



Synthesized Superabsorbent Based on Cellulose from Rice Straw for Controlled-Release of Urea

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ABSTRACT

Rice straw was used as α -cellulose sources for synthesizing a novel α -cellulose-g-poly(acrylic acid)superabsorbent by graft polymerization between α -cellulose rice straw powder and acrylic acid in aqueous solution. The synthesis and controlled-release of fertilizer from superabsorbent was carried out. The super absorbent composite was characterized by FTIR, SEM and TGA. The results of FTIR spectra showed OH of α -cellulose rice straw participated in graft polymerization with acrylic acid. The equilibrium water absorbency of super absorbent was investigated by calculating the swelling ratio. The super absorbent composite was swollen in aqueous solution of urea to load urea. Furthermore, the release of urea from loaded super absorbent was analyzed in water. Super absorbent with the highest water absorbency and the slowest profile of release controlled were obtained when the temperature of polymerization reaction was 70 °C.

Keywords: superabsorbent, rice straw, α -cellulose, controlled-release, urea.

INTRODUCTION

Super absorbent is a kind of polymer that able to absorb and hold large amount of water¹. Superabsorbent polymers have been developed and used in daily life, such as infant diapers², feminine hygiene products¹, also have been used in specific area, such as in agriculture to prohibit the large amount of evaporation³⁻⁴. Usually for synthesis and

develop super absorbent, acrylate and its derivate was used for the main ingredient. Super absorbent based only on poly(sodium)acrylate has several disadvantages such as, relatively high in production cost, not biodegradable, and not suitable to water and to soil rich with mineral contents⁵⁻⁶.

Natural polymer, such as cellulose, is possible to develop as superabsorbent polymer

through grafting modification to the main backbone of cellulose, where as the techniques of grafting polymerization process are classified into such as photo-grafting, irradiation, and chemical initiation. The development super absorbent polymer based on cellulose support by some previous researches, such as Chen Y. *et al.*⁷ provided cellulose super absorbent through copolymerization and crosslinked between cellulose and vinyl's monomer; Princi *et al.*⁸ developed super absorbent cellulose through copolymerization between cellulose and derivate of acrylate's monomer (methyl methacrylate and ethyl acrylate); and Khan *et al.*⁹ used okra fiber as cellulose's source through grafting technique to acrylonitrile's monomer with $K_2S_2O_8$ and $FeSO_4$ as initiator and catalyst, respectively. There have been many reports on introducing cellulose, inorganic clays and chitosan into pure polymeric super absorbents in order to improve swelling property, reduce production costs and ensure biodegradability¹⁰⁻¹². However, the researches that focus on super absorbent polymer based on crops residues are rare. Rice straw is one of the source of cellulose with so many advantages, such as abundantly available, biodegradable, renewable, since these are waste biomass. The composition of rice straw consists of cellulose (36,5%), hemicellulose (33,8%), lignin (12,3%), extractive compound (3,8%), ash (13,3%), and silica (70,8%)¹³.

The utilization of super absorbent in agriculture areas can provide several advantages, such as decrease the consumption of water irrigation and the death of plant, increase the water availability in soil, decrease the probability of soil hardens, prohibit the erosion, and increase the fertilizer efficiency¹⁴⁻¹⁶. The combination between superabsorbent and fertilizer in its application can increase the plant nutrition also decrease the negative impact of solvation of fertilizer¹⁷. The aim of this research focused on two points (i) synthesise of cellulose super absorbent based on cellulose from rice straw and (ii) absorption and controlled-release of urea in water.

EXPERIMENTAL

Material

Rice straw is obtained from several paddy fields in Tanjung Morawa subdistrict, regency of

Deli Serdang, North Sumatera. Acrylic acid, $K_2S_2O_8$, hydrochloric acid, sodium sulfite, sodium nitrite, sodium hypochlorite, hydrogen peroxide, sodium hydroxide, ethanol, and methanol are ordered from Merck Chemical. N, N-methylene-bisacrylamide is ordered from Sigma Aldrich. Those commercial chemicals are used without further treatments.

