THE SYNTHESIS OF CALIX[4]RESORCINARENE FROM CASSIA OIL AND ITS APPLICATION FOR SOLID PHASE EXTRACTION OF HEAVY METALS Hg(II) AND Pb(II)

RATNANINGSIH E. SARDJONO1*, GEBI DWIYANTI1, SITI AISYAH1, FITRI KHOERUNNISA1

1Department of Chemistry Education, Faculty of Mathematics and Natural Sciences, Indonesia University of Education, Jl. Setiabudi 229Bandung

* email: ratnaeksa@yahoo.com

ABSTRACT

A study on synthesis calix[4]resorcinarene from cassia oil and its application for solid phase extraction of heavy metals Hg(II) and Pb(II) has been conducted. A new extractor C-Cinnamal calix[4]resorcinarene (CCCR) was produced by one step synthesis from resorcinol, cinnamaldehyde and HCl. The synthesis was carried out at 77°C for 24 hours, and afforded the extractor in 75 %. Cinnamaldehyde was isolated from cassia oil by bisulphite methods and give cinnamaldehyde in 79% with 99.5% purify. Solid phase extraction of Hg(II) and Pb(II) was conducted in batch system and variation of pH, interaction times, and metal concentrations. Solid phase extraction of Pb(II) went optimal on pH 4, 180 minutes of contact time, and 6.6 mg/L of initial Pb(II) concentrations, followed pseudo second order kinetics models, fit well with Langmuir isotherm models, and give extraction capacity in 1.986 μmol/g or 37.2%. In other hand, solid phase extraction of Hg(II) give optimal condition, i.e. pH 4, interaction time was 180 minutes, and initial Hg(II) concentrations was 0.36 mg/L. In addition, Hg(II) extraction followed pseudo second order kinetics models, fit well with Freundlich isotherm models, and have extraction capacity in 0.71 μmol/g or 79.1%.

Key words: solid phase extraction, C-Cinnamal Calix[4]resorcinarene, Cassia Oil, Pb(II), Hg(II).
Introduction

The discharge of heavy metals into aquatic ecosystems has become a matter of concern over the last few decades. The pollutants of serious concern include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, gold, silver, copper, nickel, etc. due to pollutants’ carcinogenic and mutagenic nature. These toxic materials may be derived from mining operations, refining ores, sludge disposal, fly ash from incinerators, the processing of radioactive materials, metal plating, or the manufacture of electrical equipment, paints, alloys, batteries, pesticides or preservatives.

The commonly used procedures for removing metal ions from effluents include chemical precipitation, coagulation, ion exchange, reverse osmosis and solvent extraction. Traditional precipitation is the most economic but is inefficient for dilute solution. Ion exchange and reverse osmosis are generally effective, but have rather high maintenance and operation costs. Solid phase extraction is one of the few promising alternatives for this purpose, especially using low-cost natural extractors such as agricultural wastes (maize cob and husk\(^1\), ground pine cone\(^2\), charcoal\(^3\), fly ash\(^4\), zeolite\(^5,6\), and granular activated carbon\(^7\). But, investigated the active compound from these natural extractors was not a simple study. Structure active compound was needed to explain the extraction characteristics. New synthetic extractors have also been developed in order to describe extraction phenomena and to generate alternative materials having different properties compared to those of natural materials.

Calix[4]resorcinarenes are class of synthetic macromolecule having tetramer of resorcinol residues in a cyclic array and linked by a methyne bridge. The macromolecules are obtained by acid-catalyzed condensation of resorcinol with a variety of aldehydes. Calix[4]resorcinarenes represent an interesting family of structures which exhibit characteristic of cavity-shaped architecture. Various studies have illustrated their application as host molecules for various guests, such as cations, anions, and molecules. The family of calix[4]resorcinarenes has also been used for various functions, namely as an additive in capillary electrophoresis\(^8\), liquid membrane\(^9,10\), solvent extraction\(^9\), chemical sensing\(^11,12\), and High Performance Liquid Chromatography (HPLC) stationary phase. However, the use of calix[4]resorcinarenes as solid phase extractor of heavy metal cation was still very limited.

