Adsorption of Cd\(^{2+}\) using chitosan-linked p-t-buthylcalix[4]arene

D S Handayani\(^1\), T Kusumaningsih\(^1\), Pranoto\(^1\), N Ihsaniati\(^1\)

\(^1\)Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sebelas Maret, Jl. IrSutami 36A Surakarta Indonesia

Email: dsuci72@gmail.com

Abstract. This research aims to assess the use of chitosan-linked p-t-buthylcalix[4]arene as an adsorbent of Cd\(^{2+}\). Adsorption was done with the batch method in the variation of acidity (pH), contact time and initial concentration of Cd\(^{2+}\). The experimental results showed that the optimum pH of adsorption was pH 6 for the adsorbent chitosan and 8 for chitosan-linked p-t-buthylcalix[4]arene adsorbent. The optimum adsorption contact time was 240 minutes for both adsorbent. Study of adsorption kinetics revealed that the adsorption of Cd for two adsorbents followed the kinetics model Ho, pseudo-order 2, with adsorption rate constant 1.037x10\(^{-2}\) and 1.777x10\(^{-2}\) g mg\(^{-1}\) min\(^{-1}\) respectively. Study of adsorption isotherm presented that the using chitosan adsorbent tends to follow the Langmuir isotherm, while the adsorbent chitosan-linked p-t-buthylcalix[4]arene tend to follow Freundlich isotherm. The maximum capacity of the adsorption using chitosan and chitosan-linked p-t-buthylcalix[4]arene adsorbent 30.19 and 21.67 mol/g, with the adsorption energy 41.459 and 28.627 KJ/mol respectively.

1. Introduction

Chitosan is a polysaccharide amine resulted from deacetylation of chitin. This compound is an important natural polycationic biopolymer and can be applied in various fields such as metal and dyes adsorbent, materials for cosmetics and antibacterial agents [1]. Due to the ability to bind and to release back the metal ions by using certain solvents, thus chitosan is widely used as an adsorbent. Moreover, chitosan is able to be applied for continuous wastewater treatment [2]. The disadvantage of chitosan as the adsorbent is easily soluble in certain solvents such as acid, so it is necessary to improve the quality of chitosan by chemical modifications. Mahajan [3] found that the metal plating industry wastewater has a pH of 5 is still not meet the quality standards have permitted by the Government in accordance KEP-51/MENLH/10/1995.

Research on the use of chitosan and modified chitosan gradually increase, particularly in its application as a heavy metal adsorbent. Chitosan is available in various forms as an adsorbent, e.g. flakes [4] and powder [5], while the modified chitosan forms a crosslink chitosan [6]. Improving the ability of chitosan as an adsorbent can be conducted by modifying the chitosan to be crosslink chitosan as reported by Ngah et al. [7]. Other modifications can also be performed by crosslinking the crown ether as macromolecule on chitosan [8], or by cross-connecting between chitosan and Calix[4]arenes chelate to form the polymer. Previous research conducted by Restuti [9] also had modified chitosan with macromolecular compounds such as crown ether p-t-buthylkaliks [4] arena.

The compound p-t-buthylcalix[4]arene is one of the derivatives calixarene. Calixarene is a hollow cyclic molecule synthesized from the formaldehyde and phenols substituted by condensation under...
alkaline conditions [10]. Modifications compound p-t-butylcalix[4]arene on the fourth hydroxyl group with the addition of the carboxyl group a Quanti tative Maming et al. [11] (2007) produce acid compound p-t-butylcalix[4]arene and the use of acid p-t-butylcalix[4]arene was made by Maming et al.[12] as an adsorbent ion phosphate. Modification of chitosan compound p-t-butylcalix[4]arene by agents optocoupler DIC (N, N’-diisopropylcarbodiimide) have been undertaken by Tabakci and Yilmaz [8]. Agents optocoupler DIC has a linear shape and is often used in the field of health and synthesis of chemical compounds and biological products. In this paper, we present the adsorption of Cd metal ion using chitosan-linked p-t-buthylcalix[4]arene.

