Synthesis of mesoporous silica post-loaded by methyl eugenol as an environment-friendly slow-release bio pesticide

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Salicylaldimine, furfuralimine and benzaldehyde imine were adopted to modify mesoporous silica (MCM) respectively denoted as Sal-MCM, Fur-MCM and Ben-MCM before loading methyl eugenol (Me) for pesticide delivery. Me was adsorbed by Schiff base mesoporous silica without destructing regular hexagonal pore structure verified by the characterization results. DSC result implied that Me in amorphous state which was distributed in the pores of the mesoporous silica. The loading content of Me-Sal-MCM, Me-Fur-MCM and Me-Ben-MCM 67.89%, 73.34% and 73.84% which was higher than Me-MCM without modification (67.35%). Because the electrostatic interaction and π-π interaction between Schiff base and Me strengthened the adsorption capacity of the carrier. And the electrostatic interaction played a more important role in interaction between Me and Schiff base modified mesoporous silica. As a result, Schiff base modified sustained release system also has significantly longer sustained release time with a sequence of Me-Sal-MCM > Me-Ben-MCM > Me-Fur-MCM in release speed in negative correlation with the electric potential sequence. The behaviors of their sustained release performance can be fitted by First order kinetic model before Schiff base modification. After modification, their sustained release behaviors were consistent with Korsmeyer-Peppas equation with non-Fickian diffusion mechanism indicating that main impact on the release process after modification was no longer mainly controlled by the difference of the concentration. Finally, the highest lure rate of the modified MCM (Me-Fur-MCM) equals to the 73% of the pure Me due to its highest BET surface area and strongest interaction with Me among the three Schiff base modified samples. Therefore, the environment-friendly slow-release bio pesticide with long service life was prepared to reduce the damage on the environment caused by pesticide.

Worldwide, more effective, safer detection and control systems for invasive insect pest management become more and more important. Phenyl propanoids are attractive to numerous species of Dacinae fruit flies. Among them, methyl eugenol (Me) (4-allyl-1,2-dimethoxybenzene) is a widely distributed natural plant product and originated from more than two hundred plant species found mainly in the tropical area such as anise, nutmeg, basil, blackberry essence, bananas, citrus and so on¹. Me is also used as a flavoring in many foods due to its low toxicity². For example, clove oil contains approximately 15% Me and is generally recognized as a safe (GRAS) compound by the U.S. Food and Drug Administration as a food additive³. Other benefits used as aromatherapy, fragrance in the perfume⁴, cosmetics⁵, toiletries and detergents⁶. Methyl eugenol has been used as an anesthetic⁷ even as towing insects in combination with insecticides⁸.

In southern China, agricultural production and the product export trade were severely damaged by Bactrocera dorsalis⁹. The traditional method of controlling this pest is the application of insecticide cover sprays. However, the usage of pesticide would affect the growth of the fruits and the pesticide remained on the fruits would also damage the health of human beings¹⁰. Therefore, Me is currently the most commonly used tephritid male attractant lure. Initially, wild Bactrocera dorsalis males were successfully controlled with Me-baited traps¹¹,¹².
Nevertheless, Me discomposes quickly in soil or water at room temperature with a short half-life in air which was around 5 hours according to previous report. Recently, replacement of liquid Me and insecticides with solid formulations has drawn great interests for convenience and worker safety. In previous work, the pH responsive Schiff base modified mesoporous silica was prepared for chlorpyrifos, triazolone and avermectin delivery which showed a high performance for adsorption and sustained release. In order to improve Me stability and prolong its service life, we proposed the Schiff base modified mesoporous silica sustained release system for essential oil sustained release. The interaction of the host/guest interaction and sustained release mechanism was also studied.

**Materials and Methods**

**Preparation of salicylaldimine, furfuralimine and benzaldehyde imine grafted on APTES.** According to the literature, 4.42 g of APTES, 2.44 g of salicylaldehyde and 100 mL of ethanol were added into a flask and refluxed at 95°C for 3 h. Ethanol was removed through rotary evaporation. 20 mL of dichloromethane was added, then the products washed with deionized water 3 times. The organic layer was extracted and standing for 12 h. Then the product was filtered to remove dichloromethane to attain salicylaldimine. The furfuralimine and benzaldehyde imine were prepared through the same method illustrated above while salicylaldimine was replaced by furfuraldehyde and benzaldehyde respectively.

