Superabsorbent of nanocomposite cellulose rice husk poly (acrylate co acrylamide) applied as eco-friendly slow release fertilizer

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ABSTRACT

The results of cellulose isolation from rice husk used as a backbone to the synthesis of nanocomposite superabsorbent copolymerization. Cellulose has been isolated from rice husks and can be separated from the lignin and hemicellulose, it is not found of lignin absorption on FTIR and supported by SEM and XRD. The average rendement of cellulose-1 obtained 39.50 % and 59.50 % for cellulose-2. The diffraction pattern of XRD obtained crystallinity index of rice husk 42.60 % which increased after isolated to 67.80% for cellulose-1 and cellulose-2 60.20 %.The product of superabsorbent polymerization determined the grafting efficiency, the greater efficiency of grafting more monomers grafted, as shown by SEM. Overview of the factors that affect the swelling equilibrium has been studied. The best swelling capacity is SA2 with composition 0.1 gram cellulose, 0.5 mmol/L MBA and 7.94 mmol/L KPS with swelling capacity of water and urea 845.53 g/g, 667.80 g/g, respectively. Rate parameter of swelling fit with Voigt equation, which means that small rate parameter indicates the high swelling speed.

Keywords: *Cellulose, rice husks, superabsorbent, nanocomposite, swelling capacity*
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INTRODUCTION

Rice husk is the main byproduct produced in the rice milling process. Byproducts produced include husk (20-30%) which is part of the outer shell wrapping seeds, epidermis or bran (8-12%) and ash (5%) is part of rice were destroyed [1]. Food and Agriculture Organization of the United Nations (FAO) estimates that world rice production about 180.0 million tonnes in 2014, globally around 36-54 million tonnes of rice husks will be generated in the year. Rice production in Indonesia is third in Asia with sequence, first China, both India, and then Indonesia. The Government of Indonesia is aiming to boost rice production by 4 percent to 46.2 million tonnes (milled basis) through the provision of Subsidized fertilizers and seeds and the improvement of irrigation infrastructure [2].

Cellulose content in rice husk around 35-40%, hemicellulose 15-20% and lignin 20-25% [3]. Rice husk waste utilization is not optimal, most of the rice husk produced is used as the base for animal bedding, fuel and combustion is an alternative to remove husk rice farmers that could lead to air pollution [4]. Cellulose is polysaccharide consisting of d-glucose linked by 1,4 β -glycoside bond and is raw material for producing essential chemicals, such as; cellulosic ethanol, hydrocarbons and the basic material for the manufacture of polymers. Cellulose is polymer that is hydrophilic hydroxide groups that have great affinity to water [5-7]. Cellulose derived from rice husk which has advantages such as cheap and widely available, renewable, biodegradable and can be used as back bone superabsorbent [8-10]. Hydrophilic nature of superabsorbent is factor that determines the ability to absorb and retain large amounts of water even under certain pressure [11-13].

Based on the nature control of water release of superabsorbent are widely used in the agriculture [10], industry [14], medicine as a drug release behavior [15] and wastewater treatment [16]. System control of the water and fertilizer release in agriculture provide several advantages such as; saving water usage, reduce production costs, improve plant nutrition, reducing environmental pollution and reduces plant mortality due to overdose [17]

Currently the introduced superabsorbent of graft copolymerization of vinyl monomers on natural polymers such as; cellulose [17], starch [18], and chitosan [20]. Natural polymers used to replace synthetic polymer which is more difficult to decompose in the environment and it cost tend to be expensive [21]. In addition, the superabsorbent with high absorptions ability has great potential as coating material in the manufacture of slow release fertilizer, superabsorbent combination with fertilizer can make products have slow release fertilizer and high water-retaining [22].

In this research is similar to previous research has been conducted synthesis of cellulose superabsorbent rice straw, which observe the behavior and swelling kinetics of water and fertilizer [23]. In this work, cellulose synthesis of superabsorbent from different sources namely rice husk cellulose studied cellulose isolation results obtained, then the isolated cellulose used as back bone on the synthesis of superabsorbent. Graft copolymerization using free radical polymerization with acrylic acid (AA), acrylamide (AM) as monomer, potassium persulfate (KPS) as initiator, and N, N-methylenebisacrylamide (N, N, MBA) as crosslinking.

