

Use of Calixarenes Bearing Benzoyl Groups for the Adsorption of Heavy Metals Cations: Equilibrium and Kinetics Studies

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ABSTRACT. This study aims to examine the potential of p-tert-butylkalix[4]arene derivatives, namely 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrahydroxy-calix[4]arene (TBCA), and 5,11,17,23-tetra-tert-butyl-25-mono-hydroxy-26,27,28-tribenzoyloxycalix[4]arene (TBMTCA) as adsorbent for metal cations, such as Pb(II) and Fe(III). The synthesized compounds were characterized using FT-IR and ¹H-NMR spectroscopy. The adsorption studies were then carried out with contact time as a parameter, while the kinetics were evaluated using the Lagergren and Ho-McKay equations. The isotherms were analyzed using the Langmuir and Freundlich equations. For the kinetics of TBCA adsorbents, Pb(II) cations followed the Ho-McKay model, while Fe(III) was based on Lagergren. Furthermore, for the TBMTCA adsorbent, Pb(II) followed the Lagergren kinetic model, while Fe(III) was based on the Ho-McKay. The cation adsorption isotherms of Pb(II)-TBCA, Pb(II)-TBMTCA, Fe(III)-TBCA, and Fe(III)-TBMTCA are more in line with the Langmuir model. These results indicate that they can be used as heavy metal adsorbents, and recycled to increase their economic value.

Keywords: heavy metal, isotherm adsorption, kinetic adsorption, TBCA, TBMTCA

INTRODUCTION

Several efforts have been made to reduce the concentration of heavy metal cations in water due to their harmful effects. Wastewater is produced by various industries, and they deteriorate the public health. Several rivers in Indonesia have been polluted due to the discharge of pollutants containing hazardous metals, such as lead. Although Pb(II) has many applications in industrial activities, such as battery production, paint, and paper, it is still toxic to the environment. Strict regulations on the discharge of toxic metals need to be implemented along with the

development of various technologies for their removal from polluted streams. Adsorption processes are the most attractive methods for the effective removal of these ions from different aqueous solutions due to their high efficiency in a wide range of concentrations. They are also easy to carry out, selective, rapid, and have relatively flexible working conditions (Zaweirucha et al., 2016). Several studies revealed that the ability of macrocyclic ligands to form complexes with metal ions majorly depends on the structure and size of the cavity in the tb-calix[4]arene containing benzoyl groups, as shown in **Figure 1**.

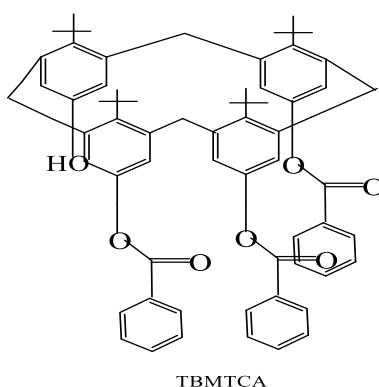


Figure 1. Structure of tb-Calix[4]arene derivative (TBMTCA).

The adsorbent material can also be recycled through appropriate desorption procedures, lowering the operational costs. Consequently, material development to obtain the ideal adsorbent for heavy metal adsorption has become the major focus of several studies. The adsorbent used must be economical, reusable, and fast. It must also have an effective adsorption and desorption processes, along with high metal selectivity (Mishra, 2014). Several techniques have been developed to overcome environmental problems, specifically the presence of pollutants in the waters, such as the extraction/absorption method. Calixarene compounds and various derivatives of Calix[4]crown can serve as materials for the production of adsorbents. Heavy metals are often contaminated with Pb(II) cations due to human activities. Furthermore, lead can interfere with the cell physiological metabolism in plants, animals, and humans by accelerating the formation of reactive oxygen species as well as inhibiting the function of bivalent and other monovalent metals in the body. Several calix[4]arene derivatives and compounds have been used as adsorbents, and they showed good adsorption. Special methods have also been used to reduce heavy metals, including. The shape of the calixarene molecule resembles a cup so that it is suitable for interacting with various receptors and is able to form complexes with heavy metal cations. (Konczyk et al., 2016; Kurniawan et al., 2019; Kamboh et al., 2018; Busroni, et al., 2017; Elcin et al., 2015; Fros et al., 2019; Kusumaningsih et al., 2012; Priastomo et al., 2021; Cataldo et al., 2021).

