Synthesis and characterization of hydrogel NaCMC-g-poly(AA-co-AAm) modified by rice husk ash as macronutrient NPK slow-release fertilizer superabsorbent

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Abstract. In this study, sodium carboxymethyl cellulose (NaCMC) based hydrogel grafted by poly (acrylate-acrylamide) by addition of rice husk ash (RHA) and NPK fertilizer to the superabsorbent with in-situ polymerization was successfully synthesized. In this work, the effect of NaCMC concentration and mass of RHA was done. The best water swelling capacity with 3 % NaCMC, 15 % RHA is 480 g/g with percentage of water release capacity is 38 %. Then, the effect of NPK fertilizer concentration on in-situ polymerization was carried out and the best swelling capacity with 5 % NPK mass is 650.10 g/g and percentage of release capacity obtained is 25.20 % for 6 days. The successful of the synthesis of hydrogels NaCMC-g-poly(AA-co-AAm) modified by rice husk ash as macronutrient NPK slow-release fertilizer superabsorbent supported by functional group was characterized by Fourier Transform Infrared (FTIR) and surface morphology by Scanning Electron Microscopy (SEM). The hydrogels based on NaCMC biopolymers and silica from rice husk ash as macronutrient NPK slow-release fertilizer superabsorbent produced slow release can be controlled and a promising material in the future and can be applied in agriculture field.

Keywords: acrylamide, acrylic acid, hydrogel, rice husk ash, superabsorbent

1. Introduction
Superabsorbent hydrogel is a three-dimensional crosslinked polymer network, which can absorb and retain liquid within its structure [1]. In agriculture sector, especially in arid areas, the usage of superabsorbent hydrogel can reduce irrigation water consumption and plants death rate, and also increase soil’s fertility [2]. In its application, adding fertilizers into superabsorbent hydrogel can increase the nutrition absorbed by plants [3].

The use of chemical fertilizers is one of the most vital factors in agricultural production [3]. To improve the products quality in agriculture, the role of chemical fertilizer is very important [4]. However, an excessive usage of chemical fertilizer may pollute the surrounding environment [5]. One of the most effective ways to overcome those issues is by modifying them into slow-release fertilizer superabsorbent in order to release nutrient in a controlled rate [6].

The utilization of polysaccharides such as cellulose has been reported as a useful material to synthesize superabsorbent hydrogel for nutrient release in plants [7]. Cellulose is an abundant, inexpensive, renewable, and biodegradable biopolymer; hence it is often used as the backbone of a hydrogel [8,9]. However, intermolecular and intramolecular hydrogen bonds among hydroxyl groups in the backbone not
only limit its solubility in water, but also make cellulose less reactive. Therefore, to increase water solubility of cellulose derivatives such as carboxymethyl cellulose is used [10]. Superabsorbent that only consists of organic materials has some weaknesses, e.g. low absorption capacity, weak mechanical strength, and prone to the change of temperature. Therefore, inorganic materials such as montmorillonite, attapulgite, kaolin, and bentonite are often used in the preparation of superabsorbent [2, 11–13]. However, recently, the use of silica as composite has drawn attention because it can be produced from rice husk ash (RHA) by calcination [14]. The presence of silica nanoparticles within the hydrogel matrix improves its swelling capacity, which is an important factor in agricultural application due to hydrophilicity effect given by silica nanoparticles to enhance water retention ability of the hydrogel composite. The interactions of hydrogen bonds between functional groups of hydrogel and hydroxyl groups of silica nanoparticles create additional physical crosslink within the hydrogel network thus increases its strength [3,15]. Moreover, silica is an essential micronutrient for plants and is easily absorbed when hydrogel has degraded in the soil medium. Silica highly affects the plants growth because silica leads to the nutrient’s imbalance within the plant. In addition, silica can also improve plants resistance to pests and cold weather [16,17].

