

Synthesis and Characterization of Controlled-Release Urea Fertilizer from Superabsorbent Hydrogels

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Abstract: It is very important to develop controlled-release fertilizers to ensure efficiency and environmental protection. This study aims to make a superabsorbent hydrogel-based controlled-release urea fertilizer. Superabsorbent hydrogels were prepared from the cellulose of corn cobs cross-linking with epichlorohydrin, and then an amount of urea as a fertilizer was stored inside the hydrogels (GEL-A). The GEL-A functionalization with carboxy-methyl was also carried out in this study to improve the hydrophilicity of hydrogels (GEL-B). GEL-A and GEL-B were immersed in water at a certain pH and temperature range and the urea concentration released from the hydrogels was monitored by a spectrophotometer. The results showed that the urea released by GEL-A and GEL-B was not much different. Respectively, the urea efficiency of GEL-A and GEL-B was around 5.29% and 5.56% for 180 min. The urea released from both hydrogels was not significantly affected by changes in the temperature of the solution. Urea release was influenced by pH, and the rate of urea release of GEL-B was faster than GEL-A, so pH control was needed in the application of this slow-release fertilizer.

Keywords: fertilizer; cellulose; superabsorbent hydrogel; slow-release fertilizer

■ INTRODUCTION

Continuous use of fertilizers in agriculture, especially nitrogen fertilizers can cause environmental problems [1]. Urea is the most widely used fertilizer because it has high nitrogen content (46%). On the other hand, the efficiency of urea uptake by plants generally ranges under 50% due to surface runoff, washing, and evaporation, causing urea to be accumulated in the water and cause very serious environmental problems [2] when converted into a toxic compound of nitrite.

Agricultural technology has developed many fertilizers that can be released slowly or controlled in the soil [3-4]. The performance of such fertilizers provides a large amount of fertilizer, but protect it from rapid release due to evaporation and infiltration. The fertilizer release mechanism is the transfer of nutrients from the fertilizer-

polymer interface to the polymer-soil interface [5] in the form of an adsorption-desorption process. The adsorption-desorption process is an equilibrium reaction, so it is influenced by changes in pH and temperature and also by the characteristics of the coating material, the type of fertilizer release material, and agronomic conditions.

The controlled release of fertilizers is carried out by materials such as hydrogels, polyolefins or resins and other polymer layers [1]. The formation of hydrogels with a cross-linking process will produce 3D macromolecules that have low solubility in water but absorb large amounts of water [6]. Hydrogels are generally obtained from natural sources (natural hydrogels) or are synthesized through chemical reactions. Naturally-sourced hydrogels are often called biopolymer-based hydrogels, which have some

advantageous attributes, unlike synthetic hydrogels, in terms of biocompatibility, biodegradability, non-toxicity, and bio-mimic traits. The appealing functions of cellulose-based hydrogels have inspired researchers throughout the globe to develop new materials for myriad applications in various fields, such as biomedical engineering (tissue engineering, wound dressing, drug delivery system), development of smart materials (sensors, actuators), advancement in healthcare and hygienic products (diapers, napkins) along with improvement in agriculture (pesticide carriers, water reservoir, water retention) [7].

Natural polymers have biocompatibility and lower toxic effects compared to the synthetic ones [8]. In this study, cellulose-based superabsorbent hydrogels was prepared using the epichlorohydrin crosslinking method to form a hollow or porous cellulose structure as a storage medium for fertilizers and release medium for the controlled release of urea.

■ EXPERIMENTAL SECTION

Materials

The materials used were corn cobs as a source of cellulose, epichlorohydrin, ethanol, CaCO₃, HNO₃, NaNO₂, Na₂SO₃, NaOCl, NaOH, CO(NH₂)₂, chloroacetic acid, 2-propanol, buffer solutions, ZnSO₄ and Nessler's reagent.

Instrumentation

The instruments used were SEM JEOL JED-2300, Bruker FTIR Spectrometer, and HACH DR-2000 Spectrophotometer.

