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Abstract

Background *Litsea cubeba* essential oil (LCEO) is a food additive that requires encapsulation to delay its release due to its irritating nature. To identify an appropriate inclusion material, gamma (γ)-cyclodextrin (CD)-metal organic frameworks (MOF) were prepared, and the sustained release of the inclusion complex (IC) was studied.

Results The γ -CD-MOF was formed using γ -CD, potassium hydroxide (KOH), cetyltrimethylammonium bromide (CTAB), and silane coupling agents through the vapor diffusion method. The highest encapsulated rate achieved was 26.02%, with a temperature of 50 °C, a stirring time of 2.5 h, and an LCEO to γ -CD dosage ratio of 1:8. During the adsorption test, the amount of LCEO gradually increased within the first 180 min. However, after this time, there was no significant change in the adsorption amount of LCEO, indicating that the γ -CD-MOF had reached adsorption equilibrium. The average release rate of the IC reached 9.76% at 11 h. By comparison, the average release rate of the IC with γ -CD was 9.30% at 10 min, resulting in a diffusion index of 0.349. Under ultraviolet (UV) scanning, the sustained-release solution of the IC exhibited a strong characteristic citral absorption peak at 238 nm. Moreover, under infrared spectroscopy scanning, the absorption peak intensity of the IC was 1.19 times higher than that of blank γ -CD-MOF at 1676 cm⁻¹. The IC, as observed through a scanning electron microscope, exhibited round pellets with a diameter of 40–60 µm. Energy dispersive spectroscopy images showed uniform distribution of potassium and sulfur elements. In X-Ray diffraction, the diffraction peaks of the IC were found at 5.27°, 7.45°, 10.54°, 12.08°, 14.20°, 14.92°, 15.84°, 16.68°, 19.24°, 21.80°, and 23.69°, with no significant change in the adsorption amount of LCEO. The Brunauer–Emmett–Teller (BET) testing revealed that the surface area of γ -CD-MOF was 5.089 m²/g, and the pore diameter was 3.409 nm by the Barrett–Joyner–Halenda (BJH) method.

Conclusion These data demonstrated that the sustained effect of the γ -CD-MOF was superior to that of γ -CD. The adsorption kinetics curve followed the Quasi-primary kinetics model, while the release curve adhered to the Ritger–Peppas model. Furthermore, the release behavior was primarily governed by the Fick diffusion mechanism, which was advantageous for achieving the sustained release of LCEO. The UV spectrum, infrared spectroscopy (IR), scanning electron microscopy–energy dispersive spectroscopy (SEM–EDS), X-ray diffraction (XRD), and BET techniques confirmed the successful formation of the IC of LCEO with γ -CD-MOF. This study offers a promising technical solution for delaying the release and improving the sustained-release product of LCEO.

Keywords y-CD, Litsea cubeba essential oil, MOF, Sustained-release, Inclusion complex

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Introduction

Litsea cubeba essential oil (LCEO) is an agricultural product obtained from the *L. cubeba* fruit, a woody plant belonging to the Lauraceae family. It serves as a raw material for food preservatives [1] and possesses various beneficial biological activities, including anti-oxidation [2], anti-bacterial [3], anti-insect [4], and anti-inflammatory [5] properties. Despite these advantages, the high volatility and irritating nature of LCEO limit its long-term application in specific environments [6].

Recent reports suggest that essential oils can be released slowly and continuously using sustained-release materials [7–9]. These materials include cyclodextrin (CD) [10], alginate [11], chitosan [12], gelatin [13], protein [14], and others. The CD is the most commonly used for encapsulating essential oils [15]. CD, also known as cyclo polyglucose, consists of three types: α -cyclodextrin (α -CD), β -cyclodextrin (β -CD), and γ -cyclodextrin

(γ -CD), containing 6, 7, and 8 glucose units, respectively. They possess internal spatial diameters of 0.6, 0.8, and 1.0 nm.

Although β -CD has been frequently reported as a sustained-release material for various essential oils in previous studies [16, 17], γ -CD offers distinct advantages. It has a larger cavity than β -CD, enabling it to encapsulate a broader range of guest molecules [18]. Moreover, γ -CD exhibits superior water solubility and contains more hydroxyl groups, making it highly effective in improving the solubility and emulsification of guest compounds [19, 20]. Another significant benefit of γ -CD is its high safety for human consumption, with no allergenicity in food applications [21, 22]. Consequently, the application prospects of γ -CD in the formation of inclusion complexes (IC) are believed to be more promising than those of β -CD.