In this study, a synthesis method of hydrogel superabsorbent nanocomposite by using sodium carboxymethyl cellulose, which was more soluble in water, is proposed, where our previous researches used cellulose [18,19]. The used silica nanoparticles from rice husk ash as filler in hydrogel matrix improved its swelling capacity and controlled release [20]. In this work, the effect concentration of NaCMC, RHA and NPK to superabsorbent nanocomposite fertilizers in-situ NPK was done and the swelling-release capacity for water and release NPK fertilizer were studied. The superabsorbent nanocomposite was characterized using Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM).

2. Experiments

2.1. Materials
The materials used were sodium carboxymethyl cellulose, NaCMC (Merck Co.) as backbone, rice husk from Bukittinggi, HCl (Merck Co.) and H2SO4 (Merck Co.) for nanosilica preparation from rice husks, nitrogen gas to eliminate dissolved oxygen, acrylic acid (Merck Co.) and acrylamide (Merck Co.) as monomers, N,N’-methylenebisacrylamide (Sigma) as crosslinking agent, potassium persulfate (KPS) as initiator, ethanol (Merck Co.) and acetone (Merck Co.) to rinse the superabsorbent, and NPK fertilizer as urea, potassium phosphate and ammonium phosphate (Merck Co.)

2.2. Nanosilica preparation from rice husk
Nanosilica has been synthesized according the protocol developed by previous researcher [20]. Rice husks were washed with distilled water. Then, the solution was dipped in HCl 3 % and heated by reflux at 100 °C for 2 hours and stirred. The same process was repeated by replacing HCl 3 % with H2SO4 10 % and filtered, washed with distilled water. Finally, rice husks were calcinated in a furnace at 900 °C, rice husk ash (RHA) was obtained.

2.3. Superabsorbent nanocomposite synthesis
Superabsorbent nanocomposite has been synthesized according the protocol developed by previous researcher [10]. NaCMC powder was dissolved in distilled water then RHA was added while being stirred until the mixture thickened. The mixture was then flowed by nitrogen gas at 60 °C and was added by potassium persulfate (KPS). Then, acrylic acid (AA), acrylamide (AAm) and N,N’- methylenebisacrylamide (MBA) were added into the solution. The solution was heated at 70 °C for 2 hours in order for the polymerization reaction to be completed. Then, the product was immersed in acetone for 24 hours. In this work, the effect of NaCMC mass (1, 2, 3) wt.% with code; SC1, SC2, SC3 and RHA (10,15, 20) wt.% with code; SC4, SC5 and SC6, it was observed the swelling-release capacity for water, NPK fertilizer and was characterized by FTIR and SEM.

2.4. Synthesis of superabsorbent nanocomposite with in-situ NPK as slow-release fertilizer
A similar procedure from our previous work was carried out to synthesize slow-release fertilizers by adding NPK fertilizer during polymerization [13]. In this work, the effect of NPK mass (3, 4, 5) wt.% with code; SC7, SC8 and SC9, respectively with the same composition of N (urea), K (potassium phosphate) and P (ammonium phosphate).

2.5. Swelling-release capacity determination

In this work, the water swelling capacity was determined by gravimetric method, 0.1 g superabsorbent was immersed in 200 mL of distilled water at room temperature with a certain time for 8640 minutes. Superabsorbent was then removed from the absorbate to measure its weight. The calculation was done by the similar equation from our previous work [13].

To determine the release capacity, swollen superabsorbent was immersed in 200 mL of 0.9 % NaCl solution, and then weighed in a certain time. Release capacity was calculated with the following equation:

\[
\text{Water release capacity} = \frac{w_0 - w_t}{w_o} \times 100 \%
\]  

(1)

where \(w_0\) is the superabsorbent weight before release and \(w_t\) is the superabsorbent weight after release at a certain time.

Meanwhile, to determine N, P and K release capacity, the similar procedure was the same as water release capacity, but the concentration of N, P and K was determined by the visible spectrophotometer. The release capacity of N, P and K was calculated with the following equation:

\[
\text{N, P and K release capacity} = \frac{C_1 - C_0}{C_0} \times 100 \%
\]  

(2)

where \(C\) is the superabsorbent concentration before release and \(C_1\) is the superabsorbent concentration after release at a certain time.