Procedure

Isolation of α -cellulose

In 75 g of corn cobs, 3.5% HNO₃ (v/v) and 10 mg NaNO₂ were mixed, and then the mixture was heated at 90 °C for 2 h and the residue was refluxed with a mixture of 2% NaOH (w/v) and 2% Na₂SO₃ (w/v) at 50 °C for 1 h. Next, it was purified with 1.75% NaOCl (v/v) at 100 °C for 1 h and was then hydrolyzed with 17.5% NaOH (w/v) at 80 °C for 30 min. In the final stage, the residue was washed with distilled water and dried in an oven at 60 °C [9-10]. The produced dry powder was characterized using FTIR.

Synthesis of superabsorbent hydrogels

Preparation of GEL-A. In 3 g of cellulose, 98 g of a mixture of 6% NaOH (w/w), 4% urea (w/w), 90% water (w/w) and CaCO₃ were added, and then the mixture was stirred for 5 min and cooled for 24 h in the refrigerator to form a transparent cellulose gel. Epichlorohydrin 10% (v/v) was added to the mixture and stirred at 30 °C for 2 h and filtered to separate the gel. The gel was then washed with distilled water and dried at 40 °C to produce GEL-A [8]. GEL-A was characterized by FTIR.

Preparation of GEL-B. A certain amount of GEL-A was functionalized by adding 6.75 g NaOH, 40 mL of 2-propanol, and 10 mL of distilled water, and then the mixture was added by 7.5 g of chloroacetic acid in 10 mL of 2-propanol. The mixture was stirred for 4 h, filtered and washed with ethanol and dried at 40 °C for 3–12 h [11] to form GEL-B. Furthermore, it was characterized by FTIR.

Swelling capacity measurement. The swelling capacity of GEL-A and GEL-B in the water was measured by soaking both gels in nylon containers filled with water for 24 h at room temperature. The swelling ratio was calculated using this equation [12]:

$$\% \text{Swelling} = \frac{M_s - M_o - M_n}{M_o} \times 100 \quad (1)$$

where M_s: swollen hydrogel weight, M₁: dried cellulose hydrogel and M_o: wet nylon bag weight.

Measurement of absorbed urea concentration. GEL-A and GEL-B were individually soaked in 100 ppm of urea solution for 24 h at room temperature and were then filtered, and the urea residue in the filtrate was measured by a spectrophotometer [13]. The amount of urea concentration absorbed into the gels is the deviation of the urea concentration in the solution from the urea concentration in the filtrate. Furthermore, the gels that had been soaked were characterized by SEM and FTIR [12].

Measurement of urea released from GEL-A and GEL-B. GEL-A and GEL-B were individually soaked in 250 mL of water for 15–180 min while being stirred constantly at room temperature. The urea which was released every 15 min was monitored by measuring the urea concentration in the solution with a

spectrophotometer [13]. In addition, the urea released from GEL-A and GEL-B was analyzed in media with pH 5–9 and temperatures 18–46 °C. The urea concentration in the solution was measured by the same technique.

■ RESULTS AND DISCUSSION

Isolation of α -Cellulose

Delignification process was carried out by a multistage pulping method using a mixture of 3.5% HNO_3 and NaNO_2 . This process converts lignin to nitro lignin while eliminating hemicellulose [14]. The surface of the fibers at this stage appeared to be rougher, showing the removal of some outer non-cellulose layers such as hemicellulose, lignin, pectin and minerals [15]. Reheating was carried out in the second stage with a mixture of 2% NaOH and 2% Na_2SO_3 to complete lignin release. The next stage was the bleaching process by adding 1.75% NaOCl , accompanied by heating to form holocellulose [14]. Next, the hydrolysis process using 17.5% NaOH was conducted to produce pure α -cellulose [16].

Synthesis and Characterization of Superabsorbent Hydrogels

Hydrogels were prepared from cellulose in an aqueous solution of NaOH /urea with the addition of CaCO_3 as a pore forming material. Kabiri and Zohuriaan-Mehr [17] reported that the swelling ratio of superabsorbent hydrogels can be enhanced through porosity formed in the hydrogel structure. The physical gelation process was carried out through cooling for 24 h and the results showed that cellulose was well dispersed in the solution. Cellulose molecules in the aqueous solution below 0 °C have strong intermolecular interactions and

relatively more rigid chains, while those above 0 °C are converted to semi flexible chain conformation. Intermolecular interactions of cellulose are much stronger than between cellulose hydrates, NaOH hydrates, urea hydrates, and water molecules below 0 °C. Therefore, cellulose can be dissolved in NaOH /urea that is cooled to -10 °C, and the cellulose solution formed cannot remain in its liquid state below 0 °C for a certain time, indicating an irreversible sol-gel transition [18].

