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SYNTHESIS OF POLY- TETRA-*p*-ALLYLCALIX[4]ARENE TETRA ACETIC ACID ADSORBENT FOR Cr(III) AND Pb(II) METAL IONS

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ABSTRACT

This paper discusses the preparation, characterization, and the evaluation of adsorption properties of resin poly-tetra-*p*-allylcalix[4]arene tetra acetic acid from the *p-t*-butylphenol. The synthesized resins were applied as an adsorbent for Cr(III) and Pb(II) metal ions. The adsorption was conducted in a batch system by investigating the effects of acidity (pH), contact time and initial concentration of a heavy metal solution. The adsorption of Cr(III) and Pb(II) metal ions on the resin had the optimum pH rating in region of 4–6 and reached the equilibrium condition in 40 minutes. The adsorption of Cr(III) and Pb(II) metal ions on the resin follows the Langmuir isothermal pattern with the linearity constant (R^2) of Cr(III) and Pb(II) adsorption, whose results were 0.9640 and 0.9716, respectively. The adsorption capacity of Cr(III) and Pb(II) metal ions is 323.0 µmole/g and 33.4 µmole/g, while the adsorption energy is 30.4 kJ/mole and 39.7 kJ/mole, respectively. Most parameters in batch systems confirm that resin is a good adsorbent for Cr(III) and Pb(II), though Cr(III) adsorption was more favorable than that of Pb(II). The outstanding adsorption abilities for Cr(III) and Pb(II) metal ions have exhibited good prospects for disposal application of polluted water and environmental protection.

Keywords: Adsorption; Metal ions*;* Poly-tetra-*p*-allylcalix[4]arene tetra acetic acid; *p-t*-butylphenol

1. INTRODUCTION

Calixarenes are cyclic oligomer of phenols linked by methylene bridges (Gutsche, 1989). They exist in a 'cup' like shape with a defined upper and lower rim and a central annulus. Their rigid conformation enables calixarenes to act as host molecules as a result of their performed activities. By functionally modifying either the upper and/or lower rims it is possible to prepare various derivatives with differing selectivity for various guest ions and small molecules. Calixarenes lend themselves well to many applications because of the multiplicity of options for such structural elaboration (Mc.Mahon et al., 2003). Calixarenes can be used in various applications because of the number of geometry variations possible within its functional groups. Ohto et al., (1997) used tetracarboxylic *p-t*-octylcalix[4]arene and tetraamide *p-t*-

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octylcalix[4]arene for the adsorbent of some heavy metal cations such as Pb(II), Cd(II), Cu(II) and Ag(I).

Research on the polymeric calixarenes is still limited. Up to now, two methods have been used to synthesize calixarene-based polymers (Yang et al., 2010). One is the grafting method, i.e. immobilization of calixarene derivatives on a polymer matrix such as dextrans (Akkus et al., 2008) and poly-acrylate (Mendrek and Trzebicka, 2009). Another method is copolymerization of calixarene with other active bi-functional monomers, such as tetraphthaloyl dichloride (Tabakci et al., 2006) and norbornone (Yang and Swager, 2007).

