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Comparative study on two different methods for fabrication of sustained release boscalid based on mesoporous silica

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Abstract

In this study, boscalid silica nanosphere nanoparticles (Bos@SNS/t Nps) and boscalid bimodal mesoporous silica material nanoparticles (Bos@BMMs Nps) were prepared using two different methods. A comparative study on characteristics and properties of two nanospheres were conducted. Both nanoparticles had spherical shapes with average diameters of 719.3 ± 6.3 nm (Bos@BMMs Nps) and 981.3 ± 4.8 nm (Bos@SNS/t Nps). The structures of nanoparticles were characterized by scanning electron microscopy, X-ray diffraction, dynamic light scattering laser particle-size analysis, and fourier transform infrared spectroscopy, indicating that Nps had a well-defined core–shell construction for efficient loading of Bos. The loading rates of Bos@BMMs and Bos@SNS/t Nps were 25.2 ± 2.3% and 27.3 ± 3.6%, respectively. The nanoparticles had obvious pH sensitivity, and the release of Bos in pH 9.0 was higher than those in pH 7.0 and pH 4.0. No significant difference in the release behavior of nanocomposites was found, and the release models were fitted with the Weibull equation. Finally, the bioactivity of the Bos-loaded nanocomposite was measured against Rhizoctonia solani, which showed that the fungicidal efficacy of Bos@SNS/t was slightly better than that of Bos@BMMs.

1. Introduction

Pesticides, owing to their efficacy, are widely used to control diseases, insects, and weeds in modern agriculture [1]. However, because of ultraviolet photolysis, poor dispersity, and application drift, the effective utilization rate of conventional pesticides is only 10% [2, 3]. A considerable amount of residual pesticides is wasted and becomes dangerous to human health and the environment [3, 4]. This issue has attracted increasingly more attention globally. Therefore, there is an urgent need to develop new technology to enhance modern agriculture in a more productive, cost-effective, and eco-friendly way [1, 5–7].

Recently, nanotechnology has been rapidly developed and applied in the fields of drugs, pesticides, and environmental engineering [8, 9]. Owing to their nanoscale size effect, large surface area, and specific targeted modification properties, nanomaterials effectively reduce the loss of pesticides and improve the utilization of active ingredients of pesticides [3, 10–12]. Theirin, various kinds of nanomaterials, such as polymers [13, 14], inorganic materials [15], and nanocomposites [16], have been used as carriers in slow- or controlled-release nano-pesticide systems. Among all of the available nanomaterials, mesoporous silica nanoparticles have been regarded as one of the most promising platforms for pesticide delivery [17, 18]. Bimodal mesoporous silica materials (BMMs) consisting of worm-like mesopores of 3 nm as well as large inter-particles pores of approximately 10–30 nm comprise an excellent drug carrier and possess high pesticide loading capacity [19, 20]. A pH-responsive thiamethoxam BMMs nanoparticle was successfully constructed in our previous research [21].
The preparation process of a nano-pesticide system based on mesoporous silica is also conventionally called the two-step method. First, the mesoporous silicon carrier (BMMs) is synthesized, and then the pesticide is loaded in the nanochannels by the solvent adsorption method. Compared with the two-step method, pesticide molecules, surfactant cetyltrimethylammonium bromide (CTAB), and ethyl orthosilicate (TEOs) are simultaneously assembled into silica nanospheres (SNSs) by quickly stirring in the one-step synthesis, eliminating the volatilization of CTAB and additional solvent adsorption of the one-step method. While greatly simplifying the originally complicated operation process, the one-step method also shortens the operation time and improves efficiency. However, few reports on the comparison of the two preparation methods exist. A schematic of the synthesis of pesticide-coated silica nanoparticles using two different methods is shown in figure 1.