Monitoring the exposure and probable intervention for reducing additional exposure to heavy metals in the environment and in humans can become a momentous step towards prevention (Jaishankar et al., 2014). Various molecular, cellular and intracellular mechanisms have been proposed to explain the toxicological profile of lead that includes generation of oxidative stress, ionic mechanism and apoptosis (Flora et al., 2012). C-4-phenacyloxy phenyl calix[4]resorcinarene with more functional groups present compare to its previously reported calix also showed good adsorption capacity against Pb(II), Cd(II) and Cr(III) (Rastuti et al., 2018; Siswanta et al., 2016). Adsorption kinetic and equilibrium parameters for Cd²⁺ and Pb(II) ions on calix[4]arene were obtained in a batch system by experimental modeling (Moradi et al., 2012; Murphy et al., 2016). Adsorption process of Fe(III) ion by chitosan-GA fitted to Freundlich and pseudo-second order models (Sugita et al., 2015). In this research, IIP was synthesized using polyeugenoxo acetate with ethylene glycol dimethacrylate to find out adsorption rate and capacity through adsorption kinetics and isotherm studies for Fe(III) adsorption (Djunaidi et al., 2021). The preparation and applications of SIRs were intensively studied for their unique advantages in recovery and separation of various metals, as high efficiency and selectivity, and

easy operation (Bao et al., 2016). The optimum condition of various parameters for the Fe(III) ions adsorption, and studied on the isotherm modeling were Langmuir and Freundlich isotherm (Mary et al., 2015).

The process took place efficiently at pH of 5 and 4, with adsorbent dosage level of 0.4 g for 60 minutes, and the maximum adsorption capacity was 161.29 mg/g for copper (II) and 1250 mg/g for Pb(II) ions when fitted in the Langmuir model (Musumba et al., 2020); Adsorption isotherm models Langmuir and Freundlich were studied and the equilibrium data was best fitted by the Freundlich isotherm model implying that the adsorption of lead ions onto the surface of WTAC and WTPC (Malise et al., 2020); The study on the effect of pH revealed that the competition between H⁺ and metal ions at low pH values is the main leading factors that affect the adsorption characteristics of SCBA, and optimum removal efficiency was achieved at pH 5.0 (Salihi et al., 2017). The current paper demonstrated the synthesis of calix[6]arene-modified PbS and its efficient cationic dye adsorption of MB dye, and the adsorption of the MB dye was in-line with the Langmuir isotherm (Rosly et al., 2021); The studied show sand and charcoal adsorbent mixture is a suitable for the removal of Fe(III) from aqueous solution (Deka et al., 2015). This modification has been proven to increase the adsorption efficiency as well as the adsorbent preparation stage. Only a few studies explored the use of calix[4]arene in the form of partially modified basic compounds as adsorbents. This is because it is more likely to be applied as an extractant. Furthermore, most of the derivatives of calix[4]arene are not soluble in water, implying they are more suitable to be used as adsorbents. The advantage of this study is that the adsorbent is relatively difficult and expensive to synthesize, indicating a non-expansive synthesis.

EXPERIMENTAL SECTION

Materials

Tribenzoyloxy-(*tert*-butyl)calix[4]arene (TBMTCA) and TBCA were synthesized based on the reported procedure (Busroni, et al., 2017). Meanwhile, other reagents were purchased from Merck and used without any special treatment or purification.

Instrumentation

The IR spectra were recorded using an FTIR Spectrometer, namely Shimadzu-Prestige 21. The melting points were determined with electrothermal 9100, while the ¹H-NMR spectra were recorded using an Agilent Varian at 400 MHz. The concentrations of metal ions in the solution were assessed with AAS Buck Scientific.

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

The synthesis of 5,11,17,23-tetra-(*t*-butyl)-25,26,27,28-tetrahydroxy-calix[4]arene (TBCA) was carried out based on the study conducted by (Busroni,

et al., 2017). Crude products were crystallized with CHCl_3 -MeOH, and dried to give white crystal powder with 46.07% concentration at 340-343 °C mp. The result of FTIR using KBr showed 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} CH_2 ; 1366 cm^{-1} CH_3 , and 1204 cm^{-1} and. The product obtained was then characterized using $^1\text{H-NMR}$ (400 MHz, DMSO). Furthermore, peaks were identified at δ 7,1757 ppm Ar-H, δ 4,3841 ppm Ar- CH_2 -Ar proton H_{axial} , δ 3,5124 ppm Ar- CH_2 -Ar proton $\text{H}_{\text{equatorial}}$, δ 10,3367 ppm Ar-OH, as well as $\text{C}(\text{CH}_3)_3$ at δ 0.67, 3.09, and 0.71 ppm.

