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Original article

Encapsulation of thymol and limonene in metal–organic frameworks for inhibition of *Colletotrichum musae* growth

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Summary Monoterpenes are the most prevalent compounds found in essential oils. They exhibit inhibitory actions against phytopathogenic postharvest fungi. Direct application limits their effectiveness due to their instability, high volatility, hydrophobicity and susceptibility to degradation. Encapsulation systems using metal–organic frameworks (MOFs) have been developed to maximise their use. In this study, four protocols were shown to encapsulate thymol and limonene in porous solids, such as ZIF-8, UiO-66-$(COOH)_2$ and zeolite 13X. Vapourisation and diffusion at 60 °C for 16 h was found to be the most efficient encapsulation process. A larger amount of thymol than limonene was loaded in the porous solids. Thymol released from MOFs slowed down the growth of *Colletotrichum musae* by up to 6 days at 25 °C. There was a sustained release of thymol even beyond the period of maximum fungal growth. This proof-of-concept study revealed the potential utility of MOFs as carriers of thymol against postharvest fungi.

Keywords *Colletotrichum musae*, encapsulation, limonene, MOFs, monoterpenes, sustained release, thymol, vapour diffusion.

Introduction

Monoterpenes, the major constituents of essential oils (EOs), are secondary plant metabolites with diverse biological activities, including fungicidal, bactericidal, insecticidal and herbicidal properties (Marei & Abdelgaleil, 2017). Thymol (2-isopropyl-5-methylphenol), a phenolic monoterpene, is commonly present in thyme (*Thymus vulgaris* L.) and oregano (*Origanum vulgare* L.) (Salehi *et al.*, 2018). Limonene (4-isopropenyl-1-methylcyclohexene), on the other hand, is a monocyclic monoterpene hydrocarbon mainly found in *Citrus* sp. (Ibáñez *et al.*, 2020).

Aside from being low cost and easy to handle (Cometa *et al.*, 2022), thymol is considered as a biocontrol agent by the European Commission and as a safe food additive by the U.S. Food and Drug Administration (Min *et al.*, 2021). It has been reported to completely inhibit the mycelial growth of 17 phytopathogenic fungi (Kordali *et al.*, 2008) including *Colletotrichum* sp., that cause diseases of tropical and subtropical fruits. Thyme oil significantly inhibited the growth of *C. musae*, a major postharvest pathogen in banana fruits, which causes latent infection during fruit development in the field, with symptoms typically emerge after harvest and often during the ripening phase (Vilaplana *et al.*, 2018).

Direct application of EOs, including monoterpenes, in liquid form limits their sustainable antimicrobial effects due to intrinsic obstacles such as instability, hydrophobicity and undesirable aroma (Wu *et al.*, 2019a; Min *et al.*, 2021). EOs are physicochemically unstable and susceptible to degradation when continuously exposed to light, oxygen, moisture and heat (Tian *et al.*, 2021). EOs also have low solubility in aqueous media and the formulated concentrations are not sufficient to exert significant biological activity (Liao *et al.*, 2021); hence, high concentrations are

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needed. However, this may lead to undesirable phytotoxic effects.

One way of preventing phytotoxicity is to apply monoterpenes in their vapour phase (Reyes-Jurado *et al.*, 2020). Thymol is considered as an active antifungal compound for vapour-phase applications (Pinto *et al.*, 2020). Encapsulation systems, as fixation methods, have been developed to overcome the instability and high volatility of EOs. Commonly used encapsulation materials include polysaccharides, proteins and polydopamine (Yi *et al.*, 2022), along with extensively developed carriers such as microcapsules and nano-emulsions.

Metal–organic frameworks (MOFs) are a relatively new class of crystalline porous coordination materials, which are composed of metal ions or clusters joined to organic ligands (Nong *et al.*, 2020). MOFs have a much larger surface area, ranging from 1000 to 10 000 m^2/g and a larger pore size than conventional adsorbent, such as zeolites (Farha *et al.*, 2012), thus making them particularly attractive for EO encapsulation. Nanocarriers provide an increased surface area and enhance the availability of encapsulated bioactive compounds compared to microsized carriers. Hence, nanoencapsulation has become one of the most significant technologies for targeted delivery of bioactive compounds (Yu *et al.*, 2018).

ZIF-8 (Zeolite Imidazole Framework), which consists of Zn^{2+} coordinated to a 2 methylimidazole ligand framework, is currently one of the most widely investigated MOFs due to its easy synthesis, relatively high stability, particular adsorption properties (*e.g.*, for xenon and water), and excellent gas separation (*e.g.*, ethane/ethylene and propane/propylene) (Lai, 2018). UiO-66 (University of Oslo), on the other hand, is a crystal containing metal nodes of a zirconium oxide complex bridged by a terephthalic acid ligand. Zirconium-based MOFs are known to have outstanding chemical and thermal stability (Cavka *et al.*, 2008).

Abdelhamid & Mahmoud (2023) recently found that copper-based MOFs embedded into carbon exhibited antifungal activity against postharvest fungi. However, research on the effectiveness of monoterpenes released from MOFs against phytopathogenic fungi is lacking. Previous *in vitro* studies have only investigated MOFs as carriers of thymol for antibacterial applications. Wu *et al.* (2019b) demonstrated that Zn@MOF loaded with thymol inhibited the growth of *E. coli* O157:H7. Min *et al.* (2021) observed antibacterial effects with thymol-loaded MOF nanofibres.

This study aimed to demonstrate the application of ZIF-8 and UiO-66-$(COOH)_2$ as novel materials for encapsulation and sustained release of volatile thymol and limonene. To the best of our knowledge, this proof-of-concept study is the first to investigate the inhibitory effect of vapour-phase thymol released from ZIF-8 and UiO-66-$(COOH)_2$ against *C. musae* incubated at 25 °C.

Materials and methods

Experimental materials

Commercially available thymol (≥98.5% purity) and limonene (97% purity) were purchased from Sigma-Aldrich Chemicals Corporation (St. Louis, MO, USA). Three porous solids were studied. ZIF-8 and UiO-66-$(COOH)_2$ were synthesised by spray-drying and precipitation, respectively.