Boscalid (Bos) is a new type of nicotinamide systemic fungicide with a broad bactericidal spectrum and displays significant antifungal activity [22, 23]. However, due to its poor water dispersibility and instability, the application of Bos has been limited [23]. In addition, it was revealed that Bos was toxic to non-target species such as zebrafish and Chlorella vulgaris in previous reports [24, 25]. In the present work, the characteristics, release behavior, and biological activity of nano pesticides prepared by the one- and two-step methods were compared. The results will provide a theoretical basis for the large-scale application of sustained-release nano pesticide systems in the future.

2. Materials and methods

2.1. Materials
Cetyltrimethylammonium bromide (CTAB, AR), ammonia (25%, AR), and ethyl orthosilicate (TEOS, AR) were supplied from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). Anhydrous ethanol (AR) and 1,3,5 - three toluene (AR) were provided from Beijing Chemical Plant (Beijing, China). Technical Boscalid (Bos, 95% effective content) was obtained from Beijing Jinyue Biological Technology Co., Ltd (Beijing, China). A dialysis bag (molecular weight cutoff 3500) was purchased from Beijing Kebiquan Biotechnology Co., Ltd (Beijing, China).

2.2. One-step synthesis of Bos silica nanosphere nanoparticles
To synthesize Bos silica nanosphere nanoparticles (Bos@SNS/t Nps), 1 g of Bos was added to 50 ml of mesitylene and sonicated for 10 min to obtain a homogeneous solution of Bos. CTAB (1.05 g) was dissolved in 23 ml of deionized water, and then 15 ml of 20 mg ml\(^{-1}\) Bos mesitylene solution was added dropwise into CATB solution with constant stirring at 40 °C for 2 h. Next, 3.2 ml of TEOs and 0.96 ml of ammonia solution were added to the solution. The pH was adjusted to 8–9 during the preparation. The system was stirred for 10 h at room temperature until a precipitate formed. The precipitate was suction-filtered and washed thoroughly with deionized water, and then dried under vacuum at 50°C overnight. Silica nanospheres loaded with Bos, which
also contain CTAB (Bos@SNS/t) were obtained. SNS/t nanoparticles were prepared using the same method and served as a negative control.

### 2.3. Two-step synthesis of BOS@BMMs Nps

#### 2.3.1. Preparation of BMMs

BMMs were produced by a sol-gel route, as previously reported. First, 1.05 g CTAB was dissolved in 23 ml of methanol water. Subsequently, 3.2 ml of TEOS was slowly added and then 0.96 ml of ammonia water was quickly added with constant stirring at a rate of 480 rpm at 40 °C until a white gel was generated. Then, the resultant white gel was suction-filtered and thoroughly washed with distilled water, followed by drying at 120 °C for 4 h to obtain a nanomaterial raw powder. The obtained raw powder was calcined at 550 °C for 5 h to remove a template to produce BMMs.

#### 2.3.2. Preparation of Bos@BMMs Nps

First, 1.0 g of BMMs was dispersed in 15 ml of Bos methanol solution with a Bos concentration of 20 mg ml⁻¹. The system was sealed and sonicated for 30 min, and then stirred at room temperature for 48 h. After being suction-filtered and washed twice with anhydrous methanol, the mixture was vacuum-dried at 50 °C for 12 h to obtain Bos@BMMs nanoparticles.

### 2.4. Characterization of Bos@SNS/t Nps and Bos@BMMs Nps

The morphology and structure of the nanoparticle were studied using scanning electron microscopy (SEM) (Zeiss Sigma 300, Oberkochen, Germany) with an accelerating voltage of 10 kV. The sizes, polymer dispersity indexes (PDIs), and zeta potentials of Bos@SNS/t, SNS/t, Bos@BMMs, and BMMs were measured by dynamic light scattering (DLS) using a Zeta Sizer Nano ZS (Malvern Instruments Ltd, Malvern, UK). X-ray diffraction studies were carried out using an x-ray powder diffractometer (D8 ADVANCE X, Bruker/AXS, Karlsruhe, Germany) with Ni-filtered Cu Kα radiation (λ = 0.154 nm). The tube voltage and tube current were 35 kV and 35 mA, respectively, and the scan speed was 0.5 min⁻¹. Fourier transform infrared spectroscopy (FTIR) spectra were conducted using a Nexus 470 FTIR spectrometer (Nexus, USA). KBr solid powder was used as a diluent and tested by the tabletting method. Spectra were recorded between 400 and 4000 cm⁻¹ at a resolution of 4 cm⁻¹.