The cross-linking reaction of cellulose increases the specific degree of swelling and stable structure [19]. Epichlorohydrin (ECH) is a cross-linking agent whose reaction is catalyzed by bases (NaOH , LiOH , etc.) and is widely used for polysaccharide chains. The cross-linking process is controlled by the synergy between the chemical and physical cross-linking processes, namely the etherification reaction between the hydroxyl group of ECH and the cellulose chain (Fig. 1), as well as the cellulose chain winding through the reconstruction of hydrogen bonds in various alkaline media (NaOH , NaOH /urea, NaOH /thiourea, or LiOH /urea) [20].

Cellulose-ECH hydrogels are functionalized under alkaline conditions because the etherification reaction can be accelerated by the alkali/protonation process [11]. The hydroxyl group ($-\text{OH}$) of the cellulose molecules is activated and converted to a more reactive alkoxide (Cell-O^-) form as shown in Fig. 2 [21]. Etherification takes place in the second stage. The role of the solvent in this reaction is to provide accessibility of the etherification reagent to the reaction center of the cellulose chain [22].

The swelling ratio has a linear correlation to the absorption capacity, where a high swelling ratio indicates

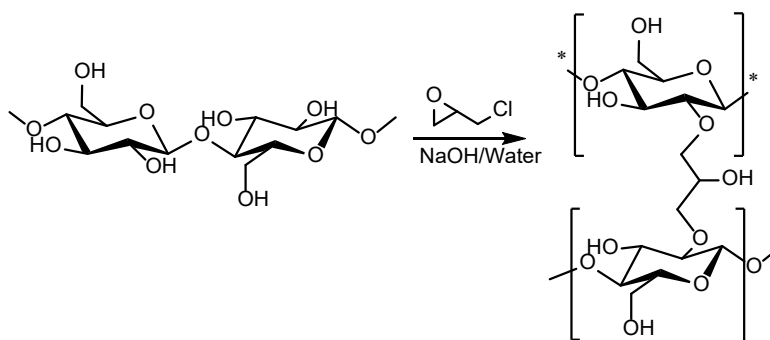


Fig 1. Mechanism of cellulose cross-linking with ECH [19]

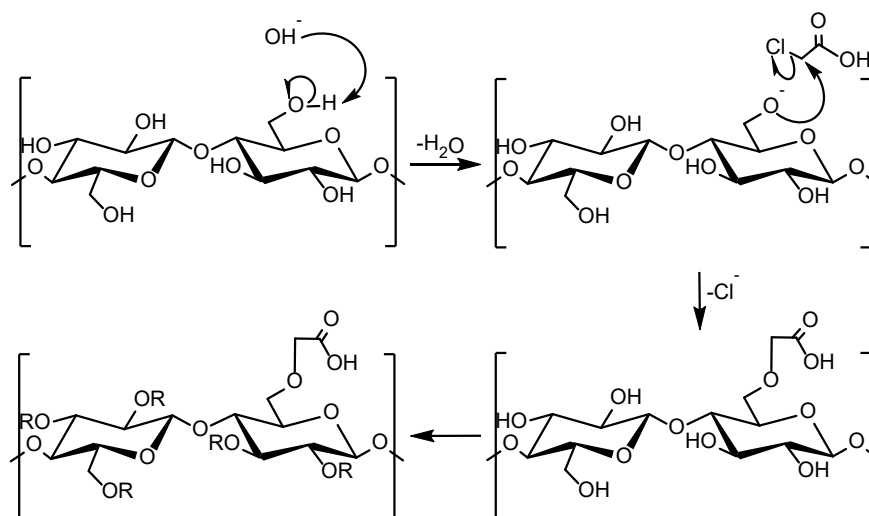


Fig 2. The mechanism for carboxymethylation of cellulose [23]