In the case of the heavy metals problem, the heavy metals and their speciation products are un-biodegradable and tend to accumulate, thus exceeding the lethal concentration (LC) levels. For the removal of toxic metal cations from aqueous media, immobilization of calixarenes on a polymer support has been reported in the literature (Yilmaz et al., 2006) and with a chitosan-linked calix[4]arene chelating polymer (Tabakci and Yilmaz, 2008). In this research, we reported the synthesis of resin poly-tetra-*p*-allylcalix[4]arene tetra acetic acid and its application to adsorption of Cr(III) and Pb(II) metal ions. This poly-tetra-*p*-allylcalix[4]arene tetra acetic acid synthesis is shown schematically in Figure 1.
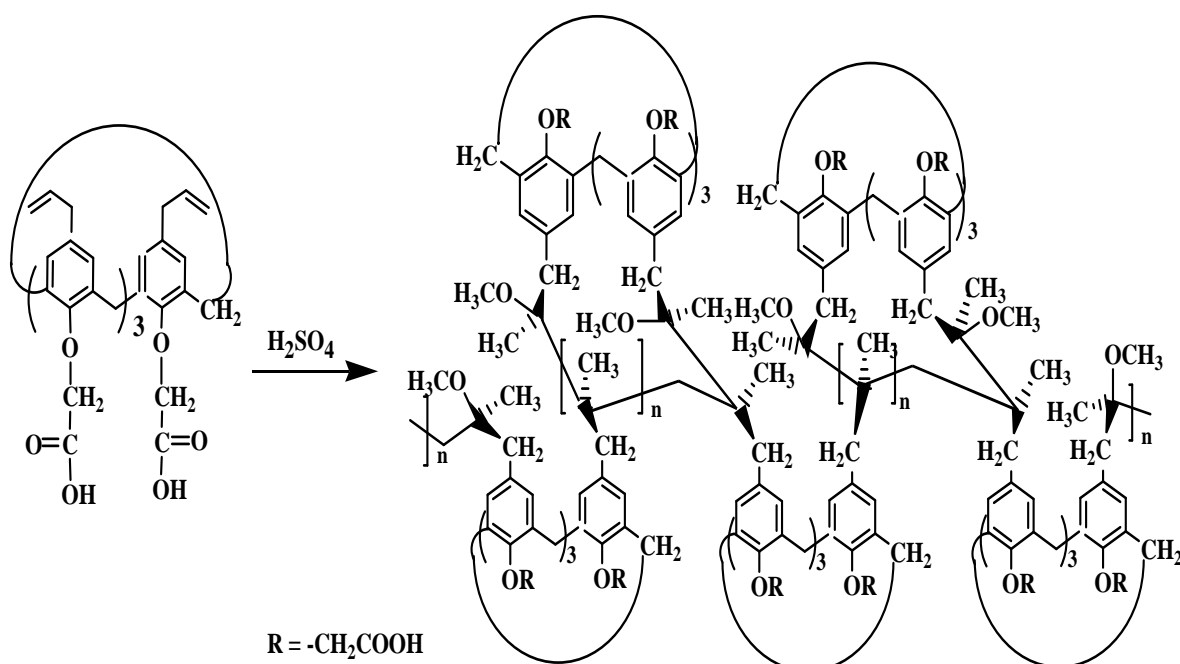

Figure 1 Synthesis of poly-tetra-*p*-allylcalix[4]arene tetra acetic acid

2. EXPERIMENTAL
2.1. Materials
p-t-Butylcalix[4]arene and tetra-hydroxycalix[4]arene were prepared according to the procedures reported previously (Gutsche, 1989). The synthesis of tetra-*p*-allylcalix[4]arene tetra acetic acid was followed the procedure reported by Kusumaningsih et al. (2010). All the chemicals were purchased from Merck or Aldrich.

2.2. Instrumentation
IR spectra were recorded on a Shimadzu Prestige-21 FTIR spectrometer as KBr pellets. H NMR spectra were obtained in the designated solvent (CdCl$_3$) on a JEOL-MY500 proton

Nuclear Magnetic Resonance Spectrometer. The surface structures characterization is from the resin using SEM. The surface area of poly-tetra-*p*-allylcalix[4]arene tetra acetic acid was characterized using SAA Quantachrome NoraWin2. Elemental analyses were performed on Perkin Elmer 3110 USA Atomic adsorbtion spectrofotometer.

2.3. Procedure

2.3.1. Synthesis of poly-tetra-p-allylcalix[4]arene tetra acetic acid

In a 100 mL three-necked flask, provided with a reflux condenser and a nitrogen pipe connector, was dissolved tetra-*p*-allylcalix[4]arene tetra acetic acid (0.15 g) in chloroform (15 mL). H_2SO_4 (0.4 mL) was then added into the mixture [0.1 mL of H_2SO_4 was added every 30 minutes]. The polymerization was performed for 5 h, which was showed by the disappearance of the starting materials in TLC plate. The reaction was then terminated by a methanol (0.5 mL) addition. The chloroform layer was washed with water until neutral, dried over Na_2SO_4 anhydrous and evaporated using a rotary evaporator. The resulted polymer was then dried in the desiccator.