**Preparation of MCM, Sal-MCM, Fur-MCM and Ben-MCM.** According to previous research, a co-condensation method was adopted to prepare salicylaldehyde modified mesoporous silica (Sal-MCM), 1.0 g of CTAB, 100 mL deionized water and 70 mL of ammonia were added to the flask to be dissolved at 60°C with stirring. 5 g of TEOS was added to the solution dropwise. 1 hour later, 1 g of APTES was added and kept on reacting for 6 h before being crystalized at room temperature, filtered, washed and dried. Finally, the template was removed by ethanol to attain Sal-MCM. Using this approach, the final products Fur-MCM and Ben-MCM (i.e salicylaldehyde replaced by furfuraldehyde and benzaldehyde imine, respectively) were prepared. In comparison, MCM was prepared as mentioned above without adding salicylaldehyde.

**Loading of methyl eugenol.** According to previous study, the supported Me was prepared via impregnation. The mesoporous silica were activated under vacuum at 80°C for 12 h. 0.25 g of samples was immersed in 250 mg Me at room temperature for 1 h, then filtered and dried. The samples obtained were denoted as Me-Sal-MCM, Me-Fur-MCM and Me-Ben-MCM respectively according to the different carrier. The amount of Me was calculated through TG method.

**Measurements.** The small angle X-ray diffraction (SAXD) were performed using a Bruker AXS D8 X-ray diffractometer (Bruker, Germany) with Cu radiation (λ = 1.5418 Å) and a graphite monochromator at 25°C, 40 kV, and 30 mA. The measurements were scanned at 2θ/min (angular range 20 = 0.5~10°) in 0.02° step size. FTIR spectra were recorded in the region 4000–400 cm⁻¹ by a Spectrum100 Fourier infrared spectrometer (PerkinElmer, USA) using the KBr slab technique. The gold particles were sprayed on the surface of samples under protection of N₂ and the samples were characterized by an S4800 scanning electron microscope (Hitachi, Japan) to observe the crystal topography. TEM observation was conducted on a FEI Tecnai G2 F20 transmission electron microscope (Thermo Fisher Scientific, USA). BET surface area of samples was determined by N₂ adsorption (Quantachrome, USA). The samples were degassed at 200°C for 12 h in vacuum before N₂ adsorption experiment. A Q200 differential scanning calorimeter (TA Instruments, USA) was used to conduct differential scanning calorimetry and detect the crystalline degree of the mesoporous silica in the particles over a heating range of 0~200°C and a heating rate of 10°C/min under the protection of N₂ (flow rate 50 mL/min). Thermal gravity (TG) measurements of these samples were carried out on an SDT-Q600 thermogravimetric analyzer (TA Instruments, USA) analyze the heat stability of particles over the heating range of 40~600°C under the condition of N₂, flow rate 50 mL/min and heating rate 10°C. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB250XI spectrometer (Thermo Fisher Scientific, USA) under a vacuum of ~2 × 10⁻⁷ Pa. Charging effects were corrected by adjusting the main C 1 s peak to a position of 284.8 eV. The zeta potential of the samples was investigated with a Zetasizer Nano ZS (Malvern, UK) in water at pH 7 through ultrasonic dispersion.
Sustained release performance test. According to previous study\textsuperscript{19}, the performance of sustained release Me particles was tested by TG method which has been adapted in our previous research\textsuperscript{20}. Drug-loaded particles (3–5 mg) were weighed and placed in a Al\textsubscript{2}O\textsubscript{3} crucible of SDT-Q600 thermogravimetric analyzer in 60 °C for 10 h, and the flow rate of N\textsubscript{2} was 50 mL/min. At intervals of (t), and the cumulative release amount of Me was calculated as \( R_t\), A \( t-R_t\) curve was drawn to study the release kinetics of Me.

