RESEARCH ARTICLE

STUDY OF PB(II) AND FE(III) METAL CATIONS ADSORPTION INTO *P*-TERT-BUTYLCALIX[4]ARENE AS ADSORBENT: KINETIC ADSORPTION.

Busroni[1], Siswanta. D[2], Santosa. S. J[2] and Jumina[2].
1. Departement of Chemistry, Faculty of Matematics and Natural Sciences, University of Jember, Indonesia.
2. Departement of Chemistry, Faculty of Matematics and Natural Sciences, Gadjah Mada University, Yogyakarta.

………………………………………………………………………………………………....

Manuscript Info	*Abstract*
……………………..	………………………………………………………………
	This research explain the study about compound of 5,11,17,23-tetra(t-Butyl)-25,26,27,28-tetrahidroxycalix[4]arene (TBCA) that will be used as adsorption material for heavy metal cations. Adsorption using immersion method with variations such as the value of acidity (pH), time of exposure and initial concentration of metal cations have been conducted. The results of each investigation showed that the optimum pH of adsorption was at pH = 5 for metal cations of Pb(II) and Fe (III). The observation results showed the optimum time exposure of cation adsorption of Pb(II) and Fe(III) was 90 minutes. Study about kinetic adsorption of Pb(II) metal cations of the adsorbent refered the Ho kinetic model, pseudo second order with rate constant of adsorption 143×10^{-3} g.mol^{-1}.min^{-1} and Fe(III) refered the Lagergren kinetics model, pseudo first order with the rate constant of 9.21×10^{-3} min^{-1}. The observation of the study showed that the isotherms adsorption for metal cations of Pb(II) and Fe(III) refered the pattern trend of Langmuir isotherm models. The value of the optimum capacity for metal cation adsorption Pb(II) and Fe(III) each was 128.46 mg/g and 156.09 mg/g respectively. Adsorption energy for Pb(II) and Fe(III) was 5.81 k.J/mol and 7.01 kJ / mol, respectively.

……………………………………………………………………………………………....

Introduction:-
The existence of the metal cations can endanger human health as heavy metals if enter into the body, because the heavy metals are toxic/poison. Heavy metals are chemical elements with a specific gravity greater than 5 g/cm^3 that located in the lower right corner of the periodic table system. Iron or Ferrum (Fe) is a silvery-white metal, clay, and can be formed. It has been conducted a study of adsorption of metal cations Fe(III) in aqueous systems using zeolite, in the determination of adsorption of metal cations Fe^{+3} performed at pH area between 1-6 [1]. Lead was widely used in the paint factory, fuel, battery industry and ammunition bullets. Lead is toxic which very influenced toward children, because the paint is widely used in residences. If the metal contains in the blood up to 10 mg/mL, it can cause illness symtoms and Pb(II) concentrations in the water does not depend on the season, but on the depth. Lead ions contained in the water can get into the body of the fish and other aquatic animals [2]. Siswanta research resulted that the adsorbent Calix[4]resorcinarene, hybrid or Calix[4]resorcinarene-chitosan and chitosan can be applied to eliminate the Pb(II) metal ions. The results of the investigation explained that the value of adsorption capacity was Calix[4]resorcinaren > Chitosan > Calix [4] resorcinarene-chitosan (hybrid) [3]. Prabawati, reported that it can be synthesized compounds of p-t.butyl-37-monoallyloxy-38,39,40,41,42-pentahidroxycalix[6]arene and p-t.butyl-

---

Corresponding Author:- Busroni.
Address:- Departement of Chemistry, Faculty of Matematics and Natural Sciences, University of Jember, Indonesia.

37,40-diallyloxy-38,39,41,42-tetrahidroxycalix[6]arene then each of them was treated by polymerization reaction in order so can be obtained poly-monoallyloxycalix[6]arene compound [PMK(6)H]arene and poly-diallyloxycalix[6]arene compound [PDK(6)H]arene and was applied to study the adsorption kinetics for Cu(II), Cd(II), and Cr(III) [4,5,6]. Calixarene can form complexes with the type of aromatic compounds in a polar solvent non water. Compounds calixaren with basketball shape has high potential as a host-guest. In this case, this calixarene compound capable to clamp the organic molecules. Calixarene compounds can be synthesized and derivatized at the "Lower Rim", therefore the part of upper rim calixarene rim is slow to develop [7]. Some type of adsorbent has been used to eliminate or reduce heavy metals, *i.e.* Poly-Calix[4]arene-Crown-6 [8,9,10,11], benzyloxycalix[4]arene [12], Calix[4]Resorcine [13,14], calixarene derivative [15], Calix[8] arene Derivative. [16], Bisazocalix[4]arene [17], t-butylcalix[4]arene derivatives [5]. Many attempts have been made to reduce the concentration of heavy metal cations, and guided by a number of facts about the consequences caused by the presence of heavy metal cations, the effort was made to reduce the concentration, especially in the waters.

