EXTRACTION OF CELLULOSE FROM KEPOK BANANA PEEL (Musa parasidiaca L.) FOR ADSORPTION PROCION DYE

EKSTRAKSI SELULOSA DARI KULIT PISANG KEPOK (Musa parasidiaca L.) UNTUK ADSORPSI ZAT WARNA PROCION

Poedji Loekitowati Hariani^{1*}, Fahma Riyanti¹ and Riski Dita Asmara¹

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, Palembang, Sriwijaya University

*email: pujilukitowati@yahoo.com

Received 9 February 2016; Accepted 4 May 2016; Available online 16 May 2016

ABSTRACT

The aim of the research was to extract a cellulose from kepok banana peel (Musa parasidiaca L.) and application to removal Procion dye. The extracted cellulose was prepared by dewaxing process to releasing of lignin, bleaching and hemicellulose removal. The cellulose identified by FTIR and SEM-EDS. The efficiency of the cellulose to adsorp Procion dye was evaluated by variation in the initial concentration of dye (5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 mg/L), solution pH (3, 4, 5, 6, 7, 8 and 9), and the contact time (15, 30, 45, 60, 75 and 90 minutes) at room temperature. The result showed that FTIR spectra of cellulose from kepok banana peel were similar with FTIR spectra of standard cellulose. The morphology of cellulose more homogenous than kepok banana peel powder. It was observed that the optimum adsorption of Procion dye by cellulose was on the initial concentration of 30 mg/L, pH solution of 5 and contact time within 30 minutes. The obtained result that cellulose has removal percentage to adsorp Procion dye more higher than kepok banana peel powder. The adsorption equilibrium showed the Langmuir isotherm was described well for adsorption process ($R^2 = 0.991$) than Freundlich isotherm ($R^2 = 0.922$).

Keywords: adsorption, banana peel, cellulose, isotherm, Procion

ABSTRAK

Penelitian ini bertujuan untuk mengekstraksi selulosa dari kulit pisang kepok (*Musa parasidiaca* L.) yang diaplikasikan untuk menyerap zat warna Procion. Ekstraksi selulosa dilakukan melalui beberapa tahap yaitu penghilangan lilin, pemutihan dan penghilangan hemiselulosa. Selulosa yang dihasilkan dikarakterisasi menggunakan FTIR dan SEM-EDS. Efisiensi selulosa untuk menyerap zat warna Procion menggunakan beberapa parameter yaitu konsentrasi awal zat warna (5, 10, 15, 20, 25, 30, 40, 45 dan 50 mg/L), pH larutan (3, 4, 5, 6, 7, 8 dan 9), dan waktu kontak (15, 30, 45, 60, 75 dan 90 menit). Hasil karakterisasi menunjukkan adanya kesamaan spektra FTIR antara selulosa yang diekstraksi dari kulit pisang kepok dengan selulosa standar, morfologi selulosa lebih homogen dibandingkan serbuk kulit pisang kepok. Kondisi optimum adsorpsi diperoleh pada konsentrasi awal zat warna 30 mg/L, pH larutan 5 dan waktu kontak 30 menit. Ekstrak selulosa dari kulit pisang kepok mempunyai persen efisiensi menyerap zat warna Procion lebih besar dibandingkan serbuk kulit pisang kepok. Isoterm adsorpsi menggunakan model Langmuir (R²= 0,991) lebih sesuai menggambarkan proses adsorpsi zat warna Procion pada selulosa dibandingkan isoterm Freundlich (R²= 0,922).

Kata kunci: adsorpsi, isoterm, kulit pisang, Procion, selulosa

INTRODUCTION

Bananas is tropical fruits that the most widely produced and used by the community Indonesian. Kepok banana (Musa parasidiaca L.) is the most widely consumed by the people of Indonesia. Currently, the peel, stems and leaves of the banana (80%) simply discarded further without processing (Tchobanoglous, Theisen, & Vigil, 2003) whereas waste of kepok banana peel containing polymers such as cellulose. hemicellulose and pectin (Klemm, Schmauder, & Heinze, 2006). Kepok banana peel also contains cellulose amounted to 18.71% (Koni, Therik, & Kele, 2013). Cellulose is a linear polymer consisting of 300 to 15.000 D-glucose linked by bonds β -(1,4) glycosidic. The empirical formula of cellulose $(C_6H_{10}O_5)_n$. The cellulose have uniform surface and form a layer of fiber-like pore structure. Porous solid has the ability as an adsorbent that can be used adsorppollutant in the environment (Wilbraham and Michael, 1992). In addition, the functional groups -OH in banana peel can be exploited into to adsorp pollutants.

