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PREPARATION AND CHARACTERIZATION OF CONTROLLED-RELEASE FERTILIZERS EXTRUSION GRANULES USING POROUS SILICON DIOXIDE

In this study, we developed Hydroxypropyl methylcellulose (HPMC)/ Ethyl cellulose (EC)/ Porous silicon dioxide (PSD) extrusion granules for controlled-release fertilizer for more than 30 days. The amount of HPMC and EC was optimized through release evaluation, and the fertilizer could be controlled for more than 30 days using PSD. The extrusion granules were manufactured by a manual round pill machine using fertilizer, HPMC, EC, and PSD in the ratio of 1:1:10:3. Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and X-ray diffraction (XRD) evaluated the physicochemical properties of the extrusion granules. In addition, the release test of the fertilizer components was performed. The fertilizer was released 80% at 30 days, which was a controlled release. Our study shows that the controlled-release fertilizer using PSD is a promising slow-release fertilizer.

Keywords: Controlled release; fertilizer; HPMC; EC; porous silicon dioxide

1. Introduction

As the global population continues to grow, the demand for food production increases, making fertilizers crucial for boosting crop yields and supporting sustainable agriculture. However, crops do not absorb most of the nutrients from fertilizers efficiently. This reduces fertilizer effectiveness and causes environmental issues, such as water pollution, air pollution, and soil compaction [1]. In addition, conventional chemical fertilizers tend to release nutrients quickly, often resulting in nutrient leaching and a mismatch between when nutrients are available and when crops need them. This inefficiency reduces the effectiveness of nutrient absorption by plants and leads to nutrient accumulation and loss. Excess nitrogen and phosphorus can seep into groundwater or be washed away by runoff, contributing to serious environmental issues like eutrophication [1]. To enhance fertilizer nutrient efficiency and reduce environmental pollution, slow-release and controlled-release fertilizers have been introduced in response to strict environmental regulations and the need for more efficient nutrient use. Currently, commercial slow-release fertilizers are primarily categorized into inorganic-coated and organic-coated types. Inorganic-coated fertilizers, however, come with certain drawbacks, including high brittleness, weak element adhesion, and challenges with transportation and storage. Organic coating fertilizers are polymer-based and receive increasing attention in release rate control [2].

It is challenging to release fertilizer components by the nutrient demand time in the crop growth cycle when using only hydrophilic single materials to produce slow-release fertilizers using bio-based polymers. Hydrophilic polymer coatings quickly absorb soil moisture, leading to rapid nutrient release. This rapid release often fails to match the nutrient uptake needs of crops. Therefore, complex components with hydrophobic properties may be more suitable for developing slow-release fertilizers as bio-based polymer coating materials [2].

HPMC is one of the polymers used to prepare hydrophilic matrices with prolonged release of active ingredients. HPMC has the advantages of being nontoxic, easy to handle, relatively inexpensive, and easy to compress [3]. EC is a kind of hydrophobic cellulose ether that is insoluble in water and is one of the polymers used for controlled release. EC is a polymer with excellent controlled release ability, durability, and low cost [4]. PSD is a nanostructured material with a large surface area (200 m^2/g) and porosity, making it an attractive active agent delivery platform. PSD is nontoxic, biodegradable with various protonated orthosilicate ions, and can be functionalized on the surface to load multiple active agents through various surface modifications such as oxidation, hydrosilylation, and silanization [5,6].

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Biodegradable controlled-release systems have been reported to be manufactured using methods such as hydrogel manufacturing or freeze-drying, which are challenging to industrialize [7]. Granulation by compression can be an exciting alternative. This technology is manufactured by applying pressure to a wet powder mixture. It is a simple, inexpensive, and quickly industrialized process [8].

This study aimed to develop a novel controlled-release fertilizer using an organic-inorganic composite system. The formulation combined hydrophilic and hydrophobic polymers with a porous inorganic carrier to regulate nutrient release effectively. Unlike previous studies that utilized either single coating material or complicated processing routes, this research proposes a scalable wet compression granulation method using HPMC for its matrix-forming and biodegradable properties, EC for sustained nutrient diffusion, and PSD for its high surface area and modifiable inorganic framework [2,7]. The physicochemical properties of extrusion granules using the generated organic-inorganic composite material were evaluated using SEM, FT-IR, and XRD. Additionally, the release properties of the fertilizer components were assessed systematically.

