International Journal of Recent Technology and Engineering (IJRTE)
ISSN: 2277-3878, Volume-8 Issue-2S7, July 2019

Optimization of Large Scale Dibuthyldithiocarbamate Synthesis by Experimental Design and Application as Extractant for Gadolinium(III)

Diana Hendrati, Erianti Siska Purnamasari, Syulastri Effendi, Uji Pratomo, Santhy Wyantuti

Abstract: The unique physical and chemical properties of Gadolinium (Gd) promote an indispensible number of its application for crucial technologies. In order to satisfy the demands of high purity, the various methods are used to separate Gd from other rare earth elements, in which a solvent extraction provides a simple separation method for these elements. However, an optimization of big scale is consequent for the solvent consumption. To overcome such a problem as a contribution in green chemistry, hereby we study the big scale synthesis optimization of dibuthyldithiocarbamate (DBDTC) by full factorial experimental design and the extraction study for Gd(III). This research start with preparing design of experiment for ligand synthesis, then perform the process of synthesis and extraction of Gd(III) according to the design of experiment. The result of synthesis and extraction were characterized by various spectroscopy methods. The highest Scale up ligand synthesis of DBDTC on this research is 20-fold times with 80.03% yield and 1.25% precision. The result shows that the optimal condition for Gd-DBDTC extraction are at pH 6, the mol ratio of gadolinium and ligand is 1:4, and 60 minutes extraction time with 76.52% yield. Therefore, the synthesis of dibuthyldithiocarbamate ligand based on the experimental design can be developed for optimization of large-scale synthesis with high Gd(III) extraction yield.

Index Terms*: *Design of Experiment, Dibuthyldithiocarbamate, Gadolinium, Solvent Extraction, Rare-Earth Elements.

I. INTRODUCTION

The rare earth elements (REE) is a series of elemental group which is very rare in earth or associated with other small metallic elements[1]. In Indonesia there are 2 types of minerals containing REE, namely monazite and xenotime. REE is generally found together with other elements, such as copper, uranium, gold, phosphate and iron, as a follow-up mineral. REE has a very wide application in various industries, therefore the price of REE oxide in its pure form is much higher than the price of its own mineral. REE’s needs are increasing with its enormous use especially in high-tech innovative products [2].

The separation of REE into its individual elements is a very difficult process, because REE's chemical properties are very similar to each other, therefore further research is needed to develop the separation process of the elements of its minerals [3]. One method of REE separation is solvent extraction. The solvent extraction method is the most commonly used method for separating REE, which has been extensively conducted on innovation-based research such as the development of extractants to form complexes with REE elements. One of the extractants used for REE extraction is dibuthyldithiocarbamate (DBDTC) which is a group of dialkyldithiocarbamate that can act as monodentat and bidentat chelate [4]. DBDTC ligand is often used for the determination of transition metal ions in trace amounts because they are capable to form stable complex compounds with various transition metal ions which, low solubility in water but highly soluble in organic solvents [5]. However, the optimization procedure for large scale synthesis of DBDTC and its application for REE extraction are still rare.

Hereby, we reported the development of optimal condition for DBDTC synthesis for scale up production. The determination of the optimal condition often requires a considerable amount of experiments, which is particularly detrimental in terms of cost, materials and time, to avoid it, we interest to utilize an experimental design which allows the study of the effects of various factors on one or more responses and to determine the mathematical model relation between these factors and responses [6]. In our previous research [7], we success to develop a synthesis procedure for DBDTC with a combination of experimental design in order to obtain a more optimal and efficient ligand synthesis procedure compared to existing synthesis procedures. We decided to use full factorial design because it can calculate all combinations between factor levels during the experiment, and to know the effect of each factor on the response and the interaction effect between different factors [8].

Revised Manuscript Received on April 25, 2019.

Diana Hendrati, Department of Chemistry, Faculty of Mathematics and Science, University of Padjadjaran, Jalan Raya Bandung Sumedang KM. 21, West Java, Indonesia.

Erianti Siska Purnamasari, Department of Chemistry, Faculty of Mathematics and Science, University of Padjadjaran, Jalan Raya Bandung Sumedang KM. 21, West Java, Indonesia.

Syulastri Effendi, Department of Chemistry, Faculty of Mathematics and Science, University of Padjadjaran, Jalan Raya Bandung Sumedang KM. 21, West Java, Indonesia.

Uji Pratomo, Department of Chemistry, Faculty of Mathematics and Science, University of Padjadjaran, Jalan Raya Bandung Sumedang KM. 21, West Java, Indonesia.

Santhy Wyantuti, Department of Chemistry, Faculty of Mathematics and Science, University of Padjadjaran, Jalan Raya Bandung Sumedang KM. 21, West Java, Indonesia.