2.3.2. Adsorption studies of Cr(III) and Pb(II) metal ions by resin

As much as 0.004 g of resin was shaken with 10 mL of aqueous solution containing of cadmium cation with various concentrations (4, 8, 12, 16, and 20 ppm) in a 20 mL-closed glass flask at 25°C, at various pH and contact time reactions and then the solution was filtered off. After filtering through 0.45 μm membrane filter, the concentration of metal ions in the supernatant was analyzed by using AAS. Sample and blank solutions were analyzed under the same condition. The amount of metal ions adsorbed was considered to be the difference between the initial and the remaining amount in the reacting solution each time a sample was analyzed.

The effect of pH on adsorption was investigated in the pH range 2.0-7.0 at room temperature. Experiments for the effect of contact time were performed from various contact times which were 5, 10, 20, 40, 80, 160 and 320 min, respectively.

3. RESULTS AND DISCUSSION

3.1. Synthesis of poly-tetra-*p*-allylcalix[4]arene tetra acetic acid

Crosslink polymerization of tetra-*p*-allylcalix[4]arene tetra acetic acid was performed by concentrated sulphuric acid as the catalyst under a nitrogen atmosphere. The reaction was terminated by adding small quantities of methanol. The resin polymer was obtained as yellow crystals with the melting point of 150°C in 85.54% yield and the relative molecular weight, obtained by Ubbelohde Viscometer, was 1.06×10^7 g/mol.

The success of the reaction can be proven by the FTIR spectrum (Figure 2 and Figure 3) and ^{1}H NMR spectrum (Figure 4). Figure 2 shows FTIR spectrum of materials before polymerization. In the FTIR spectrum (Figure 3) was shown by the disappearance of C=C aliphatic group absorption at 1647 cm^{-1}. This indicated that the double bond of the 'silly'?? group that disappeared and a new bonding polymer was formed due to polymerization addition reaction to give the expected product. The appearance of hydroxyl group at 3425 cm^{-1} is predicted from water which was trapped into poly-tetra-*p*-allylcalix[4]arene tetra acetic acid in neutralization process.
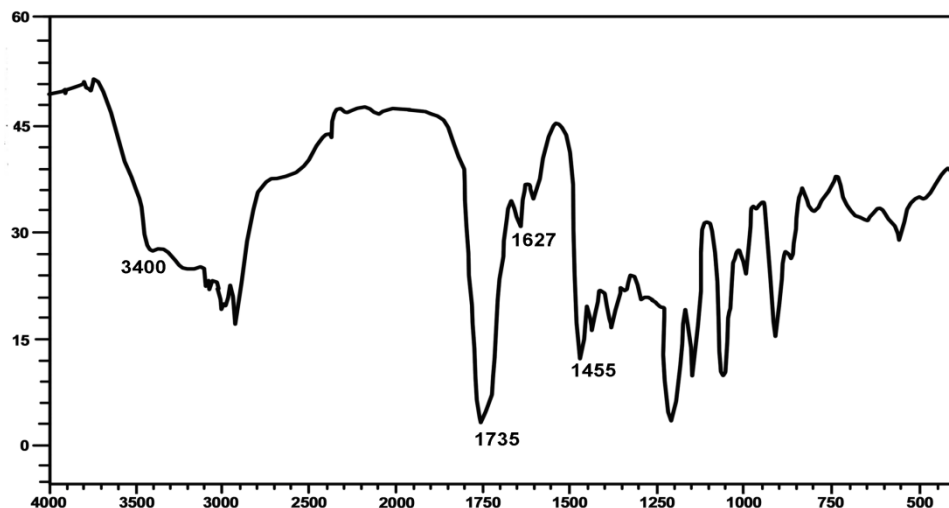
Figure 2 FTIR Spectrum of tetra-*p*-allylcalix[4]arene tetra acetic acid
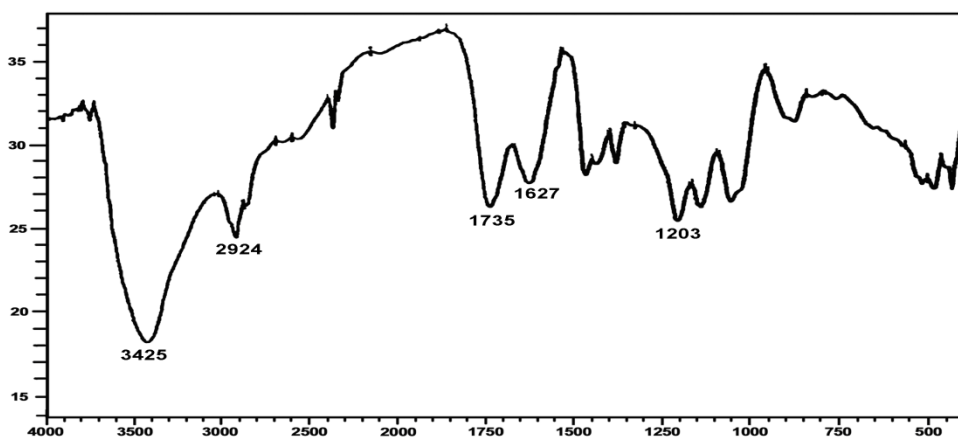(before polymerization)