A metal–organic framework (MOF) is a material with a three-dimensional network structure formed by the

self-assembly of metal ions through coordination bonds with organic ligands. This concept was first proposed by Yaghi et al. [23]. Over the past few decades, researchers have reported and studied more than 20,000 different MOFs [24]. The key advantages of MOFs include their high porosity, large specific surface area, adjustable size and internal pore diameter, and ease of chemical functionalization. These attributes make them highly suitable for applications as sustained-release materials [25–27].

In particular, the γ -CD-MOF is formed through the self-assembly of K⁺ ions with γ -CD. Compared to γ -CD, γ -CD-MOF exhibits good biocompatibility [28], high inclusion capacity for ester-type aromatics, and excellent sustained-release properties for the encapsulated aromatics. As a result, the aromatics are slowly released over an extended period, allowing them to maintain their effects while being encapsulated in the IC of γ -CD-MOF.

Despite the promising characteristics of γ -CD-MOF, there is currently no existing report on the IC of LCEO with γ -CD-MOF. Thus, this paper aims to investigate the preparation conditions of the IC of LCEO with γ -CD-MOF and study the slow release behavior of the IC.

Silane coupling agents can increase the stability of MOFs [29, 30]. Until recently, there is no report on modifying γ -CD-MOF with silane coupling agents, so we have made an innovation on γ -CD-MOF.

Materials and methods

Materials

Litsea cubeba essential oil (Hunan Nuoze Biotechnology Co., Ltd.), citral (Chengdu Alfa Biotechnology Co., Ltd.), γ -CD (Shanghai McLean Biochemical Technology Co., Ltd.), silane coupling agent KH580 (Chemical name: γ -mercaptopropyl triethoxysilane, Jiangsu Huai'an Heyuan Chemical Co., Ltd.), cetyltrimethylammonium bromide (CTAB), anhydrous ethanol, potassium hydroxide, methanol, and oxalic acid are all conventional analytical reagents.

Preparation of standard curve of citral

The primary active component of LCEO is citral, which can constitute up to 64.43% of the oil [31]. Therefore, citral serves as a marker for determining the content of LCEO in the sustained-release solution. Various concentrations of citral were prepared by diluting a specific mass of citral with anhydrous ethanol to establish the standard working curve. The UV spectrogram of citral was obtained by scanning this solution within the wavelength range of 200–400 nm using a UV–visible spectrophotometer (TU-1901, Beijing General Analysis Instrument Co., Ltd, Beijing city, China). During the scanning, it was discovered that the maximum absorption wavelength of citral occurred at 238 nm, which was subsequently selected as the detection wavelength for analysis.

Subsequently, different concentrations of citral solutions were prepared using anhydrous ethanol, and their respective absorption values were determined. By plotting the citral concentration against the corresponding absorption values, a linear equation was fitted to generate the standard working curve. This curve will be employed for accurately quantifying the content of LCEO in the sustained-release solution based on the measured absorption values of citral.

γ-CD encapsulates LCEO

To prepare the IC of LCEO with γ -CD, a certain mass of γ -CD was weighed and placed in a beaker. An appropriate amount of deionized water was added to the beaker, and the mixture was stirred with a magnetic stirrer at 60 °C for 10 min using a centralized thermostatic heating magnetic stirrer (DF-101S, Henan Gongyi Yuhua Instrument Co., Ltd, Henan province, China) to create a γ -CD saturated aqueous solution. The solution was then transferred to a water bath at 60 °C to maintain its heat.

Next, LCEO was carefully added in drops to the γ -CD saturated aqueous solution at a specific temperature, and the mixture was stirred with the magnetic stirrer for a predetermined duration. After that, the heating was stopped, and stirring continued until the solution cooled to room temperature.

The resulting solution was refrigerated at 4 °C for 24 h and centrifuged at 5000 r/min for 5 min using a centrifuge (TD5K, Dongwang Instrument, Hunan province, China) to separate and obtain the precipitate. This precipitate was then dried at 40 °C to obtain the final IC of LCEO with γ -CD.

To determine the optimal preparation method for the IC, an orthogonal design was employed to screen the most suitable conditions. Three influencing factors were selected for the design: temperature (°C), the dosage ratio of essential oil to γ -CD (mL:g), and the stirring time (h). Details of these factors are presented in Table 1.

