Article

Optimized Preparation of Methyl Salicylate Hydrogel and Its Inhibition Effect on Potato Tuber Sprouting

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Abstract: Potato tuber sprout results in nutrient loss and solanine production. Essential oils have been mentioned to reduce sprouting; however, they can easily evaporate and decompose, thus restricting their application. In this paper, the inhibition effect of methyl salicylate (MeSA) as the main component of wintergreen essential oil on tuber sprouting was evaluated, and MeSA hydrogel was prepared by using the ionic gel method to improve the sprout inhibition efficiency. Based on SEM, FTIR, XRD, and DSC images, MeSA was encapsulated successfully in calcium alginate hydrogel, and the thermal stability of hydrogel was improved. MeSA direct fumigation released sharply on the first day, while MeSA in hydrogel released slowly and steadily; the release of MeSA content was 0.0085 mg mL$^{-1}$ on the 7th day. The optimized formulations of MeSA hydrogel were as follows: 1.9% of sodium alginate, 2.2% of CaCl$_2$, 1.9:1 of core-wall ratio, and 0.15% of Tween-80. The inhibition effect of MeSA hydrogel was better than that of pure MeSA at 18 days, the sprouting rates of the MeSA and MeSA hydrogel were 42.50% and 13.33%, and the corresponding sprouting indexes were 8.57% and 2.86%, respectively. MeSA was found to inhibit potato tuber sprouting for the first time in this paper; MeSA hydrogel can enhance the inhibitory effect of MeSA on potato sprouting.

Keywords: potato tuber; sprout inhibition; methyl salicylate; hydrogel

1. Introduction

Potato (Solanum tuberosum L.) is an annual herb of Solanaceae, which is recognized as one of the most ubiquitous crops in the world, after rice, maize, and wheat. The global production of potatoes is about 368 million tons, with more than 5000 known varieties [1]. Sprouting is the main cause of loss during post-harvest storage and logistics, since it damages tuber nutrients and increases water loss of the tuber surface [2] and the production of the toxic substance solanine; therefore, the development of effective sprouting-inhibition methods is urgently needed in order to reduce tuber sprouting.

Many methods have been explored for inhibiting potato sprouting, such as reducing storage temperature [3], using chemical reagents [4] and irradiation technology [5]. During low-temperature storage (about 0°C), a large amount of reducing sugar is accumulated in tuber, and this depends on the acid invertase activity [6], resulting in browning of the potato and the formation of substances such as acrylamide, which seriously reduces the commercial value of potatoes and endangers the human health. Isopropyl N-(3-chlorophenyl) carbamate (CIPC) is widely used in potato storage due to its low cost and good inhibition effect on potato sprouting, but its degradation products may produce harmful substances to human body and pollute the environment [7]. The minimum residual amount of CIPC is limited to 30 mg kg$^{-1}$ by the Food and Drug Administration (FDA) and US Environmental Protection Agency (EPA), and the national food safety standard in China also stipulates the same; however, CIPC is no longer approved for use in the European Union [8].
effects of radiation treatment are irreversible, and gamma irradiation has harmful effects on potato quality and is currently prohibited in the European Union [9].

In recent years, essential oils have been used to inhibit potato sprouting, such as garlic essential oil [10], citronella essential oil [11], and Rosmarinus officinalis essential oil [12]. Methyl salicylate (MeSA) is the main component of wintergreen essential oil, which is classified as safe in the US (FDA) and China (GB28355-2012). Studies have shown that MeSA can enhance cold tolerance of apricots [13], control aphids [14], and enhance the resistance of rice to Xanthomonas oryzae pv. Oryzae [15]. However, the inhibitory effect of MeSA on potato sprouting has not been reported.

Additionally, essential oils are expensive, and they can easily evaporate and decompose in response to air, temperature, and light; thus, they need to be replaced every few weeks during commercial storage. Therefore, the development of transport systems that can prolong the release of essential oils will effectively suppress potato sprouting during storage and logistics. At present, essential oils are commonly encapsulated in microcapsules [16], microspheres [17], and hydrogels [18] to achieve slow release. Hydrogel is a hydrophilic polymer formed by physical or chemical crosslinking, which is widely used in drug delivery [19], tissue engineering [20], and the food industry [21]. Polysaccharide hydrogels have become a research hotspot due to their structural diversity, good biocompatibility, and biodegradability [22]. Therefore, polysaccharides, including cellulose [23], sodium alginate [24], chitosan [25], and hyaluronic acid [26], are widely used in hydrogels. Sodium alginate is a natural anionic polysaccharide compound extracted from brown algae and seaweed, consisting of  β -d-mannuronic acid (M) and  α -l-guluronic acid (G) [27]. Sodium alginate can be crosslinked with divalent cations to form hydrogels, such as Ba$^{2+}$, Sr$^{2+}$, Ca$^{2+}$, and Zn$^{2+}$ [28]. In addition, sodium alginate has been used as wall materials to encapsulate essential oil or bioactive components because of its good biocompatibility and biodegradability.