Cellulose as adsorbent for waste water treatment has an advantage of most abundant organic polymer, stable to chemicals, biodegradable, non toxic, and inexpensive. Besides that, cellulose has thermal stability, the degradation of cellulose leaded to the lost weight of 90% around 393 to 723 K (Yan, Duduku, Mariani, & Awang, 2009; Zhou et al., 2012).

Many studies used of cellulose as adsorbent to adsorp pollutant in waste water. Hejeeth (2013) extracting cellulose from sisal fiber for adsorption of Cr(VI) from aqueous solution with adsorption capacity is 280.04 mg/L. Annadurai, Ruey, and Lee (2002) used of cellulose-based wastes for adsorption of methyl orange, methylene blue, rhodamine blue, congo red, methyl violet and amido black from aqueous solution. The adsorption

capacity in the range of 10-120 mg/L. Mohadi, Nurlisa, Adi, and Aldes (2013) extracting cellulose from wood sawdust to adsorp Co²⁺ with adsorption capacity is 0.55.10⁻⁴ mol/g. Beside that, cellulose is also useful an anticoagulant, fibrinololytic and toxicological studies (Ragab et al., 2014).

In this study, cellulose extracted from kepok banana (*Musa parasidiaca* L.) performed several stages dewaxing, bleaching to release of lignin and hemicellulose removal. The dewaxing process is done by maceration using ethanol/toluena (1:1).This process increases the amorphous content, tensile strength and modulus of cellulose (Hajeeth, 2013). The bleaching process using sodium hypochlorite to degradation of lignin. The last process is the removal of hemicellulose using sodium hydroxide solution.

The cellulose was used for adsorption Procion dye using batch method. The cationic dyes released together with industry effluents such as textile, paper, plastics, cosmetics and rubber. The optimum parameters affecting the initial concentration of dye, pH solution and contact time. The equilibrium adsorption experiments were obtained fitted to Langmuir and Freundlich adsorption isotherm.

METHODS

Materials and Equipment

The kepok banana peel was obtained from a local fruit in Palembang. The analytical grade reagents such as NaOH, ethanol, toluene, NaOCl, HCl, H2O2 obtained from Merck, and Procion dye from Sigma Aldrich. The equipment includes glassware, sieve 100 mesh, oven, analytical balance, shakers, pH meter 96107 Hanna, Spectrophotometer UV-Vis UVmini-1240 Shimadzu, SEM-EDS JEOL JSM 6510-LA and FTIR Shimadzu 500.

Extraction of Cellulose

Kepok banana peel is cleaned of impurities, then dried in the sun until dry (± 5 days). Dried banana peel that has been crushed and sieved with a 100 mesh. The maceration process was carried out using 100 g powder of banana peels into ethanol/toluene (100:100) mL for 3 days. Furthermore, the process of bleaching to remove lignin using 250 mL of NaOCl (6%) solution, stirring for 3 hours and heated at 80 °C. The removal of hemicellulose carried out by using 300 mL of NaOH (4% w/v) and stirring for 4 hours at 60 °C, filtered and washed with distilled water.

The precipitated was added to 400 mL of NaOH and 200 mL of H₂O₂ (30%) in a water bath at 85 °C for one hour, filtered and washed with distilled water. The next step, the H₂O₂ (10%) 200 mL was added to precipitate, stirring at 85 °C for one hour, filtered and washed with distilled water several times until pH neutral. The precipitated was dried at 40 °C in vacuum oven for 24 hours. The Celluloses was formed identified using FTIR to determine the functional groups and SEM-EDS to study the surface morphology.

