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Preparation and Characterization of Novel Functionalized Prochloraz Microcapsules Using Silica–Alginate–Elements as Controlled Release Carrier Materials

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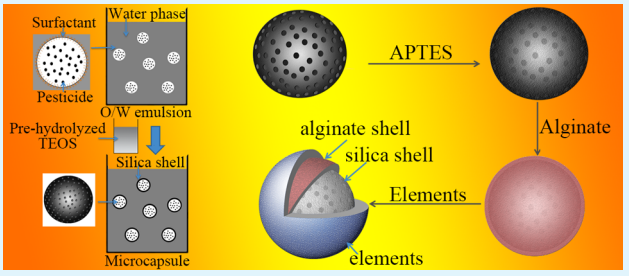
ABSTRACT: Controlled release formulation of pesticides is an effective approach to achieve the desirable purpose of increasing the utilization of pesticides and reducing the environmental residuals. In this work, a novel functionalized microcapsule using silica cross-linked with alginate, and some beneficial elements to crops, was prepared. The microcapsules were structurally characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetric analysis, and X-ray photoelectron spectroscopy. The results showed that the microcapsules had a high loading efficiency of prochloraz (about 30% w/w) and could effectively protect prochloraz against degradation under UV irradiation and alkaline conditions, showed sustainable release for at least 60 days, and also likely increased disease resistance due to the element on the surface. Given the advantages of the microcapsules, this delivery system may be extended to other photosensitive or pH-sensitive pesticides in the future.



KEYWORDS: *microcapsule, alginate, trace element, prochloraz, silica*

1. INTRODUCTION

Controlled release technology has become a growing scientific and commercial interest worldwide in the past decades. It has been remarked as a seed of new technology and widely used in the fields of medicine, pesticides, environmental engineering, cosmetics, coatings, and food.[1−5] In agriculture, the application of controlled release pesticides can provide active ingredient release at the required rate, reduce environmental problems, and save human labor.[6,7] Due to the selective permeation and conservation properties of the semipermeable membrane, microcapsules have been widely used in the pesticide field.[8−11] However, the wall materials of microcapsules are often made of thin synthetic (such as polystyrene, polyamide, and polyurethane) or natural (alginate, chitosan, lignin, starch, cellulose, and hemicellulose) polymeric membranes that cannot control the release of the core materials effectively. The release longevity of simplex microcapsules under environmental conditions is always short, so the further improvement of the controlled release property of simplex microcapsules shows broad prospects for development.[12−18]

Owing to the stable mesoporous structure, the large surface area, the good biocompatibility, and high drug loading capability relying on the changeable size, the mesoporous silica materials have shown promising applications in the encapsulation field.[19−23] However, silica-based microcapsules cannot control the release of the loaded drug without surface modification; surface functionalization has been one of the key methods toward the high utilization of mesoporous silica in different applications.[24−26] Amino-functionalized mesoporous silica particles show special characteristics in that they can not only retain the order of mesoporous channels without changing the pore size to some extent but also can strengthen the interaction force between the functional groups and the drug molecules. In addition, amino-functionalized mesoporous silica particles can be further linked with other functional groups.[27−29] Alginate is a linear anionic polysaccharide obtained from the various species of brown seaweed; it consists of two different repeating units, including 1,4-D-mannuronic acid (M) and α-L-guluronic acid (G) monomers, which are arranged in repeating GG, MM, or alternating MG blocks.[30] Due to the convenient sources, nontoxicity, excellent biocompatibility, nonimmunogenicity, and biodegradability, alginate has been widely used in the microcapsule field. Meanwhile, the rich carboxyl of alginate creates a possibility for further modifying as well as achieving better application.[31−33] Closely linked up with some catalytic processes, trace elements are significant in plant growth. Trace elements, such as copper (Cu), zinc (Zn), iron (Fe), calcium (Ca), magnesium (Mg), manganese (Mn), molybdenum (Mo), and boron (B), even in small quantities, still need to be added regularly during plant growth.[34−36] Prochloraz is a broad-spectrum, high-efficiency, and low-toxicity imidazole fungicide that is widely used in

