Havy Metal Cations Adsorption by Cinnamoyl C-methylcalix [4] Resorcinarene

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Abstract. Adsorption has been extensively studied as a cost-effective method for removing a wide variety of hazardous materials, such as dyes and heavy metals, from aqueous solutions. The aim of this research is to synthesized and applied of Cinnamoyl C-methylcalix[4]resorcinarene (CCMCR) as the Cr(III) and Cd(II) adsorbent. The cinnamoyl C-methylcalix[4]resorcinarene was synthesized in 4 steps. They were synthesis of C-methylcalix[4]resorcinarene via acid-catalyzed condensation of resorcinol and acetaldehyde, followed by O-acetylation, Friedel-Craft cinnamoylation and hydrolysis. The characterization of the target compound was performed by IR and 1H-NMR. The adsorption of Cr(III) and Cd(II) was carried out in batch system. The effect of operating parameter conditions on capacity adsorption were investigated including acidity, interaction time, and the metal ion concentration. Most parameters in batch system confirm that CCMCR is a good adsorbent for Cr(III) but not good enough for Cd(II). The Cr(III) uptake was bigger than that of Cd(II), and also Cr(III) adsorption rate was faster than Cd(II). The adsorption kinetic both of Cr(III) and Cd(II) adsorptions in batch followed pseudo 2nd order kinetics model. It is mean that the adsorption process depend on concentration and the quantity of active site. The results of adsorption equilibirium study showed that in adsorption Cr(III) and Cd(II) onto CCMCR, Langmuir isotherm model was more applicable than Freundlich model.

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

1. Introduction

Textile industry is particularly known for its high water consumption, as well as for the usage of variety and large quantity of chemicals throughout different process stages [1,2]. Two types of heavy metals that have a negative impact on human health are chromium and cadmium. At sufficiently high concentration chromiums is toxic and carcinogenic [3]. Acute inhalation exposure (high levels over a short period of time) to cadmium can damage the lungs. Chronic exposure can result in kidney, bone and lung disease [4]. Several methods such as precipitation and extraction [5], ion-exchange [6], membrane separation [7] and adsorption [8,9,10] have been reported to remove the heavy metal 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 has been extensively studied as a costeffectivemethod for removing a wide variety of hazardous materials, such as dyes and heavy metals, from aqueous solutions [11]. Calix[4]resorcinarenes are analogs of calixarenehaving two hydroxy groups on benzene rings at extra annularposition forming a macrocycle. Calix[4]resorcinarenes arresynthesized by the acid-catalyzed cyclocondensation of resorcinol with various aliphatic or aromatic aldehydes [12]. They have found application of calix[4]resorcinarenesas macrocyclic receptor [13,14]. The functionalization of the hydroxyl groups of calix[4]resorcinarenes macrocycles can increasing ability in metals cation adsorption. The application of reactants with good leaving groups, such as Br or Cl is a well known procedure for the functionalization of the hydroxyl groups of these macrocycles. However this technique is less efficient for the introduction of certain functional groups, such as amide, amine, hydrazine and others. To overcome this difficulty it was suggested toinclude such functional groups into the side chains of calix[4]resorcinarenesusingcinnamoyl chloride. The structure of CinnamoylC-methyl calix [4] resorcinarene is reported in Fig. 1.

Fig.1. Structure of Cinnamoyl C-methylcalix[4]resorcinarene

2. Materials and Methods

2.1 Materials

All reagents used were dichloromethane, acetic anhydride, resorcinol, acetaldehyde, cinnamoyl chloride, aluminum chloride anhydrous, sodium sulfate anhydrous, sulfuric acid, hydrochloric acid, dichloromethane, ethanol 96%. Metal solutions were prepared by diluting 1000 mg/L Pb(NO₃)₂, Cr(NO₃)₃ and Cd(NO₃)₂ 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. The reagents were commercially obtained from E. Merck with P.A. grade and directly used without any further purification.
2.2 Instrumentation

Structure elucidation of the synthesized compounds was performed using $^1$H-NMR and $^{13}$C-NMR (Agilent 400), as well as FT-IR (Shimadzu, Prestige 21) spectrophotometers. Adsorption process was performed using atomic absorption spectrophotometer (AAS).

2.3 Synthesis Procedure

**Synthesis of C-Methylcalix[4]resorcinarene**

Resorcinol (5.50 g, 0.05 mole), ethanol 95% (25 mL) and water (25 mL) were mixed into 100 mL round bottomed flask. The mixture was stirred for 15 minute. Acetaldehyde 2.8 mL (0.05 mole) and 1.5 mL Hydrochloric acid was then added to the homogenous solution. The mixture was heated for 24 hours at 80$^\circ$C. The product was collected as yellow solid and washed by water. The product was characterized by IR and mass spectrometer.