2. Experimental

Fertilizer containing 20% nitrogen, 20% phosphorus, and 20% calcium was purchased from Sangnoksa (Seoul, Korea). Hydroxypropyl methylcellulose (HPMC; Metholose® 90SH-100000SR) and ethyl cellulose (EC; Ethocel® Standard 7 Premium) were provided by Shin-Etus (Tokyo, Japan) and Colorcon (Darfford, UK), respectively. Porous silicon dioxide (PSD; Aerosil® 200) was purchased from Evonik (Essen, Germany). The PSD-based controlled-release fertilizer extrusion granules were prepared using the following method: First, the fertilizer, HPMC, EC, PSD were mixed manually after sieving through a 40-mesh sieve according to the compositions shown in TABLE 1. Next, an appropriate amount of distilled water was added to the previously prepared mixture and stirred thoroughly. The mixture was then extruded using a XuZhong manual round pill machine (Guangzhou, China) to obtain extrusion granules and dried at 60°C for 4 h to get the final products. The diameter of each extrusion granule was about 4 mm, and the loss on drying was within 3%.

TABLE 1

Composition of the formulations for controlled-release fertilizer

Ingredient (g)	I	II	III	IV	V	VI	VII	VIII
Fertilizer	1	1	1	1	1	1	1	1
HPMC	10	—	5	2.5	1	1	1	1
EC	—	10	5	10	10	10	10	10
PSD	—	—	—	—	—	1	3	5

Mihok et al. proposed a method to rapidly evaluate this release using electrical conductivity [9,10]. Using this method, the release of fertilizer components was assessed by soaking 0.5 g of fertilizer alone and PSD-based controlled-release fertilizer extrusion granules in 100 mL of purified water. The release was evaluated under 25 ± 1°C conditions and stirred at 80 rpm for 30 days. The conductivity of the water was measured by an electrode connected to an Orion Star A222 conductivity portable meter (Thermo Fisher Scientific, Massachusetts, USA). The release is completed when the conductivity remains constant, so the maximum release time for various systems can be measured. SEM characterized surface morphology (S-4800, Hitachi, Tokyo, Japan). The samples were fixed on a brass sampling disk and sputter-coated with platinum via EMI Teck Ion Sputter (K575 K) at a current of 15 mA and 100% turbo speed for 4 min in a vacuum (8×10^{-3} mbar) to make them electrically conductive [11]. FT-IR spectra were performed on the 3500-500 cm^{-1} samples using a PerkinElmer Frontier spectrometer (Waltham, MA, USA) [12]. The crystallinity was investigated using an Ultima IV XRD (Rigaku Co., Tokyo, Japan). The instrument was equipped with a MiniFlex goniometer and a Cu Kα1 monochromator. The instrument was operated at a current flow of 30 mA and a voltage of 40 kV at ambient temperature. The crystallinity of the samples was also observed in the two-theta angle configuration of 5-45°. Scanning was performed at an angular increment of 0.02°/s and a scan rate of 1.0 s/step [13].

3. Results and discussion

This study aimed to achieve sustained release of fertilizer components for more than 30 days by using HPMC with swelling and water solubility and EC with hydrophobicity as a matrix system [14]. HPMC controls the initial release and is non-toxic and biodegradable. EC, a hydrophobic polymer, slows nutrient diffusion and prolongs release. Together, HPMC and EC provide complementary release control. However, when only organic substances, HPMC and EC, are used, it is difficult to formulate due to low flowability and difficulty in dispersion during manufacturing, and it is not easy to control the release. Therefore, to solve these problems, controlled-release extrusion granules were manufactured using inorganic material PSD, and their effects were evaluated [15]. PSD serves multiple functions in the matrix: it enhances mechanical stability, acts as a diffusion barrier to slow water and nutrient movement, and temporarily adsorbs nutrients in its pores to delay release [15]. Moreover, a slow-release fertilizer requires a low surface area. A high surface area increases the release rate, so it is essential to reduce the surface area of the formulation containing the fertilizer component for slow-release characteristics [16]. Therefore, in this study, the extrusion granulation method was used.