a high absorption capacity [12]. Table 1 shows the comparison of the swelling ratio of the hydrogels measured for 24 h. The swelling ratio of GEL-B was greater than that of GEL-A, due to the addition of the carboxymethyl group. The acidic characteristic of carboxymethyl causes hydrogels to be more polar, easily resonated and become more stable, resulting in greater water binding ability [11]. The swelling ratio of the hydrogels is affected by the degree of cross-linking, but it can also be affected by elasticity interaction, polymer-solvent interaction, electrostatic repulsion and osmotic pressure [12]. GEL-B after swelling appeared to be more transparent (Fig. 3(d)), showing greater water absorption, and this is the same as what was stated by Chang et al. [8], the increased space in a hydrogel material is caused by a highly hydrophilic carbonyl group

that can absorb many water molecules. When applied to agricultural land, a higher water retention capability can reduce the evaporation rate of water and consequently reduce the loss of fertilizer migrating to the soil surface [24]. It should be noted that on the ground, each hydrogel particle is surrounded by soil particles under the limiting pressure from the soil. Thus, the swelling rate of hydrogels would decrease in the soil [25].

The addition of fertilizer into hydrogel material was carried out by immersing GEL-A and GEL-B into the urea solution. Based on Table 2, greater urea absorption was achieved by GEL-B. In the urea solution, there is a group that has more hydrophilic sites such as $-\text{NH}_2^+$ and $\text{C}=\text{O}$ and will interact with $-\text{COOH}$ group of hydrogels easily [26].

Table 1. Swelling ratio comparison of GEL-A and GEL-B

Sample Code	Ms (g)	Mo (g)	Mn (g)	% Swelling
GEL-A	2.4553	0.5005	0.9804	194.68
GEL B	5.4058	0.5017	0.9642	785.30

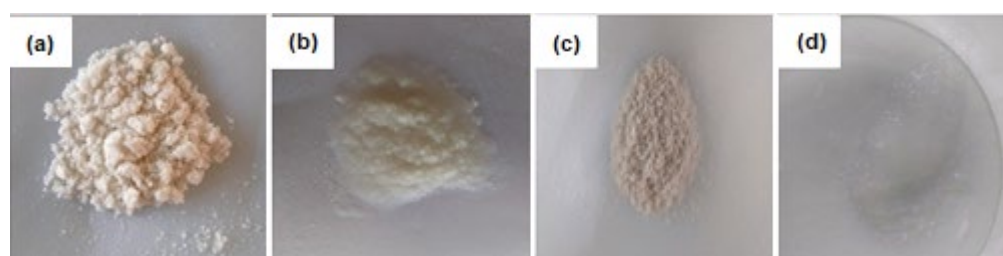
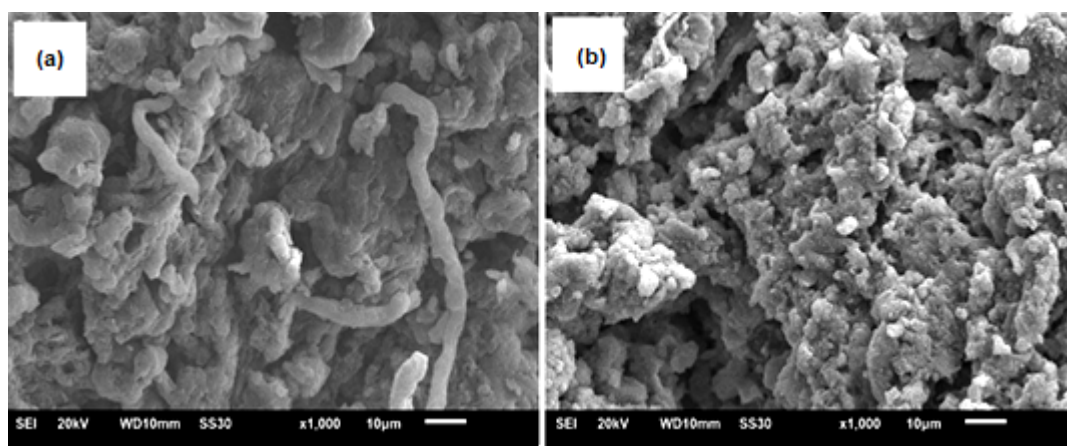


Fig 3. Hydrogels; (a) dried GEL-A, (b) swollen GEL-A, (c) dried GEL-B, (d) swollen GEL-B

