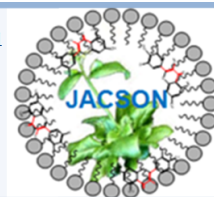


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# Synthesis and Application of C-Phenylcalix[4]resorcinarene in Adsorption of Cr(III) and Pb(II)

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## ABSTRACT

Synthesis and application of C-phenylcalix[4]resorcinarene (CPCR) as the Cr(III) and Pb(II) adsorbent has been conducted. CPCR was produced by acid-catalyzed-condensation of resorcinol and benzaldehyde. The characterization of the target compound was performed by IR, <sup>1</sup>H-NMR, and LC-MS. The adsorption process using batch system. Most parameters in batch system confirm that CPCR is a good adsorbent for Cr(III) and Pb(II). The Cr(III) uptake was bigger than that of Pb(II), and also Cr(III) adsorption rate was faster than Pb(II). The adsorption kinetic both of Cr(III) and Pb(II) adsorptions in batch followed pseudo 2nd order kinetics model. The results of adsorption equilibrium study showed that in adsorption Cr(III) and Pb(II) onto CPCR, Langmuir isotherm model was more applicable than Freundlich model.

**Keywords:** Adsorption, Synthesis, application, Pb(II), Cr(III), C-phenylcalix[4]resorcinarene, and batch system

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## 1. Introduction

Metallurgical waste is the main source of heavy metal in water environment. Heavy metal ions can be accumulated by aquatic organisms and then endanger human health through the food chain. Therefore, removal of heavy metal ions is an important topic in technology of water treatment (Zhou et al., 2011). Several methods such as precipitation and extraction (Ludwig and Dzung, 2002), ion-exchange (Sivaiah et al., 2004), membrane separation (Jain et al., 2005) and adsorption (Goswani and Ghosh, 2005; Jumina et al., 2011; Budiana et al., 2014) have been reported to remove the heavy metal ions. Zhou and Xue (1) apply spiolite to remove Cu<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> from water while Umaningrum et al. (2010) used humic acid-chitosan in reaction to adsorb Pb(II), Cd(II) and Cr(III) ions. 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 and subject to fouling. Adsorption is one of the few promising alternatives for this purpose, especially using low-cost natural adsorbents such as agricultural wastes. Unfortunately, it is difficult to figure out the active compounds or active sites in natural adsorbents because of the complexity of its contents. Therefore, it is necessary to search alternative adsorbents, especially those generated from low-cost synthetic processes (Jumina et al. 2011).

A class of synthetic macromolecules that demonstrate capabilities to function as adsorbent is calix[4]resorcinarenes. Calix[4]resorcinarenes are analogs of calixarene having two hydroxyl groups on benzene rings at extra annular position forming a macrocycle. The compounds are synthesized by the

acid-catalyzed cyclocondensation of resorcinol with various aliphatic or aromatic aldehyde (Nikod et al., 2009; Tustad et al., 1989 and Jain et al., 2005). The compounds are easily synthesized by well-established one-pot procedures (Jain et al., 2005). They have found much application of Calix[4]resorcinarenes such as macrocyclic receptor (Botta et al., 2005), host molecules (Utzig et al., 2004; Kazakova et al., 2002 and Barnes et al., 2007), dying fiber (Jain et al., 2005), building blocks for even larger supramolecular architectures assemblies such as cages, capsule, as starting materials for the preparation of more sophisticated molecules (Beyeh et al., 2006) and HPLC stationary phase (Sokolies et al., 2003 and Ruderisch et al., 2005). Calix[4]resorcinarenes is also can be applied as a sunscreen (Budiana et al., 2014). Nonetheless, there are still limited reports on the utilization of calix[4]resorcinarenes (Ruderisch et al., 2005) as adsorbent for heavy metal cations. C-phenylcalix [4]resorcinarenes (CPCR) is calix[4]resorcinarene having four benzene rings and eight hydroxyl groups (Fig. 1). CPCR was synthesized directly by acid-catalyzed condensation of resorcinol and benzaldehyde (Tunstad et al., 1989 and Gutshe, 1998). The presence of lone-pair electrons in the hydroxyl groups and p-electrons in the aromatic moieties can possibly lead to characteristic affinities to heavy metal cations especially Pb(II) and Cr(III). The former cation is considered to be a *softer pearson acid* than Cr(III), which was a *hard pearson acid*, while CPCR with hydroxyl groups and aromatic rings can form both a "hard" and a "soft" ion binding sites, respectively. So the aim of this study was to investigate the interaction of CPCR with the two said heavy metal cations (Pb(II) and Cr(III)).

## 2. Materials and Methods

### 2.1. Reagents

Metal solutions were prepared by diluting 1000 mg/L Pb(NO<sub>3</sub>)<sub>2</sub>, Cr(NO<sub>3</sub>)<sub>3</sub> and Cd(NO<sub>3</sub>)<sub>2</sub> standard solutions in aqueous nitric acid to desired concentrations. An adjustment of pH was carried out by adding slowly NaOH or HCl solution into the metal solutions followed by stirring until desired pH. Chemicals needed to synthesis CPCR were resorcinol,

benzaldehyde, HCl, and ethanol absolute. All materials required were reagent grade from E-Merck USA.