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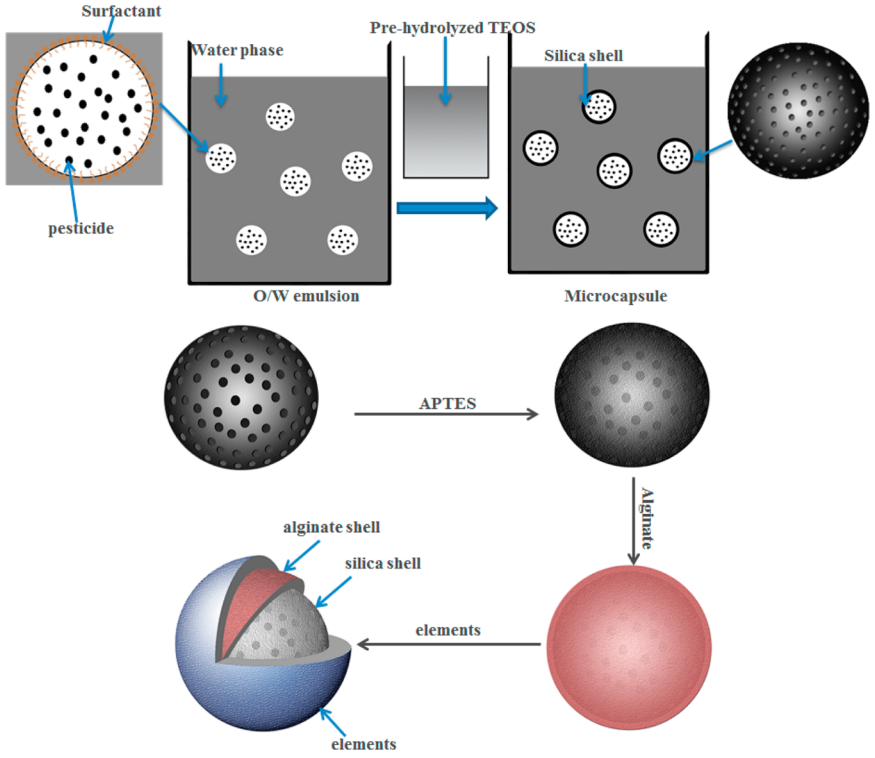
Scheme 1. Schematic Diagram of the Possible Formation Mechanism of Microencapsulation



gardening and cropping. Prochloraz has shown effective control of crop disease caused by ascomycete and adelomycete and is widely used as a fruit and vegetable fresh-keeping agent in the process of storage and transportation. However, the applicability of prochloraz is limited for it being sensitive to light and alkaline and strongly acidic conditions. Hydrolysis under alkaline conditions led to the formation of *N*-propyl-*N*-2-(2,4,6-trichlorophenoxy)ethylamine, the degradation following first-order kinetics.[37,38]

Herein, we prepared a novel functionalized microcapsule using silica cross-linked with alginate by utilizing 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide (EDC) and *N*-hydroxysuccinimide (NHS); meanwhile, the trace elements were conjugated with alginate on the surface of the microcapsule. The preparation conditions of prochloraz microcapsules, the effects of the microcapsules size, pH, and temperature on the sustained-release performance and stability of prochloraz in microcapsules were investigated.

2. EXPERIMENTAL SECTION

2.1. Materials. The model drug, prochloraz (98%), was supplied by the Institute for the Control of Agrochemicals, Ministry of Agriculture, China. Sodium alginate (SA) was purchased from Sinopharm Group Chemical Reagent Corp., Shanghai, China. Tetraethyl orthosilicate (TEOS), 3-aminopropyltriethoxysilane (APTES), hexadecyltrimethylammonium bromide (CTAB), hydrochloric acid (36%), ammonium hydroxide, ethanol (99.9%), ethyl acetate, magnesium chloride, zinc chloride, copper(II) chloride dehydrate, calcium chloride anhydrous, and ferric chloride were analytical chemicals purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., Beijing, China. 1-Ethyl-3-(3-(dimethylamino)-propyl)carbodiimide and *N*-hydroxysuccinimide were purchased from GL Biochem Ltd., Shanghai, China. Acetonitrile and methanol were high performance liquid chromatography (HPLC) grade and purchased from J.T. Baker (USA). Deionized water was applied for all reactions and treatment processes.

2.2. Preparation of Prochloraz Microcapsule. *2.2.1. Synthesis of Amino-Functionalized Silica Microcapsules.* First, 4 g of TEOS was prehydrolyzed with 1 g of water in the presence of concentrated ammonia solution (0.5 mL) at 60 °C for 90 min under constant stirring at 300 rpm.[39] The aqueous phase consisted of surfactant and deionized water was prepared by dissolving 1.5 g of cetyl trimethylammonium bromide (CTAB) (1.5% m/v of the whole system) in 89 mL of deionized water. The organic phase consisted of prochloraz and oil solution was obtained by dissolving 1 g of prochloraz in 3 mL of ethyl acetate. The organic phase was dispersed in the aqueous phase with the aid of the homogenizer (T18 digital ULTRA-TURRAX, IKA, Germany) under high speed agitation, and the mixture was homogenized at 6000 rpm for 5 min to generate a stabilized O/W emulsion. The homogeneous dispersion system was poured into a three-necked flask equipped with a temperature control magnetic stirrer and continuously stirred at 600 rpm. The prehydrolyzed TEOS was then added dropwise to the microemulsion at 70 °C for 30 min under constant stirring at 600 rpm. After the mixture was allowed to age overnight at room temperature, silica microcapsules were realized by further hydrolysis and polycondensation of TEOS precursor. Finally, 0.8 mL of (3-aminopropyl)-triethoxysilane (APTES) was added to the flask and the reaction mixture was stirred at 50 °C for a further 2 h. The microcapsules were further filtered and washed three times with distilled water, centrifuged (6000 rpm), and dried at 60 °C.[16]

