JTE HCMUTE
ISSN: 2615-9740

JOURNAL OF TECHNICAL EDUCATION SCIENCE
Ho Chi Minh City University of Technology and Education
Website: https://jte.edu.vn
Email: jte@hcmute.edu.vn

Environmentally Friendly Cassava Starch-Based Hydrogel as Absorbent with Slow Release of Fertilizer

Phuong Dong Bui, Thanh Huy Nguyen, Bui Anh Duy Nguyen, Phuoc Thiep Chau, Chi Thanh Nguyen*

Ho Chi Minh City University of Technology and Education, Vietnam

*Corresponding author. *Email: thanhnc@hcmute.edu.vn*

ARTICLE INFO

Received: 14/07/2024
Revised: 27/09/2024
Accepted: 03/10/2024
Published: 28/05/2025

KEYWORDS

Cassava starch;
Hydrogel;
Absorbent;
Slow-release fertilizer;
Environmentally friendly materials.

ABSTRACT

The environmentally friendly cassava starch-based hydrogel with controlled slow release of fertilizer replacing for fossil-based hydrogels was prepared successfully by oxidation of cassava starch using a simple reaction. The physiochemical properties of obtained hydrogel were evaluated by some reliable analytical techniques such as: X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscope (SEM), swelling ability in distilled water and various salt solutions. The XRD results showed the specific diffraction peaks corresponding to V-type crystals of starch. The results from FTIR analysis indicated the new peaks attributed to the stretching vibrations of bonding of aldehyde and carboxyl groups in the chemical structure of oxidized cassava starch. The surface morphological analysis of native cassava starch presented the smooth spherical shape. The dramatical change in morphology of hydrogel compared to that of the native cassava starch was found with the formation of a network of starch particles sticking together. The results from swelling degree of hydrogel showed that the fast water absorption at the early stage and reached the equilibrium stage in the long time of absorption. The swelling of hydrogel in salt solutions was found to be reduced with the increase of ion radius. Absorption and desorption results indicated that the obtained hydrogel had ability to absorb and release slowly some types of fertilizers such as: Urea, KNO_3, $(NH_4)_2SO_4$. This indicates that the obtained cassava starch-based hydrogel can be used as an environmentally friendly absorbent with slow release of fertilizers, having high potential for smart agricultural application.

Doi: https://doi.org/10.54644/jte.2025.1618

1. Introduction

The application of fertilizers in agriculture is crucial for enhancing crop yields, yet it is associated with significant environmental challenges, particularly with nitrogen-based fertilizers. The inefficiency of conventional nitrogen fertilizers, stemming from processes like volatilization, leaching, and denitrification, results in substantial wastage and environmental contamination. This over-application leads to severe issues, including hazardous gas emissions, groundwater pollution, eutrophication, and soil erosion. Over recent decades, extensive research has focused on the development of slow-release and controlled-release fertilizers, such as those based on urea and nitrate. These innovations aim to enhance fertilizer use efficiency while mitigating adverse environmental effects. Slow-release fertilizer carriers are designed and fabricated to release fertilizers in a manner that aligns with the plant's growth cycle, thereby reducing the risks of over-fertilization and its associated environmental impacts.

Among the diverse solutions for controlled fertilizers delivery in agriculture, hydrogels stand out as three-dimensional polymer networks capable of absorbing and retaining substantial amounts of water. These hydrogels have been extensively researched for their potential as slow-release fertilizer carriers. Notably, many hydrogels exhibit responsiveness to external stimuli, with their swelling properties being influenced by environmental changes such as temperature and pH [1], [2]. However, the majority of

these hydrogels are derived from synthetic polymers or petrochemical derivatives like acrylic acid or acrylamide [3], which results in poor biodegradability and elevated production costs [4].

To address these issues, there has been a growing interest in hydrogels based on naturally biodegradable polymers, particularly polysaccharides and proteins, for agricultural applications. Polysaccharides, in particular, are advantageous due to their high levels of hydroxyl and carboxyl groups, which can be chemically modified to create hydrogels with desirable absorption and swelling characteristics [1], [5]. Examples of such polysaccharides include chitosan, starch, and cellulose. These biopolymer-based hydrogels not only exhibit excellent biodegradability but also offer the potential for sustainable and cost-effective production, making them highly suitable for agricultural use. Through various chemical modifications, these natural polymers can form hydrogels that effectively release fertilizers in response to the needs of the plants, thereby optimizing fertilizer use efficiency and minimizing environmental impact.

Among naturally biodegradable polymers, starch has garnered significant attention for hydrogel fabrication. As one of the most abundant polysaccharides in nature, starch is widely sourced from cereals, roots, and tubers. Its biodegradability, renewability, and low cost make it an attractive polymer for a range of applications, particularly in the food industry. Nevertheless, native starch has inherent limitations, such as poor solubility, low mechanical strength, and instability under high temperatures and pH conditions during processing. To overcome these shortcomings, various chemical modifications have been explored to enhance the properties of starch-based hydrogels. These modifications primarily involve reactions targeting the hydroxyl groups in the anhydroglucose units of the starch molecule [6], [7], [8]. For example, the oxidation of starch can convert hydroxyl groups into carbonyl and carboxyl groups in the chemical structure of starch molecule, improving its functionality and reactivity. Other common modifications include esterification, etherification, and graft copolymerization, which aim to improve the solubility, mechanical properties, and thermal stability of starch.

Moreover, the development of biocomposite hydrogels incorporating other biopolymers or nanomaterials has further enhanced the performance of starch-based hydrogels. These biocomposites can provide synergistic effects, such as improved mechanical strength, enhanced water retention, and controlled release capabilities, making them highly suitable for agricultural applications like slow-release fertilizers. By leveraging these advancements, starch-based hydrogels can offer sustainable and efficient solutions for fertilizer delivery in agriculture, contributing to improved crop yields and reduced environmental impact [6].

