RESEARCH ON THE USE OF AGRICULTURAL WASTE TO MANUFACTURE HIGHLY HYGROSCOPIC MATERIALS FOR AGRICULTURAL APPLICATIONS

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Abstract - Material based on hydrogel from rice-straw with high absorption capacity and slow water release was prepared by cryogenic method, using citric acid as cross-linker and without creating waste stream to the environment. The structure and properties of the material were characterized by SEM, XRD, FTIR and TGA method. The results showed that the largest water absorbency of the material reached 30.67g/g, 4.48 times higher than the original rice-straw. The material was able to slowly release water in 6 days at room temperature and return water absorption of 3.97 g/g when reusing the material. In addition, the material is biodegradable and biocompatible. With the obtained results and simple, inexpensive, environmentally friendly method, this is a material that can be industrially produced and widely used in green agriculture.

Key words - Hydrogel; rice-straw; water absorption; slow water release; cryoge

1. Introduction

Rice-straw is a by-product of agricultural that generates millions of tons per year (about 731 million of ton per year on the worldwide) [1]. Burning rice-straw in the field after harvest season creates an amount of greenhouse gas emissions and environmental pollution such as CO_2, CH_4, CO. However, rice-straw is a source of waste that contains a lot of cellulose in its composition (about 32 – 47%) [1]. Therefore, using rice-straw as a source of biologically derived materials for synthesis of hygroscopic material will contribute to minimizing environmental problems caused by agricultural by-product and especially contribute to on maintaining moisture and improving soil after cultivation.

Currently, the research is using biologically derived materials from agricultural by-products such as straw, rice husk, sawdust, pineapple peel, corn cob, etc. to synthesize hygroscopic materials based on hydrogels or similar structures are of interest to scientists. There have been several published studies on the use of cellulose from these agricultural by-products in the synthesis of hygroscopic materials for agricultural applications. The result shows that these materials when synthesized from cellulose not only ensure water retention but also has better biodegradability and biocompatibility [2]. However, the using of three main components of rice-straw (cellulose, hemicellulose and lignin) for synthesis of hygroscopic materials based on hydrogels was not reported so far. Therefore, the intention of this study was to prepare material based on hydrogel from rice-straw by cryogenic, using citric acid as a cross-linker without generating waste stream to the environment. Cryogenic methods can improve the mechanical properties of hydrogels without affecting the compatibility, biodegradability, and non-toxicity of polymeric gels. [2] Citric acid is one of the agents commonly used for crosslinking in the formation of hydrogels from lignocellulosic sources because citric acid is a hydrophilic, non-toxic, inexpensive, environmentally friendly organic acid that has 3 groups – OH which can form a three-dimensional network of hydrogels. Citric acid improves thermal stability, mechanical strength and swelling by forming strong hydrogen bonds. [2] In this study, the authors used PVA as an additive to increase the gelling ability of lignin and hemicellulose because PVA can form hydrogen bonds with lignin, hemicellulose and cellulose to form a framework, this mechanism has been demonstrated by Huang and associates. [3] The successful synthesis of material based on hydrogel from rice-straw by simple process, low cost and friendly with the environment would open ability of wider applications in soil improvement in drought areas, especially is green agriculture field.

2. Experimental

2.1. Materials

Rice-straw is taken from the field of Quang Tri Town, Quang Tri province.

The chemicals including sodium hydroxide, polyvinyl alcohol, citric acid from Xilong Company - China and are used directly without any additional processing. All solutions were mixed with distilled water.

2.2. Alkaline hydrolysis of rice-straw

4 grams of rice-straw were hydrolyzed in NaOH 2M using heating magnetic stirrer with temperature maintained at 90^oC for 2 hours and stir continuously at a stirring rate of 200 rpm (round per minutes) [4].

2.3. Synthesis of material based on hydrogel from rice-straw

After obtaining the suspension includes cellulose, hemicellulose, lignin and NaOH, suspension was reacted with 10ml Polyvinyl alcohol (PVA) 0.4%wt solution for 30 minutes at a stirring rate of 200 rpm to increasing the gelation of lignin and hemicellulose.

