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Fabrication of Hydrogel Beads Based on Mesoporous Silica Nanoparticles/Chitosan and Application as a Slow-Release Fertilizer

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ABSTRACT

Hydrogels have gained significant attention in various applications, including agriculture, owing to their exclusive characteristics, such as great water retention and controlled delivery of fertilizers and agrochemicals. In this study, a nanocomposite hydrogel bead with exceptional slow-release capacity for urea fertilizer has been fabricated by appropriately combining urea, silica nanoparticles, and chitosan. The developed beads not only enable the efficient delivery of nutrients to plants over a long period but also enhance water retention capacity in sandy soil, resulting in minimally negative impacts on the environment. The hydrogel beads were simply prepared by dropping method. To effectively control the release of urea from hydrogel beads, mesoporous silica nanoparticles (MSNs) with a diameter of 56 nm were synthesized and used to load the urea (UM). Subsequently, the UM hybrid was incorporated into the chitosan matrix to form the hydrogel beads (UMCS). The resulting beads have a spherical shape and high stability. They exhibited a sustained release of urea for over a month and biodegradable capacity in soil. The hydrogel beads showed a good swelling degree with a maximum value of 250% at pH 3. Moreover, the hydrogel beads-embedded soil revealed a water retention capacity significantly greater than the soil without the beads. These results suggested that the nanocomposite hydrogel beads possess high application potential in fertilizer delivery and smart agriculture.

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1. Introduction

Fertilizers have played a crucial role in revolutionizing the agriculture sector, significantly increasing crop yields and feeding the world's burgeoning population. However, the efficient usage and environmental impact of chemical fertilizers, especially on soil and groundwater, are growing concerns [1]. The story of fertilizer used in agriculture is a complex issue between enhancing food production and managing unintended environmental consequences. Excessive fertilizer use can alter the natural nutrient balances, cause soil acidity, decrease microbial diversity, and damage soil structure. Moreover, the heavy use of chemical fertilizers contributes to greenhouse gas emissions, including nitrous oxide, a significant driver of climate change [2]. In particular, the efficacy of fertilizers is usually modest due to the leaching to the environment, resulting in a high agricultural cost, negative effects on groundwater quality, and environmental pollution [3], [4]. Recently, to address these environmental concerns and increase the efficiency of agrochemicals, intelligent fertilizers that can offer a controlled release capacity of fertilizers have been extensively studied and applied in practice [5], [6]. Slow-release fertilizers powered by nanotechnology are essential for research orientation. The unique advantage of nano-fertilizers lies in their ability to deliver nutrients directly to the cellular level of plants, enhancing nutrient use efficiency and potentially reducing the environmental impact associated with traditional fertilization methods. By encapsulating nutrients within nanoparticles, these fertilizers ensure a slow and more controlled release of nutrients, which can be tailored to the needs of specific plants or crop stages, optimizing growth and yield [7], [8].

Mesoporous silica nanoparticles (MSNs) play a crucial role in this context and serve as a fundamental element in soil composition. MSNs exhibit exceptional properties like non-toxicity, biocompatibility, stable isotopic structure, large surface area, pore size, and diverse surface distribution functions. Thanks to its unique properties, MSNs can enhance the solubility and loading of agrochemicals by plants and are widely used as a platform to deliver fertilizers and others [9], [10]. The application of chitosan (CS), a naturally derived biodegradable material, as a coating for fertilizer and nutrients, underscores the commitment to eco-friendly agricultural practices [11]. Chitosan's compatibility with MSNs enhances the environmental sustainability of these fertilizers, offering a compelling example of how cutting-edge science can align with the principles of green agriculture.

Recently, scientists have dedicated much effort to developing sustained-release systems for fertilizers. For example, Ding et al. (2024) investigated using mesoporous silica nanoparticles combined with other nanomaterials to improve the efficiency of nutrient delivery in agricultural applications [12]. Similarly, Gosh et al. (2023) explored different polymers and nanomaterials to prepare slow-release fertilizers that address the challenges of high production cost and limited biodegradability [13]. However, the performance and applicability of these systems remain suboptimal in practical agricultural settings.

As a critical fertilizer, urea is a vital source of nitrogen for plants, but its rapid release and high solubility can lead to environmental issues such as leaching and the release of harmful gases, such as nitrous oxide [14]. Therefore, the incorporation of urea into silica nanoparticles significantly improves the usability and effectiveness of urea, especially in sustainable agriculture. By controlling the release of urea from silica nanoparticles, it is possible to ensure that nitrogen is delivered in a controlled manner, which can enhance plant growth and reduce environmental impact. Furthermore, the integration of urea, a key nitrogen fertilizer in modern agriculture, has a unique chemical composition with amine and carbonyl groups, which allow for interactions like hydrogen bonding, especially with hydroxyl groups, facilitating its interaction with MSNs and CS, forming a urea-loaded MSNs-embedded CS hydrogel (UMCS) that optimizes nutrient release and improves soil quality. This innovative approach not only ensures that plants get a sustained provision of essential nutrients but also significantly reduces nutrient loss through leaching and runoff. Consequently, this method supports healthier plant growth and contributes to the preservation of water resources, highlighting the dual benefits of increased agricultural productivity and environmental conservation.