Research Methods:-
1. Materials and Instrumentation
Material: Compounds tb-Calix[4]arenes were synthesized following the reported procedure [18], aquabides / aquadimeneral (Lab. Organic FMIPA-UNEJ), FeCl3, Pb (NO3) 2, another reagent (Merck branded) was used without special treatment.
Instrumentation: PRESTIGE 21 Shimadzu FTIR-spectrometer with KBr, Electrothermal Digital Point, H-NMR AGILENT Varian 400 MHz, AAS Buck Scientific.

2. Methods
Effect of pH
 As many as 10 mL sample solution with a pH of 3; 4; 5; 6 was put in a 15 mL glass bottles that have been filled by 5 mg adsorbent. Each bottle was stirred using a magnetic stirrer for 3 hours, filtered with filter paper then the residue metal cation was determined using filtrate which was analyzed using atomic absorption spectrophotometer (AAS) to determine how the cations were adsorbed.

Effect of time exposure:-
Cation solution of Pb(II) and Fe(IIII) based on observation at optimum pH of 5 was prepared about 10 mL in amount and inserted into a 15 mL vial glass which was filled with adsorbent 10 mg in each. All of the test solution was stirred using a magnetic stirrer with a time variation of 10, 20, 30, 90, 180, 240 minutes. Then the solution was filtered and the filtrate was analyzed by AAS.

Effect of adsorbate concentration:-
 Each sample solution of metal cations Pb(II) and Fe(III) was prepared about 10 mL amount at optimum pH with various concentrations of 8, 16, 20, 24, 30 ppm and put in a 15 mL glass bottle sizes that have been filled adsorbent 10 mg. All solutions were stirred with optimum time. Then it was filtered and each filtrate was analyzed by AAS.

Results and Discussion:-
Effect of pH:-
Metal cation adsorption capacity was very dependent on the amount of the pH solution. At low pH /very acidic condition, the number of H^+ ions became high and it resulting in the OH groups protonation. Then the property of the OH group became positively charged and the ability as a ligand will be reduced. The positive charge on the adsorbent tb-calix[4]arenes caused repeling process between H^+ with metal ions, so that the adsorption value became small. Adsorption increased in line with the increasing of pH value around pH 5. As shown in Figure 1, it exhibited that the adsorption of metal cations Pb(II) and Fe(III) to tb-calix[4]arene depended on the pH factor. Both of metal cation Pb(II), and Fe(III) were maximum adsorbed at pH 5 with Pb(II), and Fe(III) adsorbed value was 10.52 mg / g and 14.18 mg / g. respectively (Fig. 1).
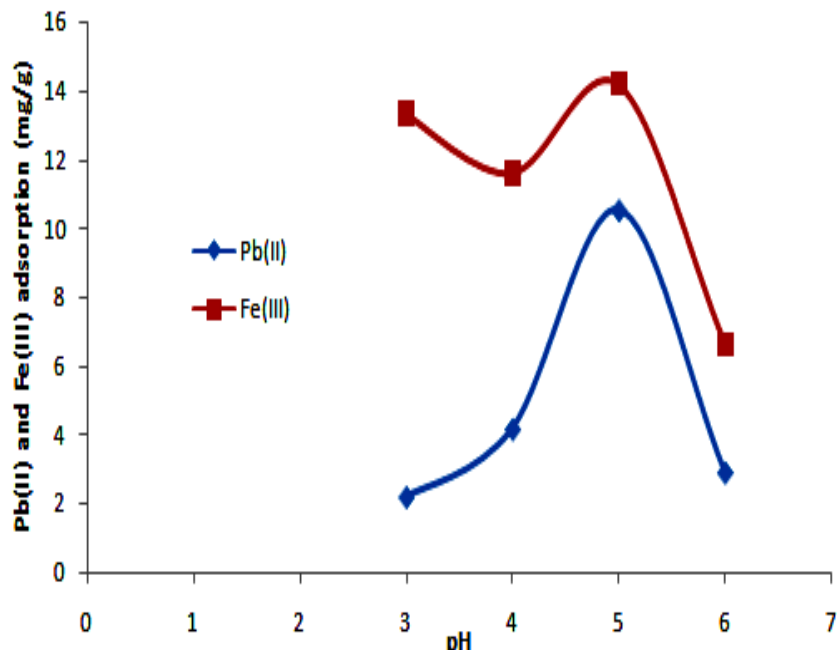
Fig.1:- Effect of pH on the Pb(II), and Fe(III) cations adsorption by p-t-Butylcalix[4]arene (TBCA)