Bacth Experimental

Batch studies used to obtain the adsorption of cellulose for Procion dye solution with parameters include initial concentration of dye, pH of solution and contact time. The effect of initial concentrations of dye was carried out in a stopper bottle containing about 50 mL of Procion dye and 0.1 g of cellulose. The initial concentration of dye in the range 5-50 mg/L. The mixture was agitated using shaker at 150rpm for 30 minutes and then filtered. The filtrate determined concentration of Procion dye at a wavelength of 542 nm using Spectrophotometer UV-Vis. Effect of pH using concentration of Procion dye 30 mg/L, pH of solutionin the range of 3-9 with 0.1 N HCl or NaOH solution. To evaluated effect of contact time determined for 15-90 minutes, so that the equilibrium time can be evaluated. The quantity of Procion dye, $q_e \pmod{g}$ at the time was calculated by following equation:

$$q_e = (C_o - C_e) \frac{v}{w}$$

The Procion dye concentration removal percentage can be expressed as follows:

$$(\% removal) = \frac{c_{o} - c_{e}}{c_{o}} \times 100 \%$$

Where C_o and C_e (mg/L) refer to the initial concentration and equilibrium liquidphase concentration of Procion dye, V(L) the volume of the Procion dye solution, and W(g) the weight of the adsorbent.

Adsorption of Isotherm

In this study, the Langmuir and Freundlich adsorption equilibrium described how the adsorption molecules distribute between liquid and solid phase. The isotherm linear equations of Langmuir calculated following:

$$\frac{C_e}{q_e} = \frac{1}{K q_m} + \frac{C_e}{q_m}$$

Where C_e (mg/L) is the equilibrium concentration of Procion dye, q_e (mg/g) is the amount of Procion dye at equilibrium concentration, q_m (mg/g) is the maximum adsorption capacity of cellulose and K (L/mg) is the Langmuir constant.

The linear equation of Freundlich isotherm:

$$\log q_e = \log K_{F+\frac{1}{n}} \log C_e$$

Where q_e (mg/g) is the amount of Procion dye at equilibrium concentration, C_e (mg/L) is the equilibrium concentration of Procion dye, n and K_F (mg/g) is the Freundlich constant.

RESULT AND DISCUSSION

Characterization of Cellulose Extracted from Banana Kepok Peel

Banana peel (*Musa paradisiaca* L) is the third part of bananas (Munadjim,

1988). Kepok banana peel has brownish yellow color, after extraction by removing the lignin, hemicellulose and bleaching process produced cellulose with white colored. Figure 1 showed the FTIR spectra of cellulose extracted from kepok banana peel and standard of cellulose. The main functional groups on the cellulose are C-H stretching vibration and hydrogen bonded O-H, cellulose is along chain of βglucose. The FTIR spectra showed that the peaks at 2920.0 and 3411.8 cm⁻¹ while compared with standard of cellulose, the peaks observed at 2900.7 and 3354.0 cm⁻¹. From these data the two main groups of cellulose are on relatively absorption area. The cellulose from kepok banana peel and standard of cellulose have the wave number at 1058.8 cm⁻¹ assigned to the stretch C-O (Alemdar and Sain, 2008).

SEM images of the surface of kepok banana peel powder and cellulose extracted from kepok banana peelare in Figure 2 at 10.000 show a magnification. From the image, cellulose and banana kepok peel powder showed different size and shape. The banana kepok peel powder has been found many small particles in the surface that cause the morphology is irregular shapes and heterogeneous, whereas the morphology of cellulose is homogeneous with the structure of dense and large particles.

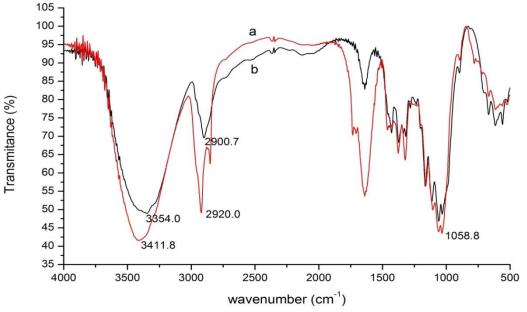


Figure 1. FTIR Spectra of (a) cellulose extracted from kepok banana peel and (b) standard of cellulose

