

# Environmentally Friendly Carboxymethyl Cellulose Hydrogels Derived from Waste Paper and Sawdust as a Urea Release Agent

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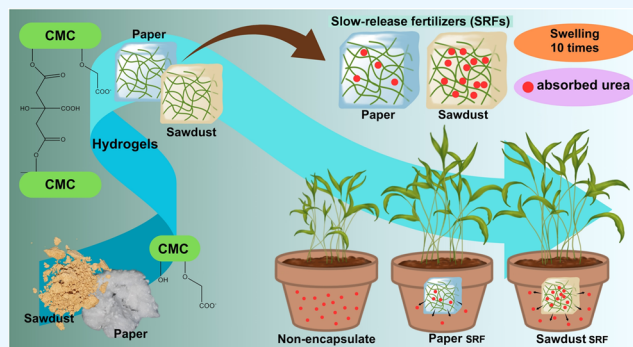


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**ABSTRACT:** This study investigates the development and application of cellulose hydrogel-based slow-release fertilizers derived from waste materials, specifically waste paper and sawdust, in cultivating water convolvulus. The slow-release fertilizers were created using carboxymethyl cellulose (CMC) derived from these waste sources with citric acid as a cross-linker, aiming to enhance nutrient efficiency and sustainable agricultural practices. The CMC hydrogels demonstrated high water swelling—approximately 10 times its dry weight, enhancing soil moisture holding levels across different soil types. Notably, the slow-release fertilizer derived from sawdust (HyU\_CMC\_SD) showed the highest urea absorption ( $330.8 \pm 2.3$  mg/g) and a high urea release rate in water and soil owing to its polymeric chain property. Cultivation trials over 25 days revealed that water convolvulus grown with the sawdust-derived slow-release fertilizer had the most extended stem growth, while the slow-release fertilizer from waste paper (HyU\_CMC\_P) provided gradual, more prolonged release, supporting consistent plant growth post-14 days of growing. Overall, slow-release fertilizers from the CMC hydrogels proved effective in slowing nutrient release, conserving soil moisture, and minimizing nutrient leaching. This research suggests that cellulose hydrogel-based slow-release fertilizers from waste materials offer a promising approach for sustainable and efficient agricultural production.



## 1. INTRODUCTION

Currently, the world has a population of approximately 8 billion people. It is speculated that between 2020 and 2050, the global population will increase by an additional 1.3–1.9 billion people, despite the slower growth rate compared to the last four decades.<sup>1,2</sup> As the population keeps rising, allocating sufficient food supplies to meet the increasing demand is a challenge for every country currently facing.<sup>3</sup> However, agricultural land is decreasing due to urban and industrial expansion. Additionally, unpredictable weather and natural disasters caused by global warming, along with heavy use of fertilizers and chemicals, accelerate crop growth and meet market demands.<sup>4,5</sup> Among the three main NPK macronutrients required for plant growth, urea is the most usually used nitrogen-based fertilizer due to its high nitrogen content and low cost.<sup>6,7</sup> Nitrogen in urea can be metabolized by urease catalysis and the nitrification process in soil to form nitrite and nitrate ions. Leaching of these excessive ions from soil by high water irrigation or heavy rainfall leads to their high concentration contamination in ground and water surface bodies, resulting in being harmful to the environment and human beings.<sup>8,9</sup> The large utility of urea also hastens soil acidification, intensifies the loss of soil fertility and organic matter, and decreases useful microorganisms.<sup>10,11</sup> It makes it difficult for soil to absorb nutrients effectively. This results in nutrient-deficient soil and poor soil quantity, negatively

impacting crop growth and yields. Thus, controlling the use of minimal, yet adequate amounts of fertilizers and chemicals throughout crop cultivation is a way to address overuse. This approach helps maintain soil nutrients and sustainably increase farmers' productivity.<sup>12</sup>

A strategy to reduce the use of fertilizers while maintaining high efficiency is using slow- or controlled-release fertilizers. This method can dwindle the fertilizer used by at least 20–30% while still yielding the same level of productivity.<sup>6,13</sup> Slow- and controlled-release fertilizers have been developed and have gained increasing attention, especially over the past 20 years for agricultural applications. Since the primary characteristic of both types of fertilizers is to slow down the nutrient release rate to efficiently deliver nutrients to plant roots, they are often collectively referred to as slow-release fertilizers (SRFs). In contrast, a real controlled-release fertilizer (CRF) described in Duan et al., should have the ability to regulate nutrient release based on the specific conditions required by plants or rely on

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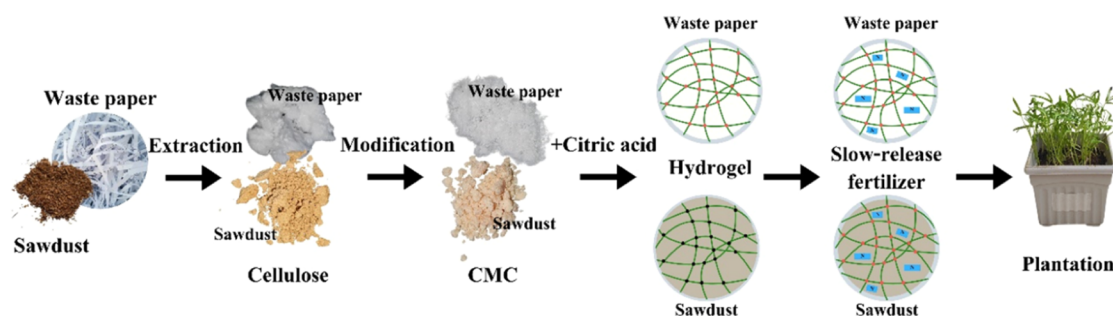
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**Scheme 1. Methodology Schematic Illustration in This Research, Considering Cellulose Extraction from Waste Paper and Sawdust, CMC Hydrogel Synthesis, Slow-Release Fertilizer Synthesis from the CMC Hydrogel and Application of the Slow-Release Fertilizer on Plantation**



the rhizosphere effect according to plant species.<sup>14</sup> Producing a true CRF that meets these specific requirements is quite challenging. Therefore, the term slow-release fertilizer (SRF) broadly refers to fertilizers with the general characteristic of slowing nutrient release. Typically, the SRF preparation involves coating or embedding fertilizers in materials that dissolve or degrade slowly in water and soil, often with a porous structure to ensure a steady and slow nutrient release into the soil.<sup>15,16</sup> Some slow-release fertilizers are generated by encapsulating or absorbing nutrient particles in hydrophobic, inorganic, or organic compounds, which serve as a diffusion wall or barrier.<sup>17</sup> By regulating the fertilizer release rate and minimizing nutrient loss, these fertilizers enhance nutrient efficiency, aligning better with the plant's lifecycle and nutrient absorption capacity.<sup>18</sup> In recent times, with an emphasis on environmental protection and green sustainability, researchers have begun to develop environmentally friendly, biodegradable, and renewable (derived from agricultural crops, industrial byproducts, or household wastes) materials for slow-release fertilizers, i.e., rubber, starch, chitosan, gelatin, pectin, and cellulose.<sup>19</sup> Cellulose, the world's most abundant natural polymer, interacts strongly with water due to its hydroxyl (–OH) groups. It is a suitable choice for agricultural applications in slow-release fertilizer starting materials. Cellulose can be processed into cellulose hydrogels, which absorb the essential nutrients needed for plant growth. Besides slowing down nutrient release, with their three-dimensional structure and water-absorbing polymer network, cellulose hydrogels help reduce irrigation frequency by enhancing moisture in the soil and reducing water evaporation. They also improve soil texture by creating more internal soil spaces for aeration and development of soil edaphon.<sup>20,21</sup> According to the previous study, since high water capacity and water retention of cellulose hydrogels in soil, cellulose hydrogels mixed in soil or covering mung bean seed had positively impacted by increasing length of mung bean's roots, stems, and leaves by 27–410% from the control (grown with soil only).<sup>22</sup> Moreover, using cellulose derivatives, i.e., carboxymethyl cellulose (CMC) hydrogel preparation, enhances water absorbency, pH sensitivity, polyelectrolyte, and ionic strength properties.<sup>23</sup> Additionally, the modification also improves the hydrogel's ability to absorb and prevent the leaching of nutrient ions such as ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ).<sup>24</sup>

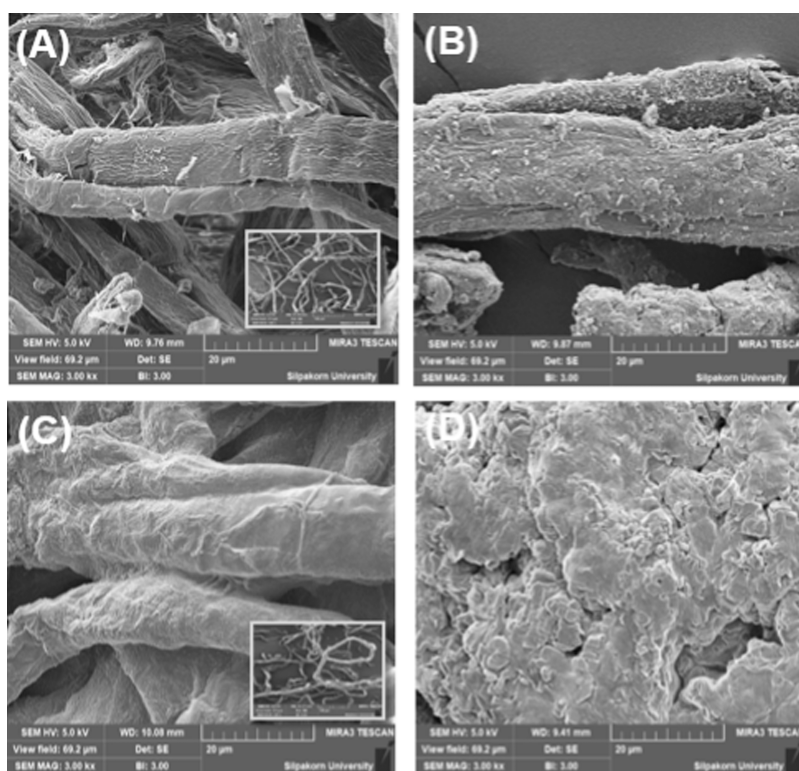
Over the past two decades, deforestation for wood has intensified worldwide, particularly in tropical regions, with an annual loss of 2,101 km<sup>2</sup>.<sup>25</sup> One primary driver of this increase is the enormous demands on the paper and pulp industry. In

2020, global paper and cardboard production reached approximately 419 million metric tons with an anticipated growth rate of 2.5–3% annually in the coming years. This uptick is primarily fueled by rising high demand from e-commerce, packaging industries, and increased office and printing needs.<sup>26</sup> The substantial demand for paper generates vast amounts of waste paper, of which about half is recycled, while the remainder is incinerated or landfilled.<sup>27</sup> Disposing of waste through landfills or incineration contributes to environmental and human health challenges. Additionally, increased global deforestation for wood products has led to significant byproducts like sawdust, a lignocellulosic material produced from sawing, planing, sanding, and milling wood. Sawdust is relatively abundant and inexpensive, but presents disposal issues. In the past decade, it has mainly been used in livestock farms and paper mills, with the surplus typically ending up in landfills without treatment.<sup>28</sup>

In response to the recent trend toward sustainable, “green” research, one promising approach involves converting waste paper and sawdust into value-added products. Here, this research explores producing carboxymethyl cellulose (CMC) hydrogel by cross-linking CMC derived from cellulose extracted from waste paper and sawdust (cellulose content between 60 and 90%),<sup>29,30</sup> with citric acid. The resulting CMC hydrogel was further treated to be loaded with urea, creating a slow-release fertilizer (Scheme 1). The CMC hydrogel and the slow-release fertilizer were analyzed for their physical and chemical properties—including surface morphology and heat stability. Key parameters such as swelling ratio, hydrogel moisture retention, and water holding capacity were also assessed for the CMC hydrogel. Furthermore, the release profiles of urea from the slow-release fertilizer were investigated in water and loamy soil to evaluate the effectiveness of the produced CMC hydrogel as a suitable slow-release fertilizer. Finally, the slow-release fertilizer was applied to cultivate water convolvulus (*Ipomoea aquatica* var. reptans), a leafy vegetable with high market demand and a significant need for nitrogen from urea as a primary nutrient (Scheme 1). This research monitored the growth of water convolvulus after adding the slow-release fertilizer, and we expect this innovative, waste-derived fertilizer to improve farming efficiency and crop productivity.

