Effect of NPK fertilizer incorporation on the characteristics of Nanocellulose-based hydrogel

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Abstract. Hydrogels are cross-linked polymers networks with high absorbing water capacity and good biocompatibility. It has been widely used as an agrochemical delivery system as well to increase the efficiency of fertilizer by releasing lower dose at a time thus protecting the environment. This research aims was to study the effect of NPK fertilizer concentration on hydrogel characteristics. The raw material used in this study was corn cobs nanocellulose. The experiment was set up in one way completely randomized design with various kinds of dose fertilizes (0, 5, 10, and 15%) with three replicates. Parameters observed were swelling ratio, moisture content, nitrogen content, potassium content, phosphorus content, texture and surface morphology. The enriched hydrogel was applied as a soil conditioner and fertilizer for chili crops. The results of analysis of variance (ANOVA) showed that the various kinds of dose fertilizers significantly influenced their physicochemical properties (p<0.05). The higher the fertilizer concentration added, the lower the swelling ratio. The addition of fertilizer with dose 5% resulted in the highest swelling ratio. This product consists of 15.82% moisture content, 1.81% of nitrogen content, 1.57% of potassium content, 0.04% of phosphorus content, and 25.17 mJ of hardness.

1. Introduction
Hydrogel are three-dimensional polymer network in hydrophilic polymer, which has the ability to imbibe large amounts of water and is not easily dissolved. Hydrogels are widely used for various purposes like diapers, wound dressings, soil conditioner, and controlled release fertilizer or agrochemical carriers. So far, most of the hydrogel made from synthetic polymers whose waste has created hazardous environmental problems since it is hard to decompose. Moreover, other problem of the overuse of mineral fertilizers, mainly fertilizers with nitrogen (ammonium and nitrate), can also cause environmental impacts [1]. The overuse of mineral fertilizers is inefficient, so it is necessary to apply several times, especially when it comes to highly mobile nutrients such as N and K. Thus, they may be leached into rivers and lakes to cause eutrophication [2].

Hydrogels can be synthesized from natural polymers such as cellulose, starch, and other polysaccharides. Hydrogels made from natural polymers promise superior properties such as being more environmentally friendly (biodegradable), non-toxic, bio-compatible and renewable. Besides, it is more affordable due to their abundance available. However, hydrogel based on carbohydrate polymers has several disadvantages, including lower water absorption and strength. In addition, it has a short nutrient release duration, less than 30 days [3].

In order to obtain such synthetic characteristics, natural polymers need to be chemically modified to increase their mechanical stability. In addition to increasing water absorption, the modification of hydrogels derived from natural polymers can also function as a carrier matrix for fertilizers to increase
its effectiveness. One of the methods to produce hydrogel is by cross-linking the polymer using such crosslinkers like epichlorohydrin, glutaraldehyde, glyoxal, sodium borate. Crosslinking addition between polymer chain affects physical properties of polymer; such as elasticity, decrease the viscosity, insolubility of the polymer, increase though and strength [4]. Good hydrogel has several criteria, including accommodate large amounts of fertilizer, release fertilizer periodically, withstand fertilizer for a long time, hold soil moisture and control soil erosion [5]. The incorporation of hydrogels with agrochemical components such as fertilizers, pesticides and other micronutrients has been quite widely studied, including the incorporation of fertilizers, pesticide cypermethrin, and copper sulfate micronutrients that have been successfully incorporated into hydrogels [6, 7].

Corn is one of important staple food in Indonesia. Corn production as 19.62 million tons of dried shelled corn and estimated produced 17.84 to 21.41 million tons of corn cobs [8]. Corn cobs are lignocellulosic rich sources having fiber content 38.99%, it has potential for producing cellulose. Hydrogel derived from cellulose exhibit unique properties such as biodegradability and biocompatibility which could be beneficial for bioengineering and agricultural purposes. Among the polymers derived from renewable sources, cellulose is highly desirable as a raw material in the production of biodegradable superabsorbent polymers because it is the most abundant natural polymer and inexpensive [9]. The research aims to study the effect of NPK fertilizer concentration on hydrogel characteristics derived from corn cobs cellulose.