This study determines how effectively the experimental design results in the ligand synthesis process, especially on a larger scale, and determines the maximum DBDTC yield on a large scale that can be produced. Moreover, we also reported its application for Gd extraction.

II. MATERIALS AND METHODS

A. Tools and Materials

The tools that used in this research are Buchner funnel, desiccator, digital analytical balance, oven, heater and magnetic stirrer PMC 502, melting point electric meter MP50 (Mettler Toledo), pH-meter MP 220 (Mettler Toledo), UV-Vis Spectrophotometer Ultraspec 3000, FTIR Pekin Elmer Spectrum 100, ESI-ToF Mass Spectroscopy (Waters). A chemical computation for experimental designs is State-Ease Version 9.0.6.2.

The materials that used in the study are perchloric acid, ammonium hydroxide, di-n-butylamine, carbon disulfide, gadolinium oxide, common organic solvents such as acetonitrile, acetone, diethyl ether, dimethyl sulfoxide, ethyl acetate, n-hexane, chloroform, and methanol. All quality chemicals derived from Merck, Aldrich, and Sigma.

B. DBDTC Ligand Synthesis Verification Based on Experimental Design

Based on the results of experimental design data processing on previous research [7], verification of laboratory scale ligand synthesis was done. The condition of ligand synthesis is shown in Table 1.

Table 1. DBDTC ligand synthesis (verification)

Dibuthylamine (mol)	CS_2 (mol)	Ammonia (mol)	Temperature (°C)	Time (sec)	Repetition (times)
1	3	4	3	30	5
1	3	4	4	30	5

C. Characterization of DBDTC ligand Synthesis Result

The DBDTC crystals were characterized by UV-Vis spectrophotometer, IR, MS, melting point and solubility test with various solvents (water, acetonitrile, dimethyl sulfoxide, ethyl acetate, n-hexane, chloroform, and methanol).

D. Synthesis of Large-Scale DBDTC Ligands

Based on the results of the previous experimental design data processing [7], the optimized parameters are: mole ratio of di-n-butylamine and CS_2 (1: 3) and the temperature of 4°C. The result of this synthesis is shown in Table 2.

Table 2. Scale up synthesis of dibuthyldithiocarbamate

No	Synthesis Scale (fold times)	Repetition (times)
1	1	5
2	5	5
3	10	5
4	20	5

E. The reaction between Gd (III) and DBDTC

A total of 10 mL of Gd(III) solution (1 equivalent) was placed in a beaker glass, then adjusted the pH with the addition of a 0.5 M ammonium hydroxide or 0.5 M perchloric acid to reach a pH 6.0. Then, a solution of DBDTC in methanol (4 equivalent) was added. The solution is stirred for 1 hour to form an optimum complex, then the solution is allowed to stand at room temperature until white crystals are formed. The crystals were filtered and then dried at room temperature and weighed. The filtrate was analyzed with ICP.

III. RESULT AND DISCUSSION

A. Characterization of DBDTC and Gd-DBDTC Complex

1) *Melting Point Test*

The ligand was melts to form a transparent yellow liquid at 43.1 °C, while the ammonium salt of DBDTC has a melting point in the area of 42°C to 44°C.

2) *Solubility Test*

The solubility character of DBDTC ligand is shown in Table 3.

Table 3. Solubility test of DBDTC

Solvent	Result
Water	Insoluble
Methanol	Soluble
Diethyl Ether	Soluble
Acetone	Soluble (forming yellow-transparent solution)
Acetonitrile	Soluble (forming yellow-transparent solution)
n-hexane	Half-soluble
DMSO	Soluble

3) *Characterization with UV / VIS Spectrometer*

DBDTC ligand was characterized by UV/Vis spectrometers. Two peaks were observed at 258 and 293 nm which is identified as the electron transition from $\pi \rightarrow \pi^*$ due to the double bond C = S and the presence of the transition electrons of $n \rightarrow \pi^*$ due to unpair electrons in S, as shown in Fig. 1.

