Materials Science Forum
ISSN: 1662-9752, Vol. 1061, pp 91-96
© 2022 Trans Tech Publications Ltd, Switzerland

Submitted: 2021-11-09
Revised: 2022-02-28
Accepted: 2022-03-09
Online: 2022-05-26

Synthesis and Characterization of Hydrogels Derived from Cellulose of Water Hyacinth (*Eichornia crassipes*) and Chitosan Using the Freeze-Thaw Method

Tur-Ridha Noer Khalifah[1,a], Hasnah Natsir[2,b], Siti Fauziah[2,c] and Indah Raya[2,d*]

[1]Postgraduate Student, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Hasanuddin University, 90245 Makassar, Indonesia

[2]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Hasanuddin University, 90245 Makassar, Indonesia

[a]noerkhalifah03@gmail.com, [b]hasnahnatsir@gmail.com, [c]stfauziah_as@yahoo.co.id, [d]indahraya@unhas.ac.id

Keywords: Absorption, chitosan, freeze-thaw, hydrogel, water hyacinth

Abstract. This study aims to determine the absorption and ability of hydrogels to hold water. The hydrogel was synthesized using the freeze-thaw method, then the absorption ability and water retention time in the hydrogel were tested and characterized by FTIR and trinocular stereo microscope. The FTIR results showed that the resulting hydrogel had N–H, O–H, aliphatic C–H, bend N–H, C–O, and C–N functional groups. The highest absorption of the hydrogel with a ratio of cellulose:chitosan:EDTA variations of 2:2.25:0.25 (g) respectively, which was 287.46% and the appearance of the hydrogel under a microscope showed that the structure of the hydrogel was rather hollow, so that it affected its absorption.

Introduction

Water hyacinth is a type of plant that floats on the water, is green in color, has a single oval-shaped leaf, and slippery has a flower in the form of grains and petals. The breeding rate of water hyacinth is very high and is recognized as one of the 10 worst weeds in the world [1]. The content of water hyacinth is very much, and the most dominating is cellulose which was 46.15% [2]. The high cellulose content in water hyacinth can be used to make hydrogels.

Hydrogel, better known as the water-absorbing gel, can absorb quite high water. This property makes hydrogels widely used as planting media, loosening dry soil, maintaining moisture in drug delivery, dye absorbents, and many more [3-5]. First, the hydrogel was successfully synthesized from the cellulose of risk husk with the addition of a crosslinker, obtaining a hydrogel with high absorption of 1162% [6]. Then, the hydrogel was successfully synthesized from chitosan and EDTA, which functions as a soil freshener and improve soybean plants' performance [7].

There are three methods of making hydrogels, namely chemical crosslinking, physical crosslinking, and radiation crosslinking [8]. This study used the physical crosslinking method, namely the freeze-thaw method, which is expected to improve the physical and mechanical properties of the hydrogel.

Several previous studies have used plasticizers from chemicals. In this study, the lime extract will be used as a plasticizer. The lime extract contains citric acid, which can reduce the intermolecular forces on the hydrogel to widen the distance between molecules, which will reduce the level of stiffness and increase polymer flexibility [9, 10]. This property will increase the hydrogel's resistance to water. This study aims to determine the cellulose content in water hyacinth and the ability of the resulting hydrogel to absorb and retain water.

Experimental Section

Materials. The materials used in this study were NH_3 13% (w/v), 15% (w/v) and 17% (w/v), water hyacinth (*Eichornia crassipes*), lime extract, EDTA, pH paper, normal filter paper, chitosan, NaOH 9% (w/v), and H_2O_2 5% (w/v).

Preparation of Water Hyacinth. Water hyacinth was cleaned of roots and leaves. Then, it was washed and cut into small pieces. The cutwater hyacinths were dried in direct sunlight. Next, it was ground and sieved with a 100 mesh sieve.

Isolation of Cellulose from Water Hyacinth. Water hyacinth powder was put into 3 maceration containers of 20 g each and soaked into 9% NaOH for 24 h. After the maceration process, the sample was filtered. The residue from the filtering process was washed with distilled water until neutral pH and dried in an oven at 105 °C. The residue was then immersed back into the NH_3 solution with a solvent variation of 13%, 15%, and 17%. Then, each mixture was heated for 60 min. After that, the mixture was filtered again, and the residue was washed with distilled water until neutral pH. Then the residue was dried again in the oven at a temperature of 105 °C. Next, the dried samples were soaked into 5% H_2O_2 solution and heated at 70 °C for 2 h. The mixtures were filtered again, and the residues were washed with distilled water until neutral pH. Finally, the mixtures were dried in an oven at a temperature of 105 °C. The resulting cellulose was analyzed using FTIR.