Determination of inclusion (adsorption) rate: The IC (200 mg) was precisely weighed and dissolved in 5 mL of anhydrous ethanol. The solution was ultrasonicated for 10 min to facilitate extraction. Next, 0.1 mL of the

 Table 1
 Orthogonal design factor and level

Factors	Level			
	1	2	3	
Temperature (°C)	40	50	60	
LCEO: γ-CD (mL:g)	1:4	1:8	1:16	
Stirring time (h)	1.5	2	2.5	

extracted solution was taken and diluted 100 times with anhydrous ethanol. The absorption value of the diluted solution was measured at 238 nm using a UV–visible spectrophotometer, and this value was utilized in the previously established linear equation of citral (section "Preparation of standard curve of citral") to calculate the concentration of citral. By applying the calculated concentration to the specific formula (1), the encapsulated (adsorbed) rate of the IC of LCEO with γ -CD-MOF was determined, allowing researchers to evaluate the efficiency of the IC in adsorbing and encapsulating citral from the LCEO.

$$M(\%) = \frac{C_1 * V * P * 10^{-3}}{m} * 100\%$$
(1)

where **M** is the encapsulated (adsorbed) rate, C_1 is the concentration of citral (µg/mL), **m** is the weighed mass of IC (mg), **V** is the volume of dissolved in anhydrous ethanol (mL), **P** is the dilution multipl(1000), and (C_1*V*P) is the adsorption amount **Q** (µg).

γ-CD-MOF encapsulates LCEO

The γ-CD-MOF was prepared using the vapor diffusion method [32]. Firstly, 4 g of γ -CD was weighed and placed in a 200 mL beaker (beaker A), followed by the addition of 100 mL of an aqueous solution of potassium hydroxide (200 mmol/L) to dissolve the γ -CD. Then, 10 mL of methanol was added to beaker A, which was then placed inside a 500 mL beaker B pre-filled with 40 mL of methanol. Beaker B was sealed with plastic film. The setup was left standing in a water bath at 50 °C for 5 h. After that, 0.88 g of CTAB was added to beaker A and incubated at room temperature for 12 h. Subsequently, the solution in beaker A was centrifuged at 5000 r/min for 5 min. The resulting precipitate was washed twice with anhydrous ethanol and methanol to remove any residual unreacted reagents. The surface residual solvent of the precipitate was removed using a chiller, and then the precipitate was dried at 40 °C until reaching a constant weight.

For the preparation of the silane coupling agent dispersion, a solution (100 mL) of anhydrous ethanol and deionized water mixed in a 9:1 volume ratio was adjusted to pH 4 with oxalic acid. Then, 10 mL of γ -mercaptopropyl triethoxysilane (coupling agent KH580) was added to beaker C and stirred with a magnetic stirrer for 1 h. Next, 3 g of γ -CD-MOF was added to the coupling agent dispersion and stirred magnetically for 4 h in a water bath at 70 °C. The mixture was then centrifuged at 5000 r/min for 5 min at room temperature, and the centrifugal precipitate was collected. The precipitate was washed three times with anhydrous ethanol to remove any residual dispersion, and the solvent on the surface of the precipitate was blown off using a chiller. Finally, the precipitate was dried in an oven at 40 °C until reaching a constant weight. The resulting product is referred to as γ -CD-MOF-SH. LCEO.

The IC of LCEO with γ -CD-MOF-SH was prepared following the method described in section " γ -CD encapsulates LCEO". The preparation process of the IC of LCEO with γ -CD-MOF-SH is illustrated in Fig. 1.

Adsorption of LCEO on y-CD-MOF

In the experiment, 100 µL of LCEO was taken in a beaker, and 250 µL of Tween 40 was added to aid in dissolution. Subsequently, 200 mL of deionized water was added to the beaker. Meanwhile, 0.75 g of blank y-CD-MOF was weighed and placed in the beaker, which was then bathed at 50 °C. At specific time intervals (0, 10, 20, 30, 40, 50, 60, 90, 120, 150, and 180 min), 1 mL of the supernatant was collected using a pipette, and each sample was diluted ten times with deionized water. The diluents were then filtered using a 0.45 µm microporous membrane, and their absorbance values were measured at 238 nm. These absorbance values were inserted into the citral linear regression equation, obtained in section "Preparation of standard curve of citral", to calculate the concentration of citral. Subsequently, the adsorption amount q was determined using Formula (2).

$$q = \frac{(C_0 - C) * V * P}{m}$$
(2)

where **q** is the adsorption amount (μ g/mg), **C**₀ is the initial concentration of the aqueous solution of LCEO (μ g/mL), **C** is the concentration of the aqueous solution after reaction time t (μ g/mL), **V** is the volume of the aqueous solution of LCEO (mL), **m** is the weighed mass of blank γ -CD-MOF (mg), and **P** is the dilution multiple [10].