### 2.2. Instruments

Elucidation the structure of the synthesized compounds was performed using Proton Nuclear magnetic Resonance (1H-Infra Red (FT-IR Shimadzu, Prestige 21), and Liquid Chromatography-Mass Spectrometer (LC-MS Mariner). pH meter (Hanna) were used for adsorption experiment and determination of heavy metals concentration using flame atomic absorption spectrometry.

### 2.3. Synthesis of CPCR

CPCR was synthesized according to the method as described by Tunstad and co-workers (Tunstad et al., 1989). Resorcinol (1.60 g, 0.015 mole) and ethanol 95% (50 mL) were mixed into 250 mL round bottomed flask. The mixture was stirred for 15 minutes. Benzaldehyde 1.59 g (0.05 mol) and 1.0 mL HCl was then added to the homogenous solution. The mixture was heated for 24 hours at 78 °C. The product was collected as yellow solid, washed by water and characterized by IR spectroscopy, <sup>1</sup>HNMR and mass spectroscopy.

### 2.4. Adsorption Procedures

Adsorption was conducted according to the method as described by Jumina et al (2011). Batch system was conducted by adding 0.01 of CPCR with particle size of 100-200 mesh into 10 mL of metal cation sample solution having concentration of about 6 mg/L. The mixture was shaken at room temperature for certain period of time. The adsorbent was filtered out and dried in desiccators. Concentration of metal ion was then measured by AAS. The data obtained was compared and corrected by a blank solution. The blank solution is similar to the adsorption sample except for the existence of the adsorbent. The amount of metal cation adsorbed was calculated from the difference between the metal cation concentration before and after the adsorption experiment. The metal uptake, q (mg metal ion/g CPCR or mmol/g) was determined as follows:  $q = (C_0 - C) \times V / m$  or  $q = (C_0 - C) \times V / (A_r \times m)$ , where C<sub>0</sub> and C are the initial and the final concentrations (mg/L) of metal ions, respectively; V is the volume of solution (mL); A<sub>r</sub> is the relative atomic mass and m is the adsorbent weight (g) in dry form.

For each metal cation, the experiment was done in 3 conditions, i.e. variation of pH, shaking time, and adsorbent concentration.

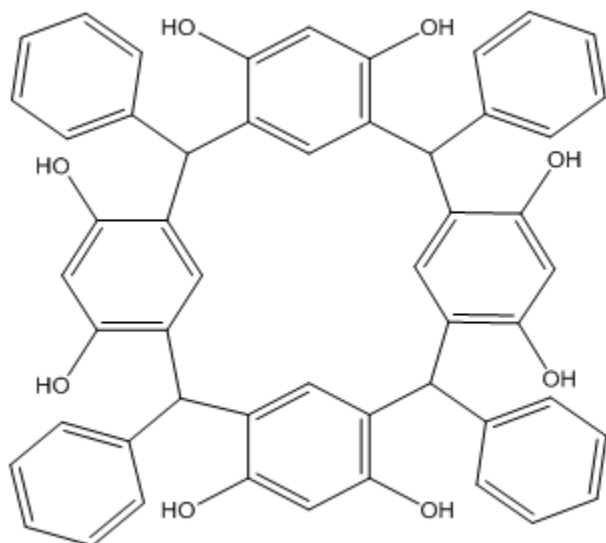


Fig. 1. Structure of CPCR

### 3. Results and Discussion

#### 3.1. Synthesis and Characterization of CMCR

Synthesis of C-phenylcalix[4]resorcinarene carried out by reacting resorcinol with benzaldehyde using HCl catalyst in absolute ethanol solvent. Synthesis of C-phenylcalix[4] resorcinarene reaction is faster than C-Methylcalix[4]resorcinarene, this is

shown by the formation of deposits in 3 hours. While C-Methylcalix[4]resorcinarene formed the deposits after 8 hours. In the beginning of C-phenylcalix[4] resorcinarene synthesis,  $H^+$  ion of HCl catalyst protonate the carbonyl group of benzaldehyde to give a carbonyl group which has positive charge. The presence of this positive charge caused unstable oxygen bond, therefore the electron of the double bonding carbonyl group shift toward oxygen atom. This shift caused the carbon atom of carbonyl group became positively charged.

