**KINETIC AND ISOTHERM STUDIES ON ADSORPTION OF Pb(II) CATIONS USING OF TB-CALIX[4]ARENE AND TB-CALIX[4]AREN DERIVATIVES**

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**ABSTRACT**

The aim research of 5,11,17,23-tetra-(t-butyl)-25-monohydroxy-26,27,28-tribenzoyloxycalix[4]arene (TBMTCA) and 5,11,17,23-tetra-(t-butyl)-25,26,27,28-tetrahydroxycalix[4]arene (TBCA) as an adsorbent of Pb2+ cations has been conducted. The adsorption method used a batch system method with variations in pH, exposure time, and initial concentration of Pb2+ cations. In addition, the optimum contact time of Pb2+ cations adsorption was 180 minutes. The adsorption kinetics of Pb2+ cations using TBCA and TBMTCA followed pseudo-2nd order and pseudo-1nd order kinetics with adsorption rate constants of the adsorption method using a batch method with variations in pH, exposure time, and initial concentration of Pb2+ cations. The results showed that the optimum at pH = 4 for the Pb2+ cations, the optimum exposure time parameter for the Pb2+ cations adsorption was 30 minutes. The kinetic models for the Pb2+ cations to the adsorbent TBMTCA and TBCA follow the Lagergren kinetics pseudo-1nd order, and pseudo-2nd order with an adsorption constant rate of 9.21 x 10-3 minute-1 and 6,91 x 10-3 minute-1 respectively. The adsorption capacity of Pb2+ cations onto adsorbent TBCA and TBMTCA were the optimum adsorption capacity for the Pb2+ cations is 137.29 mg/g and 128.46 mg/g, with adsorption energy of 6.51 kJ/mol and 5.81 kJ/mol respectively.

Keywords: TBCA, TBMTCA, adsorption capacity, adsorption energy

## **INTRODUCTION**

Water pollution is a consequence of the development of various industries and is still a big and unsolved problem and the cause of deteriorating public health, especially heavy metals pollutants that pollute several regions including Indonesia [1]. That lead statement is widely used in the paint, fuel, battery, and ammunition industries. The poisoning by lead is very influential on children and comes from the paint used on the walls of the house. If this metal is in the blood up to a scale of 6, it can cause reading disabilities [2]. The concentration of Pb metal in waters does not depend on the season but the depth of the waters. Lead ions present in water can enter the body of fish and other aquatic animals. Generally, the natural level of Pb in water is 0.03 g/mL in seawater and 0.3 g/mL in river water. In the human body, Pb metal cations react with SH groups in proteins, enzymes, blood, so that chemical reactions can be disrupted. In addition, Pb can replace the position of calcium in the bones. In animals and humans, lead can enter the body through food and drink consumed as well as through breathing and penetration of the skin. In the human body, lead can inhibit the activity of enzymes involved in the formation of hemoglobin which can cause anemia. Lead can be found in oxidation states of 0, 2+, and 4+. In aquatic environments, Pb2+ cations are more often found. Lead is found in the form of PbOH+, Pb(OH)2, Pb(OH)3, Pb2(OH)3+, Pb3(OH)42+, Pb4(OH)44+, Pb6(OH)84+ and Pb2+ [3]

Two heavy metals are often found as lead contaminants (Pb metal) in the form of Pb2+ cations concentrated due to human activities. Lead metals, in general, can be interference with physiological activities, cell metabolism in plants, animals, and humans by accelerating the formation of reactive oxygen species and by inhibiting the work of bivalent and other monovalent metals in the body. Special methods need to be carried out to reduce the heavy metals content specifically Pb2+ cations in wastewater before being released into the ecosystem [4]. Methods for removing Pb2+ cations from wastewater, several methods have been developed such as chemical deposition, ion exchange, adsorption. Low concentrations of Pb2+ cations pollutant can be separated using calix[4]arene-tetraacetate as adsorbents to remove contaminated pollutants using the droplet-based microreactor system methods [5]. The research group of organic compounds being the main focus in the development of adsorbent is tb-calix[4]arene derivatives, which can be used as heavy metal removal with good adsorption. With the modification of tb-calix[4]arene modification, it is not only limited to the addition of functional groups and has the ability to adsorption Pb2+ cations, calix[4]arene derivative materials such as: Netty Polymer [6]; Bisazocalix[4]arene [7]; Calix[4]resorcinarene derivative [8]; Pb2+ Imprinted Carboxyl Chitosan [9]; Polypropylcalix[6]arene [10]; Poly-tetra-p-allylcalix[4]arene [11]; Chitosan-calixresorcinarene [12]; Methoxyphenylcalix[4]-resocrcinarene [13]; Calixarene-grafted nanocomposites [14]; Polypyrrol-carbon composites [15]; Poliacrylamide [16]; TBCA [17-19] and [21]. Synthesized tribenzoyloxy-p-tert-butylcalix[4]arene through two reaction routes namely the synthesis of p-tert-butylcalix[4]arene (TBCA) using p-tert.butylphenol with formaldehyde in basic conditions (NaOH) and water smoke [21], and partial benzoylation of p-tert-butylcalix[4]arene using benzoyl chloride in a mole ratio of 1: 3.5 yields tribenzoyloxy-p-tert-butylcalix[4]arene (TBMTCA) [22-23]; adsorption Pb(II) using calix[4]resorcinarene derivative [8]; adsorption Pb(II) using Poly-calix[4]arene [24]. The advantage of this study is that is an adsorbent and has two types of active sites as ligands, namely the -COOPh (ester) and hydroxy groups, so that interaction can occur on the Pb2+ cations effectively

