Malays. Appl. Biol. (2019) 48(2): 109–113

CELLULOSE-BASED HYDROGEL AS HALAL AGRICULTURAL MEDIUM

SARAH HUSNAINI ZAINAL, RICA NOFRIANTI, AZWAN MAT LAZIM
and RIZAFIZAH OTHAMAN*

*Centre for Advanced Materials and Renewable Resources, Faculty of Science and Technology,
Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Malaysia*
**E-mail: rizafizah@ukm.edu.my*

Accepted 6 May 2019, Published online 31 May 2019

ABSTRACT

Waste paper has been thrown away and caused environmentally problem. Preparation of cellulose-based hydrogel from waste paper has been developed to decrease the pollution since waste paper contains more than 60% of cellulose. Cellulose-based hydrogel is produced from the waste paper solution. To make into hydrogel, the addition of crosslinking agent is needed since hydrogel is defined as a 3D network structure that is crosslinked either chemically or physically. In this study, the waste paper will be treated first to remove impurities. Sodium hydroxide/urea (NaOH/Urea) has been used as a solvent for waste paper dissolution. As hydrogel needed crosslinking to remain the network structure, we used citric acid (CA) as a chemical crosslinking agent and the heating at 60°C and 70°C before and after swelling was studied. The aim of this study is to produce halal soilless agricultural medium using cellulose-based hydrogel media from the waste paper by using non-toxic and environmental friendly solvents and CA as crosslinking agent. Waste paper hydrogel will be characterized via swelling ratio where the highest swelling is about 19% at 70°C heating temperature. Fourier-transform infrared (FTIR) shows a broad band of OH at 3339 cm^{-1} and another band was shown at 3432 cm^{-1} for 70°C heating temperature represent OH from the solvent.

Key words: Waste paper, cellulose, hydrogel, crosslinking

INTRODUCTION

Malaysian produces papers and waste paper products of about 57,000 tonnes every month which can occupy 456,000 cubic meter of landfill space. It also is the largest portion of municipal solid waste produced every year. Waste papers can form major environmental problem such as flash floods and stagnant pools for mosquitoes breed due to ending up in drains and waterways. Moreover, this will also lead to other problems such as disease, landslides and traffic congestions. Paper recovery rate in Malaysia is still considered low which is about 40%. Paper recovery is needed to reduce the number of materials being thrown at the landfill (Anon, 2015). Waste paper containing cellulose can be starting material for soilless agricultural production due to renewable resources and can decrease the environmental problem. Cellulose, a polysaccharide consists of a linear chain of numerous of *β(1-4) linked α-glucose* monomer units is the most abundant natural polymer material on earth which has characteristics of odorless, biocompatible, biodegradable and insoluble in water and most organic solvents. Due to its inexhaustible source of raw material and increase in environmentally friendly materials, cellulose has become a high demanding material (Luo & Zhang, 2010; Chang *et al.,* 2010). The waste paper contains a high amount of cellulose which is suitable biopolymer in hydrogel synthesis due to its good mechanical properties, exhibits high strength, high stiffness and low density (Choe *et al*., 2018).

The hydrogel is typically a class of gel that can be obtained by chemical stabilization and characterized by the ability to absorb and retain a large amount of liquid for a longer period time. Fabrication of hydrogel must undergo crosslinking method either chemically or physically to maintain the 3D structure of hydrogel (Koschella *et al*., 2011; Montesano *et al*., 2015). Hydrogel's ability to absorb water depends on the hydrophilic working

* To whom correspondence should be addressed.

group found on the polymer backbone while its resistance to coordination arises from the existence of cross-linkage between network chains (Pin *et al*., 2016). Hydrogel has found to apply in personal hygiene products, biomedical, pharmaceutical and mechanical engineering. This wide application of hydrogel has become a new development towards the fabrication of hydrogel (Lim *et al*., 2017). Cellulose-based hydrogel has been used widely in pharmaceutical, medical, agricultural and food industry due to cellulose characteristics such as biocompatible, biodegradable, non-toxic and environmentally friendly. Besides, hydrogel also has advantages of high hydrophilicity, good permeability and compatibility and low coefficient of friction. Combination of these advantages shows that cellulose-based hydrogel is the most significant in hydrogel fabrication (Oliveira *et al*., 2017).