C-phenylcalix[4]resorcinarene compound obtained in solid state, pale yellow with melting point of  $> 390^\circ C$ , insoluble in water, acetone and dichloromethane but soluble in DMSO. Limited solubility in organic solvents and the great melting are caused by many hydroxyl groups and phenyl groups in the molecule of C-phenylcalix[4]arene. Characterization of C-phenylcalix[4]arene by infrared spectrometer showed that C-phenylcalix[4]arene has a strong and broad absorption in  $3387\text{ cm}^{-1}$  caused by strain absorption of  $-OH$  groups, while the absorption in  $1613\text{ cm}^{-1}$  and  $1512\text{ cm}^{-1}$  area caused by absorption of  $C=C$  in aromatic rings. Absorption of  $C-H$  methylene bridge ( $-CH_2-$ ) present as a medium absorbance in  $1427\text{ cm}^{-1}$  and absorption  $C-O$  present in  $1204\text{ cm}^{-1}$ .

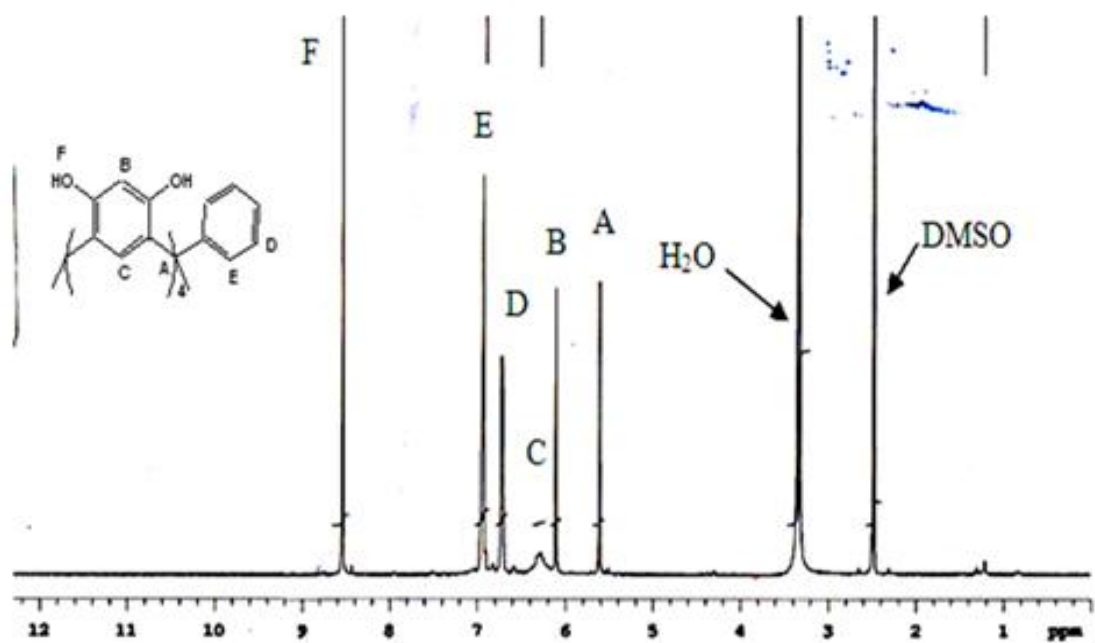


Fig. 2.  $^1H$ -NMR Spectra of C-Phenylcalix[4]resorcinarene

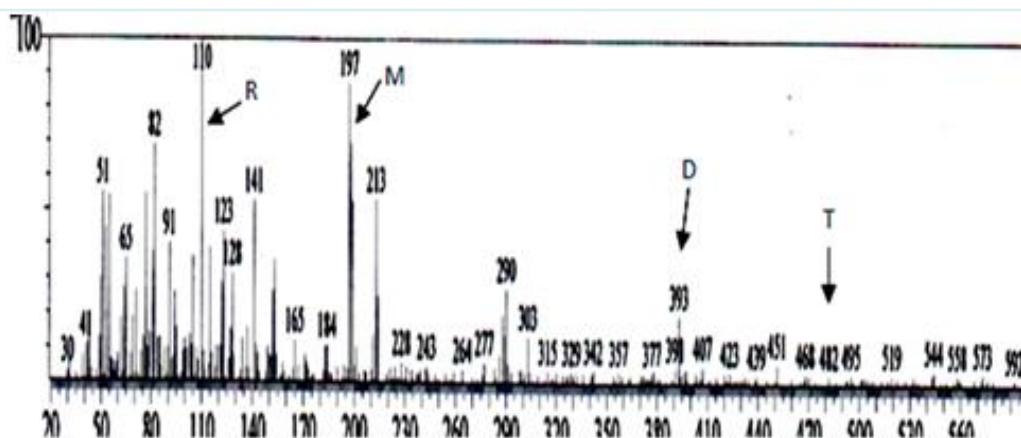


Fig. 3. Mass spectra of C-Phenylcalix[4]resorcinarene

Characterization of C-phenylcalix[4]arene by using  $^1\text{H-NMR}$  (in DMSO solvent) showed that all protons present in corresponding shift. The bridge proton present in 5,62 ppm, aromatic proton present both in 6,25 and 6,81 ppm then hydroxy proton present in 8,56 ppm. The shift in 2,55 ppm caused by DMSO solvent and shift in 3,48 areas caused by  $\text{H}_2\text{O}$  proton that probably derived from DMSO which absorb water. By comparing the obtain  $^1\text{H-NMR}$  spectra of C-phenylcalix[4]arene and  $^1\text{H-NMR}$  spectra of C-phenylcalix[4]resorcinarene, isomer models of  $\text{C}_{4v}$  dan  $\text{C}_{2v}$  were successfully separated and characterized by Tunstad et al. (1989), it turn out that C-phenylcalix[4]arene products obtained only  $\text{C}_{4v}$  (crown) isomer. This is evident from  $^-\text{OH}$  proton of resorcinol ring which present as a single peak in 8.53 ppm shift.