## **EXPERIMENTAL SECTION**

### **Materials and Instrumentation**

Synthesis tb-calix[4]arene (TBCA) according [18] and [21], tribenzoyloxy-tb-calix[4]arene (TBMTCA) according [22-23]; aquabides (Lab. Organic FMIPA-UNEJ), Pb2+ cations, acetone, Na2SO4 anhydrate, K2CO3, and used without purification. The instruments used in this study consist of laboratory glassware, heating and magnetic stirring analytical scales (Libror EB-30 Shimadzu), Buchii evaporators (R-124), melting point determinants (Electrothermal-9100), spectrophotometry infrared (FTIR, Shimadzu-8201PC), 1H-NMR spectrometry (Agilent Variant NMR 400 MHz Proton Magnetic Spectrometry, atomic absorption spectrophotometry (SSA), Buck Scientific, Pb-AA-283.2-Lib3 lamps, pH Meter (Janway 3505 pH Meter)

## **Procedure**

### **Synthesis of 5,11,17,23-tetra-(t-butyl)-25,26,27,28-tetrahydroxy-calix[4]arene (TBCA)**

Synthesis of TBCA: 5,11,17,23-tetra-(t-butyl)-25,26,27,28-tetrahydrpxy-calix[4]arene (TBCA), was synthesized according [18] and [21] crude products are being crystallized with CHCl3-MeOH, dried to give white crystal powder in 46.07%; mp 340-343 °C.FTIR (KBr) 3410 cm-1 (OH); 3055 cm-1 (C-H); 1620 and 1481 cm-1 (Ar); 2955 and 2870 cm-1 (C-H); 1481 cm-1 (CH2); 1366 cm-1 (CH3); 1204 cm-1 and characterized 1H-NMR (400 MHz, DMSO) can be identified by peaks at δ 7,1757 ppm Ar-H; δ 4,3841 ppm Ar-CH2-Ar proton H axial; δ 3,5124 ppm Ar-CH2-Ar proton H equatorial; δ 10,3367 ppm Ar-OH and C(CH3)3 at δ 0,67; 3,09; 0,71 ppm

### **Synthesis of 5,11,17,23-tetra-(t-butyl)-26,27,28-tribenzoyloxycalix[4]arene (TBMTCA)**

Synthesis of TBMTCA: 5,11,17,23-tetra-(t-butyl)-25-monohydroxy-26,27,28-tribenzoyloxy-calix[4]arene (TBMTCA) was synthesized according [22-23], procedure. mixing 1,5 grams (2,32 mmol) of the TBCA in dry CHCl3 (30 mL), and pyridine (1.35 mmol), inserted benzoyl chloride (0.95 mL; 8 mmol) in dry CHCl3 (30 mL) it was slowly. The mixture is stirred at room temperature for 3 hours. The solvent on the mixture is then to be washed in vacuo and is rinsed with aquadest and extracted with diethyl ether. Crude products are being crystallized with CHCl3-MeOH, dried to give yellow-brown powder in 94,3%; mp 306-310°C.FTIR (KBr) 3232 cm-1 (-OH), 3054 cm-1 (Csp2-H), 1605 cm-1 (C=C aromatic), 1750 cm-1 (ester C=O), 2870 cm-1 dan 2955 cm-1(Csp3-H), 1458 cm-1(-CH2-) dan 1204 cm-1 (C-O enter), and characterized 1H-NMR (400 MHz, DMSO): Partial benzoylation can be identified by peaks at δ 7.0-8.2 ppm (m, 15H, PhC=O) and δ 10.3370 ppm (s, 1H, Ar-OH). The peaks of other protons identified include two doublets at δ 4,37-δ 4,35 and 3,51-3,48 ppm from the H axial and equatorial methylene bridge, the peak of the singlet at δ 1.25 ppm from the proton group C(CH3)3/ (t-butyl), and several aromatic proton peaks were identified in the region of δ 7.0-8.2 ppm (δ 7.04 ppm (m, 4H, phenyl, J 7-10 Hz), δ 7.17 ppm (s, 8H, Ar-H, J 7-10 Hz), δ 7.33 ppm (t, 2H, phenyl, J 7-10 Hz),), δ 7.47 ppm (t, 4H, phenyl, J 7-10 Hz), δ 7.60 ppm (t, 2H, phenyl, J 7-10 Hz), δ 8,10 ppm (d, 3H, phenyl, J 7-10 Hz)

