Fabrication of γ-cyclodextrin-Based metal-organic frameworks as a carrier of cinnamaldehyde and its application in fresh-cut cantaloupes

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Abstract

Cinnamaldehyde (CA) is a promising antimicrobial agent for the preservation of fruits and vegetables due to its excellent antibacterial activity. The application is however, limited by its unstable and volatile properties. A biocompatible carbon dots hybrid γ-cyclodextrin-based metal organic framework (CD/MOF) was developed by the seed-mediated method to improve the encapsulation and sustained continuous release of CA. CD/MOF-0.5 exhibited a CA loading efficiency of 28.42% and a sustained release duration time of more than 15 days at 8 °C. The release kinetics results showed that the release behavior of CD/MOF-0.5 fitted well with the Korsmeyer-Peppas release kinetics model, indicating that its sustained release is mainly controlled by diffusion. Both the Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy analyses revealed that CD/MOF-0.5 and CA molecules were linked by hydrogen bonds. Due to the high sustained release performance, CA-loaded CD/MOF-0.5 considerably inhibited the growth of Escherichia coli, hence preventing the spoilage of fresh-cut cantaloupes. CD/MOF-0.5/CA treatment also maintained the qualities of the fresh-cut cantaloupes, prolonging their edibility to five days. This work provides a promising strategy for the prevention of spoilage in food industry.

Keywords:
γ-Cyclodextrin-based metal organic framework
Cinnamaldehyde
Sustained release
Antibacterial activity
Fresh cut

1. Introduction

Consumer demand for fresh-cut fruits and vegetables has continuously increased due to their convenience, safety, and nutritional quality (Adam et al., 2021). Fresh-cut fruits and vegetables have been observed to deteriorate more rapidly than intact ones leading to increased surface browning, textural breakdown, development of off-flavor, and microbial proliferation (Glicerina et al., 2022). Chemical fumigation agents such as SO2 and H2S are commonly used to enhance the storage and preservation of fresh-cut foods (Dou et al., 2021; Matias Ortiz et al., 2018). These chemical agents however, easily lead to the accumulation of chemical residues with a concomitant negative effect on the health of consumers and the environment (Rashid et al., 2021). Essential oils have hence been proposed as alternatives to conventional chemical agents because of their high biocompatibility and superior antibacterial activity (Yildiz et al., 2019). Nevertheless, their use is limited by their high volatility and high tendency to alter food quality when applied in high concentrations (Lin et al., 2021). This has necessitated the development of essential oil delivery systems that can stabilize and sustain the release of volatile essential oil components (Nair et al., 2022).

Many strategies have been developed for the encapsulation of essential oils. These include microcapsules, nano-emulsions, and carrier materials such as polymer particles, liposomes, solid lipid nanoparticles, mesoporous silicas spheres, and metal-organic frameworks (Jin et al., 2019; Balestri et al., 2021; Plati and Paraskevopoulou, 2022). Among the carrier materials, metal-organic frameworks, a new type of porous crystalline material constructed by the coordination of metal ions and organic ligands, have aroused great interest in catalysis, gas adsorption and separation, and drug delivery (Balestri et al., 2021; Chang et al., 2021; Rojas and Horcajada, 2020; Yang and Yang, 2020). Metal-organic frameworks show advantages over other porous materials in terms of their well-defined porous structure, large surface area, ease of synthesis, and structural diversity. Porous metal-organic framework carriers for incorporation of volatile antimicrobial essential oil components (such as...
thymol, trans-cinnamaldehyde oil, and carvacrol) have been reported to possess long-term sustained release (Gaamano et al., 2022; Liu et al., 2019; Wu et al., 2019; Yang et al., 2022). However, safety concerns about the application of the metal-organic framework in the food industry have been raised due to the presence of heavy metals such as Cd, Cu, and Zn in them (Pinar Gumus and Soyak, 2021). Therefore, cyclodextrin-based metal-organic frameworks may be a safer alternative as carriers for the incorporation of essential oils.