Sustained-release of the IC of LCEO with γ -CD-MOF

In the experiment, eight portions of the IC of LCEO with γ -CD-MOF, each weighing 2 g, were placed in separate 250 mL stoppered conical flasks. Deionized water (200 mL) was added to each flask, and the mixture was shaken at 37 °C with a speed of 200 r/min using a shaker (HY-4, Xin-rui Instrument Factory, Jiangsu province, China).

After initiating the shaking process, 1 mL of the released solution was pipetted at specific time points—5 min, 10 min, 30 min, 1 h, 2 h, 4 h, 7 h, and 11 h. Each collected sample was then diluted 10 times with deionized water and filtered using a 0.45 μ m pore diameter aqueous microporous membrane. The filtrate's absorption value was measured at 238 nm using a UV–visible spectrophotometer (TU-1901, Beijing General Analysis Instrument Co., Ltd. Beijing City, China). This



Fig. 1 Preparation of the IC of LCEO with γ -CD-MOF

procedure was repeated three times in parallel to ensure accurate results.

The obtained absorption values were inserted into the linear regression equation for citral from the previous section "Preparation of standard curve of citral", enabling the calculation of the concentration of citral in the release solution at each time point. Furthermore, the adsorption amount (Q) of the IC was determined using the method described in section " γ -CD encapsulates LCEO". Subsequently, the release rate at each time point was calculated according to Formula (3). Additionally, the same sustained-release experiments were conducted with the IC of LCEO with γ -CD for comparative analysis.

$$S(\%) = \frac{C_2 * V * 10^{-3}}{Q} * 100\%$$
(3)

where **S** is the release rate, C_2 is the concentration of citral in the release solution (μ g/mL), **V** is the volume of

release solution (mL), and ${\bf Q}$ is the adsorption amount (µg).

Ultraviolet (UV) spectrum

The IC of LCEO (0.5 g) with γ -CD-MOF was accurately weighed and dissolved in 20 mL of anhydrous ethanol. The solution was filtered through an organic phase microporous filter membrane with a pore diameter of 0.45 μ m. Subsequently, the solution of the IC was scanned under UV absorption wavelengths ranging from 200 to 350 nm to obtain its UV spectrum. A similar process was carried out for the blank γ -CD-MOF sample in the same manner.

Infrared spectroscopy (IR)

The IC of LCEO with γ -CD-MOF and the blank γ -CD-MOF were mixed with a small quantity of potassium bromide. The mixtures were then compressed into tablets after grinding. These tablets were scanned in the range of $400-4000 \text{ cm}^{-1}$ using an infrared spectrometer (Thermo Scientific Nicolet iS10, Thermo Fisher Scientific Co., Ltd, Commonwealth of Massachusetts, USA).

In addition to the IC and blank samples, LCEO was also scanned using the same infrared spectrometer. This process allowed for comparing and analyzing the infrared spectra of the IC, blank γ -CD-MOF, and the original LCEO.

Scanning electron microscope-energy dispersive spectroscopy (SEM–EDS)

A specific mass of IC of LCEO with γ -CD-MOF was subjected to gold spraying on the stage. The sample was then observed using SEM–EDS (Gemini SEM 300, Carl Zeiss AG, Oberkochen, Batenwerburg, Germany). The SEM–EDS analysis allowed for the examination of the sample's appearance and the identification and distribution of the elements present in the IC.

X-ray diffraction (XRD)

The X-ray diffractograms of both the blank γ -CD-MOF and the IC of LCEO with γ -CD-MOF were obtained using an X-ray diffractometer (D8 ADVANCE, Bruker Corporation, Free State of Bavaria, Germany) equipped with monochromatic Cu radiation (60 kV, 60 mA). The diffraction parameters used for the analysis are as follows: a scanning angle range of 5° to 85° (2 θ), a scanning step of 0.025°, and a scanning speed of 2°/min. These parameters allowed for the detailed examination of the diffraction patterns and crystal structures of both samples.