In recent years, many researchers have used calcium alginate hydrogels to embed essential oils and easily oxidized components. Shin et al. [29] encapsulated volatile and insoluble thyme white essential oil with sulfonated cellulose nanocrystals, and then embedded sodium alginate to form hydrogel beads. Aedes albopictus larvae had the highest mortality rate when treated with SA/PEs hydrogel beads formed by 0.50% CaCl$_2$. In addition, the incorporation of emulsified oils into hydrogels protects sensitive bioactive components, such as ω-3 fatty acids, from chemical degradation [30]. Potiwiput et al. prepared dual-crosslinked Alg/CMC hydrogels by using ionic crosslinking and electrostatic interaction for loading drugs tetracycline hydrochloride and silver sulfadiazine [31]. Due to the good anti-bud activity and volatility of essential oils, many researchers have developed anti-bud products in recent years. Ge et al. [32] chose HPβCD to form an inclusion complex with s- (+)-carvone to improve its instability properties and obtain a better sprout-inhibition effect; among them, the s- (+)-carvone/HPβCD complex with host–guest ratio was 1:1. The s- (+)-carvone/HPβCD composite treatment can effectively inhibit the potato sprouting; at the storage of 70 d, the sprouting rate is still less than 20%. Arnon-Rips et al. [33] prepared reactive carboxymethyl cellulose films containing coarse emulsions or nanoemulsions of citral and used them as potato packaging. After 28 days of storage, nano-emulsified citral carboxymethyl cellulose films inhibited sprouting by 80%, resulting in less weight loss and maintaining the organoleptic properties of potato tubers. In this study, we found that MeSA had the inhibition effect on potato tuber sprouting for the first time. However, MeSA is extremely susceptible to evaporation and decomposition, and has a higher price than conventional budding suppressors (such as CIPC), and this seriously limits its application. MeSA hydrogel was prepared by ionic crosslinking of sodium alginate and calcium chloride in order to improve the utilization rate of MeSA and reduce the amount of essential oil. Taking the encapsulation efficiency as the response value, the optimum preparation conditions of MeSA hydrogel were obtained by a single-factor test and response-surface optimization test, and the MeSA hydrogel was thereafter used for the inhibition test of potato sprouting. According to the release of MeSA content in hydrogel, the prepared
MeSA hydrogel has the advantage of slow release, which has a better inhibition effect on sprouting than using pure MeSA to treat potato tubers and reduces the amount of MeSA at the same time. We aim to provide a new idea for inhibiting potato sprouting during storage and logistics after dormancy release. MeSA is derived from plants, and its safety has been confirmed; therefore, MeSA hydrogel is expected to be widely used as a green and safe potato-bud suppressor.

2. Materials and Methods

2.1. Materials

Potato tubers were purchased from a local market (Jinan, China) in January 2022; they were harvested in August 2021 and stored in a refrigerator at 3 ± 0.5 °C. Potato tubers of the early variety “Favorita”, which had passed the dormant stage, were used for all experiments. The potato tubers were transported to the laboratory and screened; then uniformly sized potatoes with no mechanical damage and no pests and diseases were selected and sorted into 10 L plastic baskets.

Methyl salicylate (MeSA, purity: 99%, CAS No: 119-36-8) was purchased from Shanghai Maclin Biochemical Technology Co., Ltd. (Shanghai, China).

2.2. Inhibition Test of Potato Sprouting

Potatoes were placed in plastic baskets (10 L), with each basket containing 2 kg of potatoes, and with three baskets for each treatment. Potato tubers were treated with pure MeSA at a dose of 1.0 mL kg\(^{-1}\). The specific operation was as follows: pure MeSA was dropped onto filter paper, and the filter paper was pasted on the outside of the plastic basket for airtight fumigation. Potatoes were sealed and stored for 18 days at room temperature (25 ± 1 °C); then the sprouting rate and sprouting index were measured at 3-day intervals.

Five potatoes were randomly selected from each treatment, and the length of the longest sprout was measured by using a vernier caliper. The sprout length less than 2 mm is regarded as not sprouting or in sprouting state. The classification standards of potato tuber sprouting are as follows: 0 level (0 < L ≤ 2), 1 level (2 < L ≤ 5), 2 level (5 < L ≤ 10), 3 level (10 < L ≤ 15), 4 level (15 < L ≤ 20), 5 level (20 < L ≤ 25), 6 level (25 < L ≤ 30), and 7 level (L ≥ 30) (L: sprout length/mm) [34]. The sprouting rate and sprouting index were calculated according to the following equations:

\[
\text{Sprouting rate (\%)} = \frac{\text{no. of sprouted tubers}}{\text{total no. of tubers}} \times 100
\]

\[
\text{Sprouting index (\%)} = \left(\frac{x_1 \times 0 + x_2 \times 1 + \ldots + x_8 \times 7}{5 \times 7}\right) \times 100
\]

