Adsorption Study of Pb(II), Cd(II), Cu(II) and Cr(III) ions in Aqueous Medium using C-4-Hydroxy-3-methoxyphenylcalix[4] resorcinarene Dodecaacetate

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ABSTRACT

This research work presented the application of C-4-hydroxy-3-methoxyphenylcalix[4] resorcinarenedodecaacetate in the removal of Pb(II), Cd(II), Cu(II) and Cr(III) in aqueous medium. Various adsorption parameter such as pH, adsorbent dose and interaction time were investigated. In addition, the kinetic study was conducted by using Santosa's first order, Lagergren's pseudo-first order and Ho's pseudo-second order models. The results showed that the optimum pH for the sorption of Pb(II) and Cu(II) was 4 and that for Cd(II) and Cr(III) was 5. The optimum adsorbent dosage was 0.0175 g for all the metal ions. While the adsorption kinetic for Cd(II), Cu(II) and Cr(III) was relatively fast, the adsorption of Pb(II) occurred in slower rate. Therefore, the kinetic study be solely performed for the adsorption of Pb(II). The adsorption of Pb(II) followed the pseudo-second order of Ho with the equilibrium adsorption capacity and rate constant of 0.3936 mg/g and 0.0865 g/mg.min. respectively. From this study, C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarenedodecaacetate was expected to become an alternative adsorbent in the removal of heavy metals.

Keywords: C-4-hydroxy-3-methoxyphenylcalix[4]resorcina renedo deca acetate, adsorption, heavy metals.

INTRODUCTION

Heavy metal contamination in water is a serious problem, particularly in the health and environmental aspects. It occurs since many industries discharge their waste without any proper treatment. Most of the heavy metal are toxic and may be bio-accumulated in human body. In addition, heavy metal may cause serious health hazards[1]. In this context, WHO regulated the standard quality of metal ion in the drinking water. For instance, the regular limits for Pb(II), Cd(II), Cu(II) and Cr(III) should not exceed 0.01, 0.003, 2.0 and 0.05 mg/L, respectively[2].

To eliminate the amount of metal ions in the aquatic environment, a proper and effective wastewater treatment is highly required. Various techniques have been developed such as adsorption, ion-exchange, coagulation and precipitation. Among them, adsorption offers several advantageous such as simple operation, good efficiency and the possibility to recycle the adsorbent. It is also cheap and can be applied at low concentration of metal ions[3]. A number of natural and synthetic adsorbents have been applied in the removal of heavy metal ions such as zeolite[4], humic acid[5], modified chitosan[6-8], biosorbent[9] and calixarene[10-11].

Calixarene is a cyclic oligomer of phenol which posses unique structure and shape. The presence of cavity and the unlimited functional group modification has led this macrocycle to be mainly applied in host-guest chemistry[12]. This study will more focus on the cyclic oligomer of resorcinol namely calix[4]resorcinarene. The previous reports showed that calix[4]resorcinarene was significantly efficient in heavy metal adsorption[13-17].

The design of calix[4]resorcinarene-based-adsorbent was carried out by installing numbers of chelating atoms into its framework. The potential functional groups which display good affinity towards the metal ions include amine, alcohol, ether, phosphine, carbonyl and carboxylic acid derivatives[8, 18-21]. In the connection with our study, we have synthesized C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarenedodecaacetate containing acetoxy and alkoxy moieties. Beside the simple adsorbent preparation, it was expected that the increase of chelating atoms may be beneficial to the heavy metal sorption. Therefore, the adsorption performance of the synthesized calix[4]resorcinarene in the removal Pb(II), Cd(II), Cu(II) and Cr(III) ions will be investigated.