### **Effect of pH of Pb2+ cation solution**

Prepared sample solutions of 10 mL each with a variation of pH 3; 4; 5; 6 and added to a 20 ml glass bottle and with 5 mg adsorbent. All are stirred with a magnetic stirrer for 180 minutes. Then filtered and filtrate analyzed with Atomic Absorption Spectrophotometry (SSA)

### **Effect of exposure time**

The solution containing Pb2+ cations and the solution were conditioned as much as 10 mL at pH=5. inserted into a 15 mL bottle containing 10 mg adsorbent. Then stir using a magnetic stirrer with a time variation of 10, 20, 30, 90, 180, 240 minutes. Then filtered and analyzed with SSA

### **Effect of initial Pb2+ cation concentration**

Several 10 mL Pb2+ cations were prepared at pH 5 with a variety of concentrations of 8, 16, 20, 24, and 30 ppm into a 15 mL glass bottle containing 10 mg of adsorbent. Then stirring using a magnetic stirrer according to the optimum exposure time. Then filtered and filtrate determined using SSA

###  **Adsorption kinetics**

The tb-calix[4]arene derivatives (TBMTCA) and tb-calix[4]arene (TBCA), (10 mg) was added into 10 mL of Pb2+ cation sample solution with concentration of 8 ppm (8 mg/L) for each. The adsorption kinetics was studied by conducting the adsorption experiments in various exposure time, which were 2,4,8,20,100, and 180 minutes Concentrations of Pb2+ cation before and after adsorption than filtered and filtrate were determined using by SSA.

### **Adsorption isotherm models**

The adsorption processes were performed by stirring 10 mg of the tb-calix[4]arene derivatives (TBMTCA) and tb-calix[4]arene (TBCA) with 10 mL of Pb2+ cations sample solution having a concentration of 4, 8, 12, 16, and 20 mg/L at room temperature and the optimum pH and exposure time**.** Then, the adsorbed metal ion was measured based on the concentration of Pb2+ cation before and after adsorption then filtered and filtrate determined using by SSA

## **RESULTS AND DISCUSSION**

### **Effect of pH**

At low pH values or acidic conditions, the solution contains large amounts of proton ions, resulting in protonation of the hydroxyl groups on TBCA, and TBMTCA adsorbent, and the carbonyl group on TBMTCA adsorbent as an active group to bind metal ions. Protonated TBCA and TBMTCA adsorbent species have low electron densities, thereby reducing the ability of TBCA, and TBMTCA adsorbent to bind Pb2+ cations and even result in a repulsion effect with Pb2+ cations so that the adsorption price becomes low, increasing the pH value to a certain point can increase the adsorption of metal ions because it reduces the inactivation of active groups by H+ ionic or protons. The effect of pH on the adsorption of Pb2+ cations to the adsorbent was carried out by varying the initial pH of the solution of Pb2+ cations in the pH range of 3 - 6. Other parameters such as concentration and time are made constant Pb2+ cations concentrations were analyzed using SSA.

The ability of adsorbents in adsorption Pb2+ cations are strongly influenced by the pH of the solution. In this case, the hydroxyl groups in the adsorbent is a weak Bronsted-Lowry acid with a pKa for the first deprotonation of 4.11 [25], however, it can also act as a Lewis base because it has free electrons that can be donated to a Lewis acid in other words, at pH<pKa the one hydroxyl groups in the adsorbent can be protonated to produce a positively charged adsorbent surface [8]. The Pb2+ cations adsorption process will decrease because both have a positive charge. Conversely, if pH > pKa, one or more hydroxyl groups can be deprotonated to produce a negatively charged adsorbent surface thereby increasing interaction with positively charged Pb2+ cations. At low pH or acidic atmosphere, the solution contains H+ ions in large quantities resulting in protonation of the hydroxyl groups on the adsorbent and the carbonyl groups on the adsorbent as the active group of Pb2+ cations binding [26 - 27]. This protonated adsorbent species has a low electron density thereby reducing the ability of the adsorbent to bind Pb2+ cations. The positive charge on the protonated hydroxyl and carbonyl groups in the adsorbent even results in a repulsion effect with Pb2+ cations so that the absorption price is low. Increasing the pH value to a certain point can increase the adsorption of Pb2+ cations because it reduces the inactivation of the active group by the H+ ions. However, at higher pH, most of the Pb2+ cations are hydrolyzed and coagulated due to the formation of various hydroxides (PbOH+ / Pb(OH)2/ Pb(OH)3- so that the adsorption is lower [2].

