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Modification of Cellulose with 4.4 Diaminodiphenylether-O-Hydroxybenzaldehyde as Adsorbent and Its Application for Adsorbing Metallic Ion of Cd^{2+} In Aqueous Solution

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Abstract

This research on the modification of cellulose using 4,4-diaminodiphenylether and o-hydroxybenzaldehyde and its application to adsorb Cd^{2+} in aqueous solution has been done. The adsorption studies of cellulose and modified cellulose were done by using batch technique. The cellulose and modified cellulose were characterized by FTIR. The FTIR spectra revealed characteristic bands of 1573 cm^{-1}, 1280 cm^{-1}, 3749 cm^{-1} and 1056 cm^{-1}. It indicates function group of C=N, C=O, O-H and Si-OR bond, respectively. The FTIR spectra of cellulose and modified cellulose which interacted to Cd^{2+}, it was indicated by the shift in wavenumber of 3410 cm^{-1} to 3371 cm^{-1}. This spectral shift indicating Cd^{2+} bound to OH-group. In this research, interaction between modified cellulose with Cd^{2+} confirmed by intensities spectral changes at 1620 cm^{-1}. The adsorption capacity and energy from adsorption of Cd^{2+} ions toward cellulose were 71.43 mg/g and 4.14 kJ/mol, while toward modified cellulose were 55.56 mg/g and 0.13 kJ/mol, respectively.

Keywords: cellulose, 4,4-diaminodiphenylether-o-hydroxybenzaldehyde, adsorption, Cd^{2+}

Abstrak (Indonesian)

Telah dilakukan penelitian modifikasi selulosa menggunakan 4,4-diaminodiphenylether dan o-hydroxybenzaldehyde serta penggunaannya sebagai adsorben untuk menyerap Cd^{2+} di dalam kondisi larutan berair. Studi adsorpsi selulosa dan selulosa termodifikasi telah dilakukan menggunakan metode batch. Selulosa dan selulosa termodifikasi telah dikarakterisasi menggunakan FTIR. Spektrum FTIR menunjukkan karakteristik puncak pada 1573 cm^{-1}, 1280 cm^{-1}, 3749 cm^{-1} dan 1056 cm^{-1}. Masing-masing puncak tersebut mengindikasikan adanya gugus C=N, C=O, O-H dan ikatan Si-OR. Spectra FTIR selulosa dan selulosa termodifikasi yang telah diinteraksikan dengan Cd^{2+} menunjukkan adanya pergeseran pada panjang gelombang 3410 cm^{-1} ke 3371 cm^{-1}. Pergeseran ini menunjukkan adanya ikatan antara Cd^{2+} dengan gugus OH. Pada penelitian ini, interaksi antara selulosa termodifikasi dengan Cd^{2+} diketahui pada perubahan intensitas spektrum pada 1620 cm^{-1}. Kapasitas adsorpsi dan energi adsorpsi ion Cd^{2+} terhadap selulosa adalah 71.43 mg/g dan 4.14 kJ/mol. Sedangkan selulosa termodifikasi menghasilkan kapasitas dan energi adsorpsi sebesar 55.56 mg/g dan 0.13 kJ/mol.

Kata kunci: selulosa, 4,4-diaminodiphenylether-o-hydroxybenzaldehyde, adsorpsi, Cd^{2+}

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INTRODUCTION

Adsorption is a very efficient method to reduce the heavy metals content in the liquid media. Metallic ions adsorption by dead organisms occurs through sorption process involving the functional groups associated with proteins, polysaccharides, carboxylate, hydroxyl, sulfhydryl groups and other biopolymers contained the cell or the cell wall [1]. The adsorption process can occur chemically or physically. Physically, the adsorption process is due to Van der Waals forces that exist on the surface of the adsorbent while chemically, chemical bonding occurs between metals adsorbed on the surface of the adsorbent [2]. Adsorption capacity of the adsorbent can be improved by modification of materials using acid or alkali solution, or may be via physical treatments such as heating [3].