Isolation of α -cellulose

The α -cellulose from rice straw was isolated using method Ohwoavworhua, F.O dan T.A. Adalakun¹⁸ with some modifications. Rice straw powder (30 g) was first refluxed with 3,5% of nitric acid solution and 10 mg sodium nitrite at 90 °C for 2 hours. The resulting residues were washed and continued for further treatments with 2% of sodium hydroxide and 2% of sodium sulfite, at 50 °C for 1 hour. Residues from digestion process were washed till neutrality and the residues were hydrolyzed with 17,5% of sodium hydroxide at 80 °C for 30 minutes then continued by treating the residues in 10% of hydrogen peroxide at 60 °C for 15 minutes. The residues from bleaching process were washed till neutrality and dried in oven at 60 °C. The dried powder was characterized by FTIR, SEM, and TGA.

Preparation cellulose hydrogel

The cellulose from rice straw (800-100 mesh) and aquadest were reacted in the four-necks flask equipped with a magnetic stirrer bar, the flask is heated in a water bath at 95 °C under nitrogen atmosphere. After 30 minutes of cellulose treatment, the temperature was adjusted to 60 °C and several supported components, such as potassium persulfate, acrylic acid, and NMBA were added to the flask. The temperature then adjusted to 70-80 °C until the white color gel was obtained. The white gel was washed with methanol for 30 minutes, continued with ethanol for 5 minutes and dried in oven at 60 °C until the constant weight was obtained. The white gel then characterized, including the microstructural morphology by SEM, functional group by FTIR, and swelling ratio also controlled-release urea.

Swelling Capacity

Certain amount of dry sample, 0.1000 g, was put into a 200-mesh fastened nylon bag. Then, the bag was immersed into distilled water for 24 h to

reach the swelling equilibrium at room temperature. Subsequently, the bag was lifted from water, while the residual water was wiped up with filter paper, and weighed the bag. The swelling ratio was calculated using Eq. (1)19:

$$\text{swelling} = \frac{M_s - M_1 - M_0}{M_1} \quad \dots(1)$$

where M_s , M_1 and M_0 refer to the weight of the swollen, dried cellulose hydrogel, and wet nylon bag, respectively.

Measurement of urea absorbency

Certain amount of cellulose hydrogel was immersed into a 100 ppm of urea solution (based on N content) and allowed to soak at room temperature for 24 hours. The swollen cellulose hydrogel was filtered to remove non-absorbed water and weighted. The swollen cellulose hydrogel was dried in oven at 60 °C until the constant weight was reached. The remaining N content was measured by spectrometry UV/Vis technique.

Controlled-release of urea

To study the slow-release behavior of cellulose hydrogel in water, the following experiment was carried out: certain amount of cellulose hydrogel/urea was immersed in 250 mL of water and incubated for different periods at room temperature. After 15, 30, 45, 60, 90, 120, 150, and 180 minutes, the releasing urea in the solution was measured by spectrometry UV/vis technique.

Measurement of N content

N content of urea was measured follow Watt and Crisp method²⁰. With the volume of 5 mL of the urea solution was added to vial bottle, then the 2 mL of coloring agent was added to the solution till the equilibrium was reached and the absorbance was measured at 420 nm.

RESULT AND DISCUSSION

Isolation α -cellulose from rice straw

α -cellulose was successfully isolated from rice straw powder by following Ohwoavworhua dan

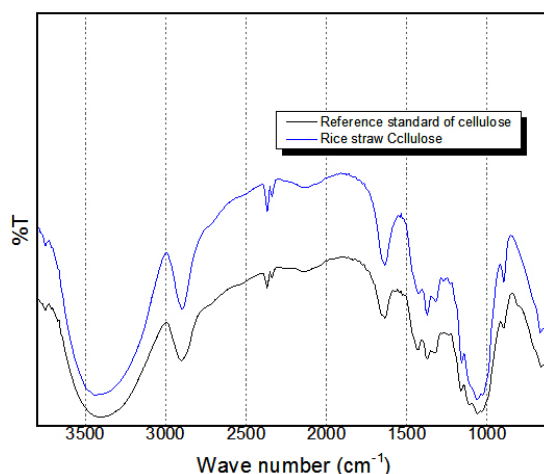


Fig. 1: Spectra FTIR of α -cellulose from rice straw and reference standard

Table 1: Yield of α -cellulose

Sample	% Yield			
	Delignification		hydrolysis	
	Weight (g)	%	Weight (g)	%
Rice straw	19,28	25,70	11,88	15,84

