

## Cerium Adsorption Using 1-Phenyl-3-Methyl-4-Benzoyl-5-Pyrazolone(HPMBP) Loaded Calcium Alginate Beads

Rusnadi Rusnadi\*, Buchari Buchari\*, M. Bachri Amran\*,  
Deana Wahyuningrum\*\*

\*(Analytical Chemistry Research Group, Faculty of Mathematics and Natural Sciences Institut Teknologi Bandung, Jl.Ganesha 10 Bandung 40132, Indonesia,)

\*\* (Organic Chemistry Research Group, Faculty of Mathematics and Natural Sciences Institut Teknologi Bandung, Jl.Ganesha 10 Bandung 40132, Indonesia,)

### ABSTRACT

1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) have been entrapped in calcium alginate beads. The uptake properties of Ce(III) on the adsorbents, HPMBP loaded calcium alginate beads (HCAB), have been investigated by batch method. The effect of various parameters such as contact time, initial solution pH and initial Ce(III) concentration has been studied. The uptake of Ce(III) was pH dependent, increased with solution pH and reached a maximum at pH 4.0. The equilibrium time of adsorption was attained within 20 hours. The adsorption data were analyzed by the Langmuir and Freundlich isotherms model. The Langmuir isotherm model best fitted the equilibrium data since it presents higher  $R^2$  value. The maximum uptake capacity of Ce(III) was 106.38 mg/g at 298 K. The value of dimensionless factor,  $R_L$  lie between 0.03 to 0.22 for the initial Ce(III) concentration range from 75 to 600 mg/L indicating favorable adsorption of Ce(III) onto the adsorbent.

**Keywords** – HPMBP, cerium, adsorption, alginate, Langmuir.

### 1 INTRODUCTION

Cerium is used as fluorescent devices, polishing compounds, magnetic substances and alloys. Cerium oxide is part of the catalyst of catalytic converters used to clean up exhaust vehicles. Removal of cerium from aqueous environment are important because of its increasing discharge is responsible for environmental pollution.[1] Various methods have been used for the removal of metals from aqueous solution, such as solvent extraction, chemical precipitation, reverse osmosis, evaporation, ion-exchange, adsorption, and electrolysis. Some of these methods are expensive or inefficient for metal removal.[2] Solvent extraction has been widely used to separate and recover metallic ions from aqueous solutions. However, large volume of solvent in solvent extraction may create health problem and cause environmental pollution. [3,4]

The immobilization of the extractant in a solid polymeric matrix possesses some advantages, for example simplicity of preparation, applicability for a wide range of extractants, and lesser loss of harmful components to the environment. [5] Alginate is a biopolymer consisting of 1,4 linked  $\beta$ -D-mannuronic (M) and  $\alpha$ -L-guluronic acid (G) residues, each containing one carboxylate group per monomeric unit. [6] Each units are organized in homopolymeric M-M and G-G blocks and heteropolymeric M-G blocks. The carboxylate groups of the polymer give it ability to form gels in the presence of calcium ions. The gel have been used as the matrix for the immobilization of microbial cells and metal extractant via entrapment.[5,7]

1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) has been extensively studied alone or in combination with other reagents in the extraction of lanthanide elements.[8] In the present study, HPMBP have been entrapped in calcium alginate to form HPMBP loaded calcium alginate beads (HCAB). The aim of this work was to investigate the uptake properties of Ce(III) onto HCAB.

### 2 MATERIALS AND METHODS

#### 2.1 Materials

Chemicals were of analytical grade and were used without further purification. Deionized water was used throughout all experiments. The Ce(III) stock solution (1000 mg/L) was prepared by dissolving cerium(III) nitrate hexahydrate (Merck) in dilute nitric acid. A series of Ce(III) solutions with different concentration were prepared by appropriate dilutions of the stock solution. Sodium alginate was purchased from Sigma Aldrich. 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone(HPMBP) was synthesized from 1-Phenyl-3-methyl-5-pyrazolone and benzoyl chloride by the method reported in the literature. [9]

#### 2.2 Methods

##### 2.2.1 Preparation of the adsorbent

Sodium alginate (2 g) was dissolved in deionized water at 60°C. Then HPMBP (2 g) were dispersed in alginate solution with constant stirring for 12 hours. The kneaded sol was added dropwise to

a 0.2 M CaCl<sub>2</sub> solution using a syringe at room temperature. Spherical gel particles were formed and stirred for 12 hours, then separated from the solution. The gels were washed several times with deionized water and air-dried for 1 day.

