ADSORPTION OF Pb(II), Cd(II), AND Cr(III) FROM AQUEOUS SOLUTION BY POLY-5-ALLYL-CALIX[4]ARENE TETRA CARBOXYLIC ACID

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ABSTRACT

The aim research is application of poly-5-allyl-calix[4]arene tetra carboxylic acid as adsorbent of heavy metal cations. Adsorption was carried out towards Pb(II), Cd(II) and Cr(III) ions in batch system. Several variables including pH, contact time and initial concentration of metal ions were determined. The optimum adsorption conditions were achieved at pH 6.0 for Cd(II) and Cr(III), while at pH 5.5 for Pb(II) ions. In addition, the optimum contact time of Pb (II), Cd(II) and Cr(III) ion adsorption were 180 min. The adsorption kinetics of Pb(II), Cd(II) and Cr(III) ions using the calixarene polymer adsorbent followed a pseudo 2nd order kinetics model, with adsorption rate constants of $2x10^{-2}$; $5x10^{-3}$, *and* $3.1x10^{-2}$ *g* $mole^{-1}$ min^{-1}, *respectively. Furthermore, the adsorption isotherm of Pb(II) and Cd(II) ions tends to follow the Freundlich isotherm, whereas the adsorption of Cr (III) tends to follow the Langmuir isotherm. The adsorption capacity of Pb(II), Cd(II) and Cr(III) metal ions were 104.04, 61.78 and 228.69 µmole/g, with adsorption energy of 24.87; 21.62 and 31.07 KJ/mole, respectively.*

Keywords: *Poly-5-allyl-calix[4]arene tetra carboxylic acid, adsorption, Cd(II), Pb(II), Cr(III), kinetics adsorption, isotherm adsorption*

INTRODUCTION

As a consequence of the industrialization process, environmental pollution become the major problems that have to be solved and controlled firmly. Many toxic heavy metals have been persistently released into the environment as industrial wastes, causing serious soil and water pollution. Heavy metals are not biodegradable and have become an ecotoxicological hazard of increasing significance owing to their harmful effect on human physiology. Lead, cadmium and chromium are examples of heavy metals that are very toxic to both man and animal.

At present, a number of technologies such as ion exchange, chemical precipitation [1], extraction [2], reverse osmosis, evaporation, membrane filtration and adsorption [3] were used for wastewater treatment. Adsorption method is relatively simple method, which could be applied for contaminant at low concentrations. Adsorption process is generally based on the interaction between metals and functional groups existed on the surface of the adsorbent through complex formation. Many kinds of functional groups such as OH,-NH,-SH and -COOH may be employed as the active sites on the surface of the adsorbent [4].

Several adsorbents have been utilized to adsorb heavy metals, such as zeolites [5], charcoal [6], activated carbon [7], fly ash [8], chitin and chitosan [9-11], biomass [12], humic acid [13] and sugarcane bagasse [14]. One group of compounds that have potential to be developed as an adsorbent is calixarene. Calixarene can be classified as macrocyclic molecules like crown ether and cyclodextrin [15]. Calixarene has active groups arranged in unique molecular geometry in the form of vase or pot in which can be used as host of cation, anion and neutral molecule [16]. Studies on adsorption of heavy metal by calixarenes have been reported by Shinkai et al. [17], Sonoda et al. [18], Ohto et al. [19], Metin et al. [20] and Dey et al. [21]. In addition, the use of calix[4]arenes, calix[4]resorsinarene and polypropilcalix[4]arenes as adsorbent was also carried out by Jumina et al. [22-23].

Studies on adsorption of heavy metal by polymer calixarene has been done by Utomo [24] and

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Handayani [25] who performed the synthesis of poly-25-allyloxy-26,27,28-trihydroxycalix[4]-arenes and poly-5-allyl-25,26,27,28-tetrahidroxycalix[4]arene. Therefore, the purpose of this research is the use of other calix[4]-arene polymer, i.e. poly-5-allyl-calix[4]arene tetra carboxylic acid as adsorbent for heavy metal ions.

EXPERIMENTAL SECTION

Materials

Metal solutions were prepared by diluting 1000 mg/L Pb, Cd and Cr standard solution in aqueous nitric acid to desired concentrations. The pH adjustment was carried out by adding slowly NaOH and/or HNO_3 solutions into the metal solutions followed by stirring until the desired pH was reached. All materials required were reagent grade from E Merck. Poly-5-allyl-calix[4]arene tetra carboxylic acid was synthesized according to Handayani et al. [26].