The organic compound can be used to modify the adsorbent, one of which is a 4.4-diaminodypenilether. The 4,4-diaminodipenileter (DDE) and ortho-hidroksibenzaldehid (o-Hb) compound can form Schiff bases (such as CN-, H, CO, OH, N_2) derived from O-Hb as polydentate ligands which can form stable complex compounds with transition metal ions. [4] The nitrogen atom in the group -N = CH- of Schiff base acts as a soft donor atom (base) so it has a high affinity to bind with metals that soft acidic character. Cellulose is one of the solids that can serve as an adsorbent because it has an active site i.e. a hydroxyl group (OH) [5]. Modification of the cellulose have been common for example with nitric acid and provide l

Meanwhile, the metal cadmium is a heavy metal that is toxic to humans because it causes bone loss and damage to the physiological systems of the body such as the lungs. Waste metals Cd can be derived from most industrial activities such as dye, batteries, photographic and electroplating industry.

In this study, a modification of cellulose with DDE and o-Hb. Cellulose adsorbent 4.4-DDE- o-Hb is then used to adsorb heavy metals Cd which belong to the category of soft acids according to the theory HSAB (Hard Soft Acid Base).arget adsorption capacity of the metals Pb and Cd [6].

EXPERIMENTAL SECTION

Materials

The materials used are cellulose, ortho-hydroxybenzildehide (o-Hb), 4.4-diaminodiphenylether (DDE), dimetilformamide (DMF), 3-chloropropilmetoxylene (CPM), Whatman filter paper, distilled water, aquadest, Cd^{2+} solution from $CdCl_2.H_2O$ HCl, NaOH, and ethanol. All the chemical was used as received. The equipment involved in this research is a set of chemical glassware, reflux, Atomic Absorption Spectrophotometer (AAS), Shimadzu FTIR spectrophotometer 8201 PC.

Methods Synthesis adsorbent cellulose 4,4-diaminodiphenylether-o-hydroxybenzaldehyde

5 g of cellulose which has been activated added to 25 mL of DMF and then mixed with 12.5 mL of 3-CPM. The mixture was refluxed for 5 hrs at a temperature of 100℃ -200℃, after refluxing, the mixture was filtered, the residue was dried in an oven. The dried residue is then mixed in a mixture of 5 g of 4,4-DDE and 25 mL of DMF. The mixture was refluxed for 3 hrs at a temperature above 80℃. The mixture was filtered and the residue dried in an oven. The residue was added to a mixture of 5.25 mL of o-Hb with 75 mL of ethanol and then refluxed for 3 hrs at a temperature of 55℃. The mixture was filtered, the residue washed with ethanol and dried. The drying result was called adsorbent 4.4 diamino dipenylether -o- hydroxybenzaldehyde (DDE-o-Hb).

Analysis of functional groups

Analysis of functional groups was determined by FTIR and using KBr pellets. The analysis included the analysis of functional groups: a. Cellulose, b. The stage of cellulose modification, c. Cellulose adsorbent 4.4-DDE-o-Hb, d. Cellulose-ion Cd^{2+} adsorbent and e. cellulose-4,4-DDE-o-Hb-ion Cd^{2+} adsorbent.

Studies of performance of cellulose-DDE-o-Hb- ion Cd^{2+} adsorbent

The influence of the interaction time

A total of 0.05 g of 4,4- cellulose-DDE-o-Hb adsorbent was mixed with 50 mL of Cd2+ ions with a concentration of 25 ppm. The mixture is shaked with a shaker with a various of interaction time of 10 minutes. Then, the solution was filtered and the concentration of filtrate was measured using AAS. The concentration of adsorbed metal ions Cd2+ was calculated from the difference between the concentration of metal ions Cd2+. With the same procedure, the interaction time increased to 30, 60, 90, 120 minutes and also performed on standard cellulose.