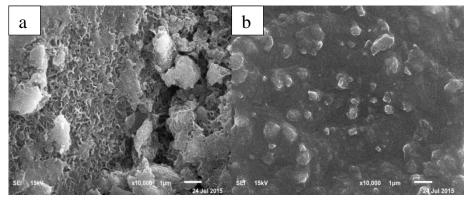


Figure 2. SEM image of (a) banana kepok peel powder and (b) cellulose extracted from banana kepok peel

Element	Mass percentage (%)	
	Banana kepok peel powder	Ectracted cellulose
С	21.94	64.67
O	36.08	31.20
Fe	3.07	-
Na	1.34	0.84
Mg	0.28	0.39
Al	10.17	-

19.95

0.49

6.68

Table 1. Elements of banana kepok peel powder and cellulose

Composition elements of banana kepok peel powder and cellulose from kepok banana peel analyze dusing ED Sare show in **Table 1**. The results indicated that differences in the elements of banana kepok peel powder and cellulose. The banana kepok peel powder contained of C 21.94% while the cellulose increased 64.67%. Some of the elements such of O, Fe, Na, Al, Si, K, and Ca in banana kepok peel powder was decreased.

Adsorption of Procion Dye

Si

K

Ca

Cl

The effect of initial concentration of removal Procion dye onto banana kepok peel powder and cellulose were evaluated in the range 5-50 mg/L of 50 mL Procion dye concentration, weight of adsorbent 0.1 g, pH of solution 5, shaking for 30 minutes at room temperature. From the **Figure 2**, it was described that adsorption Procion dye onto cellulose increases with increase initial concentration of Procion dye. When the concentration of dye was higher than 30 mg/L, the increased of removal percentage was slowly or constant. It is clear, that the amount of adsorbent was limited, but the amount of dye was increased.

The amount of Procion dye removal onto cellulose is greater than kepok banana peel powder. The same phenomenon in the adsorption of basic fuchsine using cellulose-based multicarboxyl (Zhou et al., 2013). The results indicated that the reactivity of

Procion dye increased in the adsorption using cellulose.

1.78

0.20

0.51

0.41

The range of pH solution for adsorption Procion dye onto banana kepok peel powder and cellulose were confirmed as 3 to 9, 50 mL of Procion dye with initial concentration 30 mg/L, weight of cellulose 0.1 g. Effect of the pH solution showed in the **Figure 3**. pH solution could influence the adsorption process. For the adsorption of dye using cellulose, the dye removal percentage was increased when pH solution increase from 3 to 5 and after pH solution above 5 was decrease.

Cellulose having an isoelectric point at pH solution 5 (Orelma, Ilari, Leena, Janne, & Orlando, 2011). The Procion dye is cationic dye. In low pH solution (pH <5) can be described to the electrostatic repulsion between protonated cellulose and cationic dye. In high pH solution (pH >5), electrostatic interaction between negatively of cellulose and cationic dye. Similar result of effect pH reported Suteu, Gabriela, Lacramioara, Sergiu, Gabriela (2015) for adsorption Brilliant Red HE-3B using cellulose cell optimum at pH solution of 5. Another result, Annadurai et al. (2002) obtained optimum pH solution in the range 6-7 for the adsorption of cationic dye using cellulose based wastes. Adebayo et al. (2014), get result that the adsorption was influenced by the pH of the solution.

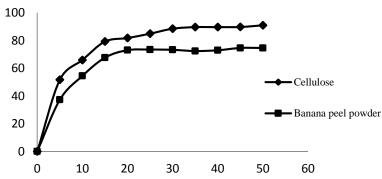


Figure 2. Adsorption curve of Procion dye at various initial concentration

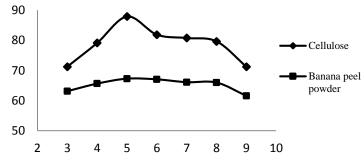


Figure 3. Adsorption curve of Procion dye at various pH solution

The removal percentage of adsorption Procion Blue MX-R dye from aqueous solution using lignin modified with aluminium and manganese in the range pH 2-10 decreased from 98% to 2%. The adsorption process of dye onto kepok peel powder perpetually banana dominated by physical adsorption. The kepok banana peel powder has pores can be adsorp the dye. The dye removal percentage at the pH solution 5 by using cellulose and banana kepok peel powder were of 87.89% and 67.25%, respectively.

