

C-Methylcalix[4]resorcinarene 에서 Pb(II)와 Cr(III)의 흡착 특징

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Adsorption Characteristics of Pb(II) and Cr(III) onto C-Methylcalix[4]resorcinarene

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요약. C-Methylcalix[4]resorcinarene(CMCR)에서 Pb(II)와 Cr(III)의 흡착 특징에 대한 연구는 수행되어왔다. CMCR은 resorcinol, acetaldehyde 그리고 HCl로 부터 1단계 합성으로 만들어졌다. 일괄처리시스템에서 대부분의 변수는 CMCR이 Pb(II)와 Cr(III)에 대해 좋은 흡착제라는 것을 확인했다. Cr(III)은 Pb(II)보다 더 크게 흡착되지만 Cr(III)의 흡착속도는 Pb(II)보다 더 느리다. Pb(II)와 Cr(III) 흡착의 흡착운동에너지는 batch안에서 유사 2차 운동 모델을 따른다. 그러나 고정상 컬럼 시스템에서 Pb(II)의 운동에너지는 일차 모델을 따른다. 흡착된 Pb(II)을 되찾기 위한 탈착 연구는 증류수와 HCl을 가지고 순차적으로 수행되었다. 그리고 그 결과는 흡착은 화학흡착에 의해 지배된다는 것을 보여주었다.

주제어: 흡착, Pb(II), Cr(III), C-Methylcalix[4]resorcinarene, 일괄처리시스템, 고정상 컬럼

ABSTRACT. A study on the adsorption characteristics of Pb(II) and Cr(III) cations onto C-methylcalix[4]resorcinarene (CMCR) has been conducted. CMCR was produced by one step synthesis from resorcinol, acetaldehyde, and HCl. Most parameters in batch system confirm that CMCR is a good adsorbent for Pb(II) and Cr(III). Cr(III) uptake was bigger than that of Pb(II), but Cr(III) adsorption rate was slower than Pb(II). The adsorption kinetic of Pb(II) and Cr(III) adsorptions in batch followed pseudo 2nd order kinetics model, but the kinetic of Pb(II) adsorption in fixed bed column system followed first order model. Desorption studies to recover the adsorbed Pb(II) was performed sequentially with distilled water and HCl, and the results showed that the adsorption was dominated by chemisorption.

Keywords: adsorption, Pb(II), Cr(III), C-methylcalix[4]resorcinarene, batch system, fixed bed column

INTRODUCTION

Several methods such as ion-exchange, membrane separation, chemical precipitation, electro-deposition, and adsorption have been used to treat industrial wastes containing heavy metal pollutants. 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 (maize cob and husk,¹ cassava waste,² banana pith,³ ground pine cone⁴), charcoal,⁵ fly ash,⁶ zeolite,^{7,8} and granular activated carbon.⁹ 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.

A class of synthetic macromolecules that demonstrate

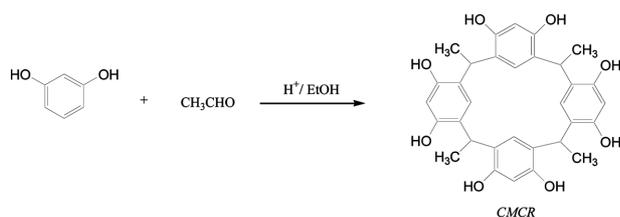


Fig. 1. Synthesis of CMCR.

capabilities to function as adsorbent are calix[4]resorcinarenes. These types of molecules consist of 4 units of resorcinol in a cyclic array which are linked by methylene bridges and are generally obtained by acid-catalyzed condensation of resorcinol with 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 cations, anions, and neutral molecules. The family of calix[4]resorcinarenes has also been used for various functions such as additive for capillary electrophoresis,¹⁰ liquid membrane,^{11,12} extraction,¹³ chemical sensing,^{14,15} and HPLC stationary phase.^{16,17} Nonetheless, there are still limited reports on the utilization of calix [4]resorcinarenes¹⁸ as adsorbent for heavy metal cations.

C-Methylcalix[4]resorcinarene (CMCR) is calix[4]resorcinarene having four benzene rings and eight hydroxyl groups (Fig. 1). CMCR was synthesized directly by acid-catalyzed condensation of resorcinol and acetaldehyde.¹⁹ The reaction proceeds easily, inexpensive, and high yielding. 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 CMCR with its hydroxyl arms and aromatic rings can form both a "hard" and a "soft" ion binding sites, respectively. Thus, it was of interest to investigate the interaction of CMCR with the two said heavy metal cations. This work will become the complement of our previous paper on the adsorption characteristics of Pb(II) and Cr(III) onto C-4-methoxyphenylcalix [4]resorcinarene in batch and fixed bed column systems recently published.²⁰

EXPERIMENTAL SECTION

Reagents

Metal solutions were prepared by diluting 1000 mg/L Pb(NO₃)₂ and Cr(NO₃)₃ standard solutions in aqueous

nitric acid to desired concentrations. An adjustment of pH was carried out by adding slowly NaOH and / or HNO₃ solution into the metal solutions followed by stirring until desired pH. Chemicals needed to synthesis CMCR were resorcinol, acetaldehyde, HCl, and ethanol. All materials required were reagent grade from E-Merck.

