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Absorption Methanyl Yellow Dye Using Hydrogel of Cassava Peel Starch (*Manihot esculenta Cranzt*)

Noer Khalifah Tur-Ridha^a, Sitti Chadijah^a, Ummi Zahra^a, Syarifah Rabiatul Adawiah^a, Rahmiani Gani^a, Firnanelty^a*

Abstract. Hydrogel of cassava peel starch was successfully decreased methanyl yellow dye. This adsorbent was employed to adsorb typical organic cationic dye contaminants from high concentration effluents. This study aimed to determine characteristic of cassava peel starch hydrogel and ability of hydrogel increased dyes. The stages of hydrogel consist of extracting cassava peel starch, making a starch solution, making hydrogel, testing water absorption, and analysing with FTIR and UV-Vis spectrophotometer. The results have obtained that the cassava peel starch hydrogel had have N-H group. Result of hydrogel had been contacted with dyes that showed N=N and S=O groups from the initial functional groups of cassava peel starch in FTIR spectum. The highest absorption of hydrogel was at 30 ppm methanyl yellow dye concentration, which was 31.72%. This result showed that the hydrogel of cassava peel starch can be used as an absorbent of methanyl yellow dye.

Keywords : Absorbent, Hydrogel, Cassava peel starch, Methanyl yellow

dyes

^a Analytical Laboratory Department of Chemistry Faculty of Science and Technology Universitas Islam Negeri Alauddin Makassar, Gowa, 92118, Indonesia Correspondence and requests for materials should be addressed to Firnanelty. (email : <u>firnanelty.rasyid@uin-alauddin.ac.id</u>)

Introduction

Cassava peels and sieviate which are by products of which harvesting and processing constitute 25% of the whole plant [1]. Cassava plants had identified many advantages. Stems, seeds, and leaves are used as vegetables which contain fibre and tubers as a source of carbohydrates. The skin of cassava tubers as tuber waste can also be used. Cassava peels have the potential used as a food source because of their nutritional content. The proximate and mineral analysis of cassava peels revealed that cassava peels are rich in nutrients especially in carbohydrate. It also contains moderate amounts of minerals [2].

About 60% of the cassava produced all over the world is used for human consumption. These peels waste were found to contain 42.6% carbohydrate, 1.6% protein, 12.1% ether extract, 5.0% total ash and 22.5% crude fibre [3]. Insufficient supply, high prices and competition with the human food and biofuel industries means there is a continuous demand for alternative energy sources for poultry. As result, cassava is becoming an increasingly important ingredient in poultry diets, largely due to its high availability. Efficient use of cassava products has been shown to reduce feed costs of poultry production. The utilisation of cassava is, however, limited by a number of factors, including its high fibre and low energy content and the presence of anti-nutritional factors, primarily hydrocyanic acid (HCN) [4].

Hydrogel or absorbent gel has the ability to absorb up to 100 times the dry weight [5]. carboxyl groups) and reusability [6][7]. Hydrogels are mostly made from synthetic polymers (petroleum -based materials), which have become more expensive given the depletion of petroleum resources. On the other hand, these materials are non-biodegradable, resulting in secondary pollution to the environment [8]. The high absorption capacity makes the hydrogel can be used as an absorbent in the absorption method. The absorption method is generally very effective in overcoming environmental or aquatic pollution [9]. Types of pollutants that are generally found in the environment are the contamination of dyes by the textile industry. One type of textile dye that can be found is methanyl yellow dye. Hydrogel based on cassava peels can be used and developed a novel high-loading adsorbent based on CMC for methyl orange (MO) removal from aqueous solutions. In terms of monomer selection, methacrylates carrying tertiary amino groups, in particular 2-(dimethylamino)ethyl methacrylate (DMAEMA) [10].

In the textile industry, the dye methanyl yellow is used to color wool and nylon, to give a bright and attractive color effect. The use of methanyl yellow dye can have an impact on environmental pollution, especially on water. Water pollution by dye waste is in the form of organic compounds containing azo compounds, and is a carcinogen [8]. During the years, various polysaccharides have been used for the development of hydrogel as a wastewater remediator. Among these tapioca starch can be used as a useful bioadsorbent because of its cost- effectiveness, high molecular weight and easy extraction from the roots of the cassava plant [11]. Based on this background, it is necessary to conduct research on the hydrogel potential of cassava peel starch (Manihot esculenta Cranz) as an absorbent of methyl yellow dye which aims to determine the characteristics of cassava peel starch and to determine the hydrogel ability of cassava peel starch as an absorbent of methyl yellow dye.