Cassia or cinnamon oil was extracted from Cinnamon, one of Indonesian natural resources. This essential oil have cinnamaldehyde as main content. Reaction of cinnamaldehyde and resorcinol give C-cinnamal calix4]resorcinarene (CCCR). This calix[4]resorcinarene has twelve benzene residues, eight hydroxyl groups, and four alkenyl (double bond) groups (Fig 1). The presence of lone-pair electrons in the hydroxyl group, also \(\pi\)-electrons in the aromatic residues and double bonds can be expected to exhibit characteristics affinities to heavy metal cations, especially \(\text{Pb}^{(II)}\) and \(\text{Hg}^{(II)}\). The \(\text{Pb}^{(II)}\) and \(\text{Hg}^{(II)}\) cation is considered to be a soft Pearson acid, while CCCR with its hydroxyl arms, double bond, and aromatic rings can form both a “hard” and a “soft” ion binding sites. Thus, it was of interest to investigate the interaction of CCCR with the \(\text{Pb}^{(II)}\) and \(\text{Hg}^{(II)}\) heavy metal cations.
Material and Methods

Reagents

Metal solutions were prepared by diluting 1000 mg/L Pb(NO$_3$)$_2$ and Hg(NO$_3$)$_2$ standard solution to desired concentrations. An adjustment of pH was carried out by adding slowly NaOH and / or HNO$_3$ solution(s) into the metal solutions followed by stirring until desired pH. Chemicals needed for synthesizing CCCR were resorcinol, HCl, cinnamaldehyde, and ethanol. All materials required were reagent grade from E Merck.

Instruments

In this experiment, equipments involving a set of reflux utilities, buchner funnels, Gas Chromatograph-Mass Spectrometer (GC-MS Shimadzu 5500), Fourier Transform Infra Red spectrophotometer (FTIR, Shimadzu 8201PC) were used for CCCR synthesis and characterization. Shaker, atomic absorption spectrophotometer (AAS; Perkin Elmer Analyst-100), pH meter (Hanna), were used for solid phase extraction experiment and determination of Hg(II) and Pb(II) concentrations.

Isolation cinnamaldehyde from cassia oil.

Cassia oil (10 g) was placed into a beaker glass, and saturated sodium bisulphite solution was added until no precipitation again. The precipitated was filtered and washed with ethanol and diethyl ether. HCl solution (250 mL, 5%) and the precipitate were refluxed at 60°C for 30 minutes. The mixture was extracted with methylene chloride (3 x 30 mL). The lower layer was combined and dried with Na$_2$SO$_4$ anhydrous. After filtration, the solution was evaporated with rotary evaporator. The residue was cinnamaldehyde resulted in 69% (6.9 mL) as yellow liquid with characteristics aroma. Purify: 99.5% (GC), MS m/z: 132 (M$^+$); FTIR $\nu$ (cm$^{-1}$): 2748, 2815, 1678, 1624.

Synthesis of CCCR

Into a solution of resorcinol (0.55 g, 5 mmol) and cinnamaldehyde (5 mmol) in 50 mL of 95% ethanol was added 0.5 mL of hydrochloric acid. The solution was stirred and refluxed at 77°C for 24 hours. The product that separated was filtered. The solid was washed using ethanol-water repeatedly and then dried to give the desired compound as a solid in 75% : mp > 390°C (dec), FTIR $\nu$ (cm$^{-1}$): 3409, 3024, 2920, 1620, 1492.
Solid phase extraction procedures

Batch experiment was conducted by adding 0.06 g of CCCR into 10 mL of Pb(II) cation sample solution having definite concentration or by adding 0.02 g of CCCR into 10 mL of Hg(II) cation sample solution having definite concentration. The mixture was shaken at room temperature for a certain period of time. The CCCR was filtered out and dried in a desiccators. Concentration of metal cation was then measured by AAS. The data obtained was compared and corrected by a blank solution. The blank solution was similar to the extraction sample except for the existence of the extractor. The amount of metal cation extracted was calculated from the difference between the metal cation concentration before and after the extraction experiment. The metal uptake or extraction capacity, \( q (\mu\text{mol metal ion/g CCCR}) \) was determined as follows:

\[
q = \left( C_0 - C \right) \times \frac{V}{m}
\]  
(1)

Where \( C_0 \) and \( C \) are the initial and the final metal ion concentrations (mg/L), respectively; \( V \) is the volume of solution (mL); and \( m \) is the CCCR weight (g) in dry form. For each metal cation, the experiment was done in 3 conditions, i.e. variation of pH, interaction time, and metal concentration.