Instruments

Equipments used for CMCR synthesis and characterization involved a set of reflux utilities, buchner funnels, nuclear magnetic resonance spectrometer (Jeol JNM-AL300 FT NMR System, 300 MHz), Fourier Transform infrared spectrophotometer (Shimadzu FTIR 8201PC), and mass spectrometer (Jeol GCmate). Pump, glass column, stirrer, shaker, atomic absorption spectrophotometer (AAS, Perkin Elmer Model 3110), and pH meter (Hanna) were used for adsorption experiment and determination of heavy metals concentration.

Synthesis of CMCR

CMCR was synthesized according to the method as described by Tunstad and co-workers.¹⁹ This method was chosen as it seems to be simpler compared to the alternative methods.^{21,22} Thus, into a solution of 5.5 g (0.05 mol) of resorcinol in 25 mL of 95% ethanol was added 25 mL of water and 1.25 mL of concentrated hydrochloric acid under nitrogen. The mixture was stirred and cooled down to 15 °C, and 2.2 g (0.25 mol) of acetaldehyde was added dropwise over 30 minutes. After that, the mixture was stirred at 50 °C for 1 hour and then allowed to cool down to 25 °C. The mixture was then stirred further at room temperature for 4 days under nitrogen and the precipitate that separated was collected. The precipitate was washed with water, and dried to give a white solid of C-methylcalix[4]resorcinarene (85%). Mp > 390 °C (dec): FTIR (KBr) ν (cm⁻¹): 3423 (OH stretching; ¹H NMR (CDCl₃) δ (ppm): 1.69-1.71 (*d*, 3H, CH₃), 4.40-4.48 (*q*, 1H, CH), 6.21 (*s*, 1H, ArH), 7.35 (*s*, 1H, ArH); ¹³CNMR (DMSO) δ (ppm): 20.202 (CH₃), 28.715 (ArCH(Ar)R), 103.90 (CH Ar), 125.26 (CH Ar), 126.18 (C Ar), 152.22 (C Ar), MS *m/z* : 544 (M⁺), 529 (M⁺-CH₃).

Adsorption Procedures

Batch system was conducted by adding 0.1 g of CMCR with particle size of 100-200 mesh into 10 mL of metal cation sample solution having concentration of about 8 mg/L. The mixture was shaken at room temperature for certain period of time. The adsorbent was filtered out and dried in desiccator. 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 CMCR 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_0 and C are the initial and the final metal ion concentrations (mg/L), respectively; V is the volume of solution (mL); A_r 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 weight.

A series of Pb(II) adsorption systems using fixed bed column were conducted in a glass column (10 cm \times 0.5 cm). The Pb(II) solutions were prepared by diluting 1000 mg/L metal cation standard solution in aqueous nitric acid to the desired concentrations (7.0 mg/L). Adjustment of pH of the metal solutions was carried out by adding slowly 0.1 M NaOH and / or 0.1 M HNO₃ solutions followed by stirring until desired pH (5.42). This metal solution was passed through the column in a down flow system at fixed flow rate of 0.5 mL/min. The weight of CMCR was 0.25 g, and its particle size was 100-200 mesh. The height of adsorbent in glass column was 2.4 cm, and its bed volume was 1.2 mL. The solution passed through the column was fractionated into 5 cm³ portions, and the effluent concentration was determined by AAS. Various fractions of the effluent were collected until the ratio of effluent concentration (C) to initial concentration (C_0) equals to one.

Desorption processes were done sequentially. Metal adsorbed was eluted with water, followed by 0.1 M HCl solution at flow rate of 0.1 mL/minute, and 5 mL fractions were collected. Elution of the desorption agents was conducted until the effluent metal concentration equals to the influent metal concentration.