### 2.2.2 Adsorption isotherm studies

The Ce (III) uptake properties on the adsorbents were studied by batch adsorption experiments. 50 mg of the adsorbents, HPMBP loaded calcium alginate beads (HCAB), were placed in 100 mL Erlenmeyer flask containing 20 mL of various concentration Ce(III) solutions. Solution pH were adjusted to the desired value with 0.1 M NaOH or 0.1 M HNO<sub>3</sub>. The flask were agitated at 150 rpm using a mechanical shaker at room temperature condition. The residual concentration of Ce (III) in the aqueous phases was determined by Arsenazo(III) method at λ = 652 nm. The percentage of adsorption (%E) and the adsorption amount of cerium (III) (q) were calculated according to equation (1) and (2).

$$\% E = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$q = \frac{(C_o - C_e)V}{m} \quad (2)$$

Where C<sub>o</sub> and C<sub>e</sub> are initial and equilibrium concentration of Ce (III) in the solutions, respectively (mg/L), V is the volume of solution (L), and m is the mass of HCAB (g).

## 3 RESULTS AND DISCUSSION

Influence of contact time on Ce(III) adsorption with HCAB can be seen in Fig. 1. The uptake of Ce(III) increases with contact time and the uptake equilibrium was attained within 20 hours.

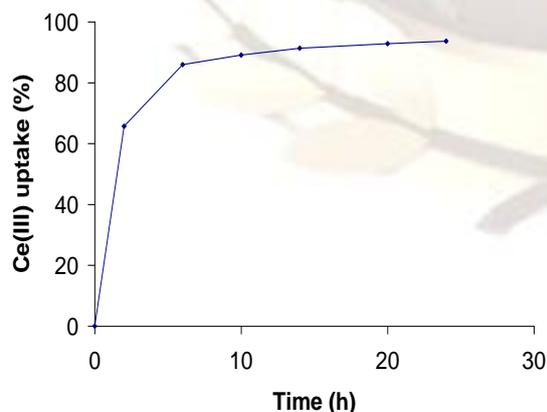


Fig 1. Effect of contact time on Ce(III) uptake by HCAB (adsorbent dosage : 50 mg ; pH : 4.0 ; Initial Ce(III) concentration : 150 mg/L)

The solution pH is one of important parameters controlling Ce(III) uptake. The influence of initial pH were studied in the range of 1-5, and the results are shown in Fig.2. The percentage adsorption was dependent on pH. It was increased from mg/g (pH ) to mg/g (pH ). At low pH values (pH<5), Cerium exist in their trivalent form. Alginate and HPMBP have pKa values 3.65 and 3.95, respectively. [4,10] At strong acidic condition there is a competition between Ce(III) and hydrogen ions to occupy the binding sites. The percentage of adsorption is lower as the result of repulsive forces between hydrogen ions and Ce(III) ions. Increasing the pH increases the number of negative sites available for Ce(III) uptake. At higher pH, hydroxide may precipitate Ce(III) ions. The optimum pH for Ce(III) adsorption was 4.0.

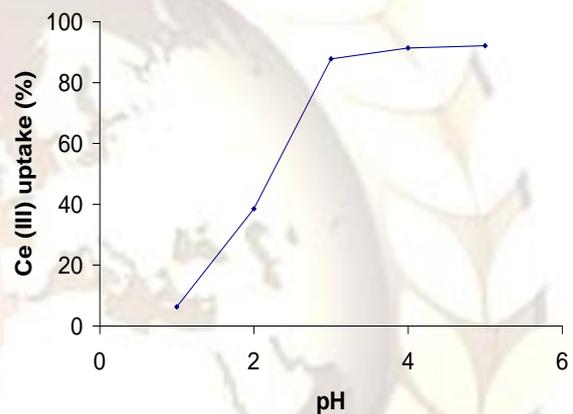


Fig.2.Effect of initial solution pH on Ce(III) uptake by HCAB (adsorbent dosage : 50 mg ; contact time : 20 h ; Initial Ce(III) concentration : 150 mg/L)