Sol obtained after adding PVA was treated at -20^oC in cryogenic zone of refrigerator within 24 hours to carry out the gelation process. After cryogenic treating, the gelation product was separated from 20 ml alkaline residual solution. The later was stored and used for the next synthesis in alkaline hydrolysis stage.

The hydrogel obtained after cryogenic will be treated by immersing in 20% citric acid solution for 20 hours [5] at ambient temperature to increase mechanical strength by forming cross-links between citric acid and cellulose molecules.

Hydrogel-based material from rice-straw is then dialyzed with water to remove free ions remaining in the cellulose hydrogel. The pH of the solution after dialysis is measured with pH paper in the range of 7-8. After successful synthesis, the material properties were investigated.

2.4. Methods to investigate physicochemical properties of hydrogel from rice-straw

2.4.1. Evaluation of sample structure and properties characterized by modern physicochemical analysis methods.

Morphology of the material was observed by using Scanning Electron Microscope (SEM, JEOL JSM-6010PLUS/LV, Japan). Phase composition of material was analyzed by X-ray Diffraction method (XRD, Rigaku – Smartlab, Japan). Diffraction graph was recorded from 5^o to 80^o with scan rate is 2^o per minute. FI-IR infrared spectrum of the sample was analyzed by FTIR Nicolet 6700 equipment. Material to be measured about 500 to 4000 cm^{-1} wave number with resolution is 4 cm^{-1}. Thermal stability of the sample was evaluated in N_2 condition by Thermal Gravimetric Analysis (TGA, STA6000, American), temperature was heated from 20 to 800^oC with heating rate is 10^oC per minute.

2.4.2. Evaluation of water absorption – releasing of the material

After fully absorbed water, the material surface was eliminated residual water and weighted to obtain the wet weight of sample(w_1). Water is released from the material at ambient temperature and its masses were recorded to demonstrate graphically the profile of water content in sample over time until getting a constant mass (w_2) [6]. The water absorption capacity was calculated and reported to 1g rice-straw hydrogel-based material (W) according to formula (1):

$$W(g/g) = \frac{w_1 - w_2}{w_2} \qquad (1)$$

After obtaining a constant weight, the sample was tested in water re-absorption and releasing for accessing the recycle ability of research material.

Procedure of synthesis and characterization of rice-straw hydrogel-based material is presented on the figure at below:

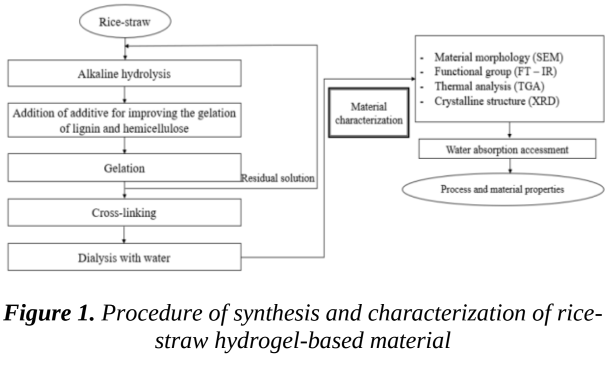

Figure 1. *Procedure of synthesis and characterization of rice-straw hydrogel-based material*

3. Results and discussions

3.1. Morphological and structural properties of the material

The morphologies of the rice-straw, rice-straw after alkaline hydrolysis, rice-straw after addition of PVA and hydrogel-based materials were observed by scanning electron microscopy. Figure 1 shows SEM images of rice-straw (A), rice-straw after alkaline hydrolysis (B), rice-straw after addition of PVA (C) and rice-straw hydrogel-based material (D) (x500 magnification).