Several oxidizing agents are commonly used to modify starch for hydrogel fabrication, such as sodium hypochlorite and hydrogen peroxide. However, sodium hypochlorite, widely employed in industrial processes, typically requires metal catalysts, which not only generates metal waste but also leads to the formation of toxic chlorine by-products. Hydrogen peroxide also necessitates metal catalysts for effective oxidation, adding to the complexity and potential environmental hazards of the process [9]. In contrast, potassium permanganate ($KMnO_4$) is an efficient oxidizing agent that can modify starch without the need for metal catalysts. $KMnO_4$'s high oxidation potential facilitates the conversion of hydroxyl groups in the chemical structure of starch to carbonyl and carboxyl groups, enhancing the hydrophilicity and functional properties of the starch. This makes $KMnO_4$ a preferable choice for eco-friendly and efficient starch chemical modification, aligning with sustainable practices in smart agriculture. By utilizing $KMnO_4$, starch-based hydrogels can be synthesized with improved mechanical strength, water absorption capacity, and controlled fertilizer release properties, thereby advancing the development of sustainably smart agricultural solutions. In this study, we used the $KMnO_4$/$NaHSO_4$ oxidation system to oxidize cassava starch to fabricate hydrogels for slow-release fertilizer carrier applications.

2. Materials and Methods

2.1. Materials

Cassava starch was purchased from Phuc Thang cassava starch production factory in Tay Ninh province, Vietnam. $KMnO_4$, Sodium Hydrogen Sulfate ($NaHSO_4$), Urea ($(NH_2)_2CO$) $(NH_4)_2SO_4$, $CaCl_2$, KNO_3, NaCl, C_2H_5OH, para–dimethylaminobenzaldehyde (DMABA), acetic acid, and Lugol 2,5 % were

purchased from Sigma Aldrich. Distilled water was supplied by the Material Technology Laboratory, Ho Chi Minh City University of Technology and Education.

2.2. Hydrogel Preparation

Cassava starch-based hydrogel materials were fabricated by mixing 5 g of cassava starch with 50 mL of distilled water into a three-neck round-bottom flask. Subsequently, the starch was gelatinized by heating the mixture at 80°C for 15 minutes. Then, the temperature of reaction was decreased to 60°C and 5 mL of distilled water was added into the reaction mixture. After that, 0.32 g of $KMnO_4$, 0.78 g of $NaHSO_4$, and 250 mL of distilled water were poured into the reactor to allow the oxidation reaction of starch to occur. The improvement of interaction between starch and chemical reagents was carried out by stirring the mixture vigorously for 4 hours at 60°C. The obtained cassava starch-based hydrogels were precipitated with 500 mL of ethanol for the purification. The final product was cleaned by washing several times with a 50% v/v EtOH/water mixture until a negative result was observed with Lugol's solution. The hydrogel samples were then dried at 40°C until a constant weight was achieved.

Figure 1. *Native cassava starch and fabricated hydrogel.*

2.3. Characterization of Materials

2.3.1. UV-Vis Spectroscopy Analysis

UV-Vis analysis was used to measure the concentration of urea fertilizer released over time. The measurements were conducted using the UV-Vis Shimadzu UV1800 system. The standard urea solutions were prepared and mixed with para–dimethylaminobenzaldehyde (DMABA) and acetic acid with various concentrations.

2.3.2. Chemical Structure

FTIR spectra of the cassava starch and hydrogels were recorded in the range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans using a Shimadzu IR Prestige-21 Fourier transform infrared spectrometer. The samples for measurement were prepared by mixing with KBr.

2.3.3. X-Ray Diffraction (XRD) Analysis

The crystalline structure of cassava starch and obtained hydrogel materials were determined using an EMPYREAN of PANalytical (Netherlands) X-ray diffraction instrument at the University of Finance Marketing in Ho Chi Minh City, Vietnam. Diffraction patterns of samples were measured in the range of 5° to 35° using CuK_α radiation at 40 kV and 45 mA. The crystallinity values (*Fc*) of samples were calculated from deconvolution of the X-ray patterns into crystalline diffraction and amorphous halo [10]-[11].

2.3.4. Morphological Analysis

The surface morphologies of the cassava starch particles and hydrogel samples were examined using a FESEM S-4800 HITACHI (Japan) scanning electron microscope with an accelerating voltage of 10

kV. To ensure the electrical conductivity of the samples, all samples were coated with a layer of platinum (Pt) before observation.

2.3.5. Thermal Stability

Thermogravimetric analysis of the cassava starch and hydrogel samples was conducted using a TGA Q500 instrument in the temperature range from 50 to 800°C at a heating rate of 10°C/min. In order to prevent oxidation, the measurement was carried out under a nitrogen atmosphere. The calibration for temperature and weight was performed before measurement.

2.3.6. Gel Fraction Determination

The gel fraction (F_g) of cassava starch and hydrogels was determined by soaking the samples in distilled water followed by filtration and dried to a constant weight. The gel fraction was calculated from the dry weights of the samples before (W_0) and after (W_f) soaking [10]:

$$F_g(\%) = \frac{W_f}{W_0} \times 100 \quad (1)$$

2.3.7. Swelling Behavior of Hydrogels Under Different Conditions

Swelling behavior of hydrogels was measured by a gravimetric method. The dry hydrogel samples were placed in a tea bag and immersed in different solutions with various concentrations for a specific period to reach equilibrium. Subsequently, the swollen hydrogels in tea bag were weighed after removing surface water. The water absorption (H) of the samples was calculated by the following equation:

$$H(\%) = \frac{W_s - W_0}{W_0} \times 100 \quad (2)$$

where Ws and W_0 represent the weight of the swollen hydrogels and the dry samples, respectively [10].

2.3.8. Method for Determining Fertilizer Absorption and Desorption

The hydrogels fabricated from cassava starch were used as an absorbent for carrying fertilizers. In this experiment, the hydrogel samples were fully immersed in fertilizer solutions (500 mL, 2000 ppm) for 24 hours. Then, the samples were filtrated and dried. The fertilizer loading was determined by weighing the hydrogel samples before and after immersion [12], [13], [14]. The fertilizer release experiment was conducted by soaking the fertilizer loaded samples in distilled water. A specific volume of solution was withdrawn from the mixture with a simultaneous addition of distilled water to ensure the same total volume at predetermined intervals. The released fertilizer concentration was measured by UV-Vis spectroscopy analysis. The percentage of fertilizer released was calculated as follows:

$$F(\%) = \frac{M_t}{M_i} \times 100 \quad (3)$$

where M_i represents the initial amount of fertilizer absorbed, and M_t represents the amount of fertilizer released at a specific time t [15].