2.2.2. Synthesis of Silica–Alginate Microcapsules. First, a solution of sodium alginate (0.2%, w/v) was prepared by dissolving 0.2 g of sodium alginate in 99.8 mL of deionized water, and then the pH was adjusted to 5 by adding dropwise 1 mol L^{-1} HCl solution. Second, 5.8 g (30 mmol) of EDC was dissolved in 50 mL of sodium alginate solution (0.2%, w/v), stirring for 30 min at room temperature. Then 0.30 g of the resulting microcapsules and 3.5 g (30 mmol) of NHS were added into reaction mixture, continuously stirring for 24 h under room temperature. Finally, the solution was centrifuged and washed twice with deionized water and ethanol successively. The functionalized prochloraz-containing microcapsules were obtained after centrifugation and dried at 60 °C in an oven.

2.2.3. Synthesis of Silica–Alginate–Elements Microcapsules. The novel functionalized prochloraz microcapsules were achieved using the

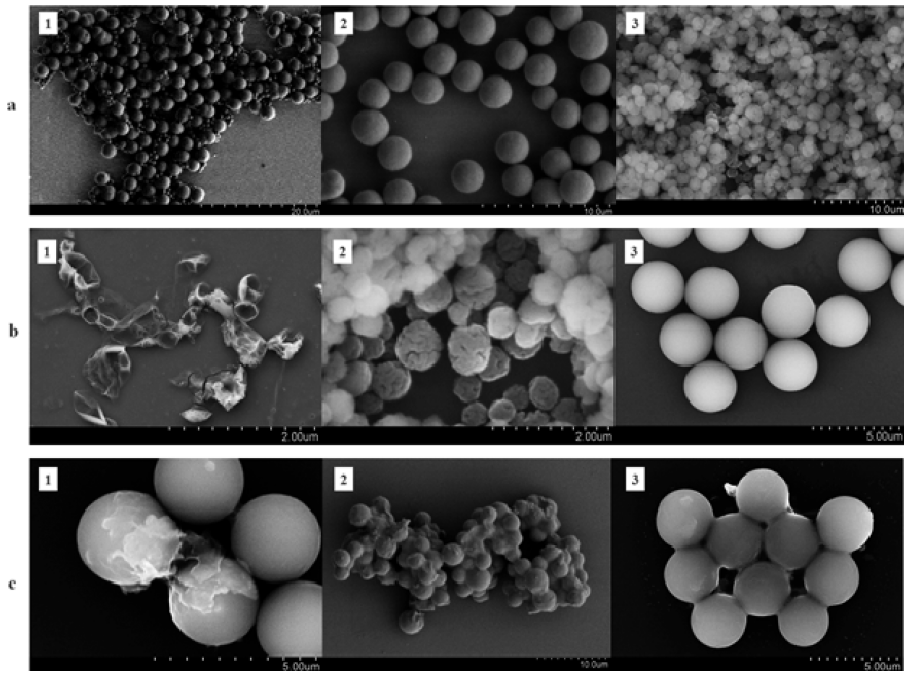


Figure 1. SEM images of the silica microcapsules prepared by various conditions: without prehydrolysis of TEOS (a-1), with prehydrolysis of TEOS at pH 9 (a-2), with prehydrolysis of TEOS at pH 4 (a-3), with concentration of CTAB 0.5% (b-1), with concentration of CTAB 2.5% (b-2), with concentration of CTAB 1.5% (b-3), with EDC/NHS 20 mmol (c-1), with EDC/NHS 40 mmol (c-2), with EDC/NHS 30 mmol (c-3).

elements to conjugate with alginate on the surface of the microcapsule. First, a mixed solution of elements was prepared by dissolving the appropriate amount of $CuCl_2$, $MgCl_2$, $CaCl_2$, $ZnCl_2$, and $FeCl_3$ in deionized water. Second, the prepared functionalized microcapsules were dispersed in water with the help of ultrasonication and poured into a three-necked flask equipped with a magnetic stirrer and continuously stirred at 300 rpm. Finally, sediments were generated by dropwise adding the mixed solution of elements, then separated by centrifuging and washed twice with deionized water. The final prochloraz microcapsules were achieved after dried at 60 °C in oven.

2.3. Characterization. *2.3.1. Fourier Transform Infrared Spectroscopy (FT-IR).* FT-IR spectra, recorded on a Jasco FT-IR 5300 spectrophotometer, were used to identify the different functional groups present in the samples. Samples were prepared as KBr pellets and scanned against a blank KBr pellet background at wavenumbers ranging from 4000 to 650 cm^{-1} with a resolution of 4.0 cm^{-1}.

2.3.2. Scanning Electron Microscopy (SEM) Observation. Scanning electron microscopy (SEM, ZEISS ULTRA 55, Germany) was used to study the morphology and structures of prochloraz microcapsules.