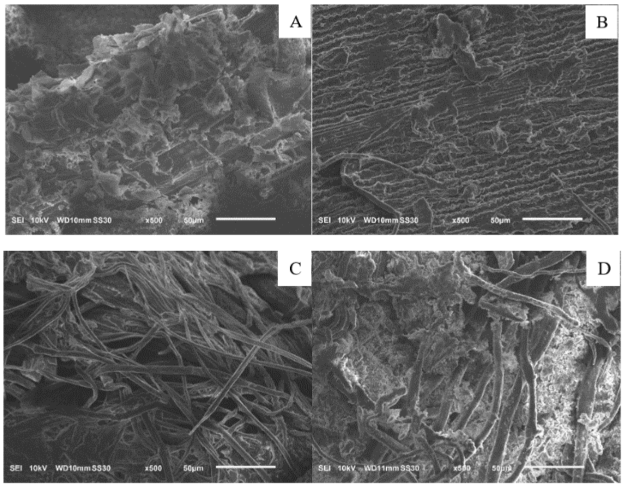

Figure 2. *SEM images of rice-straw (A), rice-straw after alkaline hydrolysis (B), rice-straw after addition of PVA (C) and rice-straw hydrogel-based material (D) (x500 magnification)*

The comparison between rice-straw structure (A) and rice-straw after alkaline hydrolysis (B) in Figure 2 shows untreated rice-straw has a stiff, block structure surrounded by lignin, while alkaline hydrolysis treatment causes structural changes. Alkaline hydrolysis separated the hemicellulose and lignin, leaving the rough surface of fibrous cellulose. Similar results were also found in the publication by Damaurai et al. when pre-treating the straw with NaOH [7]. It can be seen that the alkaline hydrolysis helped to separate lignin and hemicellulose, increasing the efficiency of cellulose access. The use of alkali increased the internal surface area of the cellulose, exposing the cellulose to PVA and citric acid during synthesis. This result is also clearly visible in the infrared spectrum of the initial rice-straw (A) and rice-straw after alkaline hydrolysis (B) in Figure 3.

Compared to the rice-straw structure after alkaline hydrolysis (B), the addition of PVA could helps disperse the lignin and hemicellulose between the cellulose fibers, producing an increase in volume of the sample compared to original straw. At the same time, PVA adheres to the surface of cellulose fibers to lose the asperity of cellulose after alkaline hydrolysis. The SEM image (D) shows the white spots formed, which are believed to be esters of PVA and citric acid, which help form a tighter bond between cellulose, lignin, and hemicellulose, which increases the mechanical resistance of the sample. This result is also compatible with the analyses of the FT-IR and XRD characterization studies.

The determination of the functional groups presenting in the structure of the rice-straw, rice-straw after alkaline hydrolysis and rice-straw hydrogel-based material was performed using the FT-IR infrared spectroscopy method shown in Figure 3.

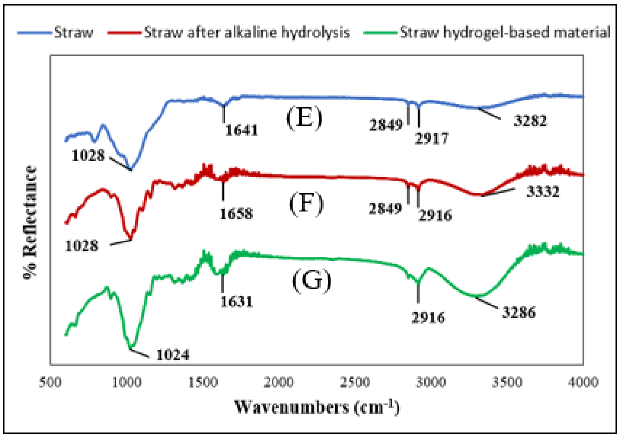

***Figure 3.** Infrared spectra of rice-straw (E), rice-straw after alkaline hydrolysis (F) and rice-straw hydrogel-based material (G)*