Cyclodextrins (CDs) are water-soluble, biocompatible, and cyclic oligosaccharides with a hydrophobic cavity and hydrophilic surface and have been used to encapsulate volatile active ingredients for controlled release through host–guest interactions (Liu et al., 2019; Zhang et al., 2019). CD-based metal-organic frameworks, derived from γ-cyclodextrin (γ-CD) and alkaline metal cations have become a rapidly developing hot research topic because of the ability of their extended porous frameworks to absorb guest molecules (Roy and Stoddart, 2021; Zhang et al., 2019). They comprise extended body-centered frameworks of (γ-CD)6 cubic units, which contain spherical pores located at the center of the cubes, and are interconnected by alkaline metal cations, forming both cylindrical and triangular channels (Roy and Stoddart, 2021). Their application is dependent on their size and shape, which are determined by the preparation method. Seed-mediated growth for the synthesis of crystalline is a versatile approach and the vast allure of this approach mainly originates from maintaining a degree of control over the size, shape, structure, and composition of crystals (Yang et al., 2014). The seeds of heterogeneous nucleation can be termed as crystallization ‘facilitators,’ in which case they can not only trigger MOF formation but also accelerate MOF growth (Doherty et al., 2014). Additionally, abundant functional groups exist on the surfaces of seeds, which make structural integration of a wide range of seeds and functional MOFs possible (Wang et al., 2017). Carbon dots have also attracted the interest of researchers in drug delivery and food preservation because they have unique surface area, multiple superficial functional groups, excellent water dispersity, low biological toxicity, and antibacterial activity (Sridharan et al., 2022; Zhao et al., 2022). However, the possibility of utilizing carbon dots as seeds in the synthesis of cyclodextrin MOF has not been examined.

In this study, N, S-doped carbon dots (CD) were for the first time used as seeds of heterogeneous nucleation to synthesize CD/MOF. Cinnamaldehyde (CA), a component of essential oil from cinnamon, with strong antibacterial activity, was selected to study the encapsulation capacity of the hybrid composites. The resultant hybrid composites were characterized by field emission scanning electron microscope (SEM), transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS). The encapsulation capacities and sustained release behaviors of CA-loaded MOF and CD/MOF, and the mechanism of interaction between CD/MOF and CA were then investigated. Finally, the antibacterial efficiency of CD/MOF/CA was assayed by testing their effects on the growth of E. coli and fresh-cut cantaloupes (Cucumis melon var. saccharinus).

2. Experimental section

2.1. Chemicals and materials

γ-Cyclodextrin was purchased from Aladdin Reagent Co. Ltd (Shanghai China). KOH and methanol were purchased from Tianjin Hengxing Chemical Reagent Co. Ltd (Tianjin, China). Cinnamaldehyde (CA; GC > 98%) and citric acid were bought from Macklin Reagent Co. Ltd (Shanghai, China). Thiourea was purchased from Xilong Chemical Co. Ltd (Foshan, China). Luria-Bertani (LB) solid medium was purchased from Sangon Biotech Co. Ltd (Shanghai, China). The violet red bile agar (VRBA) culture medium was purchased from Shanghai Shengsi Biochemical Technology Co. Ltd (Shanghai, China). Ultrapure water was obtained using a Milli-Q water purification system (Millipore, Bedford, MA, USA). All the other chemicals were of analytical reagent grade and were used as received without further purification. Cantaloupes (Cucumis melon var. saccharinus) were purchased at a local market in Xiangtan city on September 10th, 2021. Selected fruit was of uniform size and peel coloration. Non-woven bag (5.0 cm × 7.0 cm) were sealed by a vacuum sealer (14899, Deli, China). Escherichia coli strain ATCC: 25922 was kindly provided by the Department of Biotechnology and Food Engineering, Xiangtan University, Xiangtan, China.

2.2. Synthesis of CD/MOFs

The CD/MOF was synthesized by the vapor diffusion method described by (Qu et al., 2018) with minor modifications. γ-CD (324.0 mg) and KOH (112.0 mg) were fully mixed in a beaker, and fixed volumes (0, 0.25, 0.5, 1.0, and 2.0 mL) of 0.0328 g/mL CD (preparation method provided in Supplementary Information S1) added. The final volume of each mixture was adjusted to 10.0 mL with distilled water. After ultrasonic dispersion for 5 min, the clear solution was filtered through a syringe filter (0.45 μm PTFE membrane) into another beaker. Absolute ethanol (5.0 mL) was then added, and the beaker transferred into a sealed container containing 5.0 mL methanol. Vapor diffusion of methanol into the solution was conducted at 50 °C for 6 h in the closed system. 15.0 mL methanol was added dropwise into the solution by a peristaltic pump (HL-2B, Shanghai), and then incubated at room temperature for 1 h to trigger the precipitation of crystalline particles. The crystals were collected, washed with methanol, and vacuum dried at 45 °C for 6 h. The resultant crystals were denoted by CD/MOF-X (X represents the volume of the added CD), such that CD/MOF-0 is pure MOF crystals.