2.3. Preparation of MeSA Hydrogel

The preparation of hydrogel was based on the method of Mokhtari et al. [35], which was improved and optimized. Sodium alginate was added to distilled water and stirred continuously on a magnetic stirrer until dissolved to obtain a 1.0% (w/v) of sodium alginate solution. The obtained solution was sonicated for 20 min to remove the bubbles. Then 0.2% (v/v) of Tween-80 and MeSA were added to the solution and magnetically stirred for 5 min at 1000 rpm. The 1.5% (w/v) of calcium chloride (CaCl\(_2\)) solution was made by dissolving anhydrous calcium chloride in distilled water. A mixture of sodium alginate and MeSA was filled in a 1 mL syringe, extruded in calcium chloride solution, and then left for 2 h. The fabricated samples were washed with distilled water 3 times to remove excess of the crosslinker.

2.3.1. Single-Factor Experiments

The sodium alginate concentration (0.5%, 1.0%, 1.75%, 2.5%, and 3.25% (w/v), respectively), CaCl\(_2\) concentration (1.0%, 1.5%, 2.0%, 2.5%, and 3.0% (w/v), respectively), Tween-80 concentration (0.1%, 0.15%, 0.2%, 0.25%, and 0.3% (v/v), respectively), and core–wall ratio
(0.5:1, 1:1, 2:1, 3:1, and 4:1, respectively) were selected as single factors for the experiment. When investigating the influence of one factor on the encapsulation efficiency of the MeSA hydrogel, the other factors were 1.0% (w/v) of sodium alginate, 1.5% (w/v) of CaCl₂, 0.2% (v/v) of Tween-80, and 2:1 of core–wall ratio.

2.3.2. RSM Design for Optimization of Encapsulation Efficiency

Combined with the results of single-factor experiments, Response Surface Methodology (RSM) based on Box–Behnken Design (BBD) was used to optimize the encapsulation efficiency. Taking the sodium alginate concentration (A), CaCl₂ concentration (B), and core–wall ratio (C) as independent variables, and the encapsulation efficiency (Y) as a response variable, we studied the effects of various factors on the encapsulation efficiency of MeSA. Table 1 shows the response surface factors and the coded levels. Table 2 shows the specific experimental scheme, in which seventeen experiments were conducted in triplicate.

Table 1. Coded and actual values for Box–Behnken Design (BBD).

| Independent Variable | Coded Levels |
|----------------------|--------------|
|                      | -1 | 0 | 1  |
| A: Sodium alginate (%) | 1.0 | 1.75 | 2.5  |
| B: CaCl₂ (%)         | 1.5 | 2.0 | 2.5  |
| C: Core–wall ratio    | 1:1 | 2:1 | 3:1  |

Table 2. The experimental run from Box–Behnken Design (BBD).

| Run | A   | B   | C     | Y Encapsulation Efficiency/% |
|-----|-----|-----|-------|------------------------------|
| 1   | 1.75| 2.0 | 2:1   | 83.21                        |
| 2   | 1.75| 2.0 | 2:1   | 82.25                        |
| 3   | 1.00| 2.0 | 1:1   | 71.68                        |
| 4   | 1.75| 2.0 | 2:1   | 82.54                        |
| 5   | 1.75| 1.5 | 1:1   | 78.74                        |
| 6   | 2.50| 1.5 | 2:1   | 75.26                        |
| 7   | 1.75| 2.5 | 1:1   | 79.67                        |
| 8   | 1.75| 2.5 | 3:1   | 80.51                        |
| 9   | 1.75| 2.0 | 2:1   | 82.97                        |
| 10  | 1.75| 1.5 | 3:1   | 75.75                        |
| 11  | 2.50| 2.0 | 3:1   | 74.69                        |
| 12  | 2.50| 2.5 | 2:1   | 79.21                        |
| 13  | 1.00| 1.5 | 2:1   | 69.82                        |
| 14  | 1.00| 2.5 | 2:1   | 74.24                        |
| 15  | 1.00| 2.0 | 3:1   | 73.27                        |
| 16  | 1.75| 2.0 | 2:1   | 82.04                        |
| 17  | 2.50| 2.0 | 1:1   | 78.92                        |

2.3.3. Determination of Encapsulation Efficiency

The encapsulation efficiency of MeSA hydrogel was determined by a UV–Vis spectrophotometer [36]. MeSA hydrogel (0.2 g) and anhydrous ethanol solution (95%, 10 mL) were placed in a mortar and ground until completely broken. The mixed solution was sonicated for 5 min to release the encapsulated MeSA and centrifuged at 12,000 rpm for 10 min at 4 °C. The supernatant was collected and diluted to a suitable concentration, and the absorbance of the samples was measured at a wavelength of 309 nm by UV–Vis spectrophotometer. The concentration of MeSA was determined by using an appropriate calibration curve for MeSA in ethanol (y = 24.674x − 0.0649; R² = 0.9969), and the encapsulation efficiency was calculated by using the following equation:

\[
\text{Encapsulation efficiency (\%)} = \frac{\text{Total amount of loaded MeSA}}{\text{Initial amount of MeSA}} \times 100 \tag{3}
\]
2.4. Characterization of MeSA Hydrogel

2.4.1. Morphology and Size of the MeSA Hydrogel

The macro-morphology of MeSA hydrogel was observed by a digital camera. The surface morphology and the microstructure of the product were examined by using a field emission scanning electron microscope (FE-SEM Supra 55 V P, Carl Zeiss, Overkochen, Germany). Prior to analyses, the prepared hydrogels were frozen at $-80^\circ$C for 12 h and then freeze-dried for 24 h. Dried samples were glued with conductive adhesive and coated with 15 nm platinum coating.