Effect of exposure time:-

The adsorption kinetics of Pb(II) and Fe(III) cations into p-t-Butylcalix[4]arenes was presented in Fig. 2. According to the investigation results, the optimum exposure time of metal cations of Pb(II) and Fe(III) was 90 minutes, with the cation concentration that can be adsorbed was 12.69×10^{-2} mmol/g and 34.77×10^{-2} mmol/g respectively. The measurement of adsorption kinetic rate can be determined by using the interaction time required to reach a state of equilibrium adsorption. The used general parameters to study the adsorption rate was reaction rate cosntant (k). From Table 1, it can be studied that the adsorption kinetics model reffered to first order Lagergren kinetics model, and second order kinetic model [19, 20, 21]. The results of calculations were presented in Table 1.

Table 1:- Adsorption Kinetic Models

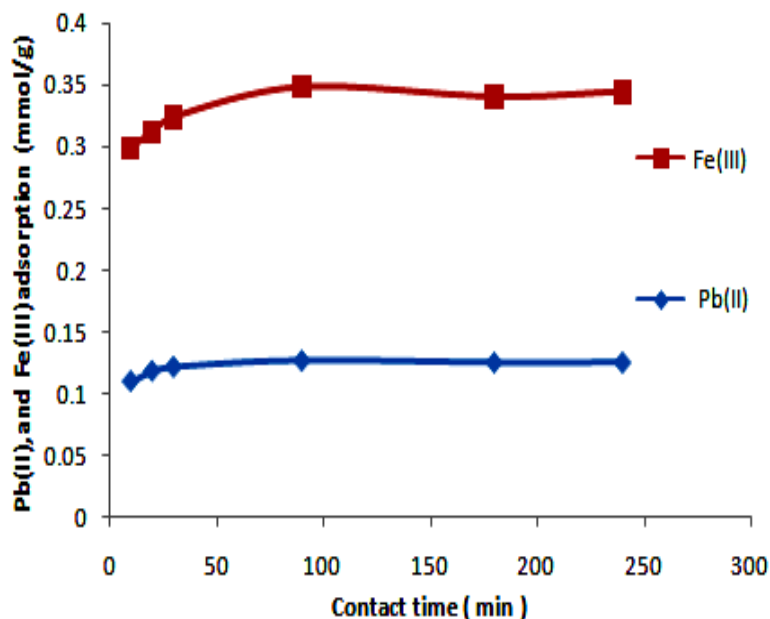| Kinetic Models	Pb(II)		Fe(III)	
	R^2	k	R^2	k
Pseudo Orde 1 (Lagergren) $$(q_e - q_t) = \log(q_t) - \frac{k_1}{2,303} t$$	0,836	$6,91 \times 10^{-3}$. (minute^{-1})	0,971	$9,21 \times 10^{-3}$ (minute^{-1})
Pseudo Orde 2 (Ho) $$t k_2 q_e^2 = \frac{q_e \cdot q_t}{(q_e - q_t)}$$	0,957	143×10^{-3} (g.mg^{-1}. minute^{-1})	0,928	16×10^{-3} (g.mg^{-1}. minute^{-1})