### 2.5. Bos loading capacity

After Bos loading, the nanoparticles were collected by centrifugation, and washed with ethanol and water three times to remove the adsorbed Bos on the surface. The Bos concentrations in the eluted solutions were analyzed by high-performance liquid chromatography (HPLC, 1200 Series, Agilent, Wilmington, USA). A ZORBAX Eclipse XDB-C18 column (4.6 × 150 mm, particle size 5μm, Agilent, Wilmington, USA) was used and operated at 30 °C. The mobile phase consisting of methanol and water (volume ratio 70:30) was programmed with a flow rate of 0.4 ml min⁻¹ at wavelength of 210 nm. The injection volume was 10 μl, and the retention time was 6 min. The Bos loading capacity in the nanoparticles was calculated with the followed equation: [26]

\[
LC(\%) = \frac{C_{\text{loading}} \times V_{\text{loading}} - C_{\text{residual}} \times V_{\text{residual}} - C_1 V_1 - C_2 V_2 - C_3 V_3}{m}
\]

where LC is the Bos loading capacity (wt.%); m is the weight of the nanoparticles (mg); \(C_{\text{loading}}, C_{\text{residual}}, C_1, C_2, C_3\) are the Bos concentrations in the original loading solution, residual solution, and eluted solutions for the first, second, and third time, respectively (mg ml⁻¹); and \(V_{\text{loading}}, V_{\text{residual}}, V_1, V_2, V_3\) are the volumes of the original loading solution, residual solution, and eluted solutions for the first, second, and third time, respectively (ml).

### 2.6. Contact-angle test

The contact angles of Bos@SNS/t Nps and Bos@BMMs Nps droplets on leaves were measured using a contact-angle apparatus (JC2000D2M, Powereach Ltd, Shanghai, China). Technical Bos solution and water were used as controls. Fresh tomato leaves were selected as model plants, and were carefully washed three times with deionized water and air-dried. Bos@SNS/t dispersion, Bos@BMMs dispersion, technical Bos solution, and water (2 μl) were dropped onto the leaves on a glass slide. Images of the droplet on the leaf surface were taken, and the corresponding contact angles were measured using a contact-angle meter (Dataphysics-TP50, Data Physical Ltd, Germany). All experiments were repeated three times.

### 2.7. Storage stability

The samples were packed and stored at 4 °C or 25 °C for 7 d, and 54 °C for 14 d. The Bos content was analyzed by HPLC.
2.8. In vitro release behavior of Bos
First, 15 mg of Bos@SNS/t Nps and Bos@BMMs Nps were dispersed separately in 3 ml of release media, and then transferred into dialysis bags with a molecular-weight cutoff of 3500 Da. Next, the dialysis bags were placed in 100 ml of methanol/deionized water mixture (70:30, v/v) with pH of 4.0, 7.0, and 9.0 respectively. The solutions were shaken at a speed of 100 rpm at room temperature, and 2 ml samples were collected at regular intervals for testing. Then the system supplemented with an equal amount of fresh medium with the same pH. The cumulative release rate of Bos from nanoparticles was calculated by determining the concentration of released Bos using HPLC. Technical Bos solution was used as a control. The test was carried out three times and the average value calculated.

