SYNTHESIS OF POLYPROPYLCALIX[6]ARENE FROM *p-t*-BUTYLPHENOL AS ADSORBENT FOR Cr(III) METAL ION

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ABSTRACT

A study has been conducted to synthesize a novel polypropylcalix[6]arene polymer using p-t-butylphenol as a starting material. It was of interest to investigate the capability of the polymer with a tunnel-like structure, as adsorbent to trap the heavy metal cation such as Cr^{3+}. The synthesis was carried out in several steps i.e (1) formation of p-t-butylcalix[6]arene from p-t-butylphenol as a starting material, (2) treatment of p-t-butylcalix[6]arene with 4.95 equivalents of allyl bromide under alkaline conditions to yield p-t-butyl-37,40-diallyloxy-38,39,41,42-tetrahydroxy-calix[6]arene, and (3) polymerization of p-t-butyl-37,40-diallyloxy-38,39,41,42-tetrahydroxycalix[6]arene by treatment with concentrated sulfuric acid to yield polypropyl-calix[6]arene. The application of polypropylcalix[6]arene for trapping Cr(III) was investigated by stirring the suspension of calixarene under variation of pH, time, and adsorbent mass. IR and ^1H NMR spectra, showed that two allyl groups had been incorporated to the lower rim of the p-t-butylcalix[6]arene and the polymer was obtained as brownish green crystals with the melting point of 108-110 °C. The study also showed that the polypropylcalix[6]arene was able to trap Cr(III) cation. The optimum adsorption conditions were achieved at pH 5, contact time 60 min and concentration 12 mg/l for every 0,008 g of polymer.

Keywords: *p-tert-butylphenol, polypropylcalix[6]arene, trapping Cr(III)*

INTRODUCTION

Calixarene-based molecules have received intense attention in the last few years. Calixarenes and their derivatives have been applied as selective binders and carriers, analytical sensors, [1-2] and in a number of instances, they were also used as catalysts in synthetic reactions and as liquid crystals [3-4].

The most attractive feature of calixarenes is their capability to serve as molecular baskets to hold other chemical guest species [5-7]. Thus calix[4]arenes and its derivatives are mainly applied as receptors in the recognition of other molecules [8-9] as well as adsorbents to trap heavy metal cations such as Pb(II) and Cr(III) cations [10-11].

To increase its polarity, it is possible to incorporate alkenyl groups such as an allyl group at the lower rim of calixarene. Ho et al. [12] and Shu et al. [13] have shown that the two allyl group at the lower rim of calix[4]arene could be incorporated by addition of allylbromide, while Jumina et al. [11] also reported that the monoallylcalix[4]-arene can be polymerized under acidic conditions to generate the corresponding polypropylcalix[4]arene polymer. Furthermore, Utomo [14] reported that the capability of this polymer to trap heavy metal cations such as Pb(II) and Cr(III)) cations are significantly greater than that of the monomer.

While considerable amount of literature there exists on calix[4]arene, its derivatives, their properties, and applications, very little has been reported on calix[6]arene. With cavity size larger than calix[4]arene, it would be interesting to study calix[6]arene and its polymerization as well as the polycalix[4]arene in regards to ability to trap heavy metals.

Treatment of calix[6]arene with allyl bromide under basic conditions is predicted to yield the allylated calix[6]arene which would undergo polymerization to further result in polypropylcalix[6]arene. Considering the cavity size of calixarene can greatly influence the complexation abilities of calixarene polymer, herein, we wish to report the synthesis of a novel polycalix[6]arene polymer and the adsorption properties to the heavy metal cation such as Cr^{3+}.

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EXPERIMENTAL SECTION

Materials

Formaldehyde, *p-tert*-Butylphenol, chloroform, potassium hydroxide and other chemicals used in this study were the highest purity available from Merck or Aldrich chemical companies and were used without further purification.

Instrumentation

Melting points were obtained with an electrothermal 9100 Model Digital Melting Point apparatus, was obtained at the Laboratory of Chemistry, State Islamic University Sunan Kalijaga of Yogyakarta. Infrared (IR) spectra were recorded on a Shimadzu FTIR 8201 PC Spectrophotometer and refer to KBr disks. ^{1}H NMR spectra were obtained in the designated solvent ($CDCl_3$) on a JEOL-MY500 proton Nuclear Magnetic Resonance Spectrometer. Concentration of cation was determined using a GBC Atomic Absorption Spectrophotometer (AAS).