To synthesise ZIF-8 (Carné-Sánchez *et al.*, 2013), a solution of 0.16 M zinc acetate in 10 mL water and a solution of 0.016 M methylimidazole in 10 mL water were separately subjected to spray-drying in a mini spray dryer using a three fluid nozzle with a 0.5 mm-in-hole spray cap, with a feed flow of 4.5 mL/min, a total flow rate of 474 mL/min, and an inlet temperature of 180 °C. The resulting powders were converted into well-dispersed and distinct crystals through ultrasonic treatment. The resulting crystals were then collected using a two-step centrifugation/redispersion cleaning method involving methanol. Finally, they were vacuum-dried for 48 h at room temperature and an additional 2 h at 300 °C.

To synthesise UiO-66-$(COOH)_2$ (Khabzina *et al.*, 2018), a 10 mmol quantity of zirconium (IV) sulphate and 11 mmol of 1,2,4-benzenetricarboxylic acid were mixed in 30 mL water. The synthesis was carried out under refluxing for 90 min.

After synthesis, the solids were washed with water, dried at 150 °C, and then kept in a gas-tight container to avoid possible contamination from air pollutants and re-humidification.

Zeolite 13X (Na exchanged, FAU structure) was also purchased from Sigma-Aldrich and used as a commercial reference sample (≈2 μm average particle size). The *C. musae* fungal strain was from Ivory Coast.

Encapsulation of monoterpenes in porous solids

The capacity of MOFs and zeolite was studied using four different monoterpene (thymol and limonene) loading protocols. Several conditions such as temperature, concentration and time duration were manipulated, primarily taking into account the nature of the monoterpenes and the characteristics of the MOFs.

For the post-encapsulation steps, the monoterpene@porous solid was washed with ethanol (Min *et al.*, 2021), along with manual filtration to remove loosely bound monoterpenes on the pore surface, then dried

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at 30 or 40 °C to ensure that no traces of ethanol were left. The dried monoterpene@porous solid was then collected and stored in a glass vial.

Loading of ethanolic monoterpenes at room temperature

Five concentrations (100%, 80%, 50%, 20%, and 0%) of ethanolic monoterpene solution (monoterpene + EtOH) were prepared (thymol – w/v; limonene – v/v). In a hermetically sealed 30-mL glass vial, 1 g of porous solid was suspended in 4 mL of each monoterpene + EtOH concentration and continually stirred at room temperature for 16 h (Fig. 1a). Pure thymol was heated to 60 °C before stirring to induce phase change. The monoterpene@porous solid was filtered manually and washed with ethanol, then dried at 30 °C for 3 h.

The encapsulated thymol, limonene, and ethanol (%) was computed as follows:

$$= \frac{\text{concentration (\%) of monoterpenes or EtOH in the solution} \times \text{encapsulation efficiency (\%) of pure monoterpenes or EtOH}}{100}$$

Vapourisation and diffusion of pure monoterpenes at 60 °C

One gram of thymol or 1 mL of limonene was placed or pipetted, respectively, in a 200-mL glass container. One gram of porous solid contained in a cylindrical aluminium foil (length: 100 mm; diameter: 20 mm; thickness: 0.01 mm) was then carefully placed inside the glass container. The top of the aluminium foil was left open and the bottom did not touch the monoterpenes. The container was then sealed and heated to 60 °C for 16 h. After washing with ethanol, the monoterpene@porous solid was dried at 30 °C for 3 h or 16 h.

Contact diffusion of pure and ethanolic monoterpenes at room temperature

One gram of porous solid was placed in a 30-mL vial (Fig. 1b). Each of the following weights or volumes of monoterpene were then added to the top of the porous solid: (a) 200 μL limonene; (b) 200 mg or 400 mg thymol; (c) 200 mg thymol +200 μL EtOH; or (d) 200 or 400 μL EtOH. The vial was sealed, then stored at room temperature for 2 days or 7 days. Once filtered and recovered, the monoterpene@porous solid was dried at 30 °C for 3 h.

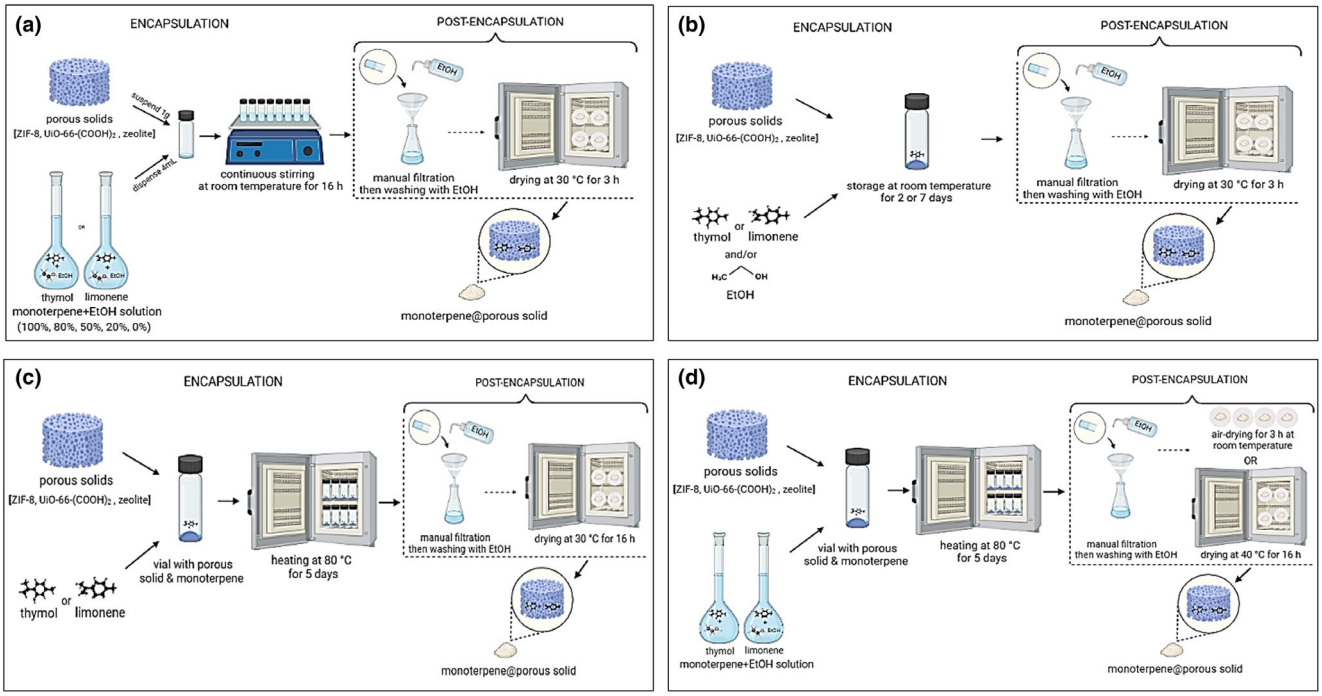

Figure 1 Loading of (a) ethanolic monoterpenes at room temperature for 16 h; (b) pure and ethanolic monoterpenes at room temperature for 2 or 7 days; (c) pure monoterpenes and (d) ethanolic monoterpenes at 80 °C for 5 days.

