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The Effect of Variation of Raw Material Ratio on Hydrogel Based on K-Carrageean - Acrylamide as a Carrier of Ammonium Nitrate Fertilizer

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Abstract

Hydrogels based on natural polymers such as carrageenan are currently being developed to improve efficiency in agriculture. By enriching hydrogels with fertilizers, they will be released slowly into the soil. Enrichment of fertilizers on carrageenan-based hydrogels was carried out and analyzed with the response of swelling ability, gel fraction value of grafting degree, to the hydrogel's ability to release the fertilizer trapped in it. Carrageenan is used because its use as a natural polymer has not been widely explored, especially in the non-food sector. The results showed that the average swelling value of carrageenan-based hydrogel to ammonium nitrate solution ranged from 750.00% - 1,633.33%. The gel fraction values obtained ranged from 74.06% to 87.51%, and the degree of grafting ranged from 85.33% to 93.59%. These values indicate a relatively high degree of tissue density and grafting of acrylamide monomer on carrageenan, which means that the carrageenan:AAm based hydrogel has strong mechanical properties. The ability to release ammonium nitrate samples from the hydrogel carrageenan-based has a value ranging from 8.86% to 44.92% in five days of observation. Interpretation of the test results, the best ratio of carrageenan:AAm is 1:1, due to its relatively low release value but still has good swelling and mechanical properties.

Keywords: *Hydrogel; Carrageenan; Acrilamyde; Fertilizer release*

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INTRODUCTION

Fertilization is an effort to increase agricultural productivity so that the agricultural products obtained is higher and the agricultural entreprises are profitable. However, the use of fertilizers is very wasteful, so the effectiveness of fertilizers is not on target. Plants do not adequately absorb the problem that occurs with fertilization. About 20-70% of the fertilizer will degrade or drift into deep groundwater, so fertilization is inefficient. It will pollute the environment with nitrogen, phosphor and potassium contents (Shaviv 1993). About 40-70% nitrogen, 80-90% phosphorus, and 50-70% potassium from fertilizers will be lost to the environment. Because they cannot be absorbed by plants (Bajpai et al. 2002) it is necessary to modify fertilizers to facilitate efficient nutrients absorption by plants. One method to overcome this problem is by making a hydrogel.

Hydrogel is a network of macromolecules capable of reversibly absorbing and releasing water based on external stimulants (Sannino et al., 2009). Unlike soil conditioners which only form a linear network so that they are water-soluble, hydrogels have a cross-linked network which, when exposed to water, will form a network of three-dimensional macromolecules with the ability to absorb water far exceeding their weight or volume (or so-called super. absorbent material) and insoluble in water (Zohuriaan-Mehr 2008). In certain conditions, the hydrogel can release stored water and then return it to its original medium, namely the soil. With the hydrogel's ability to absorb and return water to the soil based on its osmotic pressure and swelling (Rabat et al. 2016), Modified hydrogels are made by adding fertilizers to the matrix network. Fertilizers can be stored and can release into the soil in a controlled and slow manner.

Hydrogels, apart from their raw materials, which can use synthetic materials such as acrylamide or polysaccharide derivatives such as k-carrageenan, cellulose and starch, can be classified into permanent/chemical and reversible/physical hydrogels (Gulrez et al. 2011). Hydrogels made from natural polymers such as polysaccharide are more environmentally friendly, and the rate of degradation in the soil will be faster. Apart from being environmentally friendly, the use of natural polymers is also economically beneficial because of their abundant, cheap and renewable availability (Puspita et al., 2019). k-carrageenan as a natural polymer and a type of hydrocolloid produced from seaweed from the Rhodophyceae family has good prospects to be used as raw material for hydrogel synthesis. In this .

This study aims to produce an enriched hydrogel with fertilizers with excellent swelling ability, gel fraction and good mechanical properties using k-carrageenan-based acrylic-acrylamide.

MATERIALS AND METHOD

Materials

The raw material used in this research is k-carrageenan flour produced by PT Indoflora Cipta Mandiri Malang. Ammonium Nitrate Fertilizer (Blue Belt), Acrylic acid (Aldrich, cat no 147230), Acrylamide (Merck Germany, cat no 8.00830.0500), Ammonium persulfate (APS), and N, N'-Methylenbisacrylamide (MBA) (BDH England). Other technical grade chemical such as Acetone, KOH, and Methanol.