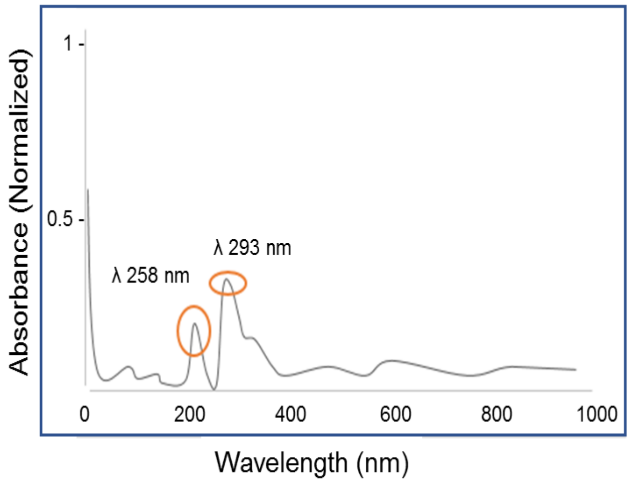

Fig. 1. UV/Vis Spectrum of DBDTC

4) *Characterization with IR Spectrometer*

The characteristics of DBDTC ligand by using infrared spectrometer are strong intensity and width area at 3094.88 cm^{-1} which is responsible to O-H stretching, sharp intensity at area 2955.29 cm^{-1} which is responsible to C-H stretching of C_4H_9, a low intensity at 1655.7 cm^{-1} (C = N stretching), strong intensity at 1402.30 cm^{-1} (C-S stretching), strong intensity at 1205.45 cm^{-1} (C-N stretching) and 947.29-529.70 cm^{-1} which is responsible for C-S binding in fingerprint area. The result of IR spectral is shown in Fig. 2.

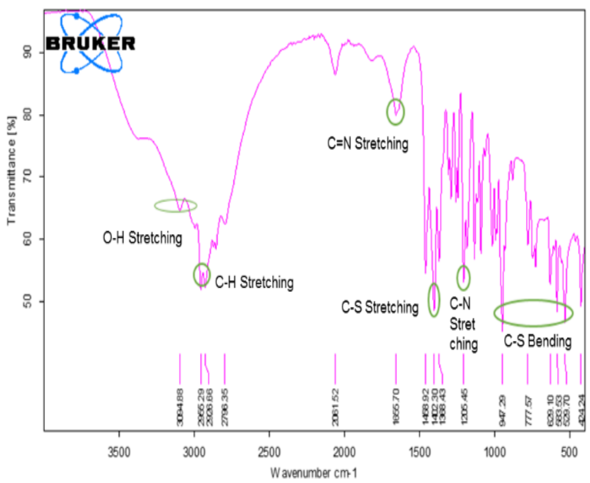

Fig. 2. IR spectral of DBDTC

5) *Characterization with Mass Spectrometer*

Characteristics of DBDTC and GD-DBDTC complex with mass spectra are shown in Figs. 3 and 4, where m/z for the DBDTC ligand obtained is 205 whereas Gd-DBDTC complex obtained at m/z of 791. Those data corresponded to the molecular weight each theoretically.

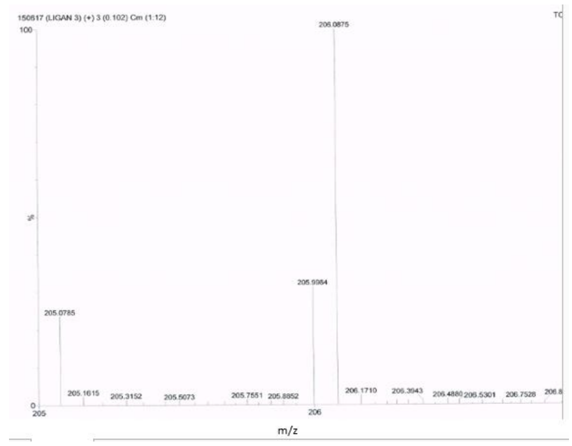

Fig. 3. Mass Spectrum of DBDTC

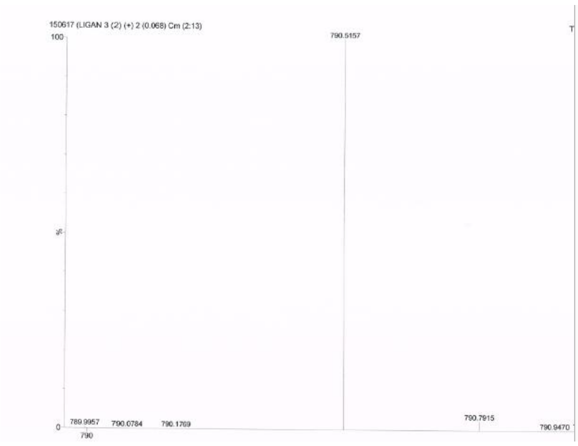

Fig. 4. Mass Spectrum of Gd-DBDTC

B. Large Scale Synthesis of DBDTC

Based on the previous research[7], we applied the optimum parameters for synthesis of DBDTC which mole ratio of di-n-butylamine and CS_2 is 1: 3 and the temperature at the synthesis is 4 ° C. The results of scale up synthesis of