RESULTS AND DISCUSSIONS

Synthesis and Characterization of CMCR

The preparation of CMCR according to the method as previously described¹⁷ afforded 85% yield of this desired compound which was found as light yellow crystals having melting point of >360 °C. Identification of the synthesized CMCR using infrared (IR), proton and carbon nuclear magnetic resonances (NMR), as well as high resolution mass spectrometers confirms the assigned structure. An accurate evidence for the synthesized CMCR was

given by its mass spectrum measured on high-resolution mass spectrometer giving molecular ion peak at $m/z = 544$ which is consistent with the molecular mass of the desired CMCR. Fragmentation of this molecular ion gave peaks at $m/z = 529, 299, 283, 257, 163, 136,$ and 110 (100%). Whereas fragment at $m/z = 529$ (M-15) is originated from the fragmentation of the molecular ion by losing one -CH₃ group, the fragment at $m/z = 110$ is corresponding to resorcinol resulted from a series of fragmentation of the molecular ion.

Effect of pH

Fig. 2 showed that the amount of metal cation adsorbed by CMCR increased in accordance with the increase of initial pH until an optimum value was reached. The optimum pH for Cr(III) cation was in the range of 5.6-5.8, whereas, for Pb(II) adsorption, it was at 4.3-4.5. At higher pH, deposition of metal ions either as their carbonate or hydroxide salts was observed. The difference between the lowest and the highest values of the uptake metals was significantly big for both of Pb(II) adsorption (0-3.4 $\mu\text{mol/g}$) and Cr(III) adsorption (0.6-7.5 $\mu\text{mol/g}$). This means that the efficiency of metal ion sorption by CMCR is controlled significantly by initial pH of the reaction mixture. The fact that the difference between the lowest and the highest values of the uptake metal for Cr(III) adsorption was bigger than those for Pb(II) showed that the effect of initial pH was more significant for the adsorption of Cr(III) rather than Pb(II) adsorption.

CMCR has 8 phenolic -OH groups that may act as the active binding sites. At low pH value, there would be strong competition between H₃O⁺ and metal ion species to interact with the binding sites. The competition would become weaker as the pH of the solution increases. Therefore, we could observe the increase of metal cation adsorption from the increase of pH of the solution. This phenomenon was observed until the optimum pH. Above

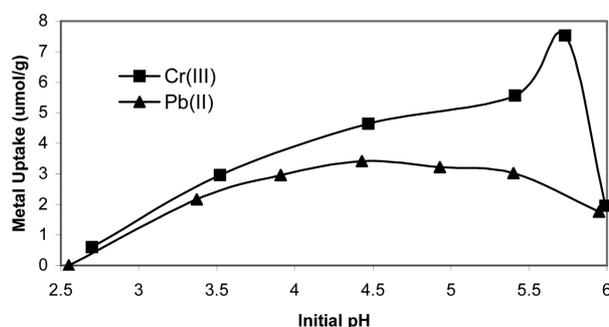


Fig. 2. Effect of initial pH on the adsorption of Pb(II) and Cr(III) onto CMCR.

the optimum pH, the binding sites of the adsorbent should be more anionic, thus stronger adsorption could be resulted. However, at higher pH value, there will be competition of the adsorption and deposition processes since the nature of a metal ion at this pH will change to another form such as its hydroxide salt. It means that if adsorption is the selected method on the experiment of metal cation removal from solution, then moderate pH values (the range of optimum pH) of the solution should be applied. It would be also the case for the application in environment when the existence of dissolved atmospheric CO₂ is unavoidable, then pH adjustment to an optimum pH will prevent the deposition of a metal ion from its carbonate salt form.

Measurements of the equilibrium pH showed that the reactions occurred during the adsorption processes caused slight increases of solution pH. This fact could be explained by the simple hydrolysis reaction of most metal ion (Mⁿ⁺) written as follows:



This reaction generates cation M(OH)⁽ⁿ⁻¹⁾⁺, and protons which contribute to the increase of acidity of Mⁿ⁺ solution. If Mⁿ⁺ is being taken up by CMCR, then the reaction above will shift to the left, leading to the depletion of protons and hence a rise in pH. In contrast, if it is M(OH)⁽ⁿ⁻¹⁾⁺ species which is adsorbed onto CMCR, then the above reaction naturally shifts to the right and the solution becomes more acidic. The pH maximum was used to predict the predominant metal ion species taken up by CMCR.

The equilibrium pH for Pb(II) and Cr(III) adsorptions increases slightly if compared to that of initial pH. This perhaps indicates that the species adsorbed by CMCR was mostly in the form of Mⁿ⁺. As result, the hydrolysis reaction would shift to the left, and accordingly the pH of the solution would increase.

Effect of Interaction Time

The effect of interaction time on the adsorption of Pb(II) and Cr(III) on CMCR was studied from 3 min to 130 minute

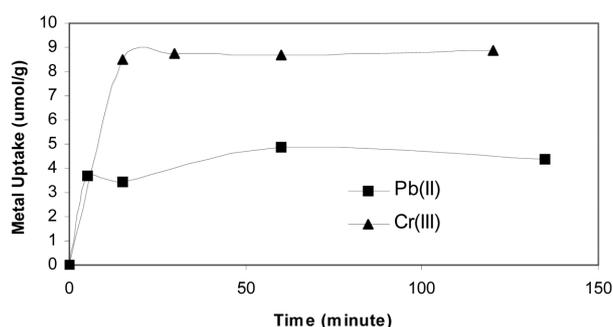


Fig. 3. Effect of interaction time on the adsorption of Pb(II) and Cr(III) onto CMCR.