The adsorption isotherm was studied for the initial Ce(III) concentration ranging from 75 – 600 mg/L at optimum condition. The data were analyzed with Langmuir and Freundlich Isotherm according to equation (3) and (4)

Langmuir isotherm :

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \quad (3)$$

where Q<sub>e</sub> is metal ion adsorbed at equilibrium (mg/g), C<sub>e</sub> is the concentration of metal ion at equilibrium (mg/L), b is the affinity constant, and Q<sub>m</sub> is maximum adsorption capacity of (mg/g).

Freundlich Isotherm :

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where n is the Freundlich exponent related to adsorption intensity and K<sub>F</sub> is Freundlich constant related to adsorption capacity.

The Langmuir plot is shown in in Fig.3. The result show that Ce(III) adsorption by HCAB follow the Langmuir isotherm with high correlation coefficient ( $R^2 = 0.997$ ). The maximum monolayer adsorption capacity ( $Q_m$ ) and the constant related to the energy of adsorption ( $b$ ) were found to be 106,38 mg/g and 0.048, respectively. From the Langmuir isotherm we can calculate  $R_L$ , a dimensionless equilibrium parameter, according to equation (5).

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

Where  $C_0$  is the initial concentration of Ce(III) in solution (mg/L). If the  $R_L$  value is between 0 to 1, the adsorption process is favorable. [11,12] The data in Table 1 show that the values of  $R_L$  lie between 0.03 to 0.22 indicating that Ce(III) adsorption process onto HCAB was favorable.

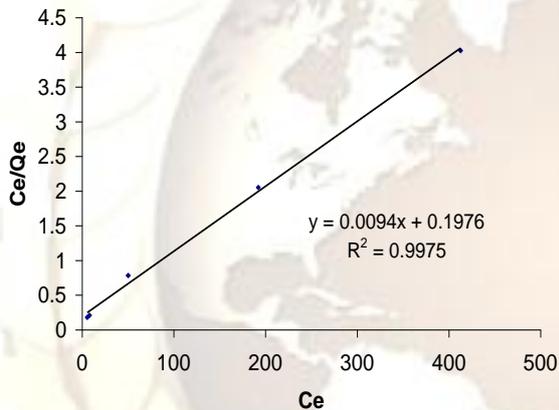


Fig.3. Langmuir plot for the Cerium(III) uptake by HCAB (adsorbent dosage : 50 mg ; pH : 4.0 ; contact time : 20 hours)

Table 1. Calculated  $R_L$  values from Langmuir Isotherm

$C_0$ (mg/L)	$R_L$
75	0.22
100	0.17
200	0.10
400	0.05
600	0.03

Fig.4 shows the Freundlich plot for Ce(III) adsorption by HCAB. The values of Freundlich constants,  $K_F$  and  $n$ , were found to be 20.6 and 3.6, respectively. The value of  $n$  was between 0 and 1 indicating that Ce(III) adsorption by HCAB was favourable. [13] However, Langmuir isotherm model best fitted the equilibrium data since it presents higher  $R^2$  value.

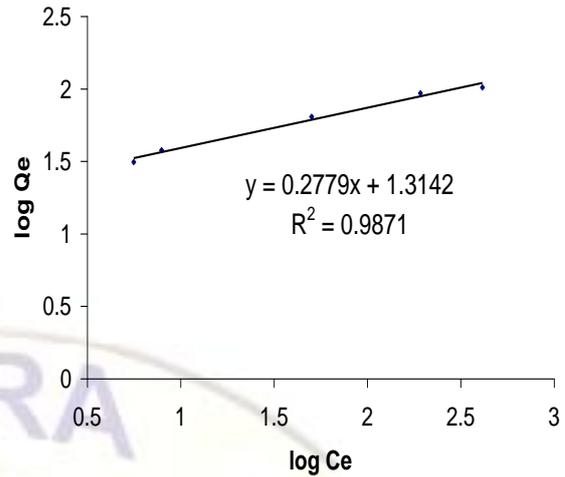


Fig.4. Freundlich plot for the Cerium(III) uptake by HCAB (adsorbent dosage : 50 mg ; pH : 4.0 ; contact time : 20 hours)