2. Research Methods

2.2 Ingredients:
Metal solutions were prepared by diluting 1000 mg/L Cd standard solution in aqueous nitric acid to desired concentrations. The pH adjustment was carried out by adding slowly NaOH and/or HNO₃ solutions into the metal solutions followed by stirring until the desired pH was reached. All materials required were reagent grade from E Merck. The material of Chitosan-p-t-butylcalix[4]arene was synthesized according to Handayani, et al. [13].

2.3 Instruments:
Atomic Absorption Spectrophotometer (AAS; AA-F-6650 Shimadzu), pH meter (Hanna), Fourier Transform Infra Red (FTIR) Prestige-21 Shimadzu, Scanning Electron Microscopy (SEM) JEOL JSM 6360 - EDX (JED-2200) and adsorption stirrer (Intan Electroplating).

2.4 Procedure:

2.4.1 Effect of solution pH solution Cd
The experiment was conducted by adding 20 mg of Chitosan-p-t-butylcalix[4]arene into 25 mL of metal cation sample solution with the concentration of 10 mg/L. The adsorptions of Cd(II) was carried out in pH 4.0; 4.5; 5.0; 5.5; 6.0 and 6.5. The mixture was then stirred at Equal room treatment performed on chitosan as a comparison measured based on the concentration of metal cation before and after the adsorption using AAS. Equal treatment performed on chitosan as a comparison.

2.4.2 Effect of Stirring Time
As much as 60 mg of the calixarene polymer was added into 30 mL of metal cation sample solution with the concentration of 10 mg/L for each. The adsorption kinetics was studied by conducting the adsorption in various contact times, which were 5, 15, 45, 135 and 405 minutes. The concentration of metal ion before and after adsorption was then measured by AAS and corrected with the blank solution. Equal treatment performed on chitosan as a comparison.

2.4.3 Influence of Solution Concentration Cd
The adsorption processes were performed by stirring 20 mg of the calixarene polymer with 30 mL of metal cation sample solution having the concentration of 2, 4, 8, 16 and 20 mg/L at room temperature and the optimum conditions achieved before. Then, the adsorbed metal ion was measured based on the concentration of metal cation before and after the adsorption using AAS. Equal treatment performed on chitosan as a comparison.

3. Results and Discussion

3.1 Determination of Optimum pH
The degree of acidity (pH) solution is one important factor in determining the course of the adsorption process, as the pH can cause changes in the charge on the surface of the adsorbent and speciation of metal ions in solution. In the process of adsorption of metal ions, the acidity of the solution effect on two things. The first presence of protons in acidic conditions to the active site of the molecule will be protonated complexing. Both under alkaline conditions will be formed hydroxide and some metal ions will experience precipitation [14].
Effect of pH on the adsorption capacity of chitosan and chitosan-p-t-buthylcalix[4]arene on Cd\textsuperscript{2+} ion and the adsorption capacity of chitosan as a comparison is presented in Figure 1. Adsorption by chitosan-p-t-buthylcalix[4]arene in Figure 1, showed an increase in the number of Cd\textsuperscript{2+} concentration adsorbed of pH 2 to pH 4. The Concentration of Cd\textsuperscript{2+} adsorbed was relatively small at pH 2. Because at low pH, adsorption process can not be maximized \cite{15}. At low pH, there is a high concentration of H\textsuperscript{+}, so the competition between H\textsuperscript{+} with Cd\textsuperscript{2+}. Competition between H\textsuperscript{+} with Cd\textsuperscript{2+} lead the interaction between Cd\textsuperscript{2+} with a hydroxyl group (OH) on chitosan p-t-buthylcalix[4]arene was reduced because of OH tend to interact with the H\textsuperscript{+}, consequently Cd\textsuperscript{2+} concentration was absorbed become small. The Concentration of Cd\textsuperscript{2+} was absorbed at pH 6 decreased again as adsorbent experiencing saturation point, consequently not capable of binding metal ions adsorbent. Adsorption of Cd\textsuperscript{2+} using chitosan-p-t-buthylcalix[4]arene reaches optimum at pH 8 with the adsorption capacity of 21.764 \times 10\textsuperscript{-3} mmol/g.