Table 2. Urea absorption comparison of GEL-A and GEL-B

Sample Code	Total Urea Concentration (ppm)	Absorbed Urea Concentration (ppm)
GEL-A	100	97.75
GEL-B	100	98.33

**Fig 4.** SEM micrograph; (a) GEL-A; (b) GEL-B

SEM characterization was used to study the morphological surface of the hydrogels. In Fig. 4, GEL-A displays a heterogeneous structure, while GEL-B has a relatively more uniform surface with the presence of several small pores. Interestingly, the structure of the fibrils can be observed on the surface (Fig. 4(a)). This fibrous structure is possible due to the cellulose chain's self-association at low temperature, which becomes more obvious and orderly with the increase of gelation concentration [8]. With the addition of the carboxymethyl group to GEL-B, it was observed that the particle size decreased. Moreover, the number of pores increased, leading to an open and loose structure (Fig. 4(b)). This shows that the electrostatic repulsion caused by the carboxylic anions ($-\text{COO}^-$) character had enlarged the space in the hydrogel network. Therefore, the swelling ratio increased because water molecules can easily diffuse in hydrogel material [27].

The differences in chemical structure between cellulose and hydrogels were characterized by FTIR, and the results are shown in Fig. 5. For the isolated cellulose spectrum (Fig. 5(a)), several typical absorption peaks can be seen, including the stretching of the $-\text{OH}$ group at wave number 3447 cm^{-1} [28-29], the $-\text{CH}$ group at wave

number 2897 cm^{-1} , the $\text{C}-\text{C}$ group at wave number $1643-1425\text{ cm}^{-1}$, reinforced by the stretching vibrations of the $\text{C}-\text{O}$ group at wave number $1273-1063\text{ cm}^{-1}$ [28], and the $1,4-\beta$ glycosidic bonds at wave number 895 cm^{-1} [30]. In the GEL-A spectrum (Fig. 5(b)), the broad absorption peak at wave number 3451 cm^{-1} is the stretching of the $-\text{OH}$ group on the polymer backbone. The stretching of the aliphatic $-\text{CH}$ group is shown at wave number 2922 cm^{-1} and the absorption peak shows the glycosidic bond ($\text{C}-\text{O}-\text{C}$) at 898 cm^{-1} . Meanwhile, in the GEL-B spectrum (Fig. 5(c)), changes in absorption bands and conical peaks for the $-\text{OH}$ group at wave number 3439 cm^{-1} have been observed. On the other hand, the aliphatic $-\text{CH}$ absorption band increases to 3173 cm^{-1} , and also the $\text{C}-\text{O}-\text{C}$ group shifts to 866 cm^{-1} with a sharper peak [11]. Compared to GEL-A, the absorption band observed at wave number 1603 and 1460 cm^{-1} can be associated with asymmetric stretching of the carboxylic anion ($-\text{COO}^-$) and buckling $-\text{OH}$ in the carboxylic spectrum [8,31]. The $\text{C}-\text{O}$ group appears at wave numbers 1139 cm^{-1} and 1059 cm^{-1} . The results showed that there is a carboxyl group in GEL-B [32].

In Fig. 5(d) and Fig. 5(e), the FTIR spectrum of hydrogels after being soaked with urea solution is shown.