2.4.2. Fourier-Transform Infrared (FTIR) Spectroscopy

The molecular structure of sodium alginate, empty hydrogel and MeSA hydrogel composite were characterized by a Fourier-transform infrared (FTIR) spectroscopy in the range of 500 to 4000 cm$^{-1}$, at a resolution of 4 cm$^{-1}$ (FTIR spectroscopy, Nicolet iS 10, Thermo Scientific, Newington, NH, USA). The samples were ground with KBr and then placed on a diamond crystal plate for scanning.

2.4.3. Differential Scanning Calorimetry (DSC) Analysis

The thermal stability of samples was carried out by using differential scanning calorimeter from 20 $^\circ$C to 200 $^\circ$C, at a heating rate of 10 $^\circ$C/min [37]. Approximately 5 mg of the samples was loaded into a closed aluminum crucible and placed in a sample tank for DSC testing (DSC, Q600, TA Instrument, New Castle upon Tyne, DE, USA).

2.4.4. X-ray Diffraction (XRD) Spectroscopy

The freeze-dried gel particles were poured into the groove to obtain a flat surface without cracks. The crystallinity of the sample was determined by X-ray diffractometry (XRD, XRD-6100, Shimadzu, Shnaghai, China), using Cu-K$\alpha$ radiation. The test conditions of the sample were a voltage of 30 kV and a current of 20 mA. The diffraction angle ranges from 5$^\circ$ to 50$^\circ$, and the scanning speed is 8$^\circ$/min.

2.5. Release Properties of MeSA Hydrogel

The release properties of MeSA hydrogel were slightly modified according to previous method [38]. In the same way, the predicted values of hydrogel were adjusted to 1.9% of sodium alginate, 2.2% of CaCl$_2$, 1.9:1 of core–wall ratio, and 0.15% of Tween-80, and a release test of MeSA was conducted. The 1 g of MeSA hydrogel was immersed in a mixture of 2 mL distilled water and 5 mL ethanol at 25 $^\circ$C for 24 h; MeSA was also treated under the same conditions. The amount of MeSA in the supernatant was measured by using UV–Vis spectrophotometer at a wavelength of 309 nm.

2.6. Inhibition of MeSA Hydrogel on Potato Sprouting

The hydrogels were prepared under the conditions corresponding to the lowest encapsulation efficiency, the highest encapsulation efficiency, and the optimal value of encapsulation efficiency in the response surface-optimization experiment. The specific preparation parameters were as follows: (1) lowest encapsulation efficiency: 1.00% of sodium alginate, 1.5% of CaCl$_2$, 2.0:1 of core–wall ratio, and 0.15% of Tween-80; (2) highest encapsulation efficiency: 1.75% of sodium alginate, 2.0% of CaCl$_2$, 2.0:1 of core–wall ratio, 0.15% of Tween-80; (3) optimal value of encapsulation efficiency: 1.9% of sodium alginate, 2.2% of CaCl$_2$, 1.9:1 of core–wall ratio, and 0.15% of Tween-80. Potatoes were treated with the kinds of MeSA hydrogels, and pure MeSA was used as the control; all the treatment doses were 0.5 mLkg$^{-1}$. After preparation of the MeSA hydrogel, the water on the surface was absorbed by filter paper and placed in a Petri dish. Potatoes were placed around the Petri dish and stored for 18 days at room temperature (25 ± 1 $^\circ$C); in the control group, pure MeSA was dropped on filter paper, and the filter paper was pasted on the outside of the plastic basket for 18 days. The above treatments were sealed with polyethylene bags of
0.03 mm thickness, and then the sprouting rate and sprouting index were measured at 3-day intervals.

2.7. Statistical Analysis

All samples were analyzed in triplicate, and the SPSS software (25.0, IBM, Armonk, NY, USA) was used to analyze the data and evaluate its significance. Differences were considered significant at a level of 95% ($p < 0.05$). The experimental design and response surface optimization analysis were performed by using Design Expert 12.0 (Stat-Ease Inc., Minneapolis, MN, USA, licensed to ICAR-CMFR). Based on the preliminary results of the single-factor experiments, we determined the variables and their ranges. The independent variables (sodium alginate concentration, CaCl$_2$ concentration, and core–wall ratio) and response variable (encapsulation efficiency) were subjected to an ANOVA and regression analysis to assess the significance of the constructed model. According to the ANOVA analysis results, the significance of linear terms, interaction terms, and quadratic terms can be obtained.