Figure 3 FTIR Spectrum of poly-tetra-*p*-allylcalix[4]arene tetra acetic acid

As expected, the ^{1}H NMR spectrum does not only show the existence of vinyl protons signals at δ 5.05–5.03 (C=CH$_2$), indicating that the vinyl groups had been polimerized. Also, the signal of 1H-NMR spectra of polymers was assigned to appropriate protons. However, it was difficult to deduce the conformation of tetra-*p*-allylcalix[4]arene tetra acetic acid units in polymers due to the absence of -CH$_2$- groups on tetra-*p*-allylcalix[4]arene tetra acetic acid skeleton and the overlapped signals for ArH. These results might indicate that they adopted the alternate or mixed conformations, which are in accordance with the conformation studies of the compounds tetra-*p*-allylcalix[4]arene tetra acetic acid. The alternate or mixed conformation was favourable for intermolecular bridging which resulted in cross-linked polymeric structures (Kusumaningsih, 2010).
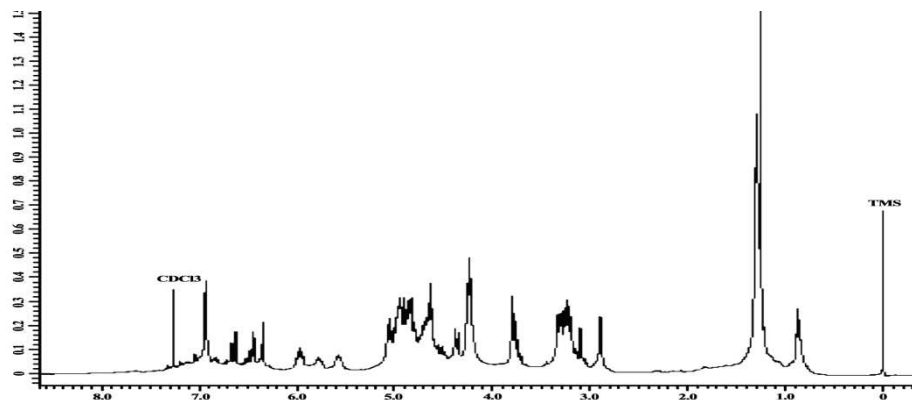
Figure 4 ^{1}H NMR Spectrum of poly-tetra-*p*-allylcalix[4]arene tetra acetic acid

The surface area of poly-tetra-*p*-allylcalix[4]arene tetra acetic acid was characterized using SAA Quantachrome NoraWin2 with physisorption analysis models using N_2 as adsorbate (m.w. 28.013 g) at temperature 77.350 K, cross section 16.200 Å2 and Liquid density 0.808 g/cc. Surface area analysis methods using *Brunauer-Emmett-Teller* (BET) and *Barrett-Joyner-Halenda* (BJH). The results were displayed in Table 1.