Fig. 2:- the effect of time exposure on removal of Pb(II) and Fe(III) cations by p-t-Butylcalix[4]arene (TBKA) adsorption
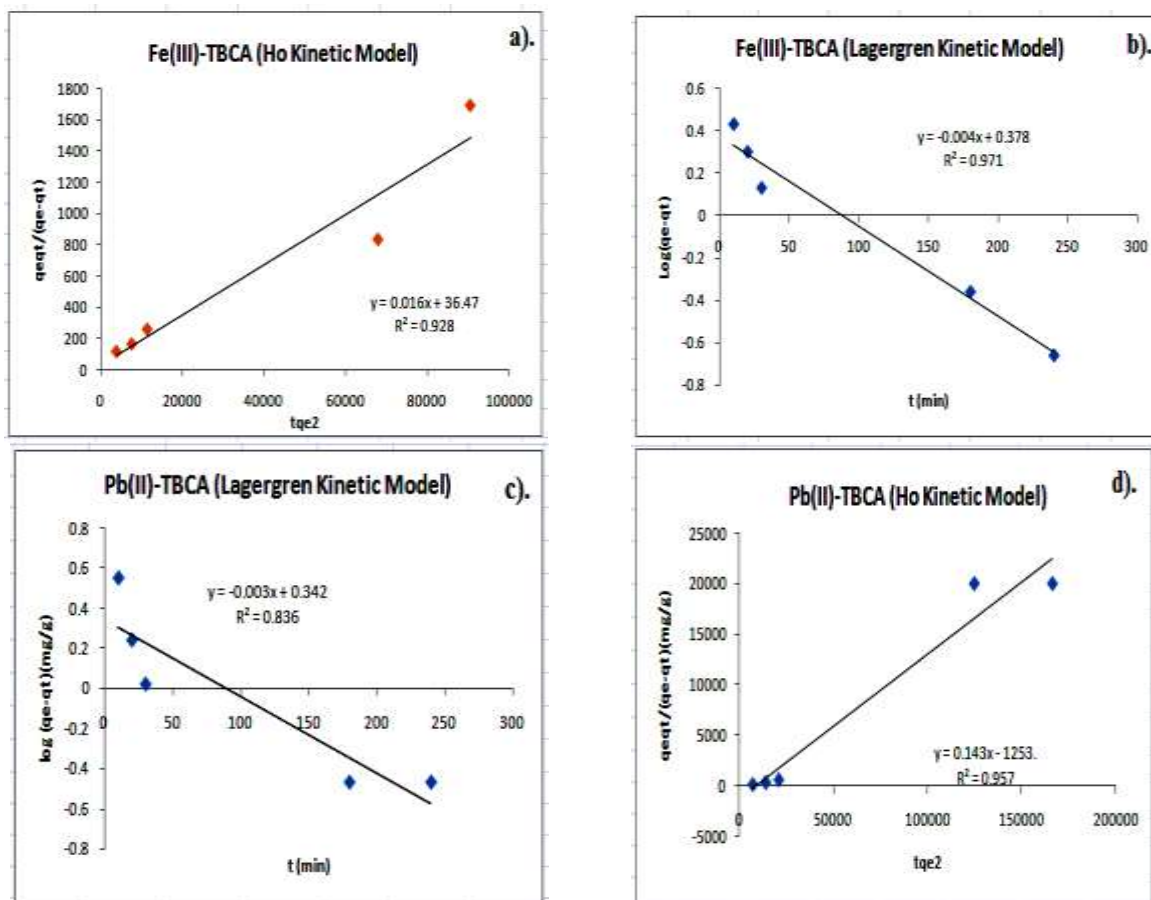

Fig. 2:- (a; b; c; and d) Pseudo first order kinetic for Pb(II), and Fe(III) adsorption on the TBCA and Pseudo second order kinetic for Pb(II), and Fe(III) adsorption on the TBCA

Based on the data analysis Table 1 and Fig. 2 (a, b, c, and d), it showed that the Ho kinetics model had higher linearity curve than the Lagergren kinetic model against metal cation of Pb(II). Otherwise, Fe(III) cation had higher linearity of Lagergren kinetic model rather than Ho kinetic model. Cation adsorption rate constant for Pb(II) can be determined based on the kinetic model of Ho as a slope, the value was 143×10^{-3} (g.mg^{-1}.min^{-1}). The adsorption constant rate of Fe(III) can be determined through Lagergren kinetic model approach as slope and the value was 9.21×10^{-1} (min^{-1}).