3. Results and discussion

3.1. Swelling-release capacity

3.1.1. Water swelling capacity. Figure 1a shows the swelling capacity to time with various concentrations of NaCMC (SC1, SC2, SC3) and RHA (SC4, SC5, SC6). The optimal swelling capacity increased by the rising of NaCMC concentration. It can be seen that superabsorbent nanocomposite with NaCMC composition of 3 wt.% has the best swelling capacity in water is 420.0 g/g (SC3). This is due to the more backbone added; the more monomers are grafted so that the active groups and swelling capacity were increased. The swelling capacity increased with the increasing of RHA weight and obtained optimum RHA 15 wt.% is 480 g/g. Addition of rice husk ash (RHA) to the superabsorbent not only increases its mechanical strength, but can also increase the swelling capacity because the electrostatic repulsion force between the –COO- group of polymer chains and the negatively charged surface of SiO₂ nanoparticles causes the superabsorbent network to be easily expanded. However, in RHA 20 wt.% there is a decrease in swelling capacity. This is caused by the excessive interaction between the surface of the -OH group of silica nanoparticles and the superabsorbent hydrogel polymer component, so that the more of the physical crosslinking increases. Therefore, the cavities between the polymer chains are reduced, resulting in the decrease swelling capacity [3]. Figure 1b shows the maximum swelling capacity of superabsorbent nanocomposite at equilibrium time of 8000 minutes in water of SC1, SC2, SC3, SC4, SC5 and SC6 are 300.60, 350.50, 420.10, 400.60, 480.30 and 450.20 g/g, respectively. It can be seen that the best swelling capacity is obtained at 480.30 with a composition of NaCMC 3 wt.% and RHA 15 wt.% (SC5).

Swelling capacity of slow release superabsorbent nanocomposite fertilizers in-situ NPK with various NPK mass; (3, 4, 5) wt.% (SC7, SC8, SC9) in water is shown in figure 2. Figure 2a shows water swelling capacity to time with various mass of NPK. The optimal swelling capacity increases by the rising of NPK mass. The presence of NPK in the superabsorbent increases the swelling capacity. This is due to the hydrophilic of the NPK group. Figure 2b shows the maximum swelling capacity of superabsorbent nanocomposite in-situ NPK at equilibrium time of 8000 minutes in water of SC7, SC8 and SC9 are
Figure 1. (a) Swelling capacity to time and (b) optimum swelling capacity SC1 to SC6

Figure 2. (a) Swelling capacity to time and (b) optimum swelling capacity SC7 to SC9

Figure 3. Water release capacity of (a) SC1 to SC6 and (b) SC7 to SC9

550.30, 610.30 and 650.10 g/g, respectively. It shows that the best swelling capacity is obtained at 650.10 with composition of NaCMC 5 wt.%, RHA 15 wt.% and NPK 5 wt.% (SC9).

3.1.2. Release capacity. Nanocomposite superabsorbents that have swollen at the maximum swelling capacity are determined by the release capacity of water. Release capacity is determined to obtain a controlled slow release superabsorbent so that the superabsorbent can hold water to be released in certain time period. The maximum release capacity of SC1 to SC6 superabsorbent nanocomposite is shown in figure 3a and the superabsorbent nanocomposite SC7 to SC9 in figure 3b. Figure 3a shows the optimal
release capacity at time 8640 minutes or 6 days with various concentrations of NaCMC (SC1, SC2, SC3) and RHA (SC4, SC5, SC6). The optimal release capacity decreased by the rising of NaCMC concentration. It shows that superabsorbent hydrogel with NaCMC composition 3 wt.% has the best water release capacity percentage of 50% (SC3). The release capacity percentage decreased with the increasing of RHA weight and obtained the optimum RHA 15 wt.% of 38%. Addition of rice husk ash (RHA) to the superabsorbent not only increases its mechanical strength, but can also decrease the release capacity. This is caused by the interaction between the surface of the -OH group of silica nanoparticles and the superabsorbent hydrogel polymer component, so that the more of the physical crosslinking, so that the ability to hold water is better and caused a decrease of water release capacity. Figure 3b shows the maximum release capacity of superabsorbent nanocomposite with various NPK concentrations of SC7, SC8, SC9 are 35.20, 30.10, 25.15 %, respectively. The release capacity percentage decreased with the increasing of NPK weight, it shows that the best release capacity percentage is obtained at 25.15 % with a composition 3 % NaCMC, 15 % RHA and 5 % NPK (SC9) at 6 days.