EXPERIMENTAL SECTION

Reagents and Chemicals
Rice husk used in this work was obtained from Bogor (Indonesia). Toluene (Merck) used to extract the cellulose in rice husk, hydrogen peroxide (Merck), potassium hydroxide (Merck) was used as an impurity removal rice husk cellulose, acrylic acid, acrylamide (Nippon Shokubai) used as a monomer, potassium persulphate (KPS; Merck) as initiator, *N,N'*-methylene*bis*-acrylamide (MBA; Sigma) as crosslinking.

Cellulose Isolation to The Rice Husk
Isolation or pretreatment of the rice husk cellulose refers to Fan et al [24] for cellulose-1 and Das et al [25] for cellulose-2. Rice husk powder (10 g) was extracted first with mixture of toluene: ethanol (2:1) by using the method of maceration while distirer to eliminate the extractive substances, then filtered and heated to 50°C for 24 hours. Hemicellulose and lignin is removed by adding 350 mL KOH 4%, 2% H_2O_2 and stirred at room temperature for 8 hours and at 90°C for 4 hours. The precipitate was filtered and washed with distilled water until neutral, then put into oven at 50°C for 24 hours. The dried sediment soaked in acetic acid of pH 3-4 at 70°C for 5 hours, centrifuged to separate the filtrate and precipitate. The precipitate washed until neutral, then put in oven at temperature of 50°C until constant weight obtained. The difference between cellulose-1 and cellulose-2 are cellulose-1 removal of lignin in dilute acid solution carried out simultaneously in one step, cellulose-2 removal of lignin in dilute acid solution done in two stages. Cellulose isolation results were analyzed by FTIR, SEM and XRD and compared with standard cellulose. The results of cellulose isolation from rice husk used as backbone to the synthesis of nanocomposite superabsorbent copolymerization, the synthesis of superabsorbent refers Helmiyati et al [23].

RESULTS AND DISCUSSION

Cellulose Isolation Result of The Rice Husk
Rice husk consist of cellulose, hemicellulose, lignin and other extractive substances are bound to each other through hydrogen bonding, Van der Waals and covalent bonding. After the pretreatment obtained average yield of cellulose can be seen in Table 1 and Figure 1.

Table 1 Average rendement of cellulose isolation

Cellulose	RHw (g)	Esa (%)	Lha (%)	Cra (%)
1	10.0	6.1	54.4	39.5
2	10.0	8.3	32.2	59.5

Rice Husk weight (RHw), Extractive substances average (Esa), Lignin and hemicellulose average (Lha), Cellulose rendement average (Cra).

In Table 1 can be seen rendement cellulose-1 is smaller than cellulose-2, this is due to the different reaction stage cellulose isolation. The cellulose-1, removal process of lignin, hemicellulose and bleaching done in one stage of reaction. While the cellulose 2, process is done gradually. Cellulose rendement weighs of cellulose-2 is greater because it still contains lignin.
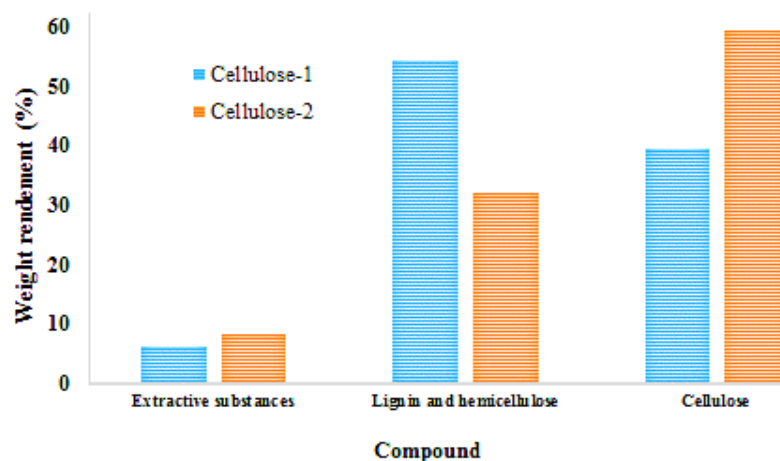
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Figure 1. The content of rice husk

Figure 1 can be seen the rice husk contains cellulose, lignin, hemicellulose and other extractive substances, cellulose can be separated from the lignin and hemicellulose quite large content of the rice husk is used.