The yield of cellulose can be calculated with the formula:

$$\%\text{yield} = \frac{\text{weight of yield cellulose}}{\text{weight of water hyacinth}'\text{spowder}} \text{ x } 100\% \tag{1}$$

Synthesis of Hydrogel. Two grams of cellulose were put in 3 containers. 2.25, 2, and 1.75 g of chitosan were added, respectively, dissolved with 50 mL of 0.6 M CH_3COOH, and stirred using a magnetic stirrer for 15 min. 0.25, 0.5, and 0.75 g of EDTA were added, respectively. Added lime juice as much as 2 mL. Add 2 M NaOH solution drop by drop to form a gel.

The gel formed was put into a mold and frozen at -20 °C for 18 h, then placed at room temperature for 6 h. The treatment was carried out for 4 cycles. Then the hydrogel was dried in an oven at 70 °C for 4 h. The results obtained were then analyzed with FTIR and a trinocular stereo microscope.

Swelling Test. The dry hydrogel was weighed first (wo) and soaked in water for 24 h, and then filtered and weighed again (wt). Finally, the difference between dry weight and wet weight was calculated.

$$\%\text{S} = \frac{\text{wt}-\text{wo}}{\text{wo}} \text{ x } 100\% \tag{2}$$

Deswelling Test. The dry hydrogel was weighed and soaked in water for 6 h. Next, it was put in a nylon bag, hung in the room at 26 °C for 15 min, and then weighed (me). Next, the nylon bag containing the hydrogel was immersed in warm water at a constant temperature of 60 °C for 10 min. Then, the hydrogel was lifted and hung in the room for 15 min, then weighed (mt). The water retention in the gel was calculated as Wr(%) with the following formula:

$$\%\text{Wr} = \frac{\text{mt}}{\text{me}} \text{ x } 100\% \tag{3}$$

Results and Discussion

Isolation of Cellulose from Water Hyacinth. Cellulose produced from the isolation of water hyacinth is a fine brownish-white powder (Fig. 1), odorless and insoluble in water. This property follows the theory put forward by Zainal [11]. The amount of cellulose obtained from each variant of NH_3 concentration can be seen in Table 1.

Table 1 shows that the highest amount of cellulose was obtained at a concentration of 13% NH_3, 32.88%. These data indicate that the higher the concentration of NH_3, the lower the cellulose obtained. An increase in the porosity of cellulose increases the conversion of cellulose to glucose [12]. Research conducted showed that the cellulose obtained with varying concentrations of 9% NaOH and 15% NH_3 was 81% [13]. This result is due to the different methods used to isolate water hyacinth and the amount of cellulose wasted during the cellulose neutralization process by the decantation method.

Fig. 1. The cellulose powder of water hyacinth

Table 1. Variation of cellulose

Concentration of NH_4OH (%)	First weight (g)	Final weight (g)	Yield of cellulose (%)
13	20	6.5769	32.88
15	20	6.2800	25.12
17	20	5.6468	22.59