3. Results and Discussions

3.1. Inhibition Test of Potato Sprouting

The tuber sprouting morphology during the storage of potatoes treated with pure MeSA is shown in Figure 1A. On the 18th day of storage, the number of potato tuber sprouts in the control check (CK) was much more than that in the pure MeSA treatment, and the terminal sprouts in the treatment were black. At the end of storage (18 d) for potato tubers, the sprouting rate and sprouting index of the pure MeSA treatment were 42.50% and 8.57% respectively, while those of the CK were 100.00% and 24.86%, respectively. These results showed that MeSA could effectively inhibit potato tuber sprouting, and the inhibitory effect of MeSA on potato tuber sprouting was first reported in this study.

![Figure 1. Effect of MeSA treatment on potato tuber sprouting (A), sprouting rate (B), and sprouting index (C). Each value represents mean ± standard deviation of three replicates.](image-url)
3.2. Preparation and Characterization of MeSA Hydrogel

3.2.1. Single-Factor Experiments

The sodium alginate concentration, CaCl$_2$ concentration, Tween-80 concentration, and core–wall ratio were taken as variables to investigate the effects of these factors on the encapsulation efficiency of the hydrogel. In this study, the sodium alginate concentration increased from 0.5% to 3.25%, and the encapsulation efficiency increased first and then decreased (Figure 2A). When the sodium alginate concentration was 1.75%, the encapsulation rate reached 77.12%. An increase in cohesion property by enhancing the sodium alginate concentration results in more MeSA being encapsulated in the matrix [35]; however, Choi et al. reported that a high sodium alginate concentration (2.5–5%) increased the viscosity of the solution and produced elongated beads [39]. The same phenomenon is also observed in this experiment, and this may be the reason why the concentration of sodium alginate is higher and the encapsulation efficiency is lower. Sevda et al. believed that increasing Na$^+$ concentration reduced the pore space in the beads and, thus, encapsulated less MeSA [40].

![Figure 2](image-url)

**Figure 2.** Effect of sodium alginate concentration (A), Tween-80 concentration (B), CaCl$_2$ concentration (C), and core–wall ratio (D) on encapsulation efficiency. Each value represents mean ± standard deviation of three replicates.

The encapsulation efficiency increased with the increase of CaCl$_2$ concentration and reached a maximum value when the CaCl$_2$ concentration was 2.0% (Figure 2C). These results are supported by Soliman et al., who found that the increase of CaCl$_2$ concentration from 0.125% to 0.5% leads the encapsulation efficiency to reach 23% for thyme. Nevertheless, the CaCl$_2$ concentration increased over 2.0%, and the encapsulation efficiency decreased gradually [41]. By increasing the CaCl$_2$ concentration, the pores in the alginate matrix become smaller, causing a decrease in the encapsulation efficiency.

The encapsulation efficiency was the highest when the Tween-80 concentration was 0.2% (Figure 2B). Due to the interaction between the emulsifier and oil molecule, the interfacial tension changed, and the oil entered the water phase to form a stable emulsion, which was embedded under the action of the ionic crosslinker. When the core–wall ratio
was 2:1, the encapsulation efficiency reached the maximum value (78.24%) and then showed a decreasing trend (Figure 2D). The reason may be that the amount of essential oil added was too high to be completely emulsified, thus forming an uneven emulsion.

3.2.2. Optimized Formulation of Encapsulation Efficiency

The effects of various factors on the encapsulation efficiency are shown in the ANOVA results in Table 3. The value of the coefficient of correlation ($R^2$) was 0.9921, indicating that 99.21% changes in response values were related to the selected factors. The adj. - $R^2$ values of the model was 0.9819, which revealed that the model fit well. The analysis of variance suggested that the model was significantly different ($p < 0.0001$), whereas the difference in the lack-of-fit term was not significant ($p > 0.05$). Sodium alginate and CaCl$_2$, as well as the quadratic terms $A^2$, $B^2$, and $C^2$, reached extremely significant levels. According to the influence of each factor on the encapsulation efficiency, the order was $A > B > C$, namely sodium alginate > CaCl$_2$ > core–wall ratio. After analyzing the data in Table 3, we determined that the quadratic multinomial regression equation was as follows:

$$Y = 82.60 + 2.38A + 1.76B - 0.5988C - 0.1175AB - 1.45AC + 0.9575BC - 6.00A^2 - 1.97B^2 - 1.96C^2$$

Table 3. Analysis of variance for determination of optimization model fit.