Adelakunmethod¹⁸. Delignification process was completely done by addition of 3,5% of HNO₃ solution and NaNO₂, those reagents caused conversion of lignin to become nitro lignin, this process provided 25, 70% of yield. On the second step, hydrolysis process, the reaction was completely done by addition of 2% of NaOH solution and 2% of Na₂SO₃, the aim of those solution is to remove hemicellulose, mineral, silica, and ash. On this step was followed by bleaching process with 1,75% of NaOCl and provided 15,84% of yield. The yield of each process was shown in Table 1. The color of the rice straw reduced in each step of processes, from brown to be white powder.

α -cellulose white powder from those processes was confirmed by FT-IR analysis (Fig. 1) and it was followed by characterizing the reference standard of α -cellulose standard.

In Fig 1. the α -cellulose from rice straw gave absorbency of OH vibration at 3411 cm⁻¹, the stretching of C-H is shown at 2900 and 894 cm⁻¹ while in reference standard α -cellulose the -OH peak is appeared at 3410 cm⁻¹ and the C-H is appeared at 2916 and 894 cm⁻¹. The details of wave number of α -cellulose absorbency were shown in Table 2.



Fig. 2: SEM images of rice straw α -cellulose

The microstructural morphology analysis of α -cellulose was shown up in Fig. 2. The morphology of α -cellulose fibers gave the appearance like fiber bundle. This result is close to the α -cellulose's morphology reported in the literature²¹.

Fig. 3 showed the TG curve analysis of α -cellulose standard and from rice straw. The thermal degradation of α -cellulose consists of a series of degradation reaction, such as dehydration and pyrolysis. The dehydration reaction occurred at 100 °C, this weight loss was mainly due to the evaporation of water that binding on α -cellulose. While the pyrolysis reaction occurred at 338, 93 °C for α -cellulose standard and 350, 01 °C for α -cellulose from rice straw. Therefore, the rice straw α -cellulose is superior to that of α -cellulose standard. Obviously, the presence of other substituent (substituted group) on that cellulose skeleton is expected to influence thermos-stability. Those results were supported by the higher residue content in α -cellulose from rice straw than standard, 10, 77% and 8,25%, respectively.

Preparation and characterization of cellulose hydrogel

The synthesized of cellulose hydrogel was done by polymerization reaction between α -cellulose and poly sodium acrylate in the presence K₂S₂O₈ as initiator and NMBA as crosslinked agent. Fig. 4 displayed the proposed mechanism reaction of crosslinked superabsorbent between α -cellulose and poly sodium acrylate.

The polymerization of cellulose and poly sodium acrylate followed the rule of polymerization step, such as initiation, propagation, and termination. During the polymerization, NMBA with two pieces of reactive double bonds can enter the chains of polymer simultaneously and form the permanent

Table 2: FTIR data of α -cellulose from rice straw and reference standard

Wave number (cm ⁻¹) Reference standard α -cellulose	Rice straw α -cellulose	Functional group
3410	3411	O-H stretching
2900898	2900894	C-H stretching
1373617	1373609	C-O stretching C-O bending