3. Results and Discussion

3.1. Morphologies of Native Cassava Starch and Hydrogels

The surface morphologies of native cassava starch and hydrogel were determined using the SEM technique (Figure 2). As clearly observed from Figure 2a, the native cassava starch sample exhibits spherical particles with flat surfaces. In comparison to the native starch sample, the hydrogel shows a significant change in surface morphology, losing the original particle structure and forming interconnected network structures of aggregated particles (Figure 2b) [10].

During the gelatinization process, starch particles swollen and absorbed water, causing the disruption of the original structure of starch particles under the oxidation of $KMnO_4$. The surface of the hydrogel samples became rougher compared to the smooth surface observed in the native starch sample [10].

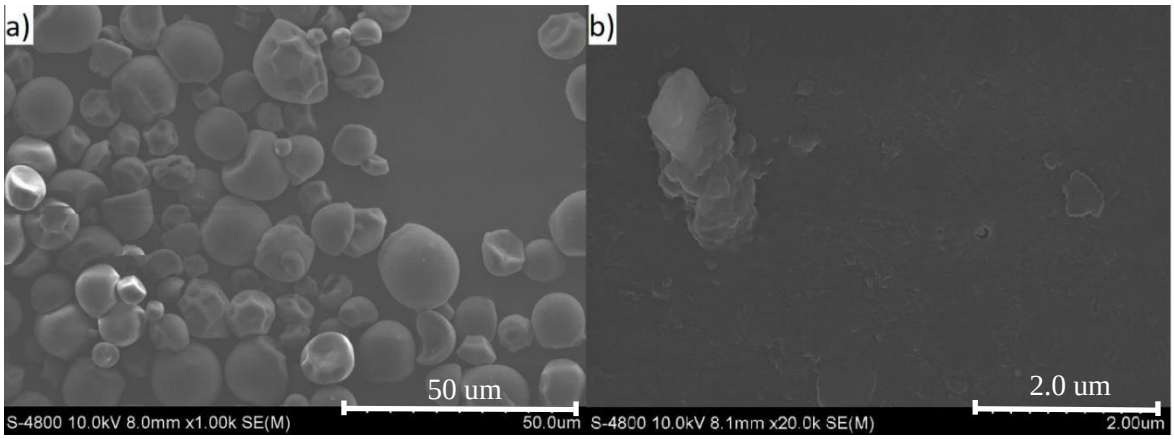

Figure 2. *SEM images of (a) native cassava starch; (b) hydrogel.*

3.2. Oxidation Process of Cassava Starch

Table 1. *Gel fraction (F_g) and relative crystallinity (F_c) of cassava starch (S) and hydrogel (H)*

Samples	F_g(%)	F_c(%)
S	85.4	38.45
H	91.0	5.34

The hydrogel was fabricated through the oxidation of cassava starch by using the $KMnO_4/NaHSO_4$ system. As observed from Table 1, the gel fraction of hydrogel is higher than that of cassava starch. Under oxidation process of cassava starch using $KMnO_4/NaHSO_4$, the hydroxyl groups first were oxidized to aldehyde groups and then to carboxyl groups. The oxidation of hydroxyl groups to carboxyl groups facilitates the formation of the hydrogels. The oxidation process caused the cross-linking reactions to occur. As a result, the hydrogel was obtained. It has been previously demonstrated [16] that carboxyl groups can form hemiacetal cross-links, enhancing the starch integrity to achieve a similar state as cross-linking with bifunctional agents.

Additionally, the $KMnO_4/NaHSO_4$ redox system generates free radicals, which may also contribute to the formation of cross-links [17]. Furthermore, the high gel fraction values obtained in all hydrogel samples (Table 1) seem to indicate that the depolymerization of starch molecules by breaking the αD-(1→4) glycosidic bonds during oxidation is relatively low compared to other systems [18].

3.3. X-ray diffraction analysis

The obtained hydrogels were also characterized by wide-angle X-ray scattering. Figure 3 displays the X-ray diffraction (XRD) patterns of native cassava starch and hydrogel. It is evident that the native starch samples exhibit a typical semi-crystalline structure, where sharp diffraction peaks are attributed to amylopectin, while broad peaks correspond to amylose [15], [16].

This semi-crystalline structure consists of granules with amorphous regions of amylose interspersed between crystalline regions of amylopectin branches arranged in a double helix. For hydrogels, the diffraction patterns reveal a new low-intensity peak ($2\theta = 5.56^o$), indicating the coexistence of both A and B polymorphs. According to previous studies, the relative crystallinity of cassava starch was determined to be 37.10% [19], [20].

The oxidation process significantly reduced crystallinity, as evidenced by the decrease in intensity and broadening of the diffraction peaks [21], [22]. This reduction in crystallinity is likely due to the increase in carboxyl group content (a result of the oxidation process). Hydrogel is characterized by three distinct diffraction peaks of type V crystals at $2\theta = 7.5°$, 13.25°, and approximately 20° [19].

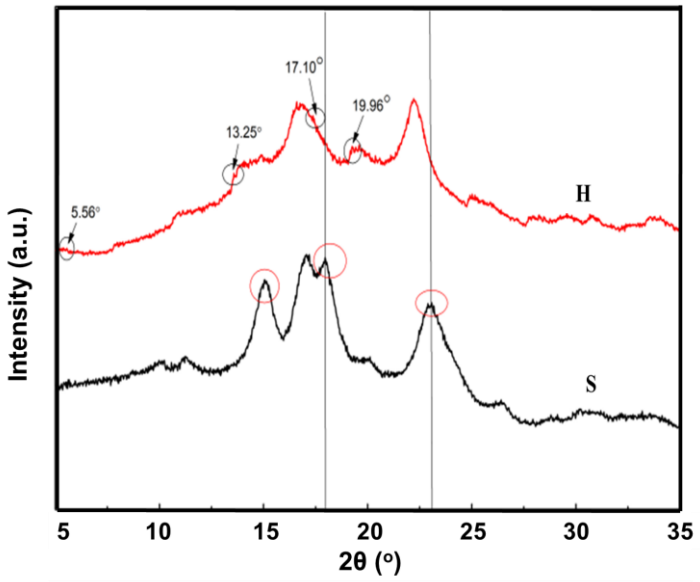

Figure 3. *XRD patterns of native cassava starch (S) and hydrogel (H).*

Overall, the diffraction patterns of oxidized starch, aside from the mentioned peaks, display an amorphous halo. This indicates that the oxidation reaction had a substantial impact on the crystalline structure of the granules. In the XRD patterns of hydrogel, the disappearance of the main diffraction peaks is clearly observed compared to native starch. H exhibits two very low-intensity peaks at 2θ = 17.13° and 22.46°. Additionally, the XRD pattern of the H sample shows a small diffraction peak at 2θ = 18.61–19.96°, while the remaining diffraction peaks disappeared [19].