Kinetic study. Sustained release curves were fitted by the first-order (Eq. (1)), Higuchi (Eq. (2)), Korsmeyer-Peppas (Eq. (3)), Quadratic (Eq. (4)), Logistic (Eq. (5)) and Weibull model (Eq. (6)). The linearized forms of these equations are expressed as below\textsuperscript{21–23}:  

\[
y = K_1[1 - \exp(-K_2t)] 
\]

\[
y = K_1t^{1/2} 
\]

\[
y = K_3t^K_4 
\]

\[
y = 100(K_2t^2 + K_3t) 
\]

\[
y = K_4[1 + \exp(-K_5(t - K_6))] 
\]

\[
y = 1 - \exp([-t^{K_7}/K_8]) 
\]

where \( y \) is the experimental accumulated rate of Me (\%) at time \( t \), respectively. \( K \) is the rate constant for the kinetic model. The correlation coefficient (\( R^2 \)) and the release exponent (\( n \)) were used to determine the best-fit kinetic model and the mechanism of the drug release.

Attraction of bactrocera dorsalis test. According to the literature\textsuperscript{8,19}, a certain among of male Bactrocera Dorsalis with sexual maturation were transferred to a 45 cm \( \times \) 45 cm \( \times \) 45 cm cage. Steiner trap was recorded to calculate the lure rate.

Results and discussion

Structure characterization. SEM and TEM images of MCM samples before and after modification were depicted in Figs. 1 and 2. The regular hexagonal pore structure and the structure integrity from MCM\textsuperscript{24} was well-maintained\textsuperscript{25} after modification and the orderings of the (100) and (110) was not affected by Schiff base co-condensation. The particle size of the four samples were 833 nm, 789 nm, 701 nm and 763 nm respectively for MCM, Sal-MCM, Fur-MCM and Ben-MCM measured from the SEM images. And the surface of MCM became rough with small particles formed on the surface as the SEM images shown in Fig. 1 after modification. Also a layer of shell structure appeared on the surface as the TEM images from Fig. 2 showed due to the precipitation of silane coupling agent\textsuperscript{26}.

Figure 3 depicted the SAXD patterns of the samples. Four characteristic peaks at 0.860°, 2.439°, 4.000° and 4.540° were ascribed to (100), (110), (200) and (210) crystal faces respectively. And the crystal faces of (100) and (110) were also shown in the TEM images as illustrated in Fig. 2 representing for the regular hexagonal pore structure in accordance with SEM and TEM images. However, the (100) diffraction of the modification samples was shown to further shift toward smaller 2\( \theta \) value due to the block of the pore by Schiff base. The 2\( \theta \) value shift of (200) and (210) crystal faces also happened for Fur-MCM. What's more, the peaks ascribed to (200) and (210) crystal faces disappeared for Sal-MCM and Ben-MCM which proved that benzene ring was introduced to the system and decreased its degree of orderliness\textsuperscript{27}.

As shown in Fig. 4a, the \( N_2 \) adsorption/desorption isotherms of MCM, Sal-MCM, Fur-MCM and Ben-MCM belong to Langmuir IV (the slope of it was decreasing) which indicated that their pore size was relatively small and also confirmed by the pore size distribution results calculated by DFT method\textsuperscript{28} as shown in Fig. 4b. The \( N_2 \) adsorption/desorption isotherms in Fig. 4 do not overlap at relative pressures <0.2 were due to \( N_2 \) chemisorbed by silanol on the surface of the pores which confirmed by our previous researches\textsuperscript{28–29}. The rapid shift of \( N_2 \) adsorption isotherms caused by capillary condensation inside the pores for MCM disappeared after modification. And the BET surface, pore size and pore volume decreased after modification due to the pore block by Schiff base. And the BET surface of Sal-MCM, Fur-MCM and Ben-MCM after modification were 225.5 m\textsuperscript{2}/g, 413.4 m\textsuperscript{2}/g and 274.8 m\textsuperscript{2}/g respectively which illustrated the difference in the degree of pore block by three different Schiff base as shown in Table 1 which was much higher than our previous research (<200 m\textsuperscript{2}/g) due to the templates removed from the samples. Fur-MCM had the highest BET surface among and largest pore size and pore volume among the Schiff base modified MCM indicating that the surface of the pores from MCM were homogeneously grafted by furalimine probably due to its strongest interaction towards to the substrate.