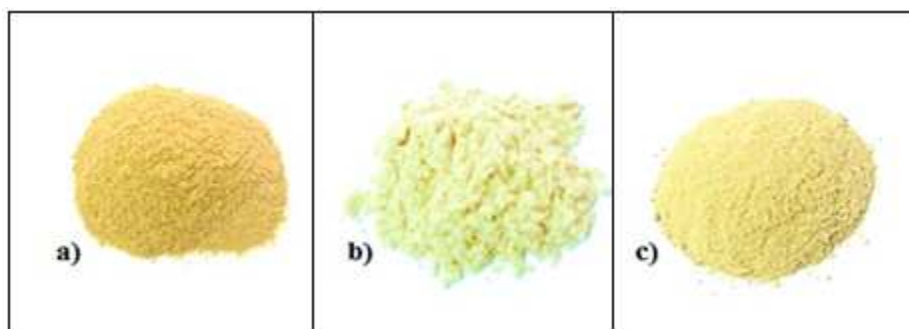The image of cellulose isolation results can be seen in Figure 2.

Figure 2. Powder of a). Rice husk, b). Cellulose-1, c). Cellulose-2

Based on Figure 2 can be seen that the samples of rice husk as raw material yellowish brown cellulose, cellulose-1 yellowish white and cellulose-2 yellowish. This result is similar to that been done by Fan et al [24] and Lu et al [26], which states that isolation process successfully. It can be seen from the color of celulose-1 yellowish white. The color change indicates that cellulose isolation process has occurred, which has been the loss of lignin in cellulose which resulted in change of color. The cellulose-2 has yellowish color and lighter than the color of rice husk. This result is similar to that carried out by Das et al [25], which states that still content lignin. These results are supported by subsequent analysis by FTIR, SEM, and XRD.

FTIR Analysis of Cellulose
FTIR analysis results shown in Figure 3.

According to Figure 3a can be seen in infrared absorptions for rice husk, the main absorption band that shows the functional groups on rice husk 1736 cm^{-1} (C=O stretching vibration), this is specific band for lignin, hemicellulose compounds and lignin compound 1520 cm^{-1} (C=C stretching vibration). The appearance of an absorption band at 3298 cm^{-1} (O-H stretching vibration) of the hydroxyl group, 1130-1175 cm^{-1} (C-O-C stretching vibration) and 496 cm^{-1} (Si-O-Si bending stretching).

Figure 3b, cellulose-1 can be seen 3296 cm^{-1} (O-H stretching vibration) and the disappearance of the absorption band at 1736 cm^{-1} indicating that it has been loss of lignin in cellulose-1. Spectra of cellulose-1 is similar to that been done Fan et al [24] , Lu *et al* [26] and Kalita et al [27]. Figure 3c, cellulose-2 can be seen 3298 cm^{-1} (O-H stretching vibration) and 1130-1175 cm^{-1} (C-O-C stretching vibration). The cellulose-2 appears absorption band 1736 cm^{-1}(C=O stretching vibration), this is specific band for lignin compounds. where the spectrum of cellulose-2 is similar to that been done Das et al [25], which is also the present of the absorptions band 1751 cm^{-1} (C=O stretching vibration). Figure. 3d, spectra of pure cellulose similarities with the spectra of cellulose-1 and cellulose-2, only cellulose-2 still lignin content.
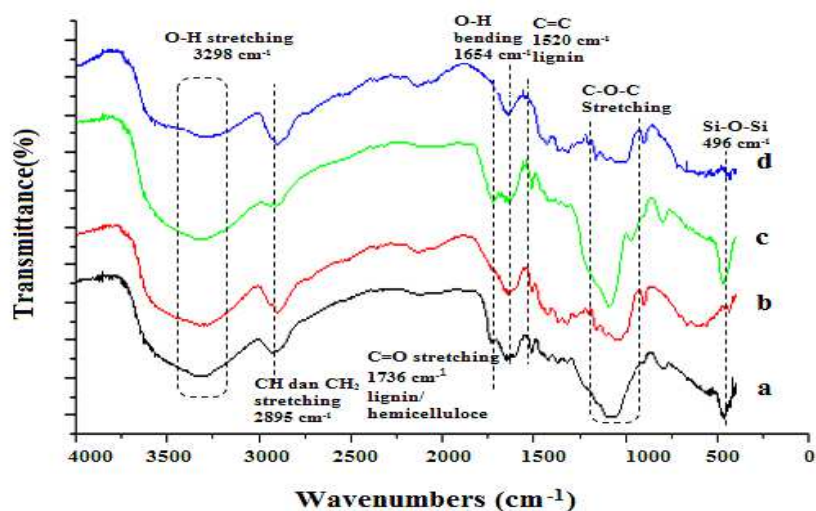
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Figure 3. Spectra of FTIR, a. Rice husk, b. Cellulose-1, c. Cellulose-2, d. Pure Cellulose