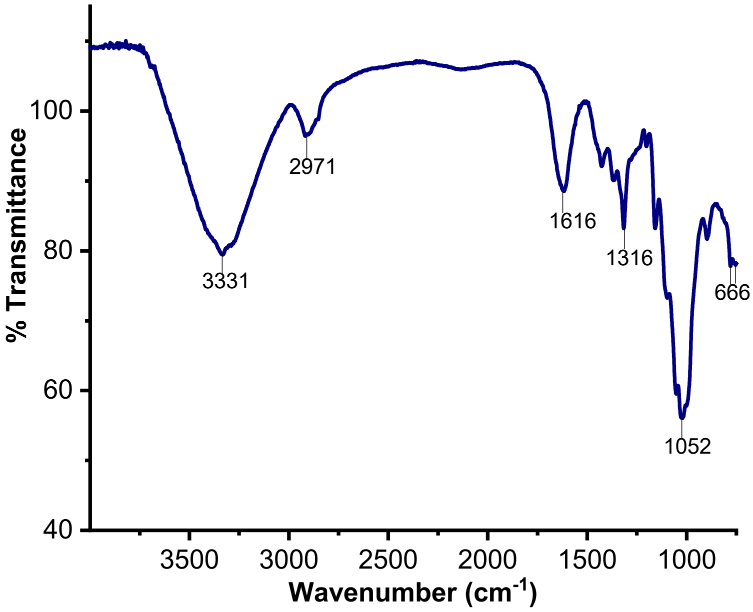

Fig. 2. FTIR spectrum of cellulose

The results of the cellulose FTIR readings (Fig. 2) showed the group of OH at a wavelength of 3331 cm^{-1}, the group of OH lignin and hemicellulose at 2917 cm^{-1}, the group of fiber OH at 1633 cm^{-1}. The CH (CH_2) group was observed at 1427 cm^{-1}, the group of CO at a wavelength of 1052 cm^{-1}, and the group of CH at 897 cm^{-1}. The OH, CH, and CO groups are the main constituents of cellulose [14].

Synthesis of Hydrogel. The hydrogel synthesized from water hyacinth cellulose and chitosan with the addition of EDTA and lime extract had a soft gel texture, brownish-yellow in color (Fig. 3). The composition of the hydrogel can be seen in Table 2.

Fig. 3. Hydrogels

Table 2. Variation of hydrogels

Cellulose (g)	Chitosan (g)	EDTA (g)	Code
2	2.25	0.25	H1
	2.00	0.50	H2
	1.75	0.75	H3

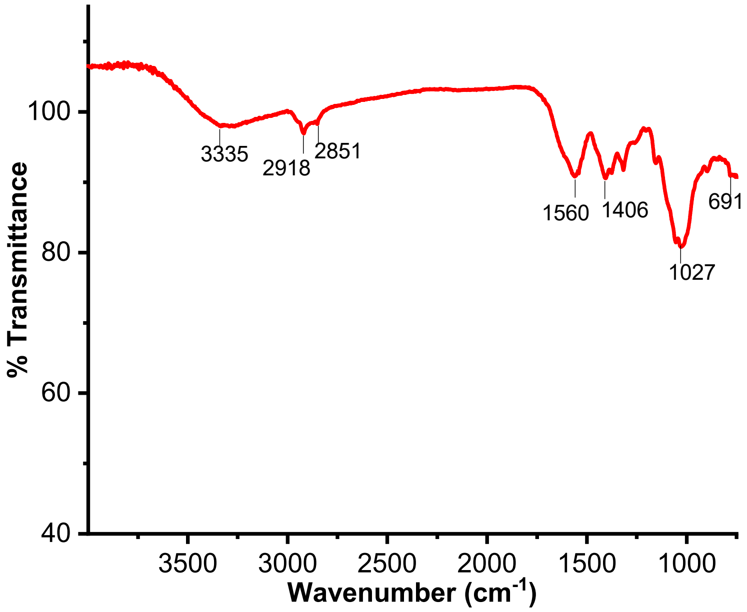

Fig. 4. FTIR spectrum of hydrogels (H1)

The infrared spectrum of the hydrogel (H1) (Fig. 4) showed the presence of N–H strain at a wavenumber of 3335 cm^{-1}, the OH group at 3292 cm^{-1}, the CH group at 2918 cm^{-1}, NH bending at 1560 cm^{-1}, the NH group at 1560 cm^{-1}, CO at 1204 cm^{-1}, and the CN group at 1317 cm^{-1}. The appearance of OH, CH, and CO groups is because these groups are constituents of cellulose water hyacinth [15]. The CO group can also be derived from EDTA and the NH group derived from chitosan [7]. In addition, the CN functional group also appears, which indicates that there is a bond between cellulose and chitosan. However, there was no strong binding due to the absence of functional groups C=O and C=N at wave number 1690–1640 cm^{-1}, which was a sign of the occurrence of bonds between chitosan-EDTA and chitosan-cellulose [16]. Thus, the hydrogel formed does not have a strong structure.we

Swelling Test. The hydrogel obtained was then evaluated for its water absorption. The results were shown in Table 3. The results indicate that the hydrogel that has the highest water absorption capacity is H1 at 287.46%, and the lowest is H3 at 194.54%. This result is in line with the theory that the more crosslinkers are added to the hydrogel, the lower the water absorption capacity because the more crosslinkers are used, the tighter the network structure will make it difficult for water molecules to enter the tissue [7]. In this case, EDTA acts as a chemical crosslinker.

