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# Adsorption study of Pb(II) onto a novel calix[4]resorcinarene-chitosan hybrid

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**ABSTRACT**

Adsorption of Pb(II) ions by a novel calix[4]resorcinarene-chitosan hybrid (CCH) compared with tetrakis-chloromethyl-C-4-allyoxy-3-methoxyphenylcalix[4]resorcinarene (CAMR) and chitosan adsorbent using the batch method has been carried out under variations of pHs, contact times, and Pb(II) ion concentrations. The optimum conditions of the adsorption of Pb(II) ions occurred at pH of 5 for CCH and CAMR adsorbent with the contact time for 2 h and at pH of 2 for chitosan adsorbent. The results show that the adsorption process of Pb(II) ions by the CCH, CAMR, and chitosan adsorbents is pseudo-second-order kinetic model with the rate constant ($k$) of $6.86 \times 10^{-2}$ g/mg min for CCH. In addition, the adsorption model of Pb(II) ions by CCH tends to follow Freundlich adsorption isotherm model, while CAMR and chitosan adsorbent tends to follow Langmuir adsorption isotherm model. Adsorption capacity ($X_m$) of CCH to Pb(II) ion is the largest than CAMR and chitosan. Thus, the CCH is the potential alternative adsorbent to absorb of Pb(II) ions.

*Keywords:* Calix[4]resorcinarene-chitosan hybrid; Adsorption; Pb(II) ion

## 1. Introduction

Industrial growth besides having a positive impact also has a negative impact, especially industries that produce waste containing heavy metals such as Pb. Compounds of Pb are mostly found in the form of Pb(II) and some Pb(IV). Considering that the negative impact caused by waste containing Pb metal is quite large, the treatment of industrial waste before being discharged into the environment becomes very important. One method that has been used in the waste treatment process containing Pb metal is adsorption. This method is quite effective, and it was performed for metal ion adsorption with various adsorbents [1–6]. In addition, there were several natural material products that have been used as adsorbents including agricultural waste such as tea waste [7], rice husks and ash [8], zeolites [9], and activated charcoal [10]. Previous researchers [11] argued that it was difficult to determine the active compound and the active side of natural adsorbents due to its complex content. Therefore, alternative adsorbents are needed, especially from cheap synthesis processes.

One of the synthesized compounds that have been used as the alternative adsorbents for heavy metal ions is calixarene compounds. One of the derivatives of this compound which has been widely studied as an adsorbent is calix[4]resorcinarene [11–15]. This compound consists of four units of resorcinol in cyclic form connected by a methylene bridge (Fig. 1). Calix[4]resorcinarene was synthesized through a reaction between resorcinol and compounds containing aldehyde groups in an acidic atmosphere [16].

Modification of functional groups of calixarenes allows it to be utilized in a variety of purposes, including: adsorbent of heavy metals [17,18], inhibitor of calcium carbonate [19,20] and calcium sulfate [21] scale formation, sunscreen

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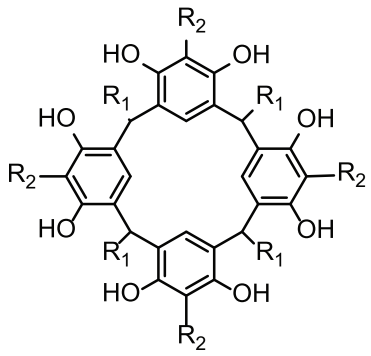


Fig. 1. Structure of calix[4]resorcinarene.

[22], drug delivery [23], and dye fibers [24]. However, the use of calix[4]resorcinarene on an industrial scale was not economical so that the application was limited. One effort to resolve these problem was to hybridize calix[4]resorcinarene with other compounds that are relatively cheap. One of the compounds as raw material of hybrid production that are relatively cheap and abundant in Indonesia is chitosan. The calix[4]resorcinarene-chitosan hybrid (CCH) compound has been synthesized and reported by previous researchers [25]. In this study, the utilization of these compounds will be reported which are new alternative compounds as adsorbent of Pb(II) ions.

## 2. Experimental procedure

### *2.1. Materials and instrumentations*

Reagents used in this work consisted of CCH resulted from synthesis in laboratory based on procedure published by previous research [25], the metal salt of $Pb(NO_3)_2$ (Merck, Germany), NaOH (Merck), HCl (Merck), and deionized water. The CCH was synthesized from reaction of tetrakis-chloromethyl-C-4-allyoxy-3-methoxyphenylcalix[4]resorcinarene (CAMR) and chitosan.

Equipment used in this research were laboratory glassware, hot plate with magnetic stirrer, atomic absorption spectroscopy (AAS) (PerkinElmer 3110, USA), and pH meter (200A Orion, USA).

