Superabsorbent nanocomposite as micronutrient slow-release fertilizer

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Abstract. In this research, sodium alginate grafted by poly(acrylate-co-acrylamide) loaded montmorillonite (MMT) and the addition of boric acid as micronutrients into the superabsorbent nanocomposite through in-situ method have been successfully synthesized. We developed superabsorbent nanocomposite with montmorillonite obtained by increasing the amount of montmorillonite, which would increase the swelling capacity and by adding boric acid micronutrients will also increase water swelling capacity. The best swelling capacity to water of superabsorbent nanocomposite obtained 426.337 g/g that formulated with MMT contents approximately 20.0 % wt and 0.1 g boric acid. The optimal release capacity of boric acid is 25.561 % for 8000 min or about 6 days. This is supported by the study of kinetics for the water swelling in pseudo second-order while the boric acid release is pseudo first-order obtained. The nanocomposite superabsorbents that are successfully synthesized show that the release of boric acid micronutrients as slow release can be controlled and denoted interesting materials to be applied in agriculture.

Keywords: montmorillonite, micronutrient, nanocomposite, sodium alginate, superabsorbent

1. Introduction
Soil nutrition control for agriculture is extremely vital because when not being fulfilled, plants will show deficiency symptoms, that is slow growth, imperfect fruit development, dry leaves, etc. [1]. Soils’ need for nutrient based on the required amount is classified into two classes, macronutrient and micronutrient. Therefore, macronutrient and micronutrient nutrition need to be controlled in order to gain ideal plants [2,3]. Micronutrient is one of the important nutrients used by plants in small amount, because micronutrient in plants usually has a role as a catalyst and thus only needed in a small amount. The amount and quality of agricultural products are highly affected by micronutrient. One of micronutrient elements for plants growth is boron [4].

Although micronutrient is needed only in a small amount, its importance in plants is as significant as macronutrient. Boron is one of micronutrients that is essential for the growth. Boron has a role in cell formation or multiplication, especially in shoots growth point, and also in the growth of pollen powder, flowers, and roots. In boron-deficient plants, sugar translocation and absorption decrease a lot. Boron may also act as inhibitor that controls the activity of enzymes that lead to the formation of toxic phenolic substances. Other symptoms of boron-deficiency are thickening, darkening, and decreasing size of leaves [5]. At present, to distribute nutrients of macro and micro fertilizers is by directly spread to the soil, so that a lot of fertilizer will be wasted. Therefore, to solve those issues, a technology such as superabsorbent nanocomposite that can release nutrients in a controlled behavior is developed, so that the amount of nutrition given to plants will not be excessive [6,7].

Superabsorbent based on alginate grafted with the monomers of acrylic acid and acrylamide have been extensively used in agriculture. The clay addition to superabsorbent nanocomposite has attracted
Table 1. Superabsorbent nanocomposite variation

| Superabsorbent nanocomposite code | MMT (%) | Micronutrient boric acid (g) |
|----------------------------------|---------|----------------------------|
| SN 1                             | 10      | -                          |
| SN 2                             | 15      | -                          |
| SN 3                             | 20      | -                          |
| SN 4                             | 10      | 0.1                        |
| SN 5                             | 15      | 0.1                        |
| SN 6                             | 20      | 0.1                        |

attention because of its high swelling capacity and controlled release [8–10]. Researches regarding superabsorbent nanocomposite have been done in various fields, such as in industry; diapers [11], drug release [12,13], agriculture [14], and waste water treatment [15].

In this study nanocomposite superabsorbents using boric acid micronutrients referred to Bortolin et al. [2], and combined with our previous study [16,17] using sodium alginate biopolymer as a backbone have been synthesized successfully. The swelling-release of superabsorbent nanocomposites of boric acid was studied. The synthesis results were supported by characterization using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR).

2. Experiments

2.1. Materials
The materials used were sodium alginate biopolymer as backbone, while served as monomers were acrylic acid and acrylamide, potassium persulfate as initiator, N,N'-Methylenebisacrylamide as crosslinking agent (all from the Merck), montmorillonite as clay (Sigma-Aldrich), and boric acid as micronutrient sources (Sigma-Aldrich).

2.2. Superabsorbent nanocomposite preparation
A superabsorbent nanocomposite preparation was referred to our previous study [17]. By modification, using montmorillonite as inorganic in various concentrations then obtained the optimum conditions and furthermore boric acid micronutrients were added. Whereas, other reagents were constant; sodium alginate is 3 wt.%., 1.2% KPS initiator is 5 mL, 20% acrylamide is 6 mL, acrylic acid: NaOH (7: 3) is 7 mL and 0.5% MBA 10 mL. The composition of montmorillonite variations can be seen in table 1.