| Source                | Sum of Squares | df | Mean Square | F-Value | p-Value |
|-----------------------|----------------|----|-------------|---------|---------|
| Model                 | 283.33         | 9  | 31.48       | 97.54   | <0.0001 |
| A: Sodium alginate (%)| 45.46          | 1  | 45.46       | 140.84  | <0.0001 |
| B: CaCl$_2$ (%)       | 24.71          | 1  | 24.71       | 76.56   | <0.0001 |
| C: Core–wall ratio    | 2.87           | 1  | 2.87        | 8.89    | 0.0205  |
| AB                    | 0.0552         | 1  | 0.0552      | 0.1711  | 0.6915  |
| AC                    | 8.47           | 1  | 8.47        | 26.24   | 0.0014  |
| BC                    | 3.67           | 1  | 3.67        | 11.36   | 0.0119  |
| $A^2$                 | 151.50         | 1  | 151.50      | 469.40  | <0.0001 |
| $B^2$                 | 16.36          | 1  | 16.36       | 50.68   | 0.0002  |
| $C^2$                 | 16.23          | 1  | 16.23       | 50.29   | 0.0002  |
| Residual              | 2.26           | 7  | 0.3228      |         |         |
| Lack of fit           | 1.31           | 3  | 0.4369      | 1.84    | 0.2799  |
| Pure error            | 0.9487         | 4  | 0.2372      |         |         |
| Cor Total             | 285.59         | 16 |             |         |         |

As shown by the 2D contour plots and 3D response surface plots (Figure 3), with the increase of the sodium alginate concentration and CaCl$_2$ concentration, the encapsulation efficiency firstly increased and then decreased slowly. The interaction between the sodium alginate concentration (A) and CaCl$_2$ concentration (B) was not significant. The addition of Ca ions to the sodium alginate solution caused the formation of an egg–box structure, and the viscosity of the solution increased with the increase of Ca ion concentration, which caused the MeSA to become encapsulated and difficult to release. The effect of the CaCl$_2$ concentration and core–wall ratio on the encapsulation efficiency is seen in Figure 3C,F. The 2D contour plot was an ellipse, and the slope of the 3D response surface plot was large, indicating a significant interaction between the two factors. For the same reason, the interaction between CaCl$_2$ concentration (B) and core–wall ratio (C) was significant.

3.2.3. Accuracy of Predictive Models

The reliability of the model was validated by comparing the predicted value with the actual value. According to the model, the optimized formulation of MeSA hydrogel was composed by 1.91% of sodium alginate, 2.2% of CaCl$_2$, 1.87:1 of core–wall ratio, 0.15% of Tween-80, and with an encapsulation efficiency of 83.25%. The adjustment conditions were 1.9% of sodium alginate, 2.2% of CaCl$_2$, 1.9:1 of core–wall ratio, 0.15% of Tween-80. Under these conditions, three validation tests were carried out, the measured encapsulation
efficiency was 83.06%. These actual values were close to the predicted values, indicating that the model had high reliability.

Table 3. Analysis of variance for determination of optimization model fit.

| Source        | Sum of Squares | df  | Mean Square | F-Value | p-Value  |
|---------------|----------------|-----|-------------|---------|----------|
| Model         | 283.33         | 9   | 31.48       | 97.54   | <0.0001  |
| A: Sodium alginate (%) | 45.46         | 1   | 45.46       | 140.84  | <0.0001  |
| B: CaCl₂ (%)  | 24.71          | 1   | 24.71       | 76.56   | <0.0001  |
| C: Core–wall ratio | 2.87          | 1   | 2.87        | 8.89    | 0.0205   |
| AB            | 0.0552         | 1   | 0.0552      | 0.1711  | 0.6915   |
| AC            | 8.47           | 1   | 8.47        | 26.24   | 0.0014   |
| BC            | 3.67           | 1   | 3.67        | 11.36   | 0.0119   |
| A²            | 151.50         | 1   | 151.50      | 469.40  | <0.0001  |
| B²            | 16.36          | 1   | 16.36       | 50.68   | 0.0002   |
| C²            | 16.23          | 1   | 16.23       | 50.29   | 0.0002   |
| Residual      | 2.26           | 7   | 0.3228      |         |          |
| Lack of fit   | 1.31           | 3   | 0.4369      | 1.84    | 0.2799   |
| Pure error    | 0.9487         | 4   | 0.2372      |         |          |
| Cor Total     | 285.59         | 16  |             |         |          |

As shown by the 2D contour plots and 3D response surface plots (Figure 3), with the increase of the sodium alginate concentration and CaCl₂ concentration, the encapsulation efficiency firstly increased and then decreased slowly. The interaction between the sodium alginate concentration (A) and CaCl₂ concentration (B) was not significant. The addition of Ca ions to the sodium alginate solution caused the formation of an egg–box structure, and the viscosity of the solution increased with the increase of Ca ion concentration, which caused the MeSA to become encapsulated and difficult to release. The effect of the CaCl₂ concentration and core–wall ratio on the encapsulation efficiency is seen in Figure 3C,F. The 2D contour plot was an ellipse, and the slope of the 3D response surface plot was large, indicating a significant interaction between the two factors. For the same reason, the interaction between CaCl₂ concentration (B) and core–wall ratio (C) was significant.