BET surface area

The surface area of the blank γ -CD-MOF was determined using the Brunauer–Emmett–Teller (BET) analysis method, following the instructions provided by Quantachrome (IQ, Florida, USA). Nitrogen (N₂) gas was used as the adsorbed gas, and the desorption temperature was set at 100 °C. The BET analysis allowed for the accurate measurement of the surface area of the blank γ -CD-MOF, providing valuable information about its porosity and specific surface characteristics.

Results and discussion

Standard curve of citral solution

Figure 2 displays the UV scanning spectrum of the citral solution, revealing that the maximum UV absorption wavelength of citral is 238 nm. Consequently, all subsequent detections are performed at 238 nm to ensure accurate measurements. Figure 3 illustrates the standard curve of the citral solution, where the linear regression equation is y=0.145x - 0.0349, with a high coefficient of determination ($R^2=0.9917$). This strong correlation

Fig. 2 UV scanning spectral profile recorded for the citral solution

250

Wavelength (nm)

275

300

225

238nm

1.2

0.9

0.6

0.3

0.0

200

Absorption



Fig. 3 Standard curve generated for the citral solution

indicates that the concentration of citral exhibits a highly linear relationship with the absorption value, validating the reliability of the method for quantifying citral in the subsequent analyses.

Determination of encapsulation conditions of the IC of LCEO with $\gamma\text{-}\text{CD}$

Tables 2 and 3 present the results obtained post the optimization of the IC of LCEO with γ -CD and variance analysis, respectively.

Based on the results of the orthogonal experiment, the following conclusions have been drawn regarding the magnitude of the effect of each factor on the encapsulated rate: temperature has the greatest impact,

	IC of LCEO with γ-CD				
	T (°C)	<i>V</i> (m)	<i>t</i> (h)	M (%)	
1	40	1:4	1.5	3.41	
2	40	1:8	2.0	9.41	
3	40	1:16	2.5	14.38	
4	50	1:4	2.0	5.83	
5	50	1:8	2.5	26.02	
6	50	1:16	1.5	14.91	
7	60	1:4	2.5	5.50	
8	60	1:8	1.5	7.24	
9	60	1:16	2.0	5.91	
K ₁	9.067	4.913	11.780		
K ₂	15.587	14.223	9.940		
K ₃	6.217	11.733	9.150		
R	9.370	9.310	2.630		

Table 2 Results obtained from the orthogonal experiments conducted with the IC of LCEO with $\gamma\text{-CD}$

M, encapsulated (adsorbed) rate

 Table 3
 Variance analysis results obtained by conducting orthogonal experiments

Source	S _T	df	F-value	F-criticality value
T (℃)	138.430	2	12.669	19.000
<i>V</i> (m)	139.389	2	12.756	19.000
<i>t</i> (h)	116.192	2	10.633	19.000
Error	10.93	2		

S_T, sum of squares of deviance; DF, degree of freedom

followed by stirring time, and the dosage ratio of LCEO to γ -CD. Visual analysis of the data revealed the optimal encapsulation conditions for achieving the highest encapsulated rate: a temperature of 50 °C, a dosage ratio of LCEO to γ -CD at 1:8, and a stirring time of 2.5 h. These conditions are expected to yield the most favorable and efficient encapsulation of LCEO with γ -CD-MOF, ensuring a high encapsulated rate and the desired sustained-release properties.

Adsorption of LCEO on y-CD-MOF

As depicted in Fig. 4, the adsorption kinetics curve of LCEO shows a gradual increase within the first 0 to 180 min of the adsorption process. However, after the 180-min mark, there is no notable change in the adsorption amount of LCEO. This observation suggests that the γ -CD-MOF has reached adsorption equilibrium by this time, indicating that further adsorption is no longer occurring. The linear fitting analysis method revealed that the adsorption kinetics curve adhered to the Quasiprimary kinetics model, which could be expressed by







Fig. 5 Quasi-primary kinetics model

the equation $\ln(q_e - q) = -0.008t + 3.104$ (as depicted in Fig. 5). Here, qe represents the adsorption amount at equilibrium. This model provides valuable insight into the adsorption rate of LCEO by γ -CD-MOF and confirms that the adsorption process follows a quasi-primary kinetics pattern.