Procedure

Synthesis of p-t-butylcalix[6]arene

A slurry of 5.0 g (33.0 mmol) of *p*-tert-butylphenol, 1.98 g (66 mmol) of paraformaldehyde, and 0.83 g (14.85 mmol) of potasium hydroxide in 50 mL of *p*-xylene was refluxed in an inert atmosphere with efficient stirring for 4 h in a 250 mL round bottomed flask equipped with a condenser and a Dean-Stark water collector. The cooled reaction mixture was filtered and the solid that was obtained was suspended into chloroform (150 mL) and shaken for 3 min. The organic phase was separated, washed with water (2 x 80 mL), dried over sodium sulfate anhydrous and concentrated in vacuum leaving approximately 50 mL of the residue. Methanol (40 mL) was added and the resulting precipitate is filtered and dried to afford a white solid (3.5 g, 65.47%), m.p. 370–372 °C); IR (KBr) 3425 cm^{-1}(OH stretching), ν (C=C aromatic) = 1627 cm^{-1}, (*t*-butyl) = 1365 cm^{-1} and ν(methylene group) = 1481 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 10.5 (s, 1, ArOH), δ 7.10 (s, 2, ArH), δ 3.9 (d, 2, CH_2), δ 1.27 (s, 9, $C(CH_3)_3$).

Synthesis of p-t-butyl-37,40-diallyloxy-38,39,41,42-tetra-hydroxycalix[6]arene

A mixture of 4.86 g (5 mmol) of *p*-*t*-butylcalix[6]arene, 1.24 g (9 mmol) K_2CO_3, 1.42 mL (16.5 mmol) allylbromide, and 100 mL of dry acetone was refluxed under dry N_2 condition for 48 h. The precipitate was filtered and acetone was evaporated. The residue was recrystallized with $CHCl_3$ and CH_3OH to yield *p*-*t*-butyl-37,40-diallyloxy-38,39,41,42-tetrahydroxycalix[6]arene, afforded 2.69 g (51.18%) of yellow white crystals: mp 141-143 °C; IR (KBr): 3410 cm^{-1}(OH stretching), ν(vinyl group,C=CH_2) 925 cm^{-1}; ^{1}H-NMR ($CDCl_3$), δ 7.06-7.24 (m, 12, ArH), δ 6.80 (m, 2, C=CH-C), δ 5.33-5.52 (m, 4H, C=CH_2), δ 4.24-4.49 (d, 4H, OCH_2C), δ 3.82-3.89 (d, 4H, $ArCH_2Ar$), and δ 1.2 (s, 54, $C(CH_3)_3$).

Polymerization of diallyloxycalix[6]arene

To 1 g of *p*-*t*-butyl-37,40-diallyloxy-38,39,41,42-tetrahydroxycalix[6]arene in 100 mL chloroform was added concentrated sulfuric acid (0.1 mL) in 0.25 mL portions every 30 min. The reaction mixture was stirred at for 8 h and the polymerization was terminated by adding 0.5 mL of methanol. The mixture was decanted and the precipitate was dissolved in diethyl ether and washed until neutral. The chloroform layer was washed until neutral and combined with the ether layer. The combined layers were dried with anhydrous Na_2SO_4 and evaporated to yield the polymer which was dried in a desiccator. The polymer was obtained as brownish green crystals 0.68 g, m.p. 108-110 °C and its relative molecular weight was 12,510 g/mol (obtained by Ubbelohde Viscometer); IR (KBr) 3363 cm^{-1}(OH stretching), ν (C=C aromatic) = 1597 cm^{-1}, ν *t*-butyl = 1365 cm $^{-1}$ and ν methylene group 1481 cm^{-1}; ^{1}H- NMR ($CDCl_3$): δ 7.06-7.24 (m, 12, ArH), δ 3.82-3.89 (d, 4H, $ArCH_2Ar$), δ 1.2 (s, 54, $C(CH_3)_3$) and the absorption peaks of vinyl's were disappeared.

Trapping of Cr^{3+}

The effects of pH, contact time and initial adsorbate concentration were investigated by conducting batch studies. Batch adsorption experiments were carried out by shaking 0.008 g of the polypropylcalix[6]arene with 10 mL of the Cr (III) solution (4-20 mg/L) at various pH (1-6) for different reaction durations (15–240 min). The pH adjustments were performed by addition of 0.1 M HCl or 0.1 M NaOH.