3.2.4. Morphology and Size of the Hydrogel

The macroscopic morphology of the empty hydrogel (without MeSA) and MeSA hydrogel is illustrated in Figure 4A,B, respectively. The empty hydrogel is transparent and smooth, while the MeSA hydrogel is milky white and not smooth. As clearly seen, the surface of the empty hydrogel is flatter, with only a few bumps and gaps, whereas MeSA hydrogel is uneven and folded (Figure 4C,D), and this may be caused by the surface shrinkage of the MeSA hydrogel after vacuum freeze-drying. Additionally, porous structures appeared on the surface of the MeSA hydrogel, indicating the presence of water between the alginate polymers before being dried [42].

3.2.5. Fourier-Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of sodium alginate, empty hydrogel, and MeSA hydrogel in the wavenumber region of 4000–500 cm⁻¹ are shown in Figure 5A. The signals in the range of 3600–3000 cm⁻¹ were assigned to the stretching vibrations of the hydroxyl group (O-H). The MeSA hydrogel exhibited a broad and strong hydroxyl stretching band at 3172 cm⁻¹; however, the hydroxyl stretching vibration peak of sodium alginate appeared at 3250 cm⁻¹. The characteristic peaks of sodium alginate at 1591 cm⁻¹ and 1397 cm⁻¹ were asymmetric and symmetric stretchings of COO⁻, respectively. These two peaks moved to 1588 cm⁻¹ and 1437 cm⁻¹ in the MeSA hydrogel, respectively. The peak of the MeSA hydrogel was 1041 cm⁻¹, which suggested the symmetric stretching vibration of C-O-C [43]. Compared with the infrared spectrum of sodium alginate, no new chemical bands appeared in the hydrogel, thus indicating that no new chemical bond formed between the alginate and MeSA.
3.2.4. Morphology and Size of the Hydrogel

The macroscopic morphology of the empty hydrogel (without MeSA) and MeSA hydrogel is illustrated in Figure 4A,B, respectively. The empty hydrogel is transparent and smooth, while the MeSA hydrogel is milky white and not smooth. As clearly seen, the surface of the empty hydrogel is flatter, with only a few bumps and gaps, whereas MeSA hydrogel is uneven and folded (Figure 4C,D), and this may be caused by the surface shrinkage of the MeSA hydrogel after vacuum freeze-drying. Additionally, porous structures appeared on the surface of the MeSA hydrogel, indicating the presence of water in the hydrogel matrix. This may be attributed to the hydrophilic and water-retaining of sodium alginate, resulting in a large amount of constant evaporation of water molecules in the hydrogel matrix. This may be attributed to the hydrophilic and water-retaining of sodium alginate, resulting in a large amount of water inside the hydrogel being lost as the temperature increases. The temperature corresponding to the absorption peak of the MeSA hydrogel was higher than that of the empty hydrogel, thus indicating that the stability of the hydrogel was improved after the crosslinking.

3.2.6. Differential Scanning Calorimetry (DSC) Analysis

The DSC thermograms of sodium alginate, empty hydrogel, and MeSA hydrogel are given in Figure 5B. The sodium alginate has a strong and narrow absorption peak at 141.92 °C, while the empty hydrogel (without MeSA) and MeSA hydrogel have a wide and weak absorption peak at 148.73 °C and 171.79 °C, respectively, which may be due to the constant evaporation of water molecules in the hydrogel matrix. This may be attributed to the hydrophilic and water-retaining of sodium alginate, resulting in a large amount of water inside the hydrogel being lost as the temperature increases. The temperature corresponding to the absorption peak of the MeSA hydrogel was higher than that of the empty hydrogel, thus indicating that the stability of the hydrogel was improved after the crosslinking.
inclusion of MeSA. The polymer chain begins to decompose at 250 °C and is completely decomposed at 300–400 °C. The maximum temperature in this study was 200 °C, so no endothermic peak of the polymer was found [44].

3.2.7. X-ray Diffraction (XRD) Spectroscopy

The XRD patterns of sodium alginate, empty hydrogel, and MeSA hydrogel are shown in Figure 5C. As shown in the figure, characteristic peaks appeared in sodium alginate and MeSA hydrogel, and the positions of their characteristic peaks were different. The typical characteristic of hydrogel is that the hydrogel formed by sodium alginate is amorphous. The characteristic peaks of sodium alginate appeared at 2θ = 13.65° and 22.71°, while those for the MeSA hydrogel appeared at 2θ = 13.77° and 22.96°, respectively. The width of the characteristic peak is closely related to the crystallinity of the material; the crystallinity increases with the decreasing characteristic peak width. The characteristic peak of sodium alginate is wide, while the characteristic peak of MeSA hydrogel is narrow and steep, indicating that the hydrogel crystal strength increases after encapsulating MeSA. The above X-ray diffraction diagram shows that MeSA is successfully encapsulated in sodium alginate hydrogel.