The effect of contact time on the adsorption process in the range 15-90 minutes at the initial concentration 30 mg/L, pH of solution 5 and weight of cellulose 0.1 g at room temperature. The results are showed in Figure 4. The trend of the adsorption showed that the dye percentage removal increases increases of contact time. The time achieved maximum removal percentage of Procion dye was 30 minutes using cellulose and 60 minutes using kepok banana peel powder, respectively. different result, Bouhdadi et al. (2011) obtained optimum contact time at 80 minutes for adsorption of cationic dye (Methylene Blue) using cellulose from Kraft pulp. Hariani, Fatma, and Zulfikar (2015) adsorption of Procion dye using activated carbon-alumina composited get optimum contact time at 2 hours. In this result, the optimum adsorption at contact time of 30 minutes with 89.94% of dye removal percentage using cellulose and kepok banana peel powder of 75.14% at 60 minutes.

Isotherm Study

The result indicated that the removal of Procion dye onto cellulose was conforming the Langmuir more to isotherm with R² = 0.991 but the Freundlich isotherm was lower, R^2 = 0.922. Langmuir isotherm is assumed that adsorption process occurs at specific homogeneous sites and monolayer adsorption while Freundlich isotherm assumption heterogeneous surface. Value of 1/n was found 0.1633 (<1) confirmed that the adsorption process followed Langmuir isotherm (Tan, Ahmad, Hameed. 2008). Similar result. adsorption dye onto cellulose from orange peel inaccording the Langmuir isotherm (Annadurai et al., 2002).

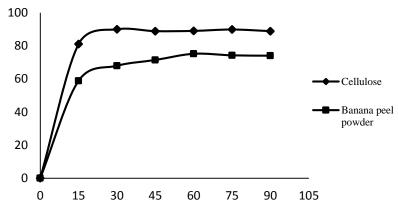


Figure 4. Adsorption curve of Procion dye at various contact time

The maximum adsortion capacity calculated was $15.585 \, \text{mg/g}$ compared with experimental was found 13.456 mg/g. Other result showed that adsorption Procion dye onto Eichharnia crassipes powder and alumina-activated carbon have adsorption capacity of 4.369 mg/g and 7.12 mg/g (Yuliasari Miksusanti, 2010; Hariani et al., 2015). Other study showed that adsorption of Procion dye using kaolin and synthetic talc accordance with Langmuir model but at different pH. The maximum adsorption capacity Procion dye using kaolin dan synthetic talc at pH solution 3.1 and 6.4 with adsorption capacity of 4.51 and 9.35 mg/g, respectively (Rahman, Takeo & Naoyuki, 2013). Table 2 summarizes of the Langmuir, Freundlich adsorption constant and their correlation coefficients.

Table 2. Langmuir, Freundlich constants for adsorption Procion dye onto cellulose

Type of isotherm model	Value		
Langmuir isotherm			
$q_m \text{ (mg/g)}$	15.585		
K (L/mg)	0.042		
\mathbb{R}^2	0.991		
Freundlich isotherm			
K_F	4.549		
1/n	0.163		
\mathbb{R}^2	0.922		

CONCLUTIONS

The cellulose extraction from kepok banana peel potential to adsorp Procion dye from aqueous solution. The FTIR and SEM-EDS characterization showed of their successful synthesis. The removal of Procion dye onto cellulose was studied by batch adsorption with the optimum condition at the initial concentration of 30 mg/L, pH solution of 5 and contact time 30 minutes. The experimental data, it was Langmuir isotherm model very well appicable for the adsorption equilibrium compared with Freundlich isotherm. The maximum adsorption capacity of cellulose to adsorp Procion dye was 15.585 mg/g.

REFERENCES

Adebayo, M.A., Lizie, D.T., Eder, C.L., Puchana, R., Renato, C., and Reinaldo, R. (2014). Adsorption of Procion blue MX-R dye from aqueous solutions by lignin chemically modified with aluminium and manganese. *Journal of Hazardous Materials*. 268, 43-50.