### **Effect of exposure time**

The study of the effect of exposure time on the adsorption of Pb2+ cations to the adsorbent is carried out by observing the time needed to reach the adsorption equilibrium point at the optimum pH until the equilibrium time is known (the adsorbent becomes saturated). The results of investigations on the effect of exposure time, then the adsorption of Pb2+ cations to the adsorbent are shown in Figure 1.

### **Effect of exposure time on the adsorption of Pb(II) cations onto TBCA and TBMTCA**

The effect of exposure time on the adsorption of Pb2+ cations on TBCA and TBMTCA was carried out by observing the time required to reach the adsorption equilibrium point. To do this, the exposure time between the ionic solution and the adsorbent was varied in the range of 0-240 minutes (known (the adsorbent became saturated). Based on observations, the optimum contact (0, 10, 20, 30, 90, 180, and 240 minutes) at the optimum pH until the equilibrium time for Pb2+ cations adsorption was 90 minutes on TBCA and TBMTCA (Figure 1)**.** As for TBCA and TBMTCA, the optimum time for Pb2+ cations absorption is 30 minutes with the number of Pb2+ cations adsorbed at 13.60 L/mol and 10.21 L/mol respectively.

**Figure** 1. Effect of exposure time Pb(II) cations adsorption on (a) TBCA, and (b) TBMTCA

From Figure 1, it can be observed that in the early minutes (t = 10-30 minutes) an increase in the number of ions adsorbed. This happens because the active groups (OH groups) on the surface of TBCA have not interacted with metal ions until the optimum time (t=30 minutes) where the active groups on the surface of TBCA have been saturated and the change in the number of metal cations adsorbed is no longer significant. also occurred in the absorbance of Pb2+ cations at TBMTCA with an optimum time of 90 minutes.

### **Adsorption kinetic models**

The adsorption kinetics of Pb2+ cations was studied based on the kinetic formulation proposed by Lagergren and Ho models. The kinetic approach used is to calculate the change in time required for the adsorption process. In Lagergren kinetic formulation [29], adsorption is seen as a pseudo-first-order reaction that follows the equation (1):

 equation (1)

where qe is the total mass of metal adsorbed (mg. g-1), qt is the mass of metal adsorbed at time t (mg/g), and k1 is the pseudo-1nd order Lagergren rate constant (minutes-1)

The adsorption kinetics can be determined as a pseudo-second-order reaction which is often known as the kinetic equation Ho in equation (2). In this Ho equation, Ho assumes that the adsorption kinetics is seen as following the second-order mechanism model which can be interpreted that the rate of adsorption kinetics (Figure 2) is the square of the adsorbate concentration. The pseudo-2nd order equation (2) Ho can be written as follows:

 equation (2)

 where k2 is a pseudo-second order rate constant (g.mg-1.min-1)



**Figure 2.** (a and b) Pseudo-1nd order kinetic for Pb2+ adsorption on the TBMTCA pseudo-2nd order kinetic for Pb2+ adsorption on the TBMTCA

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**Figure 3**.Structure of the (a). TBCA, (b). TBMTCA

### **Adsorption kinetics models**

The Lagergren kinetic model has a value of R2 almost to 1 then the Ho-McKay kinetic model so that the curve with the linearity of the Lagergren kinetics model is higher than the Ho-McKay [28 - 29], kinetics model with the Pb2+ cation. The adsorption rate constant for the Pb2+ cations can be determined through the Lagergren kinetic model as a sloping approach, a magnitude of 6.91x10-3 (minute-1) (Table 1). The results of an investigation into the effect of variations in the concentration of Pb2+ cations, versus the concentration of adsorbed metal cations are presented in Figure 4,seen at a low concentration from 8 ppm then the concentration of metal cations adsorbed is also small because of the number of Pb2+ cations. Then the number of metal cations that can be adsorbed will increase according to the increase in Pb2+ cations

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**Figure 4**. Effect of initial adsorbate concentrations Pb2+ cations on TBCA and TBMTCA

**Table 1**. Kinetic Parameters Adsorption Pb2+ cations into TBCA and TBMTCA.

|  |  |  |
| --- | --- | --- |
| Adsorbent | Kinetic Models\* | Pb2+ cations |
| R2 | k |
| TBCA | Lagergren | 0,836 | 6,91×10-3 min-1 |
| Ho-McKey | 0,957 | 143×10-3 g mg-1 min-1 |
| TBMTCA | Lagergren | 0,843 | 6,91×10-3 min-1 |
| Ho-McKey | 0,673 | 3×10-3 g mg-1 min-1 |