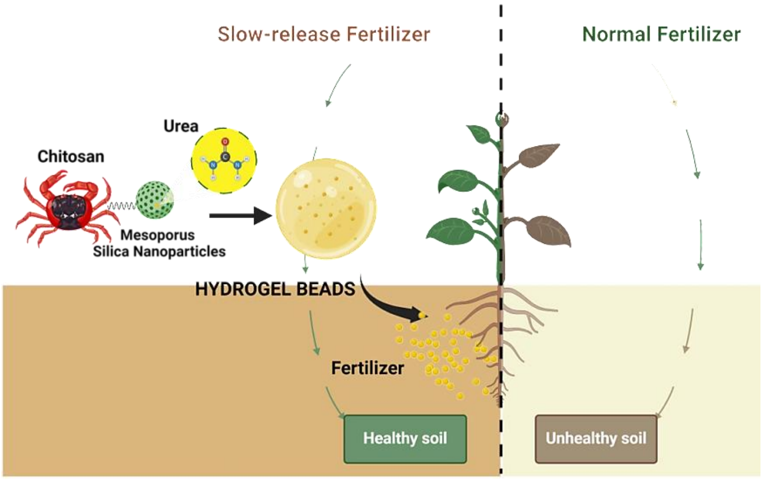


Figure 1. *Illustration of a hydrogel bead for slow-release of urea fertilizer using chitosan/MSNs/urea (UMCS bead), which aims to enhance fertilizer efficacy, overcome moisture deficiency, and minimize soil and groundwater pollution (designed by Biorender)*

Our study aims to bridge these gaps by fabricating hydrogel beads using a novel combination of MSNs and chitosan. Unlike previous studies, our approach leverages the synergistic properties of MSNs for high surface area and pore volume, coupled with the biopolymeric nature of chitosan to enhance biodegradability and environmental safety. This unique formulation not only improves the controlled release of nutrients but also offers a sustainable solution to current agricultural challenges.

Herein, the mesoporous silica nanoparticles (MSNs) were synthesized and assessed by scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) analysis. Subsequently, the UMCS hydrogel beads were fabricated by dropping method, whereas the aqueous mixture of chitosan containing urea-loaded MSNs was added dropwise to the NaOH solution. The formed hydrogel beads were investigated the swelling degree, water retention capacity, and kinetics of urea release in both water and soil media.

2. Materials and Methods

2.1. Materials

Cetyltrimethylammonium bromide (CTAB) and tetraethyl orthosilicate (TEOS), both with a purity of 99%, were obtained from Aladdin (China). Sodium hydroxide (NaOH) was supplied by Xilong (China) with a purity of over 96%. Chitosan (deacetylation degree of 85%) was obtained from Sigma-Aldrich.

2.2. Preparation of mesoporous silica nanoparticles (MSNs)

The mesoporous silica nanoparticles (MSNs) were produced by first stirring the mixture of 0.1g CTAB and 50 mL of deionized water in a two-neck round-bottom flask at 80 ºC for 20 minutes, then 0.032g of NaOH (dissolved in 0.4 mL of distilled water) was added to the above solution. Subsequently, 0.5 mL of TEOS was added dropwise to the reaction and stirred for a further 2 hours. The reaction solution was chilled to room temperature and then centrifuged at 6000 rpm for 20 minutes to obtain the precipitation, followed by washing with sequential ethanol and deionized water. Afterward, the sample was dried in an oven for 24 hours at 80 °C. Finally, the sample was calcined at 500 °C for 3 hours to produce MSNs.

2.3. Preparation of urea-loaded mesoporous silica nanoparticles (UM)

The UM was prepared by immersion method. Briefly, 60 mg of MSNs was put into a 5 mL aqueous urea solution with various concentrations of 60, 180, and 240 mg/mL. At predetermined times, the suspension was centrifuged and the precipitate was collected, followed by vacuum drying at 40 °C for 48 hours. The concentration of urea in the supernatant was identified by using an Ehrlich reagent at the absorption wavelength of 425 nm. The urea loading capacity (LC) of MSNs was calculated from equation (1).

$$\mathrm{LC\ (mg/g)} = \frac{\mathrm{W_{urea}}}{\mathrm{W_{MSNs}}} \tag{1}$$

Where W_{urea} (mg) is the weight of urea loading into the MSNs, W_{MSNs} (g) is the weight of MSNs.

2.4. Preparation of UMCS hydrogel beads

The UM with the maximum loading capacity of urea was selected for preparing hydrogel beads. In brief, chitosan was dissolved in 2% acetic acid solution to achieve a chitosan solution of 4% wt/wt. Subsequently, the UM was added to the chitosan solution with a concentration range of 0-10% wt/wt corresponding to chitosan. After the dispersion became homogenous, the system was put into a syringe of 3 mL and dropped into a beaker containing NaOH 1M solution. Finally, the beads were isolated and washed several times with distilled water, and stored for further examination.