![Figure 1](image.png)

**Figure 1.** The concentration of Cd\textsuperscript{2+} adsorbed on the pH variation using chitosan and chitosan-p-t-buthylcalix[4]arene adsorbent

### 3.2 Effect of Contact Time and Parameter Kinetics

Adsorption kinetics are determined based on the adsorption contact time. Adsorption kinetics described the rate of binding of dissolved substances on contact time change of a reaction. The results of the determination of adsorption contact time were presented in Figure 2. The contact time optimum adsorption of Cd\textsuperscript{2+} on the minutes to 240 with a concentration of Cd\textsuperscript{2+} adsorbed was 32.895 \times 10\textsuperscript{-3} mmol/g for Chitosan and 20.592 \times 10\textsuperscript{-3} mmol/g for Chitosan-p-t-buthylcalix[4]arene. Adsorption kinetics was tested using two models of the adsorption kinetics pseudo first order (Lagrgren) and pseudo second order (Ho), the results are presented in Table 1. Based on Table 1, using two adsorbents Cd adsorption kinetics followed the pseudo second order (Ho) with the adsorption rate constant of 1.037 \times 10\textsuperscript{-2} g mg\textsuperscript{-1} min\textsuperscript{-1} for chitosan and 1.777 \times 10\textsuperscript{-2} g mg\textsuperscript{-1} min\textsuperscript{-1} for chitosan-p-t-buthylcalix[4]arene.
Figure 2. Adsorption of Cd\textsuperscript{2+} on variations of contact time

Table 1. Parameters of kinetics Adsorption of Cd\textsuperscript{2+}

| Kinetic Model          | Adsorbent                  | Parameter of Adsorption |
|------------------------|----------------------------|--------------------------|
| *Pseudo* Order 1       | Chitosan                   | 0.927                    |
| (Lagergren)            |                            | 3x10\textsuperscript{-3} minute\textsuperscript{-1} |
| Log (qe-qt)=log qe-Kt  | Chitosan-calix[4]arene     | 0.948                    |
|                        |                            | 10x10\textsuperscript{-3} minute\textsuperscript{-1} |
| *Pseudo* Order 2 (Ho)  | Chitosan                   | 0.997                    |
|                        |                            | 1.037x10\textsuperscript{-2} g mg\textsuperscript{-1} minute\textsuperscript{-1} |
| \(\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{1}{q_e} t\) | Chitosan-calix[4]arene     | 0.999                    |
|                        |                            | 1.777x10\textsuperscript{-2} g mg\textsuperscript{-1} minute\textsuperscript{-1} |

3.3 Effect of Initial Concentration Dyes and Parameter Isotherm

Adsorption isotherms determined by the results of adsorption on the variation of the initial concentration of Cd\textsuperscript{2+}. Results of the adsorption by variation of the initial concentration of Cd\textsuperscript{2+} was presented in Figure 3.

Figure 3. Initial concentration of Dyes variation Remazol Yellow FG on the initial concentration of dye
The results of adsorption on the variation of the initial concentration of Cd showed that the greater the initial concentration, the greater the concentration of Cd adsorbed. The study of the adsorption isotherm shown in Table 2.

| Adsorbent                             | Parameter of Isotherm Adsorption | Parameter of Isotherm Adsorption |
|---------------------------------------|----------------------------------|----------------------------------|
|                                       | Langmuir                         | Freundlich                       |
|                                       | Xm (mol/g)                       | K x 10^3 (L/mol)                 | ∆G (kJ/mol) | R^2 | n | K(mol/g) | R^2 |
| Chitosan                              | 3.019 x 10^{-5}                 | 16560                            | 41.459      | 0.999 | 8.695 | 1.059 x 10^{-4} | 0.822 |
| Chitosan- p-t-buthylcalix[4]arene     | 2.167 x 10^{-5}                 | 96.519                           | 28.627      | 0.981 | 2.053 | 25.349 x 10^{-4} | 0.995 |