In this study, cellulose-based hydrogel from waste paper will be pre-treated to remove ink or other impurities. Then, the waste paper is dissolved in a solvent and will be transformed to hydrogel using citric acid (CA) as chemical crosslinking. CA is naturally an organic acid and generally classified as safe and halal food additives. CA also inexpensive, non-toxic chemicals and has been used to improve the performance properties of cellulose in most applications (Reddy & Yang, 2010). Thus, the media we produce is halal because most of the materials we used are safe, non-toxic and environmental friendly since the agricultural media will give the foods products. Moreover, the demand for Halal food has risen due to the increasing level of awareness of quality and hygienic value (Mujar & Hasan, 2014). From the production of the cellulose-based hydrogel, everyone can plant their own food with limit maintenance.

MATERIALS AND METHODS

Pre-treatment of paper waste

Firstly, 20 g waste paper immersed in the 20% of NaOH solution and heat at 70°C for 2 hours. After 2 hours, the sample is filtered and washed with distilled water to remove the excessive NaOH. Then, the sample is bleached with 1.5% hydrogen peroxide, H_2O_2 at pH 10 and heated at 70°C for 1 hour. After that, the sample is neutralized, filtered and dried in the oven about 50°C. The mixture of solvent NaOH/Urea/H_2O (7:12:81 w/w %) was frozen at temperature below -10°C. Then, the frozen solution is diluted and stirred at ambient temperature. Then, 3 g waste paper was added in the solvent solution and stirred until homogenous for 24 hours.

Preparation of hydrogel

In hydrogel preparation, 10 mL of CA was added in 100 mL prepared paper solution. The mixture of the solution was heated at 30-70°C and continuously stirred until the solution becomes a gel. The excess solution will be removed from the gel. Effect of heating temperature at 60°C and 70°C before and after swelling on water capacity absorption of hydrogel will be studied.

Characterization of hydrogel

In this study, the hydrogel will be characterized via swelling ratio (SR) defined as followed;

$$SR\ (\%) = \frac{(W_s - W_d)}{W_d} \times 100$$

where W_s is the weight of the sample after swollen and W_d is the weight of the sample after drying. Swelling testing was done with the addition of 10 mL of distilled water onto the hydrogel. Then, Fourier-transform infrared FTIR is used to determine the new and presence functional group.

RESULTS AND DISCUSSION

In this project, we have produced a Halal agricultural medium from waste paper. Especially in food, the choice of cultivation media and fertilizer become important factors in producing Halal products. Thus, we have produced hydrogel media for agricultural activity which is halal, safe and environmentally friendly since the Halal issue is starting to get attention in the marketplace in particularly Islamic country. Nowadays, Halal is not only restricted mean to 'pork free' especially in food. Halal will include most of the starting process, the ingredients and the products (Majid *et al*., 2015). In this study, the waste paper has been used as the source of cellulose. Figure 1 shows the step in waste paper pre-treatment. In the pre-treatment process, there is the presence of hemicellulose where hemicellulose is needed in order to improve the strength of the paper (Gandini & Pasquini, 2012). When CA was added, the solution will transform to hydrogel then dried at 60°C and 70°C to remove the access solvent. Figure 2 shows the condition of hydrogels after heating.

Figure 3 shows the FTIR spectrum for 60°C and 70°C dried waste paper hydrogel as a representative of all the samples. For all four spectrums, there is the presence of -OH groups at 3300 cm^{-1}. At 2900 cm^{-1}, there is the presence of –OH stretching from the waste paper before and after swelling for both