XRD Analysis of Cellulose
The XRD patterns of rice husk and cellulose isolated from rice husk cellulosa-1and cellulosa-2 are shown in Figure 4. that the major crystalline peak for each sample occurred at around The peak around $2\theta = 22.27^o$ which represents the cellulose crystallographic plane (2 0 0) semilar Rosa et al [4].

Figure 4a. XRD patterns rice husk, after calculation of crystallinity index obtained 42.60%. Figure 4b is pattern cellulose-1 has specific 2Θ at 15.58^0, 22.12^0, and 34.5^0 have a crystallinity index of 67.80%, and Figure 4c pattern cellulose-2 has specific 2Θ at 15.58^0, 22.12^0, and 34.5^0 the crystallinity index of 60.20%.
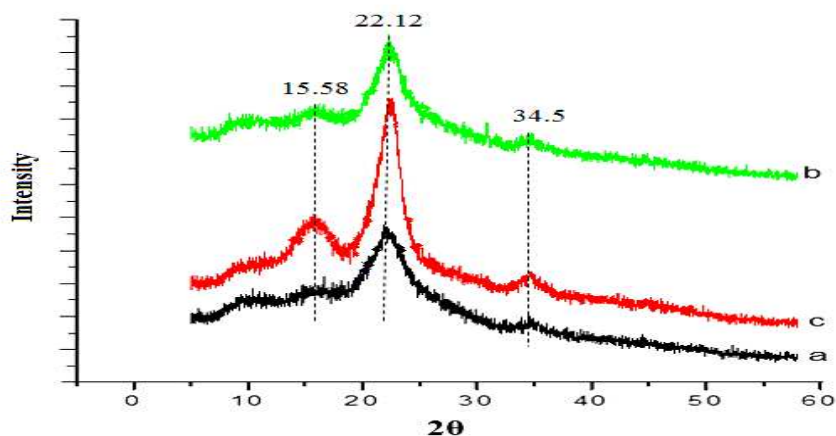

Figure 4. XRD Patterns of a. Rice husk, b. Cellulose-1, c. Cellulose-2

Patterns of cellulose-1 has higher intensity than cellulose-2 and rice husk. It can be seen that the peaks appear on the cellulose-1 and the cellulose-2 showed similarity with peak cellulose rice husk Das et al. The similarity can be seen from the 2Θ specific to cellulose Das et al on $2\Theta;16.1^0$, 22.2^0, and 34.8^0 [25]. The peak of cellulose-1 indicates that crystallinity index is higher compared to the cellulose-2. This indicates loss of lignin and hemicellulose thereby increasing the degree of crystallinity of cellulose. Crystallinity index in this study is similar to that has been done by Rosa et al, that is 67% [4].

Analysis of the Cellulose Surface Morphology by SEM
The surface morphology of cellulose can be seen in Figure 5.
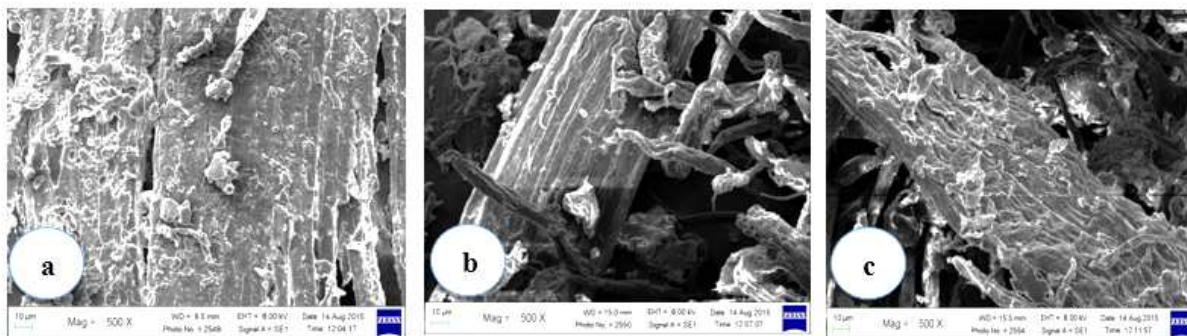
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Figure 5. Micrographs to magnification 500 times a. Rice husk, b. Cellulose-1 and c. Cellulose-2