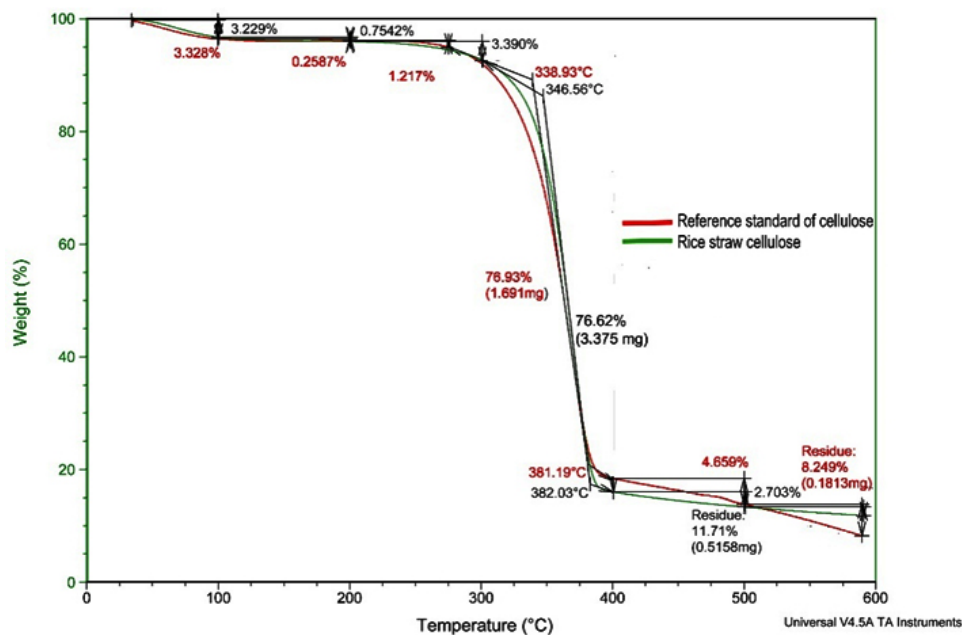


Fig. 3: TGA analysis of α -cellulose from rice straw and reference standard

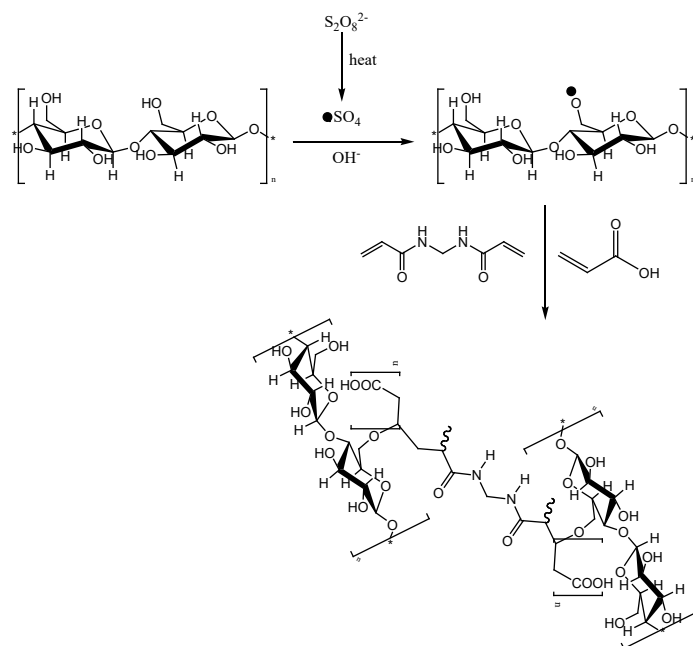


Fig. 4: Crosslinked reaction between α -cellulose and polyacrylate

Table 3: Swelling ratio of cellulose hydrogel

No.	Temperature (°C)	M_o (g)	M_t (g)	S
1	70	0.1662	37.5982	225,2226
2	80	0.1671	25.2402	150,0484

bonding between each chain (crosslinking). The degree of crosslinking influences the swelling ability of cellulose hydrogel. The swelling ability of hydrogel decrease with the increasing of degree of crosslinking. In the end of the reaction cellulose hydrogel has white color and chewy texture.

Swelling ratio has linear correlation to the absorbency capacity, the highest the swelling ratio the highest the absorbency capacity of hydrogel, in this research the hydrogel was immersed for 24 hours. The swelling ratio data is showed in Table 3 and Fig.5.