(Fig. 3). The experiments were carried out at the corresponding optimum pH values. The adsorption of metal cation increased as the interaction time increased, and it attained equilibrium or optimum value in about 15 minutes. Above 90% of metal cation adsorption occurred in the first 15 to 20 minutes, and thereafter the rate of adsorption of the adsorbate species onto CMCR was observed to be slow.

Adsorption Kinetics

The time-dependent experimental adsorption data (Fig. 3) was used for kinetic modeling. The model equations used for fitting the data are: 1st order (Lagergren), pseudo 2nd order, and second order equations. The correlation coefficient (R²) resulting from linear plot of log (q_e-q) versus t, t/q versus t, and 1/(q_e-q) versus t are shown in Table 1. The adsorption rate constant (k) was calculated using slope or intercept values from the equation, where q_e and q (both in mmol g⁻¹) are the amounts of metal ion adsorbed (metal uptake) at equilibrium and at time t (min), respectively.

Based on linear regression values, the kinetics of Pb(II) and Cr(III) adsorptions onto CMCR can be described well by pseudo 2nd order equation (R² = 0.9951 and 0.9999 for Pb(II) and Cr(III), respectively). Thus, it appears that pseudo 2nd order was the most valid kinetics model for all of metal cations adsorption. Therefore, it is possible that both adsorbent and adsorbate give contribution to the reaction

Table 1. Kinetic parameters for Pb(II) and Cr(III) adsorption by CMCR

Kinetic Model		Pb(II)	Cr(III)
1 st Order (Lagergren) equation; Log(q _e -q)=log q _e -(k/2.303)t	R ²	0.756	0.849
	k (min ⁻¹)	0.030	0.045
Pseudo 2 nd order equation; t/q = 1/2 kq _e ² + t/q _e	R ²	0.995	0.999
	k (g mmol ⁻¹ min ⁻¹)	97.344	79.589
2 nd order equation; 1/(q _e -q) = 1/q _e + kt	R ²	0.839	0.124
	k (g mmol ⁻¹ min ⁻¹)	4733.302	5.255

rate. This fact is consistent to that observed for the case of C-4-methoxyphenylcalix[4]resorcinarene (CMPCR)²⁰ in which the adsorption of Pb(II) and Cr(III) on this adsorbent both also follow the pseudo 2nd order kinetic ($R^2=0.9999$ and 0.9993 for Pb(II) and Cr(III), respectively).

The adsorption rate constant (k) of Pb(II) ($k=97.344$ $\text{g}\cdot\text{mmol}^{-1}\cdot\text{min}^{-1}$) was higher than that of Cr(III) ($k=79.589$ $\text{g}\cdot\text{mmol}^{-1}\cdot\text{min}^{-1}$) for the pseudo 2nd order equation. This indicated that the adsorption of Pb(II) onto CMCR was faster than that of Cr(III). Therefore, although the amount of the Pb(II) adsorbed was lower than that of Cr(III), but Pb(II) adsorption onto CMCR goes faster than Cr(III) adsorption. This fact was estimated to have relation to the compatibility of particle size between adsorbent and adsorbate. It is known that the adsorption mechanism of a sorbate onto the adsorbent follows three steps, namely: film diffusion, pore diffusion, and intra particle transport. The slowest step of the above three steps controls the overall rate of the process. Generally, pore and intra particle diffusions are more likely the rate-limiting step in a batch reactor, while for a continuous flow system, film diffusion is more likely the rate-limiting step.²³⁻²⁵

If the adsorption mechanism between adsorbent and adsorbate was dominated by pore diffusion, then the size compatibility between adsorbent and adsorbate certainly plays an important role in order that an effective interaction happened. Cr(III) is an ion which is smaller than Pb(II); their cation radiuses are 1.28 \AA and 2.40 \AA , respectively. Meanwhile, radius of CMCR cavity obtained from calculation result using MM+ Hyperchem 7 method was 3.058 \AA . Accordingly, Cr(III) has rather worse size compatibility against the adsorbent than Pb(II). The incompatibility of size between Cr(III) and the adsorbent could also happened if hydration effect was considered to have a role against adsorbate's size. As stated before that Cr(III) has smaller ion size and bigger positive charge, thus Cr(III) will have bigger hydration energy than Pb(II). Therefore, diffusion rate of hydrated Cr(III) cation which has big size (4.61 \AA)⁷ onto CMCR cavity will be more obstructed.