## 2. RESULTS AND DISCUSSION

### 2.1. Part I: Extraction of Cellulose from Waste Paper and Sawdust and Synthesis of CMC. 2.1.1. Surface Morphology Study by Scanning Electron Microscopy (SEM).



**Figure 1.** 3000 $\times$  Magnified SEM images showed cellulose extracted from waste paper, CP (A) (inset magnified 500 times), and from sawdust, CSD (B), Carboxymethyl cellulose derived from CP, CMC\_P (C) (inset magnified 500 times), and from CSD, CMC\_SD (D).

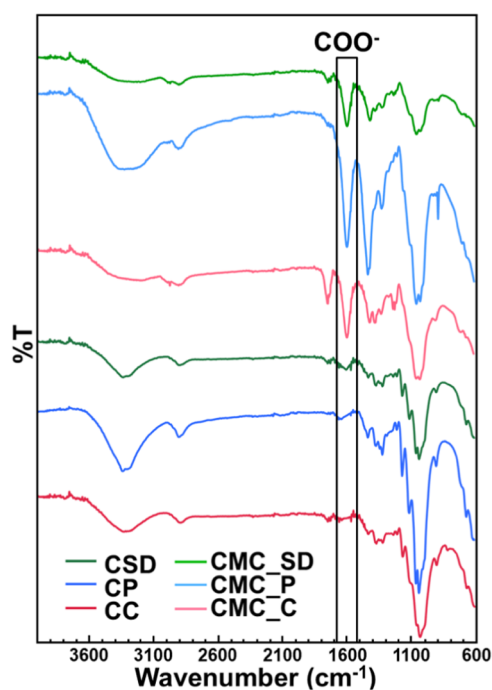
Cellulose extracted from waste paper (CP) appeared as fine white fibers, while cellulose extracted from sawdust (CSD) was a light yellow, coarse material (Figure S1). When these extracted celluloses were synthesized into carboxymethyl cellulose (CMC) through etherification with sodium monochloroacetate under basic conditions, the resulting product, CMC derived from CP (CMC\_P), appeared as a fine white powder. Meanwhile, CMC synthesized from CSD (CMC\_SD) was a fine light yellow powder lighter than the original cellulose before the CMC synthesis (Figure S1).

The morphological structure study of CP, CSD, CMC\_P, and CMC\_SD was carried out using SEM, and the SEM image is presented in Figure 1. It revealed distinctive structural changes. In a 500 $\times$  magnified SEM image of CP (inset of Figure 1A), CP fibers appeared smaller than CMC\_P fibers (inset of Figure 1C) due to substitution with carboxymethyl groups on the CMC chains. At a higher magnification (3000 $\times$ ), SEM images showed that both CP (Figure 1A) and CSD (Figure 1B) exhibited fibrous structures with rough surfaces, particularly CSD. This roughness on CP and CSD cellulose surfaces likely results from residual additives found in paper, such as clay and fillers, and compounds such as calcium oxide and silica, often present in sawdust ash content. With the appearance of light yellow on the CSD (Figure S1), there may also be residual lignin left from the extraction and bleaching processes. CMC\_P still retained a fibrous structure but with a larger fiber size and smoother surface than CP. Meanwhile, CMC\_SD (Figure 1D) appeared as a cluster with a slightly smoother surface than before modification. These findings indicated that substituting hydroxyl groups with carboxymethyl groups on cellulose chains to form CMC increases the fiber size and smooths the fiber surface.

**2.1.2. FTIR Analysis.** The study of functional groups and structures using the Fourier transform infrared (FTIR) technique on CP and CSD compared to commercially sourced cellulose (CC), as well as CMC synthesized from CP (CMC\_P) and CSD (CMC\_SD) against commercially sourced CMC (CMC\_C), revealed significant insights. The IR spectra of these substances are illustrated in Figure 2. The IR spectra for CP and CSD showed similarities to those of CC, indicating comparable functional group characteristics. The peaks at 3300–3400, 2900, 1430, 1360, 1050, and 900  $\text{cm}^{-1}$  are attributed to O–H stretching, C–H stretching,  $\text{CH}_2$  bending, C–H bending of glucose, –O stretching, and C–O–C stretching of glycosidic linkage, respectively. However, the appearance of a small peak at 1600  $\text{cm}^{-1}$  from the CSD FTIR spectrum implied that lignin or hemicellulose was not removed completely from the CSD cellulose fibers. Furthermore, the absorption bands observed around 1600 and 1420  $\text{cm}^{-1}$  in the IR spectra of the synthesized CMC indicated the substitution of carboxymethyl groups on the CMC chain with  $-\text{COO}^-$  and  $-\text{CH}_2$  groups, respectively.<sup>31</sup>

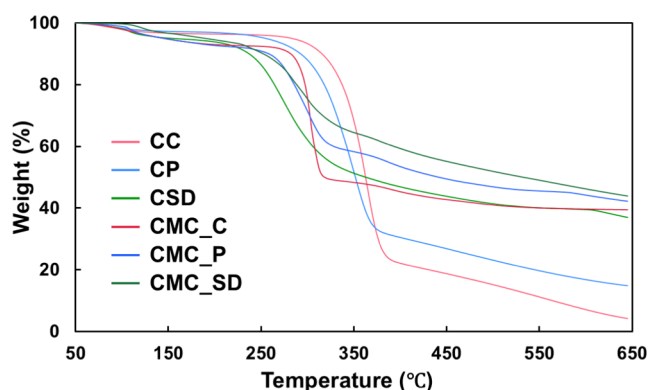
**2.1.3. TGA Analysis.** Thermogravimetric analysis (TGA) is a method used to assess the thermal stability of materials by measuring changes in weight as they are subjected to heat. The TGA results were summarized in Table S1, showing the percentage weight loss at 650  $^{\circ}\text{C}$  for each type of cellulose (CC, CP, and CSD) and CMC (CMC\_C, CMC\_P, and CMC\_SD). The weight loss for CP and CSD was found to be 69.48 and 60.01%, respectively, which was lower than that of CC at 78.52%. When cellulose was synthesized into CMC, the weight loss percentages at 650  $^{\circ}\text{C}$  were 40.99% for CMC\_P and 36.20% for CMC\_SD, which were also lower than the value for CMC\_C at 52.10%. These results indicated that the cellulose extracted from waste materials contains nonvolatile





**Figure 2.** FTIR spectra of cellulose extracted from waste paper (CP) and sawdust (CSD) were compared with commercially sourced cellulose (CC), and CMC synthesized, CMC\_P and CMC\_SD from CP and CSD, respectively, against commercially sourced CMC (CMC\_C).

components such as additives from paper or ash from sawdust.<sup>32</sup> In contrast, CC and CMC\_C exhibited higher purity levels. Figure 3 illustrates the thermogram depicting the



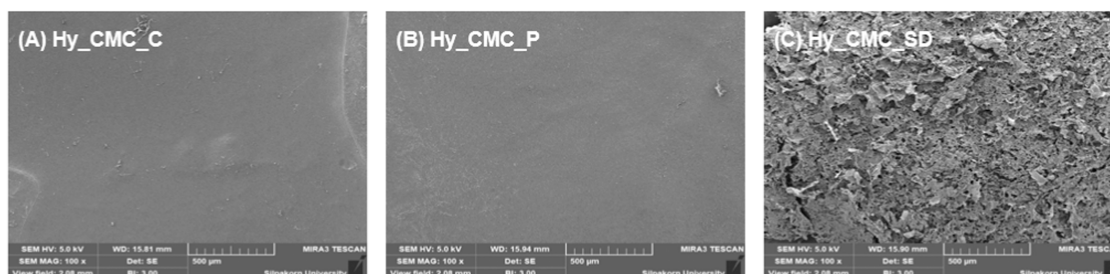
**Figure 3.** TGA thermogram of cellulose (CC, CP, and CSD) and carboxymethyl cellulose (CMC\_C, CMC\_P, and CMC\_SD).

thermal decomposition process of cellulose samples (CC, CP, CSD) and carboxymethyl cellulose samples (CMC\_C, CMC\_P, and CMC\_SD). The decomposition occurs in two main stages: The first stage showed a weight loss percentage ranging from 3.71 to 7.73%, with peak temperature ( $T_p$ ) between 88.4 and 120.1 °C, attributed to the moisture evaporation within the structure of cellulose and CMC. The weight loss in this stage was greater for CMC due to more significant spacing between polymer chains, allowing higher water molecule absorption. The second stage was the primary decomposition phase for both cellulose and CMC, where the degradation of linear polymer chains and glycosidic bonds occurred. The  $T_p$  values were presented as follows: 363.8 °C for CC, 352.1 °C for CP, and 326.8 °C for CSD (Table S1). The substitution of carboxymethyl groups on the CMC chain resulted in decreased  $T_p$  values: 305.8 °C for CMC\_C, 279.9 °C for CMC\_P, and 301.4 °C for CMC\_SD (Table S1). This reduction in thermal stability is due to decarboxylation processes converting carboxyl groups to CO<sub>2</sub> and the breakdown of the main polymer chain. The findings suggested that incorporating carboxymethyl groups into the synthesized CMC affects its polymer structure and bonding energy, resulting in lower thermal stability compared to cellulose. The reduced  $T_p$  values indicated diminished inter- and intramolecular hydrogen bonding within the polymer chains of CMC compared to cellulose.<sup>33</sup>

## 2.2. Part II: Synthesis of Cellulose Hydrogels and Characterization. 2.2.1. Surface Morphology Study by SEM.

Production of cellulose hydrogel from CMC synthesized from CMC\_P and CMC\_SD, compared to CMC\_C, utilized citric acid as a cross-linking agent. The resulting CMC hydrogels are presented in Figure S2. The hydrogels produced from CMC\_C and CMC\_P, named Hy\_CMC\_C and Hy\_CMC\_P respectively, exhibited clear and smooth film characteristics. In contrast, the hydrogel derived from CMC\_SD (named Hy\_CMC\_SD) appeared as a light yellow film (Figure S2), likely due to residual lignin remaining in the cellulose from the extraction and bleaching processes. The analysis of the morphological structure of the CMC hydrogels using scanning electron microscopy (SEM) is presented in Figure 4. The surface characteristics of the CMC hydrogels, specifically Hy\_CMC\_C (Figure 4A) and Hy\_CMC\_P (Figure 4B), at a magnification of 100×, revealed a relatively smooth texture with only slight roughness. In contrast, the surface of Hy\_CMC\_SD exhibited a significant roughness. This difference in surface morphology is attributed to the characteristics of the CMC\_SD fibers derived from the CMC synthesis process (Figure 4C).