**Synthesis of C-methylcalix[4]resorcinaryl octaacetate**

Into 100 mL round bottomed flask, C-methylcalix[4]resorcinarene (0.544 g, 0.001 mole), acetic anhydride (12 mL, 0.127 mole) and two drops of sulfuric acid was then added. The mixture was heated for 2 h at 60 $^\circ$C. The solution was cooled and crushed ice was added. The product was collected and washed by water. The product was characterized by IR and 1H-NMR.

**Synthesis of cinamoyl C-methylcalix[4]resorcinaryl octaacetate**

Cinnamoyl chloride (2.686 g, 0.016 mol) were dissolved in 50 mL dichloromethane, poured into 100 mL round bottomed flask consisted compound 2 (0.816 g, 0.001 mole). The solution was cooled to 10-20 $^\circ$C and AlCl$_3$ (2.60 g, 0.0192 mol) was then added in five portion for 2 h. Reaction mixture was refluxed for 5 h. The content of round bottomed flask was poured into a mixture of 10 g of crushed ice and 1 mL concentrated hydrochloric acid. The product was extracted from the solution by dichloromethane(3x50 mL). Organic layer was collected, washed with water (3x50 mL) and dried with anhydrous Na$_2$SO$_4$. The dichloromethane was removed by rotary vacuum evaporator and the yellow solid was collected. The product was characterized by IR and 1H-NMR.

**Synthesis of cinamoyl C-methylcalix[4]resorcinarene (CCMCR)**

Cinnamoyl C-methylcalix[4]resorcinarene (4) synthesized by hydrolyzed compound 3 with NaOH 10% for 3 h (mol ratio 1:100) at 65 $^\circ$C. The product was characterized by IR and 1H-NMR.

2.4. Adsorption Procedures

Adsorption was conducted according to the method as described by Jumina et al (2001) and Budiana et al (2016). The effect of operating parameter conditions on capacity adsorption were investigated including acidity, interaction time, and the metal ion concentration.

A. Effect of acidity (pH) on the adsorption of metal ions

Metal ion solutions are prepared by diluting cadmium nitrate solution 100 ppm with aquabides, so that a standard solution of metal ions is obtained with concentrations of 5, 10, 15, 20 and 25 ppm. In the same way another 100 mL metal ion solution was prepared at a concentration of 15 ppm with pH (2; 3; 4; 5; 6 and 7), by inserting 15 mL of 100 mg / L metal ion solution into a 100 mL flask. The pH adjustment is carried out by adding 0.1 M HCl solution or 0.1 M NaOH. A total of 10 mL metal ion solution with the desired pH is used as a blank, while 5 x 10 mL other solutions are used for the adsorption test of Cinnamoyl C-methylcalix[4]resorcinarene. The weight of the adsorbent used is 0.01 g. The mixture is then stirred for 3 hours. Experiments without using adsorbents (blank experiments) were carried out under the same conditions. After being separated by filtration, the pH of the metal solution is measured by a pH meter, while the concentration of metal ions is determined.
by the AAS. The percentage of metal ions adsorbed is calculated from the difference of the metal before absorption (blank solution) and after absorption.

B. Effect of interaction time on metal ion adsorption

A solution of 10 mL of Cd(II) that has been adjusted to the optimum pH with a concentration of 15 ppm for Cd(II) is placed in a 20 mL glass bottle filled with 0.01 g Cinnamoyl C-methylcalix[4]resorcinarene. Also included in another glass bottle is a metal ion solution that is not filled with adsorbent as a blank solution. All solutions were then stirred using magnetic stirrers for various time variations; 5, 15, 45, 135, 405 and 1215 minutes at the optimum pH. Then the solution was filtered using Whatman 42 paper and the concentration was determined with SSA. The percentage of metal ions adsorbed is calculated from the difference in the concentration of metal ions before absorption (blank solution) and after absorption.

