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Hydrogel Composite Based On Arrowroot Starch-G-Poly (Acrylamide-Co-Acrylic Acid)/Zeolite as Matrix of Controlled Release Urea Fertilizer

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Abstract: Agricultural yields can be increased through fertilization. Conventional fertilization by spreading fertilizer on agricultural land is very ineffective. As much as 40-70% of the nitrogen from urea given through conventional fertilization will be leaching. This problem can be overcome by implementing a new fertilization system, namely by applying controlled fertilizer release technology or Control Release Fertilizer (CRF). The CRF system is made by loading or mixing urea fertilizer at the time of synthesis of a composite based on Arrowroot Starch-g-poly (acrylamide-co-acrylic acid)/zeolite. Fertilizer will come off gradually during fertilizing the land. Synthesis of starch-based hydrogel composite Arrowroot Starch-g-poly (acrylamide-co-acrylic acid)/zeolite loaded or mixed with urea fertilizer, has been successfully carried out. The composite's structure characterized by IR spectroscopy and its ability as CRF has also been tested through swelling and urea release tests in distilled water, phosphate buffer pH 5, pH 7 and pH 9. The results show that the swelling capacity and urea release in distilled water > Buffer pH 7 > pH 9 > pH 5. The welling degree in distilled water, Buffer pH 5, pH 7 and pH 9 is 39.078; 18,719; 36,296 and 33,510 g.g^{-1} respectively and the release of urea is 2,129; 1,829; 2,110; and 2,091 mg.mL^{-1} respectively and they showed significant differences.

Keywords : urea, CRF, Hydrogel Composite, swelling.

INTRODUCTION

Urea fertilizer is one of the fertilizer sources of nitrogen, with a nitrogen content of 46%. Urea fertilizer applied by conventional fertilization methods (spread directly on the land), will be inefficient because not all urea will be absorbed by plants but partly lost due its leaching to the environment and carried by the wind through evaporation. According to Nielson [1], about 40-70% of nitrogen given through conventional fertilization will leaching. Inefficient fertilizer delivery will harm farmers economically. This problem can be overcome by applying new fertilization technology through controlled release fertilizer (CRF) [2].

Several ways to make CRF have been implemented. Azeem et al [3] make CRF by coating the urea. Zheng et al [4] made CRF by a static method i.e. a fertilizer solution absorbed by the polyacrylamide hydrogel would then be released again during fertilization. Liu et al [5] made CRF by introducing urea fertilizer during synthesizing hydrogels from acrylic acid monomers and maleic acid. The manufacture of CRF by Liu et al [5] method gives better results than other methods. Fertilizer coating will greatly depend on the thickness of the layer that envelops the fertilizer while for static methods it is impractical and not all fertilizers will be absorbed.

Hydrogel is a hydrophilic polymer material that is able to absorb water in wet conditions (swelling) and release water in dry conditions so that hydrogel can be used as a fertilizer release material. Hydrogels synthesized from natural polymers are called natural hydrogels or natural hydrogels. Natural hydrogel has advantages in its biodegrability and is classified as a renewable polymer. Natural hydrogel can be made from cellulose, chitosan, alginate and starch. One of the synthesis of hydrogels from natural polymers such as starch as a base chain can be done by grafting techniques using incinerators and requires the addition of cross-binding agents such as methylene bis-acrylamide as well as certain monomers such as acrylic acid, acrylamide involving radical reactions. Some types of starch that have been reported in hydrogel synthesis are corn bean starch [6], wheat starch [7], and sago starch [8]. Characteristics of successful synthesis of hydrogels through grafting can be known in the IR spectrum which displays the wave numbers of its constituent monomers and the shift of wave numbers in the methylene region [6].