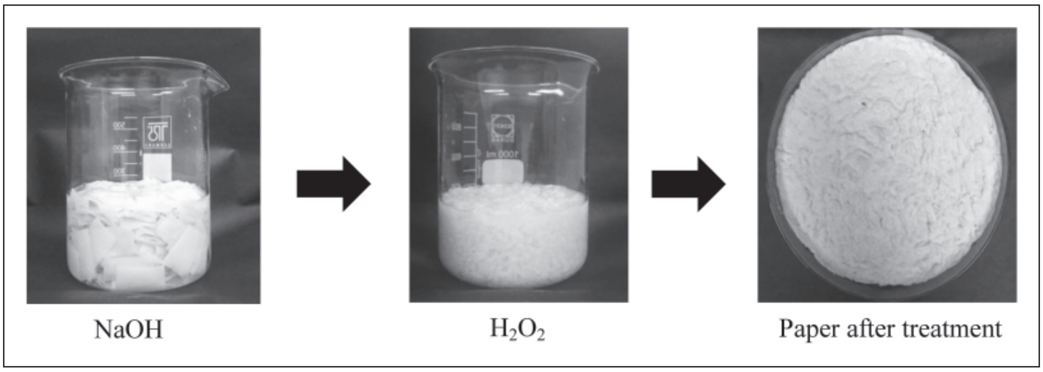

Fig. 1. Waste paper is pretreated with NaOH and H_2O_2.

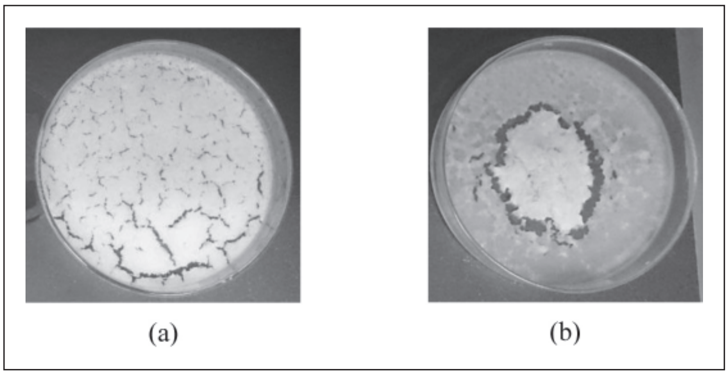

Fig. 2. The representative of the hydrogel at drying temperature (a) 60°C and (b) 70°C.

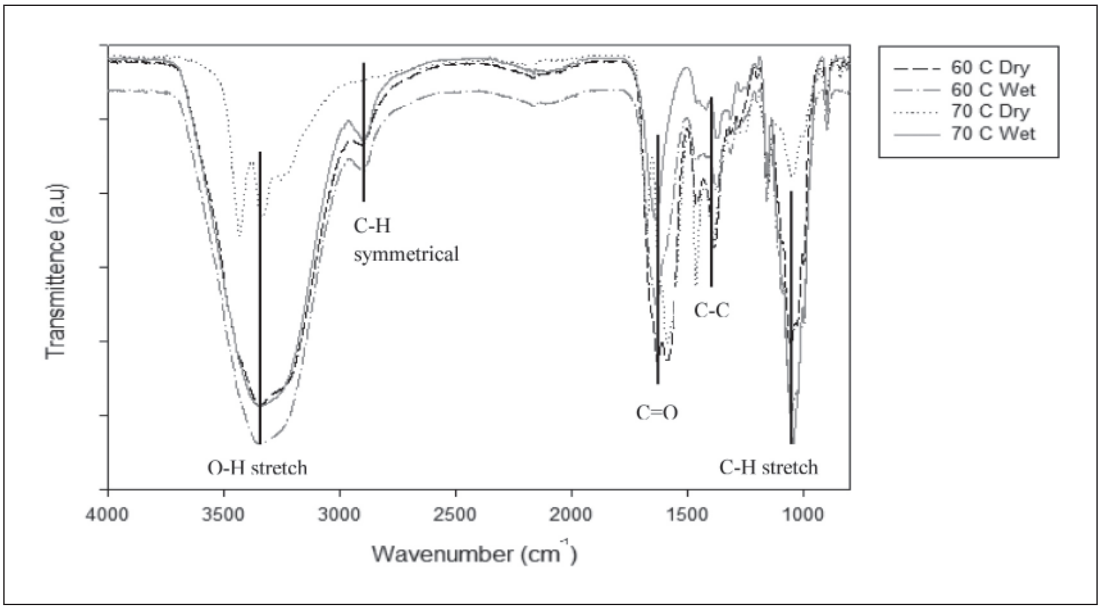

Fig. 3. FTIR spectrum at a representative drying temperature of 60°C and 70°C.