The bonding Pb2+-TBCA [17] and Pb2+-TBMTCA material is an adsorbent an excellent host for Pb2+ cations. In the adsorption of the Pb2+ cations onto 5,11,17,23-tetra(t.butyl)-25-monohydroxy-26,27,28-tribenzoyloxycalix[4]arene (TBMTCA) trending kinetics Lagergren models, with constant values adsorption rate k=6.91x 10-3 (min-1). The results of observations of the adsorption isotherm, that the adsorption for the Pb2+ cation tends to follow the Langmuir isotherm. The adsorption capacity of Pb2+ cations onto TBCA and TBMTCA was the optimum adsorption capacity for the Pb2+ cations is 137.29 mg/g and 128.46 mg/g, with adsorption energy of 6.51 kJ/mol and 5.81 kJ/mol, respectively. This is in the previous assumption which states that the interaction of Pb2+ cations with the TBMTCA or p-tert-butyl-tribenzoyloxycalix[4]arene and TBCA [17] or p-tert-butyl-tetra-hydroxycalix[4]arene compounds can be viewed as a chemical adsorption process. This is because TBMTCA compound has active sites in the form of hydroxyl groups (-OH) and ester groups (-COOPh) that can interact with Pb2+ cations, while TBCA compounds have activities in the form of hydroxyl a few compounds, which means that the adsorption process only occurs chemically. From Table 1. above it can be seen that the maximum adsorption capacity of Pb2+ uses the HSAB concept Pb2+ cations is an intermediate acid. In the HSAB concept, a soft acid will bind to a soft base, while a hard acid will bind to hard base. The active ester site on the adsorbent is the -COOPh group which is a hard base, so -COOPh will be more stable to bind to interaction with metal cations which are hard acid. While the Pb2+ cations is an intermediate acid and -COOPh in the TBMTCA compound is a hard base so it can be said that the bonding is less stable, while the -OH in the TBCA compound is a soft acid and Pb2+ cations is an intermediate base so it can be said that the bonding is more stable bonding to Pb2+ cations.

### **Kinetic adsorption of Pb(II) cations onto TBCA and TBMTCA**

Experimental data on the effect of contact time on Pb2+ cations adsorption on TBCA and TBMTCA were used and further analyzed to find the absorption kinetics model. The kinetic models that will be used are the Lagergren kinetic model (pseudo-1nd order) and the Ho-McKay kinetic model (pseudo-2nd order). To find a suitable model, the available data is processed and plotted into a straight-line equation of each kinetic model. The kinetic model with a correlation coefficient close to 1 is the most suitable model to be used in explaining the adsorption mechanism that occurs. In this study, the correlation coefficient (R2) is obtained from linear regression between log(qe-q) versus t (Lagergren kinetic model) and t/q versus t (Ho-McKay kinetic models) where qe (mmol.g-1) is the number of metal ions absorbed at the equilibrium point at time t and q (mmol.g-1) is the initial metal ion concentration. The adsorption rate constant is also calculated using the slope or intercept of the corresponding kinetic model equation (pseudo-2nd order).



**Figure 5**. The curve of Pb2+ adsorption on TBCA, based on Lagergren and Ho-McKay

The results of the adsorption data analysis of Pb2+ cations on TBCA showed that the most suitable adsorption kinetics model was the Ho-McKay kinetic model (R2=0.957) with an absorption rate constant (k) of 143×10-3 g.mg-1 min-1. In the system with TBMTCA as the adsorbent, the adsorption of Pb2+ cations tended to have a higher correlation with the Lagergren kinetic model (R2=0.843) with an absorption rate constant (k) of 6.91×10-3min-1. Details of the equations and the adsorption kinetics data of the two systems can be seen in Figure 5. and Figure 6.



**Figure 6.**  The curve of Pb2+ adsorption on TBMTCA, based on Lagergren and Ho-McKay

### **Adsorption isotherm of Pb(II) cations on TBCA and TBMTCA**

The Freundlich adsorption isotherm was obtained assuming a heterogeneous surface with non-uniform distribution of the adsorption heat over the surface. Meanwhile, in the Langmuir adsorption isotherm, then the assumption is that the absorption takes place at a specific homogeneous site in the adsorbent. The mathematical equation of the Langmuir adsorption isotherm is:

 equation (3)

where K is the adsorption equilibrium coefficient (L/mol), Xm is the adsorption capacity value (mol/L), Ce is the adsorbate concentration in equilibrium (mol/L) and qe is the amount of adsorbate adsorbed on the adsorbent (mol.g-1). The mathematical equation of the Freundlich isotherm can be written as follows:

 equation (4)

where qe is the number of grams adsorbed per gram of adsorbent, Ce is the concentration at equilibrium, while k and n are constants