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Loading of pure and ethanolic monoterpenes at 80 °C
One gram of thymol or 1 mL of limonene was placed or pipetted, respectively, in a 30-mL vial containing one gram of porous solid (Fig. 1c). The vial was sealed, then heated to 80 °C for 5 days. After washing with ethanol, the monoterpene@porous solid was dried at 30 °C for 16 h.

Four percent of ethanolic monoterpene solution was prepared. Thirty millilitres of monoterpene + EtOH solution was pipetted into a 30 mL vial containing 0.6 g of porous solid (Fig. 1d). The vial was sealed, then heated to 80 °C for 5 days. The monoterpene@-porous solid was recovered and washed with ethanol, then air-dried inside a non-ventilated fumehood for 3 h, or dried at 40 °C for 16 h.

Validation of the optimised encapsulation protocol

The optimised protocol included the same steps with vapourisation-diffusion of pure monoterpenes at 60 ± 1 °C for 16 h, except for post-treatment. The monoterpene@porous solid was dried at 30 °C for 4 h after washing with ethanol. Several trials, in triplicate per treatment, were conducted to test its consistency in attaining the highest encapsulation efficiency (% weight) computed as follows:

$$\text{Encapsulation efficiency}(\%\text{wt}) = \frac{\text{final weight of monoterpene@porous solid(g)} - \text{initial weight of porous solid(g)}}{\text{initial weight of porous solid(g)}} \times 100$$

X-ray diffraction (XRD) analysis

An XRD analysis was carried out to determine whether the monoterpene was well encapsulated in the porous solids. Pure thymol and thymol@porous solids were characterised by XRD using a D8 Advance Brücker AXS apparatus with Cu-Kα emission (λ = 1.54184 Å). Diffractograms were collected between a 2θ of 4 and 80° with a step size of 0.02° at a detector time of 0.5 s/step.

In vitro assay

Thymol loaded in ZIF-8, UiO-66-$(COOH)_2$ and zeolite obtained using the optimised protocol was used. Pure thymol and without thymol served as controls. An *in vitro* assay was undertaken to determine the inhibitory effect of volatile thymol against *C. musae*, and analyse the release profile at the same time.

A pre-weighed thymol@porous solid and a beaker filled with 100 mL of sterilised distilled water were placed on the opposite sides of a 5.5 L polypropylene container (280 × 215 × 110 mm). A 10 μL spore suspension (10^6 conidia/mL) of a 7-10-day-old *C. musae* was pipetted into the PDA plate, then placed in the middle of the container upside-down. A circular and side-perforated metal plate was used to keep the PDA plate slightly raised. The container was then hermetically sealed and stored at 25 ± 1 °C for 11 days.

In this assay, 50 mg of potentially loaded thymol in the porous solid was used. The required weight of thymol@porous solid was computed as follows:

$$\text{Weight of thymol@porous solid (mg)} = \frac{\text{potential/desired weight of thymol (mg)}}{\%\text{encapsulation}} \times 100$$

The addition of distilled water was adopted from the study reported by Lashkari *et al.* (2017) to enhance monoterpene release.

Thymol release measurements
Thymol release from the porous solids was studied by SPME/GC/MS analysis. After remaining closed for 3 days, the container was opened for around 2 min, then remained closed until the following day. The opening-closing of the container was repeated daily. Immediately after closing, a solid phase microextraction (SPME) fibre [50/30 μm divinlybenzene (DVB)/carboxen (CAR)/polydimethylsiloxane (PDMS); Supelco, Bellafonte, USA] was exposed to the headspace for 1 h to trap the thymol at 25 °C, then re-exposed for 10 min at 20 °C in a 10-mL glass vial containing 1 μL of internal standard. The fibre was then injected into an Agilent gas chromatograph 6890 series equipped with a 60 m 0.25 × 0.25 DB5 analytical fused-silica column (J&W Scientific, Folsom, CA, USA) coupled with a 5973A mass selective detector. The headspace gas was injected by thermal desorption at 250 °C for 10 min in splitless mode. The oven temperature was initially held at 100 °C, ramped up to 250 °C at a rate of 10 °C/min, then maintained at 250 °C for 15 min. The carrier gas was helium with a flow rate of 1.0 mL/min. Samples were taken in duplicate.

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To quantify the thymol trapped on the fibre, a calibration curve was created under the same sampling operating conditions in EI+ at 70 eV in SIM mode. Three serial dilutions of thymol dissolved in methanol were used against 1 μL of 3-heptanol standard solution (0.815 mg/mL) added to a 10-mL glass vial. The quantity (μg/10 mL) of thymol released was then determined using Agilent Masshunter Quantitative Analysis software version 11.1.

Growth inhibition of C. musae

The diameter of the fungal colony (mm) was measured immediately after opening the container. Three PDA plates were measured per treatment with two diameter readings per PDA plate. Percent inhibition was computed as follows:

$$\text{Inhibition}(\%) = \frac{(\text{mean diameter of treatment without thymol} - \text{mean diameter of the treatment})}{\text{mean diameter of treatment without thymol}} \times 100$$

Statistical analysis

The experiment was carried out in a completely randomised design (CRD) with each treatment in triplicate. The data were run through SAS® Studio. Treatment means were subjected to a one-way ANOVA, and significant differences among treatments were compared using HSD test at a 5% significance level. Percentage data was subjected to arcsine transformation prior to analysis.