3.4. FTIR spectroscopy analysis

The oxidation of starch samples was also studied using FTIR spectroscopy. Figure 4 shows the FTIR spectra of native starch and hydrogel samples. Compared to the FTIR spectrum of native starch, the FTIR spectrum of hydrogel shows the appearance of new peaks at 2854 cm^{-1}corresponding to the stretching vibration of the (C-H) bond of the -C(O)H group and at 1735 cm^{-1} attributed to the stretching vibration of the (-C=O) bond of aldehyde and carboxyl groups [10].

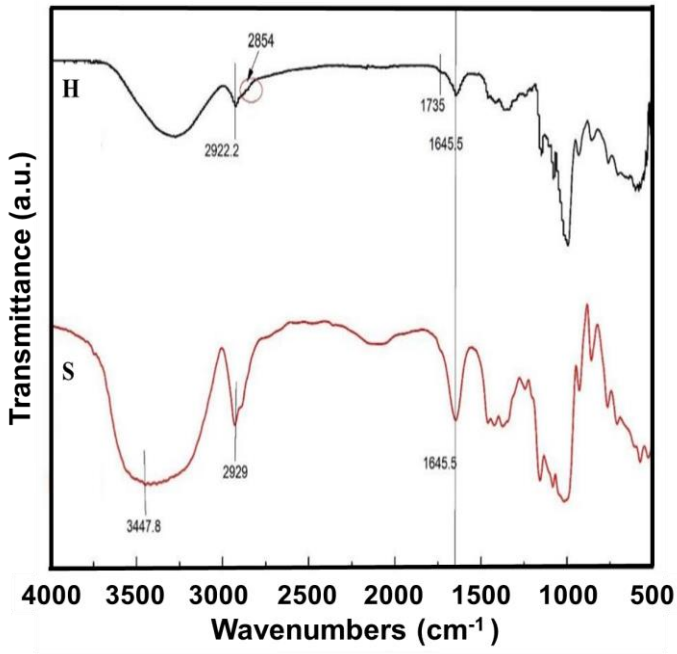

Figure 4. *FTIR spectra of native cassava starch (S) and hydrogel (H).*

JTE
HCMUTE
ISSN: 2615-9740

JOURNAL OF TECHNICAL EDUCATION SCIENCE
Ho Chi Minh City University of Technology and Education
Website: https://jte.edu.vn
Email: jte@hcmute.edu.vn

Compared to native cassava starch, the characteristic absorption peak of hydrogel at 1645 cm^{-1} significantly decreased in intensity. The peak at 2922 cm^{-1} corresponds to the asymmetric stretching vibration of the (-C-H) bond of the anhydroglucose units.

3.5. Thermogravimetric analysis (TGA)

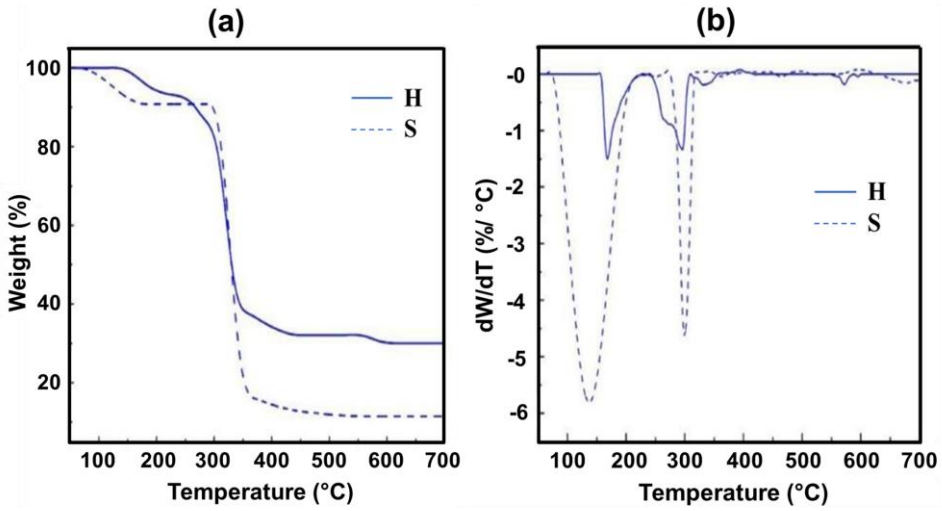

Figure 5. *Plots: (a) TGA; (b) DTG of native cassava starch (S) and hydrogel (H).*

The thermal stability of hydrogel and native cassava starch was evaluated using the thermogravimetric analysis (TGA) method. Figure 5 shows the TGA and DTG plots of the native cassava starch and hydrogel samples. As observed from Figure 5, the TGA plot of the native cassava starch sample exhibits two stages of weight loss. The first weight loss (50-150°C) is attributed to the evaporation of water and moisture, while the second stage (246-450°C) is due to starch decomposition [23], [24], [25]. The decomposition temperatures, weight loss percentages related to the thermal decomposition stages, and the percentage of remaining sample mass during the thermal decomposition process are summarized in Table 2.

Compared to the native cassava starch sample, the hydrogel sample shows a significantly higher initial thermal decomposition stage occurring at a much higher temperature range (100-245°C). This could be explained by the formation of new carboxylic groups in the chemical structure of hydrogel, which strongly absorbed water molecules [23].

The second thermal decomposition stage is the main decomposition stage, and this thermal decomposition may be attributed to the degradation and breaking of starch chains. Table 2 also indicates that hydrogel sample exhibits higher thermal stability compared to the native cassava starch sample. The hydrogel sample shows higher initial decomposition temperatures and Tmax (temperature at the maximum rate of weight loss) values compared to the native cassava starch sample [24].