#### 4 CONCLUSIONS

The immobilization of the extractant in a solid polymeric matrix is very useful technique for metal ions extraction. HPMBP loaded calcium alginate beads (HCAB) have been shown to be highly effective in for Ce(III) adsorption from aqueous solution. The optimum conditions of sorption were found to be: volume of solution 20 mL; pH 4.0 ; adsorbent dosage 50 mg ; contact time 20 hours. The adsorbents may be considered as an alternative for removal and recover Ce(III) ions from aqueous solutions.

#### 5 ACKNOWLEDGEMENT

This work was supported by Penelitian Fundamental Grant 2011.

#### REFERENCES

- [1] Y. Caiping, Adsorption and desorption properties of D151 resin for Ce(III), *Journal of Rare Earths*, 28 (special issues), 2010, 183.
- [2] I. Sharma, D. Goyal, Kinetic Modelling: Chromium(III) removal from aqueous solution by microbial waste biomass, *Journal of Scientific and Industrial Research*, 68, 2009, 640-646
- [3] O.S. Lawal, A.R. Sanni, I.A. Ajayi, O.O. Rabi, Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead(II) ions onto the seed husk of Calophyllum inophyllum, *Journal of Hazardous Materials*, 177, 2010, 829-835
- [4] D. Wu, J. Zhao, L. Zhang, Q. Wu, Y. Yang, Lanthanum adsorption using iron oxide loaded calcium alginate beads, *Hydrometallurgy*, 101, 2010, 76-83.

- [5] Y. Wu, M. Outokesh, H. Mimura, Y. Niibori, Selective uptake properties of metal ions by hybrid microcapsules enclosed with TBP, *Progress in Nuclear Energ*, 50, 2008, 487-493.
- [6] S.K. Papageorgiou, E.P. Kouvelos, F.K. Katsaros, Calcium alginate beads from *Laminaria digitata* for the removal of  $\text{Cu}^{+2}$  and  $\text{Cd}^{+2}$  from dilute aqueous metal solutions, *Desalination*, 224, 2008, 293–306.
- [7] M.Y. Arica, C. Arpa, A. Ergene, G. Bayramoglu, Omer Genc, Ca-alginate as a support for Pb(II) and Zn(II) biosorption with immobilized *Phanerochaete chrysosporium*, *Carbohydrate Polymers*, 52, 2003, 167–174
- [8] V. M. Jordanov, M. Atanassova, I. L. Dukov, Solvent extraction of lanthanides with 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone, *Separation Science and Technology*, 37(14), 2002, 3349–3356
- [9] B.S. Jensen, The Synthesis of 1-phenyl-3-methyl-4-acyl-pyrazolones-5, *Acta Chem. Scand*, 13, 1959, 1668-1670.
- [10] M. Atanassova, I. Dukov, A Comparative Study of the Solvent Extraction of the Trivalent Elements of the Lanthanoid Series with Thenoyltrifluoroacetone and 4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one Using Diphenylsulphoxide as Synergistic Agent, *J Solution Chem*, 38, 2009, 289–301.
- [11] A Ozer, D. Ozer, A. Ozer, The adsorption of copper (II) ions on to dehydrated wheat bran (DWB): determination of the equilibrium and thermodynamic parameters, *Process Biochem*, 39, 2004, 2183–2191.
- [12] W. Shao, L. Chen, L. Lü, F. Luo, Removal of lead (II) from aqueous solution by a new biosorption material by immobilizing Cyanex272 in cornstalks, *Desalination*, 265, 2011, 177-183
- [13] O.D. Uluozlu, A. Sari, M. Tuzen, M. Soylak, Biosorption of Pb(II) and Cr(III) from aqueous solution by lichen (*Parmelina tiliaceae*) biomass, *Bioresource Technology*, 99. 2008, 2972-2980