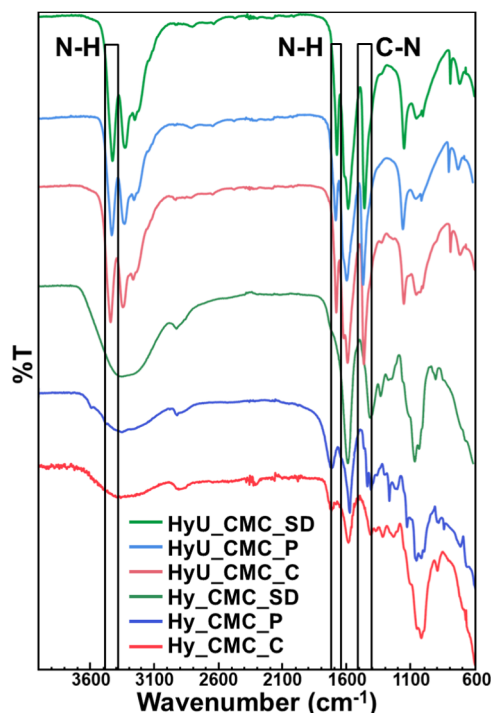
**2.2.2. FTIR Analysis.** The reaction occurred in producing CMC hydrogel using citric acid as a cross-linking agent and



**Figure 4.** SEM 100× magnified images of (A) Hy\_CMC\_C, (B) Hy\_CMC\_P, and (C) Hy\_CMC\_SD.



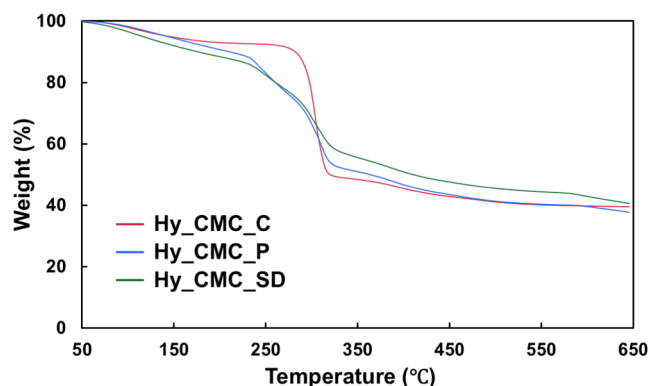
heating at 140 °C. High temperature converts citric acid to form the cyclic citric acid anhydride intermediate before it undergoes esterification with hydroxyl groups on the polymer chain of CMC (Figure S3). Examination of the structures and functional groups of the various CMC hydrogels, Hy\_CMC\_C, Hy\_CMC\_P, and Hy\_CMC\_SD, was carried out using the FTIR technique; the IR spectra of the different CMC hydrogels are shown in Figure 5. A distinct absorption



**Figure 5.** FTIR spectra of CMC hydrogels: Hy\_CMC\_C, Hy\_CMC\_P, and Hy\_CMC\_SD; FTIR spectra of slow-release fertilizers: HyU\_CMC\_C, HyU\_CMC\_P, and HyU\_CMC\_SD.

band was observed at a frequency of 1600  $\text{cm}^{-1}$ , which was attributed to the  $\text{COO}^-$  asymmetric stretching vibration, and the effects of the cross-linking reaction that formed ester bonds were observed at the absorption bands at 1730 and 1230  $\text{cm}^{-1}$  for  $\text{C=O}$  stretching and  $\text{C-O}$  stretching, respectively.<sup>34,35</sup> Thus, this confirmed that the CMC hydrogel formed according to the production method used in this research.

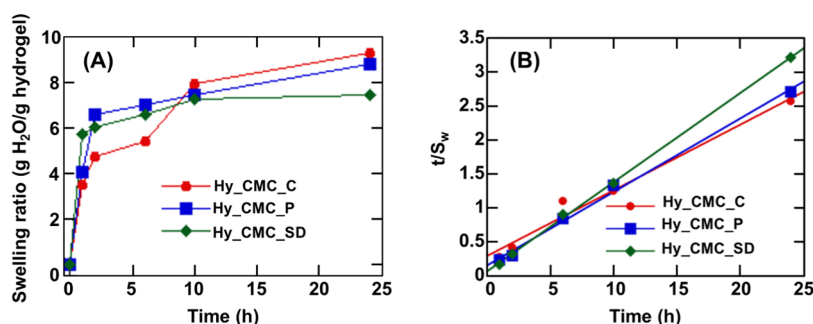
**2.2.3. TGA Analysis.** From TGA data (Table S2) of Hy\_CMC\_C, Hy\_CMC\_P, and Hy\_CMC\_SD, the decomposition process when increasing the temperature of the hydrogels from 45 to 650 °C consisted of three steps, as shown in the TGA thermogram in Figure 6. The first step of CMC hydrogel decomposition involves the evaporation of water within the CMC hydrogel structure. The next step was the decomposition of citric acid cross-linked in the hydrogel structure. The previous research indicated that citric acid began to decompose at 160 °C, while the composite hydrogel of CMC and Tamarind gum with citric acid as the cross-linking agent started the hydrogel decomposition at a temperature of 199 °C.<sup>36</sup> From Table S2, the temperature range for the decomposition of step of the cross-linked citric acid in the Hy\_CMC\_C hydrogel was between 165 and 265 °C, with a  $T_p$  of 235.4 °C, which is lower than the  $T_p$  of Hy\_CMC\_P and Hy\_CMC\_SD by 10.4 and 15.6 °C, respectively. The increase in  $T_p$  for the decomposition of cross-linked citric acid results



**Figure 6.** TGA thermogram of CMC hydrogels; Hy\_CMC\_C, Hy\_CMC\_P, and Hy\_CMC\_SD.

from the lower amount of citric acid in the hydrogel of Hy\_CMC\_P and Hy\_CMC\_SD compared to Hy\_CMC\_C.<sup>37</sup> For the final decomposition step of the CMC hydrogels, the temperature range for this step is 265–350 °C, with  $T_p$  values of 307.7, 311.6, and 304.8 °C for Hy\_CMC\_C, Hy\_CMC\_P, and Hy\_CMC\_SD, respectively. This third decomposition step involves the breakdown of the main CMC polymer chains and the ester bonds that were linked in the hydrogel. The previous research indicated that the high % weight loss observed in this last decomposition step indicated a smaller quantity of free CMC chains and effective cross-linking.<sup>37</sup> Considering the % weight loss in Table S2, it was found that % weight loss for Hy\_CMC\_C > Hy\_CMC\_P > Hy\_CMC\_SD, indicating that the hydrogel cellulose Hy\_CMC\_C had fewer uncross-linked CMC chains compared to Hy\_CMC\_P and Hy\_CMC\_SD.

**2.2.4. Swelling Ratio of CMC Hydrogel.** Due to the development of CMC hydrogels for use as a soil conditioner in agricultural applications, one of the essential properties of the hydrogels is their ability to absorb large amounts of water during the gel swelling process. This swelling results from the breakdown of hydrophilic interactions and the repulsive forces between the charges of various functional groups on the polymer when water penetrates. As shown in Figure 7A, the swelling ratio of the CMC hydrogels within 24 h indicated that all types of hydrogels exhibited rapid swelling within the first 2 h, followed by a relatively stable swelling ratio after 5–10 h. When analyzing the swelling rate of the CMC hydrogels in water according to the second-order swelling kinetic model, it was found that the swelling mechanism of hydrogel occurs through second-order kinetics, which presents the relationship between  $t/Sw_t$  and time in Figure 7B, fitted parameters and the  $R^2$  value shown in Table 1. The phenomenon of water diffusion and absorption within the polymer chains of the hydrogel controls the rate and ability to retain water in the hydrogel, depending on the surface characteristics and functional groups present in those hydrogel polymer chains.<sup>38</sup> The CMC hydrogels underwent the swelling process until they reached equilibrium, with the equilibrium swelling ratio ( $Sw_{eq}$ ) of 10.3, 9.2, and 7.6 g of  $\text{H}_2\text{O/g}$  for Hy\_CMC\_C, Hy\_CMC\_P, and Hy\_CMC\_SD, respectively (Table 1). It can be seen that the swelling ratios of the hydrogel at equilibrium Hy\_CMC\_C and Hy\_CMC\_P were quite similar (Figure 7 and Table 1). In contrast, the swelling ratio of Hy\_CMC\_SD was lower than those of other types of hydrogels (Figure 7). However, it exhibited the fastest swelling



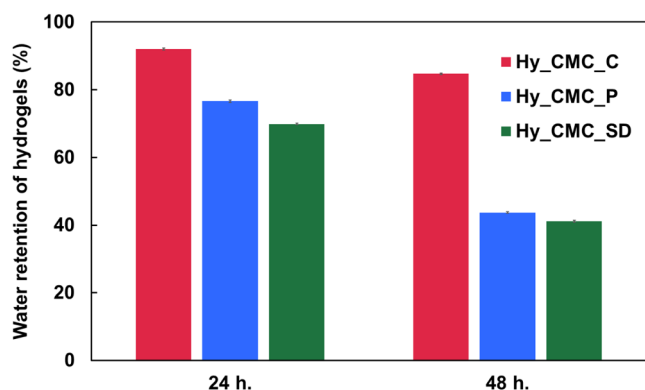
**Figure 7.** (A) Swelling of CMC hydrogels: Hy\_CMC\_C, Hy\_CMC\_P, and Hy\_CMC\_SD in water at different times within 24 h. (B) Graph showing the second-order swelling kinetic relationship of CMC hydrogels: Hy\_CMC\_C, Hy\_CMC\_P, and Hy\_CMC\_SD.

**Table 1. Parameters Obtained from the Second-Order Swelling Kinetics from the Study of CMC Hydrogel Swelling in Water: Swelling Ratio at Equilibrium ( $Sw_{eq}$ ), Swelling Rate Constant ( $k$ ), and  $R^2$  Values**

hydrogel	$Sw_{eq}$ (g H <sub>2</sub> O/g)	$k$ (g/g H <sub>2</sub> O·h)	$R^2$
Hy_CMC_C	10.3	0.03	0.9783
Hy_CMC_P	9.2	0.07	0.9954
Hy_CMC_SD	7.6	0.24	0.9994

rate, with  $k = 0.24$  g/g H<sub>2</sub>O·h (Table 1), indicating that diffusion of water into the network in Hy\_CMC\_SD occurs rapidly. Additionally, the swelling ratio ( $Sw_t$ ) depends on the interaction between the free hydroxyl groups of hydrogel cellulose and water molecules.<sup>39</sup> Although Hy\_CMC\_SD has the highest swelling rate, its swelling ratio is lower than those of other hydrogel types. The observed decrease in the swelling ratio in Hy\_CMC\_SD may be due to the lower quantity of free hydroxyl groups from the CMC chain derived from cellulose extracted from sawdust (CMC\_SD) compared to CMC\_C or CMC\_P. This is because CMC\_SD contains other components, such as silica and calcium oxide, which lead to interactions with fewer water molecules in the hydrogel structure, limiting the hydrogel polymeric chain expansion.

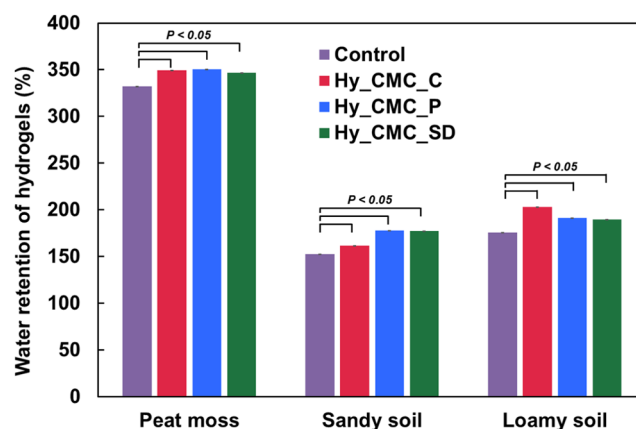
**2.2.5. Hydrogel Moisture Retention of CMC Hydrogel.** To analyze the moisture retention capability in the polymeric chains of CMC hydrogels, the water-saturated CMC hydrogels were placed under the controlled condition of approximately 40% humidity at 25 °C for 24 and 48 h. The experimental results are shown in Figure 8. It was found that all types of CMC hydrogels can retain water at levels as high as 70% after



**Figure 8.** Hydrogel moisture retention of different types of the CMC hydrogels at 25 °C and 40% humidity over 24 and 48 h.