Results and discussion

Initially, ethanolic monoterpene served as the starting material for encapsulation, since thymol and limonene are highly soluble in organic solvents such as ethanol, but not in water. Similarly, Min *et al.* (2021) loaded thymol dissolved in ethanol into MOFs known as porous coordination networks. However, ethanol could only be partially loaded in porous solids, which decreased the amount of encapsulated monoterpene. Hence, pure monoterpenes were then used due to distinct competitive adsorption between monoterpenes and ethanol in the porous solids. The release of ethanol may also be undesirable during postharvest management for safety reasons, as ethanol vapours may be flammable.

Loading of ethanolic monoterpenes at room temperature

A larger amount of monoterpenes than ethanol was loaded in both ZIF-8 and UiO-66-$(COOH)_2$ (Fig. 2). The competitive adsorption between monoterpenes and ethanol was more evident in zeolite compared to ZIF-8 and UiO-66-$(COOH)_2$. The hydrophilic nature of zeolite caused its greater affinity to highly polar alcohols like ethanol. Most zeolites are hydrophilic crystalline aluminosilicates and aluminium-deficient zeolites with low hydroxyl content become hydrophobic. Moreover, its hydrophilicity also enhanced the adsorption of hydrophobic molecules, like thymol and limonene, by creating a high surface concentration of monoterpenes and facilitating interactions with the pore surface. On the other hand, most hydrophobic zeolites are reluctant to adsorb alcohols and other polar molecules (Halasz *et al.*, 2002).

Concerning the MOFs, UiO-66-$(COOH)_2$ encapsulated a larger amount of thymol and limonene than ZIF-8. Among the porous solids, a larger amount of thymol was loaded in UiO-66-$(COOH)_2$ than in ZIF-8 and zeolite. UiO-66 may act as either a hydrophobic or hydrophilic adsorbent, which alters the adsorption of polar and non-polar molecules. With the presence of more polar molecules, like ethanol, UiO-66-$(COOH)_2$ activated its hydrophilic nature to both thymol and ethanol. In contrast, it was not efficient for UiO-66-$(COOH)_2$ to encapsulate a mixture of non-polar limonene and a highly polar molecule like ethanol.

Moreover, low temperatures, especially during synthesis of UiO-66-$(COOH)_2$, render its structure hydrophilic (Jajko *et al.*, 2022). Encapsulation was carried out at room temperature, which may have promoted more efficient loading of either thymol or limonene in UiO-66-$(COOH)_2$ than in ZIF-8. Higher limonene encapsulation efficiency was obtained in hydrophilic porous solids, like zeolite and UiO-66-$(COOH)_2$, compared to the highly hydrophobic ZIF-8.

Regardless of the monoterpenes + EtOH solution, a larger amount of thymol was loaded than limonene. Some of the major driving forces influencing diffusion of monoterpenes to porous solids are the vapour pressure and polarity of volatile terpenoids, and the interaction between structural compositions (Liu *et al.*, 2019; Ibáñez *et al.*, 2020). At room temperature (around 25 °C), thymol has a higher vapour pressure (8.5×10^{-5} bar) than limonene (4.1×10^{-5} bar) (Siddiqui *et al.*, 2021). Thymol is considered to be more polar to a certain degree, while limonene is a less polar

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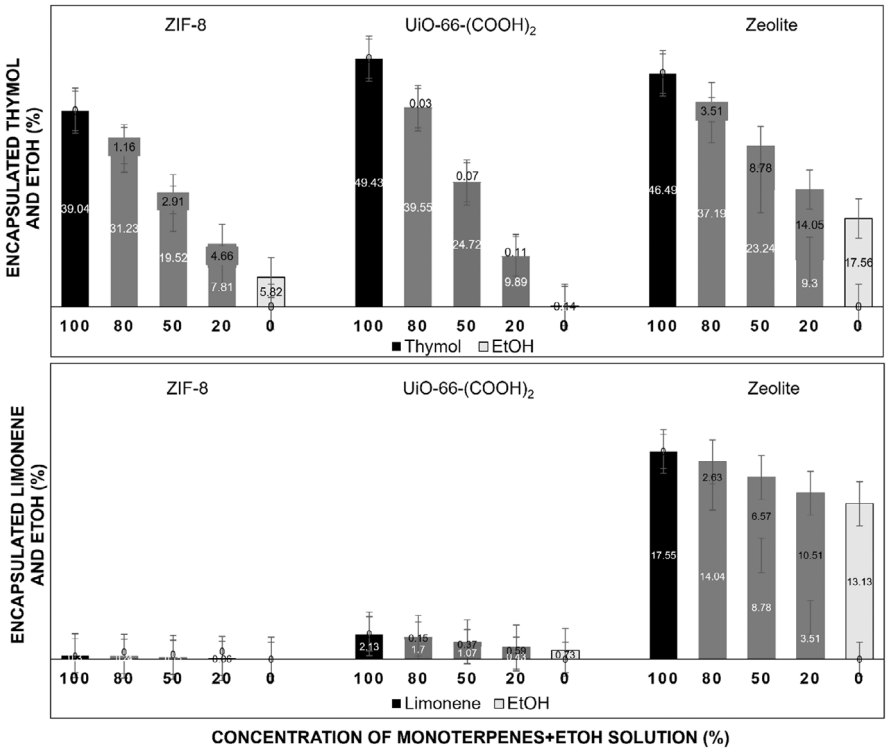

Figure 2 Encapsulated thymol, limonene and EtOH (%) in MOFs and zeolite from varying concentrations of ethanolic monoterpene solution (thymol – w/v; limonene – v/v). Values are means ± SD. The amount of encapsulated monoterpenes and ethanol using 80%, 50% and 20% ethanolic monoterpene solution was determined only in reference to the encapsulation efficiency obtained using pure monoterpenes and ethanol. No actual measurement was conducted.