EXPERIMENTAL

Materials and instrumentation
Adsorbent of C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarenedodecaacetate was prepared according to the previous study (Figure 1). The adsorbent was sieved to give the particle size of 100 mesh. The stock solutions of $Pb(NO_3)_2$, $Cu(NO_3)_2$, $Cd(NO_3)_2$ and $Cr(NO_3)_3$ (1,000 mg/L in

HNO$_3$ 0.5 M) were purchased from E. Merck. The stock solution was diluted with deionized water to give the desired concentration. The concentration of the metal ions was determined by atomic absorption spectrometer (AAS, Perkin Elmer 3110 USA) and was corrected with the blank solution. Solutions of HCl (0.1 M) and NaOH (0.1 M) were utilized to adjust the pH of the solution. The pH was determined by pH meter (Orion model 370).

Adsorption Study
The adsorption was carried out in batch system. As much as 0.1 g of the adsorbent was introduced into the 10 mL of metal solution in certain concentration and followed with the shaking at temperature ambient for certain period of time. The filtration of the mixture gave the filtrate which was analyzed by means of AAS spectrometer to determine the metal concentration. Additionally, the concentration of metals in blank solution was also measured. The adsorption capacity q (mmol/g) for such experiment was calculate based on Eq. 1.

$$q = \frac{(C_o - C_f)V}{W} \qquad \text{...(1)}$$

where C_o was the initial concentration of metal ion, C_f was the metal ion concentration after certain period of time. The volume of metal solution and the mass of the adsorbent were defined as V and W, respectively.

In this study, several adsorption parameters were evaluated including pH, mass of adsorbent and interaction time. The kinetic study was also performed

R_1 = OAc
R_2 = OMe
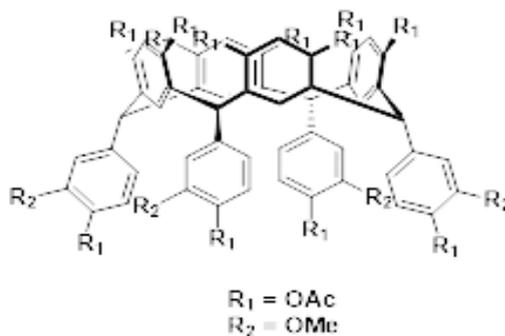
Fig. 1: The Structure of C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarenedodecaacetate

by using three models. The first-order model was proposed by Santosa[22] which was based on the concentration of the adsorbate in the aqueous phase and can be described by the eq. 2.

$$\frac{ln\left(\frac{c_o}{c_f}\right)}{c_f} = k\,\frac{t}{c_f} + K \qquad ...(2)$$

where t was adsorption time (minute), k was first order adsorption rate constant (minute^{-1}) and K was equilibrium constant (mol/L). In addition, the next two models (Lagergren and Ho) were based on the concentration of the adsorbate in the solid phase. The Lagergen's pseudo-first order and the Ho's pseudo-second order were generally expressed by eq. 3 and 4[23-24], respectively.

$$log\,(q_e - q_t) = log\,q_e - \frac{k}{2.303}t \qquad ...(3)$$

$$\frac{t}{q_t} = \frac{1}{k.q_e^2} + \frac{t}{qe} \qquad ...(4)$$

where q_e and q_t were the adsorption capacity (mg/g) at the equilibrium and contact time t, while k_1 and k_2 were the rate constants of the pseudo-first order (mg.g^{-1}.min^{-1}) and the pseudo-second order (g.mg^{-1}.min^{-1}), respectively.

RESULTS and DISCUSSIONS

We have performed adsorption study of some selected heavy metal cations (Pb(II), Cd(II), Cu(II) and Cr(III)) by using C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarenedodecaacetate as adsorbent. The study was carried out under different pH, adsorption dose and contact time in order to determine the maximum adsorption capacity. In addition, the kinetic study was also conducted to determine the kinetic mechanism of the adsorption of the heavy metals.

Effect of pH

pH is one of the important parameter in the adsorption study since it may affect the nature of both adsorbent surface and the metal ion[25]. In this study, the adsorption was carried out in the range pH of 2-6. As displayed on Figure 2, the adsorption profiles

for all metal ions were dependant to the pH value and displayed similar pattern. In acidic condition, the adsorption capacity was relatively low. Increasing the pH enhanced the capacity until the optimum pH and the higher pH led to the decrease of adsorption capacity.