Table 1 Surface area analysis of poly-tetra-*p*-allylcalix[4]arene tetra acetic acid

Methods	Parameter	poly-tetra-*p*-allylcalix[4]arene tetra acetic acid
BET	Slope	68.77
	Intercept	20.67
	coefficient of correlation	0.999684
	Constant	4.327
	Surface area	38.939
	Total volume of porous	4.922×10^{-2}
		(r < 1238.8 Å P/P_0 = 0.9922)
BJH	Surface area	29.110
	Volume of porous	0.048
	Average of radii porous	15.371

The surface structures of poly-tetra-*p*-allylcalix[4]arene tetra acetic acid were also observed by scanning electron microscopy (SEM). Figure 5 shows the SEM micrographs of poly-tetra-*p*-allylcalix[4]arene tetra acetic acid. As expected, it can be seen that poly-tetra-*p*-allylcalix[4]arene tetra acetic acid was sparsely porous and crosslinked netty architectures are shown. Also, SEM analysis indicated that structure of polymer was amorphous and heterogeneous.
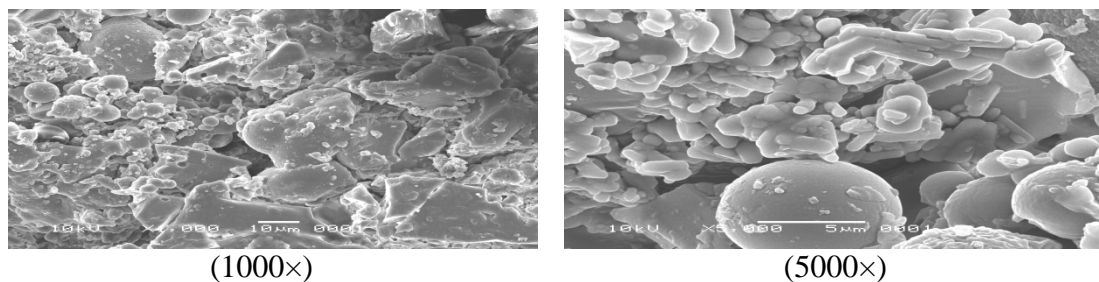

(1000×)   (5000×)

Figure 5 Micrographs of poly-tetra-*p*-allylcalix[4]arene tetra acetic acid

3.2. Adsorption of Cr(III) and Pb(II) metal ions by poly-tetra-*p*-allylcalix[4]arene tetra acetic acid

We performed solid-liquid adsorption studies of metal ions by using poly-tetra-*p*-allylcalix[4]arene tetra acetic acid as adsorbent. The adsorption capacities and energy adsorption were calculated.

3.2.1. Effect of pH

In an adsorption process, the pH of the aqueous solution is an important controlling parameter. The pH primarily affects the ionization degree of the adsorbate and the surface property of the adsorbent. Figure 6 depicts the effect of pH on the adsorption of Cr(III) and Pb(II) metal ions on poly-tetra-*p*-allylcalix[4]arene tetra acetic acid.
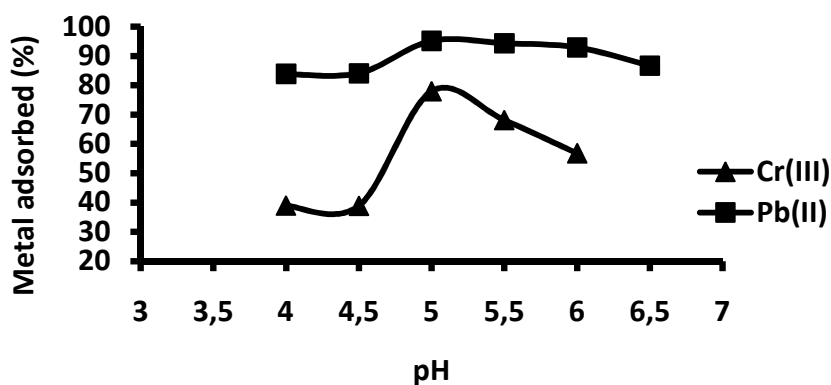