Results and Discussions

Isolation cinnamaldehyde from cassia oil

The first step of CCCR synthesis was isolation cinnamaldehyde from cassia oil. This isolation went very well and easily. The product was light yellow liquid with 99.5% purify based on GC chromatogram.

Figure 2. GC Chromatogram of cinnamaldehyde

The mass spectrum of the peak show ion molecule at \( m/z = 132 \) (MW of cinnamaldehyde) and base peak at \( m/z = 131 \). The other peaks of mass spectrum fit well with fragmentation of cinnamaldehyde.
The FTIR spectrum gives the stronger evidence about cinnamaldehyde structure. Two moderately intense bands at 2815 and 2742 cm\(^{-1}\) and intense band at 1678 cm\(^{-1}\) indicates the aldehyde groups with conjugate carbonyl groups in this compound.

**Synthesis of CCCR**

The synthesis of CCCR was conducted at 77°C in variation of time (20, 24, and 30 h). The product separated from the reaction mixture and give yields in 75% at optimum time as red brownies precipitates. The product was insoluble in many organic solvents, both polar and non polar solvent. This solubility caused difficulty in NMR analysis. The structure of CCCR was confirmed by FTIR spectrometer.

![Figure 4. FTIR spectrum of CCCR](image)

The FTIR spectrum of CCCR showed characteristics absorption at 3409 cm\(^{-1}\) due to O-H stretching vibration. It is well known that absorption bands of O-H stretching vibrations, when free, appear at around 3600 cm\(^{-1}\), and a hydrogen bonding causes these bands to shift to the lower frequencies. The weak frequencies at 3024 cm\(^{-1}\) was corresponding to C\(_{sp^2}\)-H stretching frequencies, and at 2920 cm\(^{-1}\) was corresponding to C\(_{sp^3}\)-H stretching frequencies. In addition, the IR spectrum also displayed a significantly intense C\(_{sp^2}\)-C\(_{sp^2}\) stretching frequencies at 1620 and 1492 cm\(^{-1}\).

**Solid Phase Extraction of Pb(II)**

**Effect of pH**

The effect of pH on the extraction of Pb(II) by CCCR was studied in the pH range of 2 to 5 with the initial concentration of Pb(II) solution about 10 mg/L and the results are shown in Figure 5. The amount of Pb(II) extracted consistently increased by the increase of initial pH, and it reached optimum value at initial pH value of 4.
**Figure 5.** Effect of pH on the solid phase extraction of Pb(II) onto CCCR

The fact that the amount of metal cation extracted at low pH was only little apparently was caused by the occurrence of protonation of most donating groups, especially OH groups, of CCCR. It was envisaged that the interaction between CCCR and Pb(II) cation involved an interaction between oxygen lone pair 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 oxygen pair 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 electron of CCCR and H⁺. When the initial pH was sufficiently high (about 4), there was only limited amount of H⁺ available in the system. Accordingly, the interaction occurred in the system was dominated by the interaction between oxygen lone pair electron of CCCR and vacant orbital of Pb(II). This is the reason why the amount of Pb(II) extracted at relatively high pH value was significantly high. However, increasing initial pH to a value higher than 5 is not a good idea as there has been decreation of extraction capacity.

**Effect of Contact Time**

The result of Pb(II) solid phase extraction at optimum pH with an increase of contact time is presented in Figure 6.
Figure 6. Effect of contact time on the extraction of Pb(II) onto CCCR

It was found that initially the metal uptake increased as the contact time increased. The graph indicates that the Pb(II) extraction took place quickly at the early minutes of interaction only until 2 minutes. It then decreased slowly as the interaction time was extended until reached its constant extraction value at minute of 60. After interaction process took place during 180 minutes, the amount of Pb(II) extracted did not change. Extraction process at this point has reached equilibrium between the extracted metal ions and the free ions in solution.

