



Evidence of Synergistic Behavior of Swelling and Release the Composite of Superabsorbent Hydrogel Based on Rice Husk Cellulose

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Abstract : The composite of superabsorbent hydrogel are based on cellulose isolated from rice husk is used as the backbone in the synthesis of superabsorbent cellulose-g-acrylic acid (SAA), cellulose-g-acrylamide (SAM) and compared with the superabsorbent cellulose-g-acrylic acid co acrilamida (SAA-co-SAM) using N , N-methylenebisacrylamide (MBA) as the crosslinker and potassium persulfate as initiator. In this work, we studied the behavior of swelling to water and urea. By observing the behavior of each superabsorbent swelling and supported by SEM and XRD characterization can be seen that SAA swelling capacity greater than SAM. When the two monomers are used for copolymerization process, that is the superabsorbent SAA-co-SAM get better swelling capacity, it is seen of the biggest swelling capacity. The capacity of release conducted on urea solution in the soil, obtained SAM better than SAA, and using two monomers acrylic acid and acrylamide (SAA-co-SAM) obtained the best results until 21 days, with capacity of release 70%.

Keywords : composite, superabsorbent, hydrogel, cellulose, acrylamide, acrylic acid.

Introduction

The fertilizer is important component in agriculture. Therefore fertilizer as source of nutrients for plants and should be given regularly. The main requirement to improve the quality of plant growth are water and fertilizer, so that its very important to improve the quality and the usage of fertilizers on the farm^{1,2}.

Nitrogen fertilizer is plant nutrients the widely used, but the level of utilization of nitrogen fertilizers only in the range of 30-50%. Among the nitrogen fertilizers, the most widely used is the urea, because it has high nitrogen content about 46% and relatively low of production costs. However, the urea can not easily absorbed by the soil particles before hydrolysis, so that the urea in large quantities lost, it caused washed away by water. Uncontrolled use of fertilizers not only causes economic losses and efficiency of fertilizers, but also cause environmental pollution is very serious²⁻⁸.

Weaknesses of conventional fertilizer use also overuse of the synthetic fertilizers that caused most lost of fertilizers into the soil and washed away by rain which will be serious environmental impacts. This issue has become a the focus of attention of the whole the world. One of the effort to increase of efficiency and effectiveness of fertilizer by modified become a slow release fertilizers. It has been indicates many advantages than conventional fertilizers, such as decrease in the rate of loss of fertilizers, sustainability of nutrient supply, reducing the frequency of fertilization and minimize negative impacts in the use overdosage of fertilizer. The

most effective methods to release fertilizers nutrient in the form of solution, in a controlled way to the farm by using superabsorbent^{4,8}.

Composite of superabsorbent hydrogel polymer is hydrophilic compound with three dimensional network structure which can absorb liquid 100 - 1000 times the mass and can retain a large amount of the solution even the under certain pressure⁹⁻¹¹. The absorption ability of superabsorbent hydrogel composite is very strong to the solutions, so that the superabsorbent widely used agricultural, medical and accessories daily life¹²⁻¹⁴.

Lately, many research on the synthesis of composite of superabsorbent hydrogel by using natural materials from plants as backbone, that is cellulose isolated from parts of plants such as rice straw, wheat straw, rice husk, corn straw, wheat bran, tomato and banana plant⁷⁻²¹.

Composite of superabsorbent hydrogel of graft copolymerization of vinyl monomer to natural polymer known as composite of superabsorbent hydrogel, like the chitosan, starch, cellulose and others²²⁻²⁵. Copolymerization conducted to obtain the desired properties, increase the absorption capacity. Natural polymers used to replace synthetic polymers which more difficult decomposed in the environment and prices tend to be expensive^{8,9,26}.