2.3.3. Thermogravimetric Analysis (TGA). TGA, used to determine the loading efficiency of prochloraz, was carried out with a SDT Q600 (TA Instruments-Waters LLC, USA) analyzer from 25 to 700 °C with a heat rate of 10 °C/min.

2.3.4. X-ray Photoelectron Spectroscopy (XPS) Analysis. X-ray photoelectron spectroscopy (XPS, ZEISS, Germany) was employed to analyze the chemical elements composition on the surface of prochloraz microcapsules.

2.3.5. Particle Size Analysis. A Mastersizer (Mastersizer 3000, Mlvern Instruments Co., UK) was used to determine the size distribution of prochloraz microcapsules.

2.4. High Performance Liquid Chromatography (HPLC) Analysis. The prochloraz was determined by HPLC (Shimadzu, Japan) using a Kromasil ODS C_{18} column (250 × 4.6 mm, 5 μm; DIKMA, USA) with UV detection at 220 nm. A flow rate of 1 mL min^{-1} was used with a mobile phase composition of acetonitrile and water with 0.1% acetic acid (70:30, v/v), injecting volume 20 μL. All the solvents were filtered with a 0.45 μm membrane filter.

2.5. Stability of Prochloraz Microcapsule. The 20 g of prepared microcapsules solution (2%, w/v) was packed in glass tubes and stored at 25, 35, and 45 °C for a period of 60 days, then the changes of the prochloraz were analyzed; stability against UV radiation was tested by exposing samples to a 36 W germicidal lamp (254 nm) at a distance of 20 cm for about 24 h, then to analyze the prochloraz changes, technical grade prochloraz was used as a control in the same time.

2.6. Control Release Behaviors of Prochloraz Microcapsule. The prepared microcapsules were weighted and dispersed in 500 mL of the methanol−water mixture (30:70, v/v), which was used as the release medium in order to dissolve prochloraz, and incubated at a stirring speed of 100 rpm for a given time at room temperature. The mixture at different times was then centrifuged and the prochloraz content in the supernatant determined by using HPLC to evaluate the sustained release property.

3. RESULTS AND DISCUSSION

3.1. Preparation of Prochloraz Microcapsule and the Optimization of Conditions. In this work, the functionalized microcapsules were prepared using silica cross-linked with alginate by utilizing 1-ethyl-3-(3-(dimethylamino)propyl)-carbodiimide (EDC) and *N*-hydroxysuccinimide (NHS), and the trace elements were conjugated with a residual carboxylic

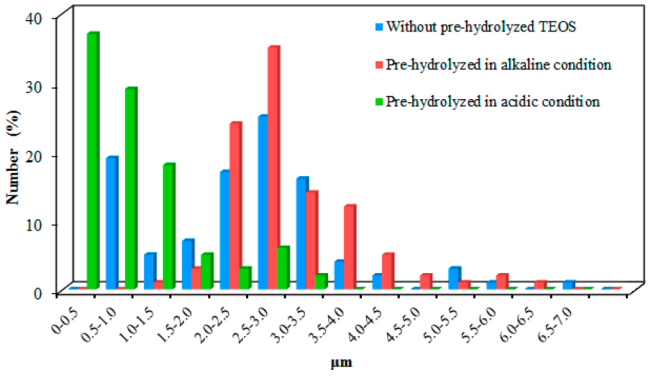


Figure 2. Particle size distribution of silica microcapsules.