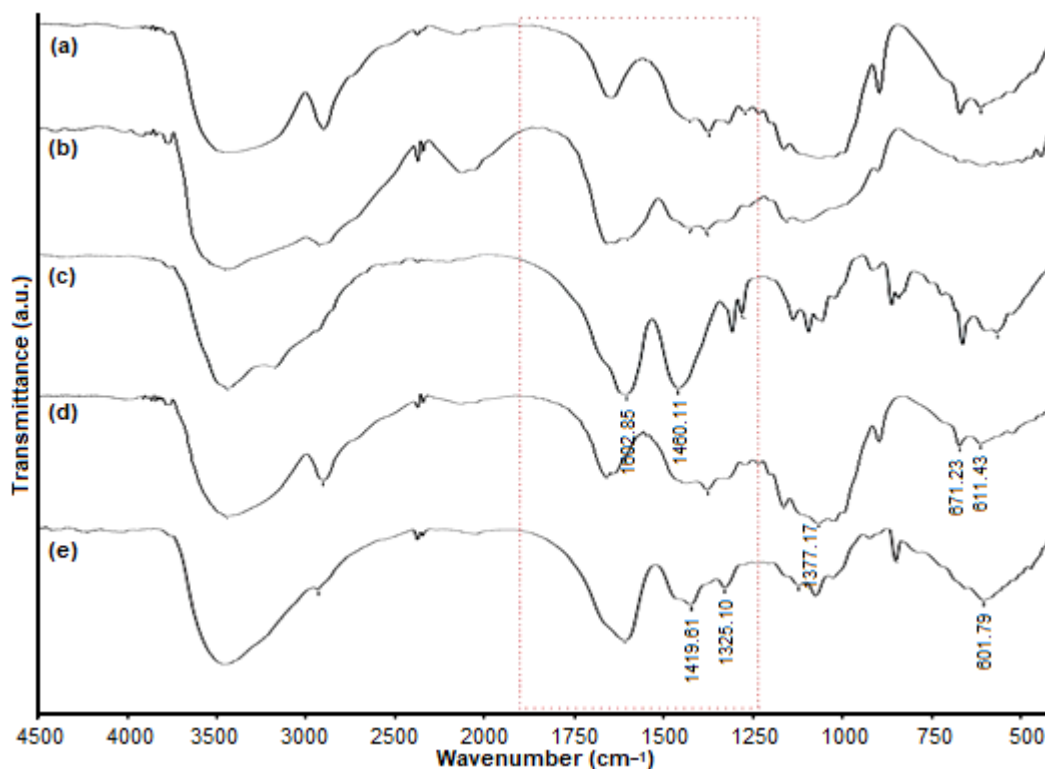


Fig 5. FTIR spectrum; (a) cellulose, (b) GEL-A before immersion, (c) GEL-B before immersion, (d) GEL-A after immersion, (e) GEL-B after immersion

The absorption peaks at wave numbers 3449 and 3445 cm^{-1} indicate the presence of the $-\text{OH}$ group and the stretching of $\text{C}-\text{H}$ was observed at wave numbers 2899 and 2928 cm^{-1} [33]. Other peaks observed are absorption bands at wave numbers 1659 and 1603, 1377 and 1325–1419, and areas around 1000–1250 cm^{-1} , indicating the presence of carboxylic anion ($-\text{COO}^-$) and $\text{N}-\text{H}$, as well as $\text{C}-\text{O}$ or $\text{C}-\text{N}$ [2,31,34]. Absorption peaks at wave numbers 611–671 and 602 cm^{-1} are associated with $\text{N}-\text{CO}-\text{N}$ flexural vibrations, showing urea involvement in GEL-A and GEL-B [34].

Urea Released from GEL-A and GEL-B

The release of urea from the hydrogels is presented in Fig. 6. Due to its high urea solubility in water, it can be assumed that without a carrier matrix, almost 100% release of urea in water will occur within minutes [25].

In the hydrogels of controlled urea, the maximum release of urea concentration from GEL-A occurred in 90 min and it was shown by a decrease in urea concentration from 95.26 ppm to 94.46 ppm. Thus, the

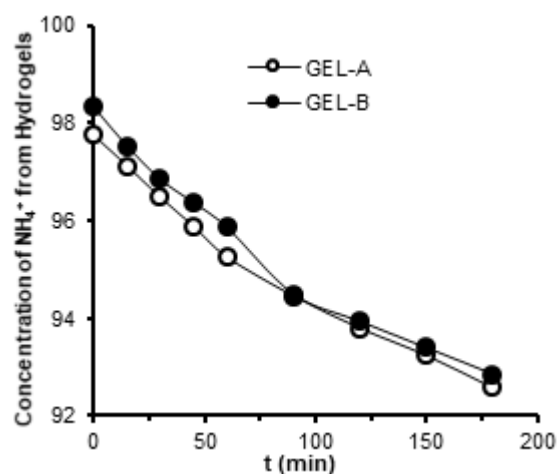


Fig 6. Slow-release of urea from hydrogels

total urea released in the 180 min period was 5.17 ppm or 5.29% of the amount of fertilizer absorbed. On the other hand, in GEL-B, the total urea released was 5.47 ppm or 5.56%. After the water entered the hydrogel layer, the fertilizer in the core was dissolved and then released in water [32]. In short, the hydrogels will gradually swell and act as a physical barrier that inhibits

