour with fruity and waxy undertones [4]. Geraniol ($C_{10}H_{18}O$) is acyclic monoterpene alcohol with the chemical formula 3,7-dimethylocta-trans-2,6-dien-1-ol as shown in Figure 2(a) [4]. The substance is known as 'Geraniol' as it is a mixture of the two cis-trans isomers geraniol (trans) and nerol (cis) as shown in Figure 2(b) [4].

Figure 1: Pelargonium Graveolens is an aromatic plant from Egypt that is composed of three main components including citronellal, citronellol and geraniol [7]

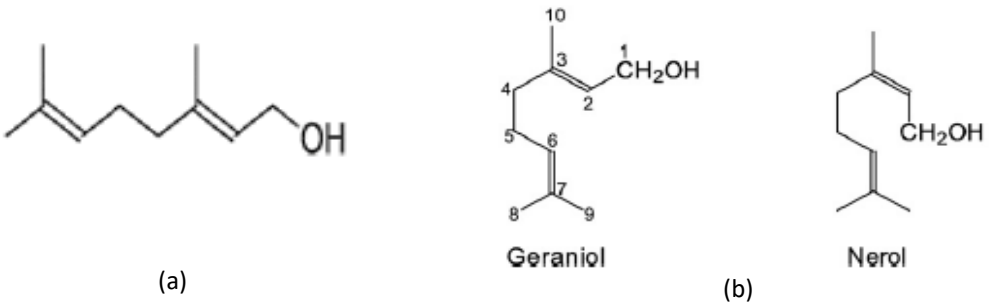


Figure 2: (a) Geraniol oil compound [8] and (b) Chemical compound structures of Geraniol and Nerol [4].

Geraniol is known to act as a mosquito repellent [9], growth inhibitor, and pesticide on food crops [10]. Its properties, such as antibacterial, antioxidant, and anti-inflammatory qualities as well as its low toxicity have been inconclusively proven by previous research [11]. Many researchers have agreed that Geraniol is effective even at low concentrations [10]. As attested by a previous study, at a concentration of 10 %, Geraniol, which is found in fragrant antibacterial perfumes, has the strongest antibacterial activity, almost as strong as Dettol [8]. Nevertheless, plant EOs, on the other hand, are severely limited in terms of their development and use. This is due to their unstable nature, ease of decomposition, and volatilization [12]. Even though Geraniol oils have many sides of specialties, it is still a type of EOs that is commonly unstable and easily volatile. Thus, the current study adapted the microencapsulation technology based on many previous investigations of Geraniol oil.

Microencapsulation is a technique for changing the physical properties of a volatile chemical to make it more manageable and protect it from a variety of external variables, such as sunlight, evaporation, humidity, alkalinity or undesired rubbing action [13]. Microencapsulation may efficiently manage the release rate of aroma compounds and EOs as needed due to its ability to ensure the life span of volatile substances [14]. This is the critical role of the technique.

Spray drying, the physical microencapsulation method, is by far the most popular method for microencapsulating EOs or volatile compounds [15]. In addition, spray drying has a low operational cost since it is 30 to 50 times less expensive than freeze drying [16]. The process entails no more than a few easy steps. Spray drying was also used in this work to create a microencapsulated Geraniol oil. Spray drying of phenolic compounds has been shown to be an excellent approach for drying and microencapsulation [17].

In addition, biodegradable compounds, such as gum Arabic and sodium alginate can be used in spray drying. A water-soluble natural polymer, such as gum Arabic with the presence of 2 % proteins provides a good emulsification property [16]. Other studies have shown that polysaccharides, such as sodium alginate, can also be used as emulsion thickeners, which gives a better encapsulation quality [18]. Several essential parameters, including the kind of wall material, the concentration of microcapsule components and spray drying conditions, have been shown to affect the microencapsulation efficiency of EOs in prior studies [16]. As a result, we investigated the effect of wall material composition, including mixed emulsifiers, on the creation and stability of Geraniol oil microcapsules.