In this work was studied the behavior of composite of superabsorbent hydrogel was made using the cellulose from rice husks is grafted with different monomer are acrylic acid (SAA) and acrylamide (SAM) and then using two monomers acrylic acid and acrylamide (SAA-co-SAM). The formed composite of superabsorbent hydrogel observed the behavior of the swelling-release of water and urea fertilizer. The novelty of this work was observed the behavior of each monomer on the capacity of swelling and release separately and compared by using two monomers that have been done on our previous work^{8,9}. The synthesis composite of superabsorbent hydrogel using methylene-bis-akrilamide (MBA) as the crosslinker and potassium persulfate (KPS) as the initiator. Then characterized using SEM and XRD.

Experimental

Preparation of Superabsorbent Hydrogel Composite

Preparation of superabsorbent hydrogel composite based on the experimental refer to our previous work^{8,9}. Cellulose solution introduced into the reactor in three-neck flask, reflux condenser and nitrogen hose. The reactor was placed in water bath at 70⁰ C. The oxygen removed from the reactor by flowing nitrogen gas into the reactor for 15 minutes. KPS is added to the reactor, and then added mixture of 20% acrylic acid and 20% acrylamide which has been dissolved. The MBA was added, then the solution was adjusted to 35 mL with the addition of distilled water. Polymerization process for 2 hours at temperature 70⁰ C. The gel obtained was washed with distilled water, ethanol and soaked in acetone for 24 hours at room temperature. The obtained gel is cut into pieces approximately 0.5 cm. Then dried at temperature 50⁰ C until constant weight.

Measurement of Swelling Capacity

The dried superabsorbent (0.5 g) dipped in water and urea solution at room temperature until get equilibrium. Swollen superabsorbent then allowed at room temperature until constant weight. Swelling capacity (Se) is calculated by the equation (1):

$$\text{Swelling capacity (g/g)} = \frac{W_s - W_d}{W_d} \quad (1)$$

Where: W_s (g) is the weight of the swollen superabsorbent, and W_d (g) is the initial weight of the dry superabsorbent.

Measurement of Release Capacity Percentage

The swelling nanocomposite superabsorbent dipped into 200 mL of distilled water at room temperature to reach equilibrium. Capacity release is calculated by the equation (2):

$$\text{Release capacity percentage (\%)} = \frac{W_s - W_t}{W_t} \times 100 \quad (2)$$

Where: W_s (g) is the weight of the swollen superabsorbent, and W_t (g) is the weight of the superabsorbent after release every time

Result and Discussion

Characterization of Composite Superabsorbent by SEM.

The surface morphology of superabsorbent hydrogel composite can be seen in Fig 1

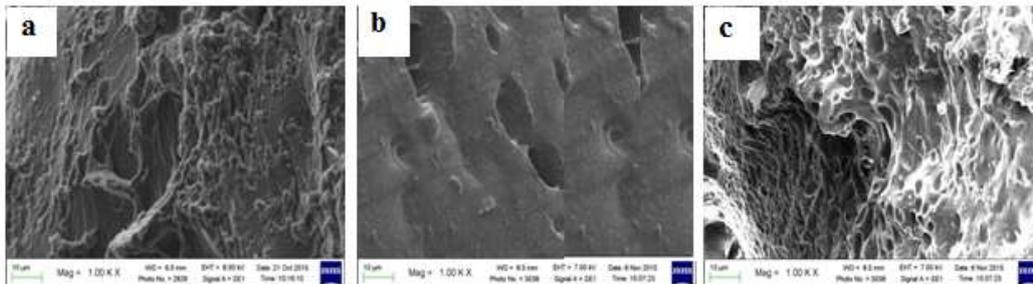


Fig. 1 Micrographs of composite of superabsorbent hydrogel SAM (a) SAA(b)SAA-co-SAM (c) with magnification 1000 times