Nonetheless, the adsorption rate constants of Pb(II) and Cr(III) on CMCR are both bigger than those discovered for the adsorption of the same ions on CMPCR²⁰ which gives adsorption rate constant of 0.490 $\text{g}\cdot\text{mmol}^{-1}\cdot\text{min}^{-1}$ for Pb(II) and 0.0985 $\text{g}\cdot\text{mmol}^{-1}\cdot\text{min}^{-1}$ for Cr(III). The occurrence of the faster adsorption of both ions on CMCR in comparison to that on CMPCR perhaps was caused by the existence of less steric barrier for the occurrence of interaction between metal ions and adsorbent in the former

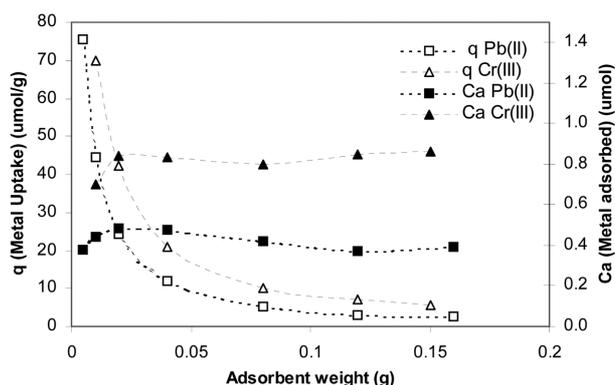


Fig. 4. Effect of adsorbent weight on the adsorption of Pb(II) and Cr(III) onto CMCR.

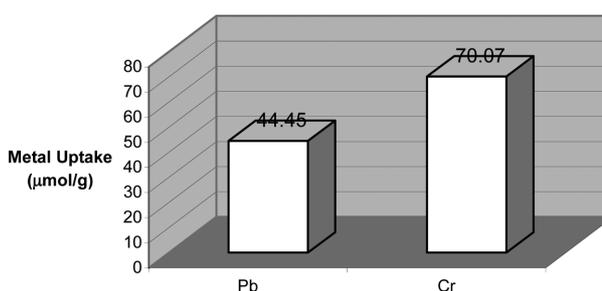


Fig. 5. Metal uptake at optimum condition.

compared to that in the latter. It is understandable that the existence of four extra methoxyphenyl rings in CMPCR would lead to a more crowded structure in this adsorbent compared to that in CMCR.

The Effect of Adsorbent Weight

Fig. 4 shows the effect of adsorbent weight on the adsorption of Pb(II) and Cr(III) onto CMCR at optimum pH and optimum contact time. There was surprising phenomenon observed here, the metal uptake (mmol/g) decreased in accordance with the increasing of the adsorbent weight. However, different phenomenon was noticed if it was the amount of the adsorbed metal in unit of mmol which was compared. From Fig. 4, it was noted that the amount of the metal adsorbed (mmol) did not decrease, but apparently it increased as the amount of the adsorbent increased until an equilibrium state was reached, that was when the adsorbent weight was as much as 0.02 g. The equilibrium state was shown by the unchangeable of the adsorbed metal amount as the adsorbent weight gain. From this fact, it was known that though the amount of the adsorbed metal raised as the adsorbent weight gained, but the increasing of adsorbent surface contact that can interact with adsorbate was not proportional (far more little) with

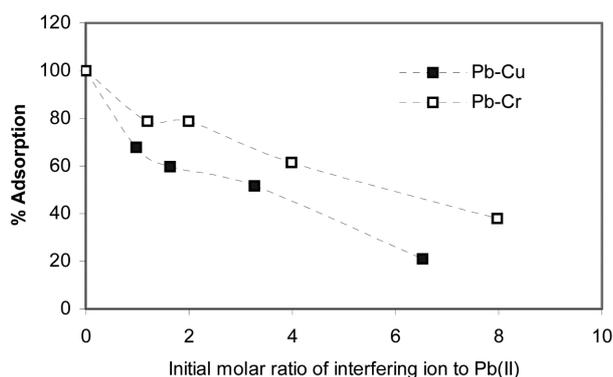


Fig. 6. Effect of the interfering ion on Pb(II) adsorption.

the addition of adsorbent weight. Thus, the amount of the adsorbed metal which is divided by the adsorbent weight will lessen exponentially.