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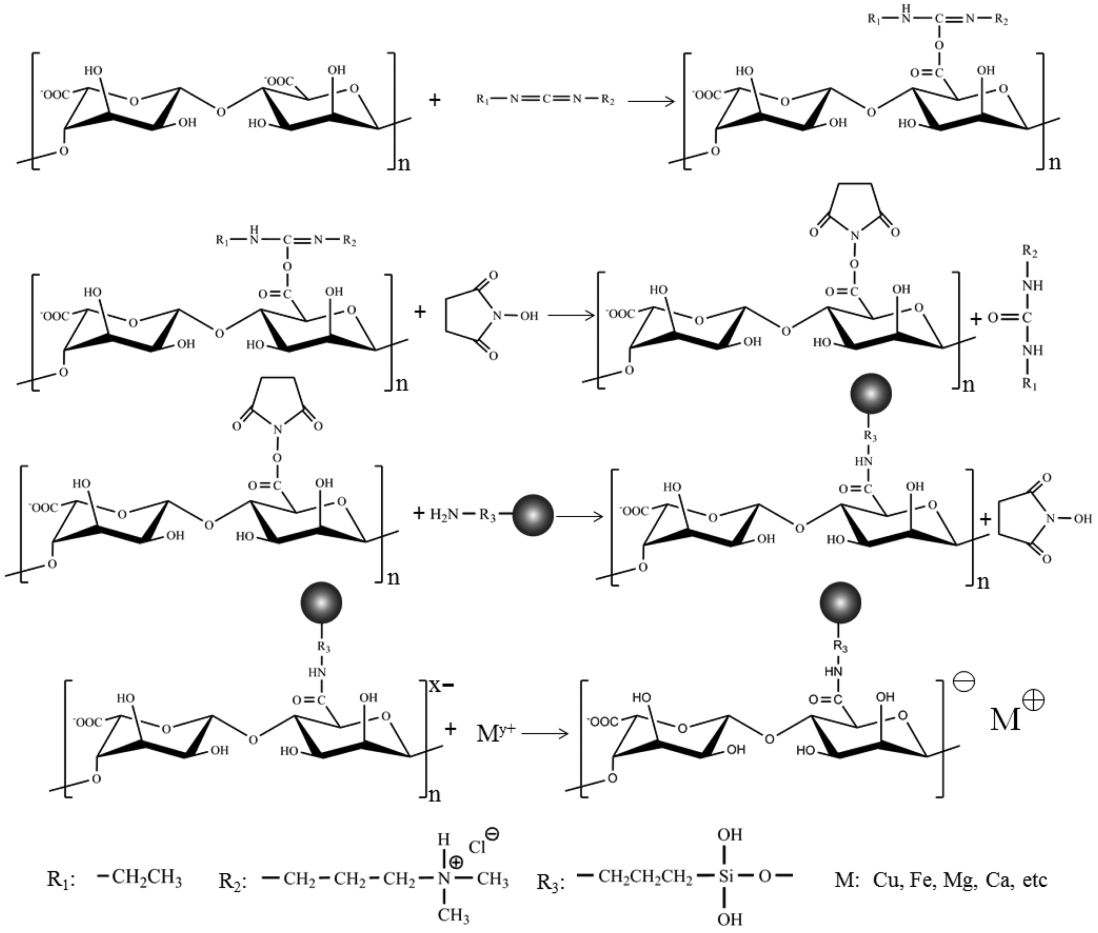
Scheme 2. Mechanism for Amino-Functionalized Silica Microcapsules



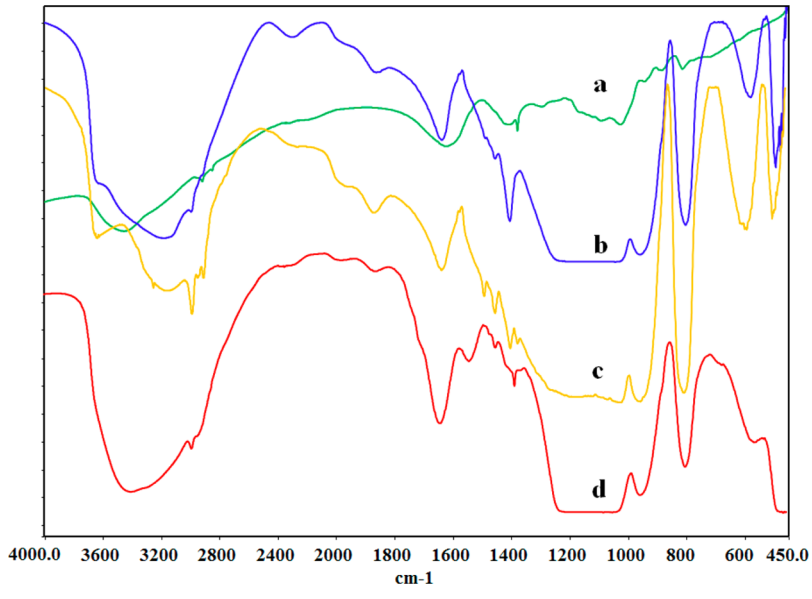


Figure 3. FT-IR spectra of sodium alginate (a), silica (b), amino-functionalized silica (c), silica−alginate (d).

group of alginate. In the procedure of preparation, O/W microemulsion droplets were used as the nanoreactor, which was composed of the water phase and the organic phase. The silica wall was formed after adding the prehydrolyzed TEOS to the O/W microemulsion via the interfacial reaction and functionalized with APTES. The formation mechanism of prochloraz microcapsules is schematically presented in Scheme 1.

3.1.1. Effects of Prehydrolyzed TEOS and Catalyst. TEOS, used as a wall material, has a significant influence on the morphology and wall thickness. The results showed that the silica microcapsules prepared without prehydrolysis of TEOS

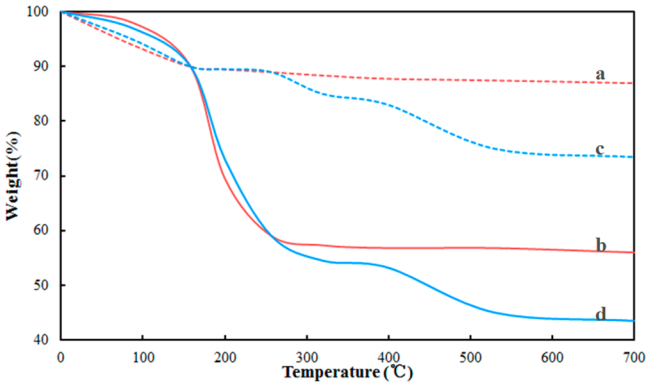


Figure 4. TGA curves of silica microcapsules (a), silica shelled prochoraz microcapsules (b), silica−alginate microcapsules (c), and silica−alginate shelled prochloraz microcapsules (d).