Alemdar, A., &Sain, M. (2008). Isolation and characterization of nanofibers from agricultural residue. *Bioresource*, 99, 1664-1671.

Annadurai, G., Ruey, S.J., & Lee, D.J. (2002). Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. *Journal of Hazardous Materials B29*, 256, 263-274.

Bouhdadi, R., Benhadi, S., Molina, S., George, B., El Moussaouiti, M., & Merlin, A. (2011). Chemical modification of cellulose by acylation application to adsorption

- of methylene blue. *Ciencia y Tecnologia*, *13*(1), 105-116.
- Hajeeth, T. (2013). Adsorption of Cr(VI) from aqueous solutions using cellulose extracted from sisal fiber. *Indian Journal od Applied Research*, 3(1), 1-5.
- Hariani, P.L., Fatma., & Zulfikar. (2015). Alumina-activated carbon composite as adsorbent for adsorption of Procion red dye from waste water songket industry. Journal Pure and *Applied* Chemistry Research, 491, 25-33
- Klemm, D., Schmauder, H.P., & Heinze, T. (2006). Cellulose, Polysaccharadies II. *Journal Poly Eukaryot*, 6, 275-320.
- Koni, T.N.I., Therik, J.B., & Kele, P.R. (2013). Pemanfaatan Kulit Pisang Hasil Fermentasi *Rhyzopus oligosporus* dalam ransum terhadap pertumbuhan ayam pedaging. *Jurnal Veteriner*, *14*(3), 365-370.
- Munadjim. (1988). *Teknologi Pengolahan Pisang*. PT Gramedia. Jakarta
- Mohadi, R., Nurlisa, H., Adi, S., & Aldes, L. (2013). Kajian Interaksi ion Co²⁺ dengan selulosa dari serbuk gergaji kayu. *Cakra Kimia Indonesia*, *1*(2), 8-15.
- Orelma, H., Ilari, F., Leena, S.J., Janne, L., & Orlando, J.R. (2011). Modifications of cellulose film by adsorption of CMC and chitosan for controlled attachment of biomolecules. *Biomacromolecules*, 12, 4311-4318.
- Ragab, T.I.M., Amer, H., Wasfy, A.A.F., Hady, M.S.A., Mossa, A.T.H., & Liebner. F. (2014).Sulfated cellulose from agriculture wastes, anticoagulant, fibrinolytic and toxicological studies. Journal Environmental Science and *Technology*, 7(5), 266-280.

- Rahman, A., Takeo, U., & Naoyuki, K. (2013). Color removal of reactive Procions dyes by clay adsorbents. *Procedia Environmental Sciences*, 17, 270-278.
- Suteu, D., Gabriela, B., Lacramioara, R., Sergiu, C., &Gabriela, N. (2015). Cellulose cellets as new type of adsorbent for the removal of dyes from aqueous media. *Environmental Engineering and Management Journal*, 14(3), 525-532.
- Tan, I.A.W, Ahmad, A.L., & Hameed, B.H. (2008). Enhancement of basic dye adsorption uptake from aqueous solutions using chemically modified oil palm shell activated carbon. *Colloids and Surfaces*, 318, 88-96.
- Tchobanoglous, G., Theisen, H., & Vigil., S.(2003). Integrated Solid Waste Management: Engineering Principles and Management Issues.McGraw-Hill. New York.
- Yan, F.Y., Duduku, K., Mariani, R., &Awang, B. (2009). Cellulose extraction from palm kernel cake using liquid phase oxidation. *Journal of Engineering and Technology*, 4(1), 57-68.
- Yuliasari, N., & Miksusanti. (2010). Studi penyerapan Procion pada limbah kain tajung menggunakan serbuk batang eceng gondok. *Jurnal Penelitian Sains*, 13(2), 1-7.
- Zhou, Y., Zhang, M., Hu, X., Wang, X., Niu, J., & Ma, T. (2013). Adsorption of cationic dyes on a cellulose-based multicarboxyl adsorbent. *Journal of Chemical and Engineering Data*, 58, 413-421.
- Wilbraham, A.C. & Michael, B.M. (1992). *Pengantar Kimia Organik dan Hayati*. Terjemahan: Suminar Achmadi. ITB. Bandung