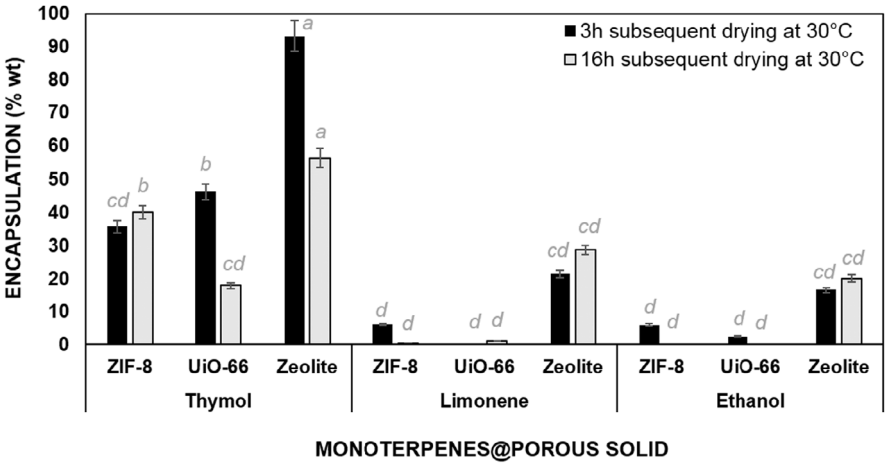

Figure 3 Encapsulation (% wt) of pure volatile fractions of thymol, limonene and EtOH in MOFs and zeolite. Monoterpenes and MOFs/zeolite were first heated to 60 °C then washed with EtOH before subsequent drying at 30 °C for 3 or 16 h. Letters indicate HSD at 5% level of significance. Each point represents the mean of three replicates.

to non-polar monoterpene. Liu *et al.* (2019) reported that more polar ester-type fragrances were adsorbed on polar hydroxyl-functionalised UiO-66 than the typical UiO-66. The formation of hydrogen bonds between polar MOFs and thymol enhanced encapsulation efficiency.

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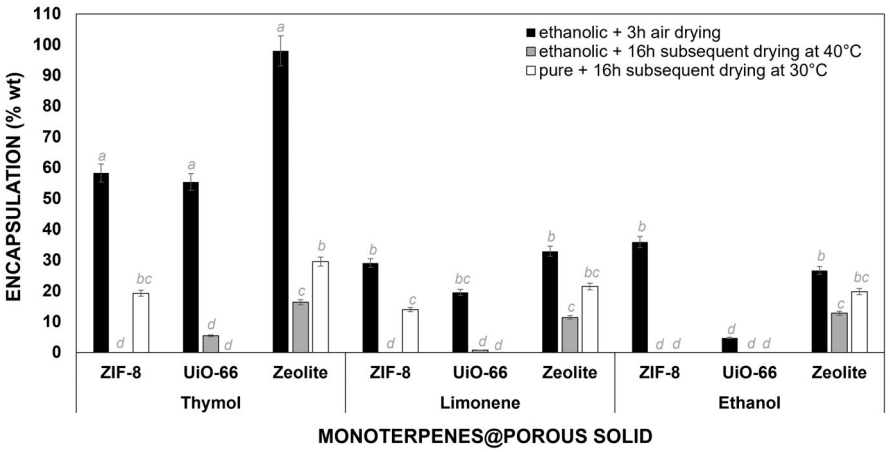

Figure 4 Encapsulation (% wt) of pure and ethanolic monoterpenes in MOFs or zeolite. Monoterpenes@porous solids were first loaded at 80 °C for 5 days then washed with EtOH before subsequent drying. Letters indicate HSD at 5% level of significance. Each point represents the mean of three replicates.

Vapourisation and diffusion of pure monoterpenes at 60 °C

As for the previous encapsulation protocol, a larger amount of thymol and limonene than ethanol was loaded in the MOFs, with more thymol loaded than limonene. High encapsulation efficiency was obtained even with only an initial 1:1 unit ratio of pure monoterpenes and porous solids used for encapsulation. A maximum of 46% and 93% of thymol was loaded in UiO-66-$(COOH)_2$ and zeolite, respectively (Fig. 3). The encapsulation efficiency of thymol@UiO-66-$(COOH)_2$ was almost the same as with the previous protocol, but almost doubled for thymol@zeolite. Liu *et al.* (2019) found that the presence of the hydroxyl group in UiO-66 enhanced the affinity of MOFs to aromatic compounds. UiO-66-$(COOH)_2$ had a hydroxyl group in the linker, compared to ZIF-8.

The encapsulation of volatile fractions of pure monoterpenes in MOFs and zeolite was facilitated by heating to 60 °C for 16 h in a tightly closed glass container without continuous stirring. Vapourisation of both thymol and limonene occurred with prolonged exposure to high temperature, which then led to the trapping of volatile fractions in the porous solids due to the increased thermal energy in the system. At high temperature, vapour pressure was high, facilitating faster diffusion of both thymol and limonene in the porous solids.

Subsequent drying was initially done to remove any traces of ethanol in the monoterpenes + MOFs/zeolite obtained during washing immediately after heating to 60 °C. However, prolonged subsequent drying at 30 °C for 16 h not only led to faster evaporation of ethanol, but also monoterpenes from MOFs, though not in zeolite. Hence, subsequent drying at 30 °C for 3 h was already enough to retain 36%–46% of thymol and 0%–6% of limonene in MOFs.

Contact diffusion of pure and ethanolic monoterpenes at room temperature

Generally, encapsulation of monoterpenes by solid-phase diffusion without any stirring, or heating at high temperature, was not efficient and yielded only 4%–26% and 14%–32% of loaded monoterpenes in MOFs and zeolite, respectively (data not shown). When the initial weight of pure thymol was doubled, it resulted in almost a double quantity of loaded thymol in ZIF-8 and UiO-66-$(COOH)_2$ after 2 days. However, the encapsulation percentage decreased when EtOH was added to pure monoterpenes. Two-day contact diffusion almost yielded the same encapsulation efficiency as that of the 7-day period, hence the 24–48 h diffusion process was already enough.

Loading of pure and ethanolic monoterpenes at 80 °C

Generally, high temperatures can increase the adsorption rate due to the increased thermal energy of the system. However, at very high temperatures combined with a prolonged encapsulation period, the loading capacity of MOFs or zeolite for certain monoterpenes may decrease due to desorption of initially adsorbed monoterpenes, or thermal degradation of the porous solid.

Encapsulation of pure monoterpenes in MOFs or zeolite through contact diffusion at 80 °C for 5 days was a less efficient process than the gaseous exchange at 60 °C for 16 h. Liédana *et al.* (2012) reported that

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ex situ prolonged contact of caffeine with ZIF-8 at 80 °C for about 3 days resulted in higher encapsulated caffeine.

For post-treatments, air-drying of the monoterpene@porous solid at room temperature for 3 h resulted in higher encapsulation than with drying at 40 °C for 16 h (Fig. 4). The observed difference was attributable to the temperature used and the drying time. With prolonged exposure at 40 °C, both thymol and ethanol evaporated from the porous solids faster due to the relatively high temperature. There could also have been an increase in the vapour pressure of thymol under these conditions. Hence, when the monoterpene@porous solid was subjected to an already prolonged heating time (5 days at 80 °C), further drying at 40 °C for 16 h was not necessary.