2.5. Swelling investigation of UMCS hydrogel beads

The UMCS samples with different ratios of UM/chitosan were examined for the swelling degree in various pH media, including pH 3, 5.5, and 7 corresponding to the simulated pH of several soil environments. The dried hydrogel beads were soaked in the media and the swollen hydrogel beads were subsequently weighed according to times. The swelling degree (SD) was determined by using equation (2), where W_o is the initial weight of the hydrogel beads, and W_t is the weight of the bead after immersion at a given time.

$$\mathrm{SD\ (\%)} = \frac{\mathrm{W_t - W_o}}{\mathrm{W_o}} \times 100\% \tag{2}$$

2.6. Investigation of water retention capacity of hydrogel beads in the soil environment

In addition to the swelling degree, water retention is essential for the agricultural application of hydrogel beads. By absorbing and retaining water, these beads help to create a reservoir of moisture for plants, especially in arid conditions. For evaluating the water retention capacity of UMCS hydrogel bead, 1 g of UMCS bead sample in dry state was mixed with 200 g of dry soil, and 200 g of soil without hydrogel was used as a control sample. Next, the samples were placed in a ceramic cup and weighed initially (W_o). Subsequently, 30 mL of tap water was slowly added to the samples, and the cup was reweighed (W_1). The cups were stored at room temperature and weighed every three days (W_i). The hydrogel beads's water retention (WR, %) was determined using the equation (3).

$$\mathrm{WR}\ (\%) = \frac{W_i - W_o}{W_1 - W_o} \times 100\% \tag{3}$$

2.7. Biodegradation test of UMCS hydrogel beads

The biodegradability of hydrogel beads can offer a safe solution for the environment, sustainable development, and green agriculture. The products generated by the degradation process of chitosan and MSNs further serve as complementary nutrients for plants. The UMCS5 hydrogel bead was examined for biodegradable characteristics for a period of 21 days in the soil environment. In particular, a space (3cm × 3cm × 10cm) was created in soil and a certain amount of UMCS5 bead sample (W_o) was buried. Afterward, 50 mL of water was poured on the soil. The sample was collected every 3 days, separated, cleaned with deionized water, dried, and then weighed (W_i). The following equation (4) was used to calculate the biodegradation rate.

$$\text{Biodegradation rate}\ (\%) = \frac{W_o - W_i}{W_o} \times 100\% \tag{4}$$

2.8. Investigation of urea release kinetics from UMCS hydrogel bead

2.8.1. Study of urea release behavior from UMCS hydrogel bead in the water medium

Briefly, 0.5 grams of UMCS5 beads were submerged in 10 mL (V_o) of distilled water. At a predetermined time, 3.0 mL (V) of the medium was withdrawn and replaced by the same volume of release medium. The concentration of urea in the medium was measured by using an Ehrlich reagent at the wavelength of 425 nm. Equation (5) was used to determine the cumulative release (CR) kinetics of urea.

$$\mathrm{CR}\ (\%) = \frac{V \times \sum_1^{t-1} C_i + V_O \times C_t}{m_O} \times 100\% \tag{5}$$

Where C_t is the concentration of urea in the release medium at time t, C_i is the concentration of urea in the release medium at time t-1, and m_o is the weight of urea in the beads.

2.8.2. Study of urea release behavior from UMCS hydrogel bead in the soil medium

To evaluate the release behavior of urea from UCMS5 hydrogel beads in the soil environment, the UCMS5 beads were kept between two layers of soil. A falcon centrifuge tube with a volume of 50 mL, and dimensions of 30 mm in diameter and 115 mm in length was utilized. The cotton fabric was placed in the bottom of a conical tube and the soil was put into the tube with a height of 60 mm, and then a layer of beads about 10 mm was placed on the top surface of the soil layer. Subsequently, the second layer of soil of 10 mm in height was put down on the beads layer. Afterward, 30 mL of distilled water was added to the plastic tube. A hole of 1 cm in diameter was created at the bottom of the tube to drain out the water into a collecting vial. Every day, 5 mL of water was collected from the bottom and the same volume was added to the system. The urea concentration in the collecting vial was identified by using the Ehrlich reagent at the absorption wavelength of 425 nm. The cumulative release of urea from the beads in the soil medium was calculated by using Equation 6.