Several studies related to hydrogel synthesis, swelling tests, and its ability as CRF, have been reported. Ren et al [9] synthesize hydrogels from Sugarcane Bagasse-g-poly (acrylic-co-acrylamide acid) by varying the ratio of acrylamide to total monomers from 0.1 to 1.0 and variations in the ratio of total monomers to Sugarcane Bagasse ranging from 2 to 8 each variation, obtaining the highest swelling yield at a ratio of ~0.6 with swelling of 260 g.g^{-1} and ratio of ~3 with swelling of 270 g.g^{-1}. Liu et al [5] synthesizing poly (acrylic acid-co-maleic acid) with urea loading variations of 6-18 grams found that the highest swelling at urea loading was ~10 g with a swelling value of 1000 g.g^{-1}. Tyliszczak et al [10] also synthesized poly hydrogel (acrylic acid) with urea variations ranging from 10 to 50% wt indicating increased swelling values ranging from 250 g.g^{-1} to 275 g.g^{-1}. The small amount of swelling value produced from hydrogel will affect the fertilizer release process. A high swelling value will lead to a rapid release of fertilizer. To overcome this mass, it can be done by adding natural minerals to reduce swelling. Zhang et al [6] added the mineral organomordenite (zeolite) in the pati-g-(polyacrylate) hydrogel with variations of 0% to 30% wt.

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The addition of minerals up to 10% indicates swelling reaches 750 $g.g^{-1}$ while for the addition of more minerals up to 30% wt causes a decrease in swelling to 450 $g.g^{-1}$.

In this article, will be discussed the synthesis of hydrogel composites based on Arrowroot Starch-g-poly(acrylamide-co-acrylic acid)/zeolite with a Arrowroot starch composition of 8 g, acrylamide monomers 16 g, acrylic acid 7.2 g, zeolite 31.20 g and urea fertilizer loaded by 6.24 to 31.20 g. The resulting hydrogel composite will be characterized by the IR spectrum and evaluated in the aquades medium, pH buffer 5, pH 7 and pH 9 to determine the effect of variations in loading urea amounts and pH variations on swelling and urea release from hydrogel composites.

METHODS

Materials

The materials used in this synthesis as is received include local Arrowroot starch (*Cap Burung*), Acrylic Acid (AA, Merck), Acrylamide (AAm, Merck), N,N-Meethylene-Bis-Acrylamide (MBA, Merck), Potassium Persulfate (KPS, Merck), Subsidized Urea Fertilizer (Brand), Standard Urea (Merck), Hydrochloric Acid p.a 37% (HCl, Merck), Universal pH, Ethanol 96% (Technical), NaOH (Merck), p-dimethylaminobenzaldehyde (DMAB, merck), KOH (technical), $NaH_2PO_4.2H_2O$ (Merck), Na2HPO4.2H2O (Merck), Aluminum Foil, Filter Paper. Equipment used includes GlassWare, Thermometer, Glass Bottle, Mixer Rod, Electric Handler, Buchner Funnel, Analytical Balance Sheet, pH Meter, UV-Vis Spectrophotometer Model 752, Shimadzu FT-IR 8400S.

Preparation of Arrowroot Starch and Zeolite

The preparation of scratch starch is basically referring to the method that has been reported by Faridah et al [11] with minor modifications. Preparations carried out in 4 stages i.e. washing with water, soaking with NaOH 0.1 M for 24 hours, washing with distilled water to neutral (standard pH 7), drying and sieving 120 Mesh. Natural zeolite preparation basically refers to the method that Zhang et al has published [12] with minor modifications. Preparations include washing with aquifers thoroughly, drying at 100 °C for 24 hours and sifting 120 Mesh.

Synthesis of Hydrogel Composite pg-g-poli (AAm-co-AA)/Zeolit

The synthesis of the Arrowroot Starch -g-Poli (AAm-co-AA)/Zeolite hydrogel composite follows the Barati [13] and Zhang et al [6] methods with minor modifications. Hydrogel composites are synthesized by heating an 8% (b/b) solution of the starch at a temperature of 55-60 °C with continuous stirring for 10 minutes for the formation of a slightly viscous gelatin (still can be flowed). The KPS initiator is added to the starch solution and stirred at a temperature of 60 °C. A mixture of comonomers (AAm and AA that have been neutralized 12.5% with KOH) is added in the starch solution and stirred until homogeneous. To the mixture is then added with MBA while stirring until homogeneous. Zeolites and urea fertilizers that have been moistened with aquifers are added to the mixture and stirred until homogeneous. The result of mixing all components in a closed container, kept in the oven for 24 hours at a temperature of 60 °C. The resulting hydrogel composite is cut into small pieces and dried at a temperature of 60 °C for 6 days. Detailed composition of hydrogel composite synthesis in Table 1.