### *2.2. Procedure*

Adsorption of Pb(II) ion by CCH was performed by batch method because this method was a simple method, cheap, easy to do, and the results can be accounted for. Adsorption was carried out through three state variations, that is, pH, contact time and concentration of adsorbate. Furthermore, adsorption of Pb(II) ions by CCH was compared with the adsorption of Pb(II) ions by CAMR and chitosan.

#### *2.2.1. Effect of pH*

A number of 0.01 g of CCH (250 mesh) was added to 10 mL of 10 ppm Pb(II) solution. Variations of pH were performed at 1, 2, 3, 4, 5, and 6. The pH adjustment was performed by adding HCl (0.1 M) and NaOH (0.1 M). The mixture was stirred with magnetic stirrer for 3 h, and then it was filtered with filter paper. Concentration of Pb(II) ion in the filtrate was determined by AAS. The experiment without addition of CCH (blank) was carried out under the same conditions. Amount of adsorbed Pb(II) ion was obtained from different metal concentrations before and after CCH addition. The optimum pH was obtained from the highest value of the ratio between the amount of adsorbed metal ions (mmol) and the adsorbent mass (g) and used for further variation.

#### *2.2.2. Effect of contact time*

A total of 0.01 g of CCH (250 mesh) was added to 10 mL of 10 ppm Pb(II) solution at optimum pH. The mixture was stirred with contact time variation of 5, 30, 60, 120, 180, and 300 min, and then it was filtered with filter paper. Concentration of Pb(II) ion in the filtrate was determined by AAS. The experiment without addition of CCH (blank) was carried out under the same conditions. Amount of adsorbed Pb(II) ion was obtained from different metal concentrations before and after CCH addition. The optimum contact time was obtained from the highest value of the ratio between the amount of adsorbed metal ions (mmol) and the adsorbent mass (g) and used for further variation.

#### *2.2.3. Effect of concentration of adsorbate*

Determination of adsorbate concentration effect was carried out at optimum condition and room temperature. The method used was the same as the determination of pH and optimum time. Concentrations of Pb(II) solution used were 5, 10, 15, 20, 30, and 50 ppm. Data obtained were applied to determine adsorption capacity, equilibrium constant, and reaction order. A similar experiment was performed on CAMR and chitosan adsorbent to compare its absorbability.

## 3. Results and discussion

### *3.1. Effect of pH on the adsorption of Pb(II) ion by CCH, CAMR, and chitosan*

Assay results of pH effect on the adsorption of Pb(II) ion by CCH, CAMR, and chitosan are shown in Fig. 2. According to Fig. 2, amount of Pb(II) ion adsorbed was affected by pH. The optimum pH at adsorption of Pb (II) ion by the three adsorbents was obtained at the medium acid level. In the CCH and CAMR, the optimum pH was obtained at pH 5, and the amount of Pb(II) ion adsorbed on this condition was 0.0365 and 0.0179 mmol/g, respectively. While on the chitosan, the amount of Pb(II) ion which is the most adsorbed was at pH 2 with the amount of Pb(II) ion adsorbed of 0.0319 mmol/g. However, it was not selected as the optimum pH because at this pH a slight change in the pH value will have a significant effect on the amount of adsorbed Pb(II) ion. The optimum pH of Pb(II) ion adsorption by chitosan was selected at pH 4. The amount of Pb (II) ion adsorbed at the pH was 0.0241 mmol/g.

### *3.2. Optimum contact time*

The determination of the optimum contact time was performed to study the kinetics of the adsorption reaction, so that information will be obtained about the time required by the adsorbate to achieve equilibrium. When equilibrium has been achieved, the adsorption rate will be proportional to the adsorbate release rate so that in this condition the amount of adsorbate adsorbed is relatively constant. Effect of contact time on the adsorption of Pb(II) ions by CCH, constituents calixarene, and chitosan are shown in Fig. 3.

According to Fig. 3, it can be observed that the amount of Pb(II) ion adsorbed increases with the increased contact time for all the adsorbents, and after 180 min of contact time the amount of Pb(II) ion adsorbed was relatively constant. This condition was called a state of equilibrium. In the equilibrium state, the adsorption rate by adsorbent was equal to desorption rate. The optimum contact time was obtained based on the time required by adsorbents to adsorb the maximum Pb(II) ion. In this test, the optimum contact time of adsorption by CCH and constituent calixarene were faster than chitosan at around of 120 min. Whereas optimum contact time of chitosan was 180 min. This was due to the suitability of the properties between the CCH and constituent calixarene with Pb(II) ion. Based on theory of HSAB that a hard acid would bind strong with a hard base. Otherwise a soft acid would bind strong with a soft base. Ion Pb(II) is an intermediate acid. It is compatible with the O–H groups attached to the aromatic ring of CCH and constituent calixarene which are classified as a medium base. Thus, process of achieving equilibrium between Pb(II) ions with CCH and constituent calixarene was faster than chitosan. The CCH and constituent calixarene were more effective to use as adsorbent Pb(II) ion than the chitosan when it was viewed from optimum contact time.