According to the Table 2 chitosan tend to follow the Langmuir isotherm, while chitosan-Calix tend to follow the isotherm Freudelich. Cd adsorption using chitosan occurred monolayer, while using chitosan-p-t-calix[4]arene occurred multilayer, the adsorption capacity of each 3.019 x 10^{-5} and 2.167 x 10^{-5} mol/g. Adsorption energy of chitosan and chitosan-Calix was 41.459 kJ/mol and 28.627 kJ/mol. Modified chitosan adsorption capacity was smaller than chitosan, because due to steric factors of the adsorbent.

3.4 Adsorbent characterization With FTIR

Results of FTIR spectra of chitosan p-t-buthylcalix[4]arene before and after adsorption can be seen in Figure 4. Figure 4 shows a new peak at wave number 3152.78 cm^{-1} indicating the typical absorption group N-H stretching and weak-sharp absorption at wave number 1565.30 cm^{-1} which were the characteristic absorption of group N-H bending [16]. Thus occurred the Cd^{2+} Interaction with the group N-H [17]. In addition, there was a wide peak at 3383.29 cm^{-1} and 1600.39 cm^{-1}. These peaks are the absorption of the hydroxy group and physically adsorbed water [18], so there was interaction Cd^{2+} with an O-H group.

![Figure 4. Spectra of FTIR chitosan p-t-buthylcalix[4]arene (a) before, (b) after adsorption](image-url)
3.5 Adsorbent characterization by SEM – EDX

Morphology adsorbent chitosan p-t-buthylcalix[4]arene before and after adsorption was characterized using Scanning Electron Microscopy (SEM) as shown in Figure 5.

![Figure 5](image)

**Figure 5.** Morphology adsorbent chitosan p-t- buthylcalix[4]arene (a) before, (b) after adsorption

Morphology adsorbent chitosan p-t-buthylcalix[4]arene before adsorption (Figure 5 (a)) showed the surface of the porous, so it was possible Cd can be adsorbed meet pores of the adsorbent. Morphology adsorbent chitosan p-t-buthylcalix[4]arene after the adsorption process (Figure 5b) surfaces look more meetings indicating that it happened adsorption adsorbate. Metals adsorbed in the adsorbent Chitosan p-t-butilkaliks [4] arena supported by the data of EDX. The composition of the adsorbent based on the EDX analysis as shown in Table 3.

| composition | p-t-butilkaliks [4] arena | Before adsorption (%) mass | After adsorption (%) mass |
|-------------|---------------------------|---------------------------|---------------------------|
| Atom C      |                           | 53.95                     | 61.57                     |
| Atom N      |                           | 18.37                     | 08.59                     |
| Atom O      |                           | 7.55                      | 28.50                     |
| Atom Cl     |                           | 20.13                     | 00.67                     |
| Atom Cd     |                           |                           | 00.67                     |

Adsorption of Cd by the adsorbent was shown from the results of EDX analysis identified the existence of Cd, which did not exist prior to the adsorption process.

4. Conclusion

Ion of Cd adsorption using chitosan-Calix had a maximum capacity and adsorption energy of 21.67 mol/g and 28 627 KJ/mol, adsorption kinetics study followed the pseudo second-order kinetics (Ho) with adsorption rate constants for 1.777x10⁻² g mg⁻¹ min⁻¹.

References

[1] Bhuvana 2006 Studies on Frictional Behavior of chitosan-Coated Fabries, *Aux. Res. J.*, Vol 6(4): 123-130.

[2] Darjito, Purwonugroho D and Nisa SN 2006 Study on Adsorption of Cd(II) by Chitosan-Alumina. *Indo. J. Chem.*, 6 (3), hal.: 238-244.