Effect of metal ion concentration

A total of 0.05 g cellulose of 4, 4-DDE-o-Hb adsorbent was added with 50 mL of Cd^{2+} ions with a concentration of 25 ppm. Then the mixture was shaked using the optimum time (the best time obtained from previous procedure). The mixture was filtered and the concentration of filtrate was measured using AAS. With the same procedure, the concentration of metal

ions Cd^{2+} increased to 50, 75, 100, 150 ppm and also performed on standard cellulose.

Effect of pH on the adsorption of metal ions

A total of 0.05 g of 4,4- cellulose DDE-o-Hb adsorbent was mixed with 50 mL of Cd^{2+} ions with a concentration of 25 ppm. The pH of solution of Cd^{2+} ion was set 4 and then shaked with a shaker during the optimum time (the best time obtained from previous procedure). The mixture was filtered and the filtrate measured concentration using AAS. With the same procedure, the pH of the solution was adjusted to 5, 6, 7, 8, 9 and also performed on standard cellulose.

RESULT AND DISCUSSION

Characterization of Adsorbent of Cellulose and Cellulose- DDE-O-Hb

The characterization was made using FTIR to the standard cellulose, the results of phase modification of cellulose and the product of cellulose DDE-o-Hb adsorbent. In addition, it was also carried out an analysis of the result of interaction of adsorbent and metallic ions Cd^{2+}. FTIR spectra of a standard cellulose, the results of phase modification, and interaction with metal ions Cd^{2+} is presented in Figure 1.

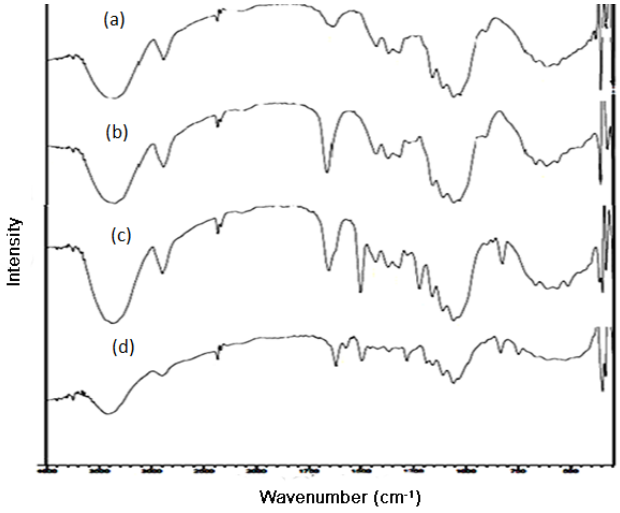

Figure 1. (a) standard cellulose, (b) cellulose- 3-CPM, (c) cellulose-3-CPM-DDE, and (d) cellulose DDE-o-Hb adsorbent.

Figure 1a is a FTIR spectra for standard cellulose. Wavenumber of 3348.42 cm^{-1} shows the stretching vibration of the hydroxyl group (OH). Wavenumber of 2900.94 cm^{-1} showed a -C-H stretching vibration [7]. Wavenumber of 1635.64 cm^{-1} and 1427 cm^{-1} shows aryl (C-C). Wavenumber of 1319.31 cm^{-1} indicating the presence -O- which is connecting to the carbon chain of cellulose, reinforced by a group of ether (C-O) at wavenumber of 1026.13 cm^{-1} [8]. In Figure 1b FTIR spectra visible difference appears at wavenumber 3927.07 cm^{-1} that showed the presence of strain OH. Absorption at Wavenumber of 1435.04 cm^{-1} showed a bending vibration of C-H functional group linking compound 3-CPM [9]. Comparation of FTIR spectra in Figure 1c to 1b shows some differences. Wavenumber of 3927.07 cm^{-1} and 3348.42 cm^{-1} derived from strain OH derived from cellulose, this area overlaps with the vibration of N-H functional group derived from the compound 4,4-DDE. Wavenumber of of 1504,48 cm^{-1} shows the C-NH derived from aromatic ring in the compound 4,4-DDE [10].