The objectives of this work were to investigate the effects of different formulations of microencapsulated Geraniol oil on the morphological structures and to identify an optimal formulation of microencapsulated Geraniol oil based on uniform microcapsules, using gum Arabic and sodium alginate as wall materials. In order to achieve more effective encapsulation and greater stability, mixing gum Arabic with sodium alginate is an alternative technique for encapsulating EOs. Initially, the Geraniol oil and wall materials were converted into slurry by homogenization, and afterwards, these slurries were converted into a spray dry. The impact of the three formulations on the microencapsulated Geraniol oil morphological structure was investigated in this study.

Materials and Methods

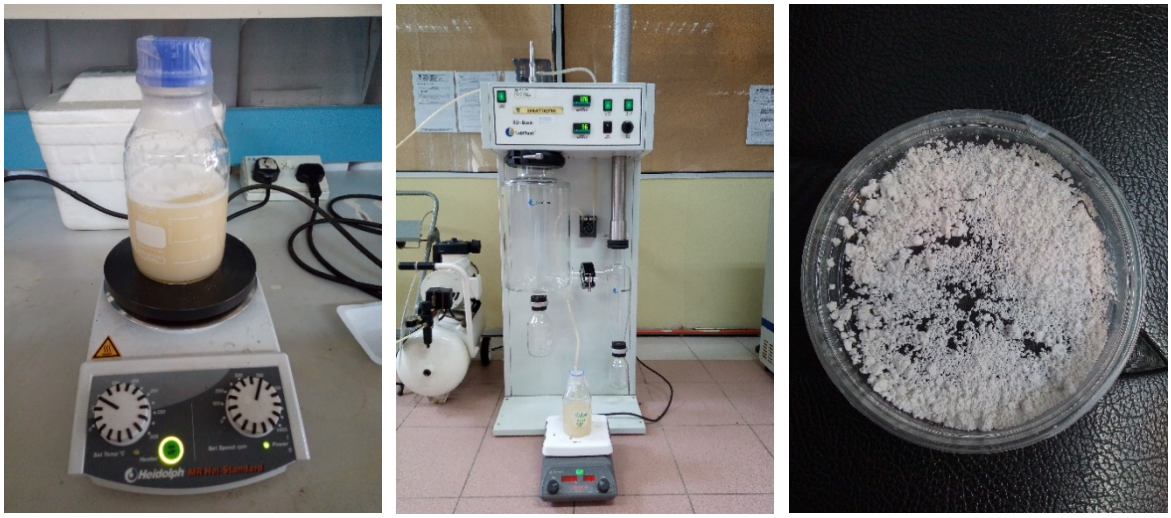
Geraniol (Pelargonium graveolens) EO, which was 100 % pure and certified organic was purchased from US Organic, (New Jersey, USA). Gum Arabic from acacia tree was purchased from Sigma-Aldrich Company (St. Louis, MO, USA), while sodium alginate was purchased from R&M Chemicals (R & M Marketing, Essex, UK). Formaldehyde solution with a minimum consumption of 37 % was purchased from Merck KGaA, Darmstadt, Germany.

Preparation of Slurry

Geraniol oil microcapsules were prepared by a two-step procedure consisting of emulsification and spray drying. 0.9 ml, 1.8 ml, and 2.7 ml were the amount of Geraniol essential oil used in the study. Those amounts were reported to exhibit the optimal amount of Geraniol essential oil formulation [19]. Briefly, 100 g of gum Arabic was prepared into 1 L total solution of distilled water for 15 min at 100 °C on magnetic stirrer hot plate with a speed at 1000 rpm to completely saturate the polymer molecules. It was followed by a mechanical mixing 10 g of sodium alginate, of which the speed was reduced to 750 rpm at 40 °C. Then, 0.9 ml Geraniol EO was added into the slurry for 40 minutes. Finally, 15 ml of formaldehyde was added into the slurry for 5 minutes and the magnetic stirrer was turned off. Similar steps were repeated for Geraniol oil formulation at 1.8 ml and 2.7 ml (Figure 3(a)).

Preparation of Microcapsules

The obtained slurry was introduced into a drying chamber of spray dryer (SD Basic model, Lab Plant, UK) with a voltage at 230 V, equipped with a fluid nozzle of 1.2 mm diameter as shown in Figure 3(b). The compressed air flow rate was 40 ml/m, feed flow rate 6.6 ml/min, pressure 45 mbar, inlet air temperature at 150 °C, and exhaust air temperature 86 °C. Prepared powders were collected in a petri dish and wrapped with parafilm to avoid volatilities as shown in Figure 3(c).