2.3. Swelling-release capacity
In this study the swelling process done in water was determined by gravimetric method and release of boric acid from superabsorbent by visible spectrophotometry. Swelling capacity was calculated using equation (1) [17].

\[
Swelling\ capacity\ (g/g) = \frac{w_t - w_o}{w_o}
\]

where \( w \) is the initial weight of the superabsorbent and \( w_t \) is the superabsorbent weight after swelling at a certain time. Release capacity was calculated using the equation (2).

\[
Release\ capacity\ (%) = \frac{m_o - m_t}{m_o} \times 100\%
\]

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

3. Results and discussion

3.1. Preparation of superabsorbent nanocomposite

3.1.1. Water swelling capacity of superabsorbent nanocomposite. In this study, preparation of nanocomposite superabsorbents with variations of montmorillonite (SN1, SN2, SN3) which have been synthesized, then determined for the swelling capacity with water, can be seen in figure 1a and
Table 2. Optimal swelling capacity of superabsorbent nanocomposite

| Superabsorbent Code | Swelling Capacity (g/g) |
|---------------------|-------------------------|
| SN 1                | 108.995                 |
| SN 2                | 156.080                 |
| SN 3                | 188.581                 |
| SN 4                | 237.313                 |
| SN 5                | 329.511                 |
| SN 6                | 426.337                 |

Figure 1. Swelling capacity of (a) superabsorbent nanocomposite and (b) with micronutrients boric acid addition.

nanocomposite superabsorbents by addition of boric acid micronutrients (SN4, SN5, SN6) can be seen in figure 1b.

As seen in figure 1a, optimal swelling capacity increases by rising montmorillonite concentration. This is due to the addition of montmorillonite (MMT), in which MMT has negative surface charge (OH group), resulting in a repulsion force between the COOH group on the sodium alginate backbone and MBA. The negative charge on the surface of the MMT results in the increasing expansion of the superabsorbent structure, so that the swelling capacity is also high [18]. As seen in figure 1b, similar things also occur with the addition of boric acid. Addition of boric acid will increase swelling capacity, where boric acid or orthoboric acid has three hydroxyl groups with negative charge on the surface, resulting in a repulsion force between the COOH group on the sodium alginate backbone and MBA. The negative charge on the nanocomposite superabsorbents surface comes from boric acid and the high MMT, so the swelling capacity by using boric acid in figure 1b is higher than the swelling capacity in figure 1a. Optimal swelling capacity of superabsorbent nanocomposite can be seen in table 2.

Boric release capacity of superabsorbent nanocomposite. Nanocomposite superabsorbents that have been swollen at the maximum swelling capacity were done with the release capacity test of boric acid determined by the visible spectrophotometer with a wavelength of 545 nm, which can be seen in figure 2. In figure 2a it can be seen swelling capacity to time and obtained an equilibrium time around 8000 min and the highest swelling capacity at the montmorillonite concentration 20 % (SN6) has a release capacity higher than the other montmorillonite concentrations. In figure 2b it can be seen the optimum release capacity of SN4, SN5 and SN6. From the results of release capacity, it can be seen that the obtained nanocomposite superabsorbent is good as a controlled slow release fertilizer with the highest release capacity of 25.561 % for 8000 min or about 6 days.
3.2. Characterization of superabsorbent nanocomposite

3.2.1. Characterization by FTIR. In figure 3a, it can be seen boric acid has characteristic peaks around 600, 750, 810, 1210, and 1400 cm\(^{-1}\), indicating the presence of BO\(^3\) ions [2]. In figure 3b, it can be seen montmorillonite (MMT) spectrum, a peak of Si-O stretching appears at 1010 cm\(^{-1}\). Figure 3c can be seen sodium alginate spectrum, the absorption band at 3200–3600 cm\(^{-1}\) are OH groups. At 675 cm\(^{-1}\) of C-H stretching, the characteristic of sodium alginate at 828 cm\(^{-1}\) of C–H vibration from β-mannuronic acid, at 960 cm\(^{-1}\) of C-H stretching vibration of guluronic acid at 1603 cm\(^{-1}\) of O-C-O asymmetric and at 1410 cm\(^{-1}\) of symmetric carboxylate stretching vibration. In figure 3d, nanocomposite superabsorbent without boric acid (SN 3) can be seen the peak of Si-O from montmorillonite shifts to 1100 cm\(^{-1}\), the characteristic of sodium alginate appears and the O-H peak is weakened due to the interaction of this group with the monomer, crosslinking component as forming superabsorbents. Figure 3e is nanocomposite superabsorbents with in-situ boric acid (SN 6) can be seen the peak of Si-O from montmorillonite shifts to 1030 cm\(^{-1}\) and the characteristic of sodium alginate appears and peak of the boric acid characteristic can be observed around 600-1400 cm\(^{-1}\) with a weaken peak. It indicates the successful synthesis of in-situ borate nanocomposite superabsorbents.