In the final stage, the cellulose-DDE adsorbent was added with o-Hb to produce cellulose adsorbent-DDE-o-Hb. The spectra cellulose-DDE-o-Hb adsorbent can be seen in Figure 1d. In Figure 1d, can be seen at wavenumber of 1573 cm^{-1} strain occurs -N = CH derived from Schiff base formed by -o-Hb with a low intensity and wavenumber of 1620.21 cm^{-1} indicating the existence of C = N. The shift action was occurred in wavenumber of 1280 cm^{-1} that showed the presence of ether C-O group of o-Hb. The shift in wavenumber of 3749.62 cm^{-1} indicating strain OH. The wavenumber of 1056.99 cm^{-1} showed the presence of Si-OR bond of 3-CPM compound with the capacity for small intens [10].

FTIR spectra of each adsorbent interaction with metal ions Cd^{2+} can be seen in Figure 2 and 3.

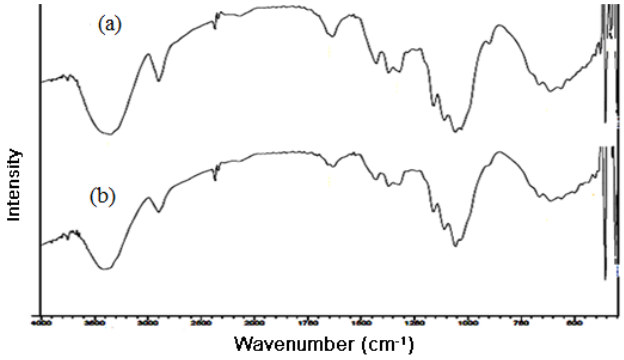

Figure 2. (a) Cellulose standard, (b) Cellulose- Metal Cd^{2+}

From the Figure 2, it can see there is a shift wavenumber from 3410.15 to 3371.57 cm^{-1}. It proved the stretching vibration of the OH group that indicated an interaction between cellulose and Cd^{2+} ions which is occurred in clusters OH [10].

In Figure 3, interaction cellulose-DDE-o-Hb adsorbent with metal ions Cd^{2+} is expected to be occur in the bond of N derived from Schiff base and also

bond O derived from the OH groups on the compound o-Hb i.e. through binding of metal ions Cd^{2+} that is indicated on the wavenumber of 1620.21 cm^{-1}. At the spectra of cellulose -DDE-o-Hb adsorbent and spectra of cellulose-DDE-o-Hb-Metal Cd^{2+} showed a shift wavenumber from 3410.15 cm^{-1} to 3371.57 cm^{-1}, which shows the stretching vibration of -OH group [10]. The shifting wavenumber indicates the bonding of Cd^{2+} ions with cellulose -DDE-o-Hb adsorbent.

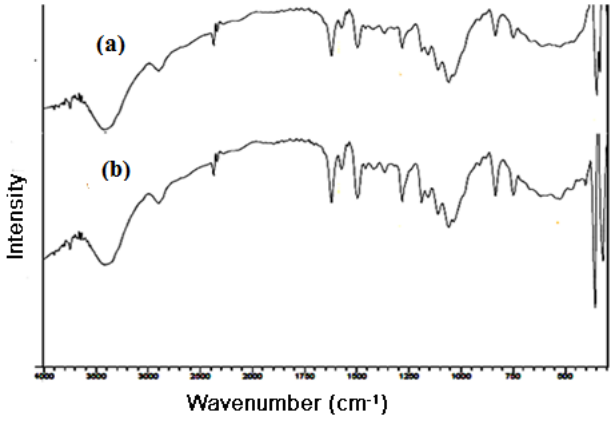

Figure 3. (a) cellulose-DDE-o-Hb, (b) cellulose-DDE-o-Hb-Metal Cd^{2+}

Adsorbent Interaction Studies with Ion Cd^{2+}

Effect of contact time

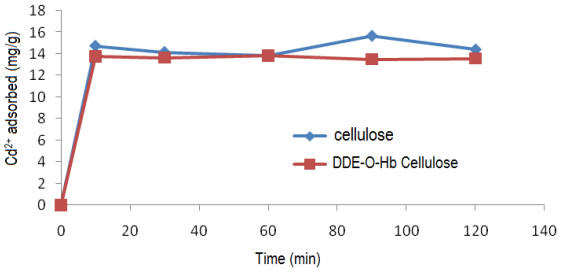

Figure 4. Effect of contact time on the extent of metal ion adsorption onto standard cellulose and modified cellulose