C. Effects of metal ion concentration

A solution of 10 mL of Cd(II) at 5, 10, 15, 20 and 25 ppm concentrations with optimum pH was put into each 20 mL glass bottle filled with adsorbents Cinnamoyl C-methylcalix[4]resorcinarene as much as 0.01 g, and also put 10 mL of metal ion solution at each optimum pH into each of the erlenmeyer that is not filled with adsorbents used as blank solutions. All solutions are then stirred using a magnetic stirrer for optimum time. Then the solution was filtered using Whatman 42 paper and analyzed with atomic absorption spectrophotometer (AAS). From the results of the SSA analysis, obtained absorbance of the sample solution. The percentage of metal ions adsorbed can be calculated by subtracting the concentration of the blank by the concentration of the metal ion of the sample filled with the adsorbent.

3. RESULT AND DISCUSSION

3.1 Mass Spectrum of C-methylcalix[4]resorcinarene

The C-methylcalix[4]resorcinarene(1) was synthesized via acid catalyzed condensation and cyclization of resorcinol and acetaldehyde. The yield of compound 1 is 80.25%. The C-methylcalix[4]resorcinarene was obtained as a yellow solid, melting point >390 °C, IR spectroscopy (KBr pellet, cm⁻¹): 3425 (-OH), 1512 and 1620 (Ar-C=C) and 1435 (C-H bridge), 1H-NMR (DMSO) δ in ppm from TMS: 4.4 (C-H bridge), 6.2 and 6.8 (Ar-H), 8.6 (H of Ar-OH) and 1.3 (H-CH3). The MS spectrum of (1) showed the appearance of a molecular peak at m/z 544 [M⁺] which indicated the molecular mass of C-methylcalix[4]resorcinarene (Fig.2). This compound is insoluble in most organic solvents and only dissolves well in dimethylsulfoxide. This limited solubility in organic solvents and high melting points is due to the presence of strong intramolecular hydrogen bonds in C-methylcalix[4]resorcinarene. This intramolecular hydrogen bond causes the conformation of C-methylcalix[4] resorcinareneshaped cones.
3.2 $^1$H-NMR Spectrum of C-methylcalix[4]resorcinarene

Compound 2 is synthesized through the acetylation reaction of compound 1 using acetic anhydride. This acetylation aims to protect the hydroxy from the Friedel-Craft cinnamoylation on the next step. C-methylcalix[4]resorcinyl octaacetate compound was obtained as a white solid with melting point 230-232 °C, insoluble in water, soluble in acetone and dichloromethane. The change of C-methylcalix[4]resorcinarene to C-methylcalix[4]resorcinyl octaacetate can be observed from the IR spectrum. The change occurred in the form of a strong absorption of C = O ester which appeared at 1759.08 cm$^{-1}$, and the absence of a strong absorption -OH group at 3423 cm$^{-1}$. This shows that the -OH group protection process takes place against the eight -OH groups. The appearance of strong absorption in the area of 1221 cm$^{-1}$ indicates the presence of C-O ether bonds. Characterization of C-methylcalix[4]resorcinyl octaacetate using $^{13}$H-NMR (CDCl$_3$ solvent) as shown in (Fig. 3), shows that the proton bridge [4]resorcinarene appears at 4.21 ppm, aromatic protons appear in the area of 6.83 ppm and 7.25 ppm while the hydroxy proton does not appear. This is caused by the replacement of the hydrogen atom by the acetyl group and is also an indication that all the -OH groups have been protected.

Fig. 2. Mass Spectrum of C-Methylcalix[4]resorcinarene

Fig. 3. $^1$H-NMR Spectrum of C-methylcalix[4]resorcinyl octaacetate
3.3 $^1$H-NMR Spectrum of C-methylcalix[4]resorcinaryl octaacetate

Synthesis of cinnamoyl C-methylcalix[4]resorcinaryl octaacetate was carried out using the Friedel-Craft acylation method by reacting C-methylcalix[4]resorcinaryl octaacetate with cinnamoyl chloride and AlCl$_3$ catalyst. AlCl$_3$ catalyst functions as a provider of empty orbitals that will take electron from Cl atoms so that the cinnamoyl group is positively charged. The cynamoylation product was obtained as a yellow solid with a melting point of 262-264 °C, 90.90% yield, insoluble in water, soluble in dichloromethane and acetone. Characterization of the reaction product with an IR spectrometer, showing an absorption at 1643.35 cm$^{-1}$ caused by the presence of a C = O carbonyl group conjugated with a benzene ring. The C=O ester group appears as a strong and sharp absorption at 1766 cm$^{-1}$. The aromatic absorption of C = C at 1574 cm$^{-1}$, C-H calix bridge at 1427 cm$^{-1}$ and the absorption of methyl groups appears at 1373 cm$^{-1}$. The proton-NMR as shown in (Fig.4) showed that the methyl proton of the calix[4]resorcinarene and methyl acetyl groups appeared at 2.22 ppm and 2.53 ppm, respectively.