Synthesis: 5,11,17,23-tetra-(*t*-butyl)-26,27,28-tribenzoyloxy-calix[4]arene

The synthesis of 5,11,17,23-tetra-(*t*-butyl)-25-monohydroxy-26,27,28-tribenzoyloxy-calix[4]arene (TBMTCA) was carried out based on the study conducted by (Kim, et al., 1997). Approximately 1.5 g of 2.32 mmol TBCA was mixed with 1.35 mmol pyridine and 0.95 mL of 8 mmol benzoyl chloride in 30 mL of dry CHCl_3 . The mixture was then stirred evenly at room temperature for 3 hours. The solvent on the mixture was washed in a vacuum, rinsed with aquadest, and then extracted with diethyl ether. The crude products were crystallized with CHCl_3 -MeOH, and dried to give yellow-brown powder with a concentration of 94.3% at 306-310 °C mp. The FTIR result using KBr showed 3232 cm^{-1} -OH, 3054 cm^{-1} $\text{C}_{\text{sp}2}$ -H, 1605 cm^{-1} C=C aromatic, 1750 cm^{-1} ester C=O, 2870 cm^{-1} and 2955 cm^{-1} $\text{C}_{\text{sp}3}$ -H, 1458 cm^{-1} CH_2 -, and 1204 cm^{-1} C-O. The product obtained was then characterized using $^1\text{H-NMR}$ (400 MHz, DMSO). Partial benzoylation was identified by peaks at δ 7.0-8.2 ppm (m, 15H, PhC=O) and δ 10.3370 ppm (s, 1H, Ar-OH). Furthermore, other proton peaks include two doublets at δ 4.37 - δ 4.35 and 3.51 - 3.48 ppm of Axial H. An increase was observed in the low single ethylene at δ 1.25 ppm from the proton group $\text{C}(\text{CH}_3)_3/(\textit{t}\text{-butyl})$. The peak of aromatic protons occurred at equatorial methylene 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, t, 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), and δ 8.10 ppm (d, 3H, phenyl, J 7-10 Hz).

Models for Kinetic and Isotherm Studies of Pb(II) and Fe(III) Adsorption

Two solutions of Pb(II) and Fe(III) containing 10 mL of Fe(III)-TBCA and Fe(III)-TBMTCA, respectively, were prepared and the pH was adjusted to 5. Each solution was poured into a 20 mL bottle glass containing 10 mg adsorbent (3). The suspensions were then stirred for 10, 20, 30, 90, 180, and 240 min. Subsequently, they were filtered, and the filtrates obtained were analyzed using SSA. The isotherm and kinetics adsorption processes were performed by mixing 10 mg of TBCA and TBMTCA with 10 mL of cation sample

solution (Pb(II) and Fe(III)) with concentrations of 4, 8, 12, 16, and 20 mg/L. The mixture was then stirred at room temperature, optimum pH, and exposure time. The adsorbed metal ion was measured using SSA based on the concentration of Fe(III) cation before and after the adsorption processes.

RESULTS AND DISCUSSION

Effect of Exposure Time Based on the Adsorption of Pb(II) and Fe(III) Cations onto TBCA and TBMTCA

Effect of exposure time on adsorption of Pb(II)-TBCA; Pb(II)-TBMTCA; Fe(III)-TBCA and Fe(III)-TBMTCA was determined by observing the time required to reach the equilibrium point. In the cationic solution and the adsorbent, a range of 10-240 minutes as obtained. At the optimum pH, the equilibrium time for Pb(II) and Fe(III) cations adsorption in Pb(II)-TBCA, Pb(II)-TBMTCA and Fe(III)-TBCA, Fe(III)-TBMTCA was 90 minutes, as shown in **Figure 2**. Meanwhile, for TBCA and TBMTCA, the optimum adsorption time was 30 minutes. Adsorption studies were often carried out by observing the changes in the amount of Pb(II) and Fe(III) metal cations adsorbed within a specified period. When there is contact between Pb(II) and TBCA, Pb(II) and TBMTCA, Fe(III) and TBCA, as well as Fe(III) and TBMTCA successively for a long time, this causes an increase in the amount of adsorbate produced. Adsorbed also occurs further until there is equilibrium/saturation with the adsorbate. The contact time for the adsorption of Pb(II) by TBCA was 0-240 minutes at a pH of 5, and cation concentration of 8-30 ppm. Changes in adsorbate concentration have a significant relationship with the contact time, as shown in **Figure 2**.

Figure 2 shows that there was an increase in the number of ions adsorbed at the early stage, namely 10-30 minutes. It was because the active OH group on the TBCA surface did not interact with the metal ions until the optimal time of 30 minutes. The functional group was also saturated, and the change in the number of metal cations absorbed was no longer significant. Similar events also occurred in the absorbance of Pb(II) cations by TBMTCA with an optimum time of 90 minutes.

Adsorption Kinetic Models

The adsorption kinetics of Pb(II) cations was studied based on the formulation proposed by Lagergren and Ho models. The approach used involves the calculation of the change in time required for the process. In the Lagergren formulation (Ho & McKay, 1999; Ho, 2004), adsorption is a pseudo-first-order reaction that follows equation (1):

$$(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (1)$$

Where q_e is the total mass of metal adsorbed ($\text{mg}\cdot\text{g}^{-1}$), q_t is the mass of metal adsorbed at time t (mg/g), and k_1 is the pseudo-first-order Lagergren rate constant (minutes^{-1}).

