SYNTHESIS, CHARACTERIZATION AND ADSORPTION TEST OF POLY-TETRA-*p*-PROPENYLTETRAHYDROXYCALIX[4]ARENE FOR CADMIUM ION

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ABSTRACT

Synthesis, characterization and adsorption test of poly-tetra-p-propenyl-tetrahydroxycalix[4]arene for cadmium ion had been done. The synthesis was carried out in five steps, which were (1) synthesis of p-t-butylcalix[4]arene from p-t-butylphenol, (2) debutylation of p-t-butylcalix[4]arene, (3) tetraallylation of 25, 26, 27, 28 tetrahydroxycalix[4]arene with NaH and allylbromide in dry tetrahydrofuran, (4) Claissen rearrangement of 25, 26, 27, 28-tetrapropenyloxy- calix[4]arene, and (5) polymerization of tetra-p-propenyltetrahydroxycalix[4]arene to yield poly-tetra-p-propenyltetrahydroxycalix[4]arene. Analysis of products was performed using melting point analysis, FT-IR, and ^{1}H NMR spectrometers. The yield of polymerization was 80.35% and m.p > 380 °C. Characterization of poly-tetra-p-propenyltetrahydroxycalix[4]arene was done using SEM and SAA. Structure of poly-tetra-p-propenyltetrahydroxycalix[4]arene was sparsely porous with crosslinked netty architectures, and possessed surface area of 46.572 m^2/g. The application of poly-tetra-p-propenyltetrahydroxycalix[4]arene in the adsorption of Cd(II) cation had also been conducted. Adsorption parameters investigated included medium pH and contact time as well as adsorption isotherm. The resin could be applied as a good adsorbent in the adsorption of Cd(II) metal cation. The adsorption followed Langmuir isotherm model, where the measured adsorption capacity, adsorption constant (K), and adsorption energy were 8.5933×10^{-2} mmol/g, 485 L/mmol, and 32.653 KJ/mol, respectively.

Keywords: *poly-tetra-p-propenyltetrahydroxycalix[4]arene, adsorption, cadmium ion*

INTRODUCTION

The synthesis of calixarene can be carried out by base-catalyzed reaction. The reaction is usually applied in calixarene synthesis from *p*-alkylphenol, especially *p*-t-butylphenol via one phase reaction between formaldehyde and the base, such as NaOH or KOH [1]. The yield of the reaction is generally high (60-90%). In addition, this reaction is cheaper and easier to be performed. With the extensive and in-depth studies of all kinds of calixarene derivatives, more and more attentions were paid to calixarene-based polymers which may be processed into materials as sorbents for heavy metal cations and derivatives of aniline [2].

Researches on the polymeric calixarenes are still limited. Up to now, two methods have been used to synthesize calixarene-based polymers [2]. One is the grafting method, i.e. immobilization of calixarene derivatives on polymer matrix such as peptide resin [3], PEG [4], polystyrene [5], dextrans [6], polysilane [7] and poly-acrylate [8]. Another method is copolymerization of calixarene with other active bis-functional monomers, such as bisphenols [9], styrene [10, 11], vinyl acetate [12], diisocyanate [13], tetraphthaloyl dichloride [14], and norbornene [15].

In the case of heavy metals problem, the heavy metals and their speciation products are un-biodegradable and tend to accumulate exceed the lethal concentration (LC) levels. There are more than 20 heavy metals, but lead (Pb), cadmium (Cd), and inorganic arsenic (As) are of special concern. They are highly toxic and can cause damaging effects even at

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very low concentrations. They tend to accumulate in the food chain and in the body and can be stored in soft (e.g., liver, kidney) and hard tissues (e.g., bone) [16]. Thus, the level of cadmium in discharged wastewater should be reduced, or recycled if possible. Due to the inherent toxicity of cadmium in most organisms [17-18], this research will focus on the adsorption of cadmium using calixarene.