Figure 4a shows that the optimal NPK fertilizer release capacity at time 8640 minutes or 6 days with various NPK mass. The total NPK release capacity percentage decreased with the increasing of NPK weight of SC7, SC8 and SC9 are 40.10, 35.15 and 30.10, respectively. This is caused by interaction between the superabsorbent hydrogel polymer components with NPK fertilizer so that the ability to hold water is better so that decreases the water release capacity. The NPK fertilizer and water are released simultaneously so the total NPK fertilizer release capacity is also decreased. It shows that the best of release capacity percentage obtained is 25.20 % with the composition 3 % NaCMC, 15 % RHA and 5 % total NPK (SC9) at 6 days.

3.2. Characterisation

3.2.1. Characterisation using FTIR. Functional groups analysis is shown in figure 5. Figure 5a shows that the peak appeared at 470 cm⁻¹ is related to Si-O-Si bending vibration. Meanwhile, the peaks at 805 and 1104 cm⁻¹ are related to symmetric and asymmetric vibrations of Si-O-Si, respectively [15]. Absorption band that appeared in rice husk ash's spectrum in 3400-3600 cm⁻¹ is related to stretching vibration of –OH of silanol [14]. In the same wavenumber range, a wide absorption band also appeared in spectrum (figure 5b) related to –OH stretching vibration [10]. A peak –COO appeared in 1597 cm⁻¹ and the peaks at 1413 and 1061 cm⁻¹, the absorption bands –CH, scissoring vibration and CH–O–CH stretching, respectively [21]. Figure 5c shows the spectrum of superabsorbent nanocomposite, a peak at 1628 cm⁻¹ is related to –COO of acrylic acid (AA) and the peaks at 3200-3600 cm⁻¹ weakened, it shows –OH from each of its components, the peak weakened due to polymerization reaction occurs which indicates the formation of a nanocomposite hydrogel. Figure 5d shows pure NPK fertilizer and figure 5e is superabsorbent nanocomposite in-situ NPK. From these two spectra peaks, it shows broad absorption bands at 3100-3600 cm⁻¹ related to –OH and overlapped with –NH group, it shows that the spectrum of pure NPK having sharp
Figure 5. FTIR Spectra of (a) RHA, (b) NaCMC, (c) SC5, (d) pure NPK fertilizer and (e) SC9

peaks. While in the superabsorbent nanocomposite in-situ NPK in figure 5e obtained the peak weaken and widen at 3100-3600 cm⁻¹, this indicates there is interaction between NPK fertilizer and components of superabsorbent. In the peak of 1719 cm⁻¹ related to –COO stretching vibrations from carboxyl methyl cellulose and acrylic monomers. The peak finger print region at 550 cm⁻¹ related to PO₄ group from NPK fertilizer and on superabsorbent nanocomposite in-situ NPK shows weak peak because there is interaction

Figure 6. Micrographs of (a) RHA, (b) NaCMC, (c) SC5, (d) pure NPK fertilizer and (e) SC9
with the component of superabsorbent. It supported that the successful synthesis of in-situ NPK nanocomposite superabsorbents.