If the reaction product is  $\text{C}_{2v}$ , the H-NMR spectrum will appear as a pair peak of  $-\text{OH}$  proton in 8,44 and 8,55 ppm area. IR and  $^1\text{H-NMR}$  data are strengthened by mass spectra data. Fragmentation pattern of C-Phenylcalix[4]arene is a bit difficult to predict because the molecular mass of C-Phenylcalix[4]arene is quite high at 792 g/mole. However, the presence of fragments may indicate that the synthesis product is actually C-Phenylcalix[4]resorcinarene. Fragment with the value of 482 near to the trimers (484), 393 fragment near to the dimers (396), 197 fragment near to the monomers (198) then 110 is resorcinol. These fragments showed that C-Phenylcalix[4]arene molecules are decompose by the high temperature. Mass spectra of C-Phenylcalix[4]resorcinarene shown in Fig. 3. The

mechanism of synthesis C-Phenylcalix[4]resorcinarene shown in Fig. 4.

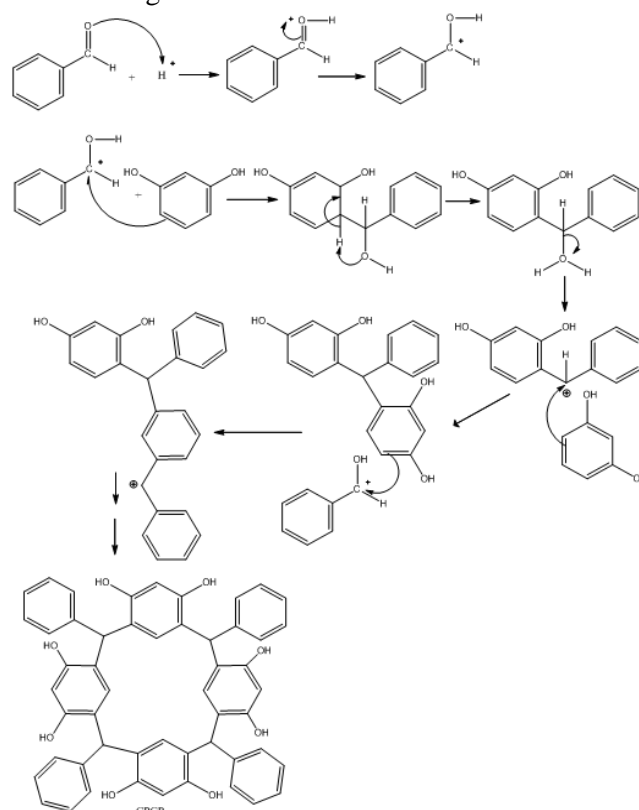


Fig. 4. The mechanism of synthesis C-Phenylcalix[4]resorcinarene

The activity test of C-Phenylcalix[4]resorcinarene as adsorbent of heavy metals cation carried out to determine the potential of this compound to be applied as adsorbent of toxic metal cations include;  $\text{Cr(III)}$  and  $\text{Pb(II)}$  both in the environment and the body (antidotum). The test conducted by batch method because this method is simple, inexpensive, easy to

perform and the result can be justified. The test was done in number of variations such as acidity degree (pH), interaction time and also the concentration of the metal cation. The variation of pH aims to determine the optimum pH of the adsorption process, by the variation of interaction time in optimum pH can be determined the Adsorption kinetics and then by the variation of concentration in optimum pH and interaction time can be concluded the isotherm adsorption pattern of benzoyl-cinnamoylcalix[4]resorcinarene also parameters of adsorption.

### 3.2. Effect of Acidity

Acidity degree is a measured concentration of  $H^+$  ion in a solution. The acidity degree is an important factor in Adsorption process, because the  $H^+$  ion can be bounded to the active sites of the base adsorbent (free electrons pair provider). As shown in Fig. 5 at low pH the percentage of Cr(III) cation which adsorbed by CPCr adsorbent is still small. Percentage of the adsorbed Cr(III) increase due to the increases of solution's pH. Maximum percentage of adsorbate that adsorbed was found on the range of pH 6 to 7 which reached 98.50%. After pH = 7, the percentage of adsorbed Cr(III) decrease to 5.43 % on pH=8. At the low pH, adsorbent's ability to adsorb Cr(III) is still small. It is because of at low pH, the concentration of  $H^+$  ion is high and it has empty orbital so is possible to

the existence of competition with metal cations which also act as a Lewis acid, for binding to the active sites on the adsorbent. There are 4 hydroxyl (-OH) groups in CPCr adsorbent which have a pair of free electrons in every oxygen atom and aromatic ring. The competition between  $H^+$  ions with cations of metal at low pH has been demonstrated by Martell and Hancock (1996), who found the complex between  $Ca^{2+}$  and EDTA are just beginning to form at pH above 3, the formed complex increased after  $H^+$  ions removed from solution by adding NaOH solution.