These results can be explained by considering electronic interaction between the adsorbent and the speciation of metal ions[26-28] in different pH. In term of metal speciation, both Pb and Cd are mainly existed as Pb^{2+} and Cd^{2+} under pH 6. On the other hand, the major species of Cr^{3+} and Cu^{2+} can be found under pH 2 and 4, respectively. Increasing the pH value allowed to these metal ion to coordinate with ligand exists on the system to form the metal complex which posses lower positive charge ($M^{(n-x)+}$).

In low pH, all the metal ions were in the form of free metal ion (M^{n+}). However, the proton was also present in the medium and was the potential Lewis acid to interact with the adsorbent. Therefore, the competition between the proton and the metal ion may decrease the adsorption capacity. The increase of adsorption capacity toward all the metal ions were observed starting from pH 3 until the optimum pH values were reached. The rationalization of these results was probably due to the decrease of the proton concentration. Therefore, the adsorbent will preferably interact with the metal ion. While the optimum pH of Pb(II) and Cu(II) was 4, the maximum adsorption capacity for Cd(II) and Cr(III) was reached at pH 5. Performing the study above the optimum pH diminished the adsorption capacity due to the increasing of the hydroxyl ion concentration. This allowed the formation of lower charge metal complex
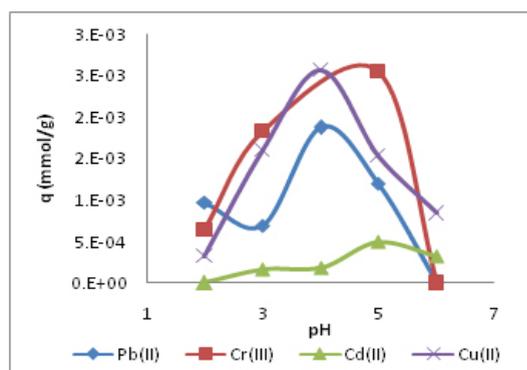
Fig. 2: The Adsorption profiles of all metal ions

and, therefore, decrease the interaction between metal and adsorbent.

Effect of adsorbent dose

The effect of the adsorption dosage on the removal of the metal ions was investigated by varying the adsorbent mass ranged from 0.0175 to 0.15 g **(**Figure 3)**.** The study was carried out at the initial metal concentration of 10 ppm at temperature ambient and under the optimum pH. It was expected that increasing the dose may supply more the adsorption sites and may, therefore, enhance the capacity. However, we observed the decrease on the adsorption capacity for all the metal ions with the increasing of the adsorption dose. The reason may be owing to the aggregation of the adsorbent due to the high concentration of adsorbent. As the

consequence, the available adsorption sites were decreased[29].

Effect of contact time

The effect of contact time to the removal of metal ion using calix[4]resorcinarene adsorbent was presented in Figure 4 and 5. The adsorption of Cu(II), Cd(II) and Cr(III) dramatically increased at 3 min. After 3 min of interaction time, the adsorption capacity of Cd(II) was relatively constant, while that of Cu(II) and Cr(III) tended to decrease. The decrease on the capacity was probably due to the weak interaction between the adsorbent and the metal ion. On the other hand, the rate of Pb(II) adsorption was relatively low comparing to the others. The rapid increase of the adsorption capacity occurred at the

Fig. 3:The effect of the adsorption dosage on the removal of the metal ions

Table 1:The three kinetic profiles of the adsorption of Pb(II) onto the calix[4]resorcinarene