The particle diameters and Zeta potential studies of MCM, Sal-MCM, Fur-MCM and Ben-MCM were investigated at pH 7 as listed in Table 2. The particle size calculated by DLS method was bigger than the particle size shown in SEM images due to the agglomeration and solvation effect since DLS measurements are conducted in solution according with previous research\textsuperscript{30}. The particle size of Sal-MCM, Fur-MCM and Ben-MCM decreased after modification. The decrease in particle size was caused by the effect of Schiff base on TEOS hydrolysis during the condensation. And the sufficient Si-OH groups on the surface MCM before modification made it Zeta
potential negative. After modification, Zeta potential of the samples shifted to be positive which confirmed the introduction of Schiff base into the mesoporous samples. Among them, Fur-MCM has the highest Zeta potential leading to its strongest electrostatic interaction with Me in consistent with BET results.

The FTIR spectra of MCM, Sal-MCM, Fur-MCM and Ben-MCM before and after loading Me were depicted in Fig. 5. Two bands appeared in 3447 cm$^{-1}$ and 968 cm$^{-1}$ for MCM ascribed to stretching and bending vibration of Si-OH respectively. 1080 cm$^{-1}$ and 810 cm$^{-1}$ were attributed to the characteristic peaks of Si-O-Si on the SiO$_2$ framework$^{30}$. Comparing to MCM, two new bands appeared at 2927 cm$^{-1}$ and 2851 cm$^{-1}$ belonging to the
symmetric and nonsymmetrical C-H stretching vibration bands from amino group for Schiff base which indicated the Schiff base was successfully grafted to MCM. After loading Me, the characteristic peaks of Me located at 3060, 2990, 2930, 1635, 1590 and 1510 cm\(^{-1}\) which proved that the Me was successfully adsorbed by mesoporous silica\(^3\). The IR spectra of Me showed a peak at 1724 cm\(^{-1}\) for carbonyl group which was gradually disappearing after loaded on mesoporous silica due to the interaction with MCM substrate. Intensity of peaks between 2800

**Figure 3.** SAXD Patterns of MCM, Sal-MCM, Fur-MCM and Ben-MCM.

**Figure 4.** N\(_2\) adsorption/desorption isotherms (a) and pore size distribution (b) of MCM, Sal-MCM, Fur-MCM and Ben-MCM.

| Sample   | BET surface (m\(^2\)/g) | Pore size (nm) | Pore volume (cm\(^3\)/g) |
|----------|--------------------------|----------------|--------------------------|
| MCM      | 681.8                    | 3.315          | 0.573                    |
| Sal-MCM  | 225.5                    | 2.531          | 0.114                    |
| Fur-MCM  | 413.4                    | 2.897          | 0.261                    |
| Ben-MCM  | 274.8                    | 2.897          | 0.156                    |

**Table 1.** The pore structural parameters of MCM, Sal-MCM, Fur-MCM and Ben-MCM.

| Sample   | SEM particle size (nm) | DLS particle size (nm) | PDI*  | Zeta potential (mV) |
|----------|------------------------|------------------------|-------|---------------------|
| Me       | —                      | —                      | —     | −38.82              |
| MCM      | 833 ± 11               | 951.79                 | 0.237 | −20.16              |
| Sal-MCM  | 789 ± 12               | 917.39                 | 0.242 | 15.77               |
| Fur-MCM  | 701 ± 12               | 740.52                 | 0.362 | 29.89               |
| Ben-MCM  | 763 ± 12               | 671.44                 | 0.371 | 25.70               |

**Table 2.** The Particle diameters and Zeta potential of MCM, Sal-MCM, Fur-MCM and Ben-MCM. *PDI: Polydispersity Index.
and 3100 cm\(^{-1}\) ascribed to the C–H stretching band was increased significantly showing that Me was successfully impregnated with mesoporous silica.