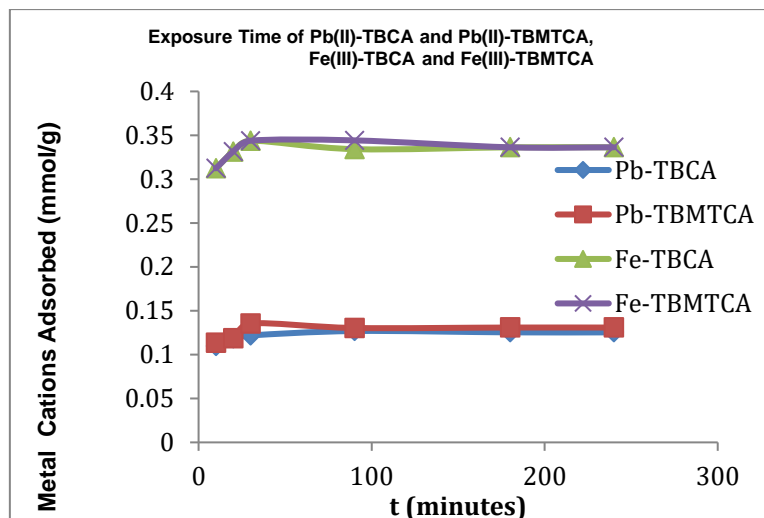


Figure 2. Exposure time of Pb(II)-TBCA (blue), Pb(II)-TBMTCA (red), Fe(III)-TBCA (green), and Fe(III)-TBMTCA (purple).

The adsorption kinetics that can be considered a pseudo-second-order reaction is known as Ho's kinetic equation, and it is illustrated below (2)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

where k_2 is a pseudo-second-order rate constant $g \text{ mg}^{-1} \cdot \text{min}^{-1}$

The Lagergren kinetic model has an R^2 value that is close to 1, followed by the Ho-McKay. The curve with the linearity of the Lagergren is higher than that of Ho-McKay (Ho & McKay, 1999; Ho, 2004), which has Pb(II) cation. Determination of the adsorption rate constant for lead(II) through Lagergren's model has an oblique approach of $6.91 \times 10^{-3} \text{ (minute}^{-1}\text{)}$, as shown in **Table 1**. **Figure 4** shows the effect of variations in the Pb(II) concentration against the adsorbed metal cation. At 8 ppm, the concentration of cation was also small due to the number of Pb(II). Furthermore, an increase in the absorption rate of the metal cations also increases the number of lead ions.

Kinetic Adsorption of Pb(II) and Fe(III) Cations onto TBCA and TBMTCA

Experimental data on the effect of contact time on Pb(II) cation adsorption on TBCA and TBMTCA were used and further analyzed to obtain the kinetics model. The models used include the Lagergren (pseudo-first-order) and Ho-McKay (pseudo-second-order). Subsequently, the available data were processed and plotted into a straight-line equation to determine the most suitable type. The model with a correlation coefficient close to 1 was the most appropriate to explain the adsorption mechanism. The correlation coefficient (R^2) was obtained from the linear regression between $\log (q_e - q)$ versus t (Lagergren's kinetic model) as well as t/q versus t (Ho kinetic model). q_e (mmol/g) is the concentration of the early metal ions. **Figure 3**, and **4** shows the value of the adsorption rate constant using the slope or interception of the corresponding kinetic models' equation (pseudo-second-order). **Figure 3**, **4**, and **5** reveal the isotherm analysis of Pb(II) and Fe(III) cations in TBCA and TBMTCA.

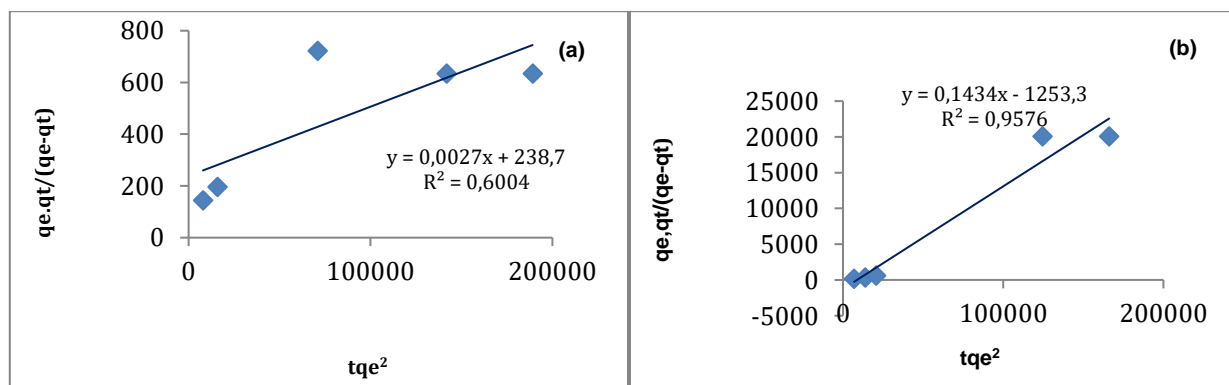


Figure 3. The curve of Pb(II) adsorption onto (a) TBMTCA, (b) TBCA, based on Ho-McKay

