Synthesis and Adsorption Study of C-4-ethoxy-3-methoxyphenylcalix[4]resorcinarena Triphenylphosphonium Chloride on $Cr_2O_7^{2-}$

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Abstract. A new compound, C-4-ethoxy-3-methoxyphenylcalix[4]resorcinarene triphenylphosphonium chloride (CEMFKRF) had been synthesized. The compounds of CEMFKRF is an orange solid with a 74.68% yield and melting point 259.7°C. Application CEMFKRF for trapping metal anions $Cr_2O_7^{2-}$ was examined by mixing the adsorbent in the sample solution in a variety of pH, contact time, and concentration. This compound was able to absorb $Cr_2O_7^{2-}$ effectively. Adsorption pattern was following the adsorption kinetics model of pseudo second order Ho & McKay and adsorption isotherm was following the model of Langmuir isotherm. Adsorption capacity was obtained as 5.64×10^{-5} mol/L. The mechanism of adsorption on the adsorbent $Cr_2O_7^{2-}$ was in the chemisorption mode ($\Delta G = 30.91$ kj/mol).

Keywords: C-4-ethoxy-3-methoxyphenylcalix[4]resorcinarene triphenylphosphonium chloride, $Cr_2O_7^{2-}$, adsorption, chemisorption

1. Introduction

Water pollution by heavy metals in the form of anion and cation is still a serious problem in Indonesia. One of the heavy metal pollutants anions that are more toxic and dangerous than in the cation form is the $Cr_2O_7^{2-}$ [1], where in small concentrations can cause cancer to humans. This has prompted researchers to develop a variety of methods to reduce the concentration, for instance by adsorption [2–4]. Various adsorbents as absorbing heavy metal cations has been developed and produced for commercial purposes. But so far as absorbing heavy metals is still very limited type and usage, e.g. talcite or hydrotalcite which were very expensive.

Recent developments are able to use calixarenes as adsorbent of heavy metal anions. One of these compounds tetrakis-N,N,N-trimethyl methyl-ammonium-C-4-hydroxy-3-methoxyphenylcalix[4]resorcin-arene that has been synthesized and developed by Utomo [4] that is prepared from anethole and eugenol. This highly effective adsorbent anion adsorb heavy metals anion such as MnO_4^-, CrO_4^-, and $Cr_2O_7^{2-}$ with the adsorption capacity was in the range 15-30 mg/g, but the compound can only be produced 40–50% yield. This is due to the large steric hindrance at the nitrogen atom which is small in terms of calix[4]resorcinarene. Steric hindrance can be minimized by replacing the nitrogen atom (atomic radius = 65 pm) by phosphorus (atomic radius = 100 pm) that can be generated by reacting CEMFKRF 4 alkyl group to the phosphorus atom in the structure of tetraalkylphosphonium halide, that will proceed easier. In addition, also in the presence of phosphorus penta-valent structure as in triphenylphosphine oxide ($Ph_3P = O$), which indicates that the steric

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hindrance in the formation of calix[4]resorcinarene tetraalkylphosphonium halide smaller than tetraalkylammonium halide analogues.

2. Experimental

2.1. Material

Chloromethyl C-4-ethoxy-3-methoxyphenyl calix[4]resorcinarene was synthesis in the previous study, n-hexane, dichloromethane, hydrochloric acid, DMF, $K_2Cr_2O_7$ (Merck), triphenylphosphine (aldrich), TLC plates, Whatman filter paper 42, aquabidest.

2.2. Instrument

Laboratory glassware, set of tools reflux, Buchii evaporator, electronic scales, chamber TLC, UV lamp 254 and 366 nm (UV-Cabinet Camac II), Buchner filter, heater and a magnetic stirrer, melting point apparatus determinants elektrotermal 9100, pH meter, spectrometer infrared (IR Shimidzu 8201 PC), nuclear magnetic resonance spectrometer (^{1}H-NMR, JEOL-MY60), nuclear magnetic resonance spectrometer (^{1}H-NMR, JEOL-MY500), and atomic adsorption spectrometer (GBC-AAS).