The release profiles of the fertilizers are shown in Fig. 1. Formulations I-V were manufactured and evaluated to confirm the influence of HPMC as a hydrophilic polymer and EC as a hydrophobic polymer on the release characteristics. The formulation I prepared with HPMC showed faster fertilizer release than the formulation II prepared with EC. It was confirmed that

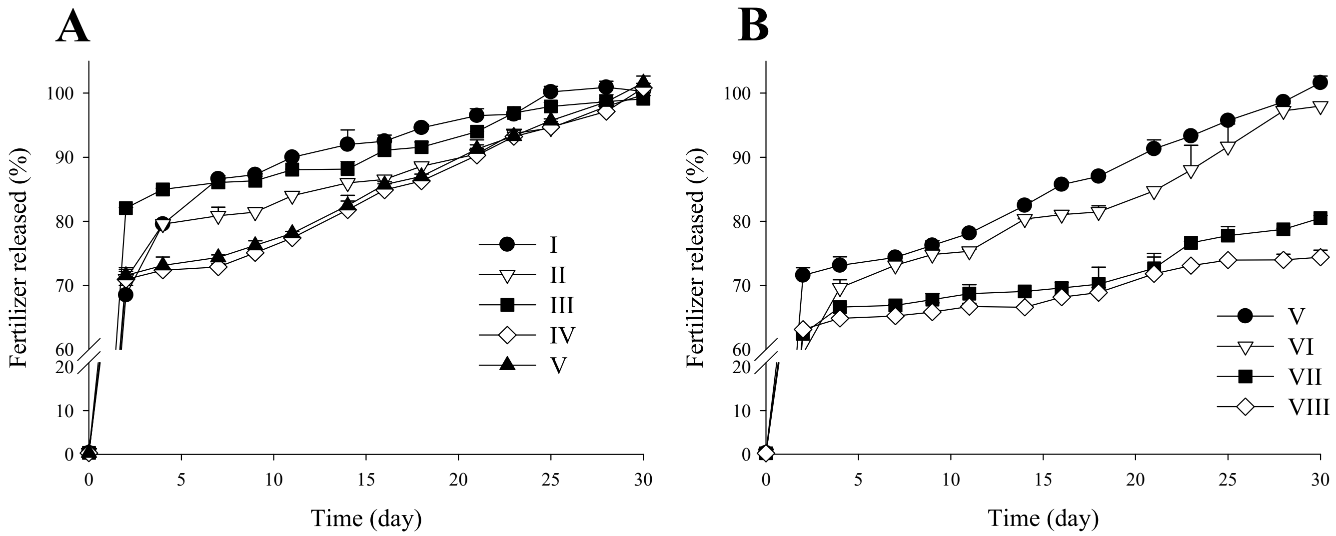

Fig. 1. Influence of the HPMC/EC ratios (A) and PSD ratios (B) on the fertilizer release from controlled-release fertilizer extrusion granules

hydrophobic polymers have a higher release control effect than hydrophilic polymers [17]. The formulation III prepared with fertilizer: HPMC: EC in a 1:5:5 ratio showed a faster initial release than when HPMC and EC were used alone (82% vs. 69% and 71%, 2nd day), but the release increase rate after the initial release was slower than when HPMC was used alone. It was confirmed that mixing HPMC and EC to form a hydrophobic polymer barrier in the swollen polymer matrix can be more effective than using HPMC or EC alone [18,19]. Both formulations IV and V showed an increased controlled release effect for 2 to 20 days compared to the case where EC, a hydrophobic polymer, was used alone. However, as the proportion of HPMC, a hydrophilic polymer, increased, the mixture's viscosity increased too much, and extruded granules were not formed. Therefore, PSD, an inorganic material with a controlled-release effect and whose viscosity did not increase during extrusion, was added, and extrusion granules were manufactured and evaluated afterward. PSD is a material suitable for biotechnological applications because of its structure and properties, characterized by highly aligned nanosized pores [20]. Formulation V, which has the highest controlled-release effect and lowest polymer ratio, was used to manufacture extrusion granules by adding PSD. In the case of formulation VI, the initial release was lower than that of formulation V, which did not contain PSD (59% vs. 71%, 2nd day). Both Formulation VII and VIII with increased PSD showed a controlled-release effect compared to Formulation V, which did not contain PSD. In addition, it was confirmed that the controlled-release impact increased as the ratio of PSD increased. Formulations VII and VIII showed that controlled release for more than 30 days was possible.