2. Materials and methods

2.1. Materials
The raw material used was corn cobs came from Sukabumi, West Java. Chemicals used were sodium hypochlorite (NaClO), sodium hydroxide (NaOH 8%), and Polyethylene glycol (PEG 4%). Equipments for cellulose preparation were autoclave, magnetic stirrer, digital balance, hot plate, cold room freezer, and oven. This research used Particle Size Analyzer (PSA) Malvern Ultrafine grinder (Masuko Corp, Japan) for hydrogel characterization, Atomic Absorption Spectrophotometer (AAS), Texture Analyzer Texture Pro CT V1.2 Build 9 and Scanning Electron Microscopy (SEM) Zeiss EVO MA10.

2.2. Preparation of nano hydrogel
The first step of nano cellulose preparation was the delignification process with NaOH dan NaOCL [10]. The method of the delignification process was as follows: 220 g of corn cobs powder and 2 L of 1 M NaOH solution were put into an autoclave and heated at 110°C for 30 minutes. After cooling, the suspension was filtered by using filter paper and rinsed with excess water. Extraction with NaOH was repeated two times and continued with two times extractions using 0.6% NaOCl for 2 hours at 80°C. After that the suspension was washed with excess water until neutral. The cellulose gel was then stored in the refrigerator. Cellulose particle size reduction was carried out on cellulose suspension using an ultra-fine grinder (Masuko, Japan) with a ratio of cellulose: distilled water = 1:10. Incorporation of NPK fertilizer was carried out by soaking the known weight of hydrogel into NPK solution as three treated concentrations and reacted for 24 hours. The absorbed NPK hydrogel was then dried using an oven at 50°C.

2.3. Analysis
Hydrogel was analysed for its performance such as swelling ratio, moisture content, nitrogen content, phosphorus content, potassium content, chemical bonds using Fourier-transform Infrared Spectroscopy (FTIR), and surface morphology using Scanning Electron Microscopy (SEM). Agronomy parameter was measured such as height plant and leaves number. The experiment was set in one way completely randomized design with various kinds of dose fertilizes (0, 5, 10, and 15%) with three replicates. All data were subjected to the analysis of variance (ANOVA) using SPSS 21 version. Differences between mean values were estimated using Duncan’s multiple range test at a confidence level of 95%. All experiments were performed in three replicates.
3. Results and discussion

3.1. Swelling ratio
The main required properties of hydrogels for agricultural purposes are the high swelling rate [11]. The swelling ratio is the ratio between the weight of hydrogel that has absorbed water and the dry weight. The swelling ratio has a linear correlation to the absorption capacity, where a high swelling ratio indicates high absorption capacity [12]. The addition of NPK fertilizer at a dose of 5% showed the highest swelling ratio compared to other treatments (Figure 1). The higher the addition of dose fertilizes, the lower the swelling ratio value. Statistical analysis showed that dose fertilizes was significantly different for swelling ratio. This happens because the compositions in NPK fertilizer that can inhibit the water absorption process in nano cellulose-based hydrogel. Swelling kinetics is greatly influenced by types of hydrophilic monomers, composition of the hydrogel, the particle size, and the surface area [13]. This is because of primarily slow water penetrating into the hydrogel through capillary and diffusion in the glassy state and then, swelling is higher at first because penetrated water is absorbed by hydrophilic groups and becomes slows down until the swelling reaching the equilibrium [14].

![Figure 1. Swelling ratio of nano cellulose-based hydrogel.](image)

3.2. Moisture content
Moisture content affects the shelf life and swelling ratio. High moisture content is suitable for fungi and it will affect the quality of hydrogels. However, for agricultural use, nanocellulose-based hydrogel with high moisture content is preferable since it could be as water reservoir or soil conditioner especially at dry condition. Addition of dose fertilizes affects the moisture content of nano cellulose-based hydrogel (Figure 2). Statistical analysis showed that among treatments different significantly for moisture content. However, there were other factors affected moisture content of hydrogel, such as the number of molecules crosslinked in hydrogel, not only fertilizer dose.
3.3. Nitrogen, phosphorus, and potassium content

Nitrogen is the essential nutrient for plant and a key contributor to agricultural productivity [15, 16]. This nutrient has the main function of synthesizing chlorophyll which is then used by plants in the photosynthesis process. Each plant requires a different amount of nitrogen, but the critical limit adequacy of nitrogen ranges from 1.5 to 4.2% [17]. Based on the critical limit of nitrogen, it can be stated that the addition of 5% NPK 15:15:15 is the optimum treatment, which is 2.44%. Statistical analysis showed that this treatment was significantly different for nitrogen content.