Figure 6 Effect of pH on adsorption efficiency of metal ions by resin

In the case of the influence of pH, the optimum pH value was predicted on the range of 4-6 as on that pH region, the best equilibrium condition occurred, where electrostatic repulsion between adsorbent and adsorbate was on its lowest. In addition, the precipitation of the metals as their hydroxide had not much occurred yet.

The fact that the amount of metal cation adsorbed at low pH was only a little apparently was caused by the occurrence of protonation of most donating groups, especially OH groups, of resin. It was envisaged that the interaction between resin and Cr(III) and Pb(II) metal cations involved an interaction between an oxygenated lone pair of electrons and metal cation vacant orbitals. As the amount of H^+ at low pH was sufficiently excessive in comparison to that of metal cation, most of the oxygen paired electrons perhaps did coordinate with H^+ and not with metal cation. The size of H^+, which is much smaller than that of metal cation, apparently also assisted the occurrence of interaction between oxygen pair electrons of resin and H^+. When the initial pH was sufficiently high (more than 5), there was only a limited amount of H^+ available in the system. Accordingly, the interaction occurring in the system was dominated by the interaction between the oxygenated lone pair electrons of resin and the metal cation vacant orbital. This is the reason why the amount of metal adsorbed at relatively high pH values was significantly high. However, increasing initial pH to a value higher than 5.0 is not a good idea as there has been precipitation of some of metal cations (Jumina, 2007).

3.2.2. 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 Cr(III) and Pb(II) by poly-tetra-*p*-allylcalix[4]arene tetra acetic acid were shown in Figure 7.
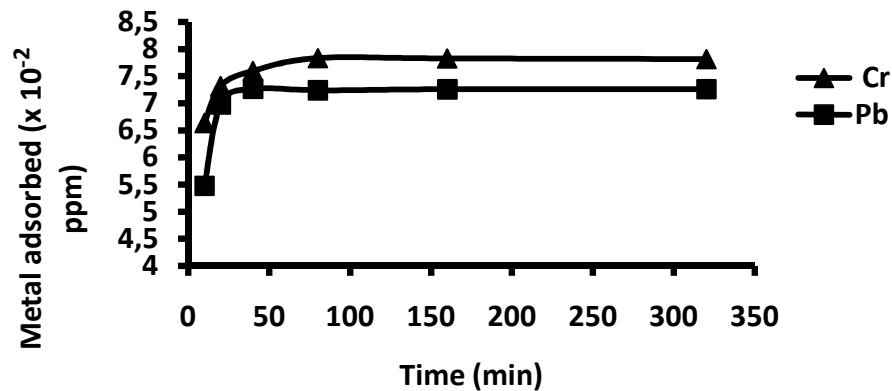

Figure 7 Effect of contact time on removal efficiency of metal ions by resin

The Cr(III) and Pb(II) adsorption occurred in the first 10 to 40 minute, and thereafter a very slow sorption was noted when determining residual Cr and Pb present in equilibrated solution. The optimum adsorption contact time for Cr(III) and Pb(II) ions were 80-minutes and 40-minutes, respectively, with the amount of Cr(III) and Pb(II) adsorbed of 7.8313×10^{-2} and 7.2642×10^{-2} ppm, respectively.

