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Article

Citronella Oil Microencapsulated in Carboxymethylated Tamarind Gum and its Controlled Release

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Abstract. Citronella oil is one of possible natural insect's repellents extracted from leaves of *Cymbopogon winterianus*. It is used extensively as a source of perfumery chemicals such as 25% citronellal, 18% citronellol and 20% geraniol. To prolong the citronella oil release, carboxymethylated tamarind gum (CTG) was used as coating material for citronella oil encapsulation and compared to crude tamarind gum (TG), using spray drying technique. Three formulas of microcapsule were prepared at different gum to oil ratios (1.25, 1.14, and 0.87). The appearance feature of CTG microcapsule from SEM images showed a smooth surface while TG microcapsule showed many holes and crack on particle surface. It was observed that increasing the gum to oil ratio increases the retention of citronella oil in microcapsules. At 1.14 gum to oil ratio, CTG microcapsules were shown longer oil retention more than one month. The citronella oil release mechanism was analyzed by different kinetic models such as Korsmeyer-Peppas, Higuchi, and Avrami's models. The microcapsules were found to release the citronella oil by Fickian-diffusion mechanism and following Avrami model release kinetics.

Keywords: Citronella oil, encapsulation, controlled release, carboxymethylated gum.

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1. Introduction

Citronella oil as essential oil is steam distilled from the leafy parts of the citronella grass. Citronella oil is a common element in perfumes and cosmetic products and is well known for its use in outdoor candles, sprays, lotions, and other camping and outdoor essentials. The functional properties of citronella oil is effective repellent activity against insects especially mosquito after the direct application on the human skin [1]. However, citronella oil is known for rapidly evaporating, causing loss of efficiency with time.

Encapsulation of essential oil in coating material can provide protection against the degradable reactions in atmosphere for improving retention, quality preservation [2], [3], [4], [5]. The most common technique in microencapsulation in the industry is spray drying [6], it is the most common and cheapest technique, equipment is readily available, which is the transformation of a feed from emulsion into dried microcapsule in spray dryer chamber. The coating material should be emulsifier when soluble in cool water and film forming characteristics. Several wall materials have been applied in essential oil encapsulation by spray drying as gum Arabic combined with maltodextrin [7], [8], modified starch [9], whey protein concentrated [10], [11], [12].

Tamarind gum is a non-ionic polysaccharide that provided from *Tamarindus indica* seeds. Its chemical structure consists of monosaccharide units (glucose, xylose, and galactose). Several drawbacks of tamarind gum are low solubility in cold water, fast biodegradability, unpleasant odor, and dull colour have been reported [13]. So, the modification of the crude tamarind gum is undertaken to overcome these disadvantages and makes it more useful for a wider range of industries. Carboxymethylation has applied for crude tamarind gum with monochloroacetic acid and sodium hydroxide [14]. Carboxymethylated tamarind gum confers an anionic that consists of carboxymethyl group thereby exposing the polysaccharide network to hydration resulting in higher solubility in aqueous media, higher viscosity and lower biodegradability. Previously, CGT was used to entrap the drug at different conditions [15], [16]. However, few studies have been published on applying CTG for essential encapsulation using spray drying technique.

Regarding the controlled release of microencapsules, it depends on several mutually dependent processes such as diffusion, swelling, erosion and fragmentation [17]. Hence, the control releasing of citronella oil microencapsulated in carboxymethylated tamarind gum was investigated by using mathematical modeling such as Korsmeyer-Peppas, Higuchi, and Avrami's equation models.

2. Materials and Methods

2.1. Materials

Tamarind gum (TG) was kindly supplied from G.M. Inchihara (Thailand) Co., Ltd. Carboxymethylated tamarind gum (CTG) (Degree of Substitution = 0.204) was a coating material. Citronella oil from *Cymbopogon winterianus* (25% Citronellal, 18% Citronellol and 20% Geraniol) was purchased from Thai-China Flavors and Fragrances Industry Co., Ltd. (Thailand).