Phosphorus is among the main limiting nutrients in soil system that creates high yield gaps [18]. The higher the dose of NPK fertilizer added to the nanocellulose, the higher the phosphorus content in the nanocellulose (Table 1). The phosphorus content in these nanocelluloses serves as a nutrient supplier for plant growth. In addition, phosphorus also has other functions, namely for the processes of photosynthesis, respiration, energy transfer and storage, and other processes in plants [19]. However, the critical limit adequacy of phosphorus also needs to be considered, where the ranges from 0.05 to 0.26% [17]. Based on the phosphorus adequacy limit, it can be stated that the addition of 5% NPK 15:15:15 fertilizer is the optimum treatment, which contains 0.191% elements. Statistical analysis showed that this treatment was significantly different for phosphorus content.

Potassium is one of the three essential macro nutrients and a key factor controlling crop productivity. Potassium contributes for tolerance against salinity as it has competing nature to sodium for binding and maintaining plant water status [20]. The potassium content that is too high or too low in nanocellulose to be applied to plants will have an impact on plant growth. The adequacy of potassium nutrient in plants ranges from 1 to 4.25% [17]. The addition of NPK 15:15:15 fertilizer by 5% is the optimum treatment which can produce potassium nutrients of 3.819%. Statistical analysis showed that this treatment was significantly different for potassium content.

| Dose fertilizes (%) | Nitrogen content (%) | Phosphorus content (%) | Potassium content (%) |
|---------------------|----------------------|------------------------|-----------------------|
| 0                   | 0.13±0.01<sup>a</sup> | 0.01±0.01<sup>a</sup>  | 0.83±0.01<sup>a</sup> |
| 5                   | 2.44±0.35<sup>b</sup>| 0.19±0.12<sup>b</sup>  | 3.82±0.12<sup>b</sup> |
| 10                  | 4.67±0.85<sup>c</sup> | 0.34±0.41<sup>c</sup>  | 4.81±0.41<sup>c</sup> |
| 15                  | 5.54±0.48<sup>d</sup> | 0.39±0.44<sup>d</sup>  | 4.84±0.44<sup>c</sup> |

Remark: numbers followed by the same letter on the same column are not significantly different based on Duncan's test 5%.

![Figure 2. Moisture content of nano cellulose-based hydrogel.](image-url)
3.4. Texture
Data from statistical analysis showed that almost all treatments were not significantly different for textures. However, there were tendencies that lower values of hardness, cohesiveness and springiness will follow on increasing on the adhesiveness. The higher swelling ability makes the presence of dissolved substances during immersion of hydrogel so that some of the crosslinking of the hydrogel weakens [21]. The addition of fertilizer could decrease the hardness and adhesiveness but increased the springiness and cohesiveness.

| Dose fertilizer (%) | Hardness (g)     | Springiness (mm) | Adhesiveness (mJ) | Cohesiveness    |
|---------------------|------------------|------------------|-------------------|-----------------|
| 0                   | 52.25±17.59<sup>a</sup> | 3.33±1.08<sup>a</sup> | 13.25±0.90<sup>b</sup> | 0.53±0.16<sup>a</sup> |
| 5                   | 25.17±7.01<sup>a</sup> | 4.23±0.32<sup>a</sup> | 9.88±2.73<sup>a</sup> | 0.62±0.03<sup>a</sup> |
| 10                  | 51.75±2.16<sup>a</sup> | 3.58±0.67<sup>a</sup> | 12.41±0.29<sup>ab</sup> | 0.52±0.14<sup>a</sup> |
| 15                  | 28.97±5.67<sup>a</sup> | 3.79±0.36<sup>a</sup> | 11.46±0.73<sup>ab</sup> | 0.67±0.20<sup>a</sup> |

Remark: numbers followed by the same letter on the same column are not significantly different based on Duncan's test 5%

Cohesiveness is an attractive attraction among similar molecules to illustrate how strong the crosslinking of hydrogel [22]. Its mean that addition of fertilizer on various dose can weaken the crosslinking of hydrogel. Springiness shows the ability of hydrogel to return to its original state after get a pressure [22]. Addition of fertilizer would increase the ability to return after get a pressure. Adhesiveness is an attractive attraction between unkind molecules that describe how weak the crosslinking [22]. It represents inversely characteristics to cohesiveness. Statistical analysis showed that this treatment was not significantly different for textures.