Table 2. *Temperature parameters of native cassava starch and hydrogel.*

Sample	Stage	Range (°C)	Weight loss (%)	T_{max} (°C)	Residual mass (%)
S	1	50 - 150	9.8	306	4.6
	2	246 - 450	85.6		
H	1	100 - 245	9.7	310	27.8
	2	265 - 450	62.5		

Previous studies on oxidized starch showed contrasting results, where the oxidation process often led to lower thermal stability due to depolymerization processes of molecular chains leading to reduced molecular weight [26], [27]. However, in the case of cassava starch oxidized by the $KMnO_4/NaHSO_4$ oxidation-reduction system, it resulted in minimal depolymerization. This could be evidenced by the

high gel fraction values obtained in hydrogel sample. Therefore, the higher thermal stability of hydrogel sample compared to that of native cassava starch may be attributed to a higher content of carboxyl groups and the formation of cross-links [28].

3.6. Swelling behavior of hydrogels in different media

The swelling behavior of hydrogel was studied in different media: distilled water, salt solutions. Figure 6 displays the amount of water absorbed (H) at various times relative to the maximum water absorption (H^{∞}) of the hydrogel sample.

It is noteworthy that the water uptake process occurred quite rapidly. At the onset of the swelling process, the graph in Figure 6 illustrates the maximum water uptake, followed by a gradual decrease in swelling to reach equilibrium over a longer period. This phenomenon is referred to as the overload effect and can be explained by physical cross-links formed by the formation of hydroxyl bonds between the carboxyl groups of the hydrogel sample [8], [29].

As can be seen from Table 3 that the hydrogel sample presents significantly higher swelling capacity compared to hydrogel prepared from corn starch in the previous studies [30].

Furthermore, the influence of ion strength on the swelling capacity of hydrogel was investigated by analyzing water uptake in salt solutions with different concentrations (NaCl, $CaCl_2$ at 0.009%, 0.09%, and 0.9%). The swelling capacity of the hydrogel samples followed the trend: NaCl > $CaCl_2$. As clearly observed from Table 3, the water absorption is higher in solutions containing monovalent cations Na^+. This ability also depends on the ionic radius, decreasing as the radius increases due to the difficulty of cation penetration into the hydrogel [31].

In the $CaCl_2$ solution medium, the swelling capacity of hydrogels decreased, possibly due to the formation of complex between divalent Ca^{2+} cations with the carboxyl groups of hydrogel sample. This provided additional cross-links [14].

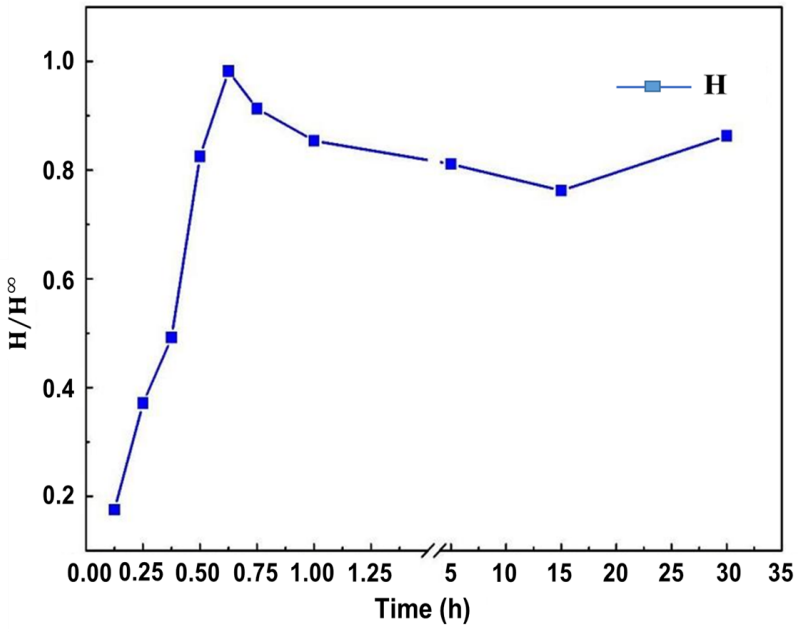

Figure 6. *Swelling kinetics of hydrogel in water.*

Table 3. *Maximum water absorption at equilibrium (H∞) of hydrogel sample (H) in distilled water and salt solutions with various concentrations.*

H^{∞} (%)	**H_2O**	**NaCl**			**$CaCl_2$**		
C (%)	-	0.009	0.09	0.9	0.009	0.09	0.9
H	3370	3763	4003	4325	1906	2408	2865

3.7. Fertilizer absorption of hydrogels

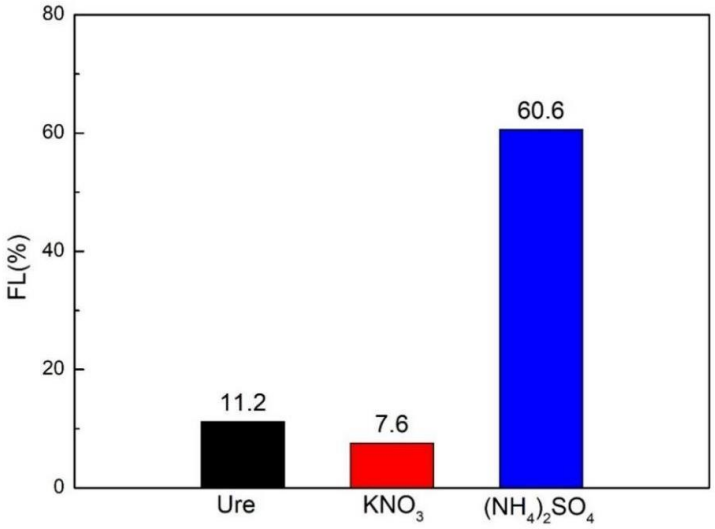

Figure 7. *Fertilizers absorption of hydrogel.*

In order to evaluate the ability of prepared cassava starch-based hydrogel to absorb and release fertilizers with controlled manner. The fertilizers absorption and release of hydrogels were investigated using various fertilizers such as urea, KNO_3, and $(NH_4)_2SO_4$. For these experiments, 500 mg of obtained hydrogel was added into urea solution with a concentration of 2000 ppm, KNO_3 solution with a concentration of 10,000 ppm, and $(NH_4)_2SO_4$ solution with a concentration of 30,000 ppm.