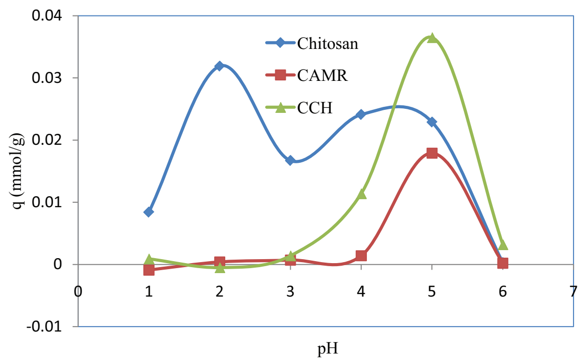


Fig. 2. Effect of pH on the adsorption of Pb (II) ion by CCH, CAMR, and chitosan (contact time of 3 h, volume of solution of 10 mL, and mass of adsorbent of 0.01 g).

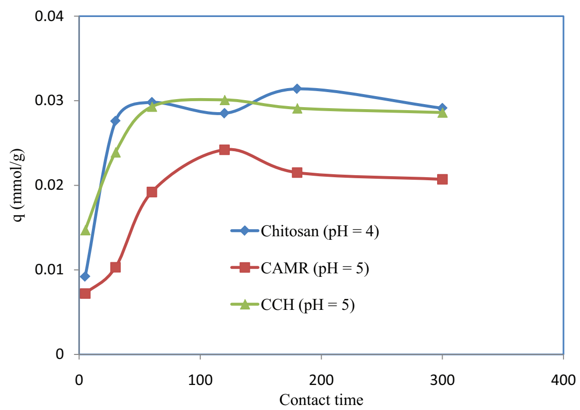


Fig. 3. Effect of contact time on adsorption of Pb (II) ion by calix[4]resorcinarene-chitosan hybrid, constituents calixarene and chitosan (volume of solution is 10 mL and mass of adsorbent is 0.01 g).

### 3.3. Adsorption kinetics

In this research, two kinetic models were often used to determine the kinetics of an adsorption process. They were namely Lagergren kinetics which was often called the pseudo-first-order kinetics and Ho's kinetics which was often called pseudo-second-order kinetic. The adsorption kinetics obtained for the three adsorbents on Pb(II) ion was determined by the value of correlation coefficient ($R^2$) of the equation of each model. Lagergren's adsorption kinetics equation was formulated as Eq. (1). While the Ho's adsorption kinetics was formulated as Eq. (2). The $q_e$ was mass of Pb(II) ion adsorbed at equilibrium. The $q_t$ was mass of Pb(II) ion adsorbed at $t$ time. The $k$ was adsorption rate constant, and $t$ was adsorbent contact time with adsorbate. In the pseudo-second-order equation, $\frac{t}{q_t}$ was plotted as the y-axis, $t$ was plotted as the x-axis, and $\frac{1}{q_e}$ was slope. The $R^2$ of each model for the three adsorbents were shown in Table 1.

$$\ln (q_e - q_t) = \ln q_e - kt \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \tag{2}$$

Based on Table 1, the $R^2$ of the three adsorbents approaches 1. So, the three adsorbents follow the second-order-pseudo kinetics model. The adsorption reaction rates of Pb(II) ions by the three adsorbents are influenced by the concentration of Pb(II) ions and number of active groups in each adsorbent.

Table 1
Correlation coefficient ($R^2$) of Pb(II) ion adsorption on Lagergren and Ho kinetics models

| Kinetics parameters | | Adsorbents | | |
|---|---|---|---|---|
| Lagergren | $R^2$ | Chitosan | CAMR | CCH |
| (pseudo-first-order) | | 0.2377 | 0.6457 | 0.3633 |
| Ho | $R^2$ | 0.9958 | 0.9814 | 0.9987 |
| (pseudo-second-order) | $k$ (g/mg min) | 0.0392 | 0.0171 | 0.0686 |

The adsorption rate constant ($k$) of each adsorbent was calculated through the equation of the pseudo-second-order linear line. The calculation of the adsorption rate constant was important because it was used to determine the contact rate between adsorbate and adsorbent. The calculation result of the adsorption rate constant showed that CCH has a greater adsorption rate constant than the constituent calixarene and chitosan as presented in Table 1. This shows that the rate of adsorption of Pb(II) ion by CCH was the greatest. This was due to the presence of active groups in the form of an intermediate base of the constituent calixarene of O–H bound to the aromatic ring and additional number of active groups of chitosan.