3.2.2. Characterization by SEM. The synthesized superabsorbent characterized using SEM can be seen in figure 4. In figure 4a shows that the surface of superabsorbent nanocomposite has a characteristic of fine fibers, has quite a rough and porous structure from sodium alginate, montmorillonite and it has big porous surface. Figure 4b shows the surface morphology of
Table 3. Kinetics order of superabsorbent nanocomposite

| Kinetic          | First pseudo order (R²) | Second pseudo order (R²) |
|------------------|-------------------------|--------------------------|
| Kinetics Swelling| 0.9325                  | 0.9995                   |
| Kinetics Release | 0.9994                  | 0.9012                   |

Figure 4. Morphology of (a) superabsorbent (b) nanocomposite with in-situ boric acid

Superabsorbent nanocomposite with in-situ boric acid as slow-release fertilizer, has smaller porous surface than figure 4a, in which its pores were not evenly distributed, due to the interaction between superabsorbents surface with boric acid, since boric acid was acidic and had an interaction with COOH group, so that it has a large swelling capacity.

3.3. Kinetics study of swelling

After obtaining the best nanocomposite superabsorbents, SN6 with a swelling capacity of 426.337 g/g and the release capacity of 25 % for 8000 min or about 6 days, furthermore, the kinetics study was determined. The determination of kinetics was carried out using the first pseudo and second pseudo reaction order. In table 3, it can be seen the R² values for first and second order kinetics swelling-release. The swelling kinetics of the first-order pseudo reaction rate was obtained at R² = 0.9325 and second-order pseudo reaction rate at R² = 0.9995, where R² of second pseudo order is higher than R² of first pseudo order. The study of kinetics swelling obtained pseudo second order for water. For the release kinetic for micronutrient, the obtained first order kinetics was R² = 0.9994 and second order R² = 0.9012. From the kinetics study the obtained release kinetics was in first order. This shows that the superabsorbent nanocomposite that was successfully synthesized has the ability to absorb large amount of water and slow release, which controls the boric acid micronutrients. From the results of the swelling and release kinetics studies, it supports the results of the discussed swelling and release capacity, in which the swelling capacity of the nanocomposite in-situ boric acid is greater and the release capacity is small. Nanocomposite superabsorbents that are successfully synthesized show that release boric acid micronutrients can be controlled.

4. Conclusions

Sodium alginate grafted by poly(acrylate-co-acrylamide) loaded montmorillonite (MMT) and the addition of boric acid as micronutrients into the superabsorbent nanocomposite through in-situ method has been successfully synthesized. This result is supported by the characterization with FTIR and SEM. Superabsorbent nanocomposite with the best swelling capacity at 20 % montmorillonite is 426.337 g/g and 0.1 g boric acid. The optimal release capacity of boric acid is 25.561 % for 8000 min or about 6 days. This is supported by the study of kinetics that obtained the swelling order in second-order with R² = 0.9995 and the order release is first-order with R² = 0.9994. The nanocomposite superabsorbents that are successfully synthesized show that release boric acid micronutrients slow release can be controlled for micronutrient slow release.
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References
[1] Tilman D, Cassman K G, Matson P A, Naylor R and Polasky S 2002 Nature 418 671–7
[2] Bortolin A, Seafim A R, Aouada F A, Mattoso L H C and Ribeiro C 2016 J. Agric Food Chem 64 3133–40
[3] Li J, Zhuang X, Font O, Moreno N, Vallejo V R, Querol X and Tobias A 2014. J. Hazard. Mater. 265 242–52
[4] Azeem B, KuShaari K, Man Z, Basit A and Trinh T T 2014 J. Controlled Release 181 11–21
[5] Koshiba T, Kobayashi M, Matsuoka K, Fujiwara T and Matoh T 2013 Soil Sci. Plant Nutr. 59 189–94
[6] Helmiyati, Abbas G H and Kurniawan S 2017 IOP Conf. Ser.: Mater. Sci. Eng. 188 012024
[7] Helmiyati, Saefumillah A and Yulianti W 2014 Asian J. Chem. 26 7337–42
[8] Hussien R A, Donia A M, Atia A A, El-Sedfy O F, El-Hamid A R A and Rashad R T 2012 Catena 92 172–8
[9] Lee W F and Chen Y C 2005 Eur. Polym. J. 41 1605–12
[10] Wu J, Wei Y, Lin J and Lin S 2003 Polymer 44 6513–20
[11] Kosemund K, Schlatter H, Ochsenhirt J L, Krause E L, Marsman D S and Erasala G N 2009 Regul. Toxicol. Pharmcol. 53 81–9
[12] Yu S H, Mi F L, Wu Y B, Peng C K, Shyu S S and Huang R N 2005 J. Appl. Polym. Sci. 98 538–49
[13] Samanta H S and Ray S K 2014 Carbohydr. Polym. 99 666-78
[14] Ni B, Liu M, Liu S, Xie L and Wang Y 2010 J. Agric. Food Chem. 58 12373–8
[15] Paulino A T, Guilherme M R, Reis A V, Tambourgi E B, Nozaki J and Muniz E C 2007 J. Hazard. Mater. 147 139–47
[16] Helmiyati and Aprilliza M 2017 IOP Conf. Ser.: Mater. Sci. Eng. 188 012019
[17] Helmiyati H and Syarifudin A 2018 AIP Conf. Proc. 2023 020080
[18] Rashizadeh A and Olad A 2014 Carbohydr. Polym. 114 269–78