If the adsorption equilibrium has been reached, the addition of the interaction time did not increase the amount of adsorbed metal. In general, the amount of metal cations adsorbed has a similar pattern in which the adsorption has increased along with the additional contact time allocated to the period whereby the additional time was no longer than the contact time was increased by the amount of adsorbate. At the 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 contact time. This shows that there has been saturation on the active sites of the adsorbent.

3.3. Adsorption kinetics

The experimental data of contact time effect on the adsorptions of Cr(III) and Pb(II) respectively were used for kinetic modeling. The model equations used for fitting the data were: 1st order (Lagergren) and pseudo 2nd order equations. The correlation coefficient (R^2) resulted from a linear plot of $\log(q_e-q)$ versus t and t/q versus t (shown in Table 2).

Table 2 Kinetic parameters for Cr(III) and Pb(II) adsorptions by resin

Kinetic model	Cr(III)		Pb(II)	
	R^2	k	R^2	k
1st order (Lagergren) equation $\log(q_e-q_t) = \log q_e - kt$	0.9111	- 0.00540 (min^{-1})	0.8656	- 0.0079 (min^{-1})
Pseudo 2nd order equation (Ho) $t/qt = \frac{1}{2} kq_e^2 + t/q_e$	0.9980	500×10^{-2} (g.mg^{-1}.min^{-1})	0.9746	21.00×10^{-2} (g.mg^{-1}.min^{-1})

The adsorption rate constant (k) was calculated using slope or intercept values from the equation, where q_e and q (both in mmol.g^{-1}) are the amounts of metal ion adsorbed (metal uptake) at equilibrium and at time t (min), respectively. Based on the linear regression values, the kinetics of Cr(III) and Pb(II) adsorptions onto resin could be well described by two equations, but the pseudo 2nd order equation was the best. Thus, it appeared that pseudo 2nd order was the most valid kinetic model.

3.4. Adsorption isoterms

The equilibrium data in the adsorbtion of Cr(III) and Pb(II) onto resin were analyzed by using Freundlich and Langmuir isotherms, i.e. log q_e = log K + 1/n log C_e and $1/q_e$ = 1/(K $q_o.C_e$) + $1/q_o$, respectively, where q_e is the amount adsorbed at equilibrium (µmol/g), C_e is the solution concentration at equilibrium (µmol/L), q_o (µmol/g) is the maximum capacity of adsorption, and K is the adsorption constant. The results of linear plots of log C_e versus log q_e (Freundlich model) and $1/q_e$ versus $1/C_e$ (Langmuir model) are shown in Table 3.

Table 3 Correlation coefficients parameters for Cr(III) and Pb(II) adsorptions

Models	Cr(III)	Pb(II)
	R^2	R^2
Langmuir	0.9640	0.9716
Freundlich	0.6610	0.8520

The data in Table 3 shows high values of correlation coefficients (R^2) indicating linear relationships, which confirm the applicability of both adsorption isotherms. The R^2 values of Cr(III) adsorption were 0.9640 and 0.6610 for Langmuir and Freundlich models, respectively. The R^2 values of Pb(II) adsorption were 0.9716 and 0.8520 for Langmuir and Freundlich models, respectively. Thus, adsorption of Cr(III) and Pb(II) onto resin tends to follow the Langmuir isotherm. This means that the process of adsorption occurred in the monolayer, with the assumption that the maximum adsorption occurred when all active sites were filled by the adsorbate and monolayer as it was formed.

Variation of Gibbs free energy (ΔG) for the retention of adsorbate on adsorbent was determined from the adsorption constant with the aid of equation ΔG = -RT ln K. Some quantitative descriptions of adsorption system (q_o, K and ΔG) on the basis of the Langmuir isotherm model are given in Table 4. Eventually, the calculated adsorption capacities (q_o), adsorption constant (K) and energy adsorption (ΔG) of Cr(III) were 323.0 µmole/g, 194 L/mole, and 30.4 kJ/mole, respectively.