The cumulative release rate (Q) of Bos in Nps is calculated according to the following equation:

\[ Q = \frac{V_0 \times C_T + V \times \sum_{N-1}^{T-1} C}{W} \times 100\% \]

where \( W \) (mg) is the loading concentration of Bos in Nps, \( V_0 \) (ml) the total volume of the sustained-release solution, and \( V \) (ml) the volume of the release medium taken at a specific interval tie. \( C_T \) (mg ml\(^{-1}\)) and \( C \) (mg ml\(^{-1}\)) are the concentrations of \( T \) and \( N \) samples, respectively. The data of the dynamic Bos sustained release from Bos@SNS/t Nps and Bos@BMMs Nps were calculated with the pseudo-zeroth-order equation, pseudo-first-order equation, Higuchi model, and Weibull model.

2.9. Biological activity test
The bioactivity of Bos@SNS/t Nps and Bos@BMMs against Rhizoctonia solani was conducted using the growth-rate method. Rhizoctonia solani cakes (5 mm diameter) were placed into the center of potato dextrose agar (PDA) petri dishes with different contents of nanoparticles (12.5, 25, 50, 100, and 200 mg l\(^{-1}\)). Technical Bos solution and distilled water were used as controls. The dishes were incubated at 28 °C and the colony diameters measured at 12 d, respectively. The relative inhibition rates and the probit regression model of two kinds of Bos nanospheres against the fungi were calculated according to the continuum equations.

2.10. Statistical analysis
All experiments were carried out three times. Data are presented as values ± standard error from triplicate analysis using SPSS 22.0 software (Chicago, Illinois, USA).

3. Results and discussion
3.1. Characterization of Bos@SNS/t Nps and Bos@BMMs Nps
SEM was performed to confirm the preparation of Bos@SNS/t Nps and Bos@BMMs Nps and to outline the particle shape and distribution. As depicted in figure 2, Bos@SNS/t Nps and Bos@BMMs Nps have excellent morphologies and uniform particle-size distribution. The nanoscale spherical shapes of nanoparticles were well maintained without aggregation, indicating that the Bos loading did not destroy the morphology of the microcapsules. The surfaces of Bos@SNS/t Nps and Bos@BMMs Nps became rough due to the Bos loading. The sizes of different nanoparticles were further measured by DLS analysis. The average particle sizes of SNS/t and BMMs were 377.4 ± 3.2 and 323.9 ± 2.9 nm, respectively. After Bos was loaded, the sizes of Nps were gradually increased to 719.3 ± 6.3 nm (Bos@BMMs Nps) and 981.3 ± 4.8 nm (Bos@SNS/t Nps). The particle size of Bos@SNS/t Nps was significantly larger than that of Bos@BMMs Nps. This may be due to the encapsulations of both CTAB and Bos in the pores of mesoporous silica when the nano pesticide system was synthesized by the one-step method. The zeta values and PDI s of the different Nps were further measured (figure 3 and table 1). The value of pH of the solution was 7.0 ± 0.1 at which the zeta potential was measured. CTAB as a cationic surfactant has been widely applied in the field of microemulsion, and the zeta value of SNS/t is 23.4 mV. After the channel was loaded with Bos, the zeta values of Bos@SNS/t Nps and Bos@BMMs Nps were −17.2 ± 2.5 and −19.5 ± 1.6 mV, respectively. Bos being negatively charged proved that these nanoparticles were successfully loaded with Bos. The high PDI values of Bos-loaded nanoparticles indicated a high degree of monodispersity and stability in the nanocomplex system.

The ordered mesoporous structure of the nanocontainers was further confirmed by X-ray diffraction. As shown in figure 3(C), two main Bragg diffraction peaks were clearly observed in the pattern and were assigned to the (100) and (110) planes [27]. Obviously, it is a typical hexagonal mesoporous structure, in agreement with the characteristic diffraction pattern of amorphous silica. The (100) peak intensity of the spectrum obviously decreased after Bos loading. The 2θ angles of SNS/t and BMMs increased from 1.86° to 1.98° and 1.97° to 2.02°, respectively, and the corresponding d-space value decreased from 47.3 to 44.50 nm and from 44.69 and 44.10.
nm, respectively, indicating that the introduction of Bos had a remarkable effect on the order of mesoporous structures and pore sizes.