One of the most important properties that must be observed is the presence of pores in the composite of superabsorbent hydrogel, the more pores will increase the effects of swelling capacity of superabsorbent Figure 1a shows the surface morphology of the superabsorbent hydrogel composite of cellulose grafting acrylamide (SAM) appear to have porous structure and uneven. Pores on the surface of the SAM superabsorbent contributes to the swelling capacity. Figure 1b, the surface morphology of the superabsorbent hydrogel composite grafting cellulose acrylate acid (SAA) appear to have few and big size pores. The swelling capacity of superabsorbent have big and many pores will has good capacity of swelling compare with slightly pores. Figure 1c shows the surface morphology of the cellulose composite of superabsorbent hydrogel acrylic acid co acrylamide (SAA-co-SAM) can be seen the surface morphology have pores of uniform, homogeneous and smooth. This is due to two monomers of acrylic acid and acrylamide better contributed in the formation of the composite superabsorbent. It is caused by combination of acrylic acid OH group with lone pair electron of NH acrylamide on grafting of cellulose. According to sadeghi et al (2013), it is suspected that these pores are the regions of water absorption and interaction hydrophilic sites with absorbate²⁴. In the presence pores on the surface of the superabsorbent will increase capacity and accelerate the occurrence of swelling in the superabsorbent. The utilization of the superabsorbent composites in the application will increase the absorption of water and fertilizer, so that it can control the release and expected to be applied on agricultural land.

Diffraction Patterns of Superabsorbent Hydrogel Composite by XRD

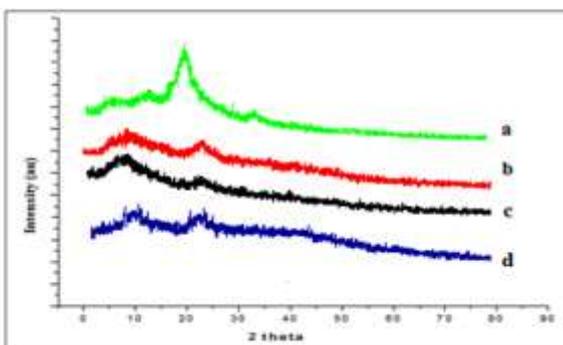


Fig 2. The diffraction patterns of rice husk cellulose (a), superabsorbent hydrogel composites of SAA (b), SAM (c) and SAA-co-SAM (d)

The diffraction patterns shown in Figure 2

Figure 2a, diffraction patterns of rice husk cellulose has specific 2θ on $15,6^\circ$, $22,6^\circ$, and $34,5^\circ$, these peaks are specific to the cellulose which has crystallinity index 55.2% indicating cellulose from rice husk has semi-crystalline properties. Figure 2b, diffraction pattern of the composite of superabsorbent hydrogel cellulose-g-acrylamide (SAM), Figure 2c, composite of superabsorbent hydrogel superabsorbent cellulose-g-acrylic acid (SAA) and Figure 2d composite of superabsorbent hydrogel cellulose-g-acrylic acid co acrylamide (SAA-co-SAM).

The three of superabsorbent cellulose composites show an amorphous structure, it indicates that there had been process of polymerisation the monomer to cellulose, besides also cellulose has spread into superabsorbent. Structure of cellulose before grafting in the form semi-crystalline, after the polymerisation it will form amorphous structure. This is according to research conducted by Wan et al (2013), in which the amorphous structure of the superabsorbent shows the success of grafting monomer to cellulose²³. The amorphous structure of the superabsorbent affect the swelling capacity of the superabsorbent. The more amorphous superabsorbent would be greater swelling capacity. It is caused by the amorphous structure arranged in an irregular manner and loose, so that solution would be easier get in and bound to the superabsorbent. Superabsorbent with the amorphous structure has a composition which not too solid but not too loose so that its swelling capacity and ability to hold water better

The Swelling Capacity of Superabsorbent Hydrogel Composite

Effect of Cellulose to Swelling Capacity

The influence of cellulose concentration to superabsorbent composite investigated in order to obtain environmental friendly superabsorbent. Cellulose is the main component of biomass plant that is widely available in nature, renewable, biocompatible and biodegradable. The influence of cellulose concentration on the swelling capacity with various superabsorbent can be seen in Figure 3