The surface elements chemical states were observed with XPS analysis as shown in Fig. 6 and Table 3. The binding energy (BE) negative shift of Si 2p as shown in Fig. 6a,b were observed after Schiff base modification due to the reaction between Si-O\(_2\)C\(_2\)H\(_5\) from Schiff base and Si-OH from MCM\(^{15}\). The N 1 s peaks as shown in Fig. 6c were observed after Schiff base modification, with a BE value of 399.98 eV, 399.74 eV and 398.65 eV for Sal-MCM, Fur-MCM and Ben-MCM. In the meanwhile, The C 1 s peaks as shown in Fig. 6d also appeared with BE value of 285.73 eV, 285.68 eV and 286.68 eV respectively for Sal-MCM, Fur-MCM and Ben-MCM which convinced the introduction of Schiff base.

Thermogravimetric analysis (TG) was used to investigate the thermal stability. As shown in Fig. 7, the loss in mass for MCM below 100 °C was caused the evaporation of water adsorbed by the samples\(^{32}\) in accordance with DSC results as shown in Fig. 8. The significant loss in mass occurred within the temperature range 160–350 °C which was caused by the decomposition of Schiff base on the mesoporous silica for Sal-MCM and Fur-MCM. While for Ben, 20% mass still existed even above 350 °C indicating that the mass loss was caused by the carbonization of Ben. After loading Me, the loss percentage in mass for Me-MCM, Me-Sal-MCM, Me-Fur-MCM and Me-Ben-MCM were calculated from loss percentage within the temperature range 160–350 °C subtracting the mass of Schiff base. The loading content of Me-Sal-MCM, Me-Fur-MCM and Me-Ben-MCM were 67.89%, 73.34% and 73.84% which was higher than Me-MCM without modification (67.35%) and much higher than the mesoporous silica prepared by our recent reported\(^{19}\) (<25%).

And the DSC thermograms of MCM, Me-MCM, Sal-MCM, Me-Sal-MCM, Fur-MCM, Me-Fur-MCM, Ben-MCM and Me-Ben-MCM were shown in Fig. 8. The fusion peaks of Schiff base modified mesoporous silica had a significant shift from 110 °C to 133 °C, 128 °C and 118 °C for Sal-MCM Fur-MCM and Ben-MCM comparing with MCM without modification which convinced the interaction between Schiff base and mesoporous silica in accordance with the XPS results. Another shift of the fusion peak happened after loading Me from 110 °C, 133 °C, 128 °C and 118 °C to 71 °C, 108 °C, 115 °C and 100 °C for Me-MCM, Me-Sal-MCM, Me-Fur-MCM and Me-Ben-MCM respectively due to the induction effect from Me. However, the disappearance of Me fusion peak proved that the Me is distributed homogeneously in amorphous state in the pores of the mesoporous silica.

**Sustained release test.** Figure 9 showed the sustained release performance of Me, Me-MCM, Me-Sal-MCM, Me-Fur-MCM and Me-Ben-MCM. The 50% accumulated release rates were attained at 389 min and 196 min for Me and Me-MCM. The rapid release for Me-MCM is probably due to the weak interaction between Me and MCM before modification. In comparison, the accumulated release rate of Me-Sal-MCM, Me-Fur-MCM and Me-Ben-MCM was less than 50% in 600 min which indicated that Schiff base modification could prevent the volatilization of Me and prolonged its service life. This slow release may be ascribed to the Schiff
base modification which strengthened the interaction with mesoporous silica by $\pi$-$\pi$ interaction between the benzene ring from Me and aromatics from Schiff base and electrostatic interaction between Schiff base with positive charge and Me with negative charge. And Fig. 9 also depicts the sustained release curves with a sequence of Me-Sal-MCM > Me-Ben-MCM > Me-Fur-MCM in release speed in negative correlation with the electric potential sequence shown in Table 2 for the three samples indicating that the electrostatic interaction played a more important role in interaction between Me and Schiff base modified mesoporous silica. And the ultimate accumulated release rate for Me, Me-MCM, Me-Sal-MCM, Me-Fur-MCM and Me-Ben-MCM were 70.82%, 82.88%, 48.59%, 56.63% and 37.21% respectively in 10 hours.