2.3. Procedure

- Synthesis of CEMFKRF

C-4-ethoxy-3-methoxyphenylcalix[4]resorcinarene triphenylphosphonium chloride (CEMFKRF) has been synthesized through several steps: (1) synthesis of 4-ethoxy-3-methoxybenzaldehyde [5], (2) condensation and cyclization with resorcinol and acid catalysts produce C-4-ethoxy-3-methoxyphenylcalix[4]resorcinarene (CEMFKR), (3) chloromethylation with paraformaldehyde, HCl, and $ZnCl_2$ catalysts produce chloromethyl C-4-ethoxy-3-methoxyphenylcalix[4]resorcinarene [4], and (4) synthesis of CEMFKRF. CEMFKRF compounds synthesized by added DMF solvent to the chloromethyl CEMFKR (1.5 mmol) while stirred for 30 minutes in a 100 mL flask and then added triphenylphosphine (7.5 mmol) and refluxed for 48 hours. The precipitate formed was filtered and washed several times with water, hexane, and dichloromethane and dried. Identification of the product is conducted by IR and NMR spectrometer.

- Adsorption of $Cr_2O_7^{2-}$

a. Effect of media acidity

Into to a 10 mL $Cr_2O_7^{2-}$ with concentrations of about 10 ppm at pH 1, 2, 3, 4, 5, and 6 was added 0.01 grams of the adsorbent and stirred for 3 hours at 25°C. Blank solution prepared with the same treatment. The solid adsorbent was filtered and the absorbance of liquid was measured using AAS spectrometry to determine the remaining $Cr_2O_7^{2-}$ concentration [6].

b. Adsorption rate

Into to a 10 mL $Cr_2O_7^{2-}$ at optimum pH with concentrations of about 10 ppm was added 0.01 grams of the adsorbent and stirred in certain time. Blank solution prepared with the same treatment. The solid adsorbent was filtered and the absorbance of liquid was measured using AAS spectrometry to determine the remaining $Cr_2O_7^{2-}$ concentration. The amount $Cr_2O_7^{2-}$ absorbed into the adsorbent was calculated based on the difference between the initial concentration (C_0) with residual concentration in solution at time t (Ca).

c. Capacity and energy of adsorption

A set of 10 mL $Cr_2O_7^{2-}$ solution of 5, 10, 15, 20, 25, 30, and 35 mg/L at pH optimum was added into 7 bottles and then add 0.01 g adsorbent. Stirred well at optimum time. The solid adsorbent was filtered and the absorbance of liquid was measured using AAS spectrometry to determine the remaining $Cr_2O_7^{2-}$ concentration. Blank solution prepared with the same treatment [4].

2.4. Result and Discussion

- Synthesis of CEMFKR

Synthesis is done by changing the fourth chloromethyl groups into quaternary phosphonium groups by reaction with chloromethyl CEMFKR and triphenyl phosphine in ethanol using HCl at a temperature 80°C for 48 hours. Products acquired an orange solid with 74.68% yield and melting point 259.7°C. IR analysis