The rate of swelling of cellulose hydrogel progresses slowly because when the hydrogel contact with water, the outer side of hydrogel is dry. The impact is the hydrogel in water will form

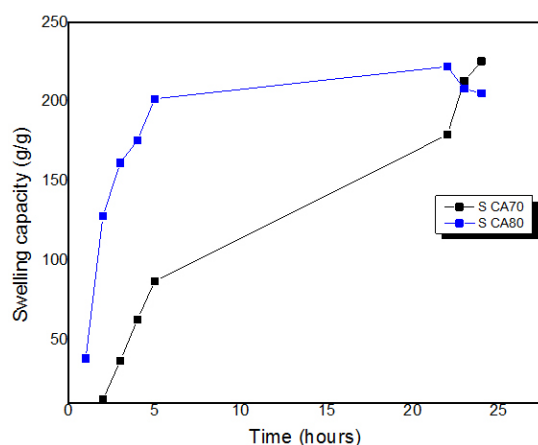


Fig. 5: Swelling ratio hydrogel vs time

two phases, such as the swollen hydrogel and dried polymer. The process of water enters into the hydrogel occurred through diffusion process²². Table 3 showed the cellulose hydrogel that prepared at 70 °C of temperature has the highest swelling ratio, 225, 2226. These differentiate are influenced by the degree of crosslinking of hydrogel. The increasing of degree of crosslinking of hydrogel can decrease the swelling ability but it can increase the mechanic properties of hydrogel²³. Those results indicated, the cellulose hydrogel that prepared at 70 °C has the lower of degree of crosslinking than cellulose hydrogel that prepared at 80 °C. Other than degree of crosslinking, the swelling ratio of hydrogel is influenced by some factors, such as (1) interaction of polymer-solvent, (2) elasticity interaction, (3) osmotic pressure, and (4) electrostatic repulsion²⁴.

The cellulose hydrogel is characterized by SEM to provide the surface morphology of hydrogel (Fig. 6). The SEM microphotograph of cellulose hydrogel C₇₀ and C₈₀ showed on the surface of hydrogel there some part of α -cellulose fiber. It indicated the α -cellulose content only reacted partially with the poly sodium acrylate and NMBA as crosslinked agent. On the hydrogel surface no pores observed, this result is close to the α -cellulose's morphology reported in the literature²², generally the pores on the surface of super absorbent polymer are random close to semi open cells. Because of the pores system of cellulose hydrogel is random close cells the urea absorbency occurred by diffusion process than capillarity²⁵.

Table 4: FTIR data of hydrogel

Wave number (cm ⁻¹) α -selulosa	HSA 70	HSA 80	Functional group
3411	3444.87	3446.79	O-H
2900	2924.09	2926.01	C-H
-	2854.65	2856.58	
894	854.47	-	
-	-	-	
-	1720.50	1722.43	C=O
-	1629.85	1629.85	
1373	1390.68	1398.39	C-O / C-N
—	—	-1168.86	
-	1043.49	1047.35	
609	584.43	582.50	