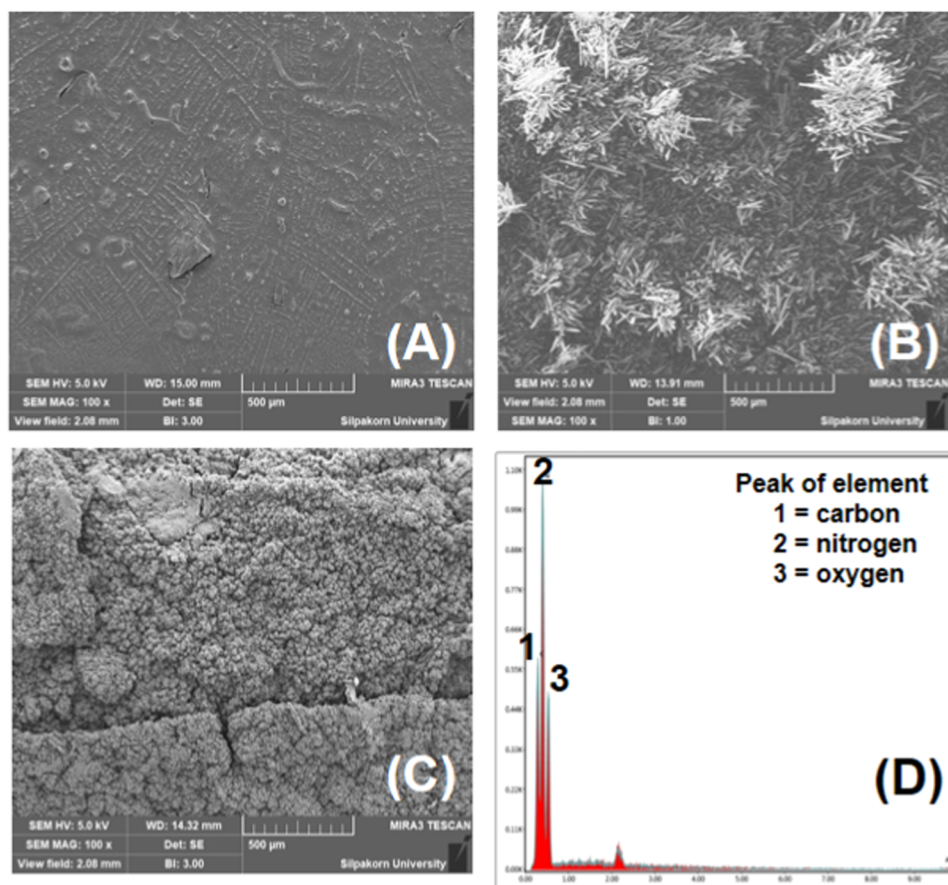
24 h, particularly Hy\_CMC\_C, which exhibited the best water retention capability at  $92.0 \pm 0.2\%$ . In contrast, Hy\_CMC\_SD had the lowest water retention capacity ( $69.9 \pm 0.2\%$ ). However, after 48 h, all three types of CMC hydrogels still demonstrated the ability to retain more than 40% water, especially Hy\_CMC\_C, which retained water at a percentage of  $84.7 \pm 0.2\%$  (Figure 8). This indicated the excellent water retention property of the CMC hydrogels, making them suitable for agricultural applications. One reason for the high capacity of moisture retention in the hydrogels, especially in Hy\_CMC\_C, is that the hydrogel contains free hydroxyl groups and  $-\text{COO}^-$  that can interact with and hold absorbed water molecules effectively within the hydrogel's chain structure.<sup>40</sup>

**2.2.6. Water Holding Capacity of CMC Hydrogel.** When analyzing the ability of the CMC hydrogels to assist in water holding in soil, 1% of the CMC hydrogel (Hy\_CMC\_C, Hy\_CMC\_P, or Hy\_CMC\_SD) was mixed into various types of soil: peat moss, sandy soil, and loamy soil. The experimental results showed that adding the CMC hydrogels increased the efficiency of water holding in the soil by 1.5–4.5% compared to the controlled soil that did not add the hydrogel (Figure 9



**Figure 9.** Effect of CMC hydrogel addition on water holding capacity in different types of soil. Statistical significance was determined using an independent  $t$  test,  $P$  value  $< 0.05$ .

and Table S3). In sandy soil with larger particle sizes, the air spaces between soil particles are large, making the soil unable to retain water effectively. However, when 1% of all CMC hydrogels were added, especially Hy\_CMC\_P and Hy\_CMC\_SD, the efficiency of water holding in the soil improved to  $29.6 \pm 1.3\%$  and  $29.5 \pm 0.1\%$ , respectively, from



**Figure 10.** SEM images at 100× magnification of the slow-release fertilizers: (A) HyU\_CMC\_C, (B) HyU\_CMC\_P, (C) HyU\_CMC\_SD. (D) EDX spectrum of elemental analysis on the surface of the slow-release fertilizer of HyU\_CMC\_SD.

$25.5 \pm 0.4\%$  in the sandy soil without the hydrogel addition. It can be observed that the water retention capacities of Hy\_CMC\_P and Hy\_CMC\_SD are higher than those of Hy\_CMC\_C, especially in sandy soil and peat moss. This result was based on the experiment where the soil was allowed to absorb water for 1 h after watering. During this period, Hy\_CMC\_C exhibited a lower swelling rate than the other hydrogels (Figure 7 and Table 1). However, all of the CMC hydrogels still help hold more water in the soil than in the soil without hydrogel addition. Therefore, the ability of the CMC hydrogels to absorb water in the soil in this experiment confirms that adding the CMC hydrogels increases the water holding capability, thereby reducing the amount needed for cultivation. However, this also depends on the duration of water absorption in the soil and the type of soil. Adding the CMC hydrogel, which is a hydrophilic soil conditioner with water-absorbing functional groups, enhances the efficiency of water retention and allows water to be held within the soil, even in soils with high air spaces between soil particles, such as sandy soil.<sup>41,42</sup>

### 2.3. Part III: Synthesis of Slow-Release Fertilizers and Characterization. 2.3.1. Surface Morphology Study by SEM.

Production of slow-release fertilizers from the CMC hydrogels was achieved by soaking the CMC hydrogels in a urea solution and drying them, resulting in the slow-release fertilizers named HyU\_CMC\_C, HyU\_CMC\_P, and HyU\_CMC\_SD. Photographs showed numerous white amorphous crystals, particularly on the surfaces of HyU\_CMC\_P and HyU\_CMC\_SD (Figure S4). These visible white crystals are urea, confirming

the absorption of urea in the CMC hydrogel through the morphological examination of the slow-release fertilizers using the SEM-EDX technique, as shown in Figure 10. When considering the SEM images of the slow-release fertilizers; HyU\_CMC\_C, HyU\_CMC\_P, and HyU\_CMC\_SD, different shapes and quantities of solid crystals adhering to the surface were observed according to the type of the slow-release fertilizer. The EDX spectrum obtained from HyU\_CMC\_SD revealed the presence of elements C, O, and N, with the nitrogen content exceptionally high at 47.4% weight or 49.6% atomic content (Table S4). This high nitrogen content confirmed that the crystals found on the slow-release fertilizer were indeed urea crystals, indicating that CMC hydrogel can absorb urea during the production process of slow-release fertilizer.

The SEM images and EDX spectrum of the HyU\_CMC\_SD in the interior (cross section) showed that the cross-sectional area (Figure S5) contained stacked layers and small porous voids that served as nutrient and water absorption spaces. Urea crystals were also found and absorbed within the hydrogel. Additionally, the presence of other elements, Si and Ca, suggested the presence of silica, silica ash, and calcium oxide derived from sawdust,<sup>32</sup> the starting material for HyU\_CMC\_SD. These components contributed to the rougher surface of the produced Hy\_CMC\_SD hydrogel compared to other types, increasing the surface area for urea absorption into the hydrogel at the surface (Figures 4 and 10).

**2.3.2. FTIR Analysis.** Results of the IR spectra for the different slow-release fertilizers, HyU\_CMC\_C, Hy-



U\_CMC\_P, and HyU\_CMC\_SD, are shown in Figure 5. The spectra display similar characteristics, with explicit signals at peaks of  $3440\text{ cm}^{-1}$ , indicating N–H stretching vibration, at  $1680$  and  $1598\text{ cm}^{-1}$  from  $-\text{NH}_2$  bending and  $\text{C}=\text{O}$  stretching vibrations, and at  $1450\text{ cm}^{-1}$  from C–N stretching vibrations.<sup>43</sup> The results of the IR spectra indicated the incorporation of urea found in all slow-release fertilizers, which occurred during the production process, when urea was absorbed into the CMC hydrogels. This confirms the presence of nitrogen, an essential nutrient for plant growth, in the slow-release fertilizers produced from the CMC hydrogels in this research.

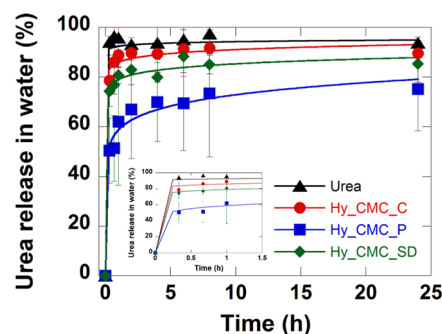
**2.3.3. Urea Amount in Slow-Release Fertilizer.** The amount of urea embedded in the slow-release fertilizers was determined by gel digesting with cellulase and reacting with *p*-dimethylaminobenzaldehyde (DMAB) to measure the amount of yellow product. Table 2 shows the amount of urea absorbed

**Table 2. Amount of Urea Absorbed in the Slow-Release Fertilizers**

slow-release fertilizer	amount of absorbed urea (mg/g slow-release fertilizer)	percentage of absorbed urea from slow-release fertilizer (%)
HyU_CMC_C	$185.0 \pm 0.9$	$18.5 \pm 0.1$
HyU_CMC_P	$226.6 \pm 1.1$	$22.7 \pm 0.1$
HyU_CMC_SD	$330.8 \pm 2.3$	$33.1 \pm 0.2$

in the different types of slow-release fertilizers, revealing that urea can be stored in the slow-release fertilizers at levels of 18.5–33.1%. The amount of urea absorbed was comparable to that in composite hydrogels containing CMC (urea amount ranging from 17.65 to 52.19%).<sup>44</sup> Notably, the amount of urea in HyU\_CMC\_SD was higher than that in other types of slow-release fertilizers, which was attributed to the increased surface area of Hy\_CMC\_SD. This increase resulted from the presence of silica and calcium oxide residues from the cellulose extraction process from sawdust, enabling the CMC hydrogel (Hy\_CMC\_SD) to absorb more urea on its surface (Figures 4C and 10C). Additionally, considering the degree of substitution of the carboxymethyl groups on each type of CMC chain (Table S5), it was found that CMC\_SD, the precursor for HyU\_CMC\_SD production, had the highest value. As a result, this reduced the intermolecular forces between CMC polymer chains, allowing water molecules and urea to penetrate and be absorbed between the polymeric chains more effectively.<sup>32</sup>

**2.3.4. Urea Release Behavior and Kinetics of Slow-Release Fertilizer in Water.** Analysis of the urea release from the slow-release fertilizers, HyU\_CMC\_C, HyU\_CMC\_P, and HyU\_CMC\_SD, in water was monitored over various time intervals of 24 h. The urea release profile of the water-release fertilizers within 24 h is presented in Figure 11. The study of free urea release (without encapsulation) in water compared to the slow-release fertilizers produced in this research found that the amount of urea released from free urea reached a high level of  $94.1 \pm 2.3\%$  within 20 min. In contrast, the amounts of urea released were lower for the slow-release fertilizers, at  $78.6 \pm 10.3\%$ ,  $50.4 \pm 13.1\%$ , and  $74.4 \pm 1.5\%$  for HyU\_CMC\_C, HyU\_CMC\_P, and HyU\_CMC\_SD, respectively (inset in Figure 11). An initial phase known as the “burst phase” was observed during the initial release study for all types of slow-release fertilizers (within the first hour). This was due to the high concentration of urea in the slow-release fertilizers (high



**Figure 11.** Release behavior of urea from the slow-release fertilizers in water (the inset shows the amount of urea released from the slow-release fertilizers throughout 1.5 h).

urea concentration gradient) and the significant dissolution and diffusion of urea from the swollen hydrogel.<sup>45,46</sup> Afterward, the urea release reached equilibrium after approximately 2–4 h.