3.3. Release Properties of MeSA Hydrogel

The release properties of MeSA are closely related to its ability to inhibit potato sprouting. When released slowly and steadily for a certain period, MeSA is beneficial for controlling potato sprouting. The time-dependent-release properties of MeSA are shown in Figure 6; MeSA in hydrogel released slowly and steadily evidently, and the release of MeSA was 0.0085 mg mL\(^{-1}\) on the 7th day, while MeSA direct fumigation released sharply on the first day, and MeSA content decreased to 0.0083 mg mL\(^{-1}\) on 4th day and 0.0011 mg mL\(^{-1}\) on 7th day, respectively. This indicated that MeSA hydrogel can continue to be released during a week of monitoring. Studies have shown that the calcium concentration and crosslinking time could affect the release amount of encapsulated substances in hydrogel; the amount of MeSA released from the hydrogel decreased as the calcium concentration was increased, while the amount of MeSA released was positively correlated with the time of crosslinking [45]. Therefore, in this study, the optimized MeSA hydrogel not only had a high encapsulation efficiency but also was released slowly and stably after encapsulation, thus achieving the purpose of sustained drug supply.

![Figure 6](image-url)  
**Figure 6.** The release properties of MeSA in hydrogel. Each value represents mean ± standard deviation of three replicates.
3.4. Inhibition of MeSA Hydrogel on Potato Sprouting

At the end of storage (18 d) for potato tubers, it was clear that the control check (CK) had longer sprouts, and the MeSA direct fumigation treatment had more sprouts, but less than the CK (Figure 7A). For the lowest encapsulation efficiency (69.82%), the highest encapsulation efficiency (83.21%), and the optimal value treatment, the lowest encapsulation efficiency treatment had the largest number of sprouts, mainly concentrated in the terminal sprouts, while the highest encapsulation efficiency and optimal value treatment had fewer and slender sprouts. Meanwhile, the sprouting rate and sprouting index of the optimal value treatment were 13.33% and 2.86%, respectively, which had a significant difference level (p < 0.05). It should be emphasized that the effective dose of hydrogel is 0.5 mL kg\(^{-1}\), which is only half of the previous effective dose of pure MeSA (1.0 mL kg\(^{-1}\)). Under the same storage conditions, the inhibition effect on the sprouting of hydrogel is significantly better than that of pure MeSA fumigation. After direct fumigation with pure MeSA (1.0 mL kg\(^{-1}\)), the sprouting rate and sprouting index of potato tubers at 18 days were 42.50% and 8.57%, respectively. These results showed that optimal value treatment effectively delayed potato sprouting and maintained the sprouting rate and sprouting index at a low level.

![Figure 7. Effect of different treatments on potato tuber sprouting (A), sprouting rate (B), and sprouting index (C). Each value represents mean ± standard deviation of three replicates.](image)

4. Conclusions

In this study, we first found that MeSA had an inhibitory effect on potato tuber sprouting. The MeSA hydrogel prepared by the RSM had an encapsulation efficiency of 83.25%, and it released slowly and steadily; the release of MeSA was 0.0085 mg mL\(^{-1}\) on the 7th day, whereas MeSA direct fumigation released sharply on the first day, and the MeSA content decreased to 0.0083 mg mL\(^{-1}\) on 4th day and 0.0011 mg mL\(^{-1}\) on 7th day. The optimized formulations of MeSA hydrogel were as follows: 1.9% of sodium alginate,
2.2% of CaCl$_2$, 1.9:1 of core–wall ratio, and 0.15% of Tween-80. After 18 days of storage, the sprouting rate and sprouting index of potato tubers in the CK group was 100.00% and 28.57%, whereas the MeSA hydrogel treatment of 0.5 mL kg$^{-1}$ showed to be the more efficient, which was 13.33% and 2.86%, respectively ($p < 0.05$). The results showed that, after the optimized preparation, MeSA hydrogel was more effective than that of pure MeSA in potato-sprouting inhibition, and the usage of MeSA can be reduced by more than half. The result suggests a promising technology for essential oils in potato-tuber-sprouting inhibition.

5. Future Work

MeSA, as a plant-derived essential oil, is non-toxic and harmless to the human body; it can be used as a new green and safe potato-sprout suppressant for promotion. However, there are still some problems to be solved in the future in theory and applications, such as (1) the specific physiological, biochemical, and molecular mechanisms of how hydrogels inhibit potato sprouting need to be further studied; (2) how to reduce or mask the odor of MeSA after use to make consumers accept it; (3) the preparation process of MeSA hydrogel is not easy to operate, so it is necessary to improve the operation process on the basis of optimizing the formula for the promotion of MeSA hydrogel sprout suppressant; and (4) at present, the application effect of MeSA hydrogel is only carried out in the laboratory. In the next step, appropriate optimization and validation of the test conditions will be carried out, and relevant experiments will be conducted under actual transportation or storage conditions, thus paving the way for the production of green and effective potato-sprout suppressant.

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