Kinetics study. To further understand the sustained release mechanism, the data of sustained release of Me and Me loaded in various mesoporous silica were fitted to different kinetic models (Table 4). The sustained release curves of Me and Me-MCM were in accordance with first-order kinetic equation proving the barrier-free diffusion of the drug. While Me-Sal-MCM, Me-Fur-MCM and Me-Ben-MCM were in consistent with Korsmeyer-Pappas kinetic equation. The diffusion coefficients of the fitting equations were between 0.45~1 controlled by a non-Fickian diffusion mechanism. The sustained release behavior of MCM changed after modification because the difference of the concentration was no longer the main factor on controlling the release performance due to the strengthened interaction between Me and the substrate. Therefore, the service life of Me was prolonged.

Attraction of bactrocera dorsalis. The practical performance of the samples was evaluated by attraction of Bactrocera Dorsalis test. The lure percentages of Me-MCM, Sal-MCM, Fur-MCM and Ben-MCM for Bactrocera Dorsalis were 40.00%, 46.67%, 53.33% and 46.67% after 72 h as depicted in Fig. 10. However, pure Me has highest lure percentage (86.67%) due to the decrease in drugs amount actually used in the experiment. While calculated from the TG results for the lure efficiency in one unit drug from Me, Me-MCM, Me-Sal-MCM, Me-Fur-MCM and Me-Ben-MCM have the equivalent of 59%, 69%, 73% and 63% pure Me lure efficiency respectively. In other words, the highest lure rate of the modified MCM (Me-Fur-MCM) equals to the 73% of the pure
Me. In summary, the sustained release system get rid of the organic solution and increases the Me service life without affecting its performance significantly.

As depicted in Fig. 11, the drug release process of mesoporous silica was illustrated by characterization results and kinetic study in this paper. Schiff base was the link between modified mesoporous silica and Me by π–π interaction between the benzene ring from Me and aromatics from Schiff base and electrostatic interaction between Schiff base with positive charge and Me with negative charge. And the electrostatic interaction played a more important role in interaction between Me and Schiff base modified mesoporous silica. As a result, the release performance of Me was proved and the service life of Me would be significantly prolonged in practical usage.
In conclusion, Schiff base (salicylaldimine, furfuralimine and benzaldehyde imine) modified mesoporous silica was prepared by co-condensation method. Then Me was post-loaded in the mesoporous silica after removing the templates in the pores. The regular hexagonal pore structure was well-maintained without agglomeration after modification. The existence of interaction between Schiff base and Me was confirmed by the characterization.