Figure 7 shows the percentage of urea absorbed (FL_{UREA}), KNO_3 (FL_{KNO3}), and $(NH_4)_2SO_4$ (FL $(NH_4)_2SO_4$) onto hydrogel sample. According to previous studies on different types of oxidized starches, oxidized cassava starch had the highest fertilizer loading capacity for all types of fertilizers [10]. This may be due to the lower gel fraction (*Fg*) and relative crystallinity (*Fc*) values of oxidized cassava starch compared to other types of oxidized starches, leading to a more flexible polymer network structure with higher molecular chain flexibility. These characteristics make oxidized cassava starch more expandable and enhance water and fertilizer absorption during the swelling process.

Oxidized cassava starch has the ability to absorb a large amount of fertilizer in decreasing order depending on the type of fertilizers as follows: $(NH_4)_2SO_4$ > Urea > KNO_3. Fertilizer absorption occurs during the swelling process in distilled water, where partially ionized carboxyl groups promote network expansion, allowing the absorption process to occur more easily.

As indicated in studies on swelling behavior in salt solutions, the ionic radius and charge of cations, as well as the quantity of cations affect water uptake and subsequently absorption ability. In this case, the radius of K^+ ions is close to that of NH_4^+ ions, so it can be explained that the higher absorption of $(NH4)_2SO_4$ may be due to the double amount of cations per molecule of $(NH_4)_2SO_4$ compared to KNO_3 [10]. Therefore, the prepared hydrogel from oxidized cassava starch absorb fertilizer in the following order: $(NH_4)_2SO_4$ > Urea > KNO_3.

3.8. Ability to release fertilizer with controlled manner of hydrogel

Table 4. *Results of urea concentration released determined by UV-Vis method.*

Time (hour)	**0.5**	**1**	**2**	**4**	**25**	**50**	**100**
Urea concentration (ppm)	32.80	131.84	137.48	143.12	134.66	131.60	140.05

JTE
HCMUTE
ISSN: 2615-9740

JOURNAL OF TECHNICAL EDUCATION SCIENCE
Ho Chi Minh City University of Technology and Education
Website: https://jte.edu.vn
Email: jte@hcmute.edu.vn

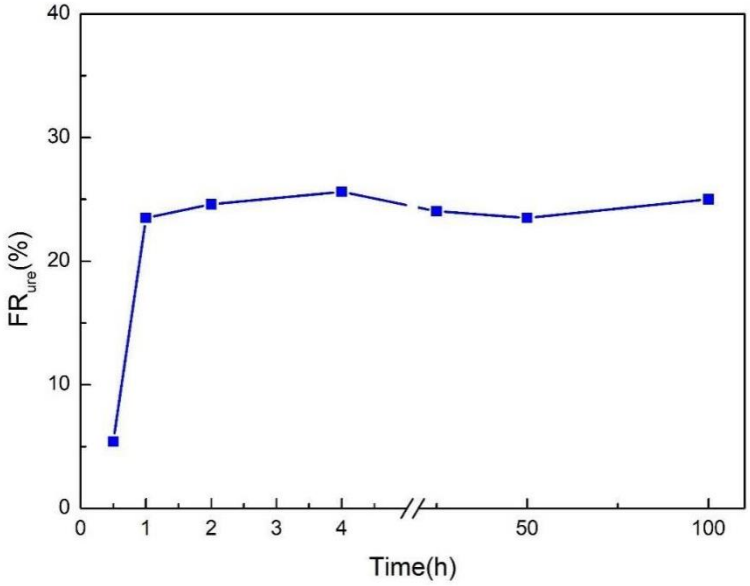

Figure 8. *The urea release kinetics of hydrogel.*

The ability to release urea fertilizer with controlled manner of obtained hydrogel was evaluated by determining the released urea concentration using UV-Vis analysis. Figure 8 illustrates the release of urea over time, where the release process exhibits a first-order release involving initially high release rates followed by rapid decline [12], [32]. This phenomenon may be associated with the desorption between water molecules and urea molecules due to the large available free volume inside the starch structure, created by the separation between chains. This results in the reabsorption at the active sites within the structure of polymer network [13]. The reduction in pore diameter or depth of inner cells and surface due to the urea molecules accumulation impedes water penetration into the structure of hydrogel [33]. This character slows down the release of fertilizer, helping control the fertilizer release rate of hydrogel.

However, as observed from Figure 8, after reaching equilibrium, the release rate slightly increased again due to the partial weakening of the structure of hydrogel as the soaking time was prolonged [34]. The high loaded urea content may also contribute to urea release as high urea loading accelerates water movement towards the sample, which can help to expand the polymer chains [12]. Additionally, incomplete urea release occurring with regard to hydrogel sample based on oxidized cassava starch is observed. This is attributed to the formation of hydrogen bonds between hydrogel and $–NH_2$ groups of urea molecules. The urea release kinetic of hydrogel seen in Figure 8 consists of three stages. The first stage is a slow-release stage, followed by a rapid-release stage where the maximum amount of fertilizer was released. The constant release rate is observed in the third stage. These results are consistent with other studies [30], [35].

4. Conclusions

The environmentally friendly cassava starch-based hydrogels were successfully fabricated through the oxidation process of cassava starch using the $KMnO_4/NaHSO_4$ redox system. The obtained results demonstrate that the oxidation process only caused minimal depolymerization of starch molecules, and all oxidized cassava starch samples yielded the high gel fraction values. The cross-linking degree and relative crystallinity were affected by the oxidation process, strongly influencing on the swelling ability of hydrogel in various media.

Oxidized cassava starch exhibited much higher swelling ability in different media compared to other oxidized starches in previous studies. This is attributed to the lower crystallinity of oxidized cassava starch compared to other starch samples studied previously. The influence of ion strength on the swelling ability of oxidized cassava starch was investigated in salt solutions with different concentrations. The results showed that oxidized cassava starch had good absorption ability for various fertilizers such as urea, KNO_3, $(NH_4)_2SO_4$. The obtained hydrogel presented the ability to release urea fertilizer with

controlled manner. This suggests that the fabricated hydrogel based on oxidized cassava starch can be applied as a slow-release fertilizer carrying material, having great application potential in smart agriculture field.