(a) (b) (c)

Figure 3: (a) Preparation of slurry, (b) Spray drying process set up and (c) Microcapsules powder

Scanning Electron Microscopy (SEM) Analysis

SEM (JSM-IT510, Japan) was used to observe the morphology of the microcapsules. The dried microcapsules were placed on the SEM stubs using a two-sided adhesive tape (Polaron, SC 7620) and then sputter coated with gold. The morphology of the microcapsules was observed at an accelerating voltage of 10 kV

Fourier Transform Infrared (FTIR) Analysis

All the Geraniol essential oil slurries were subjected to FTIR analysis (Jasco 4100, Tokyo, Japan). These samples were scanned from 400 to 4000 cm^{-1} using ATR technique.

Results and Discussion

Micrographs of the microcapsules are shown in Figure 4. In all formulations, the microcapsules existed as single discrete particles, indicating that the amount of Geraniol oil on the microcapsules' surfaces was rather low. The scattered microcapsules powder appeared with some spherical forms and the rest with concavities or a 'flat ball' effect. It is believed that the spray drying technique was able to produce a smooth surface spherical shape microcapsule as shown in Figure 4(a) to (f) only with an optimal pressure induced. The possible reason why the surface of the microcapsule became dents (as shown in all images in Figure 4) is because it was affected by high temperature pressured air in the spray drying system. A similar finding was also reported by a previous study [20]. In fact, wrinkled microcapsules created during the film formation process at the early stages of drying the atomized oil-in-water emulsions resulted from the flaws in the wrinkled microcapsules [20]. This occurrence may obstruct the ability of microcapsules to flow freely, yet it is unavoidable because these creases are the typical morphology of microcapsules produced by the spray-drying procedure [16].

The outside surfaces of the particles had no obvious holes or fractures. There were no damaged microcapsules, which is a favourable indicator of the microencapsulation efficacy of the spray drying procedure for microcapsules [20]. It has also been linked to wall materials with a high glucose content [20], which in this case, it was subjected to gum Arabic. According to SEM micrographs, the outside topography or morphology of the microcapsules was altered by the blend of the biopolymer wall material. The combination of EOs and microcapsules allows the EOs to last long, while maintaining the presence of their chemical constituent. Gum Arabic as the main wall material for microcapsules formation in this study, on the other hand, was shown to have no significant effect on the chemical composition of the spray-dried microcapsules [16]. In the current study, the addition of gum Arabic did not affect the chemical compositions of Geraniol essential oil microcapsules. From the FTIR analysis shown in Figures 5(a) to (c), the Geraniol essential oil microcapsules at 0.9 ml, 1.8 ml and 2.7 ml exhibit similar IR peaks. The IR peaks of 3295.77, 3282.43 and 3288.30 from 0.9 ml, 1.8 ml and 2.7 ml, respectively, indicate the O-H stretching of hydroxyl. Meanwhile, the IR peaks of 2159.34, 22102.63 and 2123.4 represent the C-C stretching for alkynes. The IR peaks of 1636.98, 1636.72, and 1636.42 indicate the CC stretching C=O. The peaks of C-H bending emerged at 1419.55, 1420.68, and 1419.09, respectively. The IR peaks of 1027.97, 1028.70 and 1029.10 represent the C-N stretching for amine.

The 0.9 ml formulation of microencapsulated Geraniol oil in Figure 4(a) to (c) appeared to form cluster particles. As stated in a previous study, to allow a rapid creation of a semipermeable membrane on the droplet surface, a high inlet air temperature should be employed, but not to the point of causing heat damage to the dry product or surface disturbance. Such condition is caused by an excessive bubble growth that increases the amount of water loss during drying or causes the particles to stick together. They become sticky and are quite difficult to remove when agglomerated [10]. When the intake air temperature is low, the low rate of evaporation results in the development of microcapsules with high-density membranes that flow poorly and quickly agglomerate. Sodium alginate as a wall material contributes to microcapsule homogeneity. Another study found that microcapsules appeared denser after sodium alginate was added, which formed cluster particles and should slow down the volatilization of Geraniol oil [18]. Apparently, there are two types of shapes occurred. Based on this microscopy view, dented shapes microcapsules are more dominant rather than spherical shapes. The diameter range of Geraniol oil the microcapsules for 0.9 ml concentration from 2.2127 to 14.857 μm.