Sustained-release behavior of the IC of LCEO with $\gamma\text{-}\text{CD-MOF}$

The average release rates of the IC of LCEO with γ -CD-MOF in deionized water at each time point are shown in Table 4, and the release curve is shown in Fig. 4.

As observed in Figs. 6 and 7, both the IC of LCEO with γ -CD and the IC of LCEO with γ -CD-MOF exhibit

Sample	Time					
	5 min	10 min	0.5 h	1 h		
LCEO/y-CD	7.27±1.16	9.30±0.42	13.62±0.55	14.38±0.33		
LCEO/y-CD-MOF	1.66 ± 0.06	2.23±0.15	3.10 ± 0.07	4.27 ± 0.33		
Sample	Time					
	2 h	4 h	7 h	11 h		
LCEO/y-CD	16.11±0.72	18.52±0.32	19.44±0.51	20.62±0.64		
LCEO/y-CD-MOF	6.09 ± 0.32	7.09 ± 0.53	8.66 ± 0.63	9.76±0.30		

Table 4 Average release rates of the IC ($\overline{X} \pm$ SD%)



Fig. 6 Release curve generated for IC



Fig. 7 Local amplification for Fig. 4

sustained-release effects. However, there are significant differences between the two. Within the first 10 min, the IC of LCEO with γ -CD demonstrates a burst release

phenomenon, releasing a substantial amount of the essential oil. On the other hand, the IC of LCEO with γ-CD-MOF does not exhibit a prominent burst release, indicating a more controlled release pattern. The average release rate of the IC of LCEO with y-CD reaches 9.30% at 10 min, while the average release rate of the IC of LCEO with y-CD-MOF is only 9.76% after 11 h. This indicates that the IC of LCEO with γ -CD-MOF has a superior sustained-release effect compared to that of the IC of LCEO with y-CD. This can be attributed to the regular crystal structure of γ -CD-MOF, which enhances its ability to encapsulate guest molecules, thereby reducing the release rate and prolonging the release time of LCEO. The released amount of LCEO from the material is less than 20% which is related to the absorption between LCEO and y-CD-MOF. The release kinetic curves were further analyzed using the zero-order, first-order, Higuchi, and Ritger-Peppas models, as depicted in Fig. 8. These models provide valuable insights into the release kinetics and mechanisms of the ICs, allowing for a comprehensive understanding of their sustained-release behaviors.

The equations adopted for the release kinetics are presented in Table 5. The R^2 values obtained using the Ritger–Peppas model were significantly higher than the R^2 values obtained using other models, making it the most accurate model for representing the release of LCEO from the ICs.

During the initial sudden release stage, the main influencing factor was the concentration gradient between the inside and outside of the IC. As the carrier material of the IC gradually dissolved, the release of LCEO was primarily controlled by the dissolution and diffusion permeation mechanism of the carrier material. The slope of the release equation for the IC of LCEO with γ -CD was 3.19 times greater than that of the IC of LCEO with γ -CD-MOF, indicating that the sudden release behavior of the IC of LCEO with γ -CD was sharper than that of the IC of LCEO with γ -CD-MOF.



Fig. 8 Four adopted release kinetic curves

Table 5	Kinetic	parameters	corresponding	to adopted	equations

Model	The IC of LCEO with $\gamma\text{-}CD$		The IC of LCEO with γ-CD-MOF	
	Equations	R ²	Equations	R ²
Zero-order First-order	y = 1.29x + 9.57 y = 17.74 $(1 - e^{-4.10x})$	0.4802 0.8972	y = 0.78x + 2.52 $y = 8.79(1 - x^{-0.67x})$	0.7850 0.9260
Higuchi Ritger–Peppas	$y = 5.17x^{1/2} + 6.48$ $y = 13.83x^{0.183}$	0.7426 0.9792	$y = 2.89x^{1/2} + 0.98$ $y = 4.34x^{0.349}$	0.9620 0.9932

In cyclodextrin IC with small molecules, there are two release mechanisms: diffusion and dissolution [33]. The Ritger–Peppas equation is expressed as $S = kt^n$, where *n* is the diffusion index that explains the release mechanism. For n < 0.45, the low extent of molecular release is dominated by Fick diffusion. For 0.4 < n < 0.89, the low extent of molecular release is dominated by non-Fick diffusion (a combination of diffusion and dissolution). When n > 0.89, the low extent of molecular release molecular release is dominated by dissolution. In this study, the value of n was found to be 0.349, indicating that the release of LCEO followed the Fick diffusion mechanism. This release mechanism is



Fig. 9 UV spectral profiles recorded for the IC of LCEO with γ -CD-MOF and blank γ -CD-MOF

advantageous for the sustained release of Litsea cubeba essential oil, as it prolongs its use time effectively.