Comparison of encapsulation protocols using pure monoterpenes

Even with a 1:1 ratio of monoterpenes and porous solids as the starting material for encapsulation, vapour diffusion at 60 °C with post-treatment drying at 30 °C yielded a higher encapsulation efficiency of 36% and 46% for thymol@ZIF-8 and thymol@UiO-66-$(COOH)_2$, respectively (Table 1). On the other hand, limonene exhibited encapsulation efficiency of 6% in ZIF-8 and 21% in zeolite.

A high encapsulation efficiency of 39% for thymol@ZIF-8 and 49% for thymol@UiO-66-$(COOH)_2$ was obtained with 16 h continuous stirring of pure monoterpenes at room temperature due to the higher initial weight or volume of pure monoterpenes than porous solids.

A larger amount of thymol was loaded than limonene in all the encapsulation protocols. Thymol has a higher molecular weight and is more polar than limonene. These properties influenced the impregnation of thymol to interact directly with the surface of the porous solids through hydrogen bonding, which led to stronger adsorption. In contrast, limonene is less polar and has a low molecular weight, which likely interacted with the interior of the porous solids.

Other than molecular weight and polarity, the change in vapour pressure when subjected to 60 °C also influenced monoterpene loading. The high thermal energy conditions brought about by encapsulation at 60 °C favoured the vapourisation of monoterpenes. A subsequent increase in vapour pressure then facilitated faster diffusion of both thymol and limonene in the porous solids. At 60 °C, the vapour pressure of thymol and limonene is 103 and 1515 Pa, respectively (Stull, 1947; NIST). Despite having a higher vapour pressure than thymol, limonene was not loaded efficiently in the porous solids.

Validation of the optimised loading protocol

There was more than a threefold difference in the amount of thymol and limonene loaded in the porous solids (Table 2). In the post-encapsulation steps, the additional hour of subsequent drying was used mainly to ensure that the monoterpene@porous solid was free

Table 2 Validation of encapsulation of monoterpenes in MOFs or zeolite through vapour diffusion

		Encapsulation (% wt)	
		Duration (h) of subsequent post-drying at 30 °C	
Monoterpene	**Porous Solid**	**3 h**	**4 h**
Thymol	ZIF-8	36 ± 4.3	58 ± 5.0
	UiO-66-$(COOH)_2$	46 ± 2.0	19 ± 6.3
	Zeolite	93 ± 6.2	66 ± 12.2
Limonene	ZIF-8	6 ± 0.9	18 ± 4.5
	UiO-66-$(COOH)_2$	0 ± 0	3 ± 1.5
	Zeolite	21 ± 1.2	28 ± 2.3

Table 1 Comparison of encapsulation efficiency (% wt) using pure monoterpenes

	Encapsulation (% wt)					
	Thymol			Limonene		
Encapsulation treatment	**ZIF-8**	**UiO-66-$(COOH)_2$**	**Zeolite**	**ZIF-8**	**UiO-66-$(COOH)_2$**	**Zeolite**
16 h-stirring at room temperature + 3 h-drying at 30 °C	39 ± 7.0	49 ± 6.5	47 ± 7.6	0 ± 0.1	2 ± 0.4	18 ± 1.2
16 h-vapour diffusion at 60 °C + 3 h-drying at 30 °C	36 ± 4.3	46 ± 2.0	93 ± 6.2	6 ± 0.9	0 ± 0	21 ± 1.2
16 h-vapour diffusion at 60 °C + 16 h-drying at 30 °C	40 ± 7.0	6 ± 0.5	56 ± 2.3	0 ± 0	1 ± 1.9	29 ± 7.5
5 d-contact diffusion at 80 °C + 16 h-drying at 30 °C	19 ± 4.3	0 ± 0	30 ± 2.3	14 ± 0.7	0 ± 0	21 ± 0.6

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of ethanol, which could possibly be achieved after washing. Four-hour subsequent drying increased limonene loading in all the porous solids and thymol in ZIF-8. Hence, the optimised protocol included the vapour diffusion of pure monoterpenes in porous solids at 60 °C with a post-treatment of subsequent drying at 30 °C for 4 h.

The thymol encapsulated using the optimised protocol was used in the following experiments on sustained release and determination of antifungal activity, since the encapsulation experiments revealed that a larger amount of thymol was loaded than limonene. Moreover, preliminary experiments on sustained release of both thymol and limonene also showed that thymol had higher release concentrations than limonene (data not shown).

Sustained release of volatile thymol from MOFs/zeolite

Three-day enclosure resulted in the build-up of volatile thymol in the headspace reaching a maximum release of 2250 μg/L and 1500 μg/L of volatile thymol for pure thymol and thymol@zeolite, respectively (Fig. 5). Thereafter, opening the container every day before 1 h of headspace gas sampling resulted in a decrease in the quantity of volatile thymol released. There was a continuous release of volatile thymol from porous solids for 11 days at 25 °C, with release concentrations decreasing over time, or remaining at almost the same level. The sustained release reached equilibrium within 1 h (data not shown).

Cometa *et al.* (2022) and Liu *et al.* (2019) also reported that thymol was released in a sustained manner from zeolite 4A and UiO-66-NH_2, respectively, with decreasing release rates over time. However, in contrast with the study of Cometa *et al.* (2022) on thymol loading in zeolite 4A by grinding, XRD patterns showed that thymol was well-encapsulated in MOFs and zeolite, as indicated by the absence of thymol crystals in the diffractograms (Fig. 6).

Compared to loaded thymol in porous solids, there was a rapid release of the readily available pure thymol, which was more quickly diffused into the incubation container. The higher volatility of pure thymol can be attributed to its high vapour pressure, but it still remained in solid crystalline form during the incubation period at 25 °C. The release of volatile thymol from porous solids, on the other hand, was lower than that of pure thymol. The porous solids limit the vapour pressure, since thymol was adsorbed on the surface of the porous solids as condensed molecules. The headspace gas measurement was consistent with the estimated vapour pressure extrapolated from a mathematical model comprising Antoine parameters (Stull, 1947; NIST).