were uneven and aggregated (Figure 1a-1). The uniform particle size and detached from each other microcapsules were achieved by prehydrolyzed of TEOS (Figure 1a-2). In the process of prehydrolysis, the catalyst played a critical role, and the hydrolysis of TEOS could be accomplished in acidic or alkaline conditions. In this study, the TEOS was hydrolyzed fast and finally formed a grapelike flocculated precipitate without microcapsules synthesized when under acidic conditions (Figure 1a-3), whereas the desirable microcapsules with uniform particle size were finally prepared when using ammonia solution as a catalyst (Figure 1a-2). The particle size distribution of the microcapsules affected by TEOS is shown in Figure 2.

3.1.2. Effects of CTAB. CTAB, used as a surfactant to stabilize the oil in water microemulsion, has an important role in the formation of microcapsules. With low concentrations of CTAB (<1%, v/v), it was difficult to achieve the stable microemulsion, thus resulting in oily water separation and ruptured microcapsule walls without prochloraz coating (Figure 1b-1). And the microemulsion was more stable and not layered, but the prepared capsules were not ideal with thin and unsmooth walls in high concentrations of CTAB (>2%, v/v) (Figure 1b-2). When the concentration of CTAB was in the range of 1−2%, the desirable microcapsules with uniform size and homogeneous distribution were achieved (Figure 1b-3). With the aid of EDC and NHS, the amino-functionalized silica can be coated with alginate via amide linkage between the amino group of silica and the carboxyl of alginate.

3.1.3. Effects of NHS/EDC. With the aid of EDC and NHS, the amino-functionalized silica can be coated with alginate via amide linkage between the amino group of silica and the carboxyl of alginate. The presumptive chemical reaction of amino-functionalized silica is presented in Scheme 2. The difference of coated microcapsules among the different quantity of NHS/EDC was investigated with SEM images. When the quantity of EDC/NHS was less than 30 mmol, the image (Figure 1c-1) shows that the microcapsules are partially coated with alginate, and the unstable outer shell can be easily detached from the surface of silica capsules. And the silica capsules were coated with massive alginate, and a huge number of microcapsules were coalesced in a chunk under the higher

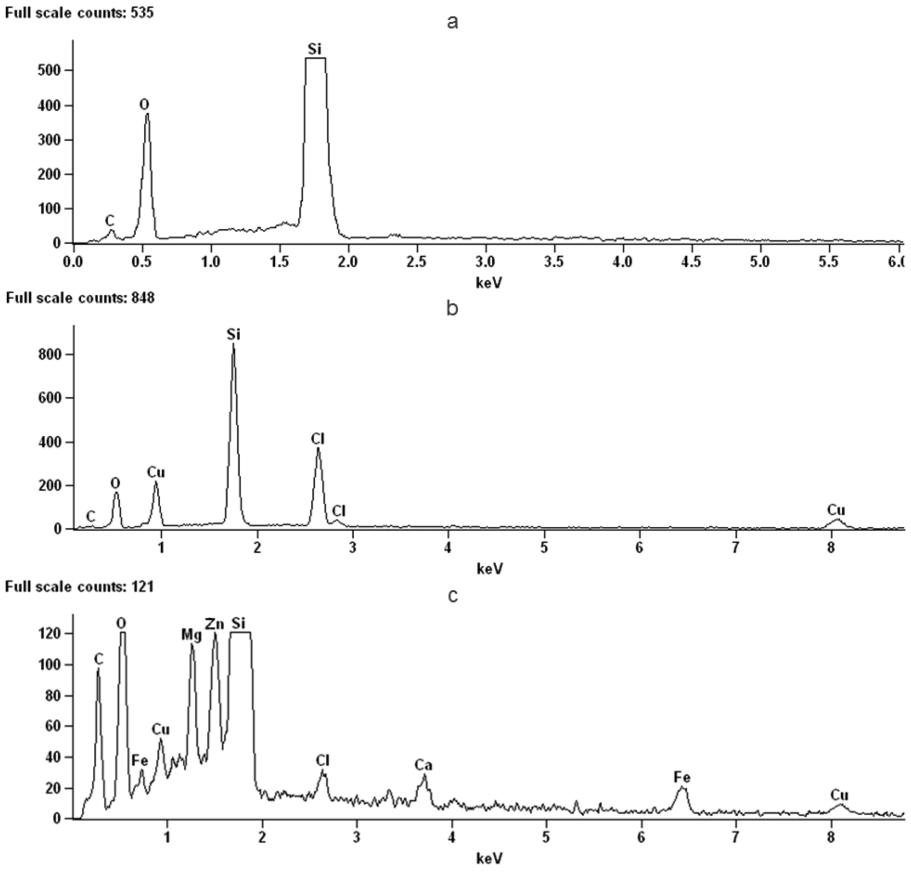


Figure 5. XPS of silica−alginate (a), silica−alginate−$Cu2^{+}$ (b), and silica−alginate−elements (c).