For the removal of toxic metal cations from aqueous media, immobilization of calixarene on a polymer support [19] and with a chitosan-linked calix[4]arene chelating polymer [20] have been reported. In this research, we report the synthesis of tetra-*p*-propenyltetrahydroxycalix[4]arene and resin poly-tetra-*p*-propenyltetrahydroxycalix[4]arene and its application in adsorption of cadmium cation.

EXPERIMENTAL SECTION

Materials

p-tert-Butylcalix[4]arene, tetrahydroxycalix[4]arene, 25, 26, 27, 28-tetra-propenyloxycalix[4]arene, and tetra-*p*-propenyltetrahydroxycalix[4]arene were prepared from *p-t*-butylphenol according to the procedures reported previously [1,16,21]. The following chemicals, potassium hydroxide (KOH), hydrochloric acid (HCl), sulphuric acid (H_2SO_4), ethanol, methanol, chloroform and sodium sulfate anhydrous (Na_2SO_4) were purchased from Merck or Sigma-Aldrich.

Instrumentation

The equipment used included infra Red (FT-IR, Shimadzu 8201 PC, KBr Pellet), Nuclear Magnetic Resonance (^{1}H-NMR, JEOL 500 MHz), Scanning Electron Microscopy (SEM, JEOL, JSM-6360LA), Surface Area Analyzer (SAA, Quantachrome NOVA 1200e) and Atomic Absorption spectrometers (AAS, Shimadzu AA-6650).

Procedure

Synthesis of poli-tetra-p-propenyltetrahydroxy calix[4]arene

Into a 100 mL three-necked round bottom flask equipped with a reflux condenser and a nitrogen pipe connector, tetra-*p*-propenyltetrahydroxycalix[4]arene (0.15 g) was dissolved in chloroform (15 mL). Sulphuric acid, concentrated (0.4 mL) was then added into the mixture (0.1 mL of H_2SO_4 every 30 min). The polymerization was performed for 7 h, which showed by the disappearance of the starting materials on TLC plate. The reaction was then terminated by the addition of methanol (0.5 mL) and gave two layers. Then, the chloroform layer was washed with water until neutral, dried with Na_2SO_4 anhydrous and evaporated using rotary evaporator. The resulted polymer was dried in a desiccator and analyzed using FT-IR, ^{1}H-NMR, SEM and SAA.

Adsorption studies

As much as 0.004 g of poly-tetra-*p*-propenyltetrahydroxycalix[4]arene was shaken with 5 mL of aqueous solution containing of cadmium cation with various concentration (4, 8, 12, 16, and 20 ppm) in 20 mL-closed glass flask at 25 °C, at various pH and contact time reaction and filtered off. After filtering through 0.45 μm membrane filter, the concentration of Cd(II) in the supernatant was analyzed by using AAS. Sample and blank solutions were analyzed under the same condition. The amount of Cd(II) sorbed was considered to be the difference between the initial and the remaining amount in the reacting solution each time a sample was analyzed.

RESULT AND DISCUSSION

Synthesis and characterization of poly-tetra-*p*-propenyltetrahydroxy-calix[4]arene

Attempts to crosslink polymerization of tetra-*p*-propenyltetrahydroxy-calix[4]arene using $BF_3O(C_2H_5)_2$ as the catalyst was also conducted in chloroform under a nitrogen atmosphere. Unfortunately, the reaction was not taken place according to TLC analysis after 7 and 30 h of polymerization. Thus, crosslink polymerization of the calixarene was performed using H_2SO_4 catalyst in chloroform under a nitrogen atmosphere. Based on TLC analysis, the polymerization was completed in 7 h. The reaction was terminated by adding small quantities of methanol. The crosslink polymerization produced brown solid having m.p. > 380 °C in 80.35% yield. This poly-tetra-*p*-propenyltetrahydroxy-calix[4]arene synthesis is shown schematically in Fig.1.

Theoretically, it can be estimated that the polymerization is taken place through cationic polymerization addition. The polymerization is initiated by the formation of secondary carbocation. The double bond of allyloxy group is protonated due to the addition of concentrated H_2SO_4. π electron in the double bond of tetraallylcalix[4]arene attacks the carbocation to form a dimer and one new carbonium is formed. This reaction is referred as a propagation step. Finally, the polymerization is terminated by adding small quantities of methanol to give poly-tetra-*p*-propenyltetrahydroxycalix[4]arene.