2.2. Emulsions

Emulsions were prepared at different gum to oil ratios: 1.25, 1.14, and 0.87 with code I, II, and III, respectively. Briefly, the carrier solution was prepared by dissolving tamarind gum into distilled water containing Tween 80 and Span 80. The mixture was left overnight under magnetic stirring for a complete hydration, after citronella oil was added drop by drop with a glass dropper. Subsequently, the mixtures were homogenized using an Ultra-Turrax homogenizer (T-25, IKA-Werke, Germany) at 16,000 rpm for 7 min.

2.3. Spray Drying Process

Emulsions were transformed into microcapsules by using mini spray dryer B-290 (BUCHI, Switzerland). The operational conditions of spray dryer were followed: inlet air temperature was 180°C, outlet air temperature was 88°C and feed rate was 4 ml/min. Then dried microcapsules were stored at 0 °C for further use.

2.4. Morphology of Microcapsule

Scanning electron microscopy, SEM (LEO 1450VP, England) was applied to observe the morphology of microcapsules. The dried microcapsules were placed on the SEM stubs using a two-sided adhesive tape (Polaron, SC 7620) and then were coated with gold. The morphology of microcapsule was observed at an accelerating voltage of 10 kV.

2.5. Chemical Components of Citronella Oil

Citronella oil components were analyzed by gas chromatrography (GC-FID). Column type: CP-Sil 8 CB (25m length, 0.53mm i.d, and 0.15μm film thickness), Flow rate: 1.2 ml/min, Injector: 250°C, Detector temperature: 320°C, Oven temperature: 50-260°C (5°C/min).

2.6. Controlled Release

Approximately, 0.1 g of microcapsules was kept into close vial, then storage at room temperature for 30 days. In these periods, the citronella oil remaining was evaluated by using similar method of total oil content determination from work of K. Khounvilay et al. (2018) [18]. Then the explanation of microcapsule release mechanism was evaluated using different kinetic models: Korsmeyer-Peppas, Higuchi, and Avram's equation models.

3. Results and Discussion

3.1. Morphology

The morphology of microcapsules was evaluated using SEM (Fig. 1). TG microcapsules had a rough surface for all tested conditions. Additionally, it has been observed that microcapsules presented small holes spreaded all over their surface. It could be that the TG contains impurities such as protein and fat inclusions, so that the cross-links between tamarind gum molecules could be interrupted at those sites. This is corroborated by the observation that microcapsules prepared from TG presented many holes, resulting in citronella oil leak. CTG microcapsules have a spherical shape and smoother surface and apparently are not fissured or cracked, which is important to provide lower oil permeability and increase oil retention. This is more evident in CTG II. CTG III shows a rougher surface shape presumably due to lower gum to oil ratio, which can be explained by the fact that there was not enough emulsifier to coat the oil droplet during spray-drying process.