The FT-IR spectra of rice-straw, rice-straw after alkaline hydrolysis and rice-straw hydrogel-based material in Figure 3, in turn observed at 3282 cm^{-1}, 3332 cm^{-1} and 3286 cm^{-1} are supposed to the -OH bond stretching vibration corresponding to the presence of alcohol and phenolic hydroxyl groups. The maximum at 2916 cm^{-1} and 2917 cm^{-1} corresponds to the stretching vibration of the C - H sp^3 bond, at 1641 cm^{-1}, 1658 cm^{-1} and 1631 cm^{-1} corresponds to the stretching vibration of the C$_{Ar}$ - H bond. The maximum observed at 1028 cm^{-1} and 1024 cm^{-1} corresponds to the C - O stretching vibration [5]. Compared to the infrared spectrum of the rice-straw, it can be clear that after the alkaline hydrolysis, there is a stretching vibration of the -OH group, the C - H sp^3, C$_{Ar}$ - H and C - O bonds of the rice-straw, which a narrower peak and higher absorbance. This can be seen that after alkaline hydrolysis, the cellulose is separated from the original lignin and hemicellulose, resulting in an increase in the density of -OH groups, C - H sp^3, C$_{Ar}$ - H bonds and C - O present in the structure from cellulose. Similar to the XRD results in Figure 3, the FT-IR results also showed that the alkaline hydrolysis helped separate lignin and hemicellulose, thereby increasing the efficiency of cellulose access.

The –OH bond stretch observation in Figure 3 for rice-straw hydrogel-based materials (G line) compared to rice-straw after alkaline hydrolysis (F line) and initial rice-straw (E line) at peaks of 3286 cm^{-1}, 3332 cm^{-1} and 3288 cm^{-1}, the rice-straw hydrogel-based material can be observed with a wider peak [8]. This result could be explained by the enhancement of intermolecular hydrogen bonds in rice-straw hydrogel-based materials between the -OH groups on the chains of cellulose and PVA. These interactions lower the vibrational energy of the -OH group therefore the peak could be shifting towards lower energy as well as widening peak width. Compared to the infrared spectrum of rice-straw and rice-straw after alkaline hydrolysis, stretching vibrations of C - H sp^3, C$_{Ar}$ - H and C - O bonds of the rice-straw hydrogel-based material can be seen it has narrower peaks and higher intensity. Here it can be observed that the hydrogel-based materials show an increase in the bond density of C - H sp^3, C$_{Ar}$ - H and C - O, respectively, the times when the PVA was involved in the formation of hydrogen bonds in lignin, hemicellulose and cellulose in the framework of the material. In addition, the citric acid involved in crosslinking also leads to an increase in the density of C - H sp^3 and C - O bonds in the structure of the material. Close to the SEM results, the FT-IR results also showed that PVA was involved in hydrogen bonding with lignin, hemicellulose and cellulose to form the structure of the material.

The structure and phase composition of the rice-straw, rice-straw after the alkaline hydrolysis and rice-straw hydrogel-based material were analyzed by X-ray diffraction. Figure 4 shows the X-ray diffraction graph of the rice-straw (a), rice-straw after the alkaline hydrolysis (b) and rice-straw hydrogel-based material (c).

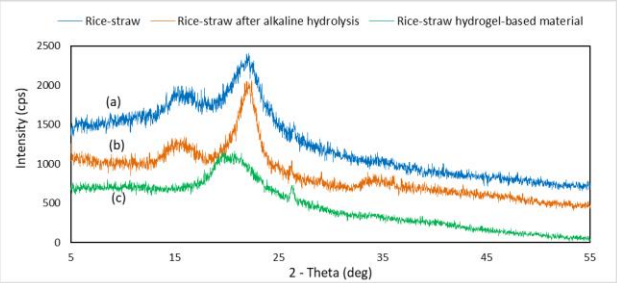

***Figure 4.** XRD measurement results of rice-straw (a), rice-straw after alkaline hydrolysis (b) and rice-straw hydrogel-based material (c)*