The type of framework and the functional groups present in the framework affects the release of thymol. There was a higher release of thymol from UiO-66-$(COOH)_2$ than ZIF-8 for 6 days, but a slower release was observed days after. The smaller pore size (approximately 0.6 nm) of UiO-66-$(COOH)_2$ might have resulted in the slow release of thymol in the latter

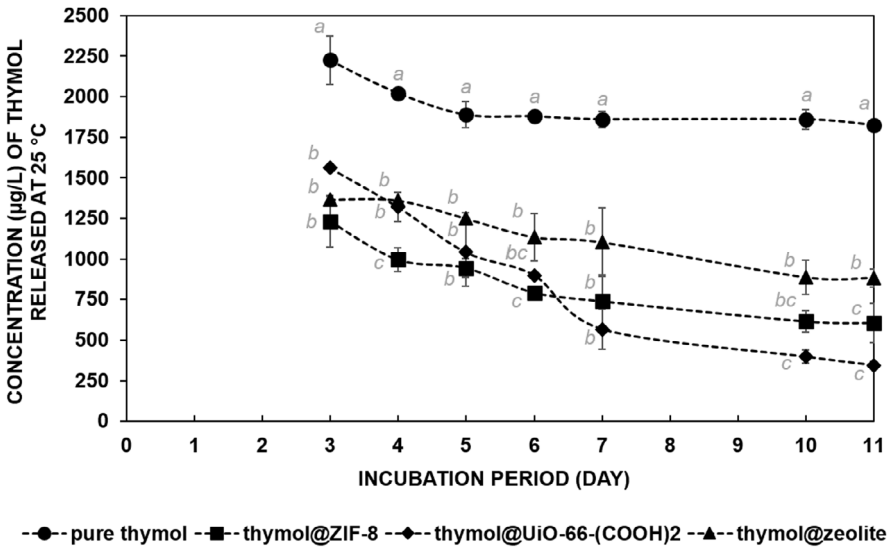

Figure 5 Concentration (μg/L) of volatile thymol released from MOFs or zeolite during *in vitro* storage at 25 °C. Letters indicate HSD at 5% level of significance. Each point represents the mean of two replicates.

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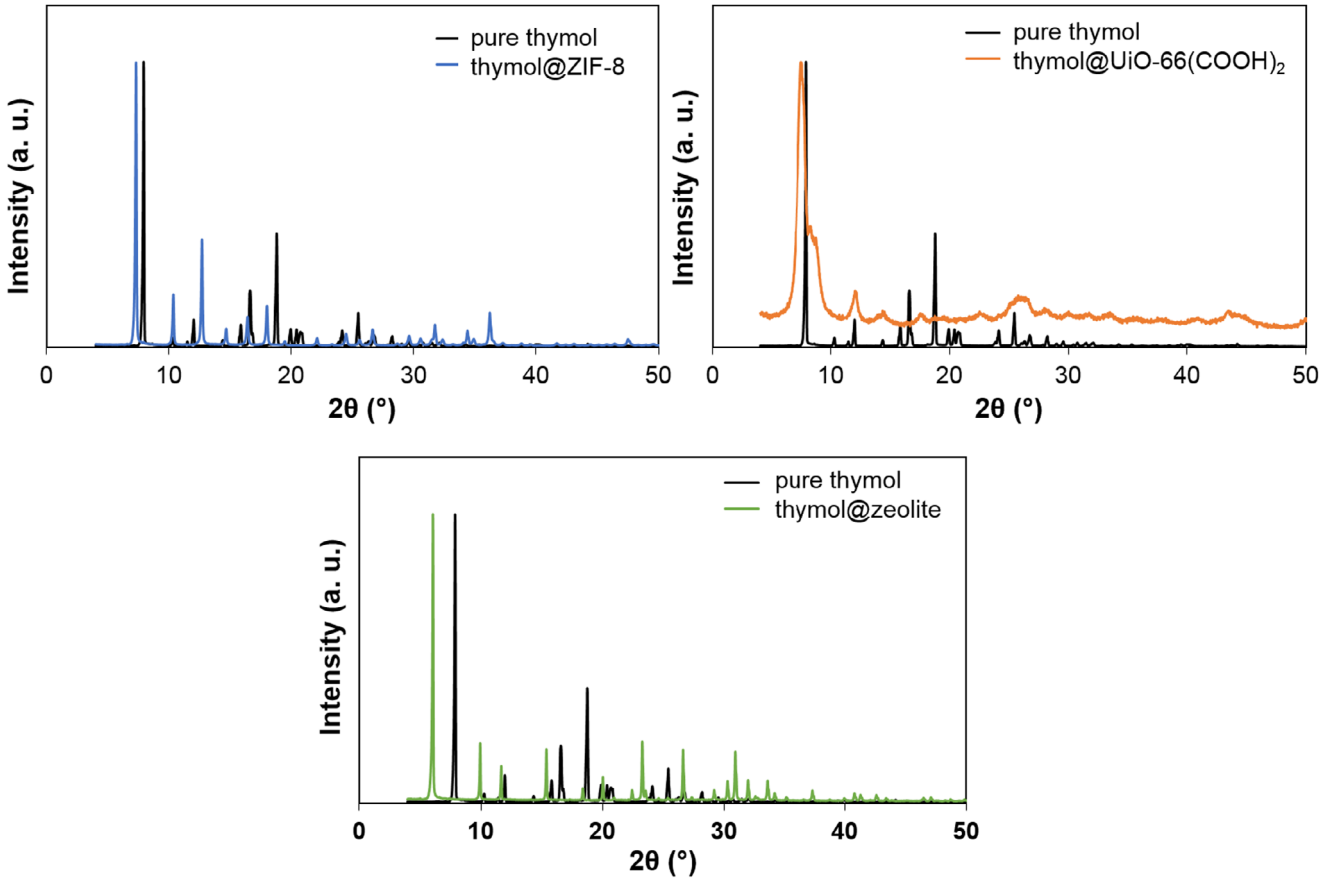

Figure 6 XRD patterns of pure thymol and thymol loaded in MOFs and zeolite after encapsulation.

part of the incubation period. Sheta *et al.* (2018) reported that smaller particle sizes of MOFs lead to an increase in specific surface area, which then enhances antibacterial activity.