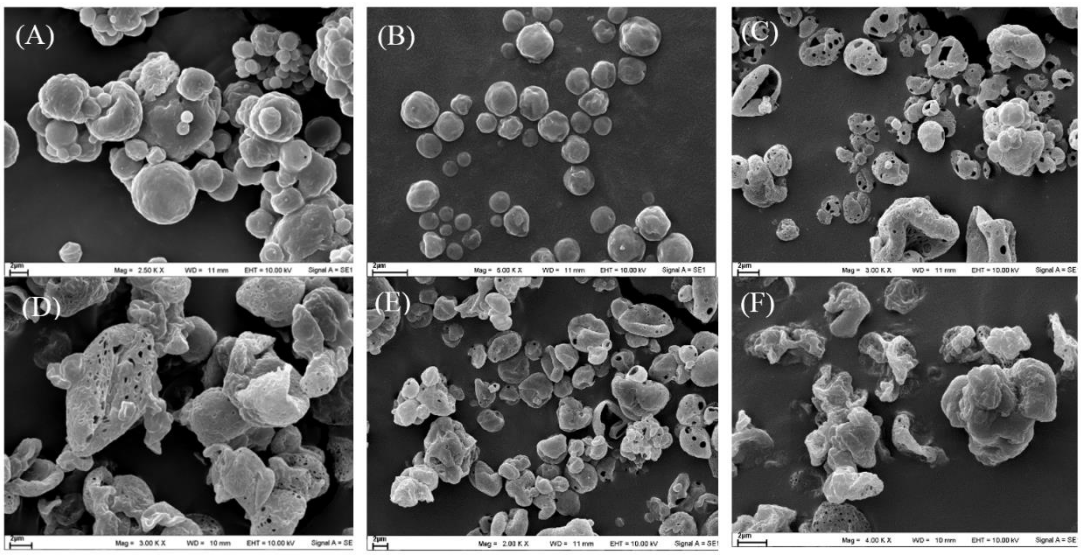

Fig. 1. SEM images of TG and CTG microcapsules: CTG I (A), CTG II (B), and CTG III (C), TG I (D), TG II (E), TG III (F).

These evidences confirm that CTG was a significantly better material to perform encapsulation than TG, in agreement with the work of S. Pal et al. (2008) [19] where compared TG and CTG for drug encapsulation. Results indicated that the CTG microcapsules possibly presented good drug stability. Due to the fact that CTG behaves as an anionic biopolymer. Modification TG with carboxymethyl group disrupts the organization of structure thereby exposing the polysaccharide network to hydration, resulting in higher viscosity and lower biodegradability thereby enhancing its good physicochemical properties [20].

3.2. Controlled Release

Citronella oil retention in both crude and carboxymethylated tamarind gums microcapsules at different gum to oil ratios were evaluated through the controlled release process. The citronella oil diffuses pass the microcapsule wall in to environmental media (hexane) for one month storage was determined by GC-FID analysis. The controlled release of citronella oil at the period of time passed TG and CTG microcapsules at different gum to oil ratios was focused. The controlled release trend line was shown the citronella oil concentration directly reduced with time which displays in Fig. 2. From the results, CTG microcapsule is a better controlled release than TG microcapsule. Due to CTG microcapsule was shown slower release than TG microcapsule which related to the morphology of TG microcapsules (Fig. 1) that had many holes on the particle surface. In addition, slower releases were found for all CTG microcapsule, especially CTG II microcapsule (Fig. 2(B)), for our studied storage period (30 days). Which is similar results of H. Yoshii et al. (2001) [21] who used maltodextrin to coat ethyl butyrate by using spray drying, their result indicated the period of time release for more than 25 days. However, at lower Fig. 2(A) and higher Fig. 2(C) gum to oil ratios were not suitable condition for spray drying technique. Due to at lower gum to oil ratio a lack of emulsifier resulted in many hole on particle, while at higher gum to oil ratio, emulsion showed high viscous which was difficult loading into spray dryer. Thus the citronella oil can be loosen during spray drying. Moreover, diffusion of the core material pass the microcapsule wall, due to the wall material properties and the action of temperature, and/or oxygen on the samples can catalyse reactions that lead to the formation of derivatives [22]. Moreover, molecular weight and solubility properties seem to play a significant role in the loss of core material since they are directly associated to the diffusion [23].