The surface morphology of fertilizer, HPMC, EC, PSD, and extrusion granules was examined using SEM (Fig. 2). Fertilizer showed a morphology containing irregularly shaped crystals (Fig. 2A). On the other hand, HPMC was an amorphous small particle powder containing irregular shapes (Fig. 2B). EC also showed amorphous containing irregular shapes but larger particles than HPMC's small particle powder (Fig. 2C). PSD showed porosity with a loose network structure (Fig. 2D). The surface morphology of the extrusion granules showed rough and coagulated particle masses and irregular surface characteristics (Fig. 2E) [21]. Enlargement of the surface of the extrusion granules revealed cracks in the cross-section (Fig. 2F). FT-IR (Fig. 3A) and XRD (Fig. 3B) were used to characterize the physicochemical properties of PSD-based controlled-release fertilizer extrusion granules. The fertilizers did not show any characteristic peaks in the FT-IR spectra. HPMC showed a broad characteristic band around 1050 cm^{-1}, representing the intense peak of the C-O-C stretching of HPMC [22]. EC exhibited distinct peaks at 940-1224 cm^{-1}, corresponding to the stretching vibrations of C-O-C in the pyranose ring and aliphatic ether groups. Additionally, it displayed characteristic peaks at 2973, 2974, and 2868 cm^{-1}, associated with the C-H stretching vibrations from CH_2 and CH_3 groups [22]. Meanwhile, PSD presented a strong peak at 820 cm^{-1}, attributed to the symmetric stretching of the Si-O-Si bond, along with a peak at 1105 cm^{-1} representing the asymmetric stretching vibration of the Si-O-Si bond [16]. The FT-IR spectrum of the final formulation of PSD-based controlled-release fertilizer extrusion granules showed similar characteristic peaks of HPMC, EC, and PSD. Therefore, the wavenumbers of the functional groups of fertilizer, HPMC, EC, and PSD were maintained in the extrusion granules, indicating no noticeable interaction among fertilizer, HPMC, EC, and PSD. The XRD pattern of fertilizer showed several high-intensity peaks, indicating the crystalline structure. The absence of specific diffraction peaks in the XRD patterns of HPMC, EC, and PSD indicates that HPMC, EC, and PSD are amorphous. In the extrusion granules, it was confirmed that the characteristic peaks of fertilizer disappeared. These results also showed that in the compressed granules loaded with fertilizer, the fertilizer was encapsulated in HPMC and EC polymers and PSD and did not crystallize. HPMC, EC, and PSD completely encapsulate the crystalline fertilizer and exhibit a long-term sustained release pattern [23-25].