Regarding to FT-IR analysis, the disappearance of C=C aliphatic group absorption at 1635.5 cm^{-1} indicated that the allylic group had polymerized to give

Table 1. Surface area analysis of poly-tetra-*p*-propenyltetrahydroxycalix[4]arene

Methods	Parameter	Value
BET	Slope	61.983
	Intercept	12.79
	coefficient of correlation	0.998416
	Constant	5.845
	Surface area	46.572 m^2/g
	Total volume of porous	$8.076.10^{-2}$ (r < 1175,8 Å P/P_0 = 0.99178)
BJH	Surface area	37.382 m^2/g
	Volume of porous	0.079 cc/g
	Average of radii porous	15.358 Å

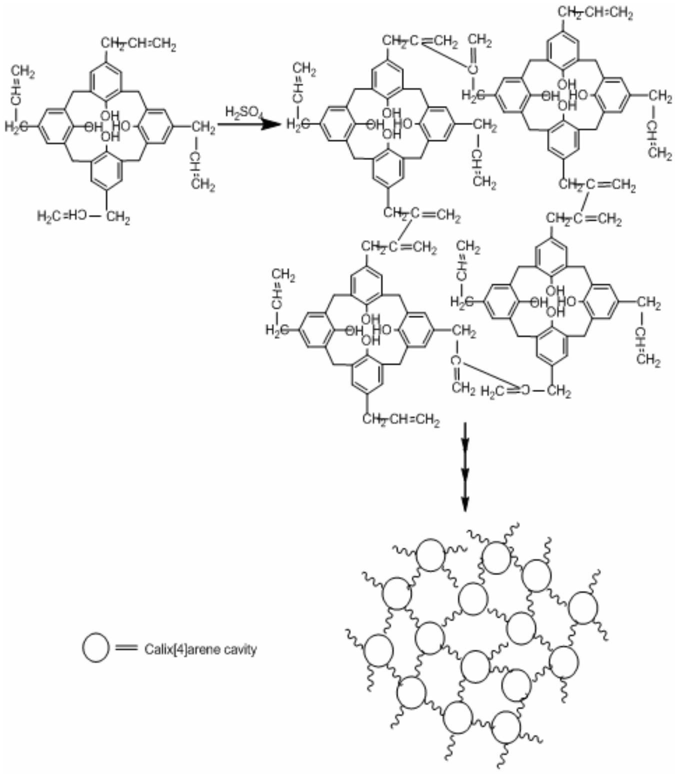

Fig 1. Synthesis of poly-tetra-*p*-propenyltetrahydroxy calix[4]arene

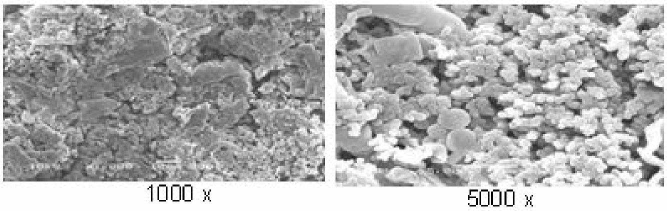

Fig 2. Micrographs of poly-tetra-*p*-propenyltetrahydroxy calix[4]arene

the product. This was the evidence that the reaction had occurred. Furthermore, the presence of hydroxy (-OH) group at 3425.3 cm^{-1} was predicted from water which was trapped into poly-tetra-*p*-propenyltetrahydroxy calix[4]arene in the neutralization process.

In the ^{1}H-NMR spectrums, it showed signal at δ = 10.1850 ppm is predicted from hydroxyl group protons. Signals at δ = 6.8616 ppm are estimated from aril (ArH) protons. The resonance of methylene group protons are estimated to appear at δ = 3.2119 ppm.