Kinetics Adsorption

The effect of cation concentration of Pb(II) and Fe(III) versus the concentration of adsorbed metal cation was exhibited in Fig.3. Observation at low concentration (about 8 ppm) showed little adsorbed metal cations, it happened because the metal cation was available in small amount. Then the amount of adsorbed metal cations increased significantly in accordance with the increase in the concentration of metal cations.
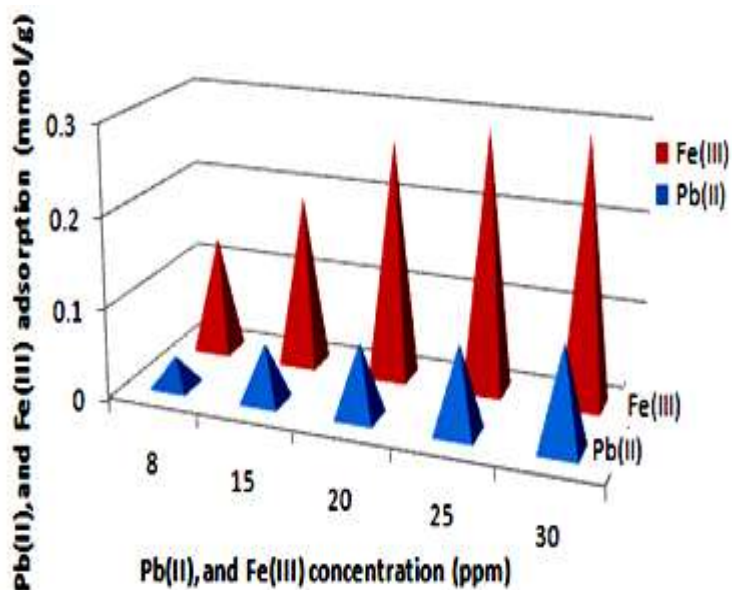

Fig. 3:- Effect of adsorbate concentrations on the Pb(II), and Fe(III) by p-t-Butylcalix[4]arene (TBCA)

Isotherms Adsorption:-

Isotherm adsorption can be determined using the data obtained from the value of the adsorbed metal cations on the variation of metal cations initial concentration (data in Fig. 3). Isotherm equation used was the equation of Langmuir and Freundlich

Langmuir Equation : $$\frac{Ce}{q_e} = \frac{1}{K.X_m} + \frac{Ce}{X_m}$$

          and Freundlich

Where :   qe   = adsorbate $\log (q_e) = \log K + n \log Ce$
            Ce   = adsorbate concentration at adsorbate phase
            Xm   = maximum adsorption capacity
            K   = equilibrium constant / intercept
            n   = slope

Indications which were obtained from Langmuir and Freundlich isotherm analysis were presented in Table 2. From Table 2 and Fig. 4 (a, b, c; and d), it can be concluded that each pattern of cation adsorption Pb(II), and Fe(III) refered the model of Langmuir isotherm adsorption. It mean that in the process of adsorption occured in a single layer (monolayer). Further it can be assumed that the maximum adsorption occured during interaction between all of the active site (OH groups) adsorbents and the adsorbate of metal cations Pb(II) or Fe(III) by forming the monolayer, with the adsorption energy value between cations Pb(II), and Fe(III) was 5.81 kJ/mol and 7.01 k J/mol

respectively. From Table 2, it showed that the maximum adsorption capacity of Fe(III) > Pb(II), this can be explained using the concept HSAB. Pb(II) was an medium acid while Fe(III) was hard acid because it had small radii and high charge. On the concept of HSAB, medium acid bound with soft acid, while the hard acid bound to a hard base. Active sites on the adsorbent was an OH group which was a hard base, so OH groups will be more stable bound to Fe (III) which belonged to the hard acid category. [22].

Table 2:- Indication of isotherm adsorption and its determination from Langmuir and Freundlich