RESULT AND DISCUSSION

Synthesis

The synthesis of *p*-*t*-butylcalix[6]arene (compound **1**) was followed the procedure reported by Gutsche et al. [2] and Jumina et al. [18]. *p*-*t*-butylphenol was treated with 2 equivalents of paraformaldehyde and 0.45 equivalent of potassium hydroxide in refluxing *p*-xylene for 4 h resulting 65.47% yield of calix[6]arene. The key step in synthesizing *p*-*t*-butylcalix[6]arene is the formation of the methylene bridge as shown in Fig. 1. The successful synthesis of *p*-*t*-butylcalix[6]arene was

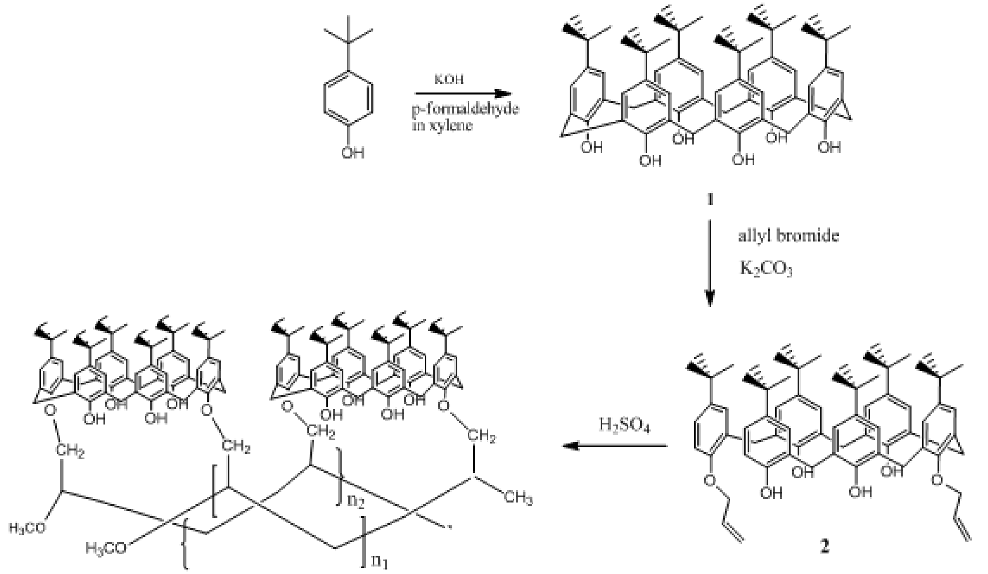

Fig 1. Polymerisation of *p*-*t*-butyl-37,40- diallyloxy-38,39,41,42-tetrahydroxy-calix[6]arene

characterized by the relatively high melting point measured (370–372 °C, decomposed), IR spectrum and ^{1}H NMR spectrum. The IR spectrum shows a strong broad band of the methylene groups at 1481 cm^{-1} and the absorption at 3425 cm^{-1}, indicating the presence of some OH groups in the molecule which possibly involve in an intramolecular hydrogen bonding. This is supported by the integration of ^{1}H NMR spectrum shows the number of hydrogen from –OH group was 6, instead of 4.

The *p*-*t*-butyl-37,40-diallyloxy-38,39,41,42-tetrahydroxycalix[6]arene (compound **2**), was prepared by treatment of *p*-*t*-butylcalix[6]arene with 4.95 equivalents of allyl bromide under dry N_2 condition. In the IR spectrum of this product (as monomer), shows a strong absorption peak at 925 cm^{-1}, indicating the presence of vinyl terminal. This is supported by the integration of ^{1}H NMR spectrum shows the number of the ether linkages of the diallyl ether (compound **2)** was 2. This indicated that the two allyl groups had been incorporated to the lower rim of the *p*-*t*-butylcalix[6]arene to form *p*-*t*-butyl-37,40-diallyloxy-38,39,41,42-tetrahydroxycalix[6]arene. This spectrum is similar to the ^{1}H NMR spectra of diallyl ether of calix[4]arene [13], and calix[4]arene syn-1,3-dibenzoate [15] which both contain two –C-O-C bond.

As a monomer, this product was polymerized with concentrated sulfuric acid to yield polypropylcalix[6] arene. The structure of polymer (compound **3**) was characterized by IR and ^{1}H NMR. In the IR spectrum, the absorption peaks of vinyl were disappeared which mean almost all of the vinyl groups were polymerized. As expected, the proton NMR spectrum does not also show the existence of vinyl protons signal which resonate at δ 6.80 ppm (C=CH-C) and δ 5.33-5.52 (C=CH$_2$), indicating that the vinyl groups had been polymerized. The polymer was obtained as brownish green crystals and the relative molecular weight, obtained by Ubbelohde Viscometer, was 12,510 g/mol.