The influence of the contact time on the adsorption of cellulose and cellulose DDE-o-Hb is shown in Figure 4. The adsorption of Cd^{2+} on modified cellulose attained an equilibrium state after 10 minutes. The adsorption occurred rapidly within first 10 minutes due to abundant availability of active sites on adsorbent. Cellulose adsorbent showed the same trend as cellulose modified

The experimental data were treated to calculated value of rate constants and correlation coefficient. Value of rate constants were calculated using pseudo-second-order kinetic equation because value of correlation coefficient to be unity. Value of rate constant of cellulose adsorbent and cellulose modified were 0,08 and 0,17 respectively

Effect of Concentration

The influence of the concentration on the adsorption of Cd^{2+} with cellulose and cellulose DDE-o-Hb is shown in Figure 5.

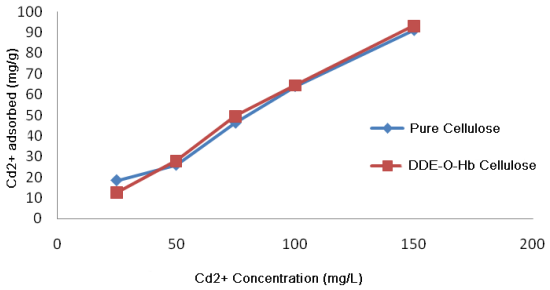

Figure 5. Effect of Cd^{2+} ion concentration with a standard cellulose and modified cellulose

The increasing of concentrations of solution always accompanied with the increasing of number of Cd^{2+} ions adsorbed on the adsorbent, for both of the standard cellulose and modified cellulose adsorbent. The higher of the concentration of metal ions Cd^{2+} so the possibility of interaction will be greater. Therefore, all of the active site of a functional group will binding to metal ions Cd^{2+} so the amount of Cd^{2+} ions adsorbed will be increased. The constant of equilibrium isotherms adsorption was calculated by the Langmuir formula. Cellulose isotherm models have equilibrium constant of 5.26, adsorption capacity of 71,43 5,26 mg/g and energy of 4.14 kJ/mol, while for cellulose modified, the equilibrium constant of 0.95; a capacity of 55, 56 mg/g and energy of 0.13 kJ/mol.

Effect of pH

The influence of pH on the adsorption of metallic ion Cd^{2+} with and cellulose DDE-o-Hb is shown in Figure 6. Based on Figure 6, the number of Cd^{2+} ions absorbed onto cellulose adsorbent increased from pH 4 to 5 and 6 to 9, while for pH 5 to 6 declined. Adsorbent from modified cellulose has more Cd^{2+} ions adsorbed at pH 5 and pH 9. When the pH lowered, the more competition between Cd^{2+} ions and H^{+} ions to interact with the adsorbent. In acidic conditions (low pH), the Nitrogen (N) atomic on the organic ligand in protonated state so it was positively charged [11]. In base solution, OH- will bind to metal ions Cd^{2+} and

form precipitate $Cd(OH)_2$. The base condition of solution caused the N atomic deprotonated thus it has partially negative charged. The partial negative charge of the N atom leads more interactions occurred so it makes the absorption increases.