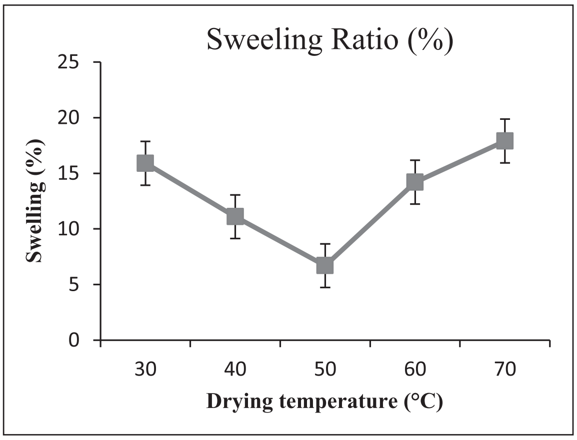

Fig. 4. Swelling ratio at a different drying temperature.

drying temperature. At 70°C dry shows a narrow peak of -OH stretching due to high temperature, -OH in cellulose become pack to each other and we can see a little bit shifting of the peak. At 60°C dry shows the high intensity of C=O at 1699 cm^{-1} indicates the carboxyl group from CA. Hydrogel dry at 70°C shows high intensity at 1055 cm^{-1} due to carboxylates from CA during the heating process (Rahman *et al*., 2014).

The dried samples were then undergoing the swelling test. Figure 4 shows the swelling ratio of the hydrogel at different heating temperature (30 – 70°C). The graph shows that, the swelling ratio decrease for the first heating temperature from 30 to 50°C. This might due to the less crosslinking attachment to –OH group of cellulose. In the other hand, cellulose/NaOH/urea aqueous solution might form irreversible gelation by heating. Thus, physical crosslinking also play an important role in the formation of hydrogel (Chang *et al*., 2010). Fig. 4 also shows that, the swelling ratio increase from 60 to 70°C heating temperature. This indicates that at high-temperature CA might start to form a strong hydrogen bond with cellulose and improves water stability in hydrogel (Reddy & Yang, 2010). Other than that, high drying temperature might give CA strong interaction with -OH groups of cellulose. Thus, the swelling ability increase due to the more linked chain in cellulose (Chang *et al*., 2010).

CONCLUSION

In conclusion, the preparation of cellulose-based hydrogel can be done using environmental friendly, non-toxic and halal material using NaOH/urea as a solvent and citric acid (CA) as a crosslinking agent. FTIR result also shows the addition of CA with high-temperature heating would affect the properties of the cellulose-based hydrogel. Based on the swelling ratio (SR), waste paper treated at 60°C and 70°C shows the significant condition of the swelling results to the highest water absorption. Thus, this hydrogel is suitable for agricultural media since it has the ability to retain a large amount of water in a longer time. This cellulose-based also can be safely used as medical applications and in biopolymers applications.

ACKNOWLEDGEMENTS

We would like to express gratitude to Faculty of Science and Technology, Universiti Kebangsaan Malaysia (UKM), Center of Research Instrumentation Management (CRIM), UKM and ST-2017-008 grant for the assistance on this project.

REFERENCES

Anon. 2015. www.thanam.com.my/paper/. Accessed on 29th August 2018.

Chang, C., Zhang, L., Zhou, J., Zhang, L. & Kennedy, J.F. 2010. Structure and properties of hydrogels prepared from cellulose in NaOH/urea aqueous solutions. *Carbohydrate Polymers*, **82**: 122-127.

Chang, C., Duan, B., Cai, J. & Zhang, L. 2010. Superadsorbents hydrogel based on cellulose for smart swelling and controllable delivery. *European Polymer Journal*, **46**: 92-100.

Chen, X., Chen, J., You, T., Wang, K. & Xu, F. 2015. Effects of polymorphs on dissolution of cellulose in NaOH/urea aqueous solution. *Carbohydrate Polymers*, **125**: 85-91.

Cheng, Y., Lu, J., Liu, S., Zhao, P., Lu, G. & Chen, J. 2014. The preparation, characterization and evaluation of regenerated cellulose/collagen composite hydrogel films, *Carbohydrate Polymers*, **107**: 57-64.

Choe, D., Kim, Y.M., Nam, J.E., Nam, K., Shin, C.S. & Roh, Y.H. 2018. Synthesis of high-strength microcrystalline cellulose hydrogel by viscosity adjustment. *Carbohydrate Polymers*, **180**: 231-237.