Hydrogel synthesis based on k-carrageenan

The research begins with making a 2% (w/w) k-carrageenan solution by dissolving carrageenan with aquadest. After that, a solution of acrylic acid - acrylamide is made by mixing acrylic acid with 16% acrylamide solution with a 1: 1 ratio, where the acrylic acid is neutralized first by adding a 10% KOH solution with a 1: 1 ratio to acrylic acid. The following preparation is mixing k-carrageenan solution 2% with APS 0.02% for 15 minutes. The acrylic acid - acrylamide solution was added with several comparisons to k-carrageenan (1:0, 1:1, 1:2) and a crosslinker in the form of an MBA with a concentration of 2%. The solution was homogenized and heated to 70ºC. The synthesis process carried out for 3 hours. This process is a modification that refers to the research of Rinawati (2011), Salim (2009), and Akalin (2019).

The sample made is then added with a solution of ammonium nitrate fertilizer with a concentration of 5% w/v. Fertilizer enrichment was carried out by soaking the sample in the fertilizer solution for 48 hours.

Analysis

The analysis and interpretation were carried out by observing the response in the form of swelling value, gel fraction, degree of grafting, loading and release of ammonium nitrate.

Swelling measurement

This test was carried out to determine the optimum swelling or swelling ability of the hydrogel to absorb water.

Dry hydrogel (m_0) was immersed in ammonium nitrate solution until there is no increase in weight (already saturated), or it is indicated that the hydrogel weight decreases overtime after reaching its highest swelling point (m_s). Equilibrium Degree of Swelling (EDS) is calculated using the following equation (Essawy et al. 2016):

$$\text{EDS}~(\%) = \frac{m_s - m_0}{m_0} \times 100\% \quad (1)$$

Gel fraction measurement

The hydrogel that has been soaked in aquadest was dried to see the remaining fraction. The number of insoluble fractions indicates the number of cross-linked bonds formed during the cross-linking mechanism carried out by the chemical cross-linking method.

100 miligram (m_0) hydrogel was immersed in 20 mL of distilled water for between 2 - 24 hours (depending on the optimum value of swelling), it was dried in an oven at 60 ° C for ± 48 hours until constant weight. Then the dry hydrogel was weighed (m1). The test was carried out in triplicates. The gel fraction is calculated using the following equation (Erizal et al. 2015):

$$\text{Gel Fraction}~(\%) = \frac{m_1}{m_0} \times 100\% \quad (2)$$

Degree of Grafting Measurement

It is the percentage of acrylate - acrylamide monomer grafted on the k-carrageenan polymer chain. After the graft polymerization process, poly graft k-carrageenan (Acrylamide-co-acrylic acid) must be extracted using a suitable solvent to remove unreacted monomers, free polymers, and additives.

Dry hydrogel (m_0) was extracted using methanol for 24 hours then washed with acetone to remove the water. After that, the samples were dried in an oven at 60 ° C and weighed again (m_g). The level of grafting can be determined using the following equation (Ediningsih et al. 2018):

$$\text{Degree of grafting (\%)} = \frac{m_g}{m_0} \text{ x } 100\% \quad (3)$$

Ammonium Nitrate Loading

The loading process was carried out by immersing the hydrogel with a specific weight in a 5% concentration of ammonium nitrate solution. The absorbance was measured, as much as 10 ml for approximately 24 hours. After immersion was done, the absorbance measurement was carried out again. the difference between the two absorbances shows the absorption capacity of the hydrogel to ammonium nitrate (Prayitno 2017).

Ammonium Nitrate Release

The hydrogel which has been immersed in ammonium nitrate solution was weighed and immersed in 20 mL of water. Absorbance measurements were carried out several times up to 5 hours on the first day and continued every 24 hours. Sampling was carried out until the 4th day. Furthermore, the release concentration value is compared with the loading value to obtain the release percentage of ammonium nitrate from the hydrogel. (Pulat 2018). The absorbance measurement used a UV-Vis spectrophotometer at a wavelength of 298 nm.