Figure 5a, shows the surface morphology of rice husk can be seen on the surface is not seen clearly fibril cellulose because it is still covered by cloud of rough and uneven found on all of its surface, it is means that the surface of rice husk cellulose still protected by hemicellulose, lignin, silica, and other extractive substances. Figure 5b and 5c show the morphology of cellulose-1 can be seen the surface morphology more clearly cellulose fibrils and homogeneous, that means that cellulose-1 has been obtained pure cellulose approached the standard cellulose. Cellulose-2, can be seen fibril cellulose but still contained lignin and hemicellulose.

Polymerization of Superabsorbent Cellulose Rice Husk
Efficiency of Grafting Superabsorbent
Efficiency of grafting shows the formation of superabsorbent. Efficiency of grafting indicate the monomer percentage grafted into cellulose, calculated from the mass ratio of monomer grafted on cellulose with mass of initial monomer, can be seen in Figure 6.
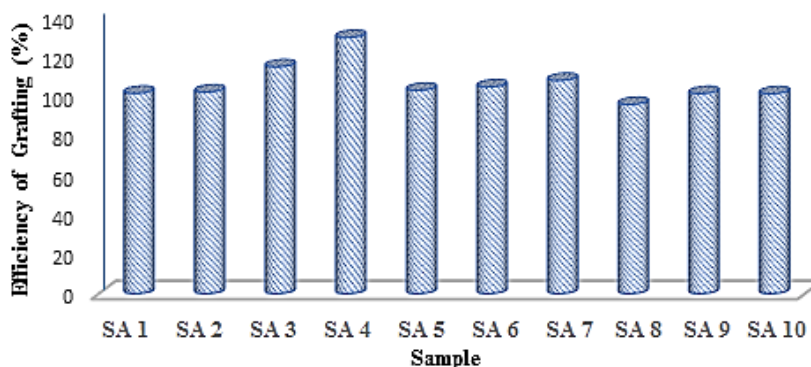

Figure 6. Efficiency of grafting cellulose with acrylic acid and acrylamide by variations

The superabsorbent of SA1 to SA4 done cellulose variations can be seen that the greater the concentration of cellulose will increase the efficiency of grafting significantly. This is caused that more backbone available to react with the monomer. Superabsorbent SA 5 to SA 7 is variation of MBA, MBA is crosslinking agent the polymer chains to one each other. Increasing the concentration of MBA will increase the efficiency of grafting. The influence of the concentration of inisiator will increase the efficiency of grafting, because KPS acts as radical formation initial at the stage of initiation that will attack cellulose. The more the concentration of KPS, cellulose radical formation increase and then it will react with the monomer, it can be seen in Figure 6, the grafting efficiency increased from SA 8 to SA 9 and constant at SA10, which means the SA 9 is optimum concentration of KPS.