3.5. FTIR
The addition of fertilizer has caused stretching of the C-O cellulose carbonyl groups at 1,057-899 cm\(^{-1}\), C-H groups at 2,807 cm\(^{-1}\) and the O-H groups at 3,125 cm\(^{-1}\) due to intermolecular hydrogen binding. Another peak at 899 cm\(^{-1}\) shows the structure of cellulose [22]. The binding of fertilizer (NPK) showed at distinct peak at 1364.75 cm\(^{-1}\) (NH\(_4\)\(^+\) bending) and 1,057.9 cm\(^{-1}\) (aliphatic P-O-C), that could refer to NPK absorption. This result is agreed with other research using NPK at cellulose hydrogel from Oil palm empty fruit bunches (OPEFB) [23].

Figure 3. FTIR spectra of nano cellulose-based hydrogel.
3.6. SEM

SEM images support the formation of interconnected pore and capillary channels. Addition 5% of NPK 15:15:15 produces a larger degree of polymer chains branching and generates an additional network. The capillary channels were clearly observed from SEM image and this may enable water to enter into the hydrogel networks (Figure 4). Increasing of crosslinking will increase pore size and swelling ratio. Compared to control, the morphological structure of hydrogel incorporated NPK fertilizer showed more open and loose structure. This structure will cause the higher swelling ratio as shown at Figure 1.

![Figure 4](image)

**Figure 4.** Surface morphology of nanocellulose-based hydrogel a) 0% of NPK 15:15:15 and b) 5% of NPK 15:15:15 (5,000x magnified).

3.7. Application of nanocellulose-based hydrogel on chili

The height of chili plants in the treatment of planting media with added nanohydrogels tended to increase compared with control. However, the highest increase in plant height at 3rd week was shown in the addition of 5% NPK fertilizer. This is in line with the optimum requirements for nitrogen, phosphorus and potassium in the treatment. It was also in line with the number of chili leaves, where the treatment of 5% NPK fertilizer addition tended to be better than other treatments at 3rd week.

**Table 3.** The percentage of height increase in chili plants in several nanohydrogel treatments.

| Treatments | Week  |
|------------|-------|
|            | I     | II    | III   |
| Control    | 0.28±0.01<sup>a</sup> | 0.73±0.02<sup>a</sup> | 0.84±0.04<sup>a</sup> |
| Dose 0%    | 3.72±0.86<sup>b</sup> | 9.83±1.06<sup>c</sup> | 13.17±2.64<sup>d</sup> |
| Dose 5%    | 0.39±0.02<sup>a</sup> | 4.71±0.85<sup>b</sup> | 16.49±1.73<sup>c</sup> |
| Dose 10%   | 0.34±0.05<sup>a</sup> | 2.74±0.76<sup>b</sup> | 7.20±1.21<sup>c</sup> |
| Dose 15%   | 3.25±0.92<sup>b</sup> | 4.58±1.10<sup>b</sup> | 3.83±0.71<sup>b</sup> |

Remark: numbers followed by the same letter on the same column are not significantly different based on Duncan's test 5%.

**Table 4.** The number of chili leaves in several nanohydrogel treatments.

| Treatments | Week  |
|------------|-------|
|            | I     | II    | III   |
| Control    | 8.00±2.17<sup>c</sup> | 6.33±1.13<sup>b</sup> | 6.67±1.32<sup>b</sup> |
| Dose 0%    | 7.00±1.38<sup>b</sup> | 5.67±0.95<sup>a</sup> | 5.67±1.20<sup>a</sup> |
| Dose 5%    | 7.33±1.25<sup>b</sup> | 7.33±1.04<sup>b</sup> | 9.00±1.10<sup>c</sup> |
| Dose 10%   | 6.00±0.84<sup>a</sup> | 4.67±1.11<sup>a</sup> | 5.33±1.16<sup>a</sup> |
| Dose 15%   | 6.33±0.99<sup>a</sup> | 4.00±1.04<sup>a</sup> | 4.33±1.07<sup>a</sup> |

Remark: numbers followed by the same letter on the same column are not significantly different based on Duncan's test 5%.
4. Conclusions
The addition of fertilizer with dose 5% produced the highest swelling ratio and improved chilli performance. This product consists of 15.82% moisture content, 1.81% of nitrogen content, 1.57% of potassium content, 0.04% of phosphorus content, and 25.17 mJ of hardness.

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