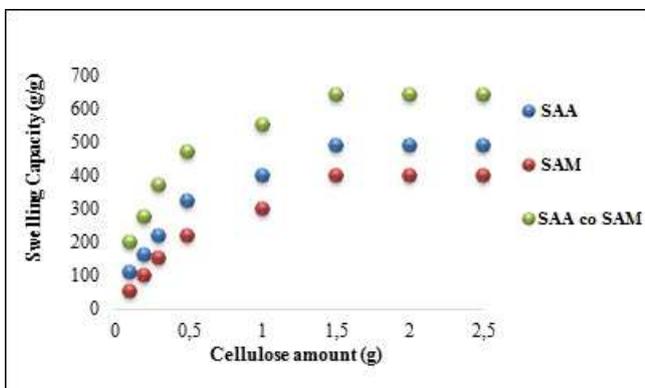


Fig 3. Swelling capacity of superabsorbent with variation of cellulose concentration

The mass of cellulose used in the polymerization of superabsorbent composites have significant influence on the result of swelling capacity. Figure 3 shows the swelling capacity of SAA superabsorbent tend to increased and optimum at 490 g/g. SAM superabsorben obtained optimum of swelling capacity at 400 g/g and superabsorbent of SAA-co-SAM optimum at 640 g/g with cellulose mass 1.5 g one each other. The greater the amount of cellulose will increase the swelling capacity of superabsorbent. Furthermore, after the optimum point was reached the increase of cellulose has no effect to swelling capacity or reach the equilibrium. The similar research have been done by Soleimani et al (2013) using various ratio of polyacrylonitrile / sucrose and obtained the maximum swelling capacity 323 g/g with polyacrylonitrile mass obtained at 1.50 g¹⁸. It is caused the more cellulose backbone is added, so that the more active group of celulose provided to bind monomer so that the active group will increase and the swelling capacity also will increase. In addition, the cellulose itself has active groups hydroxide (OH) located at the atom C2, C3 and C6 so that it can bind water and urea solution¹⁷. The swelling capacity of cellulose superabsorbent composite by using the acrylic acid monomer (SAA) is good enough compared to acrylamide monomer. It is due to the COOH group in the acrylic acid will occur interaction of hydration causing the ions in the superabsorbent from monomer attract polar molecules of water

and occur hydrogen bonds with water causing swelling capacity increasing. SAM superabsorbent swelling capacity is smaller than the SAA, due to the differences in the strength of hydrogen bonds between water and urea with superabsorbent composites, where the OH group has hydrogen bond strength greater than the NH group. This difference is also due to the SAA superabsorbent have pores of more uniform and bigger than the SAM superabsorbent shown in Figures 1a and 1b. While the swelling capacity by using two monomers are acrylic acid and acrylamide (SAA-co-SAM) obtained biggest swelling capacity. It is caused by using the two monomers, so the presence of OH and NH groups from the two monomer in the superabsorbent composites will cause the balance of the amount and the pore size obtained smooth and uniform pores can be seen in Figure 1c.

Swelling capacity to water and urea solution

Based on Figure 4, it can be seen that the superabsorbent cellulose-g-acrylic acid (SAA) has swelling capacity of water and urea solution greater than the superabsorbent cellulose-g-acrylamide (SAM). While the swelling capacity by using two monomers acrylic acid and acrylamide (SAA-co-SAM) obtained the greatest swelling capacity. Thus obtained the optimum swelling capacity of SAM, SAA and SAM co SAA in the water 245 g/g, 330 g/g and 550 g/g respectively and the optimum swelling capacity of SAM, SAA and SAM co SAA superabsorbent in urea solution are 350 g/g and 455 g/g and 700 g/g respectively. SAA swelling capacity greater than SAM superabsorbent due to the hydroxide group which can retain water and urea is greater compared to SAM. It shows that cellulose-g- acrylic acid has an important role in the absorption of water and urea solution in compared to cellulose-g-acrylamide.