Fig. 5 shows the metal uptake of Pb(II) and Cr(III) adsorptions at the optimum pH, the optimum interaction time, and the same adsorbent weight (0.01g). The figure presented that the removal of Cr(III) by CMCR ($q_e=70.07 \mu\text{mol/g}$) was significantly higher than that of Pb(II) ($q_e=44.45 \mu\text{mol/g}$). According to hard-soft acid base theory, hard acids will form strong bonding with hard bases, while soft acids will establish strong interaction with soft bases. Cation of Cr(III) is hard acid, and Pb(II) is softer than Cr(III), whereas, phenolic -OH groups from CMCR is hard base. Therefore, the interaction between Cr(III) and CMCR should be stronger than that of Pb(II) and CMCR. This is perhaps the reason why the uptake of Cr(III) is higher than that of Pb(II).

Nevertheless, the pattern of metal uptake on CMCR in which the uptake of Cr(III) is higher than that of Pb(II) is inconsistent to that found on the case of CMPCR²⁰ which gives higher metal uptake for Pb(II) ($q_e=173.00 \mu\text{mol/g}$) rather than for Cr(III) ($q_e=6.43 \mu\text{mol/g}$). The occurrence of this opposite pattern in CMPCR perhaps indicated that the presence of four extra OCH₃ groups and four benzene rings which could be classified as medium to soft bases in the molecules significantly affect the character of the adsorbent to be medium or soft ligand. Accordingly, the interaction between Pb(II) and CMPCR is more effective than that of Cr(III) and CMPCR, and hence, the metal uptake of Pb(II) on CMPCR is higher than that of Cr(III) on the same adsorbent.

Effect of Interfering Ions

The interfering effect of some ions on Pb(II) and Cr(III) adsorptions onto CMCR was investigated separately by varying the initial molar concentration ratio of each inter-

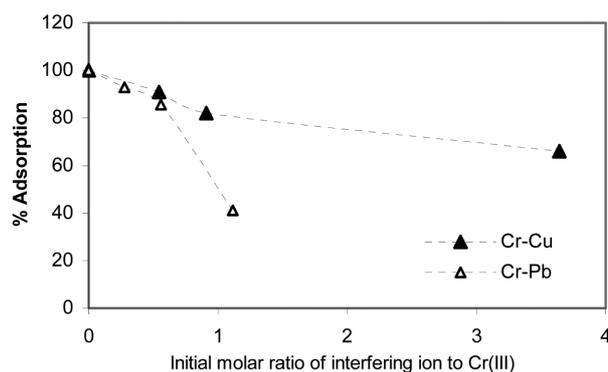


Fig. 7. Effect of the interfering ion on Cr(III) adsorption.

fering ion to Pb(II) or Cr(III). The result in Fig. 6 shows that Cu(II) and Cr(III) caused significant effect on Pb(II) adsorption when the initial molar ratio was varied from 0 to 6.52 (Cu (II)), and from 0 to 7.97 (Cr(III)). Percent of Pb(II) adsorbed decreased up to 37.98% of initial Pb(II) uptake when the initial molar concentration ratio of Cr(III), which acted as the interfering ion, to Pb(II) was up to 7.97. Value of the initial Pb(II) uptake was obtained when no interfering ions presents. Similarly, the presence of Cu(II) gives significant effect in decreasing Pb(II) uptake. The presence of Cu(II) decreased sharply up to 20.97% on initial molar ratio of 6.52. The decrease of Pb(II) adsorbed (in percent) in accordance with the increase of initial molar ratio values is presumably due to the adsorption of the interfering ions. Hence, efficiency of Pb(II) adsorption onto CMCR will decrease to some greater extent as concentration of the interfering ions increase.

It is interesting to note that Cu(II) interfered Pb(II) adsorption greater than Cr(III) did. This could occur since Pb(II) and Cu(II) both are having similar characteristics, whereas Pb(II) and Cr(III) are not. As it is known, Cr(III) is hard acid, while Pb(II) and Cu(II) are borderline acids. Therefore, it can be understood that Cr(III) could not give interfering effect as much as Cu(II) did on Pb(II) adsorp-

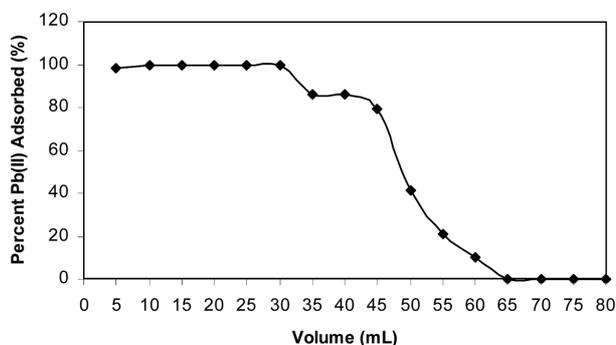


Fig. 8. Percentage of Pb(II) adsorbed by CMCR.