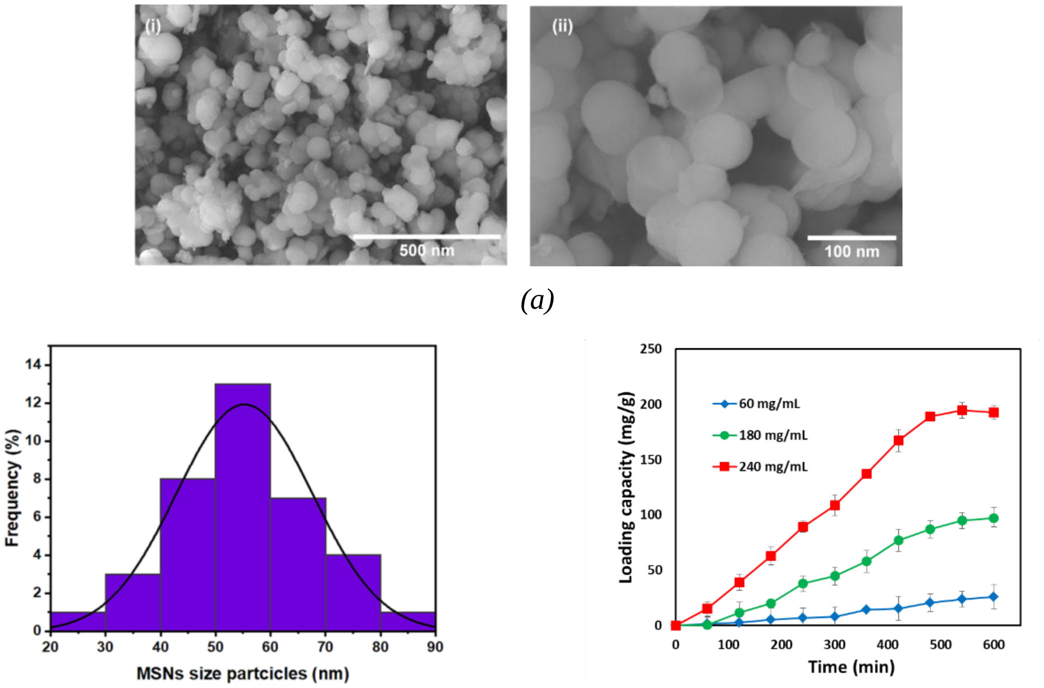
$$CR\ (\%) = \sum_{1}^{t} \frac{W_i}{W_o} \times 100\% \tag{6}$$

Where W_i is the weight of released urea at the day i, W_o is the total weight of urea.

3. Results and Discussion

3.1. Characterization of MSNs particles and loading urea into MSNs particles

The preparation and characterization of MSNs is an essential step in various scientific and industrial applications. These porous particles are well known for their exclusive characteristics such as great surface area, controllable pore size, high loading capacity of small molecules, and reinforcement function for natural polymers [15], [16]. The synthesized MSNs, derived from the TEOS precursor, exhibit a homogenously spherical shape as shown in Figures 2a(i) and 2a(ii). According to the histogram (Figure 2b) analyzed by ImageJ software, the MSNs have a size in the range of 20 and 100 nm, with an average particle size of approximately 56±1.7 nm. Overall, the result indicates a successful preparation of silica nanoparticles within the desired nano-size range. The characteristics of MSNs can be adjusted by the type and concentration of surfactants used in the sol-gel process, or by using a suitable ratio of co-solvent, such as ethanol. This accomplishment not only contributes to the advancement of nanotechnology but also opens up new possibilities for applications in various fields such as drug delivery, catalysis, and sensor technology. The MSNs sample was evaluated the porosity by using BET analysis. The result confirms the MSNs possess a large surface area of 809.431 m^2/g, indicating the great adsorption efficiency and loading capacity of the MSNs.



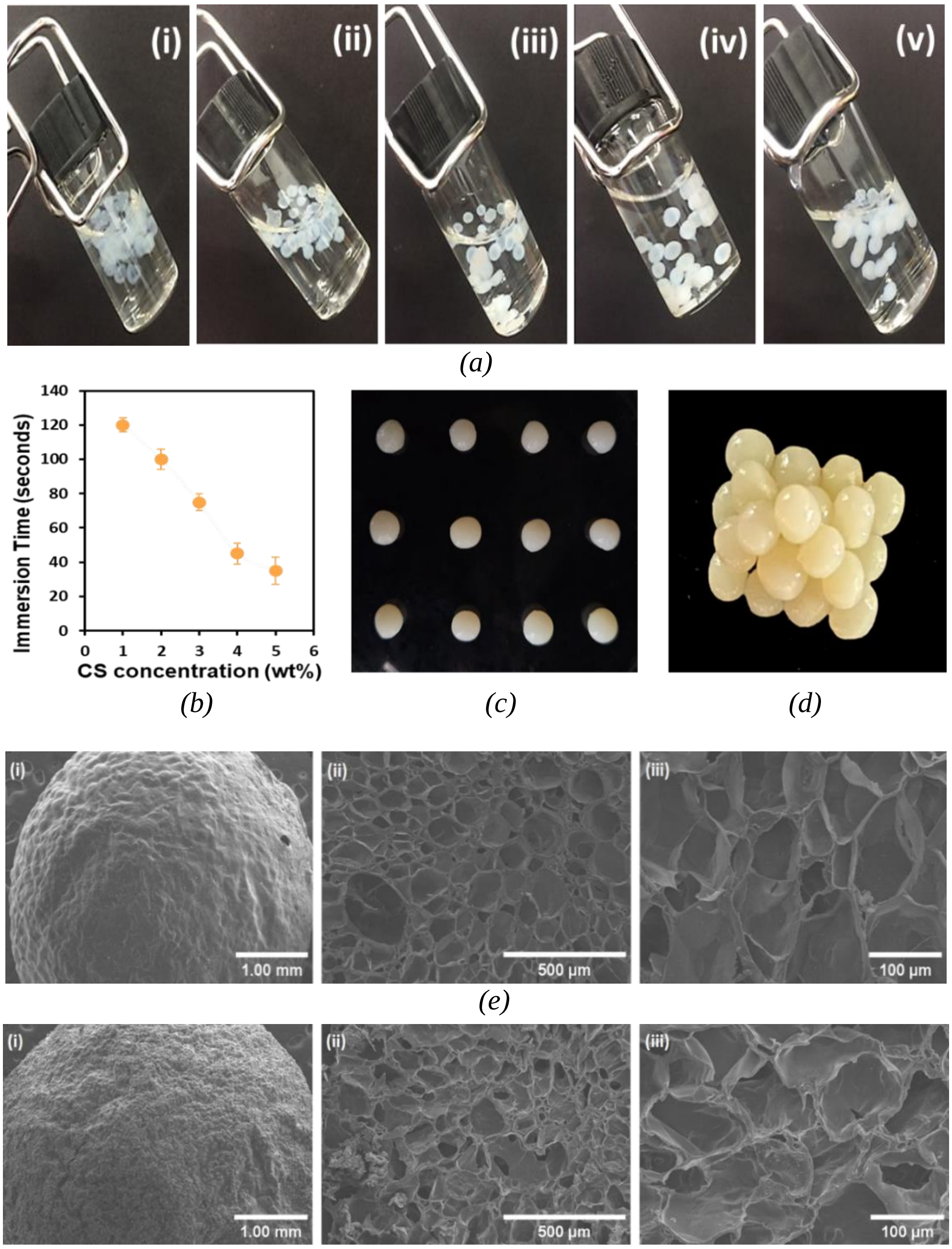
(a)