The morphology of microcapsules at 1.8 ml Geraniol oil formulation, as shown as Figure 4 (d), (e) and (f), resulted in particles with irregular sizes. Similar results were observed at 0.9 ml Geraniol oil formulation in terms of microcapsules shapes. However, a slightly different morphology was discovered when the scattered particles were not too crowded as occurred in the 0.9 ml formulation. At the 1.8 ml formulation, the slurry contains a higher amount of Geraniol essential oil, allowing the slurry to evaporate faster than the slurry at the 0.9 ml formulation. As a result, the resultant microcapsules were scattered and less dense. In addition, the appearance of some smooth surface spherical shapes microcapsules could be clearly seen. The diameter range for 1.8 ml concentration of microencapsulated Geraniol oil is from 1.683 to 24.636 μm.

Despite the fact that the particles were likely smaller, a higher number of microcapsules were identified as compared to the previous two formulations. 2.7 ml of Geraniol oil formulation as in Figure 4(g), (h) and (i) only produced dented microcapsules, not spherical microcapsules, as in the previous two formulations. It should be noted that the mechanisms involved in the concentration of Geraniol essential oil in the slurry. At a higher amount of the Geraniol essential oil, the slurry tends to evaporate faster during spray drying, causing the microcapsules to shrink and dent [10]. The diameter range of the microcapsules is approximately 1.592 to 19.236 μm.

A microscopy diagram of 2.7 ml Geraniol oil formulation as in Figure 6 shows a split microcapsule, which contains several numbers of tiny microcapsules inside it. This is most interesting in the case of microcapsules because a population of smaller particles may penetrate into the crevices between larger particles, and they take up less space [15]. It can be described that the wall material is quite thin and shares similar characteristic to egg shells, which is easily fractured.