Table 1. Composition of Hydrogel Composite Constituents

Code	Mass (g)						
	Starch solution 8% (b/b)	AAm	AA	KPS	MBA	Urea	Zeolit
H_{UZ0}	100	16	7,2	0.5	0.02	0.00	0.00
U_0	100	16	7,2	0.5	0.02	0.00	31.20
U_{20}	100	16	7,2	0.5	0.02	6.24	31.20
U_{40}	100	16	7,2	0.5	0.02	12.48	31.20
U_{60}	100	16	7,2	0.5	0.02	18.72	31.20
U_{80}	100	16	7,2	0.5	0.02	24.96	31.20
U_{100}	100	16	7,2	0.5	0.02	31.20	31.20

Note: HUZ0 code for hydrogel without urea zeolite, Code U for hydrogel composites and subscript numbers express urea variation (20-100% against total starches and monomers).

Hydrogel Composite Analysis by IR Spectroscopy

The IR spectra of solid hydrogel composite was recorded on the Shimadzu FT-IR 8400S instrument runs on wave numbers 400-4000 cm^{-1}. The same procedure is performed for Arrowroot starch, hydrogel without urea zeolite (HUZ0), natural zeolite, and composite hydrogel without urea (U0). The resulting IR spectrum is then analyzed.

Swelling Test of Hydrogel Composites

The hydrogel composite swelling test is performed by means of 0.1 g of hydrogel composite soaked in 100 mL of distilled water and phosphate buffers (pH 5, 7, and 9) for 24 hours. The hydrogel composite is filtered, left for 5 minutes and weighed. The magnitude of swelling (W) is determined using equation 1.

$$W(g.g^{-1}) = \frac{m_2 - m_1}{m_1} \qquad (1)$$

W: swelling value ($g.g^{-1}$)
m_2: wet weight (g)
m_1: dry weight (g)

Urea Released Test from Hydrogel Composite

The urea release test of the hydrogel composite is carried out by means of 0.3 g of hydrogel composite soaked in 40 mL of aquadest and Phosphate Buffer (pH 5, 7, and 9) for 7 days. Each 1-day interval of filtrate is taken as much as 2 mL and determined the concentration of urea released using the Erlich method which has been reported by Zhang et al [6], and AOAC [14] by adding DMAB reagents. The yellow color of the urea complex with DMAB reagent measured a wavelength of 420 nm using a 752 model UV-Vis spectrophotometer.

Statistical Analysis

The paired t test is performed to determine the difference in the results of urea release from hydrogel composites on the distilled water and pH 7 buffers. Paired t test conducted using α of 0.05 and assumptions as follows

H_0: The average release of urea in both mediums did not differ significantly.

H_1: The average release of urea in both mediums differs significantly.

RESULTS AND DISCUSSION

PG Hydrogel Composite -G-Poli (AAm-KO-AA)/Zeolit

Arrow root Starch-G-Poli hydrogel composite (Acrylamide-Co-Acrylic Acid)/Zeolite has been successfully synthesized. The color of the synthesized hydrogel composite is slightly different depending on the composition of its constituents. The presence of the mineral zeolite will cause the composite to be green. Hydrogels without zeolites will be orange (HUZ0). Hydrogel composites containing urea have a higher level of ductility than composites without urea.