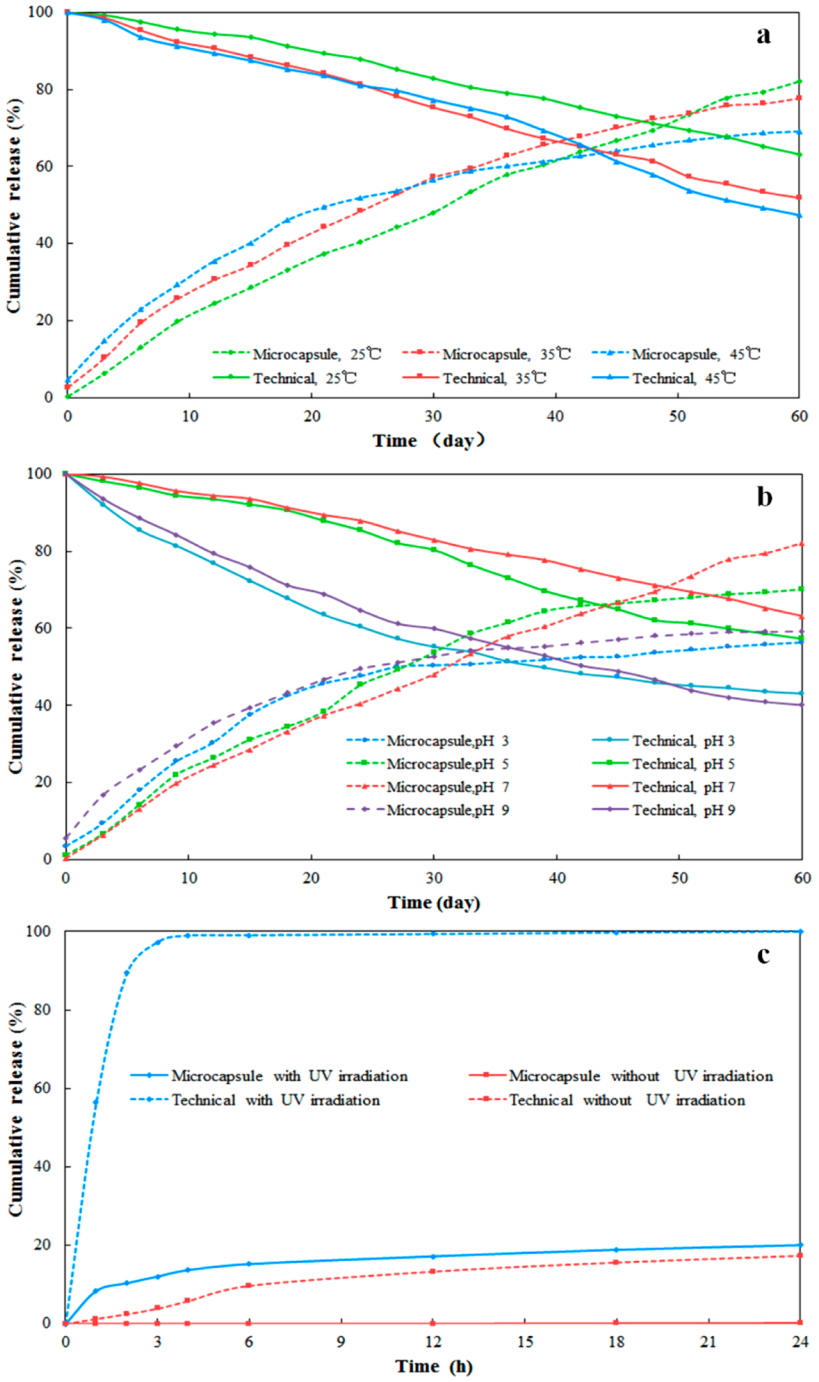


Figure 6. Effect of different temperature (a), pH value (b), and UV irradiation (c) on release behavior and stability of prochloraz microcapsules.

quantity (>40 mmol) of NHS/EDC (Figure 1c-2). The desired microcapsules with a stable outer shell were achieved by using 30 mmol NHS and EDC, respectively (Figure 1c-3).