2.3. Measurement of the loading capacity of CA

CA was encapsulated in CD/MOF-X by the soaking method (Surendhiran et al., 2022). Briefly, a total of 50.0 mg of CD/MOF-X was dispersed into 0.5 mL of CA over a period of 12 h with oscillation. The resultant crystals were washed twice with absolute ethanol to remove residual CA, and the CA-loaded samples vacuum dried for 3 h at 38 °C. CA loading capacity was then measured by gas chromatography (GC) using a GC-7900 (Techcomp, USA) (Hu et al., 2021). GC was conducted through a DB-1701 column (30 m × 320 μm × 1 μm, Agilent) with a flame ionization detector at an inlet temperature of 280 °C. The column temperature started at 100 °C for 1 min and increased to 250 °C at a rate of 30 °C/min and then held constant for 1 min. 10.0 mg of the CA-loaded samples were fully dissolved into 1.0 mL distilled water with continuous ultrasonic mixing for 30 min, and subsequently treated with 4.0 mL ethyl acetate for the extraction of CA. The supernatants were collected for further GC analysis and the amount of extracted CA was calculated from a standard curve. Loading percentage was then determined from the formula:

\[
\text{Loading percentage (\%) = } \frac{\text{Extracted CA}}{\text{Weight of CA complex}} \times 100\%
\]
analyzer (TGA/DSC1/1600, Mettler-Toledo, Switzerland), with a temperature range of 30–800 °C, at a heating rate of 20 °C/min under the airflow. XPS spectra were recorded on a Thermo Scientific K-alpha X-ray photo-electron spectrometer equipped with an Al Kα X-ray source (1486.6 eV).

2.5. CA sustained-release profiles and release kinetics at different temperature

The release of encapsulated CA from CD/MOF-0.5 was determined by the method previously described (Zhang et al., 2019). Headspace calibration curves were established using five fragrance concentrations, 0.1, 0.5, 1.0, 2.0, and 4.0 μL in a 20.0 mL headspace bottle. Additionally, 10.0 mg of CA-loaded samples were sealed in a 20.0 mL headspace bottle, respectively and stored at 8 and 28 °C, respectively. The CA released in the headspace bottle was completely extracted by HS-SPME (50/30 μm DVB/ CAR/PDMS, Supelco) at various time intervals, and its content measured by GC analysis. The percentage release of fragrance was determined by the formula;

\[
\text{Release percentage (\%) = } \frac{x_1 + x_2 + \ldots + x_n}{x_0} \times 100\%
\]

where \(x_i\) (\(i = 1, 2, \ldots n\)) is the extracted CA content at each time interval and \(x_0\) is the total CA content measured as described in section 2.5.

CA release profiles were fitted into four mathematical models namely, zero – order (3), first – order (4), Higuchi (5), and Korsmeyer – Peppas (6) equations:

\[
y = ky + c
\]

(3)

\[
y = 1 – \exp(–kt)
\]

(4)

\[
y = k t^{1/2}
\]

(5)

\[
y = k t^n + c
\]

(6)

where \(y\) is the fraction of CA released to the total CA content at time \(t\), \(k\) is the release rate constant, and \(n\) the release exponent.

2.6. Assay for the antibacterial activity in vitro

The antibacterial activity of the MOF/CA and CD/MOF-0.5/CA were evaluated by the fumigation method (Shemesh et al., 2016). E. coli were cultured at 37 °C for 3 days and a suspension of the E. coli adjusted to \(1 \times 10^8\) CFU/mL. 100.0 μL of the E. coli suspension was spread on the surface of LB solid medium and the experimental Petri dishes placed in an inverted position. Free CA (4, 5, 6, 7 μL), MOF/CA (40, 50, 60, 70 mg), and CD/MOF-0.5/CA (40, 50, 60, 70 mg) were placed in separate sterile lids cut from 10 mL centrifuge tubes. The lids were then put at the center of the respective Petri dish lids, ensuring that there was no contact between the samples and the agar. Petri dishes with E. coli but no treatment constituted the control group (CK). All the Petri dishes were then cultured at 37 °C for 3 days, the colony growth monitored daily and photos taken.

2.7. Evaluation of the antibacterial activity on the fresh-cut cantaloupes

Purchased whole cantaloupes were soaked in sodium hypochlorite (200 mg/L) for 3 min, then thoroughly rinsed with distilled water. The whole cantaloupes were manually peeled and cut into 2.5 cm × 2.5 cm × 3.5 cm size (about 5 ± 0.2 g) using a sharp sterile knife. Samples were transferred into UV-sterilized fresh-keeping polypropylene boxes (15.0 cm × 10.5 cm × 5.5 cm), each containing 7 samples. 0.3 mL E. coli suspension (1 × 10^7 CFU/mL) was then spread over the samples and dried for 10 min. A non-woven bag (a special porous bag used to hold powder and allows release of CA) containing 500 mg MOF/CA or CD/MOF-0.5/CA was stuck in the center of the fresh-keeping box cover, and a filter paper with CA used in the control group (detailed information referred to Fig. S1). The above operations were completed in a clean, sterile workbench, and the fresh-keeping boxes incubated in a refrigerator set at 8 °C for 7 days. A sample was taken out of each box every day, put into a steril bag containing 45 mL sterile sodium chloride (0.85%) and ground into a homogenate. A 10-fold incremental serial dilution of the sample homogenate was prepared, and 1 mL aliquots plated on VRBA culture mediums. The plates were then incubated at 37 °C for 24 h, and the number of E. coli counted and expressed as \(\log_{10} CFU/g\).