The FTIR spectra of Bos, BMMs, SNS/t, Bos@SNS/t, Bos@BMMs are shown in figure 3(D). SNS/t and BMMs exhibited strong characteristic peaks at 466, 738, and 1068 cm$^{-1}$ that were assigned to the bending, symmetric stretching, and antisymmetric stretching vibrations of the Si–O–Si groups, respectively, as observed in all the BMMs-related samples. The strong absorption peaks at 3282, 1577, and 1677 cm$^{-1}$ in Bos probably originated from the C–O stretching vibration and the secondary amide N–H deformation vibration of amide (–CONH–). Bos@SNS/t and Bos@BMMs had a similar FTIR absorbance as Bos, and the characteristic peaks at 1577 and 1677 cm$^{-1}$, respectively, were attributed to the presences of amides, suggesting that Bos was successfully encapsulated in the BMMs/SNS/t carriers. In addition, Bos@SNS/t possessed characteristic peaks at 2923 and 2875 cm$^{-1}$, which were assigned to the stretching–vibration absorption peaks of –CH$_2$ and –CH$_3$ in the CTAB spectra.

The loading contents of Bos in the BMMs and SNS/t were also determined by HPLC, and the loading rates of Bos@SNS/t Nps and Bos@BMMs Nps were 27.3 ± 3.6% and 25.2 ± 2.3%, respectively. The micelles were
quickly formed after adding CTAB, TEOs and Bos. The optimal concentration of CTAB was beneficial to the formation and growth of nanoparticle [28]. These observations suggest that Bos was successfully loaded into the mesopore channels of SNS/t and BMMs. There is no significant difference in the properties of the nanospheres prepared by the two different methods.

### 3.2. Foliage wettability analysis

Contact angles of the Bos@SNS/t and Bos@BMMs nanoparticles on plant leaves were measured to study the foliage wettability of sample solution. As shown in figure 4, the contact angle made by Bos@SNS/t and Bos@BMMs nano dispersion on the foliage was significantly reduced compared to the technical Bos solution and deionized aqueous solution. The contact angles of and Bos@BMMs and Bos@SNS/t on the leaves were 89.56°±0.57° and 83.31°±0.61°, respectively, which were smaller than those of deionized water (108.54°±0.43°) and Bos technical solution (96.57°±0.54°), indicating that better wettability performance of nanoparticles existed after encapsulation of Bos in SNS/t and BMMs. The leaf surface is covered with a waxy substance, and its main components include fatty acids, fatty alcohols, and fatty aldehydes. These polar functional groups on the surface of the leaves can interact with hydroxyl groups of nanoparticles, consistent with previous reports [29]. In addition, the contact angle of Bos@SNS/t was lower than that of Bos@BMMs, which may be related to the introduction of the surfactant CTAB.

| Nps          | Mean size (nm) | PDI      |
|--------------|----------------|----------|
| BMMs         | 323.9 ± 2.9    | 0.142 ± 0.01 |
| SNS/t        | 377.4 ± 3.2    | 0.081 ± 0.01 |
| Bos@BMMs     | 719.3 ± 6.3    | 0.131 ± 0.04 |
| Bos@SNS/t    | 981.3 ± 4.8    | 0.145 ± 0.03 |

Figure 3. Particle size distributions, zeta potentials, XRD patterns and the FTIR spectra of SNS/t, BMMs, Bos@BMMs Nps, Bos@SNS/t Nps.

Table 1. Mean size (nm) and polydispersity index (PDI) of nano-drug delivery system.
3.3. Storage stability
During storage or transportation, the surrounding environmental temperature may affect the stability of pesticide formulas. At high temperatures, possible thermal decomposition, curing, or volatilization will also obstruct the application of pesticides. The storage stability of Bos@SNS/t and Bos@BMMs NPs was evaluated by measuring the Bos loading contents at different temperatures (figure 5). Results showed that the nanoparticles remained stable during storage at room and low temperature. After 14 d of storage at 54 °C, the Bos contents were slightly decreased by 1.6% (Bos@SNS/t) and 1.8% (Bos@BMMs), compared with those at 4 °C, which was due to minimal degradation of Bos at higher temperature. In short, Bos-coated controlled-release microspheres exhibited good storage stability.