Kinetic Parameter		Pb(II)
q_e (mg/g)	0.4454	
Santosa's first order	k (1/min)	0.0004
	r^2	0.8823
Lagergren's pseudo -first order	k_1 (1/min)	0.0012
	q_e (mg/g)	0.2775
	r^2	0.8185
Ho's pseudo-second order	k_2 (g/mg.min)	0.0865
	q_e (mg/g)	0.3936
	r^2	0.9995
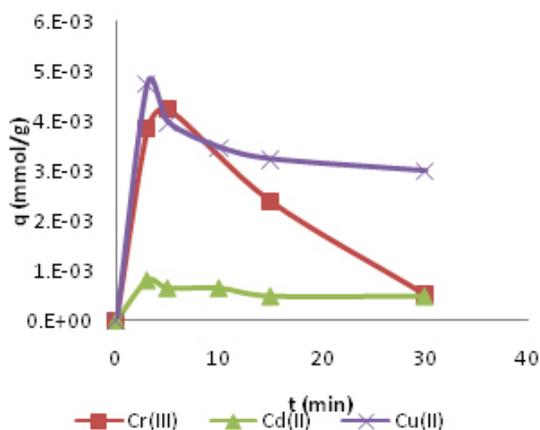
Fig. 4: The effect of contact time to the removal of Cr(III), Cd(II), and Cu(II)
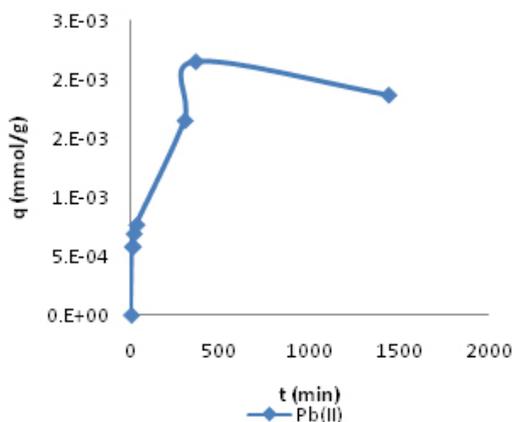
Fig. 5 :The effect of contact time to the removal of Pb(II)

first 30 minutes. The capacity gradually increased and reached the equilibrium at 360 minutes.

Kinetic study

In order to investigate the mechanism of metal sorption on calix[4]resorcinarene adsorbent, three kinetic equation models were utilized. They were first order of Santosa, pseudo first-order of Lagergren and pseudo-second order of Ho. Unfortunately, the adsorption kinetic of Cu(II), Cd(II) and Cr(III) ions could not be studied due to the very

rapid sorption at the initial stage and the decrease of capacity as the function of time.