 The adsorption isotherm can be explained based on data obtained from the Pb2+ cations values which can be adsorption at variations in the initial concentration of Pb2+ cations as in Figure 7 and figure 8. Langmuir and Freundlich isotherm models

**Table 2**. Parameters of Langmuir and Freundlich isotherm models

|  |  |  |  |
| --- | --- | --- | --- |
| Adsorbent | Metal | Langmuir isotherm models | Freundlich isotherm models |
| Xm(mol g-1) | K(L mol-1) | Eads(kJ mol-1) | R2 | n | k | R2 |
| TBCA TBMTCA | Pb2+ Pb2+  | 137.29 128.46 | 13.60 10.21 | 6.51 5.81  | 0.9710,982 | 0.3300,431 | 0,0020,008 | 0.6280,960 |

The adsorption isotherm was determined using data on the concentration of metal cations adsorbed at equilibrium points at various initial concentrations of metal cations. The adsorption isotherm in this study was analyzed using the Langmuir isotherm model (Ce/qe = 1/(K.Xm) + Ce/Xm) and Freundlich (log qe = log K + 1/n.log Ce) where qe is the number of metal cations presents adsorbed at equilibrium (mmol/g), Ce as the concentration of metal cations in solution at equilibrium (mmol/L), Xm as maximum adsorption capacity (mmol/g), and K as adsorption constant can be seen in Figure 7. and Figure 8.

**Figure 7**. Curve Pb2+ adsorption on TBCA based on Langmuir and Freundlich

**Figure 8.** Curve Pb2+ adsorption on TBMTCA based on Langmuir and Freundlich

 The adsorption isotherm analysis of each Pb2+ cations in TBCA (Figure 7), showed that the adsorption pattern of the two metal ions was more in line with the Langmuir isotherm adsorption model (R2Pb(II) = 0.971) than the Freundlich model (R2Pb(II) = 0.628). These results indicate that Pb2+ cations adsorbed on TBCA tend to form a monolayer on the TBCA surface. In addition, it can also be assumed that maximum adsorption occurs when the interaction between all active groups (hydroxyl groups) on TBCA and Pb2+ cations forms a single layer with adsorption energy for each cation of 5.81 kJ/mol. Pb2+ cations adsorption is also more by the Langmuir isotherm model (R2Pb(II) = 0.982) so that it has the same adsorption mechanism with adsorption energy for each cation of 6.51 kJ mol-1. The parameters obtained from observations on the Langmuir and Freundlich isotherms are presented in TBMTCA (Figure 8), can be explained that the adsorption pattern of Pb2+ cations, refers to the Langmuir isotherm adsorption models. In adsorption it means that it occurs in one layer (monolayer), with the adsorption pattern following the Langmuir adsorption, it can be assumed that the maximum adsorption occurs in all active sites (OH groups and C=O groups). The amount of adsorption energy between Pb2+ cations is 6.51 kJ/mol (Table 2). it can be seen that the maximum adsorption capacity of Pb2+ cations can be explained based on the HSAB concept Pb2+ cations is hard medium acid and has a small radius value. In the HSAB concept, intermediate acids will interact with soft acids, and hard acids will interact with hard bases [26 - 27]. The active site in the adsorbent is the OH group and the C=O group is a hard base, so the OH and C=O groups will be less stable to interact with the Pb2+ cations which is an intermediate acid group. The parameters obtained from observations on the Langmuir and Freundlich isotherms are presented in Table 2, can be explained that the adsorption pattern of Pb2+ cation, refers to the Langmuir isotherm adsorption models. In adsorption it means that it occurs in one layer (monolayer), with the adsorption pattern following the Langmuir adsorption, it can be assumed that the maximum adsorption occurs in all active sites (OH groups and C=O groups). From Table 2, the optimum exposure time of Pb2+ cations is 30 minutes and the amount of Pb2+ cations adsorption by adsorbent TBCA and TBMTCA is 137.29 mol/g and 128.46 mol/g. Determination of the desorption kinetics rate can be done based on the time of interaction to reach the adsorption equilibrium state. General indicators for predicting the adsorption rate are the reaction rate (k) and the correlation coefficient (R2). The adsorption isotherm parameters data of Pb2+ cations in TBCA and TBMTCA are briefly tabulated in Table 1; 2 as a comparison for adsorption studies presented in Table 3.