Figure 4 shows that the initial rice-straw and rice-straw after alkaline hydrolysis have crystalline structure with the characteristic peak appearing at angle of 2-theta of 22.2°, coinciding with the spectrum of i-alpha ($C_6H_{10}O_5$)n cellulose in the X-ray diffraction spectrum data. The XRD spectrum of rice-straw after alkaline treating showed an increase in intensity and decrease in width of the peak at 2-theta of 22.2° when compared to the one of the initial rice-straw. This XRD result evidenced that the NaOH solution has separated lignin and hemicellulose out of the cellulose surface. This phenomenon made easier the reach of hydrolysis solution to cellulose surface. In plus, the degradation of hydrogen bonds in crystalline regions of cellulose facilitating the hydrolysis of glycosidic bonds and ester bonds, may be the main reason for increasing the peak intensity of rice-straw after alkaline hydrolysis [9]. Hydrogel-based materials mainly showed peaks at 2-theta of 21° smaller than the one of initial rice-straw. This result can be explained by the increase in the distance between the faces of crystals of the alkaline hydrolyzed cellulose. Thus, the NaOH solution should have ability to remove lignin and hemicellulose out of cellulose surface and regroup them in the network between the cellulose fibers. In addition, the specific peak of citric acid was not seen in the XRD spectrum, which may indicate that citric acid was fully dispersed thank to its capacity to create the cross-linking with cellulose through the esterification reaction.

The TGA performed to evaluate the thermal stability of hydrogel-based materials and rice-straw is shown in Figures 5 and 6.

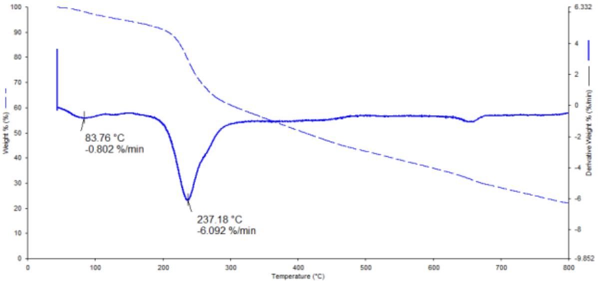

Figure 5. *TGA curve of rice-straw hydrogel-based materials*

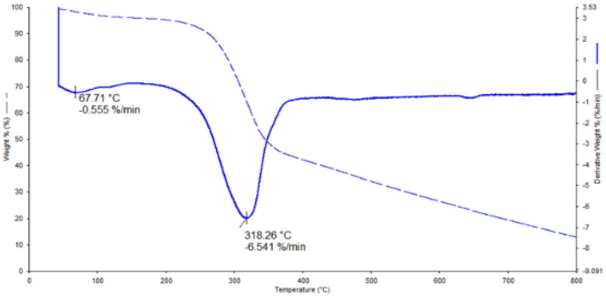

Figure 6. *TGA curve of rice-straw*

The TGA curve of the hydrogel-based material in Figure 5 shows two main stages of thermal degradation. The first stage, from about 50°C to 120°C corresponds to the loss of physically adsorbed water on the material surface. The second mass reduction between 220°C and 280°C corresponds to the decomposition of the branch or side chain of the polymer [10]. Comparing the TGA curve of the rice-straw (Fig. 6) and the resulting material, it was supposed that the hydrogel-based material would reduce the decomposition temperature of the branch or side chain of the polymer compared to the original rice-straw. This can be explained by the fact that after the straw treatment, the cellulose is not protected by lignin and hemicellulose, so the cellulose decomposes easily, the decomposition temperature is lower.

3.2. Evaluating the effectiveness of water absorption, release and reuse ability of rice-straw hydrogel-based materials

Figure 7 is an image of the hydrogel-based material obtained from rice-straw when the material absorbs the maximum amount of water (a) and the material after releasing water to a constant weight (b).

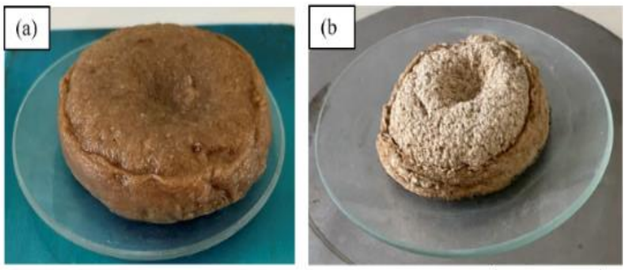

Figure 7. *Rice-straw hydrogel-based material (a) when the material maximally absorbs water (b) when the material releases water to constant mass*

Upon obtaining the data in Table 1, constructs a graph showing the water release capacity of the rice-straw hydrogel-based material over time in Figure 8.