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*-propenyltetrahydroxycalix[4]arene units in polymers due to the absence of $-CH_2-$ groups on tetra-*p*-propenyltetrahydroxycalix[4]arene 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*-propenyltetrahydroxycalix[4]arene. The alternate or mixed conformation was favourable for intermolecular bridging which resulted in cross-linked polymeric structures.

The surface area of poly-tetra-*p*-propenyltetra hydroxycalix[4]arene 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 Å^2 and Liquid density 0.808 g/cc. The results were displayed in Table 1.

The surface structures of poly-tetra-*p*-propenyltetrahydroxycalix[4]arene was also observed by scanning electron microscopy (SEM). Fig. 2 shows the SEM micrographs of poly-tetra-*p*-propenyltetra hydroxycalix[4]arene. As expected, it can be seen that poly-tetra-*p*-propenyltetrahydroxycalix[4]arene was sparsely porous and crosslinked netty architectures. Also, SEM analysis showed that structure of polymer was amorphous and heterogeneous.

Adsorption of Cd(II) by resin polymer

The synthesized poly-tetra-*p*-propenyltetra hydroxycalix[4]arene was utilized as cadmium cation

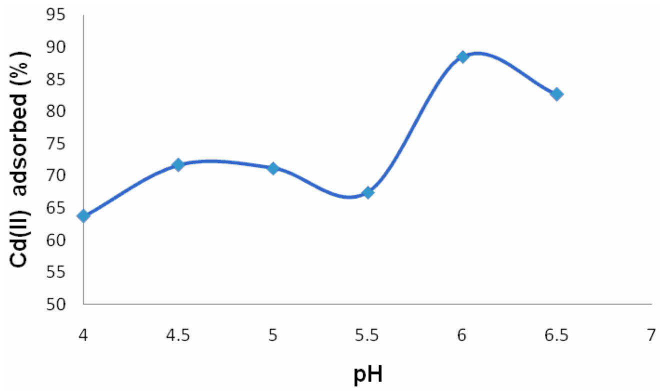

Fig 3. The effect of pH on the adsorption of Cd(II) using poly-tetra-*p*-propenyltetrahydroxycalix[4]arene

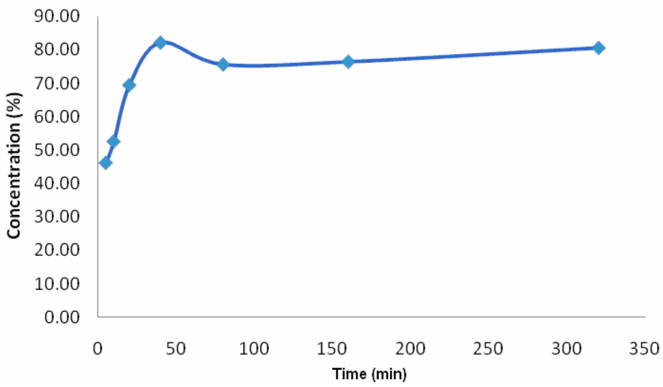

Fig 4. Effect of contact time on the adsorption Cd(II) using poly-tetra-*p*-propenyltetrahydroxycalix[4]arene

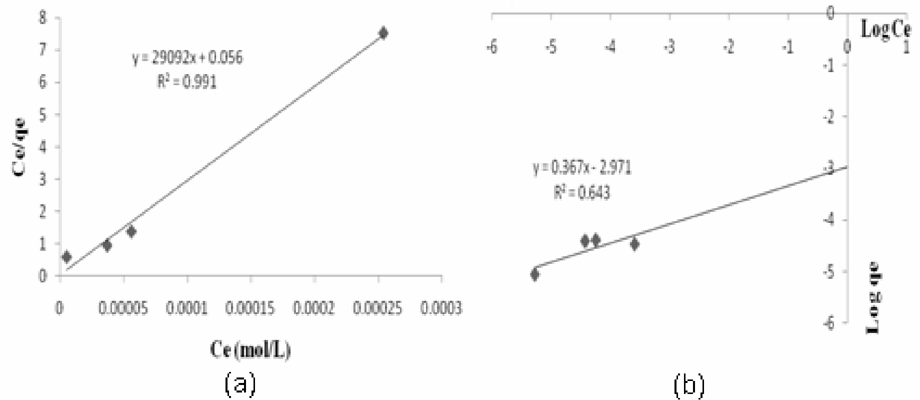

Fig 5. Adsorption Isotherm pattern of (a) Langmuir and (b) Freundlich on the adsorption Cd(II) using poly-tetra-*p*-propenyltetrahydroxycalix[4]arene

adsorbent. The investigated adsorption parameter included pH, contact time as well as adsorption isotherm.