Dutta, S., Samanta, P. & Dhara, D. 2016. Temperature, pH and redox responsive cellulose based hydrogels for protein delivery. *International Journal of Biological Macromolecules*, **87**: 92-100.

Gandini, A. & Pasquini, D. 2012. The impact of cellulose fiber surface modification on some physico-chemical properties of ensuing papers. *Industrial Crops and Products*, **35(1)**: 15-21.

Jiang, Z., Fang, Y., Xiang, J., Ma, Y., Lu, A., Kang, H., Huang, Y., Guo, H., Liu, R. & Zhang, L. 2014. Intermoleculat interactions and 3D structure in cellulose-NaOH-urea aqueous system. *Journal of Physical Chemistry*, **118**: 10250-10257.

Koschella, A., Hartlieb, M. & Heinze, T. 2011. A "click-chemistry" approach to cellulose-based hydrogels. *Carbohydrate Polymers*, **86**: 154-161.

Lim, L.S., Rosli, N.A., Ahmad, I., Lazim, A.M. & Amin, M.C.I.M. 2017. Synthesis and swelling behavior of pH-sensitive semi-IPN superabsorbent hydrogels based on poly(acrylic acid) reinforced with cellulose nanocrystals. *Nanomaterials*, **7**: 1-13.

Lindmann, B., Karlström, G. & Stigsson, L. 2010. On the mechanism of dissolution of cellulose. *Journal of Molecular Liquids*, **156**: 76-81.

Liu, G., Sun, H., Liu, G., Zhang, H., Yuan, S. & Zhu, Q. 2017. A molecular dynamics study of cellulose inclusion complexes in NaOH/urea aqueous solutions. *Carbohydrate Polymers*, **185**: 12-18.

Luo, X. & Zhang, L. 2010. New solvents and functional materials prepared from cellulose solutions in alkali/urea aqueous system. *Food Research International*, **52(1)**: 387-400.

Majid, A.A.M., Abidin, I.H.Z., Majid, H.A.M.A. & Chik, C.T. 2015. Issues of Halal food Implementation in Malaysia. *Journal Applied Environmental Biological Sciences*, **5(6S)**: 50-56.

Menzel, C., Olsson, E., Plivelic, T.S., Andersson, R., Johansson, C., Kuktaite, R., Järnström, L. & Koch, K. 2013. Molecular structure of citric acid cross-linked starch films. *Carbohydrate Polymers*, **96**: 270-276.

Montesano, F.F., Parente, A., Santamaria, P., Sannino, A. & Serio, F. 2015. Biodegradable superabsorbent hydrogel increases water retention properties of growing media and plant growth. *Agriculture and Agricultural Science Procedia*, **4**: 451-458.

Mujar, N.A. & Hasan, N. 2014. The economics of Halal Industry. Seminar UICW.

Oliviera, J.P.d., Bruni, G.P., Lima, K.O., El Halal, S.L.M., da Rosa, G.S., Dias, A.R.G. & Zavareze, E.d.R. 2017. Cellulose fibers extracted from rice and oat husks and their application in hydrogel. *Food Chemistry*, **221**: 153-160.

Piltonen, P., Hidebrandt, N.C., Westerlind, B., Valkama, J.P., Tervahartiala, T. & Ilikainen, M. 2016. Green and efficient method for preparing all-cellulose composites with NaOH/urea solvents. *Composites Science and Technology*, **135**: 153-158.

Pin, L.W., Ashari, A., Bakar, M.A., Ahmad, W.Y.W., Lazim, M.AS.M. 2016. Penyediaan dan pencirian hidrogel berasaskan kanji/akrilamida daripada ubi *Stemona Curtisii*. *Malaysian Journal of Analytical Sciences*, **20(1)**: 157-170.

Reddy, N. & Yan, Y. 2010. Citric acid cross-linking of starch films. *Food Chemistry*, **118**: 702-711.

Rahman, M.O., Hussain, A. & Basri, H. 2014. A critical review on waste paper sorting techniques. *International Journal Environmental Science Technology*, **11**: 551-564.

Zhang, S., Wang, W-C., Li, F-X. & Yu, J-Y. 2012. Swelling and dissolution of cellulose in NaOH aqueous solvent systems. *Cellulose Chemistry and Technology*, **47**: 9-10.