Instrumentation

Atomic Absorption Spectrophotometer (AAS; AA-F-6650 Shimadzu) pH meter (Hanna) and adsorption stirrer (Intan Electroplating).

Procedure

Effect of the pH of the metal ion solution

The experiment was conducted by adding 0.008 g of poly-5-allyl-calix[4]arene tetra carboxylic acid into 10 mL of metal cation sample solution with the concentration of 10 mg/L. The adsorptions of Pb(II), Cd(II), and Cr(III) were carried out in pH 4.0; 4.5; 5.0; 5.5; 6.0 and 6.5. The mixture was then stirred at room temperature for 3 h. Then, the adsorbent was filtered out and dried in a desiccator. The adsorbed metal ion was determined based on the concentration of metal cation before and after the adsorption measured using AAS.

Adsorption kinetics

The calixarene polymer (0.024 g) was added into 30 mL of metal cation sample solution with concentration of 10 mg/L for each. The adsorption kinetics was studied by conducting the adsorption experiments in various contact times, which were 5, 15, 45, 135 and 405 min. Concentration of metal ion before and after adsorption was then measured by AAS.

Adsorption isotherm

The adsorption processes were performed by stirring 0.008 g of the calixarene polymer with 30 mL of metal cation sample solution having concentration of 2, 4, 8, 16 and 20 mg/L at room temperature and the optimum pH and contact time. Then, the adsorbed metal ion was measured based on concentration of metal cation before and after the adsorption using AAS.

RESULT AND DISCUSSION

Effect of pH

The pH of the solution is an important factor in determining the rate of surface reactions. The variation in adsorption capacity in this pH range is largely due to the influence of pH on the surface of poly-5-allyl-calix[4]arene tetra carboxylic acid adsorbent. The effect of pH on the adsorption of metal ions on the adsorbent is presented in Fig. 1.

As shown on Fig. 1, the amount of Pb(II) adsorbed consistently increased by the increase of initial pH and reached the optimum value of 8.05×10^{-3} mmole g^{-1} at pH value of 5.5. Similarly, it was found that Cd(II) and Cr(III) reached optimum value at pH value of 6.0 with amount of Cd(II) and Cr(III) adsorbed 37.59×10^{-3} and 135.67×10^{-3} mmole g^{-1}, respectively.

The hydroxy (-OH) groups on polycalix[4]arene was what causes the metal cation adsorption process is strongly influenced by pH. At low pH where the concentration of H^+ ions become so high that causes the hydroxy (-OH) group would bind protons (H^+) then the poly-5-allyl-calix[4]arene tetra carboxylic acid were positively charged. The positive charge on the poly-5-allyl-calix[4]arene tetra carboxylic acid cause repelling or competition between H^+ with metal ions on cation exchange sites were positively charged, so that the adsorption becomes small.

Thus, it can be said that the adsorption of Pb(II), Cd(II) and Cr(III) by poly-5-allyl-calix[4]arene tetra carboxylic acid was influenced by the pH of the solution where it related to the existence of -OH groups as the active sites. Adsorption of metals will increase with increase in pH of the solution and in particular a higher pH has decreased due to the formation of metal hydroxide precipitate.

Effect of Contact Time

Interaction time required to reach adsorption equilibrium can be used to determine the adsorption rate. The profile of contact time effect on adsorption of Pb(II), Cd(II) and Cr(III) by the calixarene polymer were shown in Fig. 2.

The optimum adsorption contact time for Pb(II), Cd(II) and Cr(III) ions ware 135 min with the amount of Pb(II), Cd(II) and Cr(III) adsorbed of 11.24×10^{-3}, 62.29×10^{-3} and 195.83×10^{-3} mmole/g, respectively.