RESULTS AND DISCUSSION

Equilibrium Degree of Swelling (EDS)

The hydrogel swelling value will increase with the addition of acrylamide, as shown in Table 1. Acrylamide is a type of hydrophilic monomer which is often used for the making of polyacrylamide superabsorbent polymers. This hydrophilic nature causes the swelling value to increase when the acrylamide concentration increases because hydrophilic groups bind more water along the hydrogel polymer chain (Nurfadila 2020).

Figure 1 shows the highest swelling value at 50 hours of immersion. Carrageenan: AAm - 1:2 had the highest value meanwhile hydrogel without acrylamide had the lowest value. As a result, adding acrylamide can raise the swelling value. Acrylamide is a hydrophilic monomer commonly utilized in the production of polyacrylamide superabsorbent polymers.

The swelling value increases as a result of the hydrophilic properties. After 50 hours of immersion, the swelling value tends to decrease because the hydrogel has disintegrated due to the carrageenan's inability to store water after exceeding the optimum swelling value.In forming hydrogels with high swelling values, the addition of acrylamide still needs to be done. The performance of hydrogels made from natural ingredients alone is not good enough, especially in swelling and stability because the hydrogel will disintegrate very quickly.

Table 1. Effect of the ratio of raw materials to the maximum swelling value

k-carrageenan : Acrylamide	EDS (%)
1 : 0	750.00 %
1 : 1	1,219.44 %
1 : 2	1,633.33 %

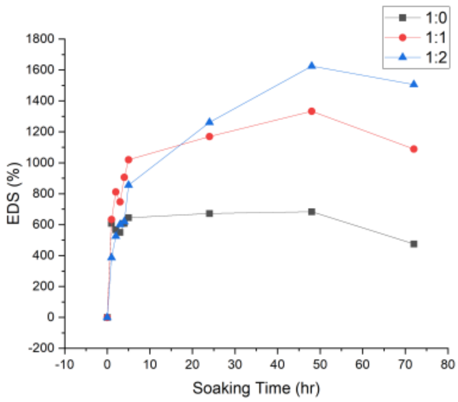


Figure 1. Effect of soaking time on the value of swelling

Meanwhile, natural polymers such as k-carrageenan will reduce the density of the polymer structure due to the competition between natural polymers and acrylamide monomer to polymerize. The addition of excess natural polymers will reduce the ability of the hydrogel to absorb water because the hydrogel cavities are getting tighter (Nuraini 2019).

In another study, the swelling value of k-carrageenan: acrylamide-based hydrogel was very high if it did not contain additives such as fertilizers or other macromolecules. swelling value could reach more than twenty thousand. However, this value dropped drastically due to the addition of fertilizer into the mixture immersion. That's natural, because this phenomenon is caused by the accumulation of ammonium nitrate that covers the pores or spaces between the polymer networks, thus limiting the number of water molecules in the hydrogel (Vanegas 2019).

Gel Fraction

The degree of cross-linking in a hydrogel, indicated by the gel fraction's value, also reflects the size of the cross-linking density that occurs between the polymers. With increasing acrylamide used, the gel fraction value tends to increase. According to Haima et al, (2020) gel fraction values above 50% have developed mechanically stable hydrogels with good gel strength so that physically, this carrageenan-based

Table 2. Effect of the ratio of raw materials to the value of the gel fraction

k-carrageenan : Acrylamide	Gel Fraction (%)
1 : 0	74.06 %
1 : 1	82.02 %
1 : 2	87.51 %

hydrogel can be used later as a fertilizer carrier in agricultural environmental conditions.

The addition of natural polymers such as k-carrageenan will reduce the value of the gel fraction on the hydrogel formed; this is due to the long chain of natural polymers is not degraded much to form radical compounds. With the addition of the MBA, the value of the gel fraction tends to decrease (Erizal et al., 2011).

Degree of Grafting

Like the gel fraction, the degree of grafting was also quite influenced by acrylamide in the sample. The grafting process based on the formation of free radicals occurs when the polymerization reaction states that the radical initiator will add monomers to the carbon double bond (Sunardi et al., 2018). This process occurs in the acrylamide monomer duplicate. The degree of grafting will increase as more monomers are grafted on k-carrageenan. The higher value of grafting, the better cross-linking between the monomers, and the sample with a 1:1 ratio has the best value. There is an anomaly for sample 1:2 has a low grafting degree, possibly due to imperfections during the synthesis process, in which not many acrylamide monomers were grafted onto the carrageenan, causing a lot of empty space in the polymeric network. However, the whole sample has a high degree of splicing, which is above 80%. The high degree of grafting indicates that all samples have strong mechanical properties.