**Table 3.** Comparative of Pb2+ adsorption in (Moradi1) [20]; Handayani2) [24]; Busroni3) [18])

|  |  |
| --- | --- |
| Adsorption Study | Adsorption Kinetic Study |
| Adsorbent | pH Optimum | Contact time(minit) | Isotherm Adsorption | Kinetic Models |
| Pb2+ -TBCA1) | 6.0 | 10 | Intra-particle diffusion | Pseudo-2nd order |
| Pb2+-Poly-Calixarene2) | 4.0 | 180 | Freundlich | Ho-McKay |
| Pb2+-TBCA3) | 5.0 | 30 | Langmuir | Ho-McKay |
| Pb2+-TBMTCA3) | 4.0 | 90 | Langmuir | Lagergren |

## **CONCLUSION**

The optimized conditions obtained were pH of 5, and exposure time of 90 minutes its TBCA and TBMTCA adsorbent for Pb2+ cations, respectively. A study of the kinetic model showed that Pb2+-TBCA and Pb2+-TBMTCA cations followed the Ho-McKay kinetics models and Lagergren kinetic models with an adsorption rate constant of 143×10-3 g mg-1 min-1 and 3×10-3 g mg-1 min-1respectively, Pb2+ cations adsorption onto adsorbent of TBCA and TBMTCA was consistent with Ho-McKay kinetics models (pseudo-2nd order) and Lagergren kinetic models (pseudo-1nd order), Adsorption isotherm study showed that Pb2+ cations adsorption for both Pb2+-TBCA and Pb2+-TBMTCA cations were consistent to Langmuir isotherm. The maximum adsorption capacity for Pb2+-TBCA and Pb2+-TBMTCA both adsorptions Langmuir isotherm models were 137,29 and 128,46 mol g-1, respectively. Adsorption energy for Pb2+-TBCA and Pb2+ -TBMTCA interactions were 6.51 k J/mol and 5.81 kJ/mol respectively.

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## **REFERENCES**

[1] Arifin, Z., Puspitasari, R. and Miazaki, N., 2012, Heavy Metal Contaminations in Indonesian Coastal Marine Ecosystems: A Historical Perspective, *Coast. Mar. Sci.,* 5(1), 227-233

[2] Roundhill, D. M., 2004, Strategies for The Removal of Toxic Metal from Soils and Waters, *Journal of Chemical Education*, 81 (2),275-282

[3] Rosas, C.C., 2010, Synthesis and Application of Manganese Dioxide Coated Magnetite for Removal of Metal Ions from Aqueous Solutions, *Dissertation* Doctor.

[4] Flora, G., D. Gupta, D., Tiwari, A., 2012, Toxicity of Lead: A Review with Recent Updates, *Interdiscip. Toxicol*., 2012, 5(2), 47-58.

[5] Kurniawan, Y.S., Ryu, M., Sathuluri, R.R., Iwasaki, W., Morisada, S., Kawakita, H., Ohto, K., Maeki, M., Miyasaki, M., and Jumina, 2012, Separation of Pb(II) Ion with Tetraacetic Acid Derivative of Calix[4]arene by Using Droplet-Based Microreactor System”, *Indones. J. Chem*., 19 (2), 368-375.

[6] Yang, F.F., Huang, Z.S., Zhang, X.Y., and Guo, H.Y., 2010, Thiacalix[4]amido-based Netty Polymers: Novel Sorbents for Heavy Metal Cations and Derivatives of Aniline, *Iranian Polymer Journal*, 19 (4), 309-318.

[7] Elcin, S., Karakus, O.O., I. Kara, I., Deligos, H., 2015, Synthesis and Structural Characterization of Bisazocalix[4]arene With Melamine: Metal ion extraction studies, *Journal of Molecular Liquids“*, 202, 134-140.

[8] Utomo, S. B., Jumina, Siswanta, D., and Mustofa, M., 2012, Kinetic and Equilibrium Model of Pb(II) and Cd(II) AdsorptionIndonesiatrakis-Thiomethyl-C-Methoxyphenylcalix[4]resorcinarene, *Indones.J. Chem*., 6(1), 49-56.

[9] Masykur, A., Santosa, S. R., Siswanta, D., and Jumina, 2014, Synthesis of Pb(II)Imprinted Carboxymethyl Chitosan and The Application as Sorbent For Pb(II) Ion, *Indones. J. Chem*., 14(2), 152-159.

[10] Prabawati. S. Y., Jumina, J., Santosa, S.J., Mustofa, and Ohto, K., 2012, Study On The Adsorption Properties Of Novel Calix[6]arene Polymers For Heavy Metal Cations, *Indo. J. Chem.*, 12 (1), 28 – 34

[11] Kusumaningsih, T., Jumina, Siswanta, D., Mustofa, Ohto, K., Kawakita, H., 2012, “Synthesis of Poly-tetra-p-Allylcalix[4]arene Tetra Acetic Acid Adsorbent Characterization and Adsorption Test of Poly-tetra-p-Propenyl For Cr(III) and Pb(II), *I.J. Tech*., (2), 93-102, ISSN 2086-9614.

[12] Siswanta, D., J. Jumina, Anggraini, M., Mardjana, M. I. D., Mulyono, P., Ohto, K., 2016, Adsorption Study of Pb(II) on Calix[4]resorcinarene-Chitosan Hybrid, *International Journal of Applied Chemistry”*, ISSN 0973-1792, Vol. 12, No. 1, 11-22.