(b) *(c)*

Figure 2. *Preparation and characterization of MSNs particles. (a) SEM images of MSNs with scale bars: (i) 500 nm, (ii) 100 nm; (b) Distribution of MSNs size analyzed from SEM images using ImageJ software; (c) Urea loading capacity of MSNs according to change of initial urea concentration and soaking time.*

The graph in Figure 2c illustrates the urea loading capacity by a variation in initial urea concentrations and soaking times. The findings suggest that the capacity of urea adsorption by MSNs directly relates to the initial urea solution concentration and immersion time. Based on the investigation conducted over 600 minutes, there is a notable increase in urea content loaded into MSNs with higher soaking time and greater concentration of urea solution. This increase could be attributed to the highly porous structure of MSNs, providing a large surface area and volume for urea molecules to diffuse into the pores of the nanoparticles. Moreover, primary amine and carbonyl groups on urea molecules enable hydrogen bonding with hydroxyl groups on the MSNs pore wall, allowing high urea encapsulating capability of MSNs. Specifically, MSNs in a urea solution with a concentration of 240 mg/mL exhibited a loading capacity of approximately 200 mg urea/g MSNs at 540 minutes. Notably, the great surface area and controllable pore size of MSNs enable them an ideal carrier for urea, as they can store a significant amount of urea and release it gradually over time. This is particularly advantageous in agricultural applications, where controlled-release fertilizers can enhance nutrient-utilizing efficacy and diminish environmental impact.

3.2. Characterization of UMCS hydrogel beads



(a)

(b) *(c)* *(d)*

(e)

(f)

Figure 3. *Characterization of CS and UMCS hydrogel beads. (a) Gelation of CS hydrogel beads at NaOH 1M and different chitosan concentrations: (i) CS 1 wt%, (ii) CS 2 wt%, (iii) CS 3 wt%, (iv) CS 4 wt% CS, (v) CS 5 wt%; (b) Formation times of hydrogel beads at different CS concentrations; (c) CS hydrogel beads; (d) UMCS hydrogel beads; (e) The surface and cross-section morphology images of CS hydrogel beads with scale bars: (i) 1.00 mm, (ii) 500 µm, (iii) 100 µm; (f) The surface and cross-section morphology images of UMCS hydrogel beads with scale bars: (i) 1.00 mm, (ii) 500 µm, (iii) 100 µm.*