Solid phase extraction kinetics

The experimental data of contact time effect on the extraction of Pb(II) were used for kinetic modeling. The model equations used for fitting the data were: pseudo 1ˢᵗ order (Lagren) and pseudo 2ⁿᵈ order (Ho). The correlation (R²) resulted from linear plot of log (qₑ-q) versus t, and t/q versus t are shown in Table 1.

Based on the linear regression values, the kinetics of Pb(II) extractions onto CCCR could be described well by pseudo 2ⁿᵈ order equation. Thus, it appeared that pseudo 2ⁿᵈ order was the most valid kinetics model.

Table 1. Kinetic model for Pb(II) extraction by CCCR

<table>
<thead>
<tr>
<th>Kinetic Model</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>pseudo 1ˢᵗ order (Lagren)</td>
<td>0.6552</td>
</tr>
<tr>
<td>log(qₑ-q)= log qₑ-(k/2.303)t</td>
<td></td>
</tr>
<tr>
<td>Pseudo 2ⁿᵈ order (Ho)</td>
<td>0.9999</td>
</tr>
<tr>
<td>t/q = ½ kqₑ² + t/qₑ</td>
<td></td>
</tr>
</tbody>
</table>

Effect of metal concentration

Figure 7 shows the effect of metal concentrations on extraction of Pb(II) onto CCCR. The amount of Pb(II) extracted consistently increased as the metal concentration increased, and it reached maximum (1.986 µmol/g, 37%) at initial metal concentration of 6.6 mg/L.
Figure 7. Effect of metal concentration on Pb(II) extraction onto CCCR

Solid phase extraction isotherms

The equilibrium data in the extraction of Pb(II) onto CCCR were analyzed by using Freundlich and Langmuir isotherms models, i.e. \( \log q_e = \log K + \frac{1}{n} \log C_e \) and \( \frac{1}{q_e} = \frac{1}{(K q_o C_e)} + \frac{1}{q_o} \), respectively, where \( q_e \) is the amount extracted at equilibrium (\( \mu \text{mol/g} \)), \( C_e \) is the solution concentration at equilibrium (\( \mu \text{mol/L} \)), \( q_o \) (\( \mu \text{mol/g} \)) is the maximum capacity of extraction, and \( K \) is the extraction constant. The results of linear plots of \( \log C_e \) versus \( \log q_e \) (Freundlich model) and \( \frac{1}{q_e} \) versus \( \frac{1}{C_e} \) (Langmuir model) are shown in Table 2. The \( K \) values could be calculated from the slopes and intercepts.

Table 2. Estimated isotherm model for Pb(II) extraction

<table>
<thead>
<tr>
<th>Isotherm Model</th>
<th>Linier equation</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>( y=0.5708x-0.795 )</td>
<td>0.6640</td>
</tr>
<tr>
<td>Langmuir</td>
<td>( y=2.8208x+2.6527 )</td>
<td>0.9023</td>
</tr>
</tbody>
</table>

The data on Table 2 shows Langmuir model give higher values of correlation (\( R^2 \)) indicating that the extraction followed the Langmuir model. The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer solid phase extraction without any interaction between extracted ions. Therefore, the model indicating to the applicability of a monolayer coverage of the Pb(II) on the surface of extractor.

Solid Phase Extraction of Hg(II)

Effect of pH

pH is an important parameter for extraction of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the extractor and the degree of ionization of the of the metal during process. To examine the effect of pH on the Hg(II) removal efficiency, the pH was varied from 3 to 6. As shown in Figure 8, the uptake of Hg(II) depends on pH, where optimal metal removal efficiency occurs at pH 5 and then decrease at higher pH.
This fact indicated that at high acidity level, protonation of most donating groups occurred, but at relatively low acidity level, it was deposition process that happened and water-solubility of extractor was getting higher.