[13] Kesuma, E. D., Jumina, Ohto, K., and Siswanta, D., 2016, Synthesis of C-4-Allyloxy-3-Methoxyphenylcalix[4]resorcinarene From Vaniline and Its Application as Adsorbent of Pb(II) Metal Cation, *Oriental Journal of Chemistry*, Vol. 32, No. 2, 769-775.

[14] Kamboh, M. A., Ibrahim, W.A.W., Nodeh, H. R., Zardani. L.A., Sanagi, M.M., 2018, Fabrication of Calixarene-grafted Magnetic Nanocomposite for the Effective Removal of Lead (II) From Aqueous Solution, *Environmental Technology.*

[15] Alghamdi. A.A., Al-Odayni, A.B., Saeed, W.S., Al-Kahtani, A., Alharthi, F.A., and Aouak, T., 2019, Eﬃcient Adsorption of Lead (II) from Aqueous Phase Solutions Using Polypyrrole-Based Activated Carbon, *Materials,* 12, 1-16.

[16] Gu, S., Wang, L., Mao, X., Yang, L., and Wang, C., 2018, Selective Adsorption of Pb(II) from Aqueous Solution by Triethylenetetramine-Grafted Polyacrylamide/Vermiculite, *Materials*, 11, 1-20.

[17] Busroni, Siswanta, D., Santosa, S.J., Jumina, 2017, Study of Pb(II) and Fe(III) Metal Cations Adsorption into p-tertbutylcalix[4]arene as Adsorbent: Kinetic Adsorption, *Int. J. Adv. Res.,* 5(9), 574-580.

[18] Busroni, 2017, Sintesis Turunan Senyawa p-Tert.Butilkaliks[4]arena Dan Penggunaannya Untuk Penjerap Kation Logam Pb(II) dan Fe(III)**,** *Disertasi* Doktor Pascasarjana, Universitas Gadjah Mada.

[19] Busroni, 2013, Synthesis and Characterization of Mono(carboxy methoxy)-tert.butylcalix[4]arenes via In Direct Alkylation, Proceeding, *The 2nd Internasional Conference Of The Indonesian Chemical Society* 2013 (ICICS), Universitas Islam Indonesia, Yogyakarta.

[20] Moradi, O., Zare, K., Zekri, A.R., and Fakhri, A., 2012, Experimental Modeling of the Adsorption Kinetics of Cd(II) and Pb(II) ions by Calix[4]arene Surface, *Journal of Physical and Theoretical Chemistry,* 9 (2), 67-76.

[21] Gutsche, C.D., Lin, L., 1988, Calixarenes 12. The Synthesis of Functionalized Calixarenes, *Tetrahedron*, 42(6), 1633-1640.

[22] Kim, J.M., Chun, J.C., and Nam, K.C., 1997, Selective Acyl and Alkylation of Monobenzoyl-p-tert-butyl Calix[4]arene, *Bull. Korean Chem.*, 18(4), 409-415.

[23] Liu, L., Huang, K., Yan, C.G., 2010, Syntheses, reaction and crystal structures of 1,3-Alternate p-t-butylthiacalix[4]arene Ester and Amide, *J. Incl Phenom Macro. Chem*., 66, 349-355.

[24] Handayani, D.S., Jumina, Siswanta, D., Mustofa, Ohto, K., and Kawakita, H., Adsorption of Pb(II), Cd(II), and Cr(III) From Aqueous Solution By Poly-5-Allyl-Calix[4]arene Tetra Carboxylic Acid, 2011*, Indo. J. Chem*., 11(2), 191-196

[25] Araki, K., Iwamoto, K., Shinkai, S., Matsuda, T., 1990, “pKa” of Calixarenes and Analogs in Nonaqueous Solvents, *Bull. Chem. Soc. Jpn*., 63(12), 3480-3485.

[26] Pearson, R. G., 1963, Hard and Soft Acids and Bases, *J. Am. Chem. Soc*., 85, 3533-3539.

[27] LoPachin, R.M., Gavin, T., DeCaprio, A., and Barber, D.S., 2012, Application of the Hard and Soft, Acid and Bases (HSAB) Theory, *Chem. Res. Toxicol*, 25, 239-251

[28] Ho, Y.S., and McKay, G., 1999, Pseudo-second order Model for Sorption Processes, *Process Biochemistry*, *Elsevier,* 34, pp. 451-465.

[29] Ho, Y. S., 2004, Citation Review of Lagergren Kinetic Rate Equation on Adsorption Reactions, *Jointly published by AkadÈmiai KiadÛ, Budapest Scientometrics, and Kluwer Academic Publishers, Dordrecht*, 59(1), 171-177