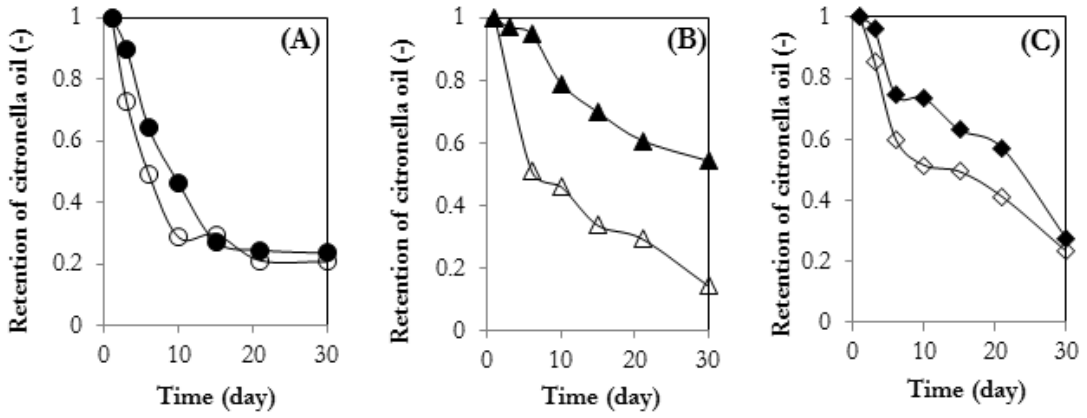

Fig. 2. The release of citronella oil components through microcapsules at different gum to oil ratios: 0.87 (A), 1.14 (B) and 1.25 (C). Open and full symbols represent TG and CTG microcapsules, respectively.

3.3. Mathematical Modeling

Generally, many mathematic models have widely been used to evaluate the core material release mechanism such as Zero order model, first order model, Avrami's equation, Korsmeyer-Peppas model, and Baker-Lonsdale model, etc. This work focuses on Korsmeyer-Peppas, Higuchi, and Avram's equation models. To obtain appropriate information, microcapsule release mechanism was evaluated using different kinetic models. The best fit or highest linearity of each model to the profile was selected to explain the release mechanism of citronella oil.

3.3.1. Korsmeyer-Peppas model

Korsmeyer-Peppas model (Eq. (1)) has widely used in pharmaceutical to predict drug release mechanism [24], [25]. However, this work used this model to predict citronella oil release from tamarind gum microcapsules.

$$\frac{M_t}{M_\infty} = kt^n \tag{1}$$

where M_t from Eq. (1) can be expressed as:

$$\ln \frac{M_t}{M_\infty} = \ln k + n \ln t \tag{2}$$

M_t/M_∞ is a fraction of core material released at time t, k is the release rate constant and n (slope) is the release exponent. In general, microcapsule from spray drying often shows the spherical sharp, when $n \leq 0.5$ the release mechanism is the Fickian diffusion operates and results in diffusion-controlled release. When, $n > 1$ depends on relaxation controlled release. In the intermediate value of n ($0.5 < n < 1$) is usually called anomalous transport (non-Fickian diffusion) [26]. This model is commonly used to describe the release of a pharmaceutical polymer system, when the release mechanism is not well known or when more than one type of release phenomena could be involved [24]. Figure 3 shows the relation between citronella oil releases by Korsmeyer-Peppas model plotting.

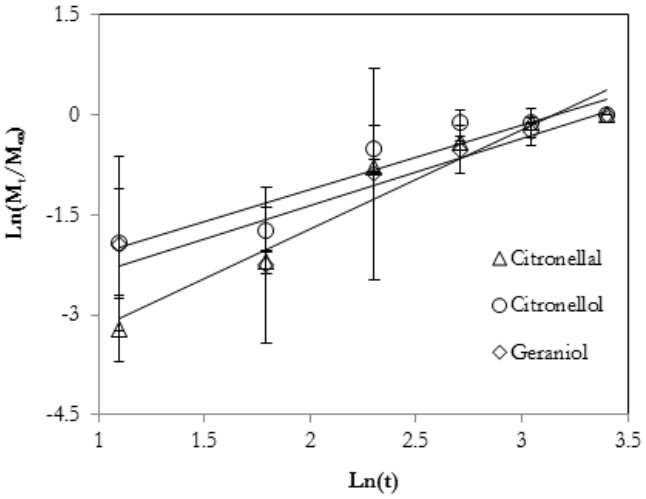

Fig.3. Correlation time of citronella oil release by Korsmeyer-Peppas model.