The competition between  $H^+$  ions and Cr (III) in the high acidity (low pH) can be illustrated (Fig. 6). In reducing of acidity (increasing of pH), the concentration of  $H^+$  ion began to decrease so that Cr(III) started more adsorbed. The increasing Cr(III) adsorption reached maximum in pH range of 6-7 and started to reducing in range of pH more than 7. The reducing of pH caused by the precipitation of Cr(III) ions to  $Cr(OH)_3$ . Adsorption ability of the test compound seems that CPCr adsorbent can adsorb the Cr(III) by approximately 98.50%. This is caused by conformity of acid-base properties between adsorbent and adsorbate. The adsorbent has many -OH group which are hard base while Cr(III) is hard acid. This is in quite good agreement with Handayani (2011) which state that in generally the hard base will form a stable

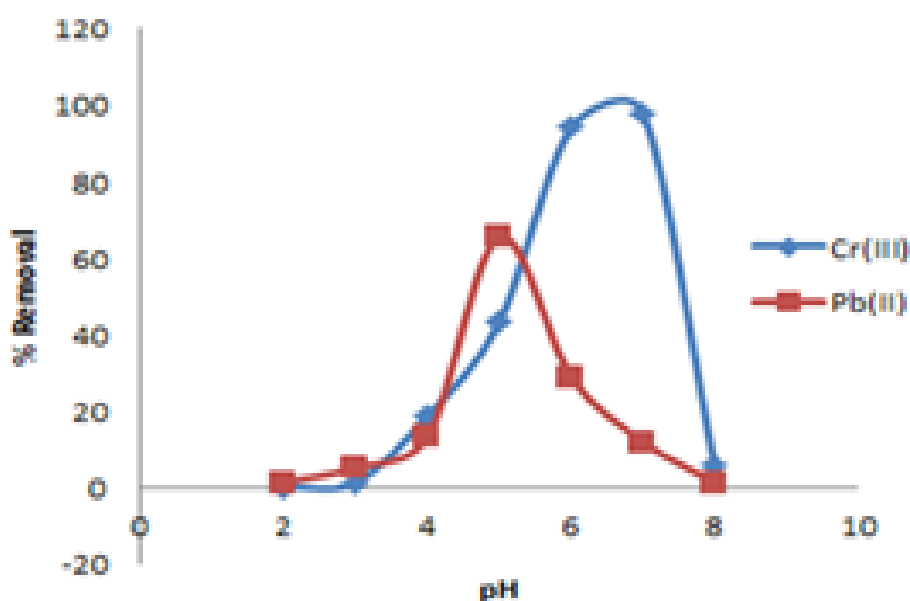


Fig. 5. Effect of initial pH on the adsorption of Cr(III) and Pb(II) onto CPCr

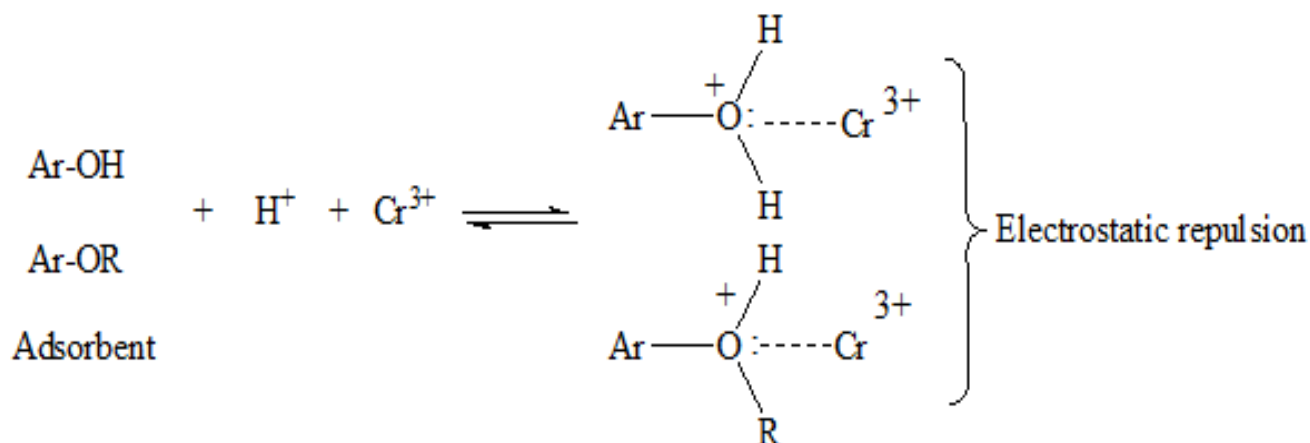


Fig. 6. Interaction between adsorbent and Cr(III) in low pH

bond with hard acid. The stable bond between the hard base adsorbent and the hard adsorbate associated with large energy differences between hard acids and bases orbitals. The large energy differences leading a charge transfer process from alkaline to acidic in highly exothermic, resulting an ionic interaction. This ionic interaction caused the bond between the adsorbent with the adsorbate is difficult to detaching.