Metal	Indcation of adsorption						
	Langmuir			Freundlich			
	Xm (mol/g)	K (L/mol)	ΔG (k J/mol)	R^2	n	K (L/mol)	R^2
Pb(II)	128,46	10,21	5,81	0,971	0,330	2,652	0,628
Fe(III)	156.09	16,62	7,01	0,946	0,456	0,016	0,813
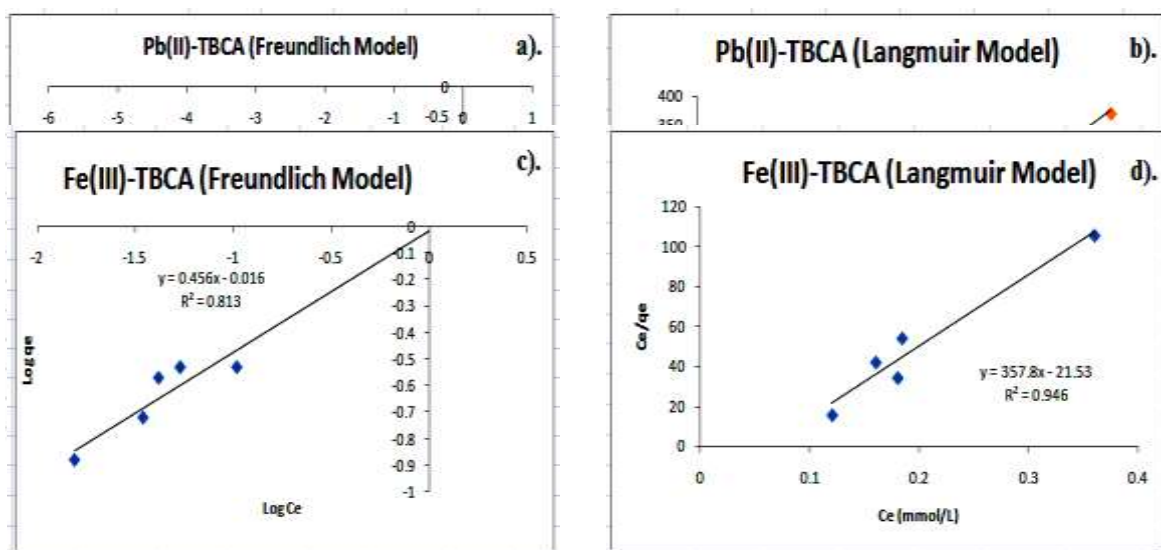
Fig. 4 (a;b;c;and d):- Isotherm Adsorption of Langmuir and Freundlich on Pb(II), and Fe(III) adsorption of the TBCA

Conclusion:-

In the process of adsorption of metal cations Pb(II), and Fe(III) using adsorbent p-t-Butylcalix[4] arenes (TBCA), it refered the Ho kinetics model, pseudo second order and had a value of adsorption rate constant k = 143x10^{-3} (g.mg^{-1}.min^{-1}), further it refered the kinetics model Lagergren, pseudo first order with the value of the adsorption rate constant was k = 9.21 x 10^{-3} (min^{-1}). From the study of the adsorption isotherm, it indicated that the adsorption process of both Pb(II) and Fe(III) cations refered the Langmuir isotherm, with a maximum capacity of cation adsorption of Pb(II), and Fe(III) was 128.46 mol/g and 156.09 mol/g respectively. Adsorption energy for Pb(II) and Fe(III) was 5.81 k.J/mol and 7.01 kJ / mol, respectively.

References:-

1. Salgado, P., Melin, V., Contresas, D., Moreno, Y., and Mansilla, H.D., 2013, Fenton Reaction Driven by Iron Ligands, J. Chil.Chem. Soc. Vol 58, no.54, Concepcion
2. Roundhill, D. M., 2004, " Strategis for The Removal of Toxic Metal from Soils and Waters, Journal of Chemical Education, " 81, (2),275-282
3. Siswanta, D., Jumina, Anggraini, M., Mardjan, M.I.D., Mulyono., and Ohto, K., 2016, " Adsorption Study of Pb(II) on Calx[4]resorcinarene-Chitosan Hybrid", International Journal of Applied Chemistry, Vol. 12, Number 1, pp. 11-22
4. Prabawaty, S., Y., Jumina, Santosa, S. J., and Mustofa , 2011, "Synthesis Of Poly-propylcalix[6]arene From p-t-Butylphenol As Adsorbent For Cr(III) Metal Ion", Indo. J. Chem. 11, (1), 37-42
5. Prabawaty, S., Y., Jumina, Santosa, S. J., and Mustofa, Ohto, K., 2012, " Study On The Adsorption Properties Of Novel calyx[6]arene Polymer For Heavy Metal Cations", Indo. J. Chem. 12, (1), 28-34

6. Prabawati, S.Y., Jumina, Santosa, S. J., and Mustofa, 2014, The Synthesis, Characterization and Properties of Calix[6]arene-Based Polymer, Int'l. J. of Adv. In Chem. Engg., & Biological Sciences (IJACEBS), Vol. 1, Issue 1, ISSN 2349-1507 EISSN 2349-1515