The application of polycalix[6]arene as adsorbent for Cr(III) metal ion

Brindle et al. [16] have reported several calix[6]-based polymers and found that some of the these polymers showed remarkable abilities to trap alkali metal ions and UO_2. Fa Fu Yang et al. [17] have also shown the adsorption properties of calix[6]amide polymers toward soft cations (Ag^+, Hg^{2+}) and hard cations (Na^+, K^+). In this paper, we report the capability of poli-diallylcalix[6]arene for trapping Cr(III) cation which is one of the major cause for water pollution in Indonesia.

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 [18]. Fig. 3 depicts the effect of pH on the adsorption of Cr(III) ion on polycalix[6]arene. It was found that Cr(III) adsorption capacity of polycalix[6]arene increased from pH 1.0 to 5.0, and decreased from pH 5.0 to 6.0, respectively and it reached maximum at pH 5.0.

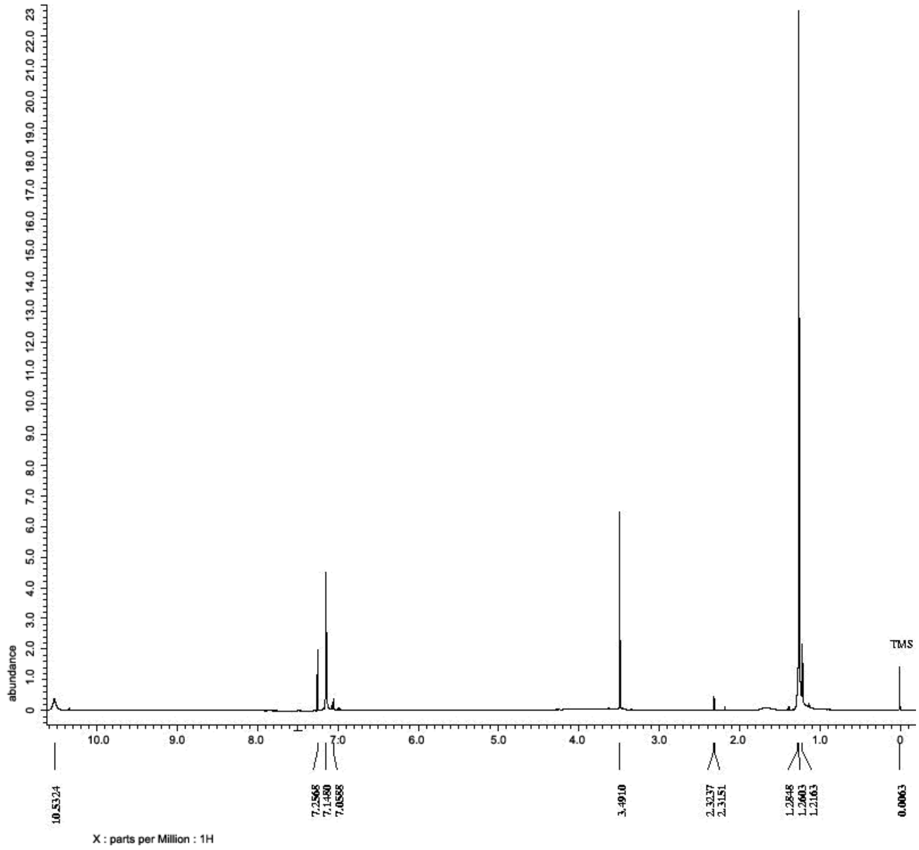

Fig 2. ^{1}H-NMR spectrum of *p*-*t*-butylcalix[6]arene

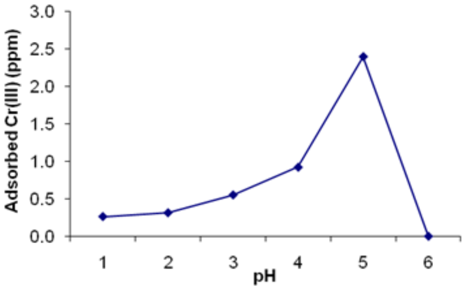

Fig 3. Effect of pH on adsorption efficiency of Cr(III) by polycalix[6]arene

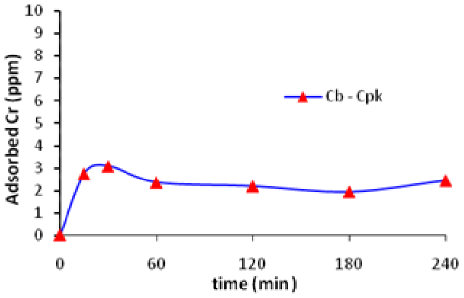

Fig 4. Effect of time on removal efficiency of Cr(III) by polycalix[6]arene

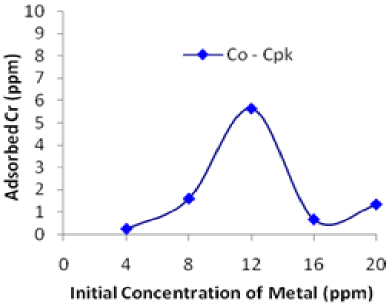

Fig 5. Effect of initial concentration of metal solution on adsorption efficiency of Cr(III) by polycalix[6]arene

This fact can be explained on the basis of surface characteristics of the adsorbent. In strong acidic solutions, the protonation takes place at O atom from the OH group which represents active sites from adsorbent so that the amount of Cr sorption would be decreased. At pH value higher than 5.0, the adsorption efficiency of Cr(III) decreased because of precipitation of $Cr(OH)_3$. A similar adsorption mechanism was presented by previous researchers on Cr(III) sorption onto *p*-(1-bromopropyl)calix[6]arene [19] and on Pb(II) sorption onto polycalix[4]arene [20].

Table 1. Langmuir and Freundlich adsorption isotherm data for Cr (III).

No	Ceq (mol/L) x 10^{-4}	m mg/g	m (mol/g) x 10^{-5}	Ceq/m x 10^{-5}	log Ceq (mg/L)	log m (mg/g)
1	0.7409	1.0021	1.9273	7.3935	0.5857	0.0009
2	1.5199	2.7426	5.2747	5.5418	0.8978	0.4382
3	1.8226	7.0675	1.3572	2.5788	0.9769	0.8493
4	3.3644	0.8439	1.6231	39.867	1.2429	-0.0737
5	4.5331	0.9494	1.8258	47.747	1.3724	-0.0226

Efect of contact time

Fig. 4 presents the time dependence of the adsorption of Cr(III). It was found that the Cr(III) adsorption increased with increasing contact time.