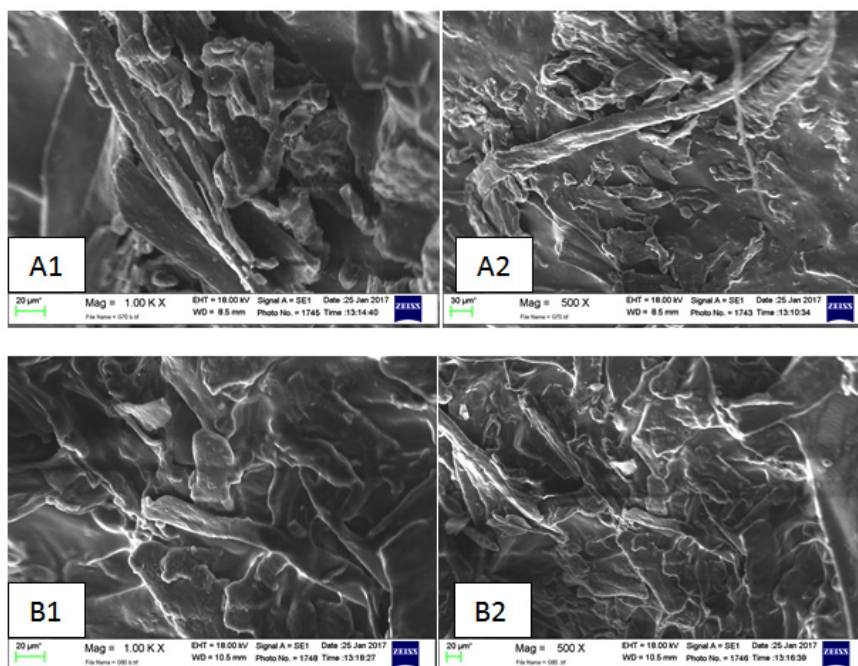


Fig. 6: SEM images of hydrogel with reaction temperature 70 °C, magnification 1000x (A1) and 500x (A2), hydrogel with reaction temperature 80 °C, magnification 1000x (A1) and 500x (A2)

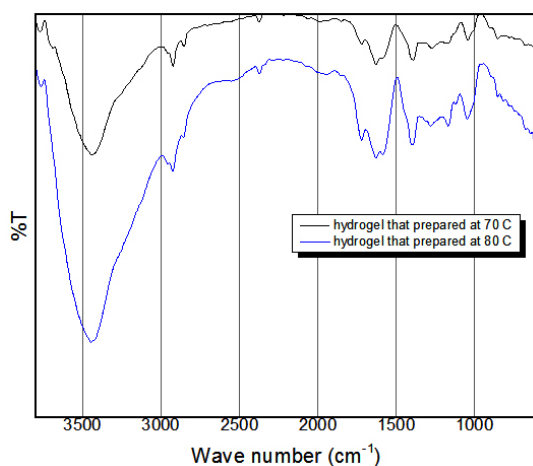


Figure 7: FT-IR spectra of hydrogel

To identify the cellulose hydrogel has been synthesized, the FT-IR spectra analysis gave the data of functional group of hydrogels (Fig. 7 and Table 4).

Fig. 7 showed, there are peak at 3446 and 3600, that indicate the presence of hydroxyl (O-H) and amino (N-H) group from cellulose and NMBA, respectively. The other peak that can prove the synthesis has been occurred are the presence of

peak at 1722-1629 and 1398-1016. Those peaks indicated the presence of carbonyl group (C=O) and C-O or C-N, respectively²⁶. The presence of C=O group in the hydrogel spectra indicated the synthesized has been occurred before the synthesis process, this peak in-appearance in the cellulose FT-IR data.

In this research, hydrogel that will be chosen for further application is the hydrogel that provide the slow rate in the releasing urea to the water. In analogy, the releasing of urea to the soil when it applied will provide controllable of hydrogel in the release of urea also it will provide the stable rate of the release urea. To measure controlled-release of urea of hydrogel, the dried one is immersed in water and the water was measured by UV-vis technique in range of 15-150 minutes at 420 nm. The reaction that occurred in the UV-vis measurement was shown in Fig. 8.

Fig. 9 showed the calibration curve of urea standard that provided regression formula, $y = 0.0019x - 0.0027$ with $R^2 = 0.9953$. In Fig. 10 provided data of the absorbance curve of controlled-release of urea in 15-150 minutes. The conversion