### *3.4. Effect of Pb(II) ion concentration and adsorption isotherm*

The effect test of Pb(II) ion concentration was performed at optimum pH and contact time that has been obtained through a previous test. This was performed to determine the isotherm model followed by the three adsorbents. Based on the isotherm model followed would be determined the maximum adsorption capacity ($X_m$), adsorption energy ($E_{ads}$), and equilibrium constant ($K$). There are two models of adsorption isotherms used in this study, namely Langmuir and Freundlich adsorption isotherms. On the Langmuir adsorption isotherm, the adsorption process takes place gradually to meet the surface. Subsequently formed a single layer (monolayer) caused by the interaction between adsorbate with the active sites between adsorbate with adsorbent. When all the active sites were already binding then, the adsorption does not happen again. Because the adsorbent surface was considered saturated. In Freundlich adsorption isotherm, the adsorption process was multilayer so that an unlimited amount of the adsorbent will be able to absorb unlimited amount of the adsorbate as well. The conclusion result of the adsorption isotherm model followed in this study was determined based on the correlation coefficient ($R^2$) which was closest to one of the two isotherm models used. The correlation coefficient ($R^2$) data of the three adsorbents using the two adsorption isotherm models is presented in Table 2.

Based on Table 2, the CCH follows the Freundlich adsorption isotherm model. While the CAMR and chitosan follow Langmuir adsorption isotherm model. The test results of effect of Pb(II) ion concentration on the amount of Pb(II) adsorbed by the three adsorbents are shown in Fig. 4.

Based on Fig. 4, it can be seen that the higher the concentration of Pb (II) ions, the higher the amount of Pb(II) ions adsorbed and at a certain concentration the amount of adsorbed ions becomes relatively constant. This occurs because all the active sites present on the surface of the adsorbent have been completely bonded with Pb(II) ion. This phenomenon can be seen in the adsorbent of calixarene and chitosan. While on the CCH adsorbent in the variation of Pb(II) ion concentration from 5 to 50 ppm looks no saturation on the active sites. It can be seen in the variation of concentration that the amount of adsorbed Pb(II) ions continues to increase. This happens because the active sites of the CCH adsorbent have not been fully bonded with Pb(II) ions. This is a positive thing because the purpose of this material synthesis is to produce adsorbents with high adsorption capacity.

Based on the adsorption isotherm followed, the maximum adsorption capacity ($X_m$), the adsorption equilibrium constant ($K$), and the adsorption energy ($E_{ads}$) were determined as shown in Table 3. Although the CCH in the variation concentrations of Pb(II) ion from 5 to 50 ppm follow the Freundlich adsorption isotherm model, the value of the quantities was still calculated using the Langmuir isotherm equation to compare with the other adsorbents.

Based on data shown in Table 3, the adsorption occurring between the Pb(II) ions and three adsorbents is classified as chemical adsorption. This is indicated from the value of adsorption energy ($E_{ads}$) three adsorbents have exceeded 20.92 kJ/mol [26]. The highest equilibrium constant value is owned by chitosan, which was $1.16 \times 10^5$ L/mol. The value of the high equilibrium constant signifies that the reaction tends to shift toward the formation of the product, that is, the adsorbate complex with the adsorbent. The adsorption capacity ($X_m$) of CCH was higher than constituent calixarene and chitosan, that is, 17.99 mg/g. The higher the adsorption

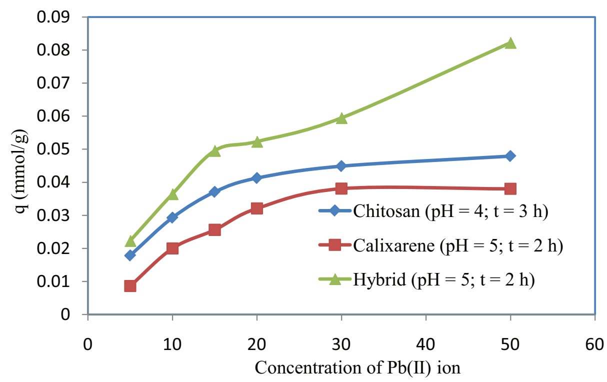


Fig. 4. The effect of Pb(II) ion concentration on the amount of Pb(II) ions adsorbed by calix[4]resorcinarene-chitosan hybrid, constituent calixarene and chitosan (volume of solution is 10 mL and mass of adsorbent is 0.01 g).