If the adsorption equilibrium has been reached, the addition of the interaction time did not increase the

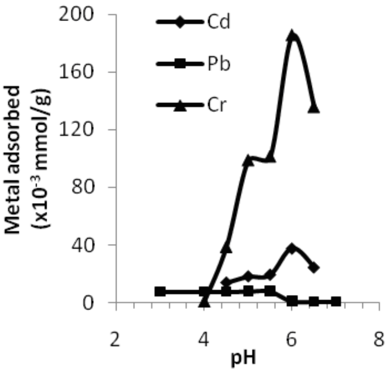

Fig 1. Effect of pH on adsorption of Pb(II), Cd(II), and Cr (III) onto poly-5-allyl-calix[4]arene tetra carboxylic acid

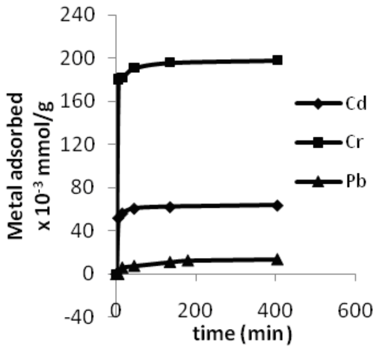

Fig 2. Effect of contact time on adsorption of Pb(II), Cd(II) and Cr(III) onto poly-5-allyl-calix[4]arene tetra carboxylic acid

Table 1. Kinetics parameters for Pb(II), Cd(II) and Cr(III) adsorptions

Kinetic Model	Pb(II)		Cd(II)		Cr(III)	
	R^2	K	R^2	K	R^2	K
Orde 1 (Santosa-Muzakky) $\frac{\ln(Co/Ca)}{Ca} = K_1 \frac{t}{Ca} + K$	0.745	3 x 10^{-3} (min^{-1})	0.563	5,2 x 10^{-2} (min^{-1})	0.778	6 x10^{-3} (min^{-1})
Pseudo Orde 1 (Lagergren) $\ln(qe - qt) = \log qe - Kt$	0.952	4 x 10^{-4} (g $mole^{-1}$ min^{-1})	0.863	6 x 10^{-3} (g $mole^{-1}$ min^{-1})	0.976	7 x 10^{-3} (g $mole^{-1}$ min^{-1})
Pseudo Orde 2 (Ho) $\frac{t}{qt} = \frac{1}{2Kqe^2} + \frac{1}{qe}$	0.988	5 x 10^{-3} (g $mole^{-1}$ min^{-1})	0.983	2 x 10^{-2} (g $mole^{-1}$ min^{-1})	0.989	3.1 x 10^{-2} (g $mole^{-1}$ min^{-1})

amount of adsorbed metal. In general, the amount of metal cations adsorbed have a similar pattern in which the adsorption has increased along with the addition of contact time to the period where the addition was no longer the contact time increases the amount of adsorbate. At initial adsorption stage, the surface of the adsorbent was still empty, so the absorption of cations by the adsorbent was rapid. The absorption will take place slowly with the addition of the contact time. This shows that there has been saturation on the active sites of the adsorbent.

Adsorption Kinetic

The experimental data of contact time effect on the adsorptions of Pb(II), Cd(II) and Cr(III) were used for kinetic modeling. The model equations used for fitting the data were: 1^{st} order (Santosa and Muzakky), pseudo 1^{st} (Lagergren), pseudo 2^{nd} order (Ho) equations.

The reaction rate can be determined by using the interaction time required to reach equilibrium adsorption. The results of kinetic calculations are presented in Table 1.

Table 1 showed that the kinetic model proposed by Ho gave a curve with a higher linearity than Santosa-Muzaky and Lagergren kinetic model for the adsorption of the three metal ions. Thus, it can be concluded that the adsorption of the three cations using poly-5-allyl-calix[4]arene tetra carboxylic acid adsorbent followed pseudo second order. Furthermore, the adsorption rate constant can be obtained from the Ho equation as a slope, which were 2×10^{-2} mmole g^{-1} min^{-1} for the adsorption of Pb(II); 5×10^{-3}mmole g^{-1} min^{-1} for Cd(II) and 3.1×10^{-2} g^{-1} mmole min^{-1} for Cr (III).

Adsorption isotherms

Adsorption isotherm was determined from data obtained from the amount of adsorbed metal ions on the variation of initial concentration of metal ions (Fig. 3).

The used isotherm equations were displayed as follow. The parameters of isotherm of Langmuir and Freundlich were also presented in Table 2.