Loading and Release of Ammonium Nitrate

The measurement of the loading value aims to determine how much the k-carrageenan-based hydrogel sample can accommodate and absorb the ammonium nitrate solution by immersing the hydrogel in the predetermined ammonium nitrate solution. The release test aims to see the phenomenon in the modified hydrogel by incorporating a substance in the form of ammonium nitrate fertilizer. With this test, the nature of the hydrogel release and whether the hydrogel can release fertilizer into the water medium can be seen. Before carrying out the loading and unloading test, it is necessary to make a standard curve first as a reference used in the future.

The loaded ammonium nitrate data is obtained from the ratio of the weight of the hydrogel sample used with its adsorption capacity. Adsorption interactions occur because of the attractive forces of atoms or molecules on the adsorbent surface, which causes the adsorbate to be absorbed. It can be seen that the more acrylamide is used, the lower the adsorption

Table 3. Effect of the ratio of raw materials to the degree of grafting

k-carrageenan : Acrylamide	Degree of Grafting (%)
1 : 0	88.60 %
1 : 1	93.59 %
1 : 2	85.33 %

Table 4. Hydrogel adsorption capacity to ammonium nitrate

k-carrageenan : Acrylamide	Hydrogel adsorption capacity (mg/g) / 10 ml of solution
1 : 0	275.25
1 : 1	154.47
1 : 2	132.57

Table 5. Ammonium nitrate loaded for each weight of the hydrogel sample used

k-carrageaan: Acrylamide	Hydrogel sample weight (g)	Loaded Ammonium Nitrate (mg)
1 : 0	0.03	8.15
1 : 1	0.02	3.48
1 : 2	0.03	4.45

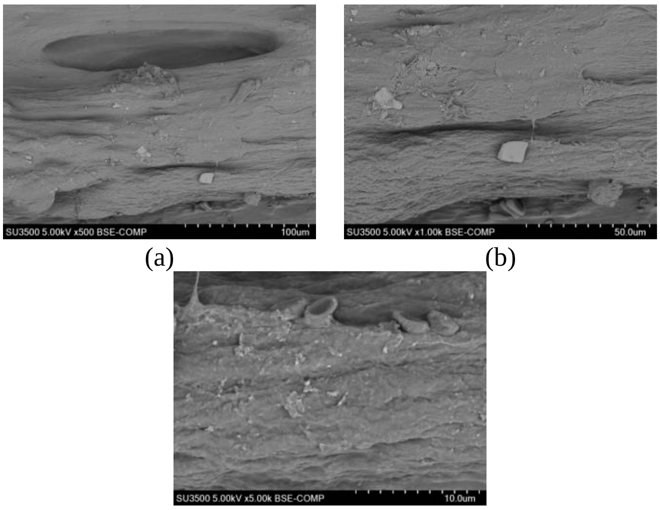
capacity of the hydrogel. This is in line with the value of this k-carrageenan-based hydrogel gel fraction.

The high level of cross-linking causes the space between the monomers to be narrower. Large particles such as fertilizers will find it difficult to enter the hydrogel matrix; this results in less fertilizer that the hydrogel can carry if excess acrylamide is used. k-carrageenan materials tend not to provide a significant difference to the adsorption capacity, so that the difference in adsorption capacity is dominated by acrylamide (Prayitno 2017)

SEM analysis was carried out to see the condition of the hydrogel surface after the ammonium nitrate enrichment process was carried out. The sample used was the k-carrageenan: acrylamide ratio 1:1 treatment. This treatment was chosen because the adsorption capacity and EDS value was in the middle of the whole treatment, which these two parameters determine the release value of ammonium nitrate.

In the SEM image (Figure 2), the pore is quite large, where the surface of the hydrogel looks quite rough. If seen further, surface roughness caused by the significant ammonium nitrate solid, which cannot enter the hydrogel's pores and only sticks to the surface; this also causes the hydrogel to be unable to absorb the ammonium nitrate solution properly because the pores are clogged.