showed no absorption at 1512.19 cm^{-1} indicating the presence of a methylene group has been the loss of (-CH$_2$Cl) and 649 – 748 cm^{-1} indicating the presence of a C-P group. ^{1}H NMR showed a loss of protons (-CH$_2$Cl) at δ 5.4233 ppm and the proton is bound to the –P-Ar$_3$ at δ 2.1 ppm [7] (see Fig. 1).
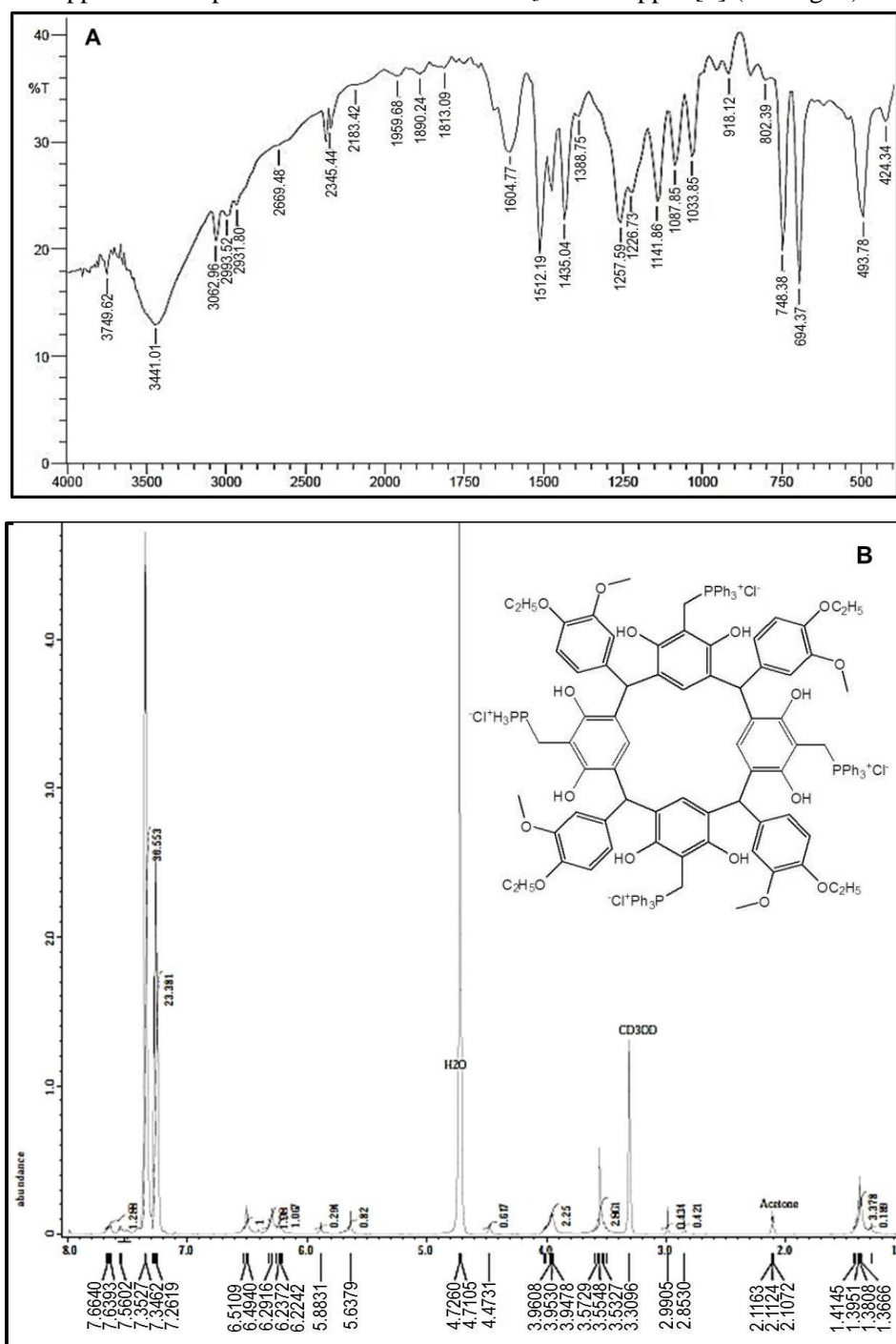

Fig. 1: Result Analysis of IR (A) and ^{1}H NMR (B) CEMFKRF

- Adsorption

Determination of pH optimum adsorption Cr$_2$O$_7$$^{2-}$ by CEMFKRF showed that adsorption took place more effectively at pH 4, which showed adsorbent has several active site of the hydroxy group, ethoxy, methoxy, and quaternary phosphonium. The positive attributes of quaternary phosphonium groups dominant in the adsorption Cr$_2$O$_7$$^{2-}$ through electrostatic interactions, while the high pH OH$^-$ concentration becomes too high, resulting in more competition between the adsorption of OH$^-$ with Cr$_2$O$_7$$^{2-}$ making effectiveness of adsorption Cr$_2$O$_7$$^{2-}$ reduced (Fig. 2A). CEMFKRF adsorption patterns on Cr$_2$O$_7$$^{2-}$ also influenced by time. The longer the alkyl group at the O-alkyl residue 4-hydroxy-3-methoxybenzaldehyde (vanillin) then resorcinarene will be a non-polar so that the diffusion process to capture resorcinarene metal targets will be long anyway. Cr$_2$O$_7$$^{2-}$

adsorption by the adsorbent in the study achieved the optimum time at 180 minute (Fig. 2B). Changes in the pattern of adsorption of the time referring to the order of the adsorption kinetics model of Lagergren [8] and the second order of Ho & McKay [9] which is based on the concentration of the adsorbate on the adsorbent. Furthermore, in order to distinguish the kinetics model with kinetic models based on the adsorbate concentration in the solution, then the model is called pseudo first order Lagergren and Ho & McKay called pseudo second order.