Since swelling and nutrient release in a medium such as water or soil rely on water penetration into the hydrogel, followed by the subsequent chain relaxation in hydrogels, the release of nutrients is also influenced by temperature, humidity, and soil biological activity. This nutrient release process is dynamic and does not occur at a constant rate. Typically, the mechanism of nutrient release occurs in three phases, lag phase, constant release phase, and decay phase. The first phase is initiated when a hydrogel absorbs water, swells, and undergoes hydration with minimal nutrient release. In the next step, nutrients diffuse steadily through the polymer matrix to reach equilibrium. Finally, the last phase, the release rate decreases due to nutrient depletion or environmental changes.<sup>47</sup> Therefore, it is essential to investigate the nutrient release mechanism by selecting an appropriate mathematical model to predict the nutrient release pattern from slow-release fertilizers (SRFs). The Korsmeyer–Peppas kinetic model<sup>47,48</sup> was applied, with the resulting values of each parameter presented in Table 3. For all three types of slow-release

**Table 3. Parameters of Urea Release Using the Korsmeyer–Peppas Model for the Different Types of Slow-Release Fertilizers in Water**

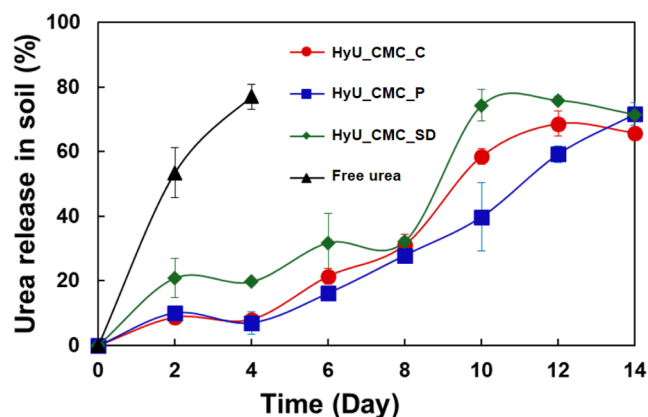
sample	parameter		
	$R^2$	$k$	$n$
free urea	0.9974	94.0	0.003
HyU_CMC_C	0.9921	86.1	0.025
HyU_CMC_P	0.9790	58.9	0.093
HyU_CMC_SD	0.9924	79.1	0.033

fertilizers, the value of  $n$  (diffusional release exponent) was less than 0.5, indicating that the mechanism of release of urea from the slow-release fertilizers follows pseudo-Fickian diffusion. This suggests that the hydrophobicity of the polymeric chains in hydrogels primarily controlled water penetration into the hydrogels, rather than chain relaxation.<sup>47</sup>

A high urea gradient on the surface of the polymer chains leads to rapid diffusion into the medium during the initial release phase before reaching a stable state (the constant release phase). Urea diffusion constants ( $k$ ) were 86.1, 58.9, and 79.1 for HyU\_CMC\_C, HyU\_CMC\_P, and HyU\_CMC\_SD, respectively. The urea release process is also

influenced by the hydrogel's strength and the hydrogel's swelling ratio.<sup>49</sup> It is evident that the urea release rate from Hy\_CMC\_P was slower than that of the other slow-release fertilizers due to its slightly lower swelling ratio compared to that of Hy\_CMC\_C. With the high hydrophilicity of the polymeric chain in Hy\_CMC\_C and its high swelling ratio, the slow-release fertilizer, HyU\_CMC\_C, was able to release urea the fastest compared to other types of slow-release fertilizers. Notably, Hy\_CMC\_SD released urea more quickly, likely due to high urea concentration gradient of Hy\_CMC\_SD and the increased surface area of the sawdust-derived hydrogel used to prepare this fertilizer (Hy\_CMC\_SD) (Figure 10C). As stated by Saruchi et al., the release mechanism of a slow-release fertilizer that is regulated and released continuously is sufficient for agricultural applications if the release mechanism follows Fickian diffusion. This depends on the diffusion rate of nutrients from the polymeric matrix of the slow-release fertilizer.<sup>50</sup> Therefore, based on the parameter values in Table 3, it can be inferred that the slow-release fertilizers produced in this research can be applied in agricultural cultivation.

**2.3.5. Urea Release of Slow-Release Fertilizer in Soil.** Testing of urea release from the slow-release fertilizers derived from the CMC hydrogels in soil involved measuring the amount of urea released over various time intervals (2, 4, 6, 8, 10, 12, and 14 days) within 14 days. The results showing the amount of urea released from different types of slow-release fertilizers are presented in Figure 12. Urea was released at 9,



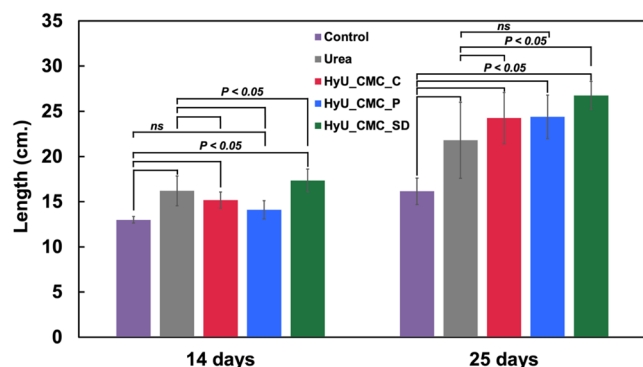
**Figure 12.** Release behavior of urea from the slow-release fertilizers in soil with different time intervals of 14 days.

10, and 20% for HyU\_CMC\_C, HyU\_CMC\_P, and HyU\_CMC\_SD, respectively, in the soil after 2 days. These amounts were less than those of free urea (without encapsulation), which reached 54% on day 2 and reached 77% on day 4. This result indicated that incorporation of urea into the CMC hydrogels can slow the release. On day 10, the urea release from HyU\_CMC\_SD was the highest (74%), followed by HyU\_CMC\_C (59%) and HyU\_CMC\_P (40%). By the final day of the experiment (Day 14), the highest amount of urea released into the soil from each SRF was recorded at 66% for HyU\_CMC\_C, 72% for HyU\_CMC\_P, and 72% for HyU\_CMC\_SD. It was observed that urea release from the slow-release fertilizers in soil was slower than in water (Figure 11). This slower release was due to the limitation of water absorption into the hydrogel, which is necessary to dissolve urea within the polymeric matrix before it diffuses into

the soil.<sup>51</sup> It was found that the release of urea from all slow-release fertilizers exhibited a lag phase during the first 8 days. The release then transitioned into a constant release phase between days 10 and 14 and remained stable throughout the experiment (Figure 12). The low swelling rate and ratio of Hy\_CMC\_P contributed to the slowest urea release from HyU\_CMC\_P. Meanwhile, the urea release trend from HyU\_CMC\_SD in soil was similar to its release behavior in water, with a high cumulative urea release of 72%. This rapid release was attributed to its significantly rough surface characteristics (Figure 4), which created a high urea concentration gradient upon release. Apart from surface characteristics and water diffusion into SRFs, soil environmental conditions also influenced urea release.<sup>14</sup> For example, polymeric chain hydrolysis by biological activity in soil played a role in the release behavior. Due to the high CMC polymer content in HyU\_CMC\_C (Figure 6), even though urea release from HyU\_CMC\_C in water occurred rapidly, the high amount of CMC chains in HyU\_CMC\_C (Figure 6) contributed to delayed urea release in soil. This delay was caused by the gel's strength and its slower degradation process. However, when compared to the standards for SRFs established by various organizations, such as the ISO standard (BS ISO 19670:2017) and China's standards (GB 15063–2001 and 2009), the SRFs produced in this study still released urea faster (in the range of 66–72% in 14 days) than the defined standard (<60% in 28 days). Therefore, although the SRFs in this study released urea more slowly than free urea, they are more suitable for crops that require short-term nutrient availability during the growing period.

**2.3.6. Application of Slow-Release Fertilizer for Water Convolvulus Cultivation.** Plant-cultivated applications of the produced slow-release fertilizers were tested by growing water convolvulus (*Ipomoea aquatica* var. *reptans*). Water convolvulus is a leafy vegetable that utilizes urea as a primary nitrogen nutrient for growth. Additionally, it is an economically significant crop that has developed into a vital export vegetable for Thailand, rich in vitamins and minerals.<sup>52</sup> Considering the appropriate timing for applying urea fertilizer in water convolvulus cultivation, typically within 7 days after sowing its seeds, followed by approximately 14–20 days of cultivation after the fertilizer application, the plants can be harvested. This timing aligns well with the urea release period from the three types of slow-release fertilizers (HyU\_CMC\_C, HyU\_CMC\_P, and HyU\_CMC\_SD), which can effectively regulate the release. Therefore, the water convolvulus is suitable for use in this experiment. The cultivation of water convolvulus with the slow-release fertilizers was conducted by adding the same amount of urea to each pot and comparing it with control pots that received no fertilizer and those treated with urea (without encapsulation). Stem length was measured on days 14 and 25 (harvest day) of the cultivation with experiments repeated 3 times. Figure S6 shows the growth of a water convolvulus on days 14 and 25. The results indicate that urea fertilizer is essential for supplying nitrogen nutrients, which are vital for the growth of leafy plants like water convolvulus. The stems of water convolvulus treated with any urea fertilizer were longer than those in pots without urea. Additionally, the leaves of water convolvulus fertilized with urea displayed a noticeably darker green color (Figure S6), indicating that water convolvulus can effectively absorb urea and convert nitrogen in urea into nitrogen-rich biomass necessary for its growth.<sup>53</sup> On day 14 of cultivation, the pots

with free urea and HyU\_CMC\_SD had longer stems than those with HyU\_CMC\_C and HyU\_CMC\_P, likely due to the faster dissolution of urea and quicker release of urea from HyU\_CMC\_SD, which allowed for faster and more substantial nutrient absorption by the plant roots. By day 25, HyU\_CMC\_SD resulted in the longest water convolvulus stems, about 28% longer than those treated with free urea. The pots with slow-release fertilizers HyU\_CMC\_C and HyU\_CMC\_P also produced longer stems than those treated with free urea (Figure 13). These results suggest that adding an



**Figure 13.** Length of water convolvulus stems (from base to tip) in centimeters was measured after cultivation on days 14 and 25 with free urea fertilizer and various types of slow-release fertilizers in the soil. Statistical significance was determined using an independent *t* test, *P* value < 0.05.

appropriate amount of slow-release fertilizer enhances yield and nutrient efficiency while reducing nitrogen and ammonium leaching from the soil.<sup>54</sup> The structural properties of the cellulose hydrogel used to prepare slow-release fertilizers, with its small pores and hydrophilic groups on the polymer chain, help absorb urea and slow the leaching rate. Typically, the cultivation of water convolvulus involves 2–3 applications of urea fertilizer, which is administered on days 7, 14, and 21 of the cultivation. These applications support plant growth during key stages, including cotyledon expansion, true leaf development, and stem formation.<sup>55</sup> However, in this study, the use of slow-release fertilizers (SRFs) involved a single nutrient application on day 7 of the growing. As a result, it was observed that water convolvulus grown in HyU\_CMC\_SD pots and those supplemented with free urea exhibited rapid early growth, as they were able to absorb readily available nutrients that were released quickly and in high amounts. At the harvest stage, however, plants in the HyU\_CMC\_C and HyU\_CMC\_P pots had stems taller than those in the free urea treatment. This can be attributed to the controlled nutrient release, which slowed nutrient release and helped prevent nutrient leaching from the soil. Nonetheless, the height of these plants remained slightly lower than that of plants in the HyU\_CMC\_SD treatment (Figure 13). This is because HyU\_CMC\_SD released a higher amount of urea compared to HyU\_CMC\_C and HyU\_CMC\_P, despite the latter two demonstrating more slow-release properties. This study concludes that applying slow-release fertilizers in vegetable cultivation depends on the release rate, quantity of nutrients, and the type of plant being cultivated to ensure optimal nutrient absorption and utilization.