![Fig. 4. $^1$H-NMR Spectrum of C-methylcalix[4]resorcinaryl octaacetate](image)

Calix bridge protons [4] resorption-narena appear at 3.75 ppm and aromatic ring protons appear at 7.45 ppm. Sinamoil protons appear at chemical shifts of 6.42 ppm, 6.53 ppm, 7.54 ppm and 7.62 ppm. Based on the results of the characterization of the reaction product using infrared spectrophotometer and proton nuclear magnetic resonance, it can be said that cinnamoyl C-methylcalix[4]resorcinaryl octaacetate are well formed.

3.4 $^1$H-NMR Spectrum of Cinnamoyl C-methylcalix[4]resorcinaryl octaacetate

Cinnamoyl C-methyl[4]resorcinarene is synthesized through the hydrolysis reaction of 3 using 10% NaOH. The reaction product is an orange solid, has a melting point > 390 °C, is insoluble in water, dichloromethane and alcohol but is slightly soluble in dimethyl sulfoxide. Characterization results using IR spectrometers showed that the product had a C = O sinamoil group that appeared at 1689 cm$^{-1}$, the -OH group as a widening peak at 3425 cm$^{-1}$, the sharp peak of the hydroxy group might have been caused by the hydrogen bonding. The results of the characterization with the proton-NMR spectrometer (fig.5) showed a chemical shift at 3.63 ppm caused by the bridge of the calix[4]resorcinarene. The high intensity of protons is probably caused by the joining of two types of protons, the proton bridge and the proton H$_2$O. Proton H$_2$O often appears if the solvent is dimethyl sulfoxide (DMSO), because in its storage process the DMSO solvent can absorb water.
The aromatic proton appears at 6.24 ppm, while the proton sinamoiil group appears as a set of signals at 6.53 ppm, 6.81 ppm, 7.45 ppm and 8.15 ppm. The weak peak at 8.52 ppm is caused by the hydroxyl group proton.

3.5 The Activity Test of Cinnamoyl C-methylcalix[4]resorcinarene as Heavy Metals Adsorbent

The activity test of Cinnamoyl C-methylcalix[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; Cr(III) and Cd(II). 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 cinnamoyl C-methylcalix[4]resorcinarene also parameters of adsorption.

3.5.1 Effect of Acidity

Studying the effect of acidity in the adsorption process is very important because through this process an optimum pH value can be determined. Optimum pH is the pH value where the maximum adsorption occurs. 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. 6 at low pH the percentage of Cr(III) and Cd(II) cation which adsorbed by CCMCR adsorbent is still small. Percentage of the adsorbed Cr(III) and Cd(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 100% and 31.58% respectively. After pH = 7, the percentage of adsorbed Cr(III) and Cd(II) decrease to 0.00 % and 3.05 % on pH=8. At the low pH, adsorbent’s ability to adsorb Cr(III) and Cd(II) 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 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. The competition between H+ ions with cations of metal at low pH has been demonstrated by [16], who found the complex between Ca²⁺ 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.
Adsorption ability of the test compound seems that CCMCR adsorbent can adsorb the Cr(III) by 100.00%. 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 [17], which state that in generally the hard base will form a stable 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.

Adsorption of Cd(II) cation by CCMCR lower than the cation Cr (III) this is in line with the nature of Cd (II) which is a metal with low acidity that will bind properly when the adsorbent also has many active group with low alkalinity such as benzene, -NH₂ and C=C.

### 3.5.2 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 reacher 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 CCMCR reached in the 135 th minute, the percentage change of Cr (III) adsorbed to the next time is not too great. In the Adsorption process of Cd(II) by CCMCR, the equilibrium state reached in the 405 th minutes. It take a lot of time to reached the equilibrium state shows that Adsorption rate of Cd(II) by the adsorbent is slow.
Fig. 7. Effect of interaction time on the adsorption of Cr(III) and Cd(II) onto CCMCR

Slow reaction rate is according to the disprapances properties of adsorbent and Cd(II) cation. All adsorbents have active site in the form of hard alkaline, while Cd(II) is a cation with intermediate alkaline properties. 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 ($q_e - q_t$) as ordinate with t(time) as the axis X. $q_e$ value is the adsorbed mass at equilibrium state (mg/g) and $q_t$ is the adsorbed mass at the time t. Slope value of Largegren is the rate constant ($k$). Ho Models studied by passing the value important to be done to determine the interaction rate that occurs between adsorbent and metal’s cation. The CCMCR rate constant of reaction ($k$) in Adsorption of Cr(III) and Cd(II) are $9.71 \times 10^{-4}$ and $5.49 \times 10^{-4}$ respectively.