Acknowledgments

We would like to thank Ho Chi Minh City University of Technology and Education for the financial support. This work belongs to project grant no. SV2024-38, funded by Ho Chi Minh City University of Technology and Education, Vietnam.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

REFERENCES

[1] Y. Zhang, X. Liang, X. Yang, H. Liu, and J. Yao, "An eco-friendly slow-release urea fertilizer based on waste mulberry branches for potential agriculture and horticulture applications," *ACS Sustain. Chem. Eng.*, vol. 2, no. 7, pp. 1871–1878, 2014, doi: 10.1021/sc500204z.

[2] T. Zheng, Y. Liang, S. Ye, and Z. He, "Superabsorbent hydrogels as carriers for the controlled-release of urea: Experiments and a mathematical model describing the release rate," *Biosyst. Eng.*, vol. 102, no. 1, pp. 44–50, 2009, doi: 10.1016/j.biosystemseng.2008.09.027.

[3] N. E. Rabat, S. Hashim, and R. A. Majid, "Effect of Different Monomers on Water Retention Properties of Slow Release Fertilizer Hydrogel," *Procedia Eng.*, vol. 148, pp. 201–207, 2016, doi: 10.1016/j.proeng.2016.06.573.

[4] R. L. Shogren, J. L. Willett, and A. Biswas, "HRP-mediated synthesis of starch-polyacrylamide graft copolymers," *Carbohydr. Polym.*, vol. 75, no. 1, pp. 189–191, 2009, doi: 10.1016/j.carbpol.2008.07.004.

[5] L. H. C. Bortolin, A., Aouada, F. A., de Moura, M. R., Ribeiro, C., Longo, E., & Mattoso, "Application of Polysaccharide Hydrogels in Adsorption and Controlled-Extended Release of Fertilizers Processes," *J. Appl. Polym. Sci.*, vol. 123, no. 4, pp. 2291–2298, 2011, doi: 10.1002/app.34742.

[6] E. V. R. Campos, J. L. de Oliveira, L. F. Fraceto, and B. Singh, "Polysaccharides as safer release systems for agrochemicals," *Agron. Sustain. Dev.*, vol. 35, no. 1, pp. 47–66, 2015, doi: 10.1007/s13593-014-0263-0.

[7] D. Soto, J. Urdaneta, K. Pernía, O. León, A. Muñoz-Bonilla, and M. Fernández-García, "Heavy metal (Cd2+, Ni2+, Pb2+ and Ni2+) adsorption in aqueous solutions by oxidized starches," *Polym. Adv. Technol.*, vol. 26, no. 2, pp. 147–152, 2015, doi: 10.1002/pat.3439.

[8] D. Soto, J. Urdaneta, K. Pernia, O. León, A. Muñoz-Bonilla, and M. Fernández-García, "Itaconic Acid Grafted Starch Hydrogels as Metal Remover: Capacity, Selectivity and Adsorption Kinetics," *J. Polym. Environ.*, vol. 24, no. 4, pp. 343–355, 2016, doi: 10.1007/s10924-016-0780-9.

[9] M. Lukasiewicz, S. Bednarz, and A. Ptaszek, "Environmental friendly polysaccharide modification - Microwave-assisted oxidation of starch," *Starch/Staerke*, vol. 63, no. 5, pp. 268–273, 2011, doi: 10.1002/star.201000124.

[10] O. León *et al.*, "Hydrogels based on oxidized starches from different botanical sources for release of fertilizers," *Int. J. Biol. Macromol.*, vol. 136, pp. 813–822, 2019, doi: 10.1016/j.ijbiomac.2019.06.131.

[11] S. Brückner, "Estimation of the background in powder diffraction patterns through a robust smoothing procedure," *J. Appl. Crystallogr.*, vol. 33, no. 3 II, pp. 977–979, 2000, doi: 10.1107/S0021889800003617.

[12] X. Liang, Y. Zhang, L. Liu, and J. Yao, "Synthesis and urea-loading of an eco-friendly superabsorbent composite based on mulberry branches," *BioResources*, vol. 8, no. 1, pp. 130–144, 2013, doi: 10.15376/biores.8.1.130-144.

[13] A. K. Bajpai and A. Giri, "Water sorption behaviour of highly swelling (carboxy methylcellulose-g-polyacrylamide) hydrogels and release of potassium nitrate as agrochemical," *Carbohydr. Polym.*, vol. 53, no. 3, pp. 271–279, 2003, doi: 10.1016/S0144-8617(03)00071-7.

[14] A. I. Raafat, M. Eid, and M. B. El-Arnaouty, "Radiation synthesis of superabsorbent CMC based hydrogels for agriculture applications," *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms*, vol. 283, pp. 71–76, 2012, doi: 10.1016/j.nimb.2012.04.011.

[15] H. A. Essawy, M. B. M. Ghazy, F. A. El-Hai, and M. F. Mohamed, "Superabsorbent hydrogels via graft polymerization of acrylic acid from chitosan-cellulose hybrid and their potential in controlled release of soil nutrients," *Int. J. Biol. Macromol.*, vol. 89, pp. 144–151, 2016, doi: 10.1016/j.ijbiomac.2016.04.071.

[16] Y. J. Wang and L. Wang, "Physicochemical properties of common and waxy corn starches oxidized by different levels of sodium hypochlorite," *Carbohydr. Polym.*, vol. 52, no. 3, pp. 207–217, 2003, doi: 10.1016/S0144-8617(02)00304-1.

[17] A. Hebeish, M. H. El-Rafie, F. El-Sisi, S. Abdel Hafiz, and A. A. Abdel-Rahman, "Oxidation of maize and rice starches using potassium permanganate with various reductants," *Polym. Degrad. Stab.*, vol. 43, no. 3, pp. 363–371, 1994, doi: 10.1016/0141-3910(94)90007-8.

[18] H. X. Xiao, Q. L. Lin, G. Q. Liu, and F. X. Yu, "A comparative study of the characteristics of cross-linked, oxidized and dual-modified rice starches," *Molecules*, vol. 17, no. 9, pp. 10946–10957, 2012, doi: 10.3390/molecules170910946.

[19] N. S. Md Shahrodin, A. R. Rahmat, and A. Arsad, "Synthesis and Characterization of Cassava Starch Nanocrystals by Hydrolysis Method," *Adv. Mater. Res.*, vol. 1113, pp. 446–452, 2015, doi: 10.4028/www.scientific.net/amr.1113.446.