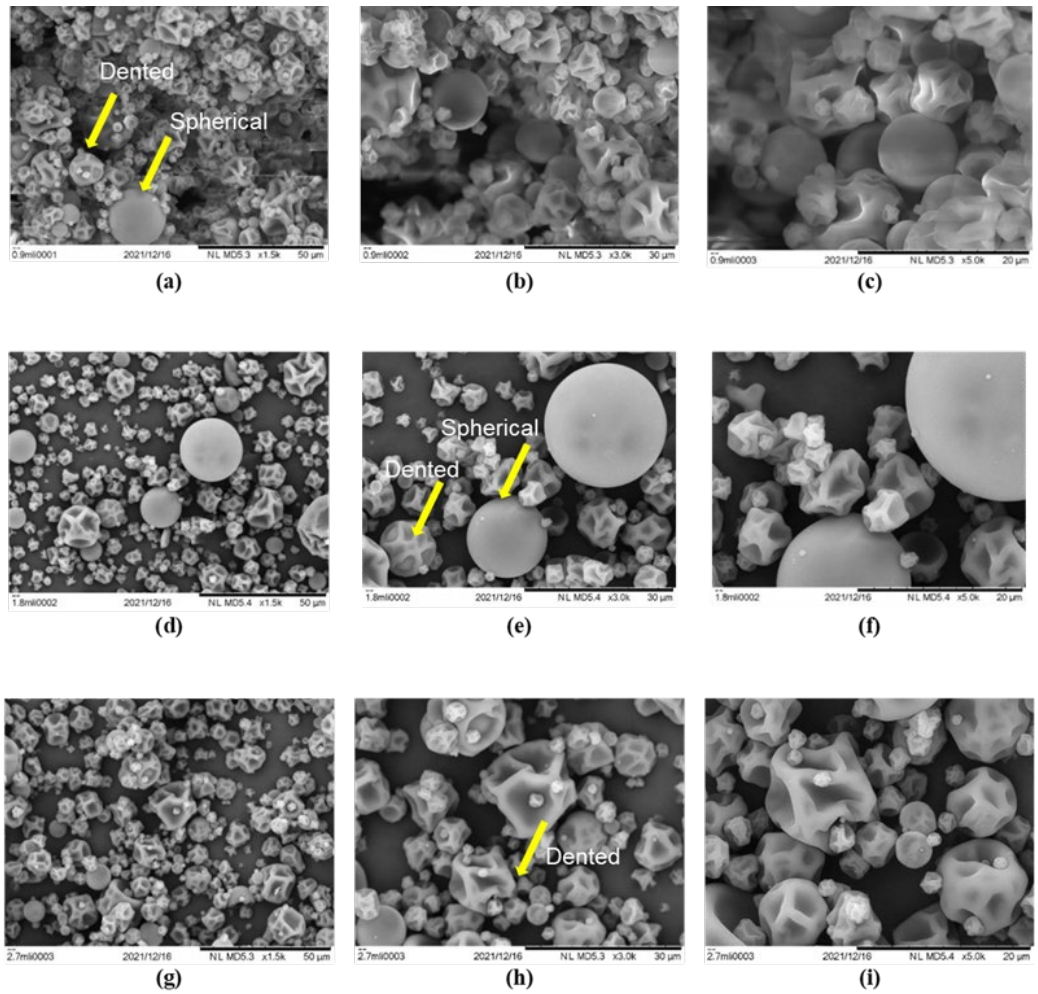


Figure 4: SEM micrographs of Geraniol oil microcapsules prepared at concentration of (a) to (c) 0.9 ml, (d) to (f) 1.8ml and (g) to (i) 2.7 ml, respectively

Microcapsules tend to form agglomerates, which are also relatively common in powders produced by spray drying. Microcapsules, which appeared with hole as shown in Figure 6, resulting in a Geraniol leak. Some distribution of Geraniol oil, which had a spherical shape and a smoother surface and was apparently not fissured or cracked, is important to provide lower oil permeability and to increase oil retention. The holes were observed inside the wall compartment of the microcapsules, suggesting that some Geraniol oil was also deposited into the membrane after the oil passed through the high-temperature spray-drying apparatus [16]. Irregular surfaces that were fragmented on microcapsules may interfere in the cell wall synthesis, directly or indirectly.