2.8. Quality analysis of fresh-cut cantaloupes

Fresh-cut cantaloupes were prepared and treated according to the method described in section 2.7, the only difference being that they were not inoculated with E. coli suspension. The cantaloupes were then stored at 8 °C for 11 days, after which the samples were randomly taken out for quality determination. Detailed methods for their treatments and quality characterization including weight loss, firmness, color, pH, total soluble solid (TSS), titratable acidity (TA), vitamin C, and microbiological analyses are provided as Supplementary Information S2.

2.9. Statistical analysis

All experiments were conducted in triplicates, and the results recorded as mean ± standard deviation (SD). The statistical significance of difference between the experimental data was analyzed by the single-factor analysis of variance (ANOVA) (P < 0.05) using SPSS version 24.

3. Results and discussion

3.1. Preparation and characterization of CD/MOFs

The N, S co-doped carbon dots (CD) were utilized as seeds of heterogeneous nucleation to synthesize CD/MOF for the first time. The obtained CD seeds were dark green in colour (inset of Fig. S2A), spherical in shape and monodispersed (Figs. S2A and B). These properties are consistent with those reported by Qu et al. (2013). The seeds had characteristic absorptions at 231 and 327 nm in ultraviolet-visible absorption spectrum (UV-vis, Fig. S2C), which were attributed to the π→π* transition of C=C bonds and the n→π* transition of the carbonyl/amine functional groups on the surface of CD, respectively (Qu et al., 2013). The adsorptions at 550 and 595 nm were ascribed to the π→π* transition of C–C=C bonds and the n→π* of C=S and S=O, which are related to the doping of sulfur (Qu et al., 2013). The nitrogen- and sulfur-rich functional groups of CD were further verified by FTIR (Fig. S2D). Peaks at 1083 and 2056 cm⁻¹ of CD seeds were assigned to C-O, which are related to the doping of sulfur (Qu et al., 2013). The nitrogen- and sulfur-rich functional groups of CD were further verified by FTIR (Fig. S2D). Peaks at 1083 and 2056 cm⁻¹ of CD seeds were assigned to C=S and C-N bonds respectively, which further confirmed that nitrogen and sulfur successfully co-doped on the carbon dots (Qu et al., 2013; Yang et al., 2020).

The SEM images and particle size of CD/MOF with and without CD seeds are shown in Fig. 1A-E. The pure MOF without CD seeds displayed a typical cubic shape (Fig. 1A), which has previously been widely reported (Zhang et al., 2019). After addition of different amounts of CD seeds, the morphologies of the resultant CD/MOFs varied from the cubic shape to other polyhedron facets (Fig. 1B-E) and the sizes fluctuated from large to small and finally to large. Additionally, redundant CD seeds were found distributed on the surface of MOF (Fig. S4), which may be due to the participation of CD in the self-assembly of MOF, leading to the coordination of K+ and hydroxyl groups (Roy and Stoddart, 2021). In most cases, the CD contained multiple functional groups including –OH, –C=N, and –C=S whose presence were confirmed by the appearance of peaks at 3452, 2065, and 1083 cm⁻¹ in the FTIR spectrum of CD (Fig. S2D). These functional groups could provide extra coordination sites for the self-assembly of CD/MOF, thereby leading to the formation of a polyhedron shape (Roy and Stoddart, 2021).
After addition of CD seeds, a schematic illustration of the synthesis of CD/MOFs through the seed-mediated method was proposed as presented in Fig. 1a. Formation of the MOF crystals comprised three steps including the appearance of a nucleus by the self-assembly of $\gamma$-CD, growth and coagulation of the crystal nucleus, and aggregation of MOF (Qiu et al., 2018). When CD seeds were added, $\gamma$-CDs were easily adsorbed onto the surface of CDs due to the interaction between CD seeds and $\gamma$-CDs. Consequently, $\gamma$-CDs could be arranged in order of easiness, which could further accelerate the formation of the nucleus. Furthermore, the aggregation of MOFs was reduced because of the monodispersed and steric effect of the CD seeds, thus forming different sizes and shapes of CD/MOFs.