Based on the values of adsorption parameters, it can be concluded that there is a curve that has the highest level of linearity can be defined as equation kinetics model that best fits the adsorption behavior of the adsorbent. $Cr_2O_7^{2-}$ interaction model CEMFKRF tends to correspond to the adsorbent and the adsorption kinetics followed the pseudo second order Ho & McKay with a high level of linearity approaching one (Fig. 3).

The effect of the concentration $Cr_2O_7^{2-}$ performed at optimum pH and adsorption time is isothermic (25°C). In this study, the optimum concentration obtained $Cr_2O_7^{2-}$ can adsorbed by CEMFKRF by 40 mg/L (Fig. 2C). Adsorption refers to the model of Langmuir and Freundlich adsorption isotherms. Through the Langmuir adsorption isotherms equation (1) and Freundlich (2), the graphs obtained are summarized in Figure 4. Based on the Langmuir and Freundlich isotherm curve, higher linearity shown by the Langmuir adsorption isotherm models indicate that the adsorption process occurs in the layer (monolayer) where maximum adsorption occurs when all active sites of adsorbent filled by the adsorbate monolayer formed. Conformity with the results of this study indicate Langmuir adsorption isotherm models and lead to second order kinetics equation model. These results are in line with the reality on the adsorption kinetics modeling approach to time following the adsorption kinetics model pseudo second order Ho & McKay. The maximum adsorption capacity (qm) were obtained by the Langmuir adsorption isotherm equation is equal to 5.64×10^{-5} mol/L.

$$\frac{1}{q_e} = \left(\frac{1}{qmKCe}\right) + \left(\frac{1}{qm}\right) \qquad (1)$$

$$\log q_e = \log K_f + \frac{1}{n} \log Ce \qquad (2)$$

where qe : concentration of adsorbate at equilibrium (mole/g), Ce : concentration of adsorbate in the aqueous phase (mole/L), qm : maximum adsorption capacity (mol/L), and K : equilibrium constant.
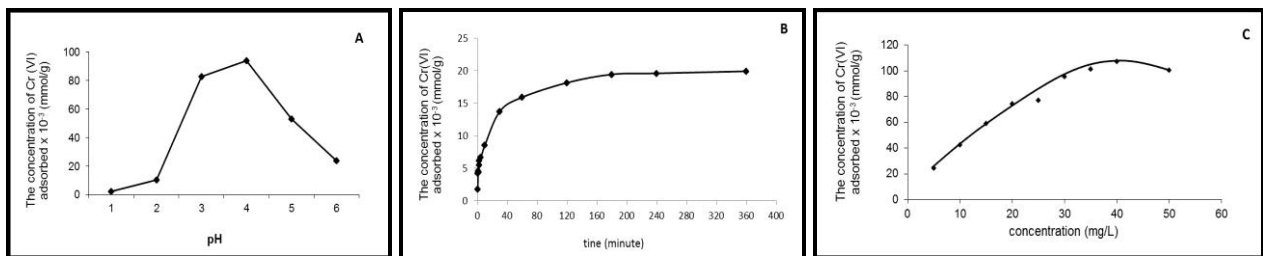