3.5.3 Effect of Metals Concentration

Metal Ion’s Concentration effect at optimum pH and time also at constant temperature aim to determine isotherm model followed by adsorption process of CCMCR to Cr(III) and Cd(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 $cn$ be convert 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;
$$\frac{Ce}{q_e} = \frac{1}{Xm.K} + \frac{Ce}{Xm}$$

The passing of Ce/qe as Y-axis and Ce/Xm then can be determined the value of equilibrium constant (K) from the value of intersection and maximum Adsorption capacity (Xm) from the slope. The important parameter to be measured in studied of isotherm adsorption is equilibrium constant (K), maximum adsorption capacity (Xm) 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 tend 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 tend to be release again. Maximum adsorption capacity (Xm) 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 Cd(II) onto CCMCR

The curve in the Fig. 8 showed that at the Cr(III) concentration (5 ppm), all of the Cr(III) ion can adsorbed by CCMCR. 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 CCMCR. It was caused by the saturation of the active site of CPCR. The values of K, Xm and E are tabulated in Table 1.

| Adsorbent | Cations | Regression Equation | Xm   | $K \times 10^4$ | E   |
|-----------|---------|---------------------|------|-----------------|-----|
| CCMCR     | Cr(III) | $Y = 6627X + 0.225$ | 150.89 | 2.94            | 25.45 |
|           | Cd(II)  | $Y = 6548X - 1.692$ | 15.27 | 3.87            | 26.8 |

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.
A 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) and Cd(II) by CCMCR 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 adsorption process.

4. Conclusion

The adsorption experiments in batch system were investigated that acidity level influence significantly the adsorption. The study of kinetic adsorption showed that CCMCR followed the kinetic model of Ho. The results of adsorption equilibrium study showed that in adsorption Cr(III) and Cd(II) onto CCMCR, Langmuir isotherm model was more applicable than Freundlich model. The tested adsorbents show that CCMCR has a good ability in adsorption of Cr(III) (100 %) but not good enough for Cd(II) (31.58%) cations. CCMCR are very potential to be developed as Cr(III) metal adsorbent in aguatic system.

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References

[1] Bansal RC, Goyal M (eds) (2005) Activated Carbon Adsorption. Taylor and Francis Group.
[2] Robinson T, McMullan G, Marchant R, Nigman P, 2001 BioresourTechnol 77 247–25
[3] Johanes Godt, Fransiska Scbeidg, Christian Grosse, Vera Esche, Paul Brandenburg, Adrea Reich and David Doneberg 2006 J Oclip Med Toxicol 1 22
[4] Risco Taufik Achmad, Budiawan and Elza Ibrahim Auerkari 2017 Annual Research and Review in Biology 133-6
[5] Ludwig R and Dzung NTK 2002 Sensor 2 398-403
[6] Jain V K, Pillai S G, Pandya R A, Agrawal Y K, and Shrivastav P S 2005 Anal Sci 21 129-33
[7] Goswani S and Ghosh UC 2005 Water SA 31 578-01
[8] Jumina, Ratnaningsih ES, Siswanta D, Santoso SJ, Ohto K J Korean Chem Soc 55 454-56
[9] Budiana I Gusti M. Ngurah, Jumina, Anwar C and Mustofa 2014 Advanced Material Research 1043, 129-32
[10] BelhachemiMeriem and Fatima Addoun 2011 Appl Water Sci 1 111–17
[11] Gutsche DC 1998 Calixarenes Revisited, Monograph In Supramolecules Chemistry The Royal Society of Chemistry Washington
[12] Jain Vinod K, Parin H. Kanaiya and Narendar Bhojak1 2008 Fibers and Polymers 9 720-26
[13] Charles L. Barnes and Eric Bosch 2007 J ChemCrystallogr 37 783-86
[14] Budiana I Gusti M. Ngurah, Jumina, Chairil Anwar, Sunardi and Mustofa 2017 Indones J Chem 17 64-65
[15] Martel E and Hancock R P 1996 Metal Complexes in Aqueous Solutions 222-224 Plenum Press New York
[17] Handayani D S 2011 Synthesis Poly-p-Propenyl calixs[4]arene and Carboxylates and Esther Derivates as Adsorbent and Antidotum Heavy Metals Disertasion Gadjah Mada University 64-71