**Figure 9.** Sustained release curves of Me, Me-MCM, Me-Sal-MCM, Me-Fur-MCM and Me-Ben-MCM.

**Table 4.** Fitting results for release curves of Me, Me-MCM, Me-Sal-MCM, Me-Fur-MCM and Me-Ben-MCM.

| Release model          | Materials    | Parameters | $K_1$     | $K_2$     | $K_3$ |
|------------------------|--------------|------------|-----------|-----------|-------|
| First-order model      | Me           | 1.6867 * 10^{-5} | 1.5388 | —         | 0.9998 |
|                        | Me-MSN       | 6.4813 * 10^{-5} | 0.8856 | —         | 0.9967 |
|                        | Me-Sal-MSN   | 3.4589 * 10^{-4} | 3.1453 | —         | 0.9999 |
|                        | Me-Fur-MSN   | 2.3984 * 10^{-4} | 3.4595 | —         | 0.9999 |
|                        | Me-Ben-MSN   | 1.0168 * 10^{-5} | 1.0188 | —         | 0.9977 |
| Higuchi model          | Me           | 0.0032 | —         | —         | 0.8965 |
|                        | Me-MSN       | 0.0044 | —         | —         | 0.9715 |
|                        | Me-Sal-MSN   | 0.0016 | —         | —         | 0.8537 |
|                        | Me-Fur-MSN   | 0.0012 | —         | —         | 0.8498 |
|                        | Me-Ben-MSN   | 0.0014 | —         | —         | 0.8804 |
| Korsmeyer-Peppas model | Me           | 0.8437 | 1.0203 * 10^{-4} | —         | 0.9996 |
|                        | Me-MSN       | 0.5699 | 0.0022 | —         | 0.9802 |
|                        | Me-Sal-MSN   | 0.9618 | 1.5311 * 10^{-5} | —         | 0.9999 |
|                        | Me-Fur-MSN   | 0.9725 | 1.0590 * 10^{-5} | —         | 0.9999 |
|                        | Me-Ben-MSN   | 0.8878 | 2.8305 * 10^{-5} | —         | 0.9991 |
| Quadratic model        | Me           | —       | 1.6677 * 10^{-12} | 2.5395 * 10^{-7} | — | 0.9999 |
|                        | Me-MSN       | —       | 1.6766 * 10^{-12} | 4.7991 * 10^{-7} | — | 0.9855 |
|                        | Me-Sal-MSN   | —       | 1.7682 * 10^{-10} | 1.0865 * 10^{-7} | — | 0.9999 |
|                        | Me-Fur-MSN   | —       | 9.4523 * 10^{-14} | 8.2606 * 10^{-8} | — | 0.9991 |
|                        | Me-Ben-MSN   | —       | 4.3702 * 10^{-13} | 1.0245 * 10^{-7} | — | 0.9976 |
| Logistic model         | Me-MSN       | 9587.6467 | 1.8295 * 10^{-4} | 0.7670 | 0.9740 |
|                        | Me-Sal-MSN   | 19117.9444 | 1.2175 * 10^{-4} | 0.3983 | 0.9914 |
|                        | Me-Fur-MSN   | 19319.6768 | 1.2142 * 10^{-4} | 0.3094 | 0.9922 |
|                        | Me-Ben-MSN   | 18804.2997 | 1.1392 * 10^{-4} | 0.3471 | 0.9926 |
| Weibull model          | Me-MSN       | 6924.9184 | 0.8838 | —         | 0.9957 |
|                        | Me-Sal-MSN   | 193080.1479 | 1.0843 | —         | 0.9992 |
|                        | Me-Fur-MSN   | 211409.7915 | 1.0636 | —         | 0.9995 |
|                        | Me-Ben-MSN   | 80909.7240 | 0.9818 | —         | 0.9978 |

**Conclusions**

In conclusion, Schiff base (salicylaldimine, furfuralimine and benzaldehyde imine) modified mesoporous silica was prepared by co-condensation method. Then Me was post-loaded in the mesoporous silica after removing the templates in the pores. The regular hexagonal pore structure was well-maintained without agglomeration after modification. The existence of interaction between Schiff base and Me was confirmed by the characterization.
results. And the negative correlation is found between sustained speed of Me and zeta potential of the samples indicating that the electrostatic interaction played a more important role in the interaction between Me and Schiff base modified mesoporous silica. Me is distributed homogeneously in amorphous state in the pores of the mesoporous silica confirmed by DSC results. The loading content of Me-Sal-MCM, Me-Fur-MCM and Me-Ben-MCM 67.89%, 73.34% and 73.84% which was higher than Me-MCM without modification (67.35%). Their sustained release curves could be described by Korsmeyer-Peppas equation in consistence with non-Fickian diffusion mechanism after Schiff base modification. Finally, the attraction of Bactrocera Dorsalis test showed the highest lure rate of the modified MCM (Me-Fur-MCM) equals to the 73% of the pure Me. In short, this sustained release system can avoid the usage of organic solution for dissolution and prolonged its service life without affecting its performance significantly through the enhancement of interaction between drug and carrier through Schiff base modification.

Data availability
The data generated or analyzed during the current study are available from corresponding author upon reasonable request.

Figure 10. Lure rate of Me, Me-MCM, Me-Sal-MCM, Me-Fur-MCM and Me-Ben-MCM.

Figure 11. The schematic diagram of drug release of Schiff base modified MCM.
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Author contributions
H.C. analyzed the results, coordinated the study and wrote the manuscript. L.C and Z.S. performed the experiments and tests. L.H. and H.X. designed the experiments. H.Z. and X.Z. directed the experiments. All authors reviewed the manuscript.

Competing interests
The authors declare no competing interests.

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