Fig. 2: Effect of pH (A), time (B), and concentration (C) in the adsorption $Cr_2O_7^{2-}$
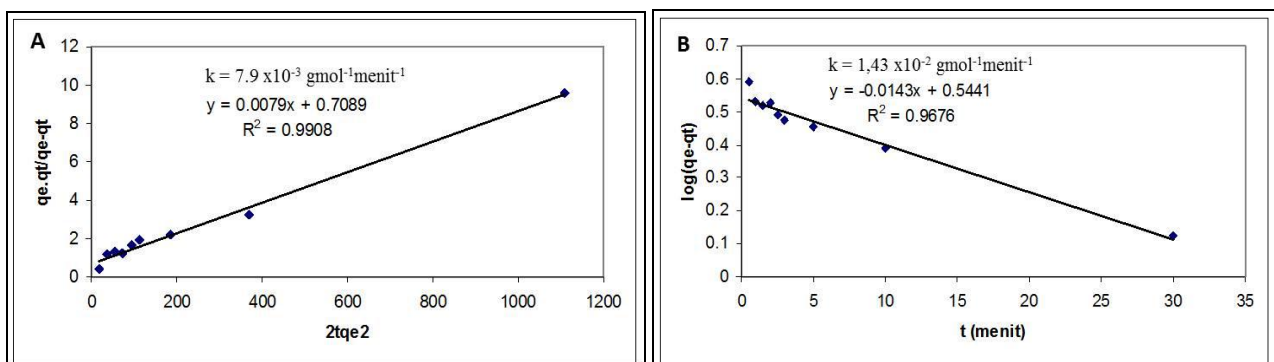

Fig. 3: Kinetics of adsorption Ho & McKay (A) and Lagergren (B)

Adsorption energy equation could be written as Eads = -$\Delta G°$. Value of ΔG can be measured from the standard state, whereas for the equation of any other state Gibbs energy (ΔG) was $\Delta G = \Delta G° + RT \ln K$, where R : the general gas constant (8.314 JK^{-1} $mole^{-1}$), T : temperature, K : adsorption equilibrium value.

According to Adamson [10], chemical adsorption energy threshold was 5 kcal $mole^{-1}$ or 20 kJ $mole^{-1}$. Thus, the adsorption process of $Cr_2O_7^{2-}$ ions onto the CEMFKRF can be classified as chemical adsorption.
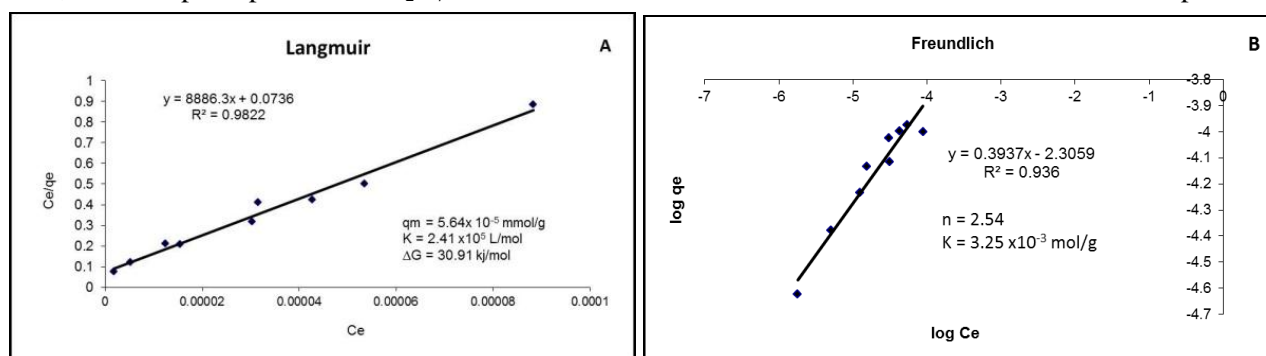

Fig. 4: Langmuir adsorption isotherms (A) and Freundlich (B)

2.5. Conclusion

Based on the IR and ^1H NMR spectra has gained an orange solid CEMFKRF compound with 74.68% yield and melting point of 259.7°C. Application CEMFKRF to trap $Cr_2O_7^{2-}$ metal anions showed optimum pH 4, the optimum time of 180 minutes, and the optimum concentration of 40 mg/L. CEMFKRF was able to effectively absorb $Cr_2O_7^{2-}$. Adsorption pattern was following the adsorption kinetics model of pseudo second order Ho & McKay and adsorption isotherm was following the model of Langmuir isotherm. Adsorption capacity was obtained as 5.64 x 10^{-5} mol/L. The mechanism of adsorption on the adsorbent $Cr_2O_7^{2-}$ was in the chemisorption mode (ΔG = 30.91 kj/mol).

3. Acknowledgements

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