Experimental

Materials

Cassava peel (Manihot ezculenta cranz) was obtained from traditional market of Gowa city, chitosan, potassium persulate, p.a, methanyl yellow, sodium hydroxide p.a, sodium tripolyphosphate, and sorbitol.

Extraction of cassava peels starch

Cassava peel starch was extracted from cassava peel following the modification method used by Sivamani [12] and Kaur [13]. The white peels part were mixed with distilled water with ratio 1:2, then mashed with blender. The solution was filtered and precipitated repeteadly then dried at 50 °C.

Preparation of cassava peels starch hydrogel

Cassava peels starch hydrogel was synthesis following the modification method used by Alifa [14]. 5 grams of cassava peel starch obtained from the extraction of cassava peel was dissolved in 100 mL of 8% sodium hydroxide. 50 mL of cas-

sava peel starch solution were put into 5 beakers, added with 0.8 grams of chitosan which has been dissolved in 30 mL of 0.6 M acetic acid. The solution was stirred for 30 minutes at room temperature. Sodium tripolyphosphate were added into solution 0, 0.3, 0.4, 0.5 and 0.6 grams respectively, then stirred for 15 minutes at room temperature. 2 mL of sorbitol and 0.2 grams of potassium persulfate were added and stirred again for 15 minutes. The hydrogel was put into glass plate and dried at room temperature. The resulting hydrogel was removed from the glass plate and cut into small pieces.

Hydrogel Application

The resulting hydrogel was applied to water and methanyl yellow dye to determine water absorption and its ability to absorb methanyl yellow dye.

Water Absorption Test

Hydrogel was put into a container filled with distilled water for 1 hour. The difference between dry weight and wet weight is calculated. Water uptake was calculated as follows :

Methanyl Yellow Absorption

A total of 0.5 grams of hydrogel was put into Erlenmeyer which contained various concen-

% water uptake =
$$\frac{final \ weights - initial \ weight}{final \ weight} \ge 100\%$$

trations 10; 20; 30; and 40 ppm of methanyl yellow. The solution was homogenized using a 160 rpm incubator shaker at 25 °C for 5 hours, then filtered.

Characterization

Functional groups of cassava peel starch and hydrogel were analyzed by using UV-vis spectrophotometer and FTIR. The FTIR analysis represented spectrum data in graphic and wave numbers of each data that provided functional groups of starch and hydrogel before and after absorpstion.

Results and Discussion

Starch was conducted from extraction of

wet cassava peel 27.26%. The characteristics of starch are a soft gel texture and brownish yellow colour. Hydrogel was made via mixture cassava peel starch, Natrium hydroxide, chitosan, sorbitol and natrum tripolyposphate. In this case, mass of Natrium Tripolyposhpate was differently used. Hydrogel are soft and brownish yellow colour.

Water absorption ability of hydrogel was successfully conducted (Table 1). The hydrogel is obtained which is good at absorbing water, namely the addition of a crosslink of 0.4 grams of 23.37% because the hydrogel is at its maximum form, which is hard and stiff, and is able to retain water for quite a long time (Adawiyah, 2016: 57). The more crosslinking is added, the lower its ability to absorb water and the structure becomes hard and strong, while the results of research that have been done show that the hydrogel that absorbs the highest water is the addition of 0.6 grams of binder. 74.82% and the lowest absorbing water was the addition of a crosslink of 0.4 grams, namely 23.37%. The factors that cause differences in the absorption process are due to the irregular surface area of the hydrogel, resulting in differences in hydrogel absorption. Apart from that, the main ingredients used are also different, thus affecting the water absorption [14].

Based on the results of the research that has been done (<u>Table 2</u>), it can be seen that the

Table 1. Water absorption ability of hydrogel.

Natrium Tripolyposh-	Initial weigth (g)	Final weight	Absorption ability (%)
pate (g)	(8)	(g)	
0	0,5001	1,8251	72,59
0,3	0,5001	1,5944	68,63
0,4	0,5001	0,6527	23,37
0,5	0,5005	1,6185	69,07
0,6	0,5000	1,9859	74,82

ability of the hydrogel to absorb methanyl yellow dye will increase along with the increase in the dye concentration up to a maximum concentration of 30 ppm of 31.7283% then decreased absorption at a concentration of 40 ppm which is equal to 30.56 % using spectrophotometer UV-Vis.