the diffusion of nutrients from the polymer tissue, then the fertilizer will gradually dissolve and be released with increasing time through water exchange when the hydrogels are applied to the soil [24]. The mechanism of urea release from the hydrogel matrix is studied using the equation:

$$M_t / M_\infty = Kt^n \quad (2)$$

where M_t is the amount of urea released at time t , M_∞ is the total amount of urea present in the initial matrix, M_t/M_∞ is the fraction of urea released at time t . $n = 1$ is a continuous zero-order release, $0.5 < n < 1$ is a non-Fickian diffusion release, and $n < 0.5$ is the release dominated by Fickian diffusion. The index n can be determined by plotting $\log M_t/M_\infty$ against the $Kt^n \log$ (Fig. 7 and Fig. 8) and determining the slope of the line obtained:

$$\log(M_t / M_\infty) = n \log(t) + \log(K) \quad (3)$$

Based on the above equation, the obtained n values of GEL-A ($n = -0.0195$) and GEL-B ($n = -0.0207$) showed the release of Fickian diffusion ($n < 0.5$). The recommended release mechanism to release the urea from the hydrogels is in a "partition" manner, where the solute moves through the interface and the area of the bound to the gel with polymer matrix [35].

The influence of pH on the release of urea from the hydrogel material is shown in Fig. 9. The release by GEL-B was faster than GEL-A. If the cation concentration increases, there is an increase in osmotic pressure in the gel system which eventually causes shrinkage within [26]. This is explained by the protonation of $-\text{COO}^-$ to

$-\text{COOH}$ and the formation of hydrogen bonds between $-\text{COOH}$ at acidic pH, which restrains the electrostatic repulsion of anions, increases the cross-linking of tissues, and consequently decreases water absorption [24]. However, in a certain pH range close to neutrality (pH 6–8), most of the base groups and acid groups are non-ionizing, so the H-bond between amine acid and carboxylic acid or carbox-amide group can produce a kind of cross-linking followed by a decreased swelling. With a further increase in pH, there is an electrostatic repulsion force between the $-\text{COO}^-$ group and ionization of the carboxylic acid group. As a result, there is an expansion of the polymeric tissue which causes an increase in water absorption and swelling, subsequently, the release of urea increases and reaches a maximum at pH 9 [36]. The presence of additional ions can obviously