Surface Morphology of superabsorbent by SEM
Morphology of superabsorbent surface derived from rice husk cellulose isolation grafted with acrylic acid and acrylamide monomer compared with superabsorbent copolymer of acrylic acid-acrylamide without cellulose, can be seen in Figure 7.
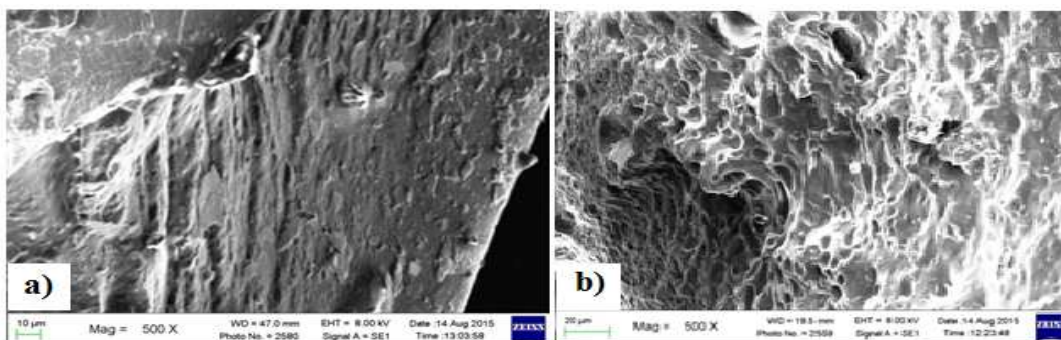
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Figure 7. Micrographs of a. copolymer of acrylic acid-acrylamide, b. superabsorbent rice husk cellulose poly (acrylic acid co acrylamide)

Figure 7a, shows the surface morphology of acrylic acid-acrylamide copolymer as control (without cellulose) can be seen smooth surface morphology with few pores. Figure 7b, shows the surface morphology of superabsorbent copolymerization rice husk cellulose poly (acrylic acid co acrylamide) can be seen porous of the surface more uniform and rough than the picture 8a, this is due to the occurrence of grafted monomer to cellulose so that the network superabsorbent formed more tightly and the pores can be function to absorb water and fertilizer when carried out the swelling process.

Swelling Capacity of Superabsorbent
The swelling capacity of superabsorbent rice husk cellulose poly (acrylic acid co acrylamide) was synthesized determined the ability to absorb water distillation and fertilizer. Grafting of acrylic acid and acrylamide monomer in cellulose would lead to interaction between the COOH, $COONH_2$ groups from monomers with OH group on the cellulose surface. This interaction will increase the ability of swelling superabsorbent [11].

The swelling capacity of water and urea in superabsorbent with various variations can be seen in Figure 8.
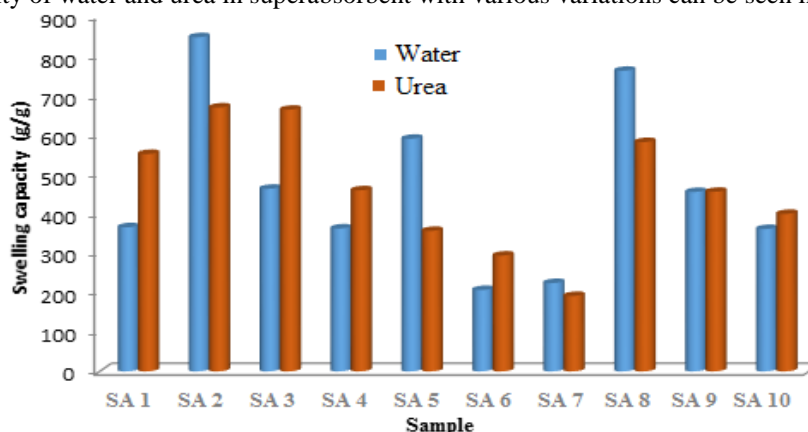

Figure 8. Swelling capacity of water and urea in superabsorbent

The process of swelling caused mainly by the presence of pores superabsorbent, active group contained in superabsorbent and the osmotic pressure. During the swelling process, the water continuously into the superabsorbent, this process caused among other things is the osmotic pressure difference between the superabsorbent with outside solution. The higher the osmotic pressure difference causes high swelling ability [28]. Based on Figure 8. Superabsorbent SA 2 have the highest swelling capacity of both the water and urea. The value of water swelling capacity SA 2 is 845.53 g/g and urea is 667.80 g/g. Swelling capacity of the water is higher than urea solution due to the urea dissolved in water will lower swelling capacity. The superabsorbent swelling ability will be reduced with the increasing number of compounds that are dissolved in water, based on Rashidzadeh et al [22]

Parameter of rate based Voigt equation model
In the preliminary study on the swelling rate of superabsorbent can be used model based on Voigt equation:

$$S_t = S_e(1 - e^{-\frac{t}{\tau}})$$
1

St is swelling at t time, Se is swelling at equilibrium and τ is the rate parameter. Rate parameters can be obtained by rearrangement the equation 1, to obtain equation 2.

$$\ln\left(1 - \frac{S_t}{S_e}\right) = -\frac{1}{\tau}t \qquad\qquad 2$$

Based on the equation 2, the rate parameters can be calculated by plotting $\ln\left(1 - \frac{S_t}{S_e}\right)$ to time. High rate parameter value indicates small swelling rate [29]. The rate parameter can be used as measure of the swelling rate, low of rate parameter value indicates high swelling rate and conversely if large rate parameter indicates the rate of the slow swelling.