The increase in the concentration of the dye methanyl yellow, the greater the ability of the hydrogel to absorb methanyl yellow dye, but the ability of the hydrogel in this study was only able to increase of concentration of 30 ppm of

31.7283% and decreased absorption at a concentration of 40 ppm of 30.5635%.

Characterization using FTIR functions to

Table 2. Absoption of Methanyl yellow dye

Methanyl yellow dye (ppm)	Absorption of Methanyl yellow dye (%)		
10	22,04		
20	28,50		
30	31,72		
40	30,56		

determine the functional groups contained in cassava peel starch, hydrogels from cassava peel starch before and after contact with dye.

Lestari (2018: 51) reports that in cassava peel starch, there are O-H groups, C-H groups, and C-O groups. Based on the results obtained, the cassava peel is known to have O-H groups in the absorption area of 3397.58 cm-1, the C-H group in the absorption area of 2931.55 cm-1 and the C-O group in the absorption area of 1239.42 cm-1. As it is known that these functional groups are constituents of starch.

Hydrogel characterization of cassava peel starch after the addition of chitosan, sodium tripolyphosphate and sorbitol using FTIR showed the presence of an OH group in the 3468.01 cm⁻¹ absorption area, the CH group in the 2931.8 cm⁻¹ absorption area, the CO group in the 1203 absorption area., 58 cm^{-1} and the NH group in the absorption area of 1575.84 cm⁻¹. When compared with the cassava peel starch functional groups, the difference lies in the emergence of a new group, namely the N-H group which is thought to originate from chitosan. In addition, the addition of chitosan and sorbitol to the starch of cassava peels causes the O-H uptake area to increase. The higher the absorption value, the more hydrogen bonds are formed, conversely, the lower the absorption value, the less hydrogen bonds are formed (Munir, 2017: 42).

The characterization of the hydrogel that has been contacted with methanyl yellow dye using FTIR shows the presence of an OH group in the 3446.79 cm⁻¹ absorption area, the CH group in the absorption area of 2924.09 cm⁻¹, the CO group in the 1259.52 cm⁻¹ absorption area, the N= N group in the 1598.99 cm⁻¹ absorption area, and the S = O group in the 1338.6 cm⁻¹ absorption area. When compared with the hydrogel prior to contact with

Table 3.	Result of	f hydrogel	obtained	was	characterized	by FTIR.
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Functional group	Wavenumber – (cm ⁻¹)	Wavenumber (cm ⁻¹)			
		Cassava peel	Hydrogel	After absorpted	
O-H	3650-3200	3397,58	3468,01	3446,79	
C-H	2970-2850	2931,55	2931,8	2924,09	
C-0	1300-1050	1239,42	1575,84	1598,99	
N-H	1640-1550	-	1203,58	-	
N=N	1630-1575	-	-	1259,52	
S=O	1375-1300	-	-	1338,60	



Figure 1. FTIR spectrum of Cassava peel starch

the dye, the difference lies in the emergence of a new group, namely the N = N and S = O groups which are thought to be derived from the methanyl yellow dye because these groups are constituents of the methanyl yellow dye. Research conducted by Lesbani (2011) states that the N = N group can be found at a wavelength of 1630-1450 cm^{-1} and the S = O group can be found at a wavelength of 1375-1300 cm⁻¹.

FTIR results show that there is a chemical bond between the hydrogel and the dye, which can be seen in the following <u>Figure 2</u> and mechanism of reaction is in <u>Figure 3</u>.



Figure 2. FTIR spectrum of hygrogel after absoption



Figure 3. Mechanism of reaction

Conclusion

Based on the research that has been done, it can be concluded:

- 1. Cassava peel starch by FTIR showed the presence of O-H, C-H and C-O groups. The hydrogel of cassava peel starch showed a new group, namely the N-H functional group and the hydrogel that had been contacted with the yellow methanyl dye showed the presence of a new group, namely the N = N and S = O groups.
- 2. The maximum absorption ability of the hydrogel decreased methanyl yellow dye at a concentration of 30 ppm is 31.7283%.