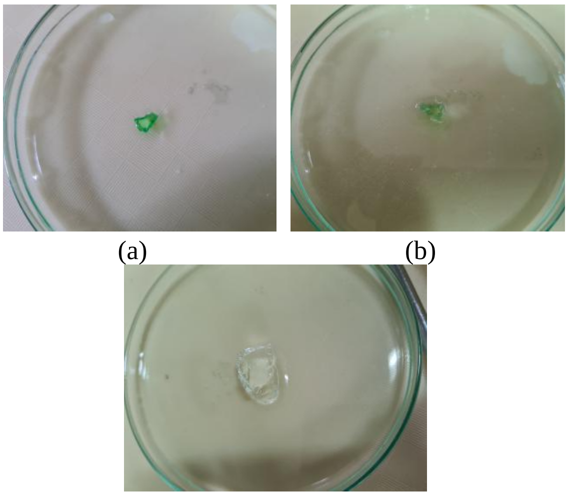
Furthermore, it can be seen in Figure 4, the released pattern of ammonium nitrate release tends to slope in all treatments; this indicates that the increase in the amount of ammonium nitrate from time to time tends to be a little, between 3% and 9% within four days of measurement. This indicates that the release of fertilizer is still in the slow category.



(a) (b)

(c)

Figure 2. Hydrogel loaded with Ammonium Nitrate, (a) magnification 500 times, (b) magnification 1000 times, (c) magnification 5000 times


(a) (b)

(c)

Figure 3. Hydrogel k-carrageenan: acrylamide - with ammonium nitrate adsorbed during release processes at water, (a) 0 hour, (b) after 1 hour, (c) after 2 hours.

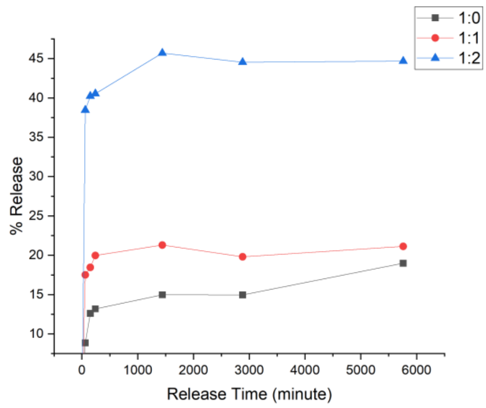


Figure 4. Value of ammonium nitrate release

The amount of substances released from the hydrogel matrix is greatly influenced by the hydrogel's ability to absorb water components. The hydrogel with the highest swelling value is the hydrogel that easily releases ammonium nitrate, absorbed in the matrix. The addition of acrylamide, which directly increases the swelling ability of the hydrogel, also has implications for the amount of ammonium nitrate released.

Of all the treatments, the hydrogel without the addition of acrylamide had the lowest swelling value, and this was in line with the results of the release test where the treatment had an initial release of below 10%, which means that very little ammonium nitrate was released in the whole release process. Moreover, compared to samples using excess acrylamide, where the usage was double the k-carrageenan used, the initial release reached 38%.

CONCLUSION

From the results, the combination of carrageenan and acrylamide can produce a fairly good hydrogel. This can be seen from the swelling value of the ammonium nitrate solution, which reached 1,633.33%. The gel fraction value reached 87.51%, and the grafting degree reached 93.59%, which indicated that this hydrogel had strong mechanical properties.

The adsorption capacity of the hydrogel showed that the hydrogel sample without acrylamide had a low value; this was due to the large size and density of the polymeric network, so that the ammonium nitrate tended to be trapped less. This also causes the ammonium nitrate load to tend to be lower.

From the SEM visualization, it can be seen that this carrageenan-based hydrogel tends to have fairly large pores and a fairly rough surface. This rough surface also indicates that ammonium nitrate tends to be more trapped on the hydrogel surface. and this can be seen in figure 3, where the release process is very visible more than the surface area.

From all observers, it can be concluded that this hydrogel has the potential as a fertilizer carrier, where ratio 1:1 is the best due to its relatively low release value but still has good swelling and mechanical properties.

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