Hydrogel Composite Characterization by IR Spectroscopy

The different pattern and peaks of absorption the of IR spectra were observed in the Arrowroot starch, the hydrogel IR spectrum of the scratch starch added KPS, MBA and monomers (AAm and AA), the zeolite, the hydrogel composite without urea, and the hydrogel composite. The existence of pattern changes and peaks of this absorption indicates that the process of hydrogel composites synthesis has been successfully carried out. The IR spectrum of the starch (Figure 1a) shows the peaks of absorption at numbers 3394, 2933, 1155 and 1020 cm^{-1} indicating the presence of OH alcohol, methylene, C-O alcohol and C-O-C ether function groups. The IR absorption of starch in hydrogel (HUZ0) with the addition of KPS, MBA and monomers (AAm and AA) are shifted and emerge in new peaks (figure 1b). The New peaks at wave numbers 2400-3600 (widened), 3196, 2947, 1715, 1680, 1618, 1456 and 1030 cm-1 indicate the presence of stretching of oh carboxylate, N-H amida, methylene CH, C=O carboxylate, C=O amida, N-H bending and C-O-C ether. Zhang et al [6] and Chang [15] mentioned that the successful of grafting was shown by a shift in the wave numbers of the methylene CH and C-O-C ether groups as well as the emergence of wave numbers from their monomers. The peak of absorption of 1618 cm^{-1} indicates the success of the process of neutralizing acrylic acid into potassium acrylic salts.

The IR spectrum of natural zeolite (figure 1c) shows the peaks of absorption in areas 3617, 3429 and 1032 cm^{-1} is evidence of Si-OH-Si, Si-OH-Al and Si-O-(Si/Al). Zeolites added to the hydrogel (HUZ0) into a urea-free hydrogel composite (U0) showed a shift in wave numbers of 3429 cm^{-1} to 3439 cm^{-1}, 1618 cm^{-1} to 1624 cm^{-1} and an increase in the intensity of peak absorption at 1048 cm-1 due to the addition of zeolite (Figure 1d). According to Zhang et al [6], this is due to the interaction of the polished ion H atom in Si-OH-Al with the COO group- in the hydrogel composite matrix. The IR spectrum of hydrogel composites the addition of urea fertilizer or U100 (Figure 1e) appears uptake of 3445.3362 cm^{-1} indicating NH_2 and increasing in intensity in C =O amide due to the addition of urea fertilizer. More details of the IR spectrum in Figure 1.

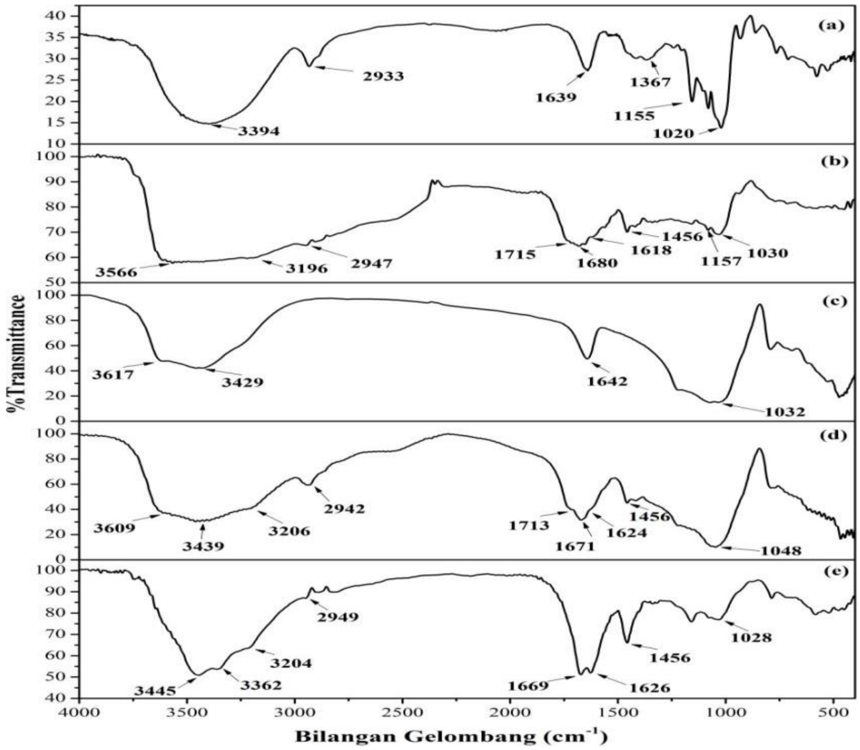

Figure 1. IR spectrum (a) Arrowroot Starch/PG; (b) hydrogel without urea zeolite/ HUZ0; (c) natural zeolite; (d) hydrogel composite without urea/U0; (e) hydrogel composite with urea/U100