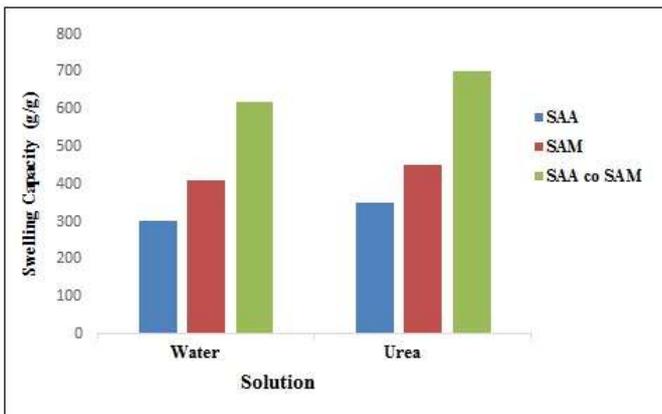


Fig 4. Swelling capacity of superabsorbent to water and urea solution

Release behavior of Superabsorbent in Soil Solution

The ability of release capacity SAA, SAM and SAA-co-SAM superabsorbent to urea solution in soil solution are shown in Figure 5.

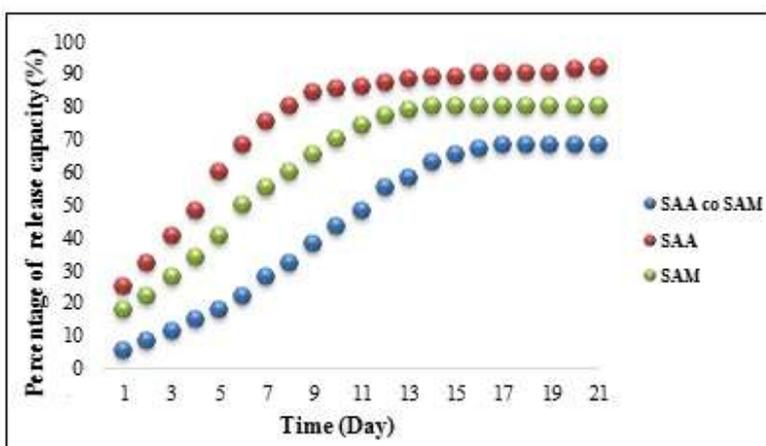


Fig 5. Percentage of Release capacity various superabsorbent in soil solution

Figure 5 shows that SAA superabsorbent has fast release to 8 days has reached 80% percentage of release. While the superabsorbent SAM undergo slower release up to 12 days reached 77%. It can be seen cellulose-g-acrylamide better release compare to cellulose-g-acrylic acid, this is due to the acrylic acid is difficult to maintain urea solution caused by OH group bind urea solution weaker than NH group, while the cellulose-g-acrylamide better caused bonding the amide groups with urea solution strong. For the superabsorbent cellulose-g-SAA-co-SAM showed more controlled release until 21 days, in which the percentage of release was 70%. From this work it can be seen that the combination of acrylic acid and acrylamide grafted on the cellulose in the synthesis of superabsorbent composite is suitable, because it can retain solution of fertilizer with more controlled release.

Conclusion

In this work has been successfully carried out the polymerization of the composite superabsorbent cellulose rice husk with acrylic acid and acrylamide monomer and has been studied the behavior of swelling and release. The results of the morphological characterization by SEM, in which SAM has more smooth pores and uneven, SAA with large pores and SAA-co-SAM has smooth pore and uniform. XRD diffraction pattern show all of this superabsorbent has an amorphous structure supporting the polymerization process is successful. The best composition of cellulose mass of the superabsorbent is 1.5 g. The optimum swelling capacity of SAM, SAA, and SAA-co-SAM in water are 245 g/g, 330 g/g and 550 g/g respectively and the optimum swelling capacity SAM, SAM co SAA and SAA in solution of urea are 350 g/g and 455 g/g and 700 g/g respectively. The release behavior of superabsorbent on soil solution obtained SAA superabsorbent has fast release for 8 days reached 80% and the percentage release of SAM with slower release for 12 days 77%. While SAA-co-SAM show more controlled release until 21 day with the release percentage 70%. The result composite superabsorbent of this work has good release and can be applied to controlled release of fertilizer nutrients on agricultural land.

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