Ultraviolet (UV) spectral profiles

The UV spectral profiles of the IC of LCEO with γ -CD-MOF and blank γ -CD-MOF are shown in Fig. 9.

Figure 9 reveals that the UV spectral profiles of the IC exhibit a robust absorption peak within the wavelength range of 210–270 nm, with the maximum value occurring precisely at 238 nm, which aligns with the absorption wavelength of citral. This provides compelling evidence that γ -CD-MOF effectively encapsulates LCEO within the IC. Moreover, the blank γ -CD-MOF displays no absorption peak in the corresponding wavelength band, signifying the absence of any background interference in the UV scanning results. This confirms the specificity of the UV scanning analysis, further supporting the successful encapsulation of LCEO within the IC.

Infrared (IR) spectroscopy

The IR profiles of LCEO, blank γ -CD-MOF, and the IC of LCEO with γ -CD-MOF are shown in Fig. 10.

In the infrared spectrum, the wavenumber range of $1050-1300 \text{ cm}^{-1}$ corresponds to the stretching vibration region of C–O–C, while the wavenumber range of $1650-1900 \text{ cm}^{-1}$ corresponds to the stretching vibration region of C=O. Additionally, the wavenumber range of $3250-3650 \text{ cm}^{-1}$ corresponds to the stretching vibration region of O–H. Given that citral serves as the main component of LCEO, the characteristic peak of C=O becomes

particularly significant. Figure 10b, c displays a robust absorption peak near 1676 cm⁻¹, which corresponds to the stretching vibration of C=O. Notably, citral does not contain O-H. Hence, a significant degree of absorption does not occur within the 3250–3650 cm⁻¹ range. Figures 10a, b reveal the spectra of γ -CD-MOF and its IC. Both spectra exhibit absorption peaks near 1070, and 3370 cm^{-1} . The wavenumber values of 1070 cm⁻¹ and 3370 cm^{-1} correspond to the stretching vibrations of C-O-C and O-H in y-CD-MOF, respectively. A significant finding emerges from these spectra: the transmissivity of 1676 cm⁻¹ in Fig. 10c is noticeably higher than that in Fig. 10b. Furthermore, the absorption intensity at 1676 cm^{-1} in Fig. 10b is 1.19 times greater than that in Fig. 10c. These results provide strong evidence to support the encapsulation of LCEO by γ-CD-MOF.

Scanning electron microscope-energy dispersive spectroscopy (SEM–EDS)

The IC of LCEO with γ -CD-MOF was examined using the SEM technique. As depicted in Fig. 11, the IC displays an irregular spherical shape with a diameter ranging from 40 to 60 μ M. Moreover, its surface appears rough, devoid of cracks and holes.

Figure 12 presents the EDS profile of the IC, while Table 6 illustrates the mass fraction of the detected EDS elements. The presence of silicon and sulfur elements can be attributed to γ -mercaptopropyl triethoxysilane, whereas the potassium element originates from potassium hydroxide (KOH). It is worth noting that, apart from carbon and oxygen elements, the content of silicon is the highest, reaching up to 4.1%. Figure 13 complements the analysis, showing that the potassium element is distributed uniformly throughout the sample. This uniform distribution serves as a strong indicator of the successful construction of the MOF.

X-ray diffraction (XRD) patterns

Figure 14 presents the X-ray powder diffraction spectra of the blank γ -CD-MOF and the IC of LCEO with γ -CD-MOF. Let's delve into the details:

Figure 14a illustrates the spectrum of the blank γ -CD-MOF, exhibiting diffraction peaks at 4.05°, 6.99°, 13.38°, 17.12°, 20.62°, and 23.16°.

On the other hand, Fig. 14b displays the spectrum of the IC of LCEO with γ -CD-MOF. This spectrum exhibits several distinct diffraction peaks at 5.27°, 7.45°, 10.54°, 12.08°, 14.20°, 14.92°, 15.84°, 16.68°, 19.24°, 21.80°, and 23.69°, respectively.