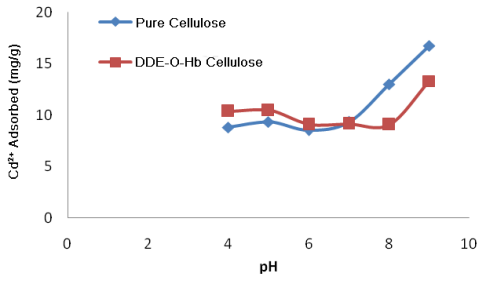

Figure 6. Effect of pH ion $Cd2^+$ to adsorbent standard cellulose and modified cellulose

CONCLUSION

1. The characterization results indicate that the 4.4-DDE-o-hidroksibenzaldehid bound to cellulose with the advent of wavenumber of 1573 cm^{-1}, 1280 cm^{-1}, 3749 cm^{-1}, 1056 cm^{-1}, which shows the characteristics of the C=N, CO, OH and Si-OR bond.
2. The shifting wavenumber from 3410.15 to 3371.57 cm^{-1} describes the OH stretching vibration, thus indicating interaction between adsorbent with metallic ions. Bond cellulose -DDE-o-Hb adsorbent with metallic ions is also indicated by the absorbance value at wavenumber of 1620 cm^{-1}. Absorbance values cellulose-DDE-o-Hb is 0.11 and cellulose adsorbent-DDE-o-Hb-Metal Cd^{2+} is 0.14.
3. Absorption of Cd^{2+} ions on the adsorbent showed the value of the standard cellulose adsorption capacity of 71.43 mg/g and a total energy of 4.142 kJ/mol, while the Cd^{2+} ion absorption on cellulose modified adsorbent showed the value of the adsorption capacity of 55.56 mg/g and an energy of 0.13 kJ/mol.

REFERENCES

[1] Drake, L. R. and Rayson, G. D, 1996, Plant derived Material for Metal Ion Selective Binding and Pre-concentration, *Analytical Chemistry*: 22-27.

[2] Kumar, P.S. and Kirthika, K., 2009, Equilibrium and Kinetic Study of Adsorption of Nickel from Aqueous Solution onto Bael Tree Leaf Powder, *Journal of Engineering Science & Technology 4(4)*:351-363.

[3] Marshall, W.E. and Mitchell, M. J, 1996, Agriculture by-Product as Metal Adsorbent: Sorption Properties and Resistence to Mechanical Abrasion, *Journal Chem Technol Biotechnol* 66:192-198.

[4] Dey, R.K., Usha, J., Singh, A.C. and Ray, A. R., 2006, Extraction of Metal Ion Using Chemically Modified Silica Gel Covalently Bonded with 4,4 Diaminodiphenylether and 4,4,-Diaminodiphenylsulfone-Salicylaldehide Schiff Bases, *Analytical Sciences*, Vol. 22: 1105- 1110.

[5] Fatoni, A., Soerja,K., and Nurlisa,H., 2015, Synthesis, Characterization of Cellulose Modified with 2-Merkaptobenzothiazole and Its Adsorption to Cu(II) ion in Aqueous Solution., Indones.J.Chem., 15(2) 194-200.

[6] Fatoni, A., Soerja,K., and Nurlisa,H., 2010, Synthesis, Characterization and Application of Diatomaceous Earth -4,4-Diaminodiphenylether-O-Hydroxybenzaldehyde As An Adsorbent of Ag(I) Metal ion, Indo.J.Chem., 10(3) 315-319.

[7] Singha, A. S and Ashish , G., 2014, Chemical Modification of cellulosic biopolymer nd its use in Removal of Heavy Metal ion , International Journal of Biological Macromolecules, 67, 409-417.

[8] Creswell,C. J., Olaf, A. R and Malcom, M. C, 1982, *Analisis Spektrum Senyawa Organik.* Edisi kedua, Institut Teknologi Bandung, Bandung.

[9] Budiman, H., Sri, H. F. and Setiawan, A.H., 2009, Preparation of Silica Modified with 2-Mercapto-imidazole and Its Sorption Properties of Chromium (III), *E-Journal of Chemistry*, 6(1): 141-150.

[10] Larkin. P., 2011, Infrared and Raman Spectroscopy: *Principles and Spectral Interpretation*, Elsevier publications.

[11] Akaninwor, J.O., Wegwu, M.O. and Iba, I.U., 2007, Removal of Iron, Zink and Magnesium from Polluted Water Samples Using Thioglicolic Modified Oil Palm Fibre, *African Journal of Biochemistry Research*, Vol. 1(2): 11-13.