To understand how CD seeds participated in the formation of CD/MOF crystals, the functional groups of CD/MOF were analyzed by FTIR. For MOF (Fig. 2A), characteristic peaks covering 3000-3700 cm$^{-1}$ reflected the $\text{-OH}$ stretching vibrations. Peaks at 2929, 1638, 1415, and 1033 cm$^{-1}$ were assigned to the $\text{–CH}$ stretching vibration, vibration of water of hydration, $\text{–OH}$ plane bending vibration, and $\text{–C–O}$ stretching vibration, respectively (Hajra et al., 2021). Notably, after addition of CD seeds, a characteristic CD peak at 2065 cm$^{-1}$ ($\text{C–N}$ bonds) occurred in the CD/MOF (Fig. 2A), signifying that CD was involved in the synthesis of MOF (Yang et al., 2020). Characteristic MOF peaks persisted as well. With the amount of CD increased, the OH vibrations of the CD/MOFs blue shifted from 3394 to 3412 cm$^{-1}$, suggesting that there was hydrogen bonding between CD and $\gamma$-cyclodextrin. The presence of the peaks of both MOF and CD in CD/MOFs indicated that the combination of MOF and CD was successful. The XRD patterns of MOF (Fig. 2B) revealed the presence of some characteristic diffraction peaks including $2\theta$ of 5.6°, 13.2°, 16.9°, and 22.1°. The XRD pattern of CD/MOFs was similar to that of MOF, indicating that its crystalline structure was included in the CD/MOFs (Yang et al., 2020). However, no characteristic peaks of CD were found due to its lower loading and crystallization extent, a consequence of the great dispersion of carbon dots on MOF (Si et al., 2020).

The surface area and porosity of the MOF and CD/MOFs were determined by $\text{N}_2$ adsorption-desorption isotherms. Their typical isotherm exhibited a high $\text{N}_2$ uptake (Fig. 2C), thus validating the porous characteristics of these materials. The BET (Langmuir) surface areas and mean pore diameters of MOF and CD/MOFs are presented in Table S1. BET (Langmuir) surface areas of CD/MOFs were all markedly higher than those of MOF. On increasing the concentration of CD seeds from 0.25 to 0.5 mL, the surface area of the CD/MOF crystals increased from 65.9 (76.8) m$^2$/g to 226.8 (261.6) m$^2$/g. The mean pore size of MOF was 2.60 nm, indicating that it was mesoporous (Mendoza et al., 2022). The pore size of CD/MOFs on the other hand, was estimated to be within the range of 1.67–1.79 nm, suggesting that it had a microporous structure (Mendoza et al., 2022). The larger surface area and lower pore diameter of the CD/MOFs could be attributed to the presence of CD. Compared with CD/MOF-0.5, CD/MOF-2 presented a lower BET (Langmuir) surface area, which was mainly because CD occupied the interior space (Wang et al., 2021), but no differences in pore width distribution between CD/MOF-0.5 and CD/MOF-2 was observed. The thermal stability
of the MOF and CD/MOFs was also studied by TGA and the results are shown in Fig. 2D. The initial weight loss of all samples between the temperature range from 30 to 150 °C was due to evaporation of the adsorbed water and residual solvent molecules (Hajra et al., 2021). The MOFs with and without CD seeds started to decompose at 205 °C and the main mass loss occurred at 320 °C, which was related to the degradation of MOF crystals. However, with the addition of CD, the thermal stability of CD/MOFs decreased. This reduction may be explained by the decreased ordering of crystallization due to the aggregation of CD and the associated blocking of the crystallization process (Qiu et al., 2018).

3.2. Enhanced encapsulation of CA

The CA loading percentages of MOF with and without CD seeds were measured (Fig. 3A). The loading percentages of the different CD/MOFs for CA were determined to be 20.25%, 28.42%, 27.17%, and 29.9%, which were significantly higher than that of pure MOF (18.02%). The loading capacities may be closely related to their porosities and surface area (Trushina et al., 2022). As shown in Table S1, the BET surface area of CD/MOF-0.5 was approximately 9.4 times broader than that of MOF. This implied that the addition of CD seeds could improve the encapsulation efficiency of CD/MOFs by increasing their surface area and porosity. There was no significant difference in the CA loading percentages of CD/MOF-0.5, CD/MOF-1, and CD/MOF-2, which might have been due to the combination of CD and CA (Farshbaf et al., 2018). Based on these results, CD/MOF-0.5 was selected for subsequent experimental studies.