Langmuir equation:

$$1/qe = (1/XmKCe) + (1/Xm)$$

Freundlich equation:

$$\log qe = \log K_f + \frac{1}{n} \log Ce$$

where

qe: concentration of adsorbate at equilibrium (mole/g),

Ce: concentration of adsorbate in the aqueous phase (mole/L),

Table 2. Parameters of Langmuir and Freundlich isotherm

Metal	Parameters of Adsorption						
	Langmuir				Freundlich		
	Xm (μmole/g)	K × 10^3 (L/mole)	ΔG (KJ/mole)	R^2	n	K (mole/g)	R^2
Pb(II)	104.04	21.405	24.87	0.984	1.487	3.81×10^{-2}	0.998
Cd(II)	61.78	5.818	21.62	0.908	1.391	1.53×10^{-1}	0.995
Cr(III)	228.69	257.223	31.07	0.968	22.73	9.441×10^{-5}	0.848

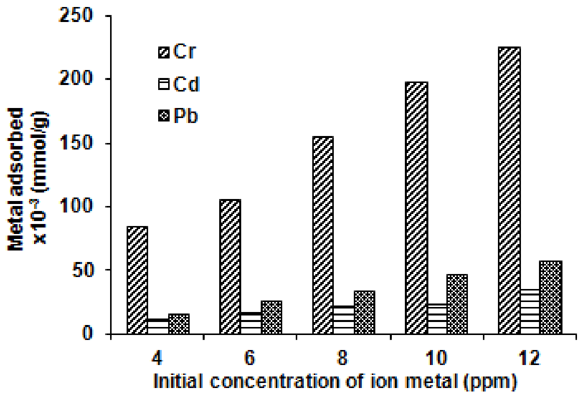

Fig 3. Effect of initial concentration of Pb(II), Cd(II) and Cr(III) by poly-5-allyl-calix[4]arene tetra caboxylate acid

Xm: maximum adsorption capacity (mole/g),
K: equilibrium constant.

Adsorption of Pb(II) and Cd(II) followed the model of Freundlich adsorption isotherm. This means that the maximum adsorption occurred when all active sites are filled by the adsorbate to form multilayer. On the other hand, the pattern of Cr(III) adsorption tends to follow the Langmuir adsorption isotherm. This implied that the process of adsorption occurred in monolayer, with the assumption that the maximum adsorption occurred when all active sites were filled by the adsorbate and monolayer was formed.

Adsorption energy equation could be written as $E_{ads} = - \Delta G^o$. Value of ΔG can be measured from the standard state, whereas for the equation of any other state Gibbs energy (ΔG) was:

$$\Delta G = \Delta G^o + RT \ln K$$

where
R: the general gas constant (8.314 J K^{-1} $mole^{-1}$)
T: temperature (Kelvin)
K: adsorption equilibrium value.

According to Adamson [27], chemical adsorption energy threshold was 5 kcal $mole^{-1}$ or 20 kJ $mole^{-1}$. Thus, the adsorption process of Pb(II), Cd(II) and Cr(III) ions onto the calixarene polymer can be classified as chemical adsorption.

Based on Table 2, the order of the maximum adsorption capacity for the metals was Cr(III)>Pb(II)>Cd(II). According to Hard Soft Acid Base (HSAB) theory of Pearson (1963), strong acids tend to interact with hard bases to form complexes, as well as soft acids with soft bases. Moreover, Cr(III) ions could be classified as strong acid, Pb(II) ion is a medium acid, whereas Cd(II) ion is a soft acid. As a consequence, poly-5-allyl-calix[4]arene tetra carboxylic acid which had the hard base active site of hydroxyl (-OH) group, would has stronger interaction with hard acids of Cr(III).

CONCLUSION

The adsorption kinetics of Pb(II), Cd(II) and Cr(III) ions using poly-5-allyl-calix[4]arene tetra carboxylic acid adsorbent followed the pseudo second order kinetics models, with rate adsorption constants of 2×10^{-2}; 5×10^{-3}, and 3.1×10^{-2} g $mole^{-1}$ min^{-1}, respectively. The adsorption isotherm of Pb(II) and Cd(II) ions tends to follow Freundlich isotherm, whereas that of Cr(III) tends to follow the Langmuir isotherm. In addition, the adsorption capacity of Pb(II), Cd(II) and Cr(III) ions were 104.04, 61.78 and 228.69 μmole/g, with adsorption energy of 24.87; 21.62 and 31.07 KJ/mole, respectively.

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