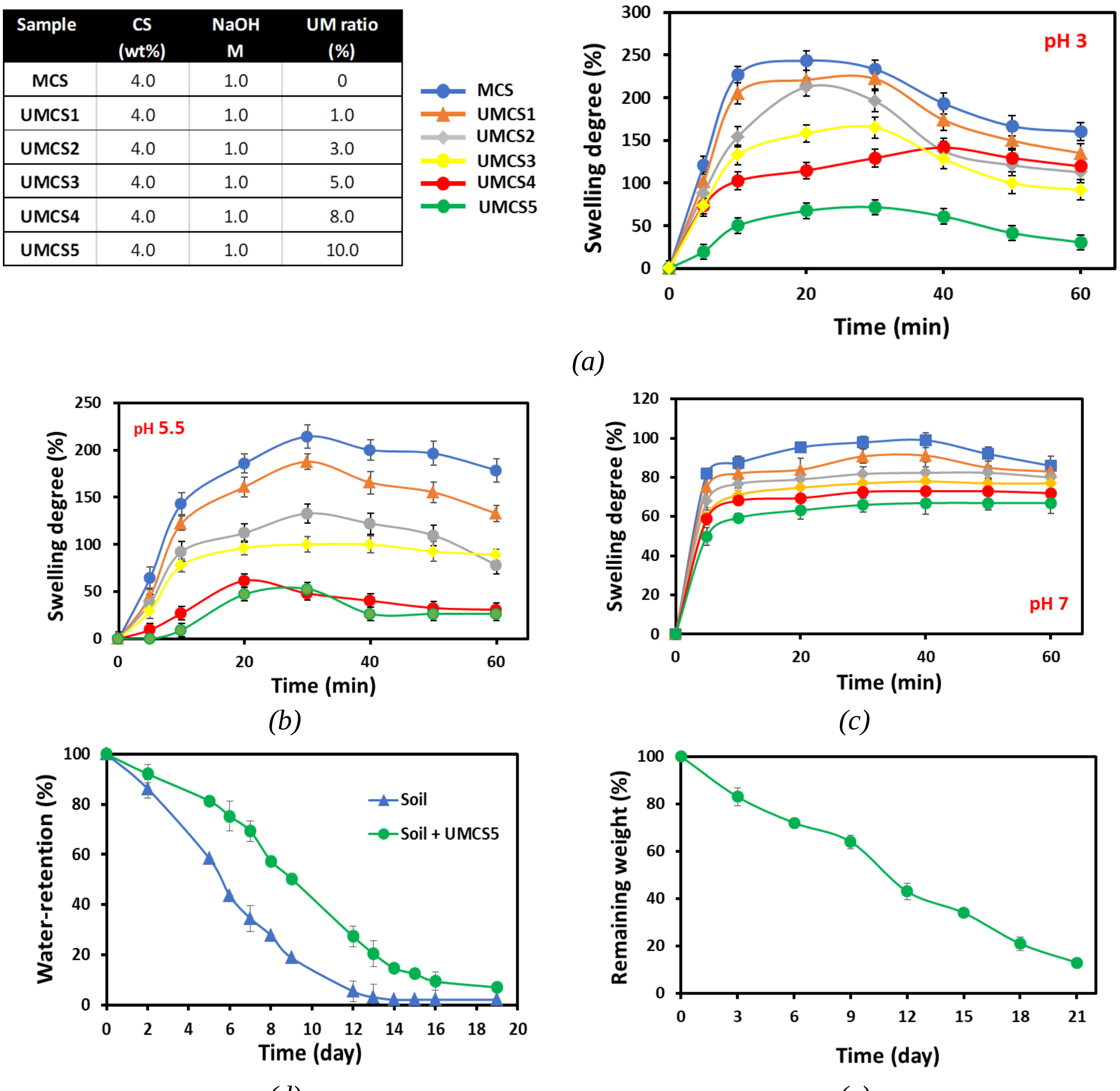
Hydrogel beads made from chitosan and mesoporous silica nanoparticles offer various applications thanks to their exclusive characteristics. Figure 3a shows the formation capacity of hydrogel beads when the chitosan solution with various concentrations is dropped into the NaOH 1M. Chitosan, a cationic polysaccharide, can be soluble in an aqueous acidic solution (usually pH < 6.0), this reason caused by the ionization of amine groups along the molecular backbone. However, in the neutral or basic solution, chitosan becomes insoluble and gelated. The size and shape of the beads can be tuned by adjusting the parameters of the gelation process, such as the concentration of chitosan and NaOH, and the incubation time. Particularly, Figure 3b indicates the gelation time depending on the concentration of chitosan. It can be observed that, under the condition of NaOH 1M and chitosan 4 wt%, the gelation time is approximately 40 seconds and the resulting hydrogel beads exhibit high stability and spherical shape. Therefore, this condition is used for further investigation. Figures 3c and 3d sequentially presented the outer shapes of CS and UMCS hydrogel beads.

Figures 3e and 3f present the SEM images of CS and UMCS hydrogel beads, respectively. From SEM observation, the surface of these hydrogel beads appears tightly packed. This surface structure plays a critical role in controlling the release of urea, ensuring a steady and controlled nutrient supply to plants, as well as improving nutrient utilization efficiency, and reducing environmental impacts associated with fertilizer runoff. Furthermore, the highly porous structure observed inside the beads enhances their water retention capability, which is essential for maintaining soil moisture levels in agriculture. This characteristic helps reduce irrigation frequency, conserve water resources, and support plant growth during dry periods [17].

3.3. Physical properties and slow-release properties of UMCS hydrogel beads

Hydrogel beads are unique materials known for their ability to swell in various solutions. This swelling property plays a pivotal role in evaluating the strength and elasticity of these beads. When submerged in a liquid, hydrogel beads absorb water and increase in size, showcasing their remarkable capacity for expansion.