Table 2
Correlation coefficient ($R^2$) Langmuir and Freundlich adsorption isotherm model of Pb(II) ion adsorption

| Adsorbents | Correlation coefficient ($R^2$) adsorption isotherm models | |
|---|---|---|
| | Langmuir | Freundlich |
| Chitosan | 0.9959 | 0.9817 |
| CAMR | 0.9526 | 0.8444 |
| CCH | 0.9624 | 0.9661 |

Table 3
The values of $X_m$, $K$, and $E_{ads}$ on Pb(II) ion adsorption by CCH, CAMR, and chitosan

| Adsorbents | Linear regression equation | $X_m$ (mg/g) | $K$ (L/mol) | $E_{ads}$ (kJ/mol) |
|---|---|---|---|---|
| Chitosan | $y = 20.09x + 0.17$ | 10.31 | $1.16 \times 10^5$ | 29.10 |
| CAMR | $y = 20.43x + 0.80$ | 10.14 | $2.56 \times 10^4$ | 25.32 |
| CCH | $y = 11.50x + 0.17$ | 17.99 | $6.87 \times 10^4$ | 27.78 |

Table 4
Adsorption capacity ($X_m$) of Pb(II) adsorbents from derived calixarene

| Adsorbents | Adsorption capacity ($X_m$) (mg/g) |
|---|---|
| Calix[4]resorcinarene-chitosan hybrid (CCH) (this research) | 17.99 |
| Tetrakis-tiomethyl-C-4-methoxyphenilcalix[4]resorcinarene | 40.33 [20] |
| C-4-hidroxy-3-methoxyphenylcalix[4]resorcinarenedodecaacetate | 0.39 [22] |
| C-4-Methoxyphenylcalix[4]resorcinarene | 4.17 [23] |
| Polypropylcalix[4]arene | 16.31 [27] |

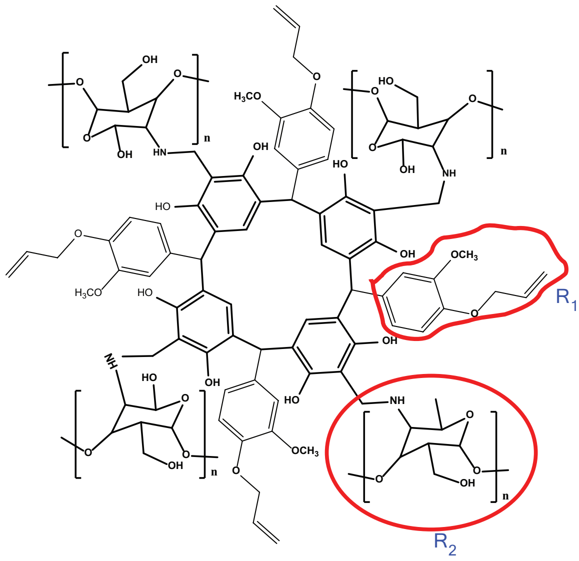


Fig. 5. Structure of calix[4]resorcinarene-chitosan hybrid (CCH).

capacity of the adsorbent the more potential the adsorbent was applied in the waste treatment process. The adsorption capacity ($X_m$) of other Pb(II) ions adsorbents from derived calixarenes is displayed in Table 4.

Adsorption between CCH adsorbent and Pb(II) ions is chemical adsorption. The structure of CCH adsorbent can be seen in Fig. 5. In chemical adsorption, the interactions between metal ions and adsorbents can occur as electrostatic interactions, hydrogen bonding, and coordinate bonds. The CCH adsorbents (Fig. 5) have nucleophile groups such as –OH groups attached to aromatic rings as well as chitosan, amine (–NH–), and ether (–OR) groups. The nucleophile groups will interact with the Pb(II) ions through the ion-dipole force.

## 4. Conclusions

CCH can be used as the potential adsorbent of Pb(II) ions. The adsorption ability of CCH to Pb(II) ions is due to the nucleophile groups such as –OH groups attached to aromatic rings as well as chitosan, amine (–NH–), and ether (–OR) groups which can interact with Pb(II) ions through ion-dipole interactions. The optimum adsorption of Pb(II) ion by the CCH is at the pH of 5 and the contact time for 2 h. The adsorption kinetics model of this adsorbent tends to follow pseudo-second-order kinetics model with the adsorption rate constant ($k$), that is, $6.86 \times 10^{-2}$ g/mg min. The CCH adsorption capacity ($X_m$) of Pb(II) ions is 17.19 mg/g.

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