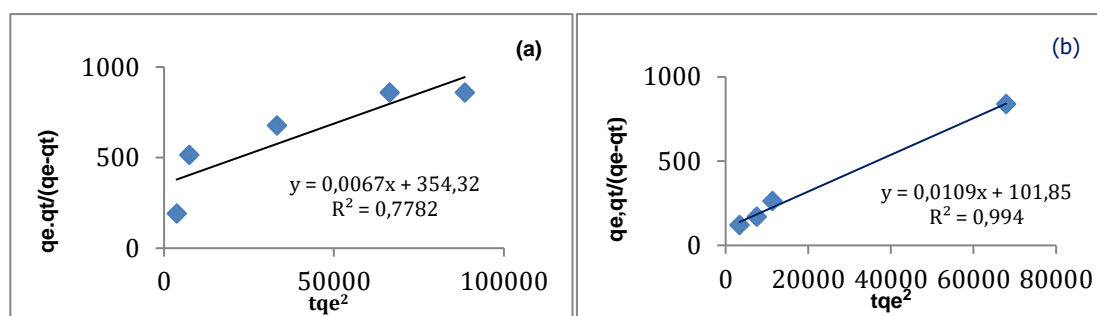


Figure 4. The Curve of Fe(III) adsorption onto (a) TBMTCA, (b)TBCA, based on Ho-McKay

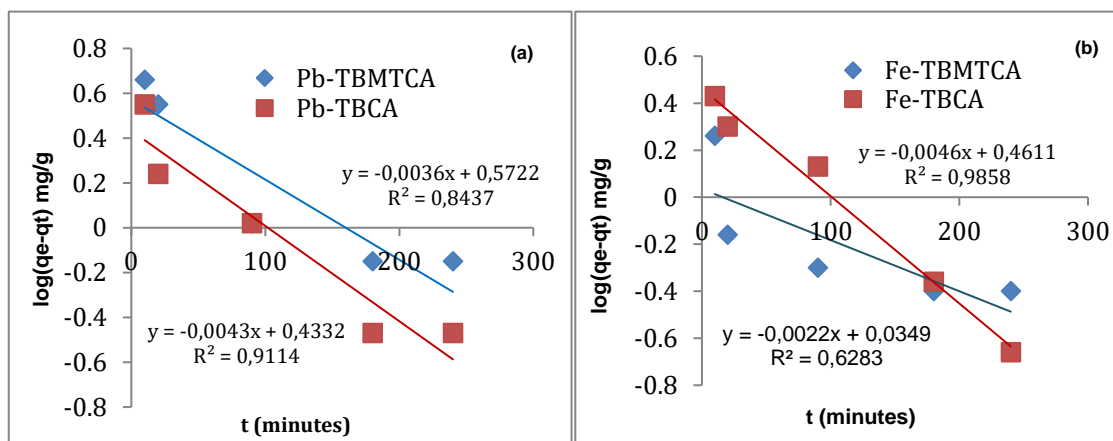


Figure 5. The curve of (a) Pb(II) and (b) Fe(III) adsorption onto TBCA, and TBMTCA, based on Lagergren.

Table 1. Kinetic models in Fe(III) cations for TBCA and TBMTCA adsorptions.

Adsorbent	Kinetic Models	Fe(III)-TBCA		Pb(II)-TBMTCA	
		R ²	k	R ²	k
TBCA	Lagergren	0.986	$9.21 \times 10^{-3} \text{ min}^{-1}$	0.9114	$9.21 \times 10^{-3} \text{ min}^{-1}$
	Ho-McKay	0.994	$0.016 \text{ g mg}^{-1} \text{ min}^{-1}$	0.9576	$143 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$
TBMTCA	Lagergren	0.628	$4.61 \times 10^{-3} \text{ min}^{-1}$	0.6004	$6.91 \times 10^{-3} \text{ min}^{-1}$
	Ho-McKay	0.778	$6 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$	0.8437	$3 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$

The bonding Pb(II)-TBCA (Busroni et al., 2017) material is an adsorbent as well as an excellent host for Pb(II)cations. The adsorption of the bonding Fe(III)-TBCA was based on the Lagergren models. The observation result of the isotherm showed that the adsorption of Pb(II) tends to follow the Langmuir isotherm. This is in line with a previous assumption, which stated that the interaction of lead (II) ions with p-tert-butyl-tribenzoyloxycalix[4]arene (TBMTCA) and p-tert-butyl-tetra-hydroxycalix[4]arene (TBCA) compounds can be viewed as a chemical adsorption process. The TBMTCA compound has active sites in the hydroxyl (-OH) and ester groups (-COOPh), which interact with the cation. Meanwhile, TBCA has activities in the form of hydroxyl and few combinations, which indicates that the adsorption process only occurs chemically. Table 1 shows that the maximum adsorption capacity of Fe(III) and Pb(II) using the HSAB

concept is similar to an intermediate acid. In the concept, a weak acid is expected to bind with a soft base, while a hard acid binds to a hard floor (Pearson, 1963; LoPachin et al., 2012).