3.4. Sustained-release behavior and release kinetics analysis
The release behavior of Bos from entrapped Bos@SNS/t NPs and Bos@BMMs NPs in the methanol/deionized water mixture (70:30, v/v) with pH of 4.0, 7.0, and 9.0 was investigated. As shown in figures 6(A), (C), Bos@SNS/t NPs and Bos@BMMs NPs exhibited an obvious sustained release. The release ratios of Bos from Bos@SNS/t and Bos@BMMs NPs increased obviously from 65.4 to 87.3% and 60.3 to 78.9%, respectively, at 220 h with the increasing pH from 4.0 to 9.0, indicating that the release of Bos from Bos@SNS/t and Bos@BMMs nanospheres could be adjusted by pH, and the cumulative release rate of Bos in alkaline condition was higher than those in acidic and neutral conditions. This was mainly due to the instability of the silicon-oxygen bond leading to the collapse of the mesoporous structure with the increase of pH values from 4.0 to 9.0. Therein, the pesticides in the samples were released relatively easily, which is consistent with previous reports [30, 31]. In addition, Bos@SNS/t NPs and Bos@BMMs NPs exhibited similar release behavior, i.e., a high initial release rate at the beginning stage followed by a slow release of Bos. The results obtained showed that there was no significant difference in the release behavior of the nanocomposites obtained by the two different preparation methods. The sustained-release properties of Bos@BMMs NPs and Bos@SNS/t NPs can extend the duration of pesticide activity on crops, and improve the pesticide utilization rate.

To further elucidate the release mechanism, the release kinetics of Bos from Bos@SNS/t and Bos@BMMs NPs were analyzed according to the zeroth- and first-order equations, Higuchi kinetic model [32], and Weibull model [33]. The Weibull function emerges due either to the creation of a concentration gradient near the releasing boundaries of the Euclidian matrix or to the ‘fractal kinetics’ behavior associated with the fractal geometry of the environment. As shown in table 2 and figures 6(B), (D), the Bos release curves followed the Weibull model, wherein the R² value was greater than 0.99. In addition, the a0 values increased significantly with the increase of pH, which was similar to the release behavior of nanoparticles. The a0 values of Bos@SNS/t and
Bos@BMM were 0.768 and 0.773 at pH9, respectively, and the \( a_0 \) values were greater than 0.75, indicating that the release exhibited a complex mechanism. Not only did Fick diffusion influence the release of Bos, but other factors, such as concentration and electrostatic interaction, did as well [34, 35].

Figure 5. The Bos contents of Bos@BMMs Nps and Bos@SNS/t Nps after 14 days.

Figure 6. The Cumulative release profiles and fitting models of Bos released from Bos@SNS/t Nps (A), (B) and Bos@BMMs (C), (D) Nps at different pH values.
3.5. Bioactivity test

To evaluate the biological properties of Bos@SNS/t and Bos@BMMs, the effects of nanoparticles with different concentrations on *Rhizoctonia solani* were investigated. The technical Bos solution was used as a positive comparison. The growth inhibitions of two microspheres and Bos at 8 d are summarized in Figure 7.

Compared to the control, 25.1% (Bos@SNS/t) and 19.2% (Bos@BMMs) inhibition-rate increases were observed at Bos-as-an-active-ingredient contents of 25 mg l\(^{-1}\) at 8d, due to the sustained release of Bos in the nano-delivery systems. The fungicidal efficacy of Bos@SNS/t was slightly superior to that of Bos@BMMs, which was consistent with the release results of nanoparticles. In addition, the antibacterial activity of CTAB were reported in previous study [36], and the existence of CTAB in Bos@SNS/t was also a possible reason for the excellent antibacterial effect. These data show that the biological activity of the microcapsules against fungi was better than that of Bos.