Effect of pH

The effect of pH on the adsorption of Cd(II) by the calixarene was studied in the pH range of 4.0 to 6.5 with the initial concentration of cadmium solution of 10 mg/L. The results are displayed in Fig.3.

The amount of Cd(II) adsorbed varied with the value of initial pH and reached the optimum value at initial pH of 6.0 were 88.50 in percentage ($6.30.10^{-2}$ mmol/g). The fact that the amount of metal cation adsorbed at low pH was only a little mainly due to the protonation of the donating groups, especially hydroxyl (-OH) groups, of resin. The interaction between resin and the cation involved an interaction between oxygen lone pair electrons and the cation vacant orbitals.

Effect of Contact Time

The effect of contact time on the adsorption of Cd(II) by the calixarene was studied in the time range 5 to 320 min with pH 6.0 and the initial concentration of cadmium solution of 10 mg/L. The result is shown in Fig.4.

As shown in Fig.4, it was found that the trend of metal uptake increased along with the increase of contact time. It also showed that the Cd(II) adsorption occurred quickly in the early minutes until approximately 20 min giving the amount of Cd(II) adsorbed as much as 69.45%. Then, the Cd(II) adsorbed increased slowly as the interaction time was extended and reached its maximum adsorption value of 82.16% in 40 min. After 40 min, the amount of Cd(II) adsorbed was relatively constant indicating that equilibrium between the adsorbed metal ions and the free ions in solution had been reached.

Adsorption Isotherms

Approach of either Langmuir and Freundlich adsorption isotherm was also applied to study equilibrium of adsorption Cd(II) by the resin. Adsorption Isotherm pattern of Langmuir and Freundlich was presented in Fig.5.

Fig. 5 showed high values of correlation coefficients (R^2) indicating linear relationships, which confirmed the applicability of both adsorption isotherms.

Table 2. Quantitative descriptions of Cd(II) adsorption on the basis of the Langmuir isotherm

Cation	q_0(mmol/g)	K(L/mmol)	ΔG(kJ/mol)
Cd(II)	$8.5933.10^{-2}$	485	32.653

The R^2 values of Cd(II) adsorption were 0.993 and 0.64 for Langmuir and Freundlich models, respectively. Thus, it can be stated that the adsorption data fitted the Langmuir model test.

The equilibrium data of the adsorption of Cd(II) onto resin was then analyzed using Langmuir isotherm,

$$\frac{1}{q_e} = \frac{1}{(K.q_0.C_e)} + \frac{1}{q_0} \qquad (1)$$

where

q_e = the amount adsorbed at equilibrium (µmol/g);
C_e = the solution concentration at equilibrium (µmol/L);
q_0 = the maximum capacity of adsorption;
K = the adsorption constant

The results of linear plots of $1/q_e$ versus $1/C_e$ (Langmuir model) were presented in Table 2. Eventually, the calculated adsorption capacities, adsorption constant (K) and energy adsorption were 8.5933×10^{-2} mmol/g, 485 L/mmol, and 32.653 KJ/mol, respectively.

CONCLUSION

Preparation and characterization of resin poly-tetra-*p*-propenyltetra-hydroxy-calix[4]arene was successfully achieved. Structure of resin was amorphous and heterogen with surface area was 46.572 m^2/g. The resin could be applied as a good adsorbent in the adsorption of Cd(II) metal cation. The outstanding adsorption abilities for cadmium cation have exhibited good prospects for disposal application of polluted water and environmental protection.

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