The Cr(III) adsorption occurred in the first 15 to 30 min, and thereafter a very slow sorption was noted when determining residual Cr present in equilibrated solution. However, the contact time required for maximum Cr(III) adsorption onto polycalix[6]arene was found to be relatively stable at 60 min.

Effect of initial concentration of metal solution

The effects of initial concentration of metal solution on the adsorption of Cr(III) is shown in Fig. 5.

The data indicates that the adsorption increases with the increasing of initial concentration of metal solution. The maximum uptakes of Cr(III) is exhibited at 12 mg/L of metal solution.

Adsorption Isotherms

The analysis of the isotherm data is important in representing the adsorption results and for design purposes. The following two isotherm models were used for fitting the experimental data obtained at room temperature and pH 5.0.

Langmuir isotherm model: C/m = 1/bK + C/b.
Freundlich isotherm model: log m = log B + 1/n (log C).
where: C, the equilibrium concentration in solution
m, metal sorbed per g sorbent at equilibrium
b, Langmuir's sorption capacity
K, sorption affinity
B, Freundlich's sorption capacity

Table 1 displays the experimental data of this research. The R^2 of data plots based on Langmuir and Freundlich isotherm models are 0.8696 and 0.0496, respectively. Since the linearity of the data plot based on the Langmuir isotherm model is greater than that based on the Freundlich isotherm model. It can be concluded that the adsorption of Cr (III) by polycalix[6]arene follows the Langmuir isotherm model. Therefore, it can be assumed that the adsorption process occurs on the monolayer instead of multilayer.

Adsorption capacity of polycalix[6]arene towards Cr(III) ion was 1.47 x 10^{-5} mol/g. The value of equilbrium constant (K) was calculated from the graphic C/m versus C. Adsorption energy was calculated from the equation: $E = \Delta G° = - RT \ln K$. The value of adsorption equilibrium constant and adsorption energy were 1.2228 x 10^4 L/mol and 23.2511 kJ/mol, respectively.

CONCLUSION

Based on the results of the experiment as described above, it was concluded that polycalix[6]arene was obtained as brownish green crystals with the melting point of 108–110 °C and the relative molecular weight was 12,510 g/mol. The polypropylcalix[6]arene was able to trap Cr(III) cation with the adsorption equilibrium constant = 1.2228 x 10^4 L/mol. Capacity and energy of adsorption were 1.47 x 10^{-5} mol/g and 23.2511 kJ/mol, respectively.

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