### 3. CONCLUSIONS

Slow-release fertilizers are increasingly applied in agricultural cultivation to boost productivity efficiently and sustainably, reduce production costs by lowering the need for supplemental nutrients, and decrease excess chemical runoff into the environment; the slow-release fertilizers control water permeability to dissolve nutrients within the materials and release them slowly into the soil. Cellulose hydrogel is a popular material for making slow-release fertilizers due to its porous, three-dimensional structure, which can absorb and retain water and nutrients effectively. It is also biodegradable and environmentally friendly. This research focuses on producing cellulose hydrogel-based slow-release fertilizers derived from waste paper and sawdust, divided into four main parts: (I) production of slow-release fertilizers from CMC hydrogels derived from waste paper and sawdust, (II) studying the produced CMC hydrogels' structural properties, swelling behavior, and water retention, (III) investigating the amount and mechanism of urea release (a primary nitrogen source for plants) in water and soil, and (IV) applying the slow-release fertilizers to water convolvulus cultivation. This study successfully produced CMC hydrogels and slow-release fertilizers from waste paper and sawdust. The CMC hydrogels showed good water swelling capability about 10 times from its dry weight and enhanced water retention in sandy soil, loamy soil, and peat moss. The hydrogel effectively absorbed urea, especially the slow-release fertilizer derived from sawdust (HyU\_CMC\_SD), which stored the highest amount of urea ( $330.8 \pm 2.3$  mg/g). This high urea absorption is due to the rough surface and increased surface area of this type of CMC hydrogel (Hy\_CMC\_SD), which enhances urea absorption, especially on the fertilizer's surface. HyU\_CMC\_SD also demonstrated a higher release rate of urea in water and soil compared with the other slow-release fertilizer types. Meanwhile, the slow-release fertilizer made from paper (HyU\_CMC\_P) released urea more slowly in water and soil. In tests on water convolvulus cultivation over 25 days, the slow-release fertilizer derived from sawdust produced the longest-stem plants. Notably, after 14 days, the pot treated with slow-release fertilizer from waste paper and commercial CMC showed higher growth than those with free urea. Nonetheless, the height of the water convolvulus stems remained slightly lower than that of plants in the HyU\_CMC\_SD treatment. This result is attributed to the gradual urea release from this slow-release type, maintaining optimal release of urea levels in the soil for plant absorption throughout the cultivation period. Additionally, adding slow-release fertilizer to the soil reduced nutrient leaching compared to that of free urea. In summary, the slow-release fertilizers developed in this research are effective for agricultural applications as they regulate nutrient release, optimize water use, and reduce nutrient leaching into the environment.

### 4. METHODS

**4.1. Chemical Reagents and Materials.** Cellulose fibers were extracted from waste paper and sawdust. Waste paper from office paper and printed paper was collected from the Department of Chemistry, Faculty of Science, Silpakorn University. Wood sawdust was collected from a local furniture company in Bang Phae district, Ratchaburi, Thailand. Cellulose commercial grade was  $\alpha$ -cellulose powder and was obtained from Sigma-Aldrich. Carboxymethyl cellulose commercial



grade was ultrahigh viscosity and highly purified (Sigma-Aldrich). Sodium monochloroacetate (NaMCA, 98%) was obtained from Acros Organics (Belgium). Citric acid used was of analytical reagent grade from Merck (Germany). Sodium hydroxide, ethanol, and glacial acetic acid were of analytical reagent grade (Sigma-Aldrich). Isopropanol and urea were American Chemical Society grade and supplied from Merck (Germany). Deionized water was used throughout all of the experiments. Peat moss was purchased from the ChiaTai Company, Thailand. Sandy and loamy soils were purchased from a local farming supplier in Ratchaburi, Thailand.

**4.2. Cellulose Extraction from Waste Paper and Sawdust.** (I) Preparation of waste paper and sawdust before cellulose extraction: Penetrated the sawdust through a sieve (40 mesh) to separate large wood matters. For wasted paper, it was cut into small pieces, boiled in hot water (80 °C) for 1 h, and then blended until finer. For sawdust, it was washed with water twice. The blended waste paper or washed sawdust was filtered to remove excess water with a sieve (200 mesh) before being rinsed with water twice, squeezing water out as much as possible. Then, it was rinsed again with 5% sodium hydroxide 2 times. (II) Cellulose extraction: the waste paper or sawdust from the previous step was added with a solution of 5% sodium hydroxide with a ratio of 1 g of the solid per 20 mL of the solution and then stirred for 24 h at 50 °C. After 24 h of stirring, the mixture was sieved and rinsed with water until the pH of the residue was neutral. To gain purer extracted cellulose from the waste paper and sawdust, we repeated the extraction step once. The extracted cellulose was dried at 50 °C in a hot-dry oven. The cellulose extracted from waste paper (CP) was obtained and characterized. Another step in obtaining cellulose extracted from sawdust (CSD) was delignification to eliminate lignin using a sodium hypochlorite solution (6%). Then, the delignified cellulose from sawdust was rinsed with water to remove the bleaching solution and the byproducts, checking with silver nitrate solution (0.05 M). The cellulose was dried in the oven until it reached a constant weight at 50 °C. The cellulose extracted from sawdust and delignified was called CSD.

**4.3. Preparation of Carboxymethyl Cellulose (CMC).** Cellulose extracted from waste paper (CP) and sawdust (CSD) was synthesized to carboxymethyl cellulose (CMC) via etherification with sodium chloroacetate in isopropanol/NaOH. The milled cellulose (CP or CSD) (5 g) was soaked in 100 mL of isopropanol and 20 mL of 15% sodium hydroxide and then stirred at room temperature overnight. Then, carboxymethylation on the cellulose was conducted by adding 6 g of ground sodium chloroacetate and stirring for 3 h at 55 °C. After the reaction, the mixture was centrifuged, and the supernatant was decanted. Isopropanol was added to the rest of the sediment, and the pH was adjusted to neutral with an acetic acid solution. Then, centrifugation was used to separate and collect the sediment. To eliminate byproducts from the reaction, solutions of 70, 75, 80, 85, 90, and 95% ethanol were used to rinse the sediment. Finally, the residue was baked to dryness at 50 °C, resulting in the carboxymethyl cellulose product derived from CP (CMC\_P) and CSD (CMC\_SD). The substitution of hydroxyl groups (–OH) with carboxymethyl groups (–CH<sub>2</sub>COOH) on a cellulose polymeric chain was assessed via the USP XXIII standard for Croscarmellose sodium and reported in the [Supporting Information](#).

**4.4. Preparation of CMC Hydrogel.** The preparation of the cellulose hydrogel used carboxymethyl cellulose (CMC),

which consisted of three types: 1. commercial CMC (CMC\_C, ultrahigh viscosity, highly purified grade), 2. CMC derived from cellulose extracted from waste paper (CMC\_P), and 3. CMC derived from cellulose extracted from sawdust (CMC\_SD), with citric acid as a cross-linking agent. The details for preparing the CMC hydrogel were as follows: Weighed 2 g of CMC and dissolved it in 98 g of distilled water, stirring the solution at room temperature overnight until a clear CMC solution. Then, 0.40 g of citric acid was added to the CMC solution and mixed thoroughly for approximately 30 min. The resulting hydrogel solution was poured into a glass Petri dish (100 mm × 15 mm) with a hydrogel thickness of about 1 cm. The Petri dish was covered with its lid and was then sealed on the edge with two layers of parafilm on the edge and wrapped with aluminum foil. The prepared hydrogel was then baked at 60 °C for 24 h, followed by heating at 140 °C for 5 h. Subsequently, the hydrogel was soaked in water at room temperature for 12 h to remove residues before being dried at 60 °C. The resulting CMC hydrogels were designated as Hy\_CMC\_C, Hy\_CMC\_P, and Hy\_CMC\_SD for the hydrogels prepared from CMC\_C, CMC\_P, and CMC\_SD, respectively.

**4.5. Preparation of Slow-Release Hydrogel.** The CMC hydrogel (Hy\_CMC\_C, Hy\_CMC\_P, or Hy\_CMC\_SD) was soaked in a urea solution at a concentration of 50 g/L for 24 h. After absorption of the urea solution, the CMC hydrogel was dried at 50 °C. This process yields a slow-release urea fertilizer made from the cellulose hydrogel produced from CMC. The slow-release fertilizers were designated as HyU\_CMC\_C, HyU\_CMC\_P, or HyU\_CMC\_SD which were produced from the CMC hydrogel; Hy\_CMC\_C, Hy\_CMC\_P, or Hy\_CMC\_SD, respectively.

**4.6. Sample Characterization.** Cellulose, CMC, CMC hydrogels, and slow-release fertilizers were monitored functional groups using a Fourier transform infrared (FTIR) spectrometer (PerkinElmer, Inc.) at wavenumber ranging from 400 to 4000 cm<sup>−1</sup>, morphology using scanning electron microscopy (SEM), and mineral components of the material using energy-dispersive X-ray spectroscopy (EDX) (Tescan: Mira 3, Czech Republic) and thermogravimetric analysis using a TGA Analyzer (PerkinElmer Pyris 1, PerkinElmer, Inc.).

**4.7. Swelling Ratio of CMC Hydrogel.** The experiment was conducted to determine the swelling ratio of the CMC hydrogel in water by cutting each prepared CMC hydrogel type into pieces (1 cm × 1 cm). A dry CMC hydrogel with a known weight ( $W_d$ ) was soaked in water, and the weight of the swollen hydrogel was measured at various time intervals (1, 2, 6, 10, and 24 h) as  $W_t$ . The swelling ratio ( $Sw_t$ ) of the CMC hydrogel at different times within 24 h was calculated using eq 1.

$$\text{swelling ratio, } Sw_t = (W_t - W_d) / W_d \quad (1)$$

The swelling behavior and swelling rate of CMC hydrogel in water can be analyzed using the second-order swelling kinetics model, as shown in eq 2.<sup>56</sup>

$$\frac{t}{Sw_t} = \frac{1}{kSw_{eq}^2} + \frac{t}{Sw_{eq}} \quad (2)$$

where  $Sw_t$  = swelling ratio of CMC hydrogel in water at different times,

$Sw_{eq}$  = swelling ratio of CMC hydrogel when swelling has reached equilibrium,

$k$  = swelling rate constant of cellulose hydrogel (g/g of H<sub>2</sub>O h).