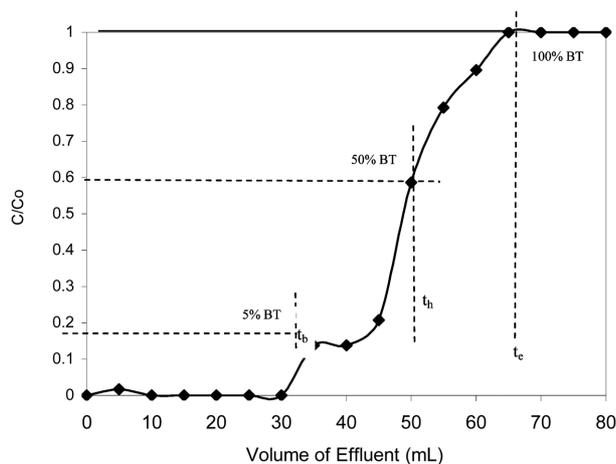


Fig. 9. Breakthrough curve of Pb(II) adsorption by CMCR.

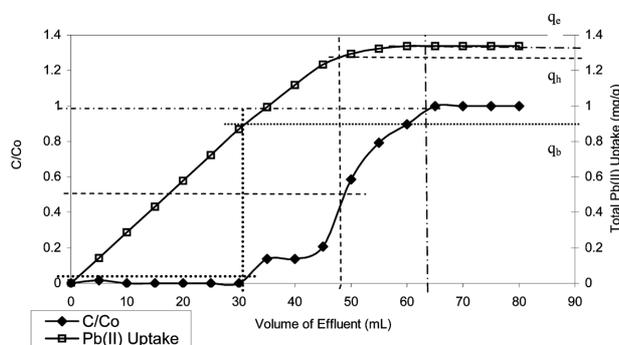


Fig. 10. Total uptake of Pb(II) by CMCR.

tion.

The results of interfering ion effect on Cr(III) adsorption is presented in Fig. 7. The figure above shows that Cu(II) and Pb(II) gave significant effect on Cr(III) adsorption when the initial molar ratio was varied from 0 to 1.67 (Pb(II)), and from 0 to 3.64 (Cu(II)). Percent of Cr(III) adsorbed decreased up to 32.14% of initial Cr(III) uptake when the initial molar concentration ratio of Pb(II), which acted as the interfering ion, to Cr(III) is up to 1.67. Value of the initial Cr(III) uptake was obtained when no interfering ions presents. Meanwhile, the presence of Cu(II) as the interfering ion caused smaller effect in decreasing percent of Cr(III) adsorbed. The presence of Cu(II) decreased sharply but only up to 66.01% on the initial molar ratio of 3.64. Such big the interfering effect caused by Pb(II) might be happened since the compatibility of size between CMCR and Pb(II) is better than between CMCR and another heavy metal cation, as previously stated. Accordingly, the presence of Pb(II) ion which was not far different in ratio with Cr(III) has decreased the adsorbed Cr(III) very significantly.

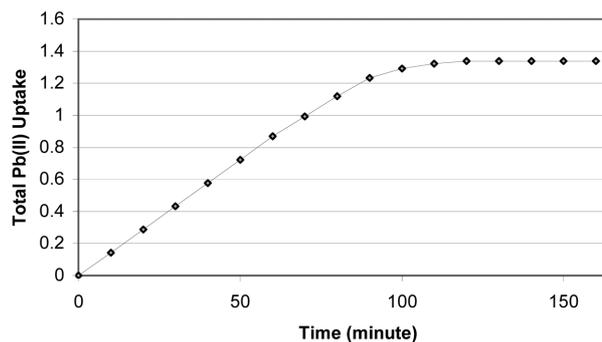


Fig. 11. Kinetics of Pb(II) adsorption by CMCR.

Fix Bed Column Adsorption of Pb(II)

Fig. 8 depicts the percentage of Pb(II) metal adsorbed through the fix bed column adsorption experiment. At some early fractions until about 6 fractions (30 mL), Pb(II) was adsorbed completely (about 100%). In the next fractions, percent of Pb(II) adsorbed decreased sharply until column exhausted, i.e. when concentration of Pb(II) of effluent was the same with concentration of Pb(II) of influent. This column exhaustion has occurred since 13th fraction (75 mL) wherein the throughput volume applied to the column was 80 mL.

Fig. 9 demonstrates the breakthrough curve of Pb(II) adsorption by CMCR. It can be seen that the curve line has a steep slope. The 5% breakthrough point (BT), 50% BT, and 100% BT occurred after passing about 30 mL, 48 mL, and 65 mL, or about 25 bed volume (BV), 40 BV, and 54 BV, respectively. Based on the breakthrough curve, Pb(II) adsorption by CMCR is potential to give a high efficiency since it has steep shape and it only required short period of time for its elution.