The values of each parameter that predicted by Korsmeyer-Peppas model were shown in Table 1. It shows the release profile of citronella oil by Korsmeyer-Peppas model plotting of both crude and carboxymethylated tamarind gum microcapsules. Each citronella oil component (citronellal, citronellol and geraniol) release was observed by fitting the Korsmeyer-Peppas model. R^2 was in the range of 0.7642 to 0.9885. From results, TG microcapsule shows both Fickian and non- Fickian diffusion mechanisms, which observed the n value in the case of Fickian diffusion n value in ranged 0.31 to 0.48 which similar to the research of B. Wilson et al. (2009) [27] who studied the drug (tacrine) release from chitosan microcapsule, the release mechanism presented the Fickian diffusion due to $n = 0.30$. In contrast, CTG microcapsule displays only non- Fickian diffusion due to n value indicated that $0.5 < n < 1$. Only, citronellal component was displayed the relaxation controlled release due to $n > 1$ which similar report of P. C. Ferrari et al. (2009) [28] who found that the n value in ranged 1.02 to 1.50 for drug release mechanism from chitosan microcapsule.

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Table 1. Release rate constant k and the parameter n of Korsmeyer-Peppas model under various release conditions.

	Citronellal			Citronellol			Geraniol		
	n	k (1/day)	R^2	n	k (1/day)	R^2	n	k (1/day)	R^2
TG									
I	0.55	0.20	0.7642	0.27	0.40	0.9391	0.48	0.20	0.9329
II	0.31	0.33	0.8874	0.90	0.05	0.9850	0.29	0.35	0.8445
III	0.82	0.07	0.8651	0.95	0.04	0.8023	0.54	0.18	0.8882
CTG									
I	1.12	0.034	0.8170	0.52	0.197	0.8493	0.57	0.160	0.8859
II	1.48	0.068	0.9417	0.96	0.048	0.8862	0.89	0.014	0.8634
III	1.23	0.014	0.9885	0.62	0.121	0.8440	0.97	0.039	0.8313

Moreover, citronellal showed faster release more than other components maybe due to it physical properties as showed in Table 1. Generally, this model has been applied to control release drug delivery. But it rarely applied to predict citronella oil release from biopolymer microcapsule. However, recently numerous researches also used it to predict oil release through biopolymer microcapsule. H. C. B. Paula et al. (2011) [29] produced *Lippia sidoides* essential oil microcapsule with chitosan/cashew gum as wall material using injection dropping technique. While E. F. de Oliveira et al. (2014) [30] used spray drying technique. They were successful applied Korsmeyer-Peppas model to predict oil release mechanism. Their result showed that n value from injection dropping technique was illustrated at higher than 0.50 which characterized in non-Fickian diffusion. In contrast, the oil release from microcapsule by spray drying was shown n= 0.50, also indicated Fickian diffusion. Similar research of F. O. M. S. Abreu et al. (2012) [31] indicated that n= 0.50.

3.3.2. Higuchi model

Higuchi model or Square root of time release model is frequently referred as square root of time release, providing compound release is linear with the reciprocal of the square root of time. The release rate is then given as:

$$\frac{M_t}{M_\infty} = kt^{1/2} \tag{3}$$

where k_h is Higuchi constant. It is the slope which obtained from $\frac{M_t}{M_\infty}$ plotted against $t^{1/2}$. Generally, this model describes drug release as diffusion process based on Fick's law when R^2 is nearly 1.0. This relation can be used to describe the drug dissolution from several type of modified release. Fig. 4 shows the relation between citronella oil releases at period of time by Higuchi model plotting. The values of each parameter from Higuchi model prediction were shown in Table 2.

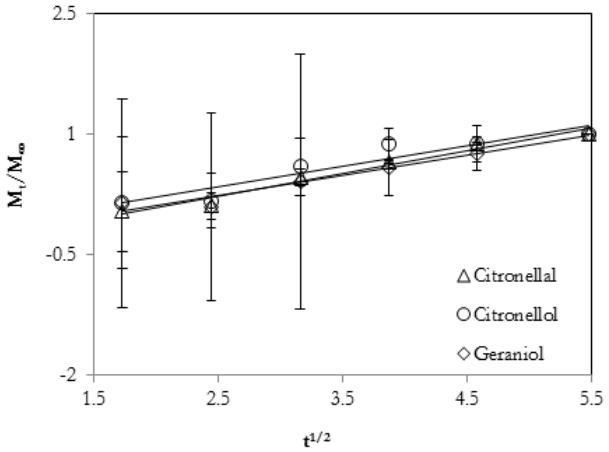

Fig. 4. Correlation time of citronella oil release by Higuchi model.

