Release of encapsulated citronella oil in Tween 80 solution

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Abstract. Microencapsulation is a technique in which small particles are enclosed by a coating wall. Microencapsulation has been widely used in applications such as the controllable release of essential oils and improvement of the stability of the core substances and many other fields. Volatiles liquids and solids are easily damaged during long term use, due to their external environment. This leads to degradation and loss of function. In preventing this drawback, encapsulation of essential oils by embedding them into polymer wall has been introduced. In this study, citronella oil (CO) encapsulated by gelatin-chitosan was prepared by complex coacervation technique. Report on release study of encapsulated CO and its applications in floor cleaning solution is very limited. Hence, release rate and release mechanism of the microcapsules in simulated floor cleaning solution (Tween 80 solution) were investigated. Morphology of the microcapsules was determined through optical microscope. The release of CO was observed through the formation of rupture on the spherical microcapsule. The release rate of encapsulated CO increases with the increase of temperature from 25°C to 75°C. The release mechanism of the CO, based on Fick’s law was classified as following the Korsmeyer-Peppas controlled release model of super case II, whereby the release is due to wall erosion.

1. Introduction
Citronella oil (CO) is from Cymbopogon genus plant family. CO is a volatile compound and has been widely used in fragrances and personal care products. The antiseptic property of CO has promoted its application in soaps, household cleaners, and detergents [1]. Most of the essential oils are volatile, therefore encapsulation should be introduced to control release of the evaporation [2]. Encapsulation is a process of enclosing solids, liquid or gaseous materials in small closed capsule which can release their core materials at a controlled rate under particular conditions. This technique depends on the physical and chemical properties of the material to be encapsulated. The most crucial part in encapsulation is to stop the deterioration of the core materials during the encapsulation process, hence choice of microencapsulation method is very important [3–6]. Among the microencapsulation techniques, complex coacervation is suitable in encapsulating high value active molecules and unstable substances such as polyphenols which are the major constituents in CO [7]. Complex coacervation is about neutralization of two oppositely charged wall materials (polymers) in aqueous solution. Concentration of the wall material and pH of the aqueous solution are the most essential characteristics in the process. Moreover, cross-linking agent such as formaldehyde or glutaraldehyde is commonly used to harden the wall material [8]. Basically, the complex coacervation process...
consists of three steps: i) formation of emulsion, ii) formation of coating, and iii) stabilization of the coating [9]. The most favorable coating material is a combination of gelatin-arabic gum [10–12]. However, recently gelatin-chitosan has been considered because of its excellent thermal stability [13–15]. Release rate of the core material to the surrounding medium is related to the diffusion mechanism. The wall material characteristics such as thickness and composition; the properties of the core material; and the surrounding medium; determine the diffusion mechanism [8,16]. Release behavior of the core material can be determined by Fick’s law of diffusion using Korsmeyer-Peppas controlled release model:

\[ \frac{M_t}{M_\infty} = k t^n \]  

where \( t \), a time of fractional release; \( k \), a release rate constant; \( n \), a characteristic of release mechanism; \( M_t \), the amount of release at specified time; and \( M_\infty \), the amount of release at infinity time [16,17].

2. Experimental

2.1 Materials

Gelatin-B (type B, 260 bloom, from bovine) was supplied by a local company (Halagel Sdn. Bhd., Malaysia). Citronella oil, Java (85/35%) was purchased from Sigma-Aldrich, United States. Glutaraldehyde (50% aqueous solution) and chitosan (medium molecular weight) were obtained from R&M Chemicals, Malaysia. Tween 80 was bought from Systrem, Malaysia.

2.2 Microencapsulation of CO by Complex Coacervation

In preparing chitosan-gelatin solution, 0.1 g chitosan was dissolved in 100 mL of 1% acetic acid at room temperature producing chitosan solution. On the other hand, 3.5 g Gelatin-B (dissolved in 350 mL of deionized water) was mixed with 3.6 g CO and conditioned at 500 rpm, 50°C for 30 min. The mixture was then blended with the prepared chitosan solution before further conditioned at 500 rpm, 50°C and pH 5 for 30 min. The mixture was then diluted with 350 mL deionized water prior to addition of 2 mL of 25% glutaraldehyde and conditioning at 200 rpm with temperature below 10°C for 60 min. Finally, the mixture was settled down for 24 hours before filtration for harvesting the encapsulated CO (ECO).

2.3 Characterization of ECO

The shape and morphology of ECO were determined by using an optical microscope (RZ-5, Meiji Techno, Japan). Confirmation on the release of CO can be seen under optical microscope through the ruptured capsule wall.

2.4 Release rate of CO

Effect of ECO concentration in simulate clean floor solution was investigated by mixing 3 different weights of ECO 0.5, 1.0 and 1.5 g with 100 mL of simulated floor cleaning solution (0.3 wt% Tween 80 solution) and kept in separate closed containers for 30 days at room temperature, which simulated the clean floor storage condition. Effect of temperature on all of the mixtures was observed by exposing the samples at different temperatures 25°C, 50°C and 75°C. A 5 mL of each sample was collected at specified time with 5-day intervals and filtered to remove the ECO. The filtrate was collected for release rate study using UV-Vis spectrometer. The release rate was calculated as equation (2):

\[ \text{Release Rate (\%)} = \frac{C_t}{C_{\text{max}}} \times (100\%) \]  

(2)
where $C_t$ is the concentration CO at the specified time and $C_{\text{max}}$ is the concentration of CO when the capsule is 100% ruptured.