The results of the adsorption data analysis of Pb(II) cations onto TBCA showed that the most suitable kinetics model was the Ho-McKay ($R^2=0.957$) with a rate constant (k) of $143 \times 10^{-3} \text{ g.mg}^{-1} \text{ min}^{-1}$. In the system with TBMTCA as the adsorbent, the adsorption of Pb(II) had a higher correlation with the Lagergren ($R^2=0.843$) with a rate constant (k) of $6.91 \times 10^{-3} \text{ min}^{-1}$. The data analysis for Fe(III) cations on TBCA showed that the most suitable model was the Ho-McKay ($R^2=0.994$) with a rate constant (k) of $16 \times 10^{-3} \text{ g.mg}^{-1} \text{ min}^{-1}$. In the system with TBMTCA as the adsorbent, the adsorption of Fe(III) had a higher correlation with the Ho-McKay ($R^2=0.778$) with a constant (k) of $6 \times 10^{-3} \text{ min}^{-1}$.

Adsorption Isotherm

Freundlich isotherm by assuming that adsorption occurred on a heterogeneous surface with non-uniform distribution of heat over the surface, was obtainable. Meanwhile, in Langmuir isotherm, the assumption is that the process occurred at a specific homogeneous site in the adsorbent. The mathematical equation of the Langmuir adsorption isotherm is:

$$\frac{c_e}{q_e} = \frac{1}{K \cdot X_m} + \frac{c_e}{X_m} \quad (3)$$

Where K is the adsorption equilibrium coefficient (L/mol), X_m is the adsorption capacity value (mol/L),

C_e is the concentration of adsorbate at equilibrium (mol/L), q_e is the amount of adsorbate absorbed (mol.g⁻¹).

The mathematical equations of the Freundlich isotherm is:

$$\log(q_e) = \log k + (n) \log C_e \quad (4)$$

Where q_e is the number of adsorbate (g) adsorbed per gram of adsorbent, C_e is the concentration at equilibrium, and k and n are constants.

The isotherms adsorption was analyzed with the isothermal models, and the constants obtained were for Langmuir and Freundlich, as shown in **Figures 6, 7, 8, and 9.**

Table 2. Langmuir and Freundlich Isotherm Constants for the adsorption of Pb(II) and Fe(III) cations onto TBCA and TBMTCA adsorbents.

Adsorbent	Metal	Langmuir				Freundlich		
		X_m (mol g ⁻¹)	K (L mol ⁻¹)	E_{ads} (kJ mol ⁻¹)	R^2	n	k	R^2
TBCA	Pb(II)	128.46	10.21	5.81	0.871	0.330	0,002	0.628
	Fe(III)	156.09	16.62	7.01	0.946	0.456	0,963	0.813
TBMTCA	Pb(II)	137,29	13,60	6,51	0,982	0,431	0,008	0,961
	Fe(III)	164,81	25,40	8,07	0,977	0,363	0,774	0,894

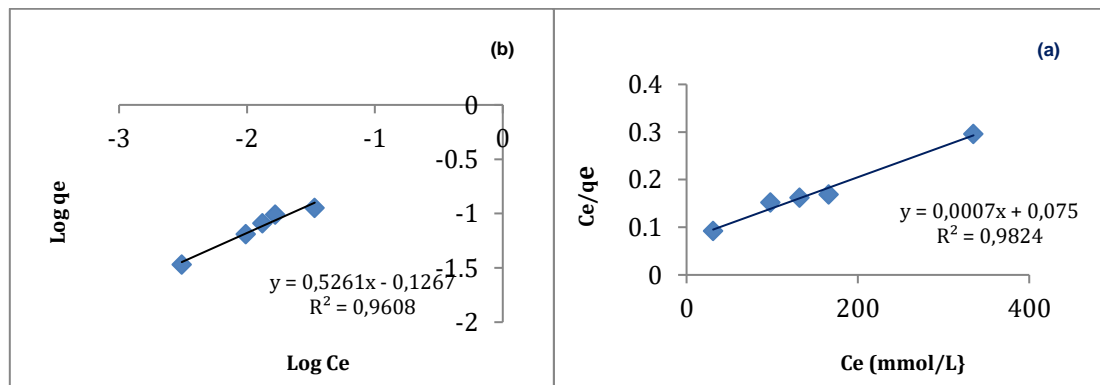


Figure 6. Curve Pb(II) adsorption onto TBMTCA based on (a) Langmuir, (b) Freundlich.