Fig. 5 shows the swelling of the hydrogel that has been in contact with water. The swelling is up to several times than that of hydrogel before contact with water and it still retains the same shape. The addition of a plasticizer into hydrogels is supposed to increases the elasticity and water resistance of the resulted gels [17].

Table 3. Swelling of hydrogels

Hydrogel	First weight (g)	Final weight (g)	Swelling (%)
H1	0.3477	1.3472	287.46
H2	0.3283	1.0417	217.30
H3	0.2306	0.6792	194.54

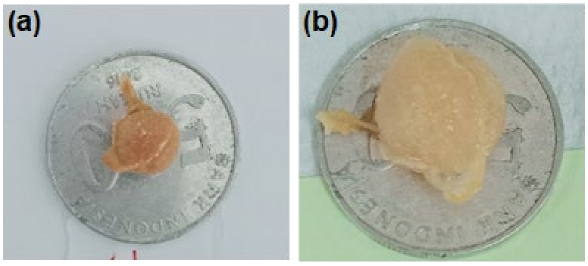

Fig. 5. Hydrogel (a) Before the swelling test, (b) After swelling test

As the hydrogel observed under a trinocular stereo microscope, it can be seen that the more crosslinkers added, the more solid the hydrogel surface. The solid surface shape allows the hydrogel to have low water absorption [7]. It can be seen in Fig. 6.

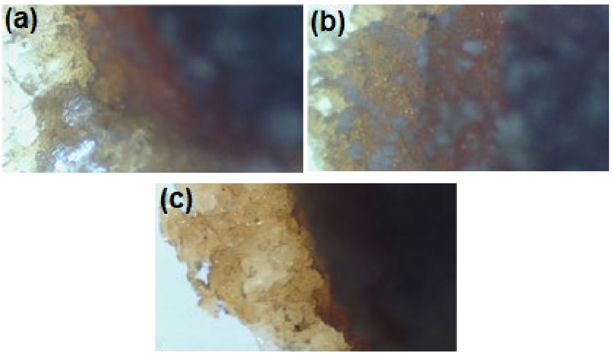

Fig. 6. Hydrogels observation under a trinocular stereo microscope (a) H1, (b) H2, (c) H3

Deswelling Test. Water retention ability in hydrogel can be seen in Table 4. Hydrogels that have absorbed water can experience structural damage if extreme changes in their environment, such as high-temperature changes. This change can cause the hydrogel structure to break down.

Table 4. Deswelling of hydrogels

Hydrogel	Weight before heating (g)	Weight after heating (g)	Deswelling (%)
H1	0.2932	0.2907	99.15%
H2	0.2370	0.2278	96.12%
H3	0.1881	0.1776	94.42%

From the data in Table 4, the greatest water resistance at high temperatures is in hydrogels with H1 variation of 99.15%, and the lowest is the hydrogels with H3 variation of 94.42%. This result shows that the more crosslinkers are added, the lower the water resistance in the hydrogel will be. When the temperature increases, the longer the polymer chains will close tightly so that it will be difficult for water to enter the network [18].

Conclusion

The results of cellulose isolation from water hyacinth, which were dignified with NaOH and NH_3 solution, were the highest at a concentration of 13% NH_3, which was 32.88%, and the highest water absorption and resistance of the hydrogel produced were found in the H1 variation, which respectively was 287.46% and 99.15%.

References

[1] I. Harun, H. Pushiri, A.J. Amirul-Aiman, Z. Zulkeflee, Invasive water hyacinth: Ecology, impacts and prospects for the rural economy: Review, Plants 10 (2021) 1613.

[2] F. Fitrya, N.A. Fithri, D.P. Wijaya, E.P. Sembiring, Optimization of acid concentration and hydrolysis time in the isolation of microcrystalline cellulose from water hyacinth (*Eichornia crassipes* solm), Trop. J. Nat. Prod. Res. 5 (2021) 503–508.