### 2.5 Release rate behavior
Release rate behavior of the CO was analyzed using Fick’s law of diffusion. A plot of log (fractional release, $M_t/M_\infty$) versus log (release time, $t$), as in equation (3) was developed from Korsmeyer-Peppas controlled release model as to determine the release kinetics. Release behavior of the CO can be determined from the $n$ value of the plot.

\[
\log \left( \frac{M_t}{M_\infty} \right) = n \log t + \log k \quad (3)
\]

In determining the $M_t$ and $M_\infty$, mixture of 0.5 g of ECO per 100 mL of simulated clean floor solution was kept into 6 separate closed containers at 25°C. For $M_t$, 2 mL of sample mixture was taken out at 30, 60, 90, 120, 180, 240 and 300 minutes. For $M_\infty$, the sample mixture was taken out at 1440 min (24 hours). The collected samples were filtered and the filtrates were scanned in the range 200 - 400 nm by using UV-Visible spectrometer, Perkin Elmer, Lambda 750.

### 3. Results and discussion
#### 3.1 Release rate of CO
Figure 1 shows the effect of temperatures on the release rate of CO in simulated floor cleaning solution at different concentrations of ECO. The increase of temperatures from 25°C to 50°C and 75°C has increased the release rate of CO, which was applicable for all concentrations of ECO this study. The increase of temperature resulted in increase of the diffusion activation energy which led to higher release rate of CO. Similar finding was observed by Hsieh et al. [14] where chitosan encapsulated citronella oil was placed in an Infrared Moisture Determination Balance. The release rate increased drastically in a linear pattern within the first 10 days and reached equilibrium from day 11 onwards. In the first 10 days, the release rate was due to the rapid release (burst release) discharge of CO from the surface matrix of wall film as explained by Xu et al. [18]. The burst release was due to high CO content on the surface of ECO. Furthermore, from day 11 onwards, CO migrated from the deep matrix of wall film to the surface leading to a lower release rate until the equilibrium level was achieved. Figure 2 shows the effect of different concentrations of ECO towards the release rate of CO in the simulated clean floor solution. The results revealed that the release rate of CO for all temperatures in this study was not very much affected by the concentration of ECO in the solution. These findings are in agreement with Gautam et al. [19] where the release rate of core material is very much influenced by several factors such as stirring rate, temperature, viscosity, pH and composition of the solution medium.
Figure 1. The effect of temperatures on the release rate of CO in simulated floor cleaning solution at different concentrations of ECO; (a) 0.5 g ECO, (b) 1.0 g ECO and (c) 1.5 g ECO.
Figure 2. The effect of ECO concentrations on the release rate of CO in simulated floor cleaning solution at different temperatures; (a) 25°C, (b) 50°C and (c) 75°C.
3.2 Release behavior of microcapsules

Figure 3 shows the Korsmeyer-Peppas controlled release model for ECO in simulated floor cleaning solution. The high $R^2$ value indicates that the release mechanism of ECO is fitted well with Korsmeyer-Peppas controlled release model. The value of $k$ (release rate constant) is $-2.778 \text{ k(min}^{-1}\text{)}$ and $n$ is 0.9476. The $n$ value which is larger than 0.85, indicates that the release mechanism is according to super case II. Super case II (relaxation) reveals that acceleration of the encapsulation release is due to stresses and swelling of capsule wall in the solution media which lead to erosion [19,20]. This finding is further confirmed by the morphology of the ECO.

![Graph showing the Korsmeyer-Peppas controlled release model for ECO in simulated floor cleaning solution.](image)

**Figure 3.** Korsmeyer-Peppas controlled release model for ECO in simulated floor cleaning solution.

3.3 Morphology of encapsulated citronella oil

Figure 4 shows the ECO in simulated floor cleaning solution under optical microscope. The morphology shows that the CO capsules were in spherical shape with irregular size. Evidence of wall ruptures can be observed on the ECO on day 1 and became worse on day 4. On day 6, 12 and 14, some of the ECO were completely ruptured and distorted. The observation confirmed the above finding on the release rate of CO towards exposure time in floor cleaning solution. Consequently, this finding is in agreement with the Korsmeyer-Peppas controlled release model of super case II prediction, whereby the release is due to wall erosion.
4. Conclusions
Release rate and release mechanism of CO from ECO were very much affected by temperature but not very much affected by concentration of ECO in the simulated clean floor solution. The release mechanism of the CO, based on Fick’s law was classified as following the Korsmeyer-Peppas controlled release model of super case II, whereby the release is due to wall erosion. It was confirmed by the formation of rupture on the spherical ECO which indicates the physical release mechanism of CO from ECO.

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