3.3. Interaction between CA molecules and CD/MOF-0.5

The interaction between CA molecules and CD/MOF-0.5 was studied by FTIR, XRD, TGA, and XPS analyses. Characteristic peaks of CA at 1626 and 1676 cm⁻¹ were observed (Fig. 3B), which belonged to the C=C double bond and C=O stretching vibration, respectively (Yildiz et al., 2019). It was noticed that CA experienced some changes, for example, peaks within the range of 500–1250 cm⁻¹ significantly reduced or totally disappeared. This may be because the hydrophobic CA molecules preferentially entered the hydrophobic cavity of the cyclodextrin, hence the characteristic absorption band of phenyl was covered (Xiao et al., 2019). It may also indicate that the phenyl group of the CA entered the cavity of the γ-cyclodextrin. Interestingly, the peak of C=O originally located at 1676 cm⁻¹ shifted to 1675 cm⁻¹, which usually suggests the formation of hydrogen bonds between CA and the matrix (Ke et al., 2019). The same C=O peak at 1676 cm⁻¹ disappeared in MOF or CD/MOF-0.5, indicating that CA had formed complexes with both MOF and CD/MOF-0.5 (Yildiz et al., 2019). The XRD patterns of the MOF, CD/MOF-0.5, and CA-loaded samples are presented in Fig. 3C. The appearance of new peaks at 13.0° after loading the CA molecules indicated that CA may have participated in the loading process and hence altered the original crystal structure of both MOF and CD/MOF-0.5. Furthermore, the characteristic diffraction peak values of the CA complex at 5.6°, 13.2°, 16.9°, and 22.1° were higher than those of MOF and CD/MOF-0.5. This might be ascribed to the higher crystallization of MOF and CD/MOF-0.5 induced by the uniformly dispersed CA (Zhang et al., 2020). The thermal stabilities of CD/MOF-0.5 with and without CA were studied using TGA. As shown in Fig. 3D, CA was only thermally decomposed between 104 and 500 °C with an observed weight loss of 100%. Compared with CD/MOF-0.5, CD/MOF-0.5/CA presented the highest weight loss at 250 °C due to the release of CA, indicating that CA was successfully loaded into the MOF. Furthermore, majority of the CA was decomposed at about 220 °C, whereas MOF/CA and CD/MOF-0.5/CA presented a gradual loss of CA until 300 °C. This suggested that MOF and CD/MOF-0.5 could delay the thermal evaporation and decomposition of the CA. All these pointed to the fact that MOF and CD/MOF-0.5 could increase the stability of CA by preventing its thermal evaporation and decomposition.
To further clarify the interaction between CD/MOF and CA, the surface chemical compositions of MOF, CD/MOF-0.5, and CD/MOF-0.5 loaded with CA were analyzed by XPS (Fig. 4). From the results O1s, K2s, K2p, C1s of MOF and N1s, S2p of CD were observed in the survey spectrum of CD/MOF-0.5 (Fig. 4A and B), indicating that CD was bound to the MOF-0.5 through some kind of interactions. By comparing the high-resolution XPS for C1s (Fig. 4D, E) and O1s (Fig. 4G and H) chemical states between the MOF and CD/MOF-0.5, new peaks of C-N/C-O (285.9 eV) and C-N (288.7 eV) were observed in CD/MOF-0.5. This indicated that as a seed, CD participated in the formation of CD/MOF-0.5 (Qu et al., 2013), which is consistent with the FTIR analysis results. The peak (162.9 eV) of the S2p was assigned to S-K bond (Fig. S4), thus it was reasonable to presume that S in CD was coordinated to K+ in MOF (Ke et al., 2019). Compared with the C1s (Fig. 4E, F) and O1s (Fig. 4H and I) spectra of CD/MOF-0.5, CD/MOF-0.5/CA retained its characteristic peaks, which suggested that the main structure of CD/MOF-0.5 persisted even after adsorption of CA. But their binding energies and relative content (Table S2) varied significantly after the adsorption of CA, implying that interactions occurred in the process of adsorbing CA. The binding energy of O1s in CD/MOF-0.5/CA exhibited an obvious shift to low binding energy compared to that in CD/MOF-0.5 (Fig. 4H and I), suggesting that C-O, O-H, and C=O interactions occurred between the CA and CD/MOF-0.5 (Yang et al., 2020). These results further suggest that the prepared CD/MOF-0.5 had a high adsorption performance for CA.

3.4. CA release behavior

To evaluate the capability of CD/MOF-0.5 as carriers for the encapsulation and controlled release of CA molecules, the release profiles of free CA, MOF/CA, and CD/MOF-0.5/CA at 8 °C and 28 °C were measured. As shown in Fig. 5A, at 8 °C, free CA was rapidly released within 4 days, but all CA loaded in MOF/CA and CD/MOF-0.5/CA presented sustained-release profiles. The release rates were in the order of free CA > MOF/CA > CD/MOF-0.5/CA, indicating the superiority of CD/MOF-0.5 in the controlled release of CA. The ability of CD/MOF-0.5 to hold CA for a long period of time might be due to the formation of hydrogen bonds between CD/MOF-0.5 and the CA molecules (Liu et al., 2019). The sustained-release profiles of Free CA, MOF/CA, and CD/MOF-0.5/CA at 28 °C (Fig. S5A) displayed a similar trend to that at 8 °C, but the higher temperature increased the cumulative release of CA.