Acidity effect to the Pb(II) cation adsorption by CPCR showed in Fig. 5 shown that CPCR begin to adsorb Pb(II) cation at pH of 2 and this is somewhat different with Cr(III) cations which are just beginning to be adsorbed by the adsorbent at pH of 3. Just like to the Adsorption of Cr(III) cation, in low pH or in the high acidity, percentage of adsorbed Pb(II) cation is still small. This is caused by existence of competition between  $\text{H}^+$  of acid with Pb(II) cations (Fig. 6). Because of the acidic nature of  $\text{H}^+$  ion is higher than the Pb (II), the Pb (II) lost the competition for binding to the sides of the active adsorbent which is alkaline. The  $\text{H}^+$  ions are covalently bound to the active cluster coordination of the adsorbent so the adsorbent consequently positively charged. This is what causes the occurrence of electrostatic repulsion between the protonated adsorbent with Pb (II) so that the adsorption process could not be run properly. Adsorption of Pb(II) cation by five CPCR lower than the cation Cr (III) this is in line with the nature of Pb (II) which is a metal with medium acidity that will bind properly when the adsorbent also has many active group with medium alkalinity such as  $\text{N}_2$ ,  $\text{N}_3$ ,  $\text{NO}_2$ ,  $\text{C}_6\text{H}_5\text{NH}_2$  and Br.

### 3.3. Effect of Interaction Time

Effect of interaction time between calix[4]resorcinarene (adsorbent) with metal's cation (adsorbate) is important to be studied in order to determine the reaction kinetics of Adsorption. Through the determination of interaction time effect on the percentage of adsorbed adsorbate, will be known the time required by adsorbate to reach equilibrium.

After reached the equilibrium, adsorption rate comparable to the rate of the release adsorbate so that in this state the percentage of the adsorbed adsorbate relatively constant. The curve in the Fig. 7 showed that at the first 5 minutes, adsorbent can adsorb Cr(III) above 50%. After the increase of interaction time, in generally the adsorbed Cr(III) also increase. This is concluded that there are free active sites so the adsorbent still adsorb at any given time the percentage of adsorbed metal cation not significantly increased. In this condition, the adsorption process is said to have reached an equilibrium state. The equilibrium state is achieved due to the adsorption rate that has been offset by the rate of desorption. Fig. 7 shows that the optimum time of adsorption on the adsorbent CPCR reached in the 45<sup>th</sup> minute, the percentage change of Cr (III) adsorbed to the next time is not too great.

In the Adsorption process of Pb(II) by CPCR, the equilibrium state reached in the 405<sup>th</sup> minutes. It take a lot of time to reached the equilibrium state shows that Adsorption rate of Pb(II) by the adsorbent is slow. Slow reaction rate is according to the discrepancies properties of adsorbent and Pb(II) cation. All

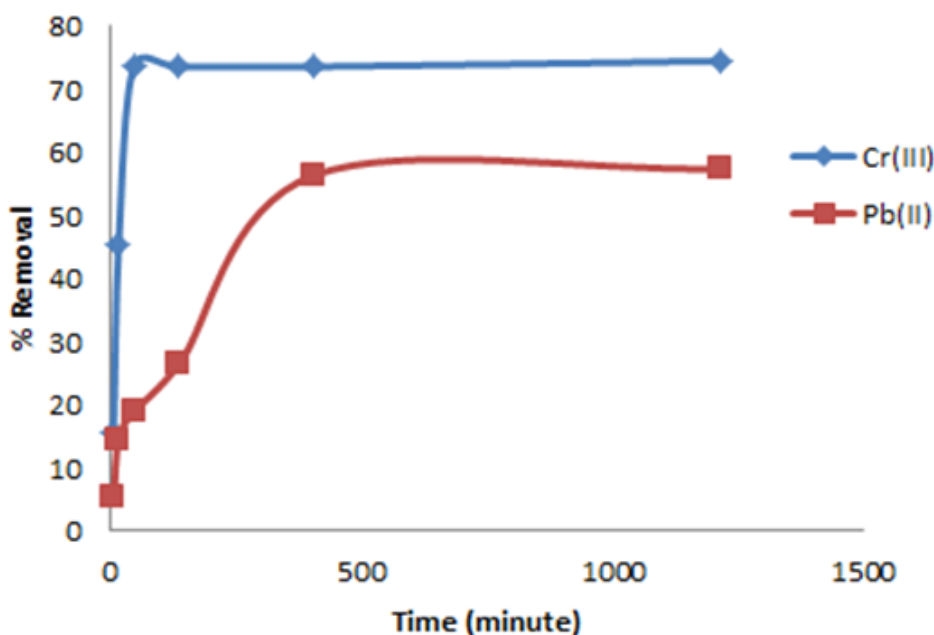


Fig. 7. Effect of interaction time on the adsorption of Cr(III) and Pb(II) onto CPCr