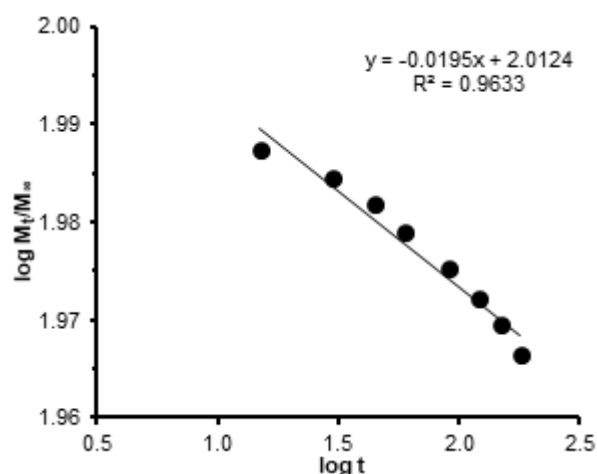


Fig 7. Index n of GEL-A

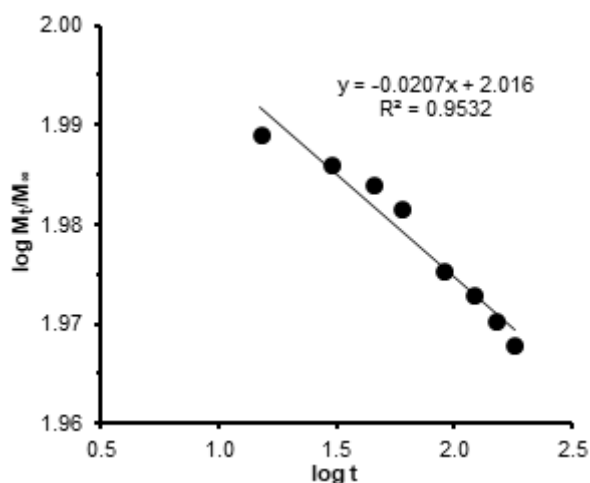


Fig 8. Index n of GEL-B

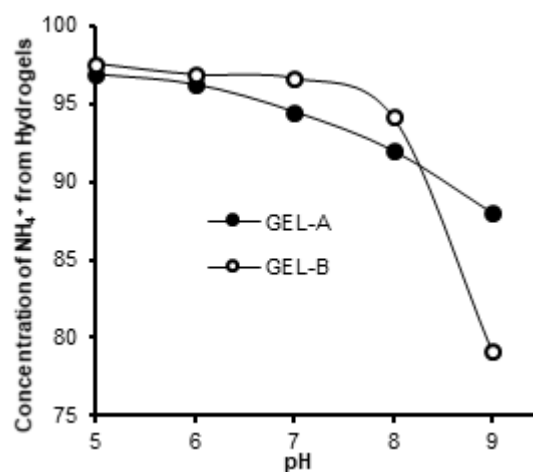


Fig 9. Effect of pH on urea release from hydrogels

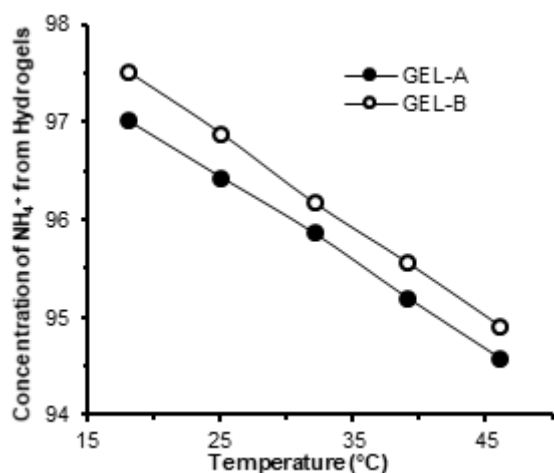


Fig 10. Effect of temperature on urea release from hydrogels

cause a slower rate of swelling and lower swelling capacity. Existing cations can produce greater fertilizer diffusion. Ions derived from the addition of a buffer solution can also play a role in increasing the concentration of urea in the release media. This means that the cations in water can accelerate the release of fertilizers by competing for adsorption sites, competitive complexing, etc. [37].

Slow-release fertilizer or controlled-release fertilizer can release nutrients due to two factors: humidity and temperature. Generally, the higher the temperature and the more available water vapors are, the faster the release of urea is [38]. This statement is in accordance with the graph in Fig. 10 which shows that as the temperature increases, the release of urea takes place quickly. Thus, the amount of urea in GEL-A has decreased from an initial concentration of 97.75 to 94.59 ppm. Whereas in GEL-B, the amount of urea released decreased from the initial concentration of 98.33 to 94.52 ppm. In the hydrophilic region, water molecules are connected by side chains through hydrogen bonds and work cooperatively to form a stable hydration shell around the hydrophobic groups. All of these interactions cause good solubility at room temperature. When the temperature rises, this system needs more energy to destroy this interaction and free trapped water molecules [39]. Lee and Yuan [40] also explained that the hydrophilic group in the polymer structure will form intermolecular hydrogen bonds between molecules with the surrounding water at low temperatures. Therefore, water that penetrates into the gel

is bound to a low temperature. The water molecule will gain enthalpy during the rise in temperature, and the hydrophilic groups in the gel will be converted into intramolecular hydrogen bonds under this condition. At the same time, hydrophobic strength will increase. These two results make the water molecules in the gel change from a bonded state to a free state and detached from the gel tissue with the release of urea. The level of immersion of the hydrogels that are sensitive to temperature also depends on the degree of water distribution. Faster response rate can be achieved if the water trapped in the hydrogels can quickly spread [36].

CONCLUSION

Superabsorbent hydrogels have been successfully synthesized and have shown their performance as the release material of controlled-release urea fertilizer. The formed GEL-A was better than GEL-B because the combination of urea and hydrogels produced a stable release of urea with a relatively lower amount of urea released (5.29%). Hydrogel application requires pH control.

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