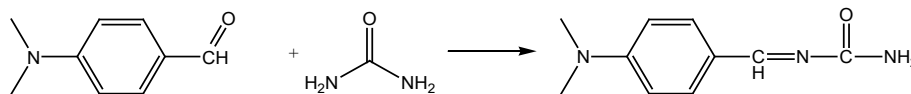


Fig. 8: Reaction of urea and DMAB

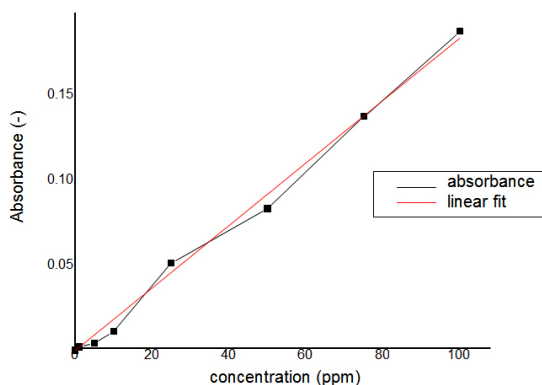


Fig. 9: Calibration curve of urea standar

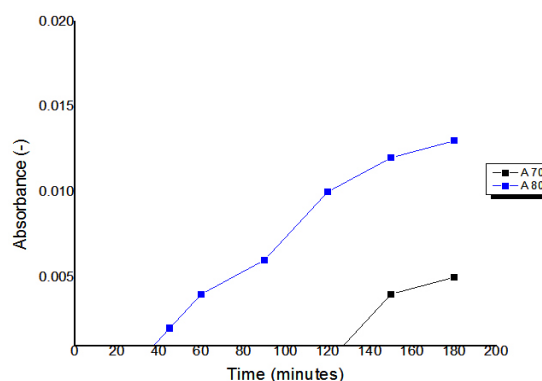


Fig. 10: Graphic of controlled-release urea (based on absorbance)

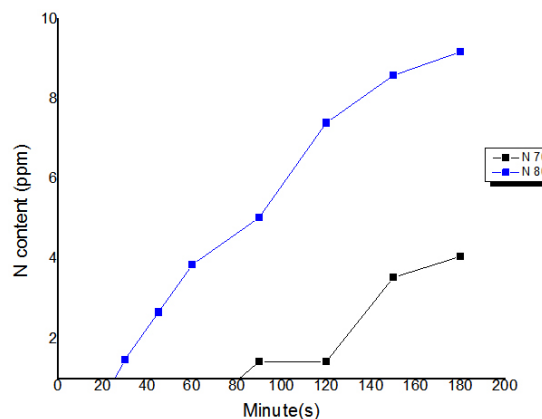


Fig. 11: Graphic of controlled-release urea (based on N content)

of absorbance value will provide other data, that is N% content value by substituting the absorbance value to the regression formula. After substituting those value, the N% content of each treatment was displayed in Fig. 11.

The hydrogel that prepared at 70 °C of temperature has the slowest controlled-release of urea, which showed the first released of urea held in minutes of 90 with N% content of 0.3684 ppm and at minutes of 180 this hydrogel also gave the low value of N% content of 4.05263 ppm. In other side, the hydrogel that prepared at 80°C the first released of urea held in minutes of 30 with N% content of 1.4210 ppm and at minutes of 180 this hydrogel also gave the low value of N% content of 8.2631 ppm.

The objective of this research is to obtain the model of hydrogel with two properties, where it was related to each other. Both are high absorbency capacity and slow in the release of urea. Therefore, the suited model of hydrogel that has both properties is the hydrogel which prepared at 70 °C of reaction temperature. It is altogether reasonable to conclude that the hydrogel which prepared at 70 °C is the suited model of hydrogel for applied in slow-release of urea, because of this hydrogel has the slowest number in the release of urea. Besides that, this hydrogel has the highest absorbency capacity, it means it can load much number of urea. The highest absorbency capacity is linear to the ability of hydrogel to expand itself in the urea solution, that calculated as swelling capacity. The highest the swelling ration and absorbency capacity, the lowest the number of crosslinking unit in the hydrogel that prepared in 70 °C of reaction temperature.

CONCLUSION

The α -cellulose-g-poly(acrylic acid) super absorbent composite was synthesized by graft copolymerization reaction of α -cellulose rice straw and AA in aqueous solution. The highest water absorbency and the slowest profile of release controlled were obtained when the temperature of polymerization reaction was 70 °C.

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