Figure 8 indicated that the differences of pH values caused the differences of extraction capacity significantly. Therefore, best extraction needs a pH control tightly. Generally, the increase of pH value happened accompanies the extraction, and pH value increased with increasing extraction capacity. This fact support that the predominant species extracted was $M^{n+}$. In water, the most metals were hydrolyzed as follows:

$$ Mn^{n+} + H_2O \rightleftharpoons M(OH)_{m(n-m)+} + H^+ $$

If $M^{n+}$ is being taken up, the reaction above shifts to the left, leading to the depletion of protons and hence a rise in pH.

**Effect of contact time**

The result of Hg(II) solid phase extraction at optimum pH with an increase of contact time is presented in Figure 9. Some of extraction parameters such as dose of extractor, pH of solution and agitation speed were kept optimum, while temperature was kept at room temperature. The results indicate that extraction capacity increased with an increase in contact time. It can be seen that Hg(II) extraction capacity increased when contact time was increased from 30 to 180 min, but equilibrium condition hasn’t been reached.
Solid phase extraction kinetics

The rate of extraction of an ion onto a surface is an essential parameter when designing batch solid phase extraction systems, consequently it is essential to establish the time dependence of such systems under various process conditions. In an attempt to describe the extraction rate and confirm the reaction mechanism of Hg(II) onto CCCR, two kinetic models were applied to the experimental data. The first model was a pseudo first order rate kinetics from Lagergren. This model was tried without success. Hence, the experimental data were further evaluated based on the pseudo-second order kinetic rate model.

According to Ho et al. (in Ahalya et al\textsuperscript{13}) if the plot is linear, then the solid phase extraction process may be described as chemically extraction. The experimental data were fitted into Ho equation and a plot of $t / q_i$ vs. $t$ made and a linear relationship was observed. Thus, it appeared that pseudo 2\textsuperscript{nd} order was the most valid kinetics model.

Table 3. Kinetic model for Hg(II) extraction by CCCR

<table>
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<tr>
<th>Kinetic Model</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pseudo 1\textsuperscript{st} order (Lagergren) \log(q_e - q) = \log q_e - (k/2.303)t</td>
<td>0.9076</td>
</tr>
<tr>
<td>Pseudo 2\textsuperscript{nd} order (Ho) $t/q = \frac{1}{2} k q_e^2 + t/q_e$</td>
<td>0.9817</td>
</tr>
</tbody>
</table>

Effect of metal concentration

The effect of metal concentrations on extraction of Hg(II) onto CCCR shows in Figure 10. The amount of Hg(II) extracted consistently increased as the metal concentration increased, and it reached maximum (0.71 $\mu$mol/g, 79.1\%) at initial metal concentration of 0.36 mg/L, but equilibrium condition hasn’t been reached.
Solid phase extraction isotherms

The Hg(II) extraction capacity onto CCCR was evaluated using the Langmuir and Freundlich solid phase extraction isotherms. The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir isotherm is based on these assumptions, metal ions are chemically extracted at a fixed number of well defined sites; each site can hold only one ion; all sites are energetically equivalent and there is no interaction between the ions. 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 4.

Table 4. Estimated isotherm model for Hg(II) extraction

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<td>Freundlich</td>
<td>$y=3.3901x+1.28$ 6</td>
<td>0.994 9</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$y=2.679x-5.7328$</td>
<td>0.999 9</td>
</tr>
</tbody>
</table>

The data on Table 4 shows the extraction data fit well with the Langmuir and Freundlich isotherm models. But, the linier equation of Langmuir model gives negative intercept, an impossible value in order to data interpretation. Therefore, the extraction Hg(II) onto CCCR followed the Freundlich model better.

Conclusions

CCCR produced from cassia oil could be solid phase extractor of Hg(II) and Pb(II). Solid phase extraction of Pb(II) went optimal on pH 4, 180 minute of contact time, and 6.6 mg/L of initial Pb(II) concentrations, followed pseudo second order kinetics models, fit well with Langmuir isotherm models, and give extraction capacity in 1.986 μmol/g or 37.2%. In other hand, solid phase extraction of Hg(II) give optimal condition, i.e. pH 4, interaction time was 180 minutes, and initial Pb(II)
concentrations was 0.36 mg/L. In addition, Hg(II) extraction followed pseudo second order kinetics models, fit well with Freundlich isotherm models, and have extraction capacity in 0.71 μmol/g or 79.1%.

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Reference