**Table 2.** Kinetic parameters of Bos released from Bos@SNS/t Nps and Bos@BMMs Nps at different pH values.

| Fitting model | Formula | Sample        | pH | \(a_0\) | \(a_1\) | \(R^2\) |
|---------------|---------|---------------|----|---------|---------|--------|
| Zero-order    | \(y = a_0x\) | Bos@SNS/t     | 4  | 0.289   | /       | 0.870  |
|               |         | 7             | 0.310 | /       | 0.866  |
|               |         | 9             | 0.290 | /       | 0.872  |
|               |         | Bos@BMMs      | 4  | 0.263   | /       | 0.896  |
|               |         | 7             | 0.292 | /       | 0.890  |
|               |         | 9             | 0.325 | /       | 0.849  |
| First-order   | \(y = a_0(1 - \exp(-a_1x))\) | Bos@SNS/t     | 4  | 60.127  | 0.026  | 0.864  |
|               |         | 7             | 68.632 | 0.069  | 0.868  |
|               |         | 9             | 76.081 | 0.058  | 0.961  |
|               |         | Bos@BMMs      | 4  | 54.702  | 0.023  | 0.955  |
|               |         | 7             | 61.373 | 0.026  | 0.924  |
|               |         | 9             | 66.978 | 0.047  | 0.920  |
| Higuchi       | \(y = a_0x^{0.5} + a_1\) | Bos@SNS/t     | 4  | 5.307   | 15.100 | 0.982  |
|               |         | 7             | 4.829  | 14.004 | 0.973  |
|               |         | 9             | 4.499  | 3.824  | 0.981  |
|               |         | Bos@BMMs      | 4  | 4.051   | 2.879  | 0.987  |
|               |         | 7             | 4.501  | 5.092  | 0.982  |
|               |         | 9             | 5.075  | 7.882  | 0.963  |
| Weibull       | \(y = 1 - \exp(-a_0x^a_1)\) | Bos@SNS/t     | 4  | 0.626   | 29.997 | 0.997  |
|               |         | 7             | 0.818  | 18.194 | 0.995  |
|               |         | 9             | 0.768  | 19.887 | 0.998  |
|               |         | Bos@BMMs      | 4  | 0.639   | 15.123 | 0.996  |
|               |         | 7             | 0.798  | 18.081 | 0.998  |
|               |         | 9             | 0.773  | 16.953 | 0.997  |

**Figure 7.** Fungicidal efficacy of Bos@SNS/t Nps and Bos@BMMs Nps against *Rhizoctonia solani* at 8d.
4. Conclusions

In this work, controlled-release Bos nanoparticles based on mesoporous silica were successfully fabricated using two different methods. The appearances of the prepared nanospheres were regular spheres, and the small particle sizes of Bos@SNS/t NPs and Bos@BMMs Nps improved the dispersibility in water and increased the wettability on the leaf surface. Bos@SNS/t NPs and Bos@BMMs Nps had remarkable loading rates for Bos (27.3 ± 3.6% and 25.2 ± 2.3%, respectively), and could effectively protect Bos against thermal degradation. The nano-delivery system had good adhesivity and slow release of Bos properties. The release rate of Bos under alkaline condition (pH 9.0) was higher than those under neutral (pH 7.0) and acidic (pH 4.0) conditions, and the release models were fitted with the Weibull equation. A sustained fungicidal efficacy against Rhizoctonia solani compared with the technical Bos solution indicated that the microcapsules could effectively improve the utilization of Bos by reducing the amount of Bos used. In conclusion, there is no obvious difference between the properties and efficacy of Bos@SNS/t NPs and Bos@BMMs Nps. However, the preparation process was simplified and the operation time was short, i.e., a one-step method, which is helpful for the promotion and large-scale utility of nanoparticles in future agriculture.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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