**4.8. Water Retention of CMC Hydrogel.** Each type of CMC cellulose hydrogel, with 1 cm × 1 cm dimensions, was saturated with water to reach a known weight ( $W_s$ ). The hydrogel was then placed on a Petri dish under controlled humidity (approximately 40%) at 25 °C. The weight of the hydrogel was measured at different time intervals ( $W_{rt}$ ). The water retention percentage of the CMC hydrogel was calculated by using eq 3.

$$\% \text{ water retention} = (W_{rt}/W_s) \times 100 \quad (3)$$

**4.9. Water Holding Capacity of CMC Hydrogel in Soil.** Experiments were carried out with peat moss, loamy soil, and sandy soil to test the water holding capacity of the CMC hydrogel. Each soil type was prepared by sieving through an 8-mesh screen and drying at 60 °C. The dried soil was then mixed with the prepared CMC hydrogel at a soil-to-hydrogel ratio of 10:0.1 g (1% w/w hydrogel in each soil type). A known weight of soil mixed with the CMC hydrogel ( $W_{ds}$ ) was placed in a container with 2 holes at the bottom to allow water drainage. Water was added for each soil type (60 mL,  $V_{H_2O}$ ) to saturate the soil, and the mixture was left for an hour. In a while, the top of the container was sealed with aluminum foil and secured with rubber bands. After the set time, water was released from the container's bottom (until the water dripping stopped). The weight of the soil with retained water ( $W_{ws}$ ) was then measured, and the water holding percentage of the CMC hydrogel in the soil was calculated using eq 4.

$$\% \text{ water holding in soil} = ((W_{ws} - W_{ds})/V_{H_2O}) \times 100 \quad (4)$$

**4.10. Urea Content Analysis in Slow-Release Fertilizer.** To measure the urea content in the slow-release fertilizer made from the CMC hydrogel derived from waste paper and sawdust, a known weight (20 mg) of the dry slow-release fertilizer was added to 2 mL of 10 mM phosphate buffer pH 7.0. An 8 mg/mL cellulase enzyme solution (0.2 mL) was added into the mixture and then incubated at 37 °C and 250 rpm for 4 days to release urea. The released urea was analyzed using colorimetric spectrophotometry<sup>57</sup> by reacting the solution with *p*-dimethylaminobenzaldehyde (DMAB, 16 mg/mL) for 10 min. The reaction solution was measured absorbance at 420 nm using a range of 0.04–0.36 mg/mL standard urea for the calibration curve. The percentage of urea content in slow-release fertilizer was calculated using eq 5.

$$\% \text{ urea content} = \frac{\text{amount of released urea (g)}}{\text{weight of dry slow-release fertilizer (g)}} \times 100 \quad (5)$$

**4.11. Urea Release Analysis and Kinetics in Water from Slow-Release Fertilizer.** To analyze the release of urea from the hydrogel-based fertilizer in water over time, 20 mL of water was added into a known weight (0.1 g) of the slow-release fertilizer and placed in a 50 mL conical tube. The released urea samples were collected at intervals of 0.33, 0.67, 1, 2, 4, 6, 8, and 24 h. Each sample was analyzed to quantify urea content using the colorimetric spectrophotometry described in Section 4.10. Release behavior and release rate of urea from each type of slow-release fertilizer were investigated using Korsmeyer–Peppas shown in eq 6.<sup>48</sup>

$$\frac{M_t}{M_\infty} = kt^n \quad (6)$$

where  $M_t/M_\infty$  = fraction of urea released,

$k$  = diffusion constant,

$t$  = release time (h),

$n$  = diffusion exponent ( $n < 0.45$  indicates Fickian diffusion,  $0.45 < n < 0.89$  indicates non-Fickian,  $n > 0.89$  indicates case II transport).

**4.12. Urea Release Analysis in Soil from Slow-Release Fertilizer.** To analyze the release of urea in soil, 0.1 g of the slow-release fertilizer in a tea bag was placed between a two-layer portion of 10 g of loamy soil in a cup, and soil moisture was maintained at 60% over 14 days. The soil samples were collected on days 2, 4, 6, 8, 10, 12, and 14 to analyze the released urea quantity. The collected soils were dried at 50 °C to constant weight. 30 mL of water was added to the soil, vortexed, and then incubated at 30 °C, 250 rpm for 1 h. The soil mixture was centrifuged at 10,000 rpm for 15 min. Quantification of released urea in a clear solution was conducted. This experiment measured the untreated soil (no fertilizer addition) as a baseline urea level.

**4.13. Application of Slow-Release Fertilizer in Water Convolvulus Cultivation.** The experiment (in triplicates) started by adding 5 g of dried coconut coir cube and 80 g of dried loamy soil into a 3-inch pot. After the soil was added at the specified weight, 35 mL of water was added to moisten it thoroughly. Presoaked water convolvulus seeds were then planted (25 seeds per pot). The seeds were covered with an additional 10 g of dried soil and watered with another 10 mL of water. All pots were placed in a small greenhouse in a well-lit area with soil moisture maintained at 60%. After 7 days, a slow-release fertilizer from CMC hydrogel was added to the soil in equal amounts of urea (50 mg of urea/100 g of loamy soil by mixing the fertilizer with 10 g of dried loamy soil before evenly spreading in the pot). For the two control pots, one with no added fertilizer and the other with direct urea application (without encapsulation). Watering was continued to maintain soil moisture at 60%. Water convolvulus was harvested on days 14 and 25 to monitor growth by measuring the length of the stems (15 plants per pot).

## ■ ASSOCIATED CONTENT

### Data Availability Statement

Software: ChemBioDraw Ultra 14.0 was used to draw chemical structures. Excel charts and graphs and KaleidaGraph were used to create graphs and analyze data.

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.4c09928>.

Methods: degree of substitution (DS) of CMC; results: cellulose extracted from waste paper and sawdust; photographs of CMC hydrogels; TGA data for cellulose (CC, CP, and CSD) and carboxymethyl cellulose (CMC\_C, CMC\_P, and CMC\_SD); cross-linking reaction involved in the production of cellulose hydrogel from CMC using citric acid as a cross-linking agent; TGA data for CMC hydrogels; percentage of water holding capability of the CMC hydrogels in different types of soil; photographs of slow-release fertilizers; percentage of element content in HyU\_CMC\_SD from EDX analysis; SEM image at 1000× magnification of the

interior (cross section) of HyU\_CMC\_SD and the EDX spectrum of the elemental analysis of the slow-release fertilizer of HyU\_CMC\_SD in the cross section; degree of substitution (DS) of carboxymethyl group on CMC; growth of water convolvulus cultivated on days 14 and 25 was observed with various types of the slow-release urea fertilizers (PDF)

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### Author Contributions

C.T. and S.A. initiated the project; P.L., S.A., and C.T. designed the experiments and analyzed the data. P.L. and C.T. wrote the manuscript.

### Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

CC, commercial cellulose; CP, cellulose extracted from waste paper; CSD, cellulose extracted and delignified from sawdust; CMC, carboxymethyl cellulose; CMC\_C, carboxymethyl cellulose (commercial grade); CMC\_P, carboxymethyl cellulose synthesized from CP; CMC\_SD, carboxymethyl cellulose synthesized from CSD; Hy\_CMC\_C, CMC hydrogel derived from CMC\_C; Hy\_CMC\_P, CMC hydrogel derived from CMC\_P; Hy\_CMC\_C, CMC hydrogel derived from CMC\_SD; HyU\_CMC\_C, slow-released fertilizer derived from Hy\_CMC\_C; HyU\_CMC\_P, slow-release fertilizer derived from Hy\_CMC\_P; HyU\_CMC\_SD, slow-release fertilizer derived from Hy\_CMC\_SD

## REFERENCES

- (1) Gu, D.; Andreev, K.; Dupre, M. E. Major Trends in Population Growth Around the World. *China CDC Weekly* **2021**, *3*, 604–613.
- (2) Lawencia, D.; Wong, S. K.; Low, D. Y.; Goh, B. H.; Goh, J. K.; Ruktanonchai, U. R.; Soottitantawat, A.; Lee, L. H.; Tang, S. Y. Controlled Release Fertilizers: A Review on Coating Materials and Mechanism of Release. *Plants* **2021**, *10*, No. 238.
- (3) Kamal, B. How to eradicate rural poverty, end urban malnutrition. *Third World Econ.* **2017**, *648*, 13–15.
- (4) Guo, L.; Wang, Y.; Wang, M.; Shaghaleh, H.; Hamoud, Y. A.; Xu, X.; Liu, H. Synthesis of bio-based MIL-100(Fe)@CNF-SA composite hydrogel and its application in slow-release N-fertilizer. *J. Cleaner Prod.* **2021**, *324*, No. 129274.
- (5) Wen, P.; Wu, Z.; Han, Y.; Cravotto, G.; Wang, J.; Ye, B.-C. Microwave-Assisted Synthesis of a Novel Biochar-Based Slow-Release Nitrogen Fertilizer with Enhanced Water-Retention Capacity. *ACS Sustainable Chem. Eng.* **2017**, *5* (8), 7374–7382.
- (6) Gil-Ortiz, R.; Naranjo, M.A.; Ruiz-Navarro, A.; Caballero-Molada, M.; Atores, S.; García, C.; Vicente, O. New Eco-Friendly Polymeric-Coated Urea Fertilizers Enhanced Crop Yield in Wheat. *Agronomy* **2020**, *10*, No. 438.
- (7) Versino, F.; Urriza, M.; García, M. A. Eco-compatible cassava starch films for fertilizer controlled-release. *Int. J. Biol. Macromol.* **2019**, *134*, 302–307.
- (8) Savci, S. Investigation of Effect of Chemical Fertilizers on Environment. *APCBEE Procedia* **2012**, *1*, 287–292.
- (9) Messiga, A. J.; Dyck, K.; Ronda, K.; van Baar, K.; Haak, D.; Yu, S.; Dorais, M. Nutrients Leaching in Response to Long-Term Fertilization and Broadcast Nitrogen in Blueberry Production. *Plants* **2020**, *9*, No. 1530.
- (10) Wu, L.; Xu, H.; Xiao, Q.; Huang, Y.; Suleman, M. M.; Zhu, P.; Kuzyakov, Y.; Xu, X.; Xu, M.; Zhang, W. Soil carbon balance by priming differs with single versus repeated addition of glucose and soil fertility level. *Soil Biol. Biochem.* **2020**, *148*, No. 107913.
- (11) Paharvi, H. N.; Rafiya, L.; Rashid, S.; Nisar, B.; Kamili, A. N. Chemical Fertilizers and Their Impact on Soil Health. In *Microbiota and Biofertilizers, Vol 2: Ecofriendly Tools for Reclamation of Degraded Soil Environments*; Dar, G. H.; Bhat, R. A.; Mehmood, M. A.; Hakeem, K. R., Eds.; Springer International Publishing, 2021; pp 1–20.
- (12) Krasilnikov, P.; Taboada, M. A.; Amanullah. Fertilizer Use, Soil Health and Agricultural Sustainability. *Agriculture* **2022**, *12*, No. 462.
- (13) Trenkel, M. E. *Slow- and Controlled-Release and Stabilized Fertilizers: An Option for Enhancing Nutrient Use Efficiency in Agriculture*; International Fertilizer Industry Association: Paris, France, 2010.
- (14) Duan, Q.; Jiang, S.; Chen, F.; Li, Z.; Ma, L.; Song, Y.; Yu, X.; Chen, Y.; Liu, H.; Yu, L. Fabrication, Evaluation Methodologies and Models of Slow-release Fertilizers: A Review. *Ind. Crops Prod.* **2023**, *192*, No. 116075.
- (15) Rahman, M. H.; Haque, K. M. S.; Khan, M. Z. H. A review on application of controlled released fertilizers influencing the sustainable agricultural production: A Cleaner production process. *Environ. Technol. Innovation* **2021**, *23*, No. 101697.
- (16) Mansouri, H.; Ait Said, H.; Noukrati, H.; Oukarroum, A.; Ben youcef, H.; Perreault, F. Advances in Controlled Release Fertilizers: Cost-Effective Coating Techniques and Smart Stimuli-Responsive Hydrogels. *Adv. Sustainable Syst.* **2023**, *7* (9), No. 2300149.
- (17) Vejan, P.; Khadiran, T.; Abdullah, R.; Ahmad, N. Controlled release fertilizer: A review on developments, applications and potential in agriculture. *J. Controlled Release* **2021**, *339*, 321–334.
- (18) Govil, S.; Van Duc Long, N.; Escribà-Gelonch, M.; Hessel, V. Controlled-release fertiliser: Recent developments and perspectives. *Ind. Crops Prod.* **2024**, *219*, No. 119160.
- (19) Cannazza, G.; Cataldo, A.; De Benedetto, E.; Demitri, C.; Madaghiale, M.; Sannino, A. Experimental Assessment of the Use of a Novel Superabsorbent polymer (SAP) for the Optimization of Water Consumption in Agricultural Irrigation Process. *Water* **2014**, *6*, 2056–2069.
- (20) Li, Z.; Zhang, M. Progress in the Preparation of Stimulus-Responsive Cellulose Hydrogels and Their Application in Slow-Release Fertilizers. *Polymers* **2023**, *15*, No. 3643.