Growth inhibition at 25 °C

The sustained release of volatile thymol from the porous solids slowed down the growth of *C. musae* by up to 6 days at 25 °C (Fig. 7), which was 2 days longer than those treated without thymol. The volatile thymol was released continuously even beyond the period when the fungus had already reached its maximum growth after a week of incubation. Li *et al.* (2022) reported that thymol was released from cyclodextrin-MOFs for 35 days. The sustained release of thymol allowed its exposure to the fungal cells for a longer period.

Potential growth inhibition was more evident during the initial period of incubation, which coincided with the largest amount of volatile thymol released into the headspace. A maximum of 40% inhibition was observed in thy@UiO-66-$(COOH)_2$ even with lower volatile thymol released compared to thymol@zeolite, and even with pure thymol. The comparative advantage of volatile thymol released from UiO-66-$(COOH)_2$ lasted for 5 days. There was not much difference between thymol released from ZIF-8 and zeolite except for the third day of incubation.

The structural framework of UiO-66-$(COOH)_2$ was likely dissolved during the encapsulation process (Fig. 6), resulting in the dissolution of zirconium linkers, which could also have an indirect inhibitory effect against *C. musae*. Abdelhamid & Mahmoud (2023) reported that copper oxide MOFs alone embedded into carbon (CuO@C) exhibited increased inhibition zones of postharvest pathogens such as *Alternaria alternata*, *Fusarium oxysporum*, *Penicillium digitatum* and *Rhizopus oryzae*.

Thymol was more effective in slowing down the growth of *C. musae* when it was initially present in volatile form as released from MOFs or zeolite than in solid crystalline form when not encapsulated. The desirable effect was evident in porous solids even with

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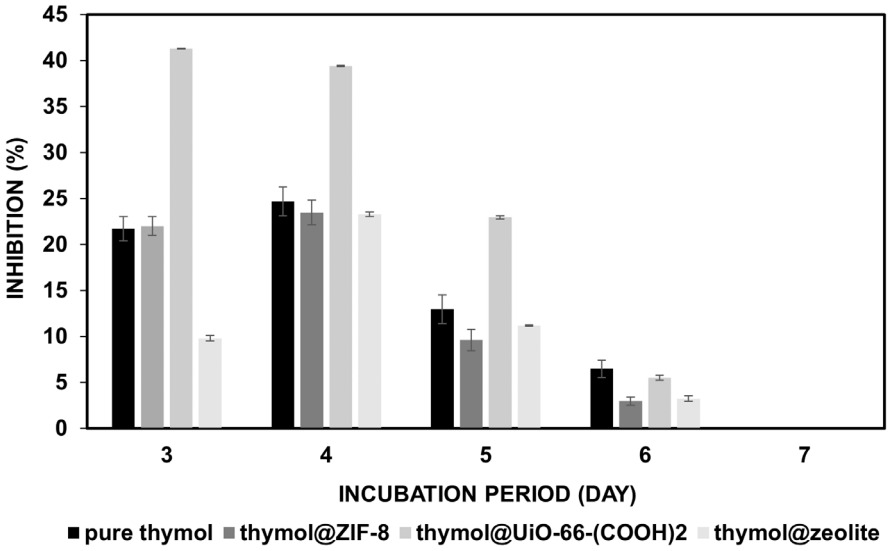

Figure 7 Growth inhibition (%) of *C. musae* exposed to thymol encapsulated in MOFs or zeolite, then incubated at 25 °C. There was no growth inhibition in the treatment without thymol. Values are means ± SD. Each point represents the mean of three replicates.

only a small quantity of thymol released. An increase in surface area provided by MOFs or zeolite and their porous nature resulted in high contact interaction between the fungus and condensed thymol, hence improved antifungal efficiency. Thymol can easily penetrate fungal cell walls and may reach the cytoplasm, where it can interact with and disrupt fungal cellular processes. In contrast, when thymol was in pure solid form, its vapourisation was very slow, which might limit its potential maximum inhibitory interaction against *C. musae*.

The effect of thymol released from porous solids has also been studied in the control of foodborne pathogens. Similar to this study, the sustained release of thymol loaded in Zn@MOF resulted in the inhibition of *E. coli* O157:H7 growth, without an exponential growth phase 24 h after incubation (Wu *et al.*, 2019b).

Conclusion

In all encapsulation protocols, a larger amount of thymol was loaded in porous solids compared to limonene. Vapour diffusion at 60 °C for 16 h, followed by post-drying at 30 °C, was efficient for loading pure thymol or limonene in a 1:1 ratio with porous solids. This resulted in a substantial encapsulation efficiency of 36% and 46% for thymol when loaded in ZIF-8 and UiO-66-$(COOH)_2$, respectively.

A slight increase in encapsulation efficiency to 39% and 49% for thymol loaded in ZIF-8 and UiO-66-$(COOH)_2$, respectively, was achievable with a higher initial weight or volume of pure monoterpenes and loading under continuous stirring for 16 h at room temperature.

The encapsulation of pure monoterpenes during a 5-day loading period was less efficient even with higher temperature, such as 80 °C. Furthermore, subsequent drying at higher temperature and for longer durations was not necessary.

The sustained release of volatile thymol from porous solids slowed down the growth of *C. musae* up to 6 days at 25 °C. A maximum of 40% inhibition was attained with 1560 μg/L of volatile thymol released from UiO-66-$(COOH)_2$, even the release concentration was lower than pure thymol. In addition, the release of volatile thymol was sustained even beyond the period of maximum fungal growth.

Further studies are essential to validate the full potential of MOFs as carriers of monoterpenes for *in vitro* postharvest fungal applications.

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Author contributions

Johnrell Zuniega: Investigation (lead); formal analysis (equal); methodology (equal); writing – original draft

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(lead). **Joël Grabulos:** Formal analysis (equal); methodology (equal); supervision (equal). **Marc Lebrun:** Formal analysis (equal); methodology (equal); supervision (equal). **Thibaud Aumond:** Formal analysis (equal). **Cécile Daniel:** Data curation (equal); formal analysis (equal). **Pierre Brat:** Conceptualization (equal); funding acquisition (lead); methodology (lead); project administration (lead); supervision (lead); writing – review and editing (lead). **David Farrusseng:** Formal analysis (lead); methodology (lead); project administration (lead); supervision (lead); writing – review and editing (lead).

Conflict of interest statement

The authors declare no conflict of interest.

Peer review

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Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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