The kinetic profiles of the adsorption of Pb(II) onto the calix[4]resorcinarene by using the three kinetic models were depicted in (Figure 6a-c and Table 1). By comparing the value of the linear regression value (R^2) of each model, it was found that Ho's pseudo-second order ($R^2 = 0.9995$) had the highest linearity comparing to Santosa's first order ($R^2 = 0.8823$) and Lagergren's pseudo-first order
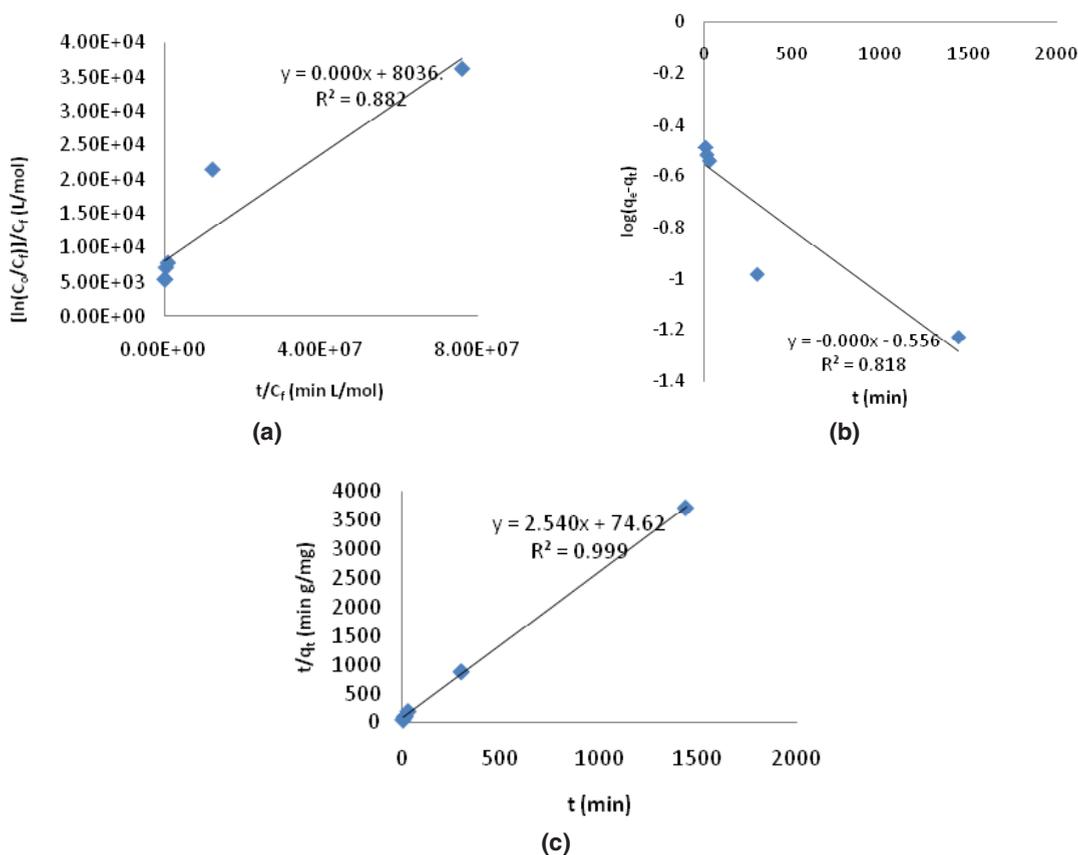
Fig. 6 : The three kinetic models (a) Santosa's first order (b) Lagergren's pseudo-first order (c) Ho's pseudo-second order

($R^2 = 0.8185$). It indicated that that adsorption process could be better described by the second order of Ho.

According to the Ho's equation, the adsorption capacity at the equilibrium can be determined from the slope of the plot of t/q_t vs t. The capacity was 0.3936 mg/g and was more closer to the experimental adsorption capacity. Moreover, the

calculated rate constant (k_2) was found to be 0.0865 g/mg.minutes.

CONCLUSION

Adsorption study of several heavy metal ions of Pb(II), Cd(II), Cu(II) and Cr(III) onto C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarenedodecaacetate

has been successfully carried out. The results showed that the adsorbent was effective to remove Pb(II) and Cu(II) at pH 4 as well as Cd(II) and Cr(III) at pH 5. It was noticed that the increase of the adsorbent dose led to the decrease of adsorption capacity. It has been also found that the adsorption rate for Pb(II) was relatively lower than the that for the others. Moreover, the adsorption of Pb(II) followed the pseudo second order model of Ho. From this study, C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarenedodecaacetate was expected to become an alternative adsorbent in the removal of heavy metals.