Effect of Urea Variation on Swelling and Urea Release

The effect of variations in the amount of urea on swelling and urea release is carried out in the water. The results of the swelling test showed that the swelling of the hydrogel composite from U0 to U20 increased the swelling value by 2,927 $g.g^{-1}$ while for loading the larger amount of urea U20 to U100 decreased by about 2,176 to 12,945 $g.g^{-1}$ (Figure 2a). The increase in swelling due to the presence of urea can form hydrogen bonds with water and work synergistically with the coo^{-}, COOH and NH2 hydrophilic groups derived from acrylamide monomers and acrylic acids located in hydrogel composites [5] while the loading of larger amounts of urea decreases due to urea filling the matrix tighter and stiffer thus lowering swelling.

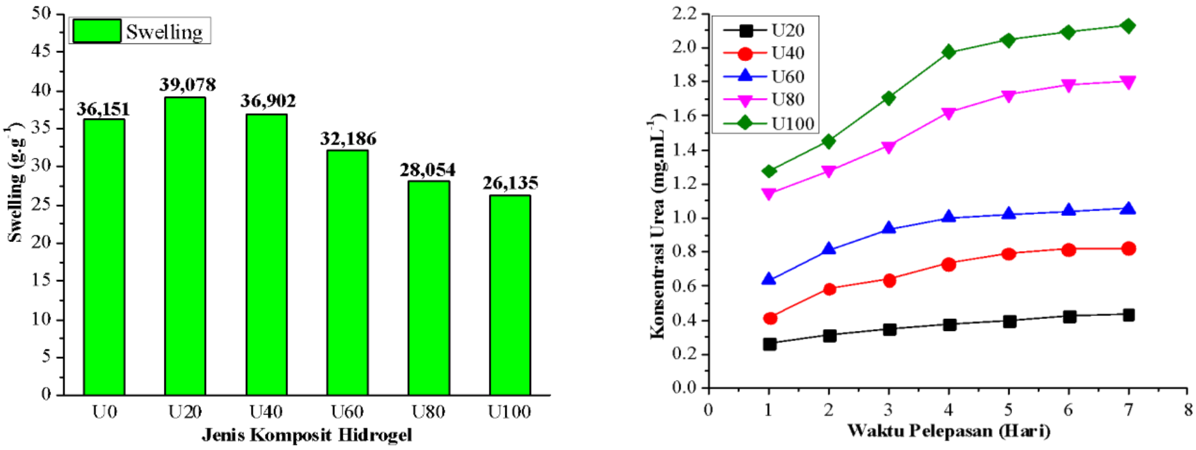

Figure 2. Effect of Variation in Urea Amount on Swelling (a) and Urea Release (b)

Figure 2b. Shows the largest urea release occurred in hydrogel composites with the highest loading amount of urea (U100) for 7 days reaching 2,129 mg.mL^{-1}. This is because when water enters the composite hydrogel (swelling) with the loading of a larger amount of urea then the soluble urea is greater. The more urea dissolved, the faster the mobility of urea to diffuse from within the hydrogel composite to the outer environment of the hydrogel composite matrix due to a much higher difference in concentration gradients resulting in greater urea loading resulting in a greater release of urea.

Effect of pH Variation on Swelling and Urea Release

The effect of pH variations on swelling and urea release is carried out on the phosphate buffer medium (pH 5, 7 and 9). The swelling results show swelling at pH 7 > pH 9 > pH 5. The swelling values on the medium buffer pH 5, pH 7 and pH 9 each produce consecutive swelling values with a range of 14.123-18.719 g.g^{-1}; 25,069-36,296 g.g^{-1} and 22,123-33,510 g.g^{-1} shown in Figure 3.