[3] Mahajan SP 2002 Pollution Control in Process Industries, Tata McGraw-Hill Pub. Co. Ltd., New Delhi.
[4] Wu FC, Tseng RL, and Juang RS 2010 A review and experimental verification of using chitosan and its derivatives as adsorbents for selected heavy metals, Journal of Environmental Management, Elsevier, Vol. 91, Issue 4, Pages 798–806

[5] Airoldi C and Oryton AC 2000 Chitosan–organosilane hybrids—Syntheses, characterization, copper adsorption, and enzyme immobilization, Journal of Polymer Applied Science, volume 77, Issue 4, hal 797-804

[6] Ngah WSW, Endud CS, and Mayanar R 2002 Removal of copper(II) ions from aqueous solution onto chitosan and cross-linked chitosan beads, Reactive and Functional Polymers, Elsevier, Vol. 50, Issue 2, 181-190

[7] Ngah WSW, Teong LC, and Hanafiah M 2011 Adsorption of dyes and heavy metal ions by chitosan composites: A review, Carbohydrate Polymers, Elsevier, Vol.3, Issue 4, Pages 1446–1456

[8] Tabakci M, and Mustafa Y 2008 Synthesis of a Chitosan-linked Calix[4]arene chelating Polymer and Its Adsorption ability toward Heavy Metals and dichromate anions, Bioresour. Technol., 99: 6642-6645.

[9] Restuti A 2012 Sintesis dan Karakterisasi p-t-Butilikaliks[4]arena yang diikatkan pada kitosan, Skripsi, Surakarta : FMIPA Universitas Sebelas Maret.

[10] Gutsche CD 1998 Calixarene Revisited, Monograph in Supramolecular Chemistry, Royal Society of Chemistry, Cambridge.

[11] Maming 2008 Transpor Cr(III), Cd(II), Pb(II) dan Ag(I) melalui Membrane Cair Ruah mengandung Turunan Karboksilat, Ester, dan Amida p-t-butilkaliks[4]arena sebagai Pengemban Ion, Disertasi, PPS-UGM, Yogyakarta.

[12] Maming, Jumina, Siswanta D and Sastrohamidjojo H 2007 Transport of Cr3+, Cd2+, Pb2+, and Ag+, Ions Through Bulk Liquid Membrane Containing p-tert-Butylcalix[4]Arene-Tetracarboxilic Acid as Ion Carrier, Indo. J. Chem, 7(1), 172-179.

[13] Handayani D S, Kusumaningsih T and Restuti A 2014 Modification and Characterization a New Polymer Chitosan-p-t-b-calix[4]arenes, Prosiding ICOPIA part of series: Advance in Physic Research Atlantis Press 21-25

[14] Mollah. MYA, Schennach R, and Parga JR 2001 Electrocoagulation (EC)-science and applications, Journal of hazardous, Elsevier, Vol. 84, Issue 1, Pages 29–41

[15] Buhani, Narsito, Nuryono and Kunarti ES 2010 Chemical Stability of Cd(II) and Cu(II) Ionic Imprinted Amino-Silica Hybrid Material in Solution Media, Eksakta, 13 (1-2), hal.: 1-10.

[16] Sastrohamidjojo H 1991 Spektroskopi, Liberty Yogyakarta, Yogyakarta.

[17] Amri A, Supranto, and Fahrurozi M 2004 Kesetimbangan Adsorpsi Optional Campuran Biner Cd (II) dan Cr (III) dengan Zeolit Alam Terimpregnasi 2-merkaptobenzotiazol, Jurnal Natur Indonesia, 6 (2), hal.: 111-117.

[18] Taba P, Natsir H, Fauziah, and Ismail M 2010 Adsorpsi Ion Cd (II) oleh Kitosan-Silika Mesopori MCM-48, Marina Chimica Acta,11(1), hal.: 13-22.

Acknowledgment
The financial support from Indonesian Directorate General of Higher Education through the research project of Penelitian Unggulan Perguruan Tinggi (PUPT) 2015 is greatly appreciated.