REFERENCES

1. Bailey, S.E.; Trudy, J.; Olin, T.J.; Bricka, M.R.; Adrian,D.D. *Water.Res*. **1999**,*33*(11), 2469–2479.
2. W.H.O. Guidelines for drinking-water quality, 4th Ed., Geneva,*WHO Press* **2011**..*327,*340, 383.
3. Ren, Y.; Zhang, M.; Zhao, D. *Desalination* **2008**, *228*, 135-149.
4. Blanchard, G.M. ; Maunaye ; Martin, G. *Water. Res.***1984**,*18*(12), 1501-1507.
5. Jin, X. ; Bailey, G.W. ;Yu,Y.S., Lynch, A.T.*Soil Science***1996**, *161*(8), 509-520.
6. Tabakci, M.; Yilmaz, M. *Bioresour. Technol*. **2008**,*99*, 6642-6645.
7. Li, H-B.; Chen, Y-Y.; Liu, S-L. *J. Appl. Polym. Sci.* **2003**,*89*, 1139-1144.
8. Siswanta, D.;Jumina ;Anggraini, M; Mardjan, M.I.D.;Mulyono, P.;Ohto, K. *Int. J. Appl. Chem.***2016**,*12* (1), 11-22.
9. Dang, V.B.H.;Doan,H.D.; Dang-Vuc, T.;Lohi, A. *Bioresour. Technol.* **2009**,*100*, 211-219.
10. Tabakci,M.; Yilmaz,M. *J. Hazard Mater*. **2008**,*151*, 331-338.
11. Tabakci, M.; Erdemir, S.;Yilmaz, M. *J. Hazard Mater*. **2007**,*148*, 428-435.
12. Gutsche,C.D. Calixarenes, Monograph in Supramolecular Chemistry,Cambride,*Royal Society of Chemistry*. **1989**.
13. Al-Trawneh, S.A. *Jordan J. Earth Env. Sci.***2015**,*7* (1), 1-9.
14. Utomo, S.B.;Jumina; Siswanta, D.;Mustofa. *Indones. J. Chem.* **2012**.,*12* (1), 49-56.
15. Jumina;Sarjono, R.E.;Paramita, B.W.; Siswanta, D.;Santosa, S.J.; Anwar, C.;Sastrohamidjojo, H.;Ohto, K.;Oshima, T. *J. Chin. Chem. Soc.* **2007**,*54* (5), 1167-1178.
16. Jumina;Sarjono, R.E.; Siswanta, D.;Santosa, S.J.;Ohto, K. *J. Korean Chem. Soc.* **2011***, 55* (3). 454-462.
17. Kesuma, F.E.;Jumina;Ohto, K.; Siswanta, D. *Orient. J. Chem.* **2016**,*32* (2), 769-775.
18. Handayani, D.S.;Jumina; Siswanta, D.;Mustofa;Ohto, K.;Kawakita, H. *Indones. J. Chem.* **2011**,*11* (2), 191-195.
19. Adhikari, B.B.;Kanemitru, M.;Kawakita, H.;Jumina;Ohto, K. *Chem. J. Eng.* **2011**,*172*, 341-353.
20. Adhikari, B.B.;Ohto, K.; Schramm, M.P. *Chem. Commun.* **2014**,*50*, 1903-1905.
21. Adhikari, B.B.;Gurung, M.;Chetry, A.B.;Kawakita, H.;Ohto, K. *RSC. Adv.***2013**,*3*, 25950-25959.
22. Santosa, S.J.; Siswanta, D.;Sudiono. S.;Sehol, M. *Surf. Sci.* **2007**,*601*, 5148-5154.
23. Ho, Y.S.; McKay, G. *Process Biochemistry***1999**,*34*, 451-465.
24. Ho, Y.S. *J. Hazard. Mater.***2006**,*136*, 681-689.
25. Wu, Y.H.; Jiang, L.;Mi, X.M.; Li, B.;Feng, S.X. *Korean J. Chem. Eng*. **2011**,*28* (3), 895-901.
26. Berber-Mendoza, M.S.;Leyva-Ramos, R.; Alonso-Davila, P.; Mendoza-Baron, J.; Diaz-Flores, P.E. *J. Chem. Tech. Biotech.* **2006**,*81*, 966-973.
27. Odisitse, S.; Jackson, G.E.;Govender, T.; Kruger, H.G.; Singh, A. *Dalton Trans.* **2007**, 1140-1149.
28. Santos, V.C.G.D.;Salvado, A.D.P.A.;Dragunski, D.C.;Peraro, D.N.C.;Tarley, C.R.T.; Caetano, J. *Quim. Nova.* **2012**,*35* (8), 1606-1611.
29. Ramesh, A.; Hasegawa, H.; Maki, T.; Ueda, K. *Sep. Purif. Technol.***2007**,*56* (1), 90-100.