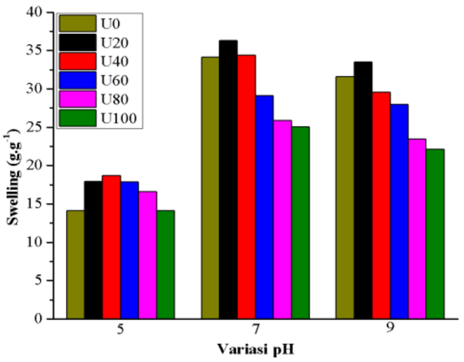

Figure 3. PH Variations against Swelling

In the medium buffer pH 5 will cause the COO^- and $-NH_2$ groups to be protonated into COOH and NH_3^+. The NH_3^+ group formed will cause the interaction of ions in the form of attraction between the NH_3^+ group and the negative charge of Al on the zeolite structure so that hydrogel composites are more difficult to swell. A hydrogel composite at pH 7 compared to pH 9 of the COOH function group that is deprotonated into a COO group-more at pH 9 than pH 7. The COO group- which is formed more causes the interaction of the ions in the form of COO-attraction-with more and more Na^+ ions resulting in a hydrogen bond that occurs between the NH_2 and COOH groups with more water molecules at pH so that the resulting swelling value is high pH 7 [6, 9].

Hydrogel composites in the pH 7 and pH 9 mediums do not experience the interaction of ions in the form of attraction with zeolite so that in both mediums is easier to experience swelling than in the pH 5 buffer. Medium buffer pH 5 which involves the interaction of ions in the form of pull of the NH_3^+ group with a negative charge of the zeolite causes for maximum swelling required higher urea (U40) while at pH 7 and 9 which has greater swelling ability only a lower amount of urea (U20) is needed for maximum swelling limited by cross-binding agents [6]. Hydrogel composites at various pH show urea release at pH 7 > pH 9 > pH 5 (Figure 4). The resulting urea release trend is in accordance with the swelling trend. Higher swelling will absorb water higher, causing higher amounts of soluble urea resulting in a higher release. The review for the variation in loading the amount of urea for each pH showed that the higher the amount of urea loaded, the higher the soluble urea so that the faster the diffusion process resulted in the high release of urea. The highest urea release occurs at U100 for medium buffer pH 5, 7 and 9 until it reaches 1.829; 2,110 and 2,091 mg.mL^{-1}.