7. Tung C. H., and Ji, H. F., 1997, A Novel Host Molecule p-[1-(4-hidroxyphenyl)-1-methylethyl]-calix[8]arene. Synthesis and Complexation Properties in non-aqueous Polar Solution, J. Chem. Soc., Perkin Trans 2, 185-188

8. Kusumaningsih, T., Jumna, Siswanta, D., Mustofa, Ohto, K., and Kawakita, H., 2012, Synthesis of Poly-Tetra-p-Allylcalix[4]arene tetra acetic acid Adsorbent for Cr(III) and Pb(II) Metal ions, Internatiol Journal of Technology, 2, 93-102

9. Ulewicz, M., Bochenska, M., Lesinska, U., Walkowiak, W., 2005, " Studies On Removal Of Zn(II), Cd(II), and Pb(II) Ions In Polymer Inclusion Membrane Transport With Calix[4]-Crown-6 Derivatives ", Physicochemical Problems of Mineral Processing, 39, 107-116

10. Yang, F. F., Zhao, X., Huang, C. Y., Guo, H., Y., Zheng, S. N., Peng, Q., 2006, Synthesis and Complexation Properties of Novel Biscalixarene Composed o. Calix[4]arene and Thiacalix[4]arene Subunits, *Chinese Chem. Latters*, Vol. 17, No. 8, pp 1029-1032Yang, F. F., Huang, Z. S., Zhang. X. Y., and Guo, H. Y., 2010, " Thiacalix[4]amido-based Netty Polymer: NovelSorbent for Heavy Metal Cations and Derivatives of Aniline", Iranian polymer Journal, 19(4), 309-318 Gharib, F., Ganjali, S.T., Eslamipanah, M., Mazooji, R., and Ebrahimi, S., 2006, " Complexation of Di and Tetra-Benzyloxy Ether Derivatives of Calix[4]arene With Alkali Metal Cations ", Acta Chim. Slov., 53, 427-415

11. Kesuma, E.D., Jumina, Ohto, K., and Siswanta, D., 2016, " Synthesis of C-4-Allyloxy-3-Methoxyphenylcalix[4]resorcinarene from Vanilin and Its Application as Adsorbent of Pb(II) Metal Cation ", Oriental Journal of Chemistry, Vol. 32, No. 2, Pg. 769-775

12. Vyas, D.J., Makwana, B. A., Bhatt, K. D., Jain, V. K., 2013, "Octa-O-Methoxy Resorcin[4]arene Amberlite XAD-4 Polymeric Chelating Resin for Solid Phase Extraction, Preconcentration, Separation and Trace Determination of Ni(II), Cu(II), Zn(II) and Cd(II) Ions, "American Journal of Analytical Chemistry, 4, 238-251[4=19] Ho, Y.S. dan McKay, G., 1999, Pseudo-second Order Model for sorption Processes, Elsevier, 34, 451-465

13. Maming, 2008, " Transpor Cr(III), Cd(II), Pb(II), dan Ag(I) melalui membrane cair ruah yang mengandung turunan karboksilat , ester, dan amida p-tert.butilkaliks[4]arena sebagai pengemban ion, Disertasi Doktor Pascasarjana, Universitas Gadjah Mada, YogyakartaQureshi, I., Memon, S., and Yilmas, M., 2008, " Extraction and Binding Efficiency of Calix[8]arene Derivative Toward Selected Transition Metals", Pak. J. Anal. Environ. Chem., Vol. 9, No. 2, 96-100

14. Elcin, S., Karakus, O. O., Kara, I., Deligos, H., 2015, "Synthesis and structural caharacterization of bisazocalix[4]arene with melamine: Metal ion extraction studies, " Journal of MolecularLiquids, " 202, 134-140

15. Gutsche, C.D and M. Iqbal, 2005, " Organic Synthesis ", Inc. All Rights Reversed, Coll. 8, 75

16. Ho,Y.S.and McKay, G., 1999, Pseudo-second Order Model for sorption Processes, Elsevier, 34, 451-465

17. Ho, Y.S., 2004, Citation Review of Lagergren Kinetic Rate Equation on Adsorption Reaction, Scientometrica, 59, 1, 171-177

18. Rosas, C. C., 2010, Synthesis and Application of Manganese Dioxide Coated Magnetite for Removal of Metal Ions from Aqueous solutions, Dissertation Doctor

19. Pearson, R.G., 1963, Hard and Soft Acid Bases, J. Am.Soc., 85, 3533-3539