Plot $\ln\left(1 - \frac{S_t}{S_e}\right)$ against time for the superabsorbent with swelling capacity in water and urea for SA 2 of cellulose-1 and SA 4 of cellulose-2 is presented in Figure 9.
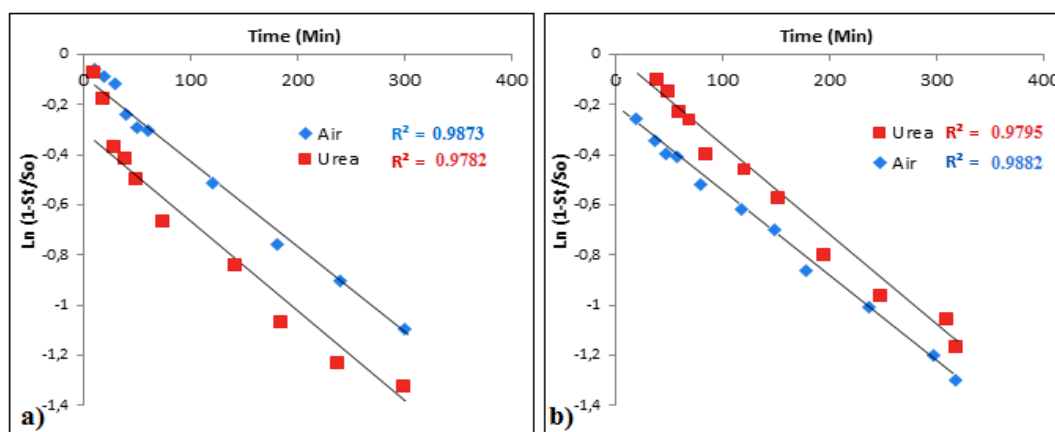

Figure 9. Plot $\ln\left(1 - \frac{S_t}{S_e}\right)$ versus time a). Cellulose-1, b). Cellulose-2

Figure 9, can be seen that line equation for cellulose-1 had regression (R^2) to water and urea respectively 0.9873 and 0.9782 and cellulose-2 had regression (R^2) to water and urea respectively 0.9882 and 0.9795, meaning swelling rate parameters according to the Voigt equation model, which means that small rate parameter indicates the highest swelling rate.

CONCLUSION

Cellulose has been isolated from rice husk and can be separated from the lignin and hemicellulose. This is indicated by color change in powder straw, it is supported by the FTIR spectra of lignin loss absorption at 1520 cm^{-1} and 1736 cm^{-1}. The average rendement obtained was 39.50% for cellulose-1 and 59.50% for cellulose-2. Crystallinity index of rice husk obtained of XRD is 42.60%, which increased after isolated into 67. 80% and 60.20% cellulose-1 cellulose-2, respectively. Cellulose isolation used as the backbone in the synthesis of superabsorbent, the grafting success characterized of the greater grafting efficiency. Results synthesis supported by SEM. This superabsorbent has great affinity to water as evidenced by high swelling. Swelling capacity of the cellulose-1 the best for the SA 2 with composition of 0.1 grams cellulose, 0.5 mmol / L concentration of MBA and 7.94 mmol / L concentration KPS with water swelling capacity of 845.532 g/g and urea 667.808 g/g and for cellulose-2 is SA 4. Rate parameter of cellulose-1 generally smaller than cellulose-2. SA 2 on cellulose-1 has the lowest rate parameter in the water and urea, namely 296.70 and 301.98, this according to the value of water and urea swelling capacity at most. SA 4 on cellulose-2 has the lowest rate parameters in the water and urea are 335.34 and 171.12 and gain the swelling capacity are greatest for water and urea.

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