[20] C. Mutungi, F. Rost, C. Onyango, D. Jaros, and H. Rohm, "Crystallinity, thermal and morphological characteristics of resistant starch type iii produced by hydrothermal treatment of debranched Cassava starch," *Starch/Staerke*, vol. 61, no. 11, pp. 634–645, 2009, doi: 10.1002/star.200900167.

[21] D. Kuakpetoon and Y. J. Wang, "Structural characteristics and physicochemical properties of oxidized corn starches varying in amylose content," *Carbohydr. Res.*, vol. 341, no. 11, pp. 1896–1915, 2006, doi: 10.1016/j.carres.2006.04.013.

[22] N. L. Vanier *et al.*, "Physicochemical, crystallinity, pasting and morphological properties of bean starch oxidised by different

concentrations of sodium hypochlorite," *Food Chem.*, vol. 131, no. 4, pp. 1255–1262, 2012, doi: 10.1016/j.foodchem.2011.09.114.
[23] A. Gunaratne and R. Hoover, "Effect of heat-moisture treatment on the structure and physicochemical properties of tuber and root starches," *Carbohydr. Polym.*, vol. 49, no. 4, pp. 425–437, 2002, doi: 10.1016/S0144-8617(01)00354-X.
[24] U. Federal, D. M. Gerais, B. Horizonte, U. Federal, D. O. Preto, and O. Preto, "Thermal behaviour of starch and oxidized starch," vol. 296, pp. 141–148, 1997.
[25] B. Wei, H. Li, Y. Tian, X. Xu, and Z. Jin, "Thermal degradation behavior of hypochlorite-oxidized starch nanocrystals under different oxidized levels," *Carbohydr. Polym.*, vol. 124, pp. 124–130, 2015, doi: 10.1016/j.carbpol.2015.01.081.
[26] L. S. Guinesi, A. L. da Róz, E. Corradini, L. H. C. Mattoso, E. de M. Teixeira, and A. A. d. S. Curvelo, "Kinetics of thermal degradation applied to starches from different botanical origins by non-isothermal procedures," *Thermochim. Acta*, vol. 447, no. 2, pp. 190–196, 2006, doi: 10.1016/j.tca.2006.06.002.
[27] Y. R. Zhang, X. L. Wang, G. M. Zhao, and Y. Z. Wang, "Preparation and properties of oxidized starch with high degree of oxidation," *Carbohydr. Polym.*, vol. 87, no. 4, pp. 2554–2562, 2012, doi: 10.1016/j.carbpol.2011.11.036.
[28] A. Hebeish, M. H. El-Rafie, A. M. Rabie, M. A. El-Sheikh, and M. E. El-Naggar, "Ultra-microstructural features of perborate oxidized starch," *J. Appl. Polym. Sci.*, vol. 131, no. 8, pp. 1–9, 2014, doi: 10.1002/app.40170.
[29] Y. Yin, X. Ji, H. Dong, Y. Ying, and H. Zheng, "Study of the swelling dynamics with overshooting effect of hydrogels based on sodium alginate-g-acrylic acid," *Carbohydr. Polym.*, vol. 71, no. 4, pp. 682–689, 2008, doi: 10.1016/j.carbpol.2007.07.012.
[30] X. Liu, Y. Yang, B. Gao, Y. Li, and Y. Wan, "Environmentally Friendly Slow-Release Urea Fertilizers Based on Waste Frying Oil for Sustained Nutrient Release," *ACS Sustain. Chem. Eng.*, vol. 5, no. 7, pp. 6036–6045, 2017, doi: 10.1021/acssuschemeng.7b00882.
[31] E. M. Ahmed, "Hydrogel: Preparation, characterization, and applications: A review," *J. Adv. Res.*, vol. 6, no. 2, pp. 105–121, 2015, doi: 10.1016/j.jare.2013.07.006.
[32] R. Liang, H. Yuan, G. Xi, and Q. Zhou, "Synthesis of wheat straw-g-poly(acrylic acid) superabsorbent composites and release of urea from it," *Carbohydr. Polym.*, vol. 77, no. 2, pp. 181–187, 2009, doi: 10.1016/j.carbpol.2008.12.018.
[33] S. Mishra, J. Bajpai, and A. K. Bajpai, "Evaluation of the water sorption and controlled-release potential of binary polymeric beads of starch and alginate loaded with potassium nitrate as an agrochemical," *J. Appl. Polym. Sci.*, vol. 94, no. 4, pp. 1815–1826, 2004, doi: 10.1002/app.21096.
[34] Y. Zhang, F. Wu, L. Liu, and J. Yao, "Synthesis and urea sustained-release behavior of an eco-friendly superabsorbent based on flax yarn wastes," *Carbohydr. Polym.*, vol. 91, no. 1, pp. 277–283, 2013, doi: 10.1016/j.carbpol.2012.08.041.
[35] Y. Niu and H. Li, "Controlled release of urea encapsulated by starch-g-poly(vinyl acetate)," *Ind. Eng. Chem. Res.*, vol. 51, no. 38, pp. 12173–12177, 2012, doi: 10.1021/ie301684p.

Bui Phuong Dong studying Materials Technology at Ho Chi Minh City University of Technology and Education.
Email: 20130020@student.hcmute.edu.vn. ORCID: https://orcid.org/0009-0007-5228-4980

Nguyen Thanh Huy received his Bachelor Engineering degree in Materials Technology from Ho Chi Minh City University of Technology and Education in 2024.
Email: huynt171201@gmail.com. ORCID: https://orcid.org/0009-0004-1110-286X

Nguyen Bui Anh Duy received the Bachelor Engineering degree in Materials Technology from Ho Chi Minh City University of Technology and Education in 2024.
Email: anhduy240901@gmail.com. ORCID: https://orcid.org/0009-0004-6535-8027

Chau Phuoc Thiep received his Bachelor Engineering degree in Materials Technology from Ho Chi Minh City University of Technology and Education in 2023.
Email: 17130043@student.hcmute.edu.vn. ORCID: https://orcid.org/0009-0008-3969-6355

Nguyen Chi Thanh received his Bachelor degree in Materials Science from Ho Chi Minh City University of Sciences, Viet Nam and the Ph.D. degree in Polymer Engineering from Suranaree University of Technology, Thailand. He is currently a lecturer at Ho Chi Minh City University of Technology and Education, Viet Nam.
Email: thanhnc@hcmute.edu.vn. ORCID: https://orcid.org/0000-0003-3638-9903