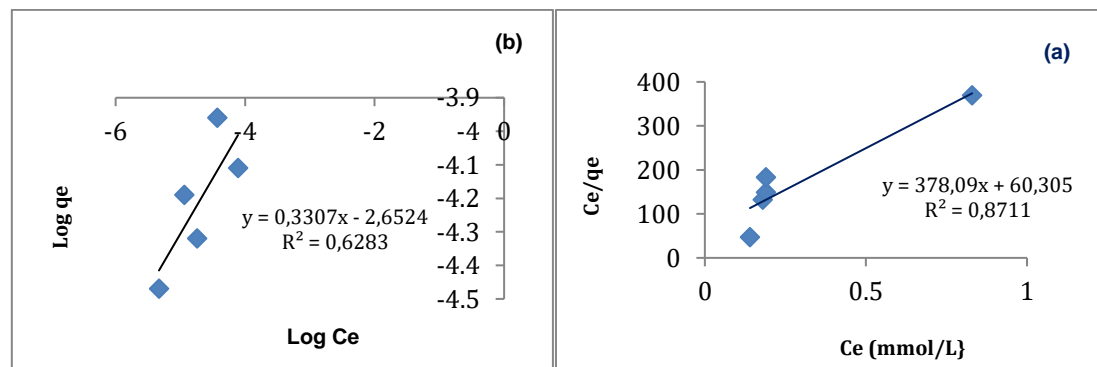


Figure 7. Curve Pb(II) adsorption onto TBCA based on (a) Langmuir, (b) Freundlich.

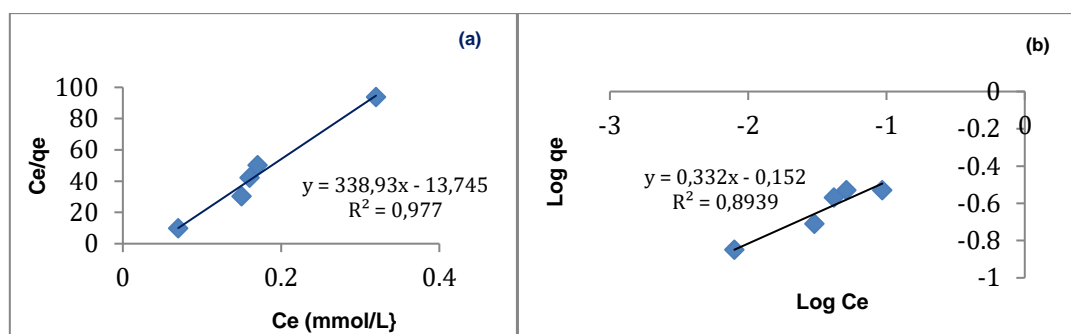


Figure 8. Curve Fe(III) adsorption onto TBMTCA based on (a) Langmuir, (b) Freundlich.

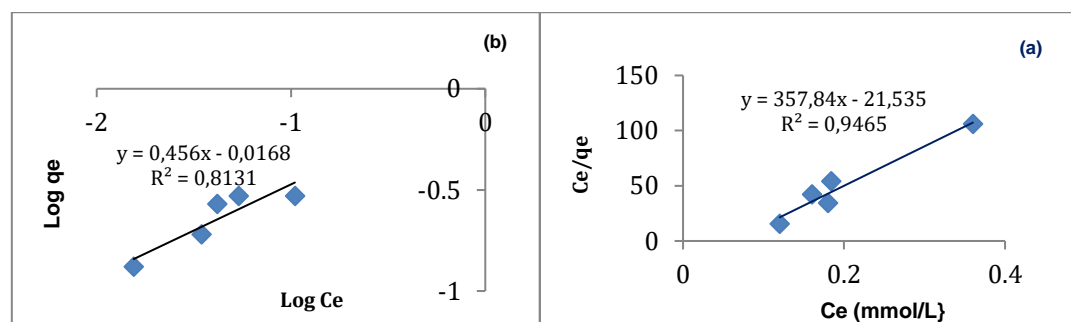


Figure 9. Curve Fe(III) adsorption onto TBCA based on (a) Langmuir, (b) Freundlich.