Table 2. Release rate constant k_h and R^2 of Higuchi model under various release conditions.

	Citronellal		Citronellol		Geraniol	
	k_h (1/day)	R^2	k_h (1/day)	R^2	k_h (1/day)	R^2
TG						
I	0.18	0.6954	0.13	0.9322	0.17	0.9175
II	0.13	0.8856	0.25	0.8774	0.12	0.9537
III	1.64	0.8651	1.90	0.8023	1.01	0.8882
CTG						
I	0.25	0.8539	0.18	0.8412	0.19	0.8903
II	0.28	0.9688	0.25	0.8880	0.25	0.9603
III	0.22	0.9094	0.18	0.8795	0.21	0.9032

R^2 displayed from 0.6954 to 0.9537 and 0.8412 to 0.9688 for TG and CTG microcapsules, respectively. These results showed the citronella oil release from TG and CTG microcapsule displayed non-Fickian and Fickian diffusion. Previously this model have been applied to predict citronella oil release through the nanoemulsion as presented in the work of U. Sakulku et al. (2009) [32]. X. Jun-xia et al. (2011) [33] was successful used this model to predict sweet orange oil release from chaitosan-alginate microcapsule, which observednin the Fickian diffusion. Moreover, this model have been used to describe the drug dissolution from several types of modified release pharmaceutical dosage forms, as in the case of some transdermal systems and matrix tablets with water soluble drugs [34]. Recently, E. F. de Oliveira et al. (2014) [30] prepared using spray drying, the aiming at development of a biopolymer blend for encapsulation of an essential oil. Their research was successful applied Higuchi model to predict essential oil release mechanism, which indicated in Fickian diffusion process.

3.3.3. Avrami's equation model

Avrami's equation model (Eq. (4)) has widely been used to predict release mechanisms of core material [21], [35], [36]. This model was applied to observe the kinetics of liberated ethyl esters and limonene compounds [37].

$$R=e^{-(kt)^n} \tag{4}$$

Equation (5) can be expressed as a linear equation plotting.

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$$\ln(-\ln R) = n \ln k + n \ln t \quad (5)$$

where R is the retention of flavor during release, t is time, n (slope) is a parameter representing the release mechanism, and k is the release rate constant. This model originally developed to express the crystal growth of polymers [38]. If $n = 1$ correspond to the first order reaction, if $n < 1$ correspond to the Fickian diffusion mechanism, and if $n > 1$ the release mechanism is rapidly release. Figure 5 shows the relation between citronella oil releases and storage time by Avrami's equation model plotting. The values from fitting of each parameter were shown in Table 3.

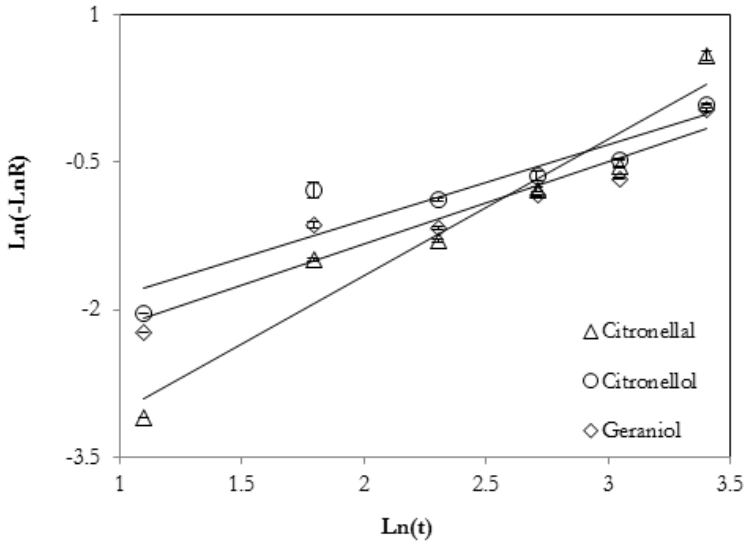

Fig. 5. Correlation time of citronella oil release by Avrami's equation model.