The resin was able to trap Pb(II) cation with the adsorption constant was 8320 L/mole. Capacity adsorption and energy of adsorption were 33.4 µmole/g and 39.7 kJ/mole, respectively.

Table 4 Quantitative descriptions of Cr(III) and Pb(II) adsorptions on the basis of the Langmuir isotherm

Cation	q_o (µmole/g)	K (L/mole)	ΔG (kJ/mole)
Cr(III)	323.0	194	30.4
Pb(II)	33.4	8320	39.7

Based on Table 4, the order of the maximum adsorption capacity for the metals was Cr(III) > Pb(II). According to Hard Soft Acid Base (HSAB) theory, 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 acids whereas Pb(II) ion is a medium acid. As a consequence, poly-tetra-*p*-allylcalix[4]arene tetra acetic acid which had the hard base active site of hydroxyl (-OH) group, would has stronger interaction with had acid of Cr(III).

Adsorption capacities of resin poly-tetra-*p*-allylcalix[4]arene tetra acetic acid comparison with other adsorbent metal ions were presented at Table 5.

Table 5 Comparison of adsorption capacities of resin poly-tetra-*p*-allylcalix[4]arene tetra acetic acid with other adsorbents

Adsorbent	Adsorption capacities (µmol/g)		References
	Cr(III)	Pb(II)	
resin poly-tetra-*p*-allylcalix[4]arene tetra acetic acid	323	33	This research
C-4-Methoxyphenylcalix[4]resorcinarene	6	173	Jumina, 2007
calix[4]arene-based chitosan polymer	-	360	Tabakci, 2008
chitosan	-	244	Kelesoglu, 2007

Based on Table 5, for the adsorption of Cr(III), adsorption capacities of resin poly-tetra-*p*-allylcalix[4]arene tetra acetic acid higher than C-4-methoxyphenylcalix[4] resorcinarene, but adversative matter happened at Pb(II) adsorption. Resin poly-tetra-*p*-allylcalix[4]arene tetra acetic acid is resin polymer from tetra-*p*-allylcalix[4]arene tetra acetic acid which has four benzene residues, four hydroxyl groups, and four carbonyl groups. The structure of poly-tetra-*p*-allylcalix[4]arene tetra acetic acid was sparsely porous with crosslinked netty architectures. This matter can improve adsorption capacities of resin.

Capacities adsorption of Pb(II) by resin poly-tetra-*p*-allylcalix[4]arene tetra acetic acid compared to calix[4]arene-based chitosan polymer, shows a smaller result, as according to similar result from Tabakci, 2008. Research from Kelesoglu (2007), is known to indicate that adsorbent chitosan is good for Pb(II) adsorption.

4. CONCLUSION

Preparation and characterization of resin poly-tetra-*p*-allylcalix[4]arene tetra acetic acid was successfully achieved. A resin of poly-tetra-*p*-allylcalix[4]arene tetra acetic acid was obtained as a yellow solid with m.p. of 150ºC in 85.54% yield. The adsorption study of Cr(III) and Pb(II) metal ions were performed by poly-tetra-*p*-allylcalix[4]arene tetra acetic acid in batch system. The adsorption of Cr(III) and Pb(II) metal ions on the resin follow the Langmuir isothermal pattern with the linearity constant (R^2) of Cr(III) and Pb(II) adsorption rates were 0.9640 and 0.9716, respectively. Interaction between adsorbent poly-tetra-*p*-allylcalix[4]arene tetra acetic acid with Cr(III) and Pb(II) metal ions had adsorption capacities, occurring in a row of 323.0 µmole/g and 33.4 µmole/g, with adsorption energy is 30.4 kJ/mole and 39.7 kJ/mole, respectively. Most parameters in batch systems confirm that resin is a good adsorbent for Cr(III) and Pb(II), although Cr(III) adsorption was more favorable than that of Pb(II). The outstanding adsorption abilities for Cr(III) and Pb(II) metal ions have exhibited good prospects for disposal application of polluted water and environmental protection.

5. ACKNOWLEDGEMENTS

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