The isotherm analysis of Pb(II) in TBMTCA revealed that the adsorption pattern was more in line with the Langmuir model ($R^2_{Pb(II)} = 0.9824$) than Freundlich ($R^2_{Pb(II)} = 0.9608$), as shown in **Figure 6**. In TBCA, the cations were also more in line with the Langmuir model ($R^2_{Pb(II)} = 0.8711$) than Freundlich ($R^2_{Pb(II)} = 0.6283$), as shown in **Figure 7**. These results indicate that the Pb(II) adsorbed on TBCA tend to form a monolayer on its surface. Furthermore, it can be assumed that the maximum adsorption occurs when the interaction between all active hydroxyl groups on TBCA and Pb(II) cations forms a single layer. The parameters were obtainable from the observations of both isotherms in TBMTCA, as shown in **Figure 6** and **7**. The isotherm analysis of Fe(III) in TBMTCA showed that the adsorption pattern was more in line with the Langmuir model ($R^2_{Fe(III)} = 0.977$) than Freundlich ($R^2_{Fe(III)} = 0.8939$), as shown in **Figure 8**. In TBCA, the cations were also more in line with Langmuir ($R^2_{Fe(III)} = 0.9465$) than the Freundlich ($R^2_{Fe(III)} = 0.8131$), as shown in **Figure 9**. These results indicate that Fe(III) adsorbed onto TBMTCA tends to form a monolayer on its surface. It can also be assumed that maximum adsorption occurs when the interaction between all active hydroxyl groups on TBMTCA and Fe^{3+} forms a single layer. The parameters were obtainable from observations of Langmuir and Freundlich isotherms present in the adsorbent, as shown in **Figure 8** and **9**. The parameters used for the observations can be reviewed in **Table 2**. The adsorption pattern of Pb^{2+} and Fe(III) cations refers to the Langmuir models, which indicate that they occurred in one layer (monolayer). It can also be assumed that the

maximum adsorption occurs in all active sites, namely OH and C=O groups. Furthermore, **Table 2** shows that the optimum exposure time of Pb(II) was 30 minutes, and the amount of cations adsorbed by a TBCA and TBMTCA was 137.29 mol/g and 128.46 mol/g, respectively. The kinetics rate can be determined based on the time of interaction to reach the equilibrium state. General indicators for predicting adsorption are the reaction rate (k) as well as the correlation coefficient (R^2). This is in line with the previous assumption that the interaction of Fe(III) cations with p-tert-butyl-tribenzoyloxy-calix[4]arene (TBMTCA) and p-tert-butyl-tetra-hydroxy-calix[4]arene (TBCA) as adsorbents can be viewed as a chemical adsorption process (Busroni, et al., 2017). This is because TBMTCA compounds have active sites in the form of hydroxyl groups (-OH) and ester groups (-COOPh) that can interact with the cations. Meanwhile, TBCA compounds have an active site in the form of hydroxyl groups (-OH), which indicates that the adsorption only occurs chemically. **Table 1** shows that the maximum adsorption capacity of Fe(III) using the HSAB concept is similar to a hard acid. In the concept (Pearson, 1963; LoPachin, et al., 2012), a soft acid is expected to bind to a soft base, while a hard acid bind to a hard base. The active ester site on the adsorbent is the -COOPh group, which is a hard base. This indicates that it is more stable to bind with metal cations, which are hard acids. Fe(III) in TBMTCA is a hard acid and the -COOPh is a hard base, hence, the bonding is more stable. In TBCA compounds, the -OH is a soft acid and the Fe(III) cations is a hard acid, indicating the bonding is less stable. The parameters

obtained from the observation of Langmuir and Freundlich isotherm were presented in **Table 1**, where the maximum adsorption capacity in Fe(III)-TBMTCA was larger than Fe(III). This can be explained by the HSAB concept, where Fe(III) and Fe(III)-TBMTCA were categorized as soft and hard acid, respectively. Furthermore, Fe(III)-TBMTCA has a smaller atomic radius and higher charge than Fe(III)-TBCA. In the HSAB concept, soft acid reacts strongly with soft acid and inversely.

CONCLUSIONS

The results showed that the adsorption pattern of Pb(II)-TBCA and Pb(II)-TBMTCA follow the Ho-McKay kinetic model. This study was carried out to determine the contact time, and the kinetics were studied using the Lagergren and Ho equations. Furthermore, the isotherms were analyzed using the Langmuir and Freundlich equations. For adsorption kinetics on TBCA adsorbents, Pb(II) and Fe(III) cations followed the Ho-McKay model and Lagergren, respectively. Meanwhile, in TBMTCA, the adsorption of Pb(II) and Fe(III) cations followed the Lagergren and Ho models, respectively. The cation isotherms of Pb(II)-TBCA, Pb(II)-TBMTCA, Fe(III)-TBCA, and Fe(III)-TBMTCA are more in line with the Langmuir model with an adsorption energy of 5.81 and 7.01 kJ/mol for TBCA as well as 6.51 and 8.07 kJ/mol for TBMTCA. Based on the results, they can be used as heavy metal adsorbents. The materials can also be recycled and reused to increase their economic value. The adsorption capabilities for heavy metal cations indicate that they are prospects in polluted water disposal applications and environmental protection.

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