- (21) Ranganathan, N.; Bensingh, R. J.; Kader, M. A.; Nayak, S. K. Cellulose-Based Hydrogels for Agriculture. In *Cellulose-Based Superabsorbent Hydrogels*; Mondal, M. I. H., Ed.; Springer International Publishing, 2018; pp 1–21.
- (22) Phomsombut, K.; Saohong, S. S.; Buntan, R. Cellulose Hydrogel and Its Impact on Mung Bean Growth. *Curr. Appl. Sci. Technol.* **2023**, 23, No. 4.
- (23) Nasution, H.; Harahap, H.; Dalimunthe, N. F.; Ginting, M. H. S.; Jaafar, M.; Tan, O. O. H.; Aruan, H. K.; Herfananda, A. L. Hydrogel and Effects of Crosslinking Agent on Cellulose-Based Hydrogels: A Review. *Gels* **2022**, 8, No. 568.
- (24) Demitri, C.; Scalera, F.; Madaghiele, M.; Sannino, A.; Maffezzoli, A. Potential of Cellulose-Based Superabsorbent Hydrogels as Water Reservoir in Agriculture. *Int. J. Polym. Sci.* **2013**, 2013, No. 435073.
- (25) Hansen, M. C.; Potapov, P. V.; Moore, R.; Hancher, M.; Turubanova, S. A.; Tyukavina, A.; Thau, D.; Stehman, S. V.; Goetz, S. J.; Loveland, T. R.; et al. High-Resolution Global Maps of 21st-Century Forest Cover Change. *Science* **2013**, 342 (6160), 850–853.
- (26) Lopez, A. M. Five key factors shaping the global outlook for paper packaging. 2024.
- (27) Abushammala, H.; Masood, M. A.; Ghulam, S. T.; Mao, J. On the Conversion of Paper Waste and Rejects into High-Value Materials and Energy. *Sustainability* **2023**, 15, No. 6915.
- (28) Mallakpour, S.; Sirous, F.; Hussain, C. M. Sawdust, a versatile, inexpensive, readily available bio-waste: From mother earth to valuable materials for sustainable remediation technologies. *Adv. Colloid Interface Sci.* **2021**, 295, No. 102492.
- (29) Ferede, E. Evaluation of Mechanical and Water Absorption Properties of Alkaline-Treated Sawdust-Reinforced Polypropylene Composite. *J. Eng.* **2020**, 2020 (1), No. 3706176.
- (30) Sahin, H. T.; Arslan, M. B. A Study on Physical and Chemical Properties of Cellulose Paper Immersed in Various Solvent Mixtures. *Int. J. Mol. Sci.* **2008**, 9, 78–88.
- (31) Rachtanapun, P.; Luangkamin, S.; Tanprasert, K.; Suriyatem, R. Carboxymethyl cellulose film from durian rind. *LWT Food Sci. Technol.* **2012**, 48 (1), 52–58.
- (32) Chenevert, B. C.; Kramlich, J. C.; Nichols, K. M. Ash characteristics of high alkali sawdust and sanderdust biomass fuels. *Symp. (Int.) Combust.*, **1998**, 27 (2), 1719–1725.
- (33) El-Sakhawy, M. A.; Tohamy, H. A. S.; Salama, A.; Kamel, S. Thermal properties of carboxymethyl cellulose acetate butyrate. *Cellul. Chem. Technol.* **2019**, 53, 667–675.
- (34) Demitri, C.; Sole, R. D.; Scalera, F.; Sannino, A.; Vasapollo, G.; Maffezzoli, A.; Ambrosio, L.; Nicolais, L. Novel superabsorbent cellulose-based hydrogels crosslinked with citric acid. *J. Appl. Polym. Sci.* **2008**, 110 (4), 2453–2460.
- (35) Heise, K.; Kirsten, M.; Schneider, Y.; Jaros, D.; Keller, H.; Rohm, H.; Kalbitz, K.; Fischer, S. From Agricultural Byproducts to Value-Added Materials: Wheat Straw-Based Hydrogels as Soil Conditioners? *ACS Sustainable Chem. Eng.* **2019**, 7 (9), 8604–8612.
- (36) Mali, K. K.; Dhawale, S. C.; Dias, R. J.; Dhane, N. S.; Ghorpade, V. S. Citric Acid Crosslinked Carboxymethyl Cellulose-based Composite Hydrogel Films for Drug Delivery. *Indian J. Pharm. Sci.* **2018**, 80, 657–667.
- (37) Aswathy, S. H.; NarendraKumar, U.; Manjubala, I. Physicochemical Properties of Cellulose-Based Hydrogel for Bio-medical Applications. *Polymers* **2022**, 14, No. 4669, DOI: 10.3390/polym14214669.
- (38) Kaşgöz, H.; Durmus, A. Dye removal by a novel hydrogel-clay nanocomposite with enhanced swelling properties. *Polym. Adv. Technol.* **2008**, 19 (7), 838–845.
- (39) Bauli, C. R.; Lima, G. F.; de Souza, A. G.; Ferreira, R. R.; Rosa, D. S. Eco-friendly carboxymethyl cellulose hydrogels filled with nanocellulose or nanoclays for agriculture applications as soil conditioning and nutrient carrier and their impact on cucumber growing. *Colloids Surf., A* **2021**, 623, No. 126771.
- (40) Lv, Q.; Wu, M.; Shen, Y. Enhanced swelling ratio and water retention capacity for novel super-absorbent hydrogel. *Colloids Surf., A* **2019**, 583, No. 123972.
- (41) Al-Darby, A. M. The hydraulic properties of a sandy soil treated with gel-forming soil conditioner. *Soil Technol.* **1996**, 9 (1), 15–28.
- (42) Al-Humaid, A. I.; Moftah, A. E. Effects of Hydrophilic Polymer on the Survival of Buttonwood Seedlings Grown Under Drought Stress. *J. Plant Nutr.* **2007**, 30 (1), 53–66.
- (43) Grdadolnik, J.; Maréchal, Y. Urea and urea–water solutions—an infrared study. *J. Mol. Struct.* **2002**, 615 (1), 177–189.
- (44) Charoenchaitrakool, M.; Tulathon, P.; Meesangnil, W.; Niamnuy, C.; Seubsai, A.; Nunta, S.; Sudsakorn, K. Carboxymethyl cellulose and gelatin composite hydrogel for environmentally friendly urea delivery. *Colloids Surf., A* **2024**, 690, No. 133774.
- (45) de Souza, A. G.; Junqueira, M. T.; de Lima, G. F.; Rangari, V. K.; Rosa, D. S. A New Proposal of Preparation of Different Polymorphs of Nanocellulose from *Eucalyptus citriodora*. *J. Polym. Environ.* **2020**, 28 (4), 1150–1159.
- (46) Ahmad, D. F. B. A.; Wasli, M. E.; Tan, C. S. Y.; Musa, Z.; Chin, S.-F. Eco-friendly cellulose-based hydrogels derived from wastepapers as a controlled-release fertilizer. *Chem. and Biol. Technol. Agric.* **2023**, 10 (1), No. 36.
- (47) Song, Y.; Ma, L.; Duan, Q.; Xie, H.; Dong, X.; Zhang, H.; Yu, L. Development of Slow-Release Fertilizers with Function of Water Retention Using Eco-Friendly Starch Hydrogels. *Molecules* **2024**, 29, No. 4835.
- (48) Korsmeyer, R. W.; Gurny, R.; Doelker, E.; Buri, P.; Peppas, N. A. Mechanisms of solute release from porous hydrophilic polymers. *Int. J. Pharm.* **1983**, 15 (1), 25–35.
- (49) Kiran, Tiwari, R.; Krishnamoorthi, S.; Kumar, K. Synthesis of cross-linker devoid novel hydrogels: Swelling behaviour and controlled urea release studies. *J. Environ. Chem. Eng.* **2019**, 7 (4), No. 103162.
- (50) Saruchi; Kumar, V.; Mittal, H.; Alhassan, S. M. Biodegradable hydrogels of tragacanth gum polysaccharide to improve water retention capacity of soil and environment-friendly controlled release of agrochemicals. *Int. J. Biol. Macromol.* **2019**, 132, 1252–1261.
- (51) Ni, B.; Liu, M.; Lü, S.; Xie, L.; Wang, Y. Environmentally Friendly Slow-Release Nitrogen Fertilizer. *J. Agric. Food Chem.* **2011**, 59 (18), 10169–10175.
- (52) Wilaiporn, S. Effect of aerobic compost and chemical fertilizers on water convolvulus yield. *Thai Agric. Res. J.* **2019**, 37, 48–57.
- (53) Luyen, L. T.; Preston, T. R. Effect of level of urea fertilizer on biomass production of water spinach (*Ipomoea aquatica*) grown in soil and in water. *Livest. Res. Rural Dev.* **2004**, 16 (10), No. 81.
- (54) Abg Ahmad, D. F. B.; Wasli, M. E.; Tan, C. S. Y.; Musa, Z.; Chin, S.-F. Eco-friendly cellulose hydrogels as controlled release fertilizer for enhanced growth and yield of upland rice. *Sci. Rep.* **2023**, 13 (1), No. 20453.
- (55) Chat, T. H.; Dung, N. T.; Binh, D. V.; Preston, T. R. Effect on yield and composition of water spinach (*Ipomoea aquatica*), and on soil fertility, of fertilization with worm compost or urea. *Livest. Res. Rural Dev.* **2005**, 17, No. 108.
- (56) Schott, H. Swelling kinetics of polymers. *J. Macromol. Sci., Part B: Phys.* **1992**, 31 (1), 1–9.
- (57) Potts, T. J. Colorimetric Determination of Urea in Feeds (Report of AOAC Committee). *J. Assoc. Off. Anal. Chem.* **1967**, 50 (1), 56–58.