Figures 4a, 4b, and 4c show that, in the early stages (first 20 minutes), the hydrogel beads have a very high swelling ability due to their good water absorption ability. But gradually in the following stages, the beads begin to stabilize and absorb less water. After 60 minutes as above, we can see that the swelling of the beads in pH 3, 5.5, and 7 solutions is very high, up to more than 85% of the initial mass of MCS hydrogel beads (see Figure 4c). However, MCS hydrogel beads have a swelling degree higher than that of UMCS hydrogel beads, and UMCS hydrogel beads with a urea: MCS ratio of 10% (UMCS5) have the lowest swelling level. The presence of MSNs and urea within the chitosan hydrogel beads plays a crucial role in modifying the hydrogel’s structural properties. MSNs, with their well-defined porous structure, introduce a new phase within the hydrogel matrix, potentially resulting in a rise in the cross-linking density of the chitosan network. This enhanced cross-linking density could stint the extent of swelling by limiting the amount of water the hydrogel can absorb. Urea, on the other hand, serves a dual function. Firstly, urea molecules can fill the pores within the hydrogel beads, further inhibiting water uptake. Secondly, urea can engage in hydrogen bonding with the chitosan matrix, thereby contributing to the overall stiffness of the hydrogel structure. These hydrogen bonds may also reduce the availability of functional groups in chitosan that are responsible for water absorption, leading to a decrease in swelling. Therefore, the swelling ability of UMCS5 hydrogel beads is suitable for slow and controlled fertilizer release properties [18], [19]. Furthermore, Zhu et al. (2022) explored urea-modified chitosan hydrogels and highlighted urea’s role in reducing water uptake by filling hydrogel pores and forming hydrogen bonds with the polymer matrix. This is consistent with the dual function of urea described in chitosan-MSNs-urea hydrogel beads, where it inhibits rapid swelling, thus supporting controlled fertilizer release [20]. Similarly, Liu et al. (2020) investigated chitosan/MSNs composite hydrogels and noted their slow swelling properties, contributing to sustained drug release behavior. This parallels the controlled release potential observed in UMCS hydrogel beads for fertilizer applications [21]. By comparing these findings from recent literature, it becomes evident that the slow swelling property of chitosan-MSNs-urea hydrogel beads aligns with similar systems developed for controlled release applications. This comparison underscores the potential of our hydrogel beads in achieving effective and sustained fertilizer release properties.



Sample	CS (wt%)	NaOH M	UM ratio (%)
MCS	4.0	1.0	0
UMCS1	4.0	1.0	1.0
UMCS2	4.0	1.0	3.0
UMCS3	4.0	1.0	5.0
UMCS4	4.0	1.0	8.0
UMCS5	4.0	1.0	10.0

(a)

(b)

(c)

(d)

(e)

Figure 4. *Physical properties of UMCS hydrogel beads. (a)Swelling of UMCS hydrogel beads at pH 3; (b) Swelling of UMCS hydrogel beads at pH 5.5; (c) Swelling of UMCS hydrogel beads at pH 7; (d) Water-retention capacity of soil with or without UMCS5; (e) Biodegradation of UMCS hydrogel beads in the soil.*

Adequate water extent ensures that soil maintains sufficient moisture for healthy plant growth and development. The impact of hydrogel beads on soil water retention is a remarkable illustration of how modern agricultural technologies can enhance the water-holding capacity of soil. Hydrogel beads, when mixed with soil, act as mini reservoirs of water. They absorb water and swell during wet conditions, and then gradually release water back into the soil in drier conditions, thereby ensuring a more consistent level of soil moisture, which is particularly beneficial during the initial stages of plant growth. As depicted in Figure 4d, the comparison between soil samples with and without these hydrogel beads reveals a stark contrast in water retention capabilities. Soil samples devoid of hydrogel beads experience a rapid decline in moisture levels, becoming arid by the twentieth day. This demonstrates the challenge of maintaining soil moisture solely through natural or traditional irrigation methods, which can be inefficient and unsustainable, especially in arid regions or during periods of drought. On the other hand, soil samples that incorporate UMCS hydrogel beads show a remarkable improvement in water retention. These beads act like tiny reservoirs, slowly releasing water as the surrounding soil dries, thereby maintaining a more consistent level of moisture. On day 20, these enhanced soil samples retained moisture levels that were 8% higher than their non-hydrogel counterparts. In particular, Wang et al. (2021) investigated pH-sensitive hydrogel beads based on chitosan and mesoporous silica nanoparticles

(MSNs) and reported significant improvements in water retention capacity. The porous structure of MSNs facilitated water absorption and retention within the hydrogel matrix, similar to the mechanism expected in UMCS hydrogel beads [22]. Additionally, Xiao et al. (2022) illustrated hydrogel beads specifically designed to improve water retention in soil [23]. These references provide a diverse set of comparisons for the water retention capacity of hydrogel beads, reinforcing the notion that UMCS hydrogel beads not only ensure a steady nutrient supply but also improve soil moisture retention. This dual functionality enhances plant growth and reduces the frequency of both watering and fertilizer applications, making these hydrogel beads a promising solution for sustainable agriculture.

Figure 4e provides a visual comparison of the UMCS5 hydrogel beads before and after a set period of decomposition in soil, illustrating a significant transformation over just 21 days. This controlled degradation is a key feature of the UMCS hydrogel beads, designed to break down under specific conditions without leaving harmful residues in the soil, with a reduction of approximately more than 58% in weight after 12 days, and a further 30% reduction after 21 days. The degradation process of these hydrogel beads is not only crucial for understanding their environmental impact but also for evaluating their effectiveness in applications such as soil moisture retention and nutrient delivery. The controlled manner in which these beads decompose suggests that they can provide targeted benefits to crops during critical growth phases before seamlessly integrating with the soil. This characteristic minimizes the environmental footprint of their use, making them an attractive option for eco-conscious agricultural practices. The ability to control the degradation rate of these beads opens up new possibilities for precision agriculture, where resources are delivered more efficiently and sustainably to crops, enhancing yield while protecting the environment.