The total Pb(II) uptake of the column test (q_e) is presented in Fig. 10. The figure shows that the total Pb(II) uptake was 1.388 mg Pb(II) per g of CMCR or 6.458 mmol/g. The initial breakthrough occurred (5% BT) at column loading of about 0.90 mg of Pb(II) per g of CMCR (q_b). This means that the amount of the Pb(II) adsorbed has reached 64.8% of the total uptake, although Pb(II)

Table 2. Kinetic parameters for Pb(II) adsorption by CMCR with fixed bed column

Kinetic Model	Pb(II)	
	R ²	k
1 st Order (Lagergren) Equation; Log($q_e - q$) = log $q_e - (k/2.303)t$	0.8655	$6.9 \times 10^{-3} \text{ min}^{-1}$
Pseudo 2 nd order equation; $t/q = 1/2 kq_e^2 + t/q_e$	0.7844	$4.7 \times 10^{-3} \text{ g mmol}^{-1} \text{ min}^{-1}$
2 nd order equation; $1/(q_e - q) = 1/q_e + kt$	0.4697	$4.0 \times 10^{-3} \text{ g mmol}^{-1} \text{ min}^{-1}$

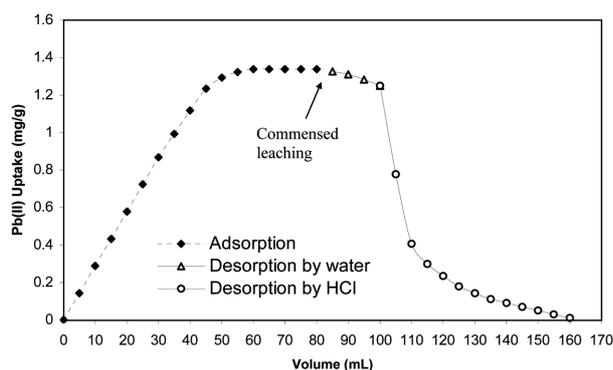


Fig. 12. Sequential desorption of Pb(II) by water and HCl 1 M.

solution applied only 37.5% of total volume or 62.5% operating costs will be consumed for taking 35.2% of the rest of Pb(II). Likewise, at $C/C_0 = 0.5$ in which C = concentration of metal cation in the effluent and C_0 = initial concentration of metal cation, the amount of Pb(II) adsorbed reached almost 92.9%, i.e. 1.29 mg Pb(II) per g CMCR and consumed as much as 60% operating cost, or 40% operating costs will be consumed for taking 7.1% of the rest of Pb(II). Therefore, it was inefficient to run the column fully since the highest efficiency has taken place at column operation until $C/C_0 = 0.5$ (about 50 mL).

Kinetic Aspect

The kinetic aspect of Pb(II) adsorption by CMCR are shown in Fig. 11. The time needed to reach equilibrium was 130 minutes. Based on the graph, the kinetic of Pb(II) adsorption by CMCR occurred rapidly until the state of equilibrium was reached.

In order to figure out a reaction rate order, adsorption can be modeled by the first order Lagergren equation, the pseudo second order rate equation, and the second order rate equation. The rate constant (k) values can be calculated from the slopes or intercepts of the related equation.

According to Table 2, from the three model, the first-order reaction rate model adequately described the kinetics of adsorption of lead with the highest correlation coefficient ($R^2 = 0.86$), and the rate constant (k) of $6.9 \times 10^{-3} \text{ min}^{-1}$. Therefore, it was only adsorbate that gave contribution to the reaction rate.

Desorption

In order to recover the column and to investigate the adsorption mechanism, desorption test of Pb(II) adsorbed by CMCR was done sequentially. In this experiment, desorption was done by water and HCl. Water was used to liberate the adsorbed Pb(II) by physical adsorption via trapping

mechanism, whereas acid solution (HCl) was used to leach the adsorbed Pb(II) by chemical adsorption via ion exchange or hydrogen bond mechanism.

Fig. 12 exhibits the result of Pb(II) desorption experiment. According to the graph, water leached Pb(II) poorly, only about 6.44%, whereas 0.1 M HCl solution leached Pb(II) up to 98.2%. According to the data, Pb(II) adsorption by CMCR was dominated by chemisorption (more than 93%). On the contrary, physisorption ruled adsorption mechanism only in little portion (about 6.44%). Based on these data, it is estimated that Pb(II) ion was adsorbed by CMCR through ionic and hydrogen bonding mechanisms. Thus, there is apparently no chelate or complex formation involved in the adsorption of Pb(II) on CMCR. This phenomenon is consistent to that found on the case of CMPCR²⁰ in which the interaction between Pb(II) and CMPCR is also dominated by chemisorption (>98%).

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