adsorbents have active site in the form of hard alkaline, while Pb(II) is a cation with intermediate alkaline properties. If Judging from the achievement of equilibrium time that take a lot of time which almost 7 hours, the from the economic stand point those adsorbent are less favorable to applied for Pb(II) Adsorption. Long reaction time certainly required a lot of effort and operational cost.

The conclusion about the kinetics model followed in the adsorption experiments are based on the value of the correlation coefficient ( $R^2$ ) for each model. Largegren model studied by passing  $\log(q_e - qt)$  as ordinate with  $t$ (time) as the axis X.  $q_e$  value is the adsorbed mass at equilibrium state (mg/g) and  $qt$  is the adsorbed mass at the time  $t$ . Slope value of Largegren is the rate constant ( $k$ ). Ho Models studied by passing the value of (Y axis) with the time  $t$ , and as the value of slope.

Correlation coefficient showed that almost all Ho model have  $R^2$  value close to 1 and larger than  $R^2$  value of Largegren. Based to these data, the reaction rate of both Cr(III) and Pb(II) cations by CPCr are determined by the active sites quantity of adsorbent and also adsorbate concentration. Value of rate constant ( $k$ ) is measured by intersection between X-axis (time) and Y-axis (time ( $t$ )/adsorption mass at time ( $qt$ )) by determined the adsorption mass at equilibrium state of slope first). The measurement of rate constant

important to be done to determine the interaction rate that occurs between adsorbent and metal's cation. The CPCr rate constant of reaction ( $k$ ) in Adsorption of Cr(III) and Pb(II) are  $15.36 \times 10^{-4}$  and  $4.18 \times 10^{-4}$  respectively.

### 3.4. Effect of Metal Ion's Concentration and Isothermal Adsorption

Metal Ion's Concentration effect at optimum pH and time also at constant temperature aim to determine isotherm model followed by adsorption process of CPCr to Cr(III) and Pb(II) cations. Based to the followed isotherm pattern, there can be measure the maximum adsorption capacity ( $X_m$ ), Adsorption energy ( $E$ ) and equilibrium constant ( $K$ ). The adsorption models studied in this research are Freundlich and Langmuir isotherm adsorption. In the Freundlich isotherm the adsorption process is multilayer which the adsorbent with unlimited concentration able to unlimited adsorb the adsorbate.

While in the model of Langmuir isotherm adsorption, the adsorption process takes place gradually until it meets the surface and form a single layer (monolayer) caused by the interaction between the adsorbate with the active sites of the adsorbent. When all of the active sites already binds the adsorption does not happen again, because the surface of the adsorbent is considered saturated. Freundlich

isotherm models defined by the equation;

$$\log q_e = \log K + \frac{1}{n} \log C_e$$

Where  $q_e$  is the adsorbate concentration adsorbed by adsorbent at the equilibrium states (mole/g) which the units can be converted into mole/L.  $C_e$  is the concentration of adsorbate in liquid state (mole/L). By passing  $q_e$  as the ordinate and  $C_e$  as the abscissa then the value of equilibrium constant (K) and amount of n layer can be measured by the intersection and the slope. Langmuir isotherm models defined by the equation;

$$\frac{C_e}{q_e} = \frac{1}{X_m \cdot K} + \frac{C_e}{X_m}$$

The passing of  $C_e/q_e$  as Y-axis and  $C_e/X_m$  then can be determined the value of equilibrium constant (K) from the value of intersection and maximum

Adsorption capacity  $X_m$  from the slope. The important parameter to be measured in studied of isotherm adsorption is equilibrium constant (K), maximum adsorption capacity ( $X_m$ ) and adsorption energy (E).

Equilibrium constant related to the comparison between concentrations of reaction product and remains reactant at the equilibrium state. If the value of K is larger it means the reaction tends to shift toward product, in this case complex between adsorbent and adsorbate. Otherwise, if the value of K is smaller the equilibrium reactions tend to shift toward reactant which also means that metal ion tends to be released again. Maximum adsorption capacity ( $X_m$ ) value is also important to be measured because it involves the ability of an adsorbent in adsorbing metal cations. The effect of concentration on the adsorption of Cr(III) and Pb(II) onto CPCr described in Fig. 8.