3.4. The slow-release characteristic of UMCS under a water and soil environment

The unique properties of UMCS hydrogel beads make them ideal for various applications, especially in controlled release systems. By leveraging its exceptional swelling and water retention abilities, UMCS has shown promise in effectively regulating the release of urea. The intercalation of urea between the pores of MSNs plays a significant role in this process, allowing for a gradual and controlled release mechanism.

The study of urea release in agricultural applications has taken a significant leap forward with the introduction of UMCS hydrogel beads. Figure 5, which illustrates the release curves of UMCS hydrogel beads into water and soil environments over 30 days, reveals a noteworthy distinction in their behavior. The UMCS hydrogel beads demonstrate a markedly slow-release rate, with about 90% of the urea content being released into the water and more than 75% into the soil after 30 days. This slow-release rate observed in UMCS hydrogel beads can be attributed to the innovative combination of mesoporous silica nanoparticles (MSNs) and chitosan, which together facilitate a controlled release mechanism. The MSNs, known for their high surface area and mesoporous structure, along with the hydrogel-forming capability of chitosan, create a matrix that effectively encapsulates the urea molecules. The physical and hydrogen bonds between urea molecules and the pore walls of MSNs create a barrier because the surface of MSNs is rich in silanol (Si-OH) groups, which slows down urea dissolution into the water and soil [24]. When introduced into the system, urea diffuses into the pores of the MSNs and interacts with the silanol groups on the surface. This interaction results in the adsorption of urea within the mesoporous structure [25]. These diffusion and interaction processes are vital for the controlled release of nutrients like urea. Nayan et al. (2018) demonstrated that urea diffuses from inside the hydrogel beads into the surrounding environment gradually, ensuring a steady supply of nutrients to plants over an extended period [26]. Similarly, Swify et al. (2023) also found that hydrogel-based fertilizers encapsulate urea inside the gel particles and release it slowly, reducing volatilization and leaching, thereby decreasing environmental pollution [27]. The hydrogel matrix serves as a reservoir, capturing urea molecules and gradually releasing them into the soil solution.

Thus, the study on chitosan/MSNs hydrogel beads has achieved a significant milestone in the controlled release of urea, demonstrating an extended-release period of 30 days in a water environment. This duration surpasses the typical 2-3 weeks reported in other studies, showcasing the superior performance of the chitosan/MSNs hydrogel system. For example, Song et al. (2022) developed double-network hydrogel beads using sodium alginate combined with other polymers to achieve a slow release of urea. The study demonstrated that these hydrogels could effectively sustain nutrient release for approximately 2-3 weeks. The prolonged-release period ensures a consistent supply of nutrients, enhancing plant growth and reducing the frequency of fertilizer applications [28].

The implications of this research for agriculture are profound. The controlled release of urea from UMCS hydrogel beads aligns more closely with the nutrient uptake kinetics of plants, ensuring that nitrogen is available when plants are most capable of assimilating it. This not only has the potential to enhance plant growth and yield but also minimizes the environmental impact associated with the leaching of nitrogen into water bodies. By reducing the rapid dispersal of urea into the environment, this technology offers a promising solution to one of the significant challenges in agricultural fertilization practices, paving the way for more sustainable and efficient use of urea-based fertilizers.

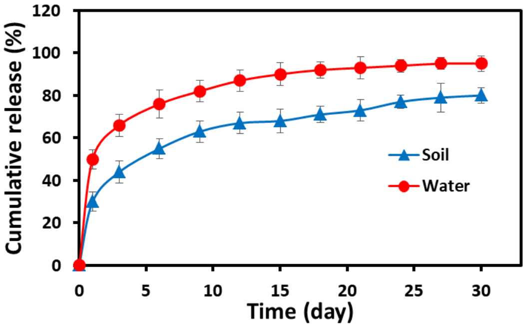


Figure 5. *Cumulative release of urea from the UMCS5 hydrogel bead in water and soil environments*.

4. Conclusions

The development of a unique hydrogel bead based on urea-mesoporous silica nanoparticles-chitosan (UMCS) represents a promising advancement in the field of agricultural technology, particularly in the realm of controlled-release fertilizers. These UMCS hydrogel beads, with their meticulously engineered composition comprising 4 wt% chitosan (CS), a 10% mixture of urea and MSNs exhibit remarkable properties that could revolutionize the way fertilizers are used in farming. The synthetically produced MSNs particles possess a high surface area and a well-defined porous structure with pore sizes ranging from 20 nm to 90 nm, peaking at approximately 55 nm. This makes them ideal for absorbing and storing urea through physical adsorption and hydrogen bonding interactions. Additionally, the prepared UMCS beads displayed a smooth, spherical shape with a porous internal morphology. Their swelling ability at different pH levels (pH 3, pH 5.5, and pH 7) supports slow and controlled fertilizer release properties, particularly evident in the UMCS5 sample. Moreover, these beads maintain their spherical shape and release urea slowly in both water and soil environments over a 30-day period, with rates exceeding 90% and 75% respectively. This ensures efficient and sustainable nutrient delivery to plants. The extended-release duration guarantees a steady nutrient supply, promoting plant growth and reducing the need for frequent fertilizer applications.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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