Table 1. *Data table of sample weight obtained over time*

Time (hour)	Sample weight (g)
0	34.36
24.5	24.85
72	11.51
96	8.47
120	5.90
144	3.69
168	3.73
192	3.70
216	3.67
240	3.67

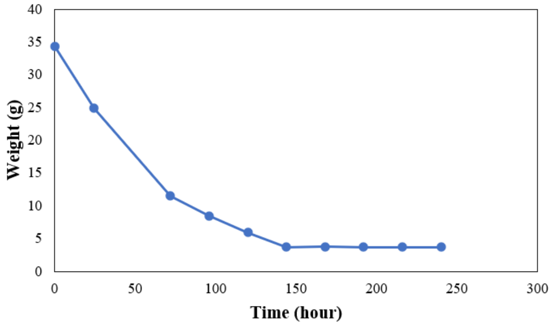

Figure 8. *Graph of water release at ambient temperature over time of hydrogel-based materials from rice-straw*

From Figure 7 and the graph in Figure 8, the hydrogel-based material of the straw can retain water for 144 hours (6 days) at ambient temperature and release water slowly. With the maximum mass of the material after water absorption is 34.36 g (w_1) and the constant weight obtained is 3.69 g (w_2) calculated by the formula (1), the results obtained are the water absorption capacity of material is 7.67g water/g material. Compared with the measured results of the water absorption capacity of the original straw of 1.71g water/g straw, the hydrogel-based material of the rice-straw has a water absorption of 4.48 times greater than of that of original straw. In addition, in contrast to the rapid dehydration of rice straw, the hydrogel-based material of rice straw was able to retain water for 6 days, exhibiting a slow drainage capacity. The five last values in Table 1 describe the stable weight of sample so the average value of 3.69g with the standard deviation of 0.03g.

Experimental results on reuse of rice-straw hydrogel-based materials as water absorbent are presented in Table 2 and Figure 9.

Table 2. *Water absorption of reused rice-straw hydrogel-based materials over time at room temperature*

Time (hour)	Sample weight (g)
0	3.69
24	15.50
120	18.70
144	19.58
240	19.70
264	19.73

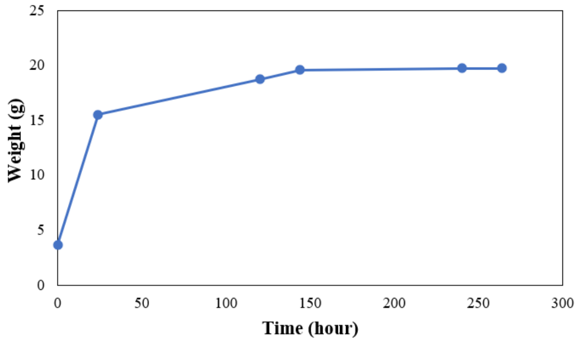

Figure 9. *Graph showing the reusability of rice-straw hydrogel-based materials over time at room temperature*

Experimental results presented on Figure 9 evidence the reuse possibility of the rice-straw hydrogel-based material. After 144 hours (6 days) of soaking in water, the material has a maximum water absorption capacity of 5.35g water/g material. The lower amount of water absorbed compared to the one of the first time can be explained by the degradation the structure of the material. The three last values in Table 2 describe the average stable weight of 19.64g with the standard deviation of 0.08g.

4. Conclusion

Rice-straw hydrogel-based materials with slow water uptake and release were successfully synthesized by cryogenic freezing using citric acid as a crosslinking agent and without releasing any waste component into the environment. The results show that the maximum water absorption capacity of the material is 7.67g water/g, i.e., 4.48 times greater than that of original straw. The studied material can slowly release water in 6 days at room temperature. In addition, the material is reusable with a water absorption of 5.35 g water/g material. This is a study to synthesis an environmentally friendly material with a simple and inexpensive synthesis method. Rice-straw hydrogel-based materials open up potential applications in green agriculture and can be used in industrial production to retain water and improve soil quality in arid regions such as the South Central Region of our country.

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