References

- [1] F. A. Aderemi and F. C. Nworgu, "Nutritional Status of Cassava Peels and Root Sieviate Biodegraded With Aspergillus niger," Am. J. Agric Environ. Sci, vol. 2, no. 3, pp. 308–311, 2007.
- M. A. Otache, S. T. Ubwa, and A. K. Godwin, "Proximate Analysis and Mineral Composition of Peels of Three Sweet Cassava Cultivars," vol. 3, no. 4, pp. 1–10, 2017, DOI: <u>10.9734/</u> AJOPACS/2017/36502.
- [3] A. O. Obadina, O. O. B. S. L. O, and S. S. Abiola, "Fungal enrichment of cassava peels proteins," *African J. Biote*, vol. 5, no. February, pp. 302–304, 2006, DOI: <u>10.5897/AJB05.360.</u>
- [4] N. K. Morgan and M. Choct, "Cassava: Nutrient composition and nutritive value in poultry diets," *Anim. Nutr. J.*, 2016, DOI: <u>10.1016/j.aninu.2016.08.010</u>.
- [5] E. Erizal and F. Lukitowati, "Synthesis and Characterization of Superabsorbent Sodium Alginate-G-Poly (Potassium Acrylate) Hydrogels Prepared By Using Gamma Irradiation," no. July, 2017, DOI: <u>10.24817/jkk.v39i1.2727.</u>
- [6] L. Chen, Y. Zhu, Y. Cui, R. Dai, Z. Shan, and H. Chen, "Fabrication of starchbased high-performance adsorptive hydrogels using a novel effective pretreatment and adsorption for cationic methylene blue dye: Behavior and mecha-

nism," Chem. Eng. J., vol. 405, no. 2021, p. 126953, 2021, DOI: <u>10.1016/</u> j.cej.2020.126953.

- [7] H. Mondal, M. Karmakar, P. K. Chattopadhyay, and N. R. Singha, "Starch-gtetrapolymer hydrogel via in situ attached monomers for removals of Bi(III) and/or Hg (II) and dye(s): RSM-based optimization," *Carbohydr. Polym.*, vol. 213, no. January, pp. 428–440, 2019, DOI: <u>10.1016/</u> j.carbpol.2019.02.035.
- [8] H. Al-Aidy and E. Amdeha, "Green adsorbents based on polyacrylic acid-acrylamide grafted starch hydrogels: the new approach for enhanced adsorption of malachite green dye from aqueous solution," Int. J. Environ. Anal. Chem., pp. 1–21, 2019, DOI: 10.1080/03067319.2020.1711896.
- [9] L. Cundari, A. N. Utari, and M. Septikarini, "Adsorption Capacity and Isotherm of Methylene Blue Removal in Aqueous Solution onto Regenerated Activated Carbon," *IOP Conf. Ser. Mater. Sci. Eng.*, 2019, DOI: 10.1088/1757-899X/543/1/012088.
- [10] A. Salama, N. Shukry, and M. El-Sakhawy, "Carboxymethyl cellulose-g-poly(2-(dimethylamino) ethyl methacrylate) hydrogel as adsorbent for dye removal," Int. J. Biol. Macromol., vol. 73, no. 1, pp. 72–75, 2015, DOI: <u>10.1016/j.ijbiomac.2014.11.002</u>.
- [11] D. Sarmah and N. Karak, "Double network hydrophobic starch based amphoteric hydrogel as an effective adsorbent for both cationic and anionic dyes," *Carbohydr. Polym.*, vol. 242, no. January, p. 116320, 2020, DOI: <u>10.1016/j.carbpol.2020.116320.</u>
- [12] S. Sivamani, K. Archana, N. Sivarajasekar, and N. Prasad, "Synthesis and characterization of starch nanoparticles from cassava Peel," J. *Bioresour. Bioprod.*, vol. 3, no. 4, pp. 161–165, 2018, DOI: <u>10.21967/jbb.v.</u>
- K. Kaur, P. Ahluwalia, and H. Singh, "Cassava: Extraction of starch and utilization of flour in bakery products," *Int. J. Food Ferment. Technol.*, vol. 6, no. 2, p. 351, 2016, DOI: <u>10.5958/2277-</u> <u>9396.2016.00059.3.</u>
- [14] D. F. Alifa, D. Izak Rudyardjo, and J. Ady, "Sintesis dan Karakterisasi Hidrogel Kitosan-Glutaraldehid dengan Penambahan Asam Laurat Sebagai Plasticizer Untuk Aplikasi Penutup Luka," Jurnal Fisika dan Terapannya, vol. 2, no. 3, pp. 16-36, 2013.