3.2. Structural Characterization of Prochloraz Microcapsule. *3.2.1. Results of Fourier Transform Infrared Spectroscopy (FT-IR).* The FT-IR results (Figure 3) show the infrared spectra of silica, amino-functionalized silica, silica−alginate, and sodium alginate. Compared with silica, the amino-functionalized silica shows the characteristic vibration bands of the amine ($-NH_2$) at 3300 cm^{-1} and the absorption band of the methylene group ($-CH_2-$) at 2980 cm^{-1} appears, which indicated that the APTES was successfully attached onto the surface of silica. The sodium alginate showed a broad band at about 3425 cm^{-1}, assigned to stretching vibration modes of O—H groups. The weak peak toward 2930 cm^{-1} was attributed to the C—H antisymmetrical stretching vibration. Two peaks at 1710 and 1390 cm^{-1} are assigned to C═O and −COOH, respectively. The spectrum of the silica−alginate exhibits a much stronger absorption band of the amide group (−CONH−) at about 1640 cm^{-1}. Besides, the absorption band of the amine ($-NH_2$) at 3300 cm^{-1} is replaced by a broad band of the alginate at about 3425 cm^{-1}, demonstrating that the alginate was conjugated with the amino-functionalized silica.

3.2.2. TGA Curves of Microcapsules. The TGA curves of blank silica microcapsules, silica microcapsules with prochloraz, silica−alginate microcapsules, and silica−alginate−elements

microcapsules with prochloraz are illustrated in Figure 4. The results exhibited that the weight loss before 158 °C was probably ascribed to the water evaporation in the microcapsules and the weight loss between 158 and 260 °C might be ascribed to the evaporation and decomposition of prochloraz, whereas the weight loss when the temperature was over 260 °C could be due to the decomposition of alginate shells. The total weight losses of microcapsules in the range of 158−700 °C were about 75.0% and 45.0%, so the loading efficiency of prochloraz was about 30%.

3.2.3. XPS Analysis of Microcapsules. The XPS spectra (Figure 5a) show that carbon, oxygen, and silicon are detected on the surface of silica−alginate microcapsules, which indicates that the wall material is mainly composed of these three elements. Figure 5b demonstrates that the Cu^{2+} is attached to the surface of silica−alginate−Cu^{2+} microcapsules. Figure 5c illustrates the microcapsules have attached a variety of elements on the surface, including iron, magnesium, zinc, cuprum, and calcium elements. Therefore, the silica microcapsules coated with alginate have potential capacity to be conjugated with many trace elements which can increase the disease-resistance, reduce the disease invasion and provide the nutrient element to the crops.

3.3. Release Behaviors and Stability of Silica−Alginate−Elements Microcapsule. *3.3.1. Effects of Temperature.* Figure 6a shows the effects of different temperatures (25, 35, and 45 °C) on release behaviors and stability of silica−alginate−elements microcapsules (about 2.5 μm) at pH 7 while keeping constant stirring at a speed of 100 rpm. For prochloraz technical, the degradation rate of prochloraz increased with increase of the temperature and only 47.4% of the prochloraz remained in the solution at the 60th day at 45 °C. For prochloraz microcapsules, at 45 and 25 °C, the accumulated release rates were increased from 69.2% to 82.1% at the 60th day. In comparison with prochloraz technical, the prochloraz microcapsules showed a sustained release performance and good stability.

3.3.2. Effects of pH. Figure 6b shows the release behaviors and stability of the silica−alginate−elements microcapsule (about 2.5 μm) under different pH values (3.0, 5.0, 7.0, and 9.0) at room temperature while kept constantly stirring at a speed of 100 rpm. For prochloraz technical, only 43.1% and 40.2% remained in the solution at the 60th day under strong acidic (pH 3) and alkaline (pH 9) conditions. For prochloraz microcapsules, at pH 3 and 9, the cumulative release rates were 50.3% and 52.8% at the 30th day, respectively, and were nearly unchangeable from 30 to 60 days. The results illustrated that prochloraz microcapsules were nonsensitive to the pH with high stability and desirable sustained-release properties.

3.3.3. Effects of Light. Figure 6c shows the effects of UV radiation on release behaviors and stability of the silica−alginate−elements microcapsule (about 2.5 μm) at pH 7, 25 °C. The decomposition rate of prochloraz technical reaches up to 97.3% after 3 h of UV irradiation, much higher than that of the microcapsules, which exhibits less than 13.2% decomposition. In dark conditions, the decomposition rate of microcapsules was unobserved and the technical exhibited 13.3% decomposition after 12 h. The results demonstrated that prochloraz could be protected by the microcapsules wall.

4. CONCLUSION

In this communication, we described a novel modification on the surface of silica capsules that had shown the potential to be further conjugated with other desirable substances such as trace elements, nutriments, and so on. On the basis of this novel modification, the silica−alginate−elements microcapsules were used to prepare the prochloraz microcapsules to protect prochloraz against the degradation under UV irradiation and alkaline conditions. The results showed that the silica−alginate−elements microcapsules had remarkable advantages of sustained-release and stability under different pH values, different temperatures, and UV irradiation, as well as with high loading efficiency of prochloraz (about 30% w/w). The elements on the surface of microcapsules could supply the nutriment and increase the disease-resistance ability of crops. This delivery system may be extended to other photosensitive or pH-sensitive pesticides in the future.

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Notes

The authors declare no competing financial interest.

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