To better understand the CA sustained release kinetics and mechanisms, four mathematical models including zero–order, first–order, Higuchi, and Korsmeyer–Peppas models were employed at 8 °C (Fig. 5B–E) and 28 °C (Figs. S5B–E). The relative kinetic parameters and coefficient of determination (R²) are summarized in Table S3 and Table S4, respectively. At 8 °C, the experimental data of free CA was best suited for the first–order model in which the highest R² value (0.9699), and the CA release was mainly controlled by the concentration gradient (Salehi et al., 2022). The release profile of MOF/CA and CD/MOF-0.5/CA were all well-fitted by the Korsmeyer–Peppas model (R² > 0.9945), indicating that sustained release pattern was mainly controlled by diffusion. The “n” value in the Korsmeyer–Peppas equation depicts the diffusion mechanism. For n < 0.45, the release mechanism was Fickian diffusion; for 0.45 < n < 0.89, the diffusion mainly resulted in non–Fickian diffusion; and n > 0.89 was the skeleton dissolution mechanism (Binesh et al., 2021). As shown in Table S3, the
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diffusion index $n$, of both MOF/CA and CD/MOF-0.5/CA was greater than 0.45 but less than 0.89, indicating that the release behavior was controlled by non–Fickian diffusion. CD/MOF-0.5/CA showed similar CA release kinetics at 28 °C as at 8 °C (Figs. S5B–E and Table S4).

3.5. Antibacterial activity of CD/MOF-0.5/CA

*E. coli* was selected for evaluating the antibacterial activity of the prepared CD/MOF-0.5/CA. The effect of different amounts of CA, MOF/CA, and CD/MOF-0.5/CA on *E. coli* were examined. As shown in Fig. 6A, the *E. coli* inhibition zone for the pure CA-, MOF/CA-, and CD/MOF-0.5/CA-treated samples increased with increase in their amounts. The released CA accumulated in the Petri dish environment and at a certain minimum concentration, exhibited a growth inhibitory effect against the *E. coli*. Compared to free CA, the *E. coli* inhibition zone in Petri dishes treated with MOF/CA and CD/MOF-0.5/CA were much smaller at the beginning of the experiment (Fig. 6B and C). This was attributed to the low diffusion speed of CA from the MOF/CA and CD/MOF-0.5/CA to the enclosed microbial environment. Consequently, the limitation to the antibacterial capability of MOF/CA and CD/MOF-0.5/CA at the beginning of the experiment was the speed of release of CA (Jin et al., 2019). However, the *E. coli* inhibition zone of the free CA-treated samples steadily decreased with an increase in time, as opposed to those of MOF/CA- and CD/MOF-0.5/CA-treated samples which only decreased on the second day and remained constant on the third day. This is because CD/MOF-0.5/CA retained the CA and released it over a longer period of time, thus as CA was getting depleted from the free CA-treated samples (by day three, about 90% CA had been released), CD/MOF-0.5/CA continued to release CA beyond the second day (by day 3, only ~ 20% of total CA had been released by CD/MOF-0.5/CA-70 mg, for example). This demonstrates the effectiveness of CD/MOF-0.5/CA in inhibiting the growth of *E. coli* over a prolonged period of time. The encapsulation system, therefore, exhibited a sustained-release behavior to improve the duration and extent of inhibition on the growth of *E. coli* (Perumal et al., 2022). A similar phenomenon was previously described in which the inhibition of nanoencapsulation eugenol against bacteria was slightly lower than that of free eugenol (Jin et al., 2019). In the current study, the inhibition zone of the *E. coli* fumigated with CD/MOF-0.5/CA was larger than that fumigated with MOF/CA. This is because CD/MOF-0.5 has a better CA loading capability, thus it can preferentially be used to inhibit the growth of *E. coli*.

3.6. Effect of CD/MOF-0.5/CA on growth of *E. coli* in fresh-cut cantaloupes

The inhibitory effect of free CA, MOF/CA, and CD/MOF-0.5/CA on the growth of *E. coli* in fresh-cut cantaloupes was examined. The results are presented in Fig. 7. No *E. coli* were detected in freshly cut cantaloupes (0 day). In the early stages of treatment (1–3 d), the *E. coli* counts in free CA, MOF/CA, and CD/MOF-0.5/CA treated samples were significantly lower ($P < 0.05$) than in the control samples (CK). The antibacterial activity of free CA gradually weakened from the fourth day to the seventh day, which could be due to depletion of the available free CA (Fig. 5A). The antibacterial activity of MOF/CA was generally lower than that of CD/MOF-0.5/CA during the entire storage time. This might be because the latter has a stronger loading capability and higher sustained-release ability than the former. It should be noted that, on the seventh day, the antibacterial activity of CD/MOF-0.5/CA was significantly ($P > 0.05$) higher than those of CK, free CA, and MOF/CA, confirming the excellent sustained-release performance and strong