[3] B. Qu, Y. Luo, Chitosan-based hydrogel beads: Preparations, modifications and applications in food and agriculture sectors – A review, Int. J. Biol. Macromol. 152 (2020) 437–448.

[4] M. Mahinroosta, Z.J. Farsangi, A. Allahverdi, Z. Shakoori, Hydrogels as intelligent materials: A brief review of synthesis, properties and applications, Mater. Today Chem. 8 (2018) 42–55.

[5] M.M. Golor, D. Rosma, S.P. Santoso, F. Soetaredjo, M. Yuliana, S. Ismadji, A. Ayucitra, Citric acid-crosslinked cellulosic hydrogel from sugarcane bagasse: Preparation, characterization, and adsorption study, J. Idn. Chem. Soc. 3 (2020) 59–67.

[6] A. Abdulhameed, H.M. Mbuvi, E.O. Changamu, Synthesis of cellulose-based superabsorbent hydrogel from rice husk using a microwave, Am. J. Mater. Sci. 10 (2020) 1–8.

[7] H. Ritonga, A. Nurfadillah, F.S. Rembon, L.O.A.N. Ramadhan, M. Nurdin, Preparation of chitosan-EDTA hydrogel as soil conditioner for soybean plant (*Glycine* max), Groundwater Sustainable Dev. 9 (2019) 100277.

[8] S. Alven, B.A. Aderibigbe, Chitosan and cellulose-based hydrogels for wound management, Int. J. Mol. Sci. 21 (2020) 9656.

[9] I. Purwaningsih, K. Kuswiyanto, Perbandingan perendaman asam sitrat dan jeruk nipis terhadap penurunan kadar kalsium oksalat pada talas, Jurnal Vokasi Kesehatan 2 (2016) 89–93.

[10] M.G.A. Vieira, M.A. da Silva, L.O. dos Santos, M.M. Beppu, Natural-based plasticizers and biopolymer films: A review, Eur. Polym. J. 47 (2011) 254–263.

[11] S.H. Zainal, N.H. Mohd, N. Suhaili, F.H. Anuar, A.M. Lazim, R. Othaman, Preparation of cellulose-based hydrogel: A review, J. Mater. Res. Technol. 10 (2021) 935–952.

[12] N. Novia, I. Utami, L. Windiyati, Pembuatan bioetanol dari sekam padi menggunakan kombinasi soaking in aqueous ammonia (SAA) pretreatment – acid pretreatment – hidrolisis – fermentasi, Jurnal Teknik Kimia 20 (2014) 46–53.

[13] I. Kurniaty, U.H. Hasyim, D. Yustiana, I. Fajriahmuti, Proses delignifikasi menggunakan NaOH dan amonia (NH_3) pada tempurung kelapa, Jurnal Integrasi Proses 6 (2017) 197–201.

[14] V. Hospodarova, E. Singovszka, N. Stevulova, Characterization of cellulosic fibers by FTIR spectroscopy for their further implementation to building materials, Am. J. Anal. Chem. 9 (2018) 303–310.

[15] L. Setyaningsih, E. Satria, H. Khoironi, M. Dwisari, G. Setyowati, N. Rachmawati, R. Kusuma, J. Anggraeni, Cellulose extracted from water hyacinth and the application in hydrogel, IOP Conf. Ser.: Mater. Sci. Eng. 673 (2019) 012017.

[16] F. Sebayang, R. Bulan, E.Z. Nasution, M.Z.E. Sinaga, W.A. Putri, Making Hydrogel with Crosslinked Reaction between Chitosan and Dialdehyde Cellulose from Coconut Fiber as Wound Headers, Proceedings of the 1st International Conference on Chemical Science and Technology Innovation (ICOCSTI 2019), SCITEPRESS–Science and Technology Publications, 2019, pp. 204–210.

[17] K. Chapain, S. Shah, B. Shrestha, R. Joshi, N. Raut, R. Pandit, Effect of plasticizers on the physicochemical properties of bioplastic extracted from banana peels, J. Inst. Sci. Technol. 26 (2021) 61–66.

[18] L. Anah, N. Astrini, Sintesa dan karakterisasi hidrogel super absorben polimer (SAP) berbasis selulosa menggunakan crosslinking agent water-soluble carbodiimide (WSC), Jurnal Selulosa 5 (2015) 1–6.