The release of citronella oil through the TG and CTG microcapsules fitted well with Avrami's equation model which confirmed by R^2. The tendency of release rate constant (k) increased when the gum to oil ratio decreasing. While the higher gum to oil ratio prolonged the oil release due to the thickness of microcapsule wall.

TG microcapsule showed rapidly release at lower and higher gum to oil ratio which observed from n value that more than 1.0 (citronellal and citronellol). Due to in spray drying process, the lower amount of wall material lacks of emulsifier to protect core material, while the highest amount of wall material shows higher viscous which is difficult to disperse in emulsion system and difficult to load emulsion into a spray dryer. Moreover oil rapidly release due to its physical properties as volatility which could be observed from it boiling point temperature, solubility, molecular size. The highest volatility lower boiling point temperature showed faster release and lower oil retention [23].

CTG microcapsule showed Fickian diffusion $n < 1$ (citronellol and geraniol). This mean CTG microcapsule showed slower releases than TG microcapsule which related to the morphology in Fig. 1 had many holes on surface, while CTG microcapsule had smooth surface. Which similar results of H. Yoshii et al. (2001) [21] they studied the essential oil encapsulation by using spray technique and their result showed that release profile is a function of time (t), the values of n was in the range of 0.2–1.0, indicated that the release of encapsulated flavour is controlled by the Fickian diffusion mechanism through the microcapsule wall. In addition, citronellal component showed Fickian diffusion ($1 < n$) and rapid release ($n > 1$), similar results of S. T. Chin et al. (2010) [35] who used gum arabic blend with maltodextrin to encapsulate flavors from durian powder using spray drying technique. Their results showed that $n = 2.51$. Moreover previous work of H. Shiga et al. (2001) [39] used Avrami's equation to predict d-limonene and n-hexanoate release mechanism. Their result showed that d-limonene displayed a rapid release ($1.2 < n < 1.4$) because of lower boiling point and molecular mass, while n-hexanoate showed Fickian diffuse ($n < 1$).

Table 3. Release rate constant *k* and the parameter *n* of Avrami's equation under various release conditions.

	Citronellal			Citronellol			Geraniol		
	n	*k* (1/day)	R^2	*n*	*k* (1/day)	R^2	*n*	*k* (1/day)	R^2
TG									
I	1.38	0.17	0.9382	1.18	0.08	0.9169	0.67	0.05	0.9455
II	0.57	0.14	0.7519	0.45	0.04	0.9805	0.46	0.04	0.9129
III	1.16	0.18	0.9958	1.43	0.04	0.9060	0.68	0.04	0.9083
CTG									
I	2.12	0.11	0.9789	0.68	0.04	0.9025	0.79	0.03	0.8988
II	0.87	0.04	0.9652	0.85	0.01	0.9779	0.89	0.01	0.9991
III	1.39	0.04	0.9383	0.78	0.03	0.8636	0.84	0.02	0.9059

To obtain appropriate information, the mechanical of microcapsules release were evaluated using different kinetic models (Korsmeyer-Peppas, Higuchi, and Avrami's equation models). The model with highest coefficient of determination (R^2) was accepted as more appropriate model for the present conclusion data. The release patterns from all the microcapsules were best explained by Avrami model because of the highest linearity. Thus citronella oil release mechanism was followed in Avrami model.

4. Conclusions

To prolong the oil release through microcapsule, controlled release was observed. TG microcapsule showed faster release than CTG microcapsule, especially in CTG II could prolong oil release more than one month. Mathematical models were used to predict the citronella oil release mechanism. The best fit of these models to the profile was investigated; the model with highest coefficient of determination (R^2) was accepted as more appropriate model for the present conclusion data. The release patterns from all the microcapsules were best explained by Avrami model because of the highest linearity.

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