Profiles recorded for (a) blank γ -CD-MOF, (b) IC of LCEO with γ -CD-MOF, and (c)

LCEO

Fig. 10 Infrared spectrogram of LCEO, blank y-CD-MOF, and the IC of LCEO with y-CD-MOF

The X-ray diffraction pattern of the IC is markedly different from that of the blank γ -CD-MOF. When the LCEO molecule was included in the cavity of γ -CD, as shown in Fig. 14b, most of the crystalline diffraction peaks of γ -CD appeared after complexation with LCEO, such as the characteristic diffraction peaks at 2θ value of 10.54°, 12.08°, 14.20°, 14.92°, 15.84°, and 16.68° were appeared. The alteration in the crystal structure of the blank γ -CD-MOF indicates the successful encapsulation of LCEO within the γ -CD-MOF cavity. This encapsulation results in a significant change in the crystal form and the formation of a new phase.

Overall, the observed differences in the XRD patterns support the conclusion that LCEO interacts with γ -CD-MOF to form the IC, leading to significant modifications in the crystal structure of the host material.

BET surface area

Surface area and pore size analyses of γ -CD-MOF materials were conducted using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. The results are as follows:

BET analysis revealed that the surface area of the γ -CD-MOF material was 2.540 m²/g. This result is inconsistent with literature, communicated with analysts of BET, it only micropores and mesopores (0.35–50 nm) can be counted by instrument. However, the



(a) 100 x magnification, (b) 200 x magnification

Fig. 11 SEM images of the IC



 Table 6
 Atomic percentages of elements

Element	At (%)
C	75.11
0	17.18
Si	4.10
S	3.59
К	0.02
Totals	100

pore size of γ -CD-MOF may exceed this range sometimes, so the data of BET will be low.

These analyses provide valuable insights into the surface characteristics and porosity of the γ -CD-MOF material, helping to better understand its physical properties and potential applications.



Fig. 13 Potassium element distribution image

Conclusion

Gamma-cyclodextrin (γ -CD), γ -mercaptopropyl triethoxysilane, and KOH were used as raw materials to prepare γ -CD-MOF using the vapor diffusion method. Under the following conditions: temperature of 50 °C, a dosage ratio of LCEO to γ -CD as 1:8, and a stirring time of 2.5 h, LCEO was encapsulated by γ -CD-MOF into a sustained-release body. The average release rate of LCEO with γ -CD-MOF reached 9.76% at 11 h, while the average release rate of LCEO with γ -CD was 9.30% at 10 min. This indicated that the sustained-release effect of γ -CD-MOF was more pronounced than that of γ -CD.

The release behavior of LCEO with γ -CD-MOF followed the Ritger–Peppas model, with a diffusion index



Fig. 14 XRD spectral profile

(*n*) value of 0.349. This value fell within the range that conforms to the Fick diffusion mechanism for LCEO. UV, IR, SEM-EDS, XRD, and BET characterization results confirmed the successful structuring of LCEO with y-CD-MOF. SEM analysis showed the diameter of the IC to be 40–60 μ M. EDS revealed the elements present in the IC, including C, O, Si, S, and K. XRD diffraction peaks appeared at 5.27°, 7.45°, 10.54°, 12.08°, 14.20°, 14.92°, 15.84°, 16.68°, 19.24°, 21.80°, and 23.69°. The significant surface area was 5.089 m^2/g , and the pore diameter was 3.409 nm, as determined from the BJH and BET profiles. In the future, we plan to investigate the sustained-release behavior of LCEO with y-CD-MOF under various environmental conditions. By further modifying the structure of y-CD-MOF, we aim to tailor the sustained-release behavior in response to factors such as temperature, pH, and magnetic fields, ultimately maximizing the effectiveness of LCEO.

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Author contributions

Wenxi Zheng wrote the main manuscript, Sheng Zhang proposed the concept and revised the manuscript, and Jie Chen conducted the experiments. All authors reviewed the manuscript.

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Availability of data and materials

The datasets used and/or analyzed are available from the corresponding author upon reasonable request.



Declarations

Ethics approval and consent to participate

There are no ethical/legal conflicts to declare.

Consent for publication

All authors have read and approved the content and agreed to submit the paper for publication in your journal.

Competing interests

The authors declare that they have no competing interests.

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