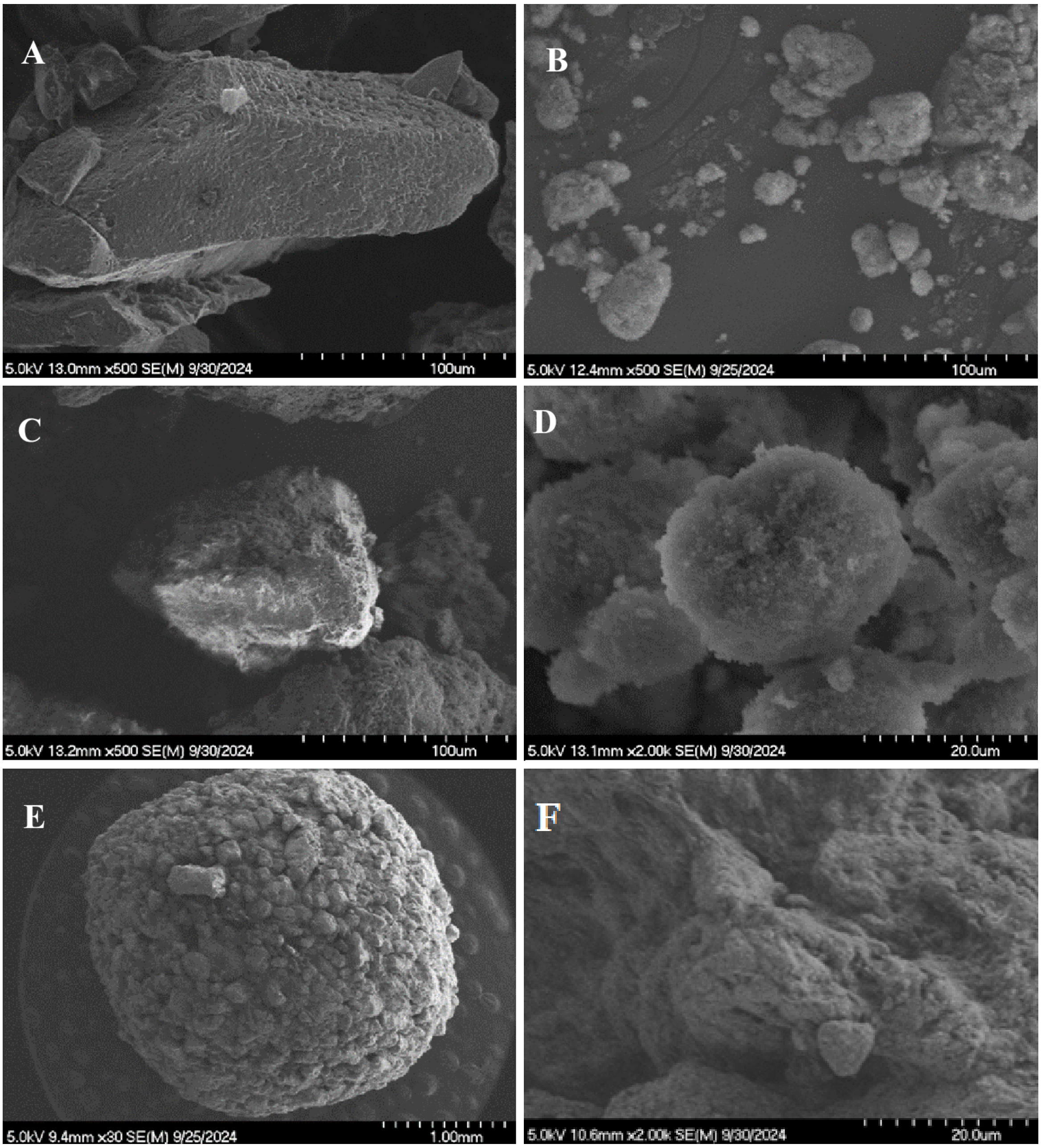

Fig. 2. SEM images of Fertilizer (×500) (A), HPMC (×500) (B), EC (×500) (C), PSD (×2,000) (D), PSD-based controlled-release fertilizer extrusion granules (formulation VII, ×30) (E), and PSD-based controlled-release fertilizer extrusion granules (formulation VII, ×2,000) (F)

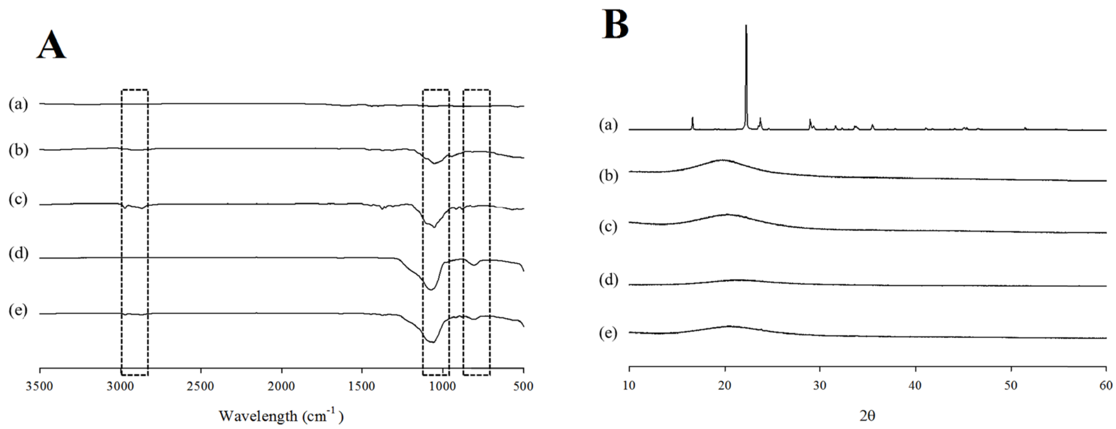

Fig. 3. FT-IR spectra (A) and XRD patterns (B) of Fertilizer (a), HPMC (b), EC (c), PSD (d), and PSD-based controlled-release fertilizer extrusion granules (formulation VII) (e)

4. Conclusions

The ratio of HPMC and EC was optimized for the sustained release of fertilizer, and the extrusion granules were optimized using PSD. When fertilizer, HPMC, EC, and PSD were mixed in a ratio of 1:1:10:3, the optimized result was obtained, and the release control rate was 62% on the 2nd day and 80% on the 30th day. The compressed shape of the extrusion granules was confirmed through SEM measurement, and FT-IR measurement confirmed that there was no interaction among fertilizer, HPMC, EC, and PSD. In addition, we were able to verify that the fertilizer components were encapsulated in HPMC, EC, and PSD through XRD measurements. In summary, PSD-based granules showed effective long-term nutrient release. These results suggest that PSD is a promising inorganic material for future controlled-release fertilizer formulations.

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