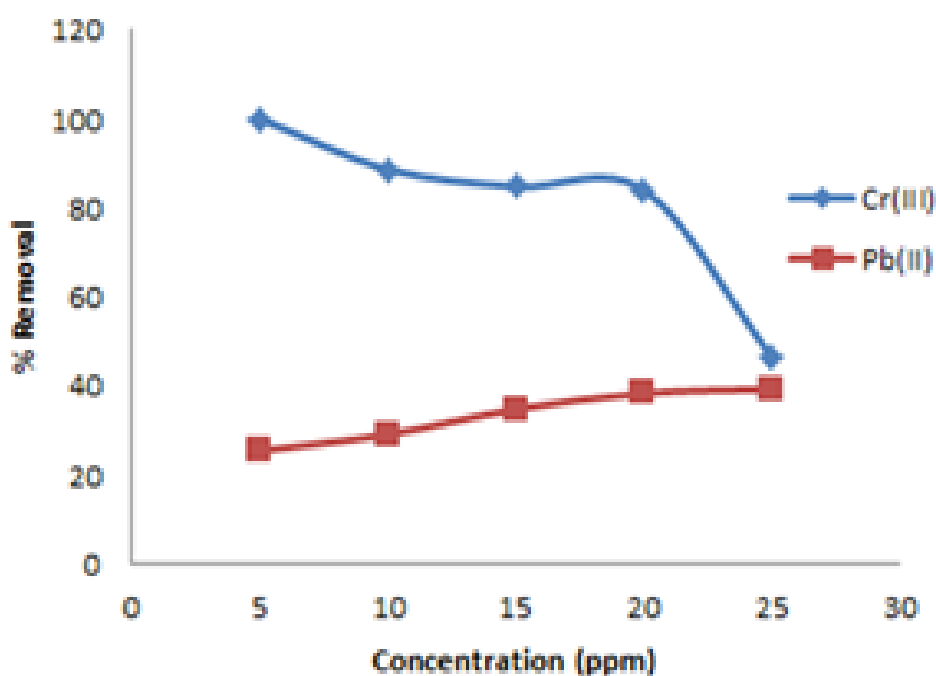


Fig.8. The effect of concentration on the adsorption of Cr(III) and Pb(II) onto CPCr

Table 1. Values of K,  $X_m$  and E in Adsorption of Cr(III) and Pb(II) by CPCr Adsorbent

Adsorbent's Name	Cations	Regression Equation	$X_m$ ( $\mu\text{mole/g}$ )	$K \times 10^4$ (L/mole)	E (kJ/mole)
CPCr	Cr(III)	$Y = 1769x + 0.087$	565,29	2,033	24,58
	Pb(II)	$Y = -19854x + 20.36$	50,37	22,821	30,57



The curve in the Fig. 8 showed that at the Cr(III) concentration (5 ppm), all of the Cr(III) ion can adsorbed by CPCR. It caused by the amount of active site of the adsorbent too much greater than amount of the metal ions. The greater concentration the smaller amount of the metal that is absorbable by CPCR. It was caused by the saturation of the active site of CPCR. The values of K, X<sub>m</sub> and E are tabulated in Table 1.

The greater adsorption capacity means the adsorbent is better, this is because the increases of adsorbate quantity that adsorbed by an adsorbent. Value of adsorption energy (E) indicates the type of adsorption involved, because value of E measured by Gibbs energy equation;  $\Delta G = -RT \ln K$ . R is an ideal gas constant (8.314 J/K mol), T is the temperature in Calvin and K is the equilibrium constant. Adsorption energy more than 20 kJ/mole indicate that the involve adsorption is a chemical adsorption. Energy adsorption value less than 20 kJ/mole indicate that the involve reaction is a physic adsorption. Chemical adsorptions occur by the strongly chemical bond between adsorbent and adsorbate. The chemical bond can be pure covalent bonds, ionic bonds or hydrogen bonds.

The adsorption energy data in table 1 showed that all adsorption energies are more than 20 kJ/mole. Based to this adsorption data, the adsorption type in adsorption process of Cr(III) and Pb(II) metals by adsorbent are chemical adsorption. In the reaction between adsorbed solid and soluble substance, this adsorption is specifically and involve the greater force than the physic adsorption.

The adsorption of metal cation such as Cr(III), Pb(II) and Cd(II) by CPCR are following Langmuir isotherm adsorption model as indicated in the V attachment. According to Langmuir, the adsorbed molecules are detained on the surface by the same valence force as occur in the atoms of molecule. By the presence of a chemical bond then in the surface of the adsorbent will be formed a layer wherein the formation of the layer will further inhibit the absorption process.

#### 4. Conclusion

C-Phenylcalix[4]resorcinarene (CPCR) could be synthesized only in one step of the reaction i.e.

condensation of the resorcinol with benzaldehyde using HCl catalyst. The adsorption experiments in batch system were investigated that acidity level influence significantly the adsorption. The study of kinetic adsorption showed that CPCR followed the kinetic model of Ho. The results of adsorption equilibrium study showed that in adsorption Cr(III) and Pb(II) onto CPCR, Langmuir isotherm model was more applicable than Freundlich model. The tested adsorbents show that CPCR has a good ability in adsorption of Cr(III) (98.50%) and Pb(II) (65.8%) cations.

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