![Fig. 4. XPS, C1s, and O1s spectra of MOF (A, D, G), CD/MOF-0.5 (B, E, H) and CD/MOF-0.5/CA (C, F, I).](image-url)
antibacterial activity of CD/MOF-0.5/CA during the storage period. These findings strengthen our observation that CD/MOF-0.5/CA may be a promising antibacterial material for a long-lasting inhibition of the growth of \textit{E. coli} in fresh-cut cantaloupes.

3.7. Quality analysis of fresh-cut cantaloupes

The total bacterial counts on fresh-cut cantaloupe samples with or without fumigation treatment are displayed in Fig. 8. On day zero, the colony number was determined to be $0.782 \pm 0.019 \log_{10} \text{CFU/g}$ which may be attributed to the presence of endophytic bacteria that thrive inside plants (Glassner et al., 2015). Generally, throughout the experimental period, the total bacterial count in CD/MOF-0.5/CA-treated samples were significantly lower ($P < 0.05$) than in the CK samples.

Fresh-cut cantaloupes in which the total number of microbial colony counts were less than $4 \log_{10} \text{CFU/g}$ were considered fresh (Ji et al., 2017). On the 2nd day, the total bacterial count on CK sample was $4.1 \log_{10} \text{CFU/g}$, thus the cantaloupes had lost their edibility. Samples treated with free CA, and MOF/CA also lost their edibility on 4th and 2nd days respectively, but those treated with CD/MOF-0.5/CA maintained their edibility to the 5th day. Weight loss, $\Delta E$, and TA content of all fresh-cut cantaloupes increased throughout the storage time (Table S5). After the 5th day, the weight loss and TA contents of CD/MOF-0.5/CA-treated samples were significantly lower ($P < 0.05$) than those of the CK group. On the contrary, all samples showed a decrease in firmness, pH, TSS, and VC contents of fresh-cut cantaloupes during the treatment period. However, the firmness, pH, and TSS of fresh-cut cantaloupes treated with CD/MOF-0.5/CA were significantly

![Release profiles of free CA, MOF/CA, and CD/MOF-0.5/CA at 8 °C](A); CA release curves of free CA, MOF/CA, and CD/MOF-0.5/CA fitted using a zero-order (B), first-order (C), Higuchi (D), and Korsmeyer-Peppas model (E).
Fig. 6. Effects of different treatments on the growth of E.coli.
higher (P < 0.05) than those of the CK group (Table S5). There were no significant differences in the color index and VC content between CD/MOF-0.5/CA-treated samples and the CK samples (P > 0.05). The results also indicate that the total bacterial counts were positively correlated with weight loss, and negatively correlated with firmness and pH (Table S6). Un-treated cantaloupes which had high microbial growth demonstrated a faster rate of weight loss and decrease in pH. CD/MOF-0.5/CA slowed down microbial growth rate thus limited the loss of moisture and decrease in firmness. Our current findings suggest that CD/MOF-0.5/CA can strongly inhibit bacterial growth and maintain the quality of fresh-cut cantaloupes, which provides a promising strategy for the preservation of fresh-cut fruits and vegetables.

4. Conclusions

In summary, we have successfully synthesized CD hybrid MOF through the seed-mediated method. The synthesized CD/MOF-0.5 had an excellent porous structure that enabled it to encapsulate CA. CD/MOF-0.5 effectively controlled a sustained release of CA via H-bonding, and the release behavior fitted well with the Korsmeyer–Peppas release kinetics model, indicating that the sustained release was mainly controlled by diffusion. The CD/MOF-0.5/CA exhibited a strong and long-lasting antibacterial activity when tested against E. coli in vitro and on fresh-cut cantaloupes. It maintained the fruit quality, and prolonged the edibility of fresh-cut cantaloupes, suggesting that CD/MOF-0.5 as a carrier of cinnamaldehyde can be effectively applied in the preservation and storage of fresh-cut fruits and vegetables.

CRediT authorship contribution statement

Jinxin Che: Conceptualization, Methodology, Writing – review & editing, Funding acquisition, Project administration. Keqin Chen: Writing – original draft, Software, Data curation. Jaorao Song: Writing – original draft, Investigation, Data curation. Ying Tu: Investigation, Data curation. Okwong Oketch Reyimick: Writing – review & editing. Xiumei Chen: Supervision, Writing – review & editing, Funding acquisition. Nengguo Tao: Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.crfss.2022.10.025.

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