3.2.2. Characterization using SEM. Morphology analysis using SEM is shown in figure 6. Figure 6a shows that the RHA has particles with irregular size and shape and with rough surface with large porosity. Figure 6b shows NaCMC has smooth and uniform fiber that is evenly spread. While figure 6c shows that superabsorbent nanocomposites which are a combination of NaCMC, RHA and other components have smooth surface and it can be observed that fibers from NaCMC as backbone and RHA as fillers are evenly distributed with fine pores. Figure 6d shows NPK fertilizer has an evenly distributed granule-like surface derived from urea as N, potassium phosphate as K and ammonium phosphate as P sources. Figure 6e shows superabsorbent nanocomposite in-situ NPK has smooth pores and NPK fertilizer distributed on the surface has the similarity of pure NPK fertilizers (figure 6d). The surface morphology by SEM proves that the NPK fertilizer has been successfully encapsulated into the superabsorbent nanocomposites.

4. Conclusions
In this study, we developed superabsorbent nanocomposite and slow-release fertilizers in the form of superabsorbent through in-situ polymerisation. The result shows that the optimal NaCMC and RHA composition are 3 wt.% and 15 wt.%, respectively. Superabsorbent nanocomposite in-situ is synthesized by varying the NPK fertilizers mass, increasing of mass lead to increase the swelling capacity and decreasing release capacity. The optimal swelling capacity of superabsorbent nanocomposite with in-situ NPK in water is 650.10 g/g. The optimal total NPK release capacity of superabsorbent nanocomposite with in-situ NPK is 25.20 %. The successful of the synthesis of hydrogels nanocomposite in-situ NPK fertilizer superabsorbent supported by functional group were characterized by FTIR and surface morphology by SEM. The hydrogels NaCMC-g-poly(AA-co-AAm) modified by rice husk ash as macronutrient NPK slow-release fertilizer superabsorbent that are successfully synthesized show that NPK fertilizers slow release can be controlled and could be an interesting material for the future application in agriculture.

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References
[1] Alla S G A, Sen M and El-Naggar A W M 2012 Carbohydr. Polym. 89 478–85
[2] Wu L, Liu M and Liang R 2008 Bioresour. Technol. 99 547–54
[3] Olad A, Gharekhani H, Mirmohseni A and Bybordi A 2017 Polym. Bull. 74 3353–77
[4] Zhang S, Guan Y, Fu G, Chen B, Peng F, Yao C and Sun R 2014 Journal of Nanomaterials 2014 ID 675035
[5] Rashidzadeh A and Olad A 2014 Carbohydr. Polym. 114 269–78
[6] Hemvichian K, Chanthawong A and Suwanmala P 2014 Radiat. Phys. Chem. 103 167–71
[7] Zhong K, Lin Z T, Zheng X L, Jiang G B, Fang Y S, Mao X Y and Liao Z W 2013 Carbohydr. Polym. 92 1367–76
[8] Chang C and Zhang L 2011 Carbohydr. Polym. 84 40–53
[9] Sannino A, Demitri C and Madaghièele M 2009 Materials 2 353–73
[10] Bao Y, Ma J and Li N 2011 Carbohydr. Polym. 84 76–82
[11] Liang R and Liu M 2006 Ind. Eng. Chem. Res. 45 8610–6
[12] Schexnaldler P and Schmidt G 2009 Colloid Polym. Sci. 287 1–11
[13] Helmiyati and Syarifudin A 2018 AIP Conf. Proc. 2023 020080
[14] Chandrasekhar S, Pramada P N and Praveen L 2005 J. Mater. Sci. 40 879–87
[15] Suriyaprabh R, Karunakaran G, Yuvakkumar R, Prabu P, Rajendran V and Kannan N 2012 J. Appl. Polym. Sci. 123 879–87
[16] Yuvakkumar R, Elango V, Rajendran V, Kannan N S and Prabu P 2011 Int. J. Green Nanotechnol. 3 180–90
[18] Helmiyati and Apriliza M 2017 *IOP Conf. Ser.: Mater. Sci. Eng.* **188** 012019.
[19] Helmiyati, Fitriyani A and Meyanti F 2017 *IOP Conf. Ser.: Mater. Sci. Eng.* **188** 012051
[20] Gharekhani H, Olad A, Mirmohseni A and Bybordi A 2017 *Carbohydr. Polym.* **168** 1–13
[21] Biswal D and Singh R 2004 *Carbohydr. Polym.* **57** 379–87