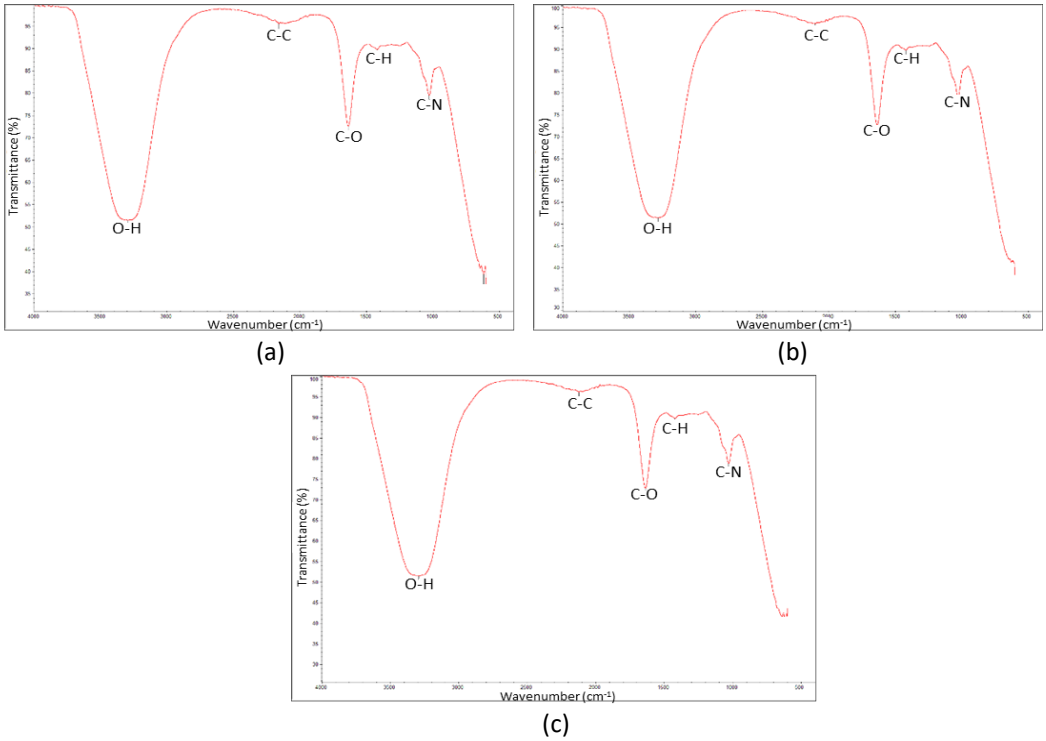


Figure 5: IR spectra of (a) 0.9 ml, (b) 1.8 ml and (c) 2.7 ml Geraniol essential oil slurry

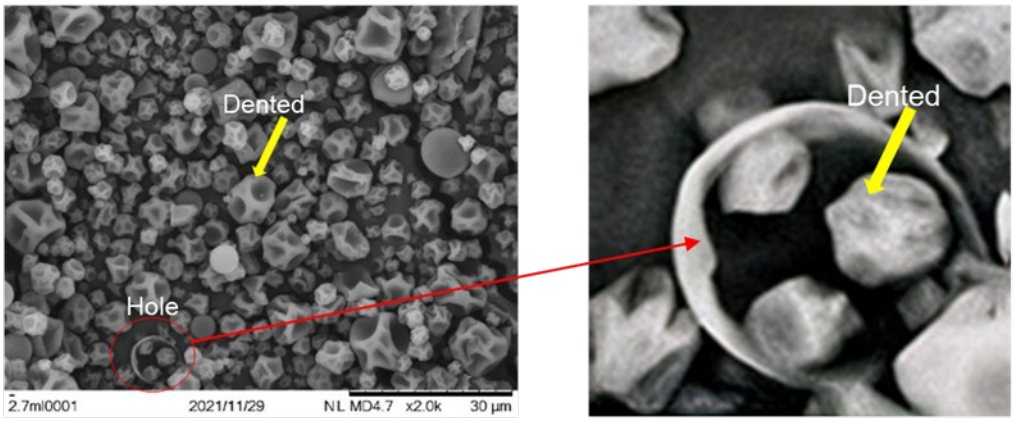


Figure 6: Scanning electron microscopy (SEM) micrographs of split microcapsules at 2.7 ml formulation

Some of the microcapsules presented had smooth surfaces, but most of the capsules had dented surfaces. The depressions created in some surfaces can be related to the contraction and collapse of droplets during the drying and solidification stages [21]. Overall, the 2.7 ml was the best among other concentrations (0.9 ml and 1.8 ml), producing uniform dent shapes of the microcapsules.

Conclusions

The formation and characterization of microencapsulated Geraniol oil on the morphological structures were investigated in this study and the results were achieved. In the present study, three different concentrations were used, which were 0.9 ml, 1.8 ml and 2.7 ml, respectively. The result shows that the Geraniol oil concentration did affect the morphological structures of microcapsules since they varied in diameter, which were in the range of 1 to 24.636 μm. Microcapsules produced by 1.8 ml and 2.7 ml concentrations exhibited single discrete particles with various particle sizes. However, microcapsules produced by 1.8 ml presented some smooth surfaces spherical morphologies compared to microcapsules produced by 2.7 ml, which dominantly appeared as dents. On the other hand, microcapsules produced by 0.9 ml had cluster particles, were believed to be affected by the stickiness properties of sodium alginate, low solution concentration, and high solution surface tension. From these findings, the study shows that the optimal concentration for microencapsulated Geraniol oil is 2.7 ml due to the existence of a smooth surface morphology with tiny range sizes of microcapsules. Thus, the 2.7 ml formulation microencapsulated Geraniol oil is recommended for future studies, particularly, in the development of mosquitoes repellent for textile clothing.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work

Disclosure of Conflict of Interest

The authors have no disclosures to declare

Compliance with Ethical Standards

The work does not require any ethical procedures.

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