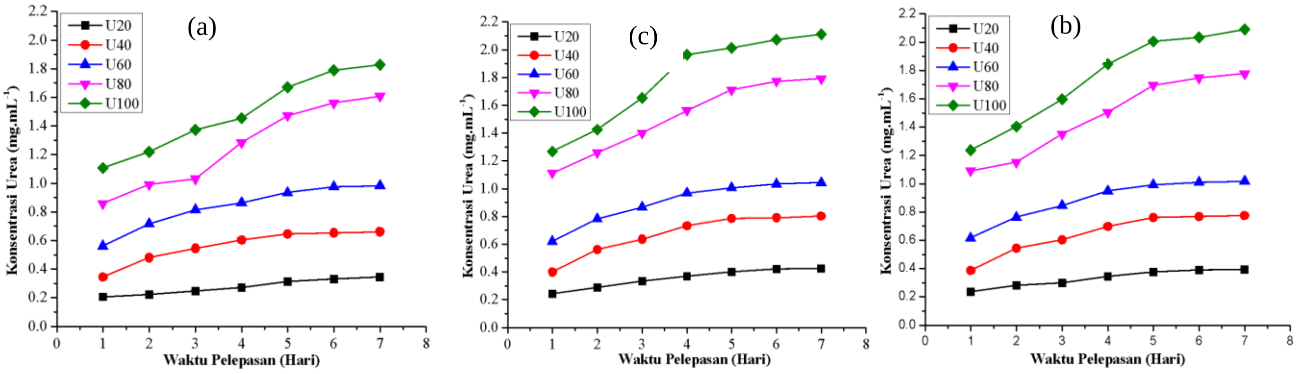

Figure 4. Urea Release (a) pH buffer 5; (b) pH buffer 7; (c) Buffer pH 9

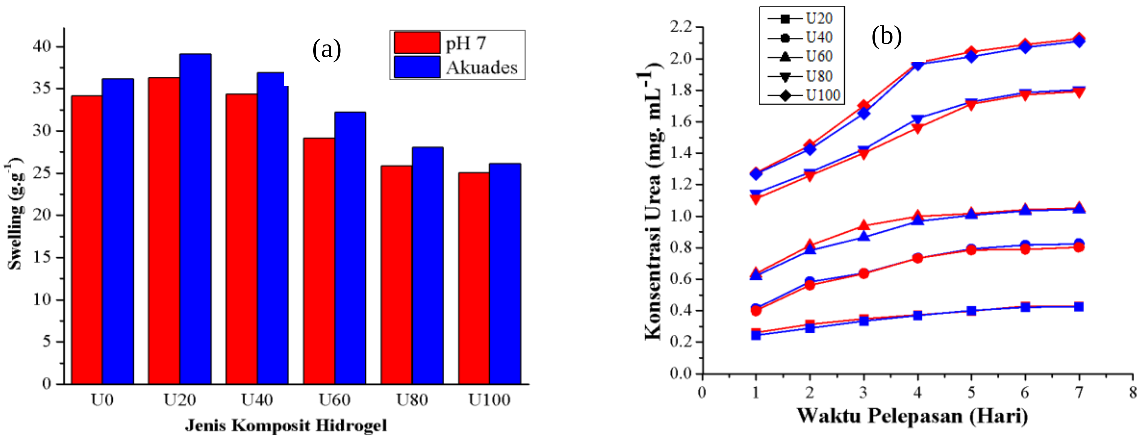

Figure 5. (a) Swelling and (b) Urea Release from Hydrogel Composites in distilled water and buffer pH 7

Effect of Distilled Water and Buffer pH 7 on Swelling and Urea Release

The results of swelling and release of urea from hydrogel composites in distilled water pH 7 and pH buffer 7 of the hydrogel composites U20, U40, U60, U80, and U100 on both mediums showed different swelling capabilities and had consecutive differences of 2,782; 2,526; 3,054; 2,189 and 1.066 g.g^{-1} are higher at distilled water (Figure 5a). The results of urea release tests on both mediums also showed that urea release in the distilled water was higher than the buffer pH 7 (Figure 5b). This is because in the distilled water system consists of H_2O molecules while in the pH 7 buffer consists of NaH_2PO_4, Na_2HPO_4 and H_2O. Ren et al [9] and Zhang et al [6] stated that the contribution of Na^+ ions to the pH 7 buffer resulted in the interaction of ions with coo groups- so that the interaction of polished ions that occur is lower than in distilled water. Low dipole ion interactions cause higher swelling and urea release in the distilled water.

The release of urea in both mediums that have similar values is carried out in pairs. The results of the t test showed that the t-count value for all types of hydrogel composites was higher compared to the t-table so it could be taken that the release of urea in both mediums differed significantly or reject H0 (Figure 6).

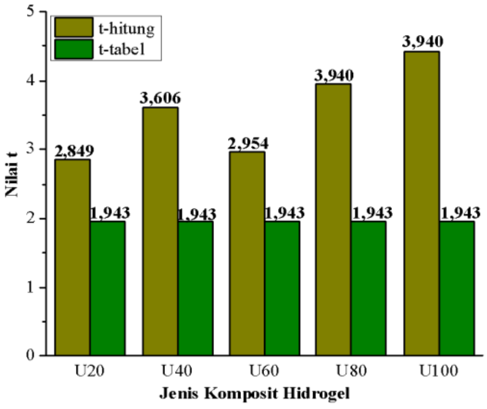

Figure 6. T test pairs urea release in distilled water and buffer pH 7

CONCLUSION

Hydrogel composite was successfully synthesized from arrowroot starch, Acrylic Acid, Acrylamide and zeolite which was characterized by the appearance of IR absorption peak of OH carboxylates, N-H amides, C=O carboxylates/amides, Si-O-(Si/Al). The greater the amount of urea loaded hydrogel composites, the greater the release of urea from the hydrogel composite. Swelling and release of urea at pH 7 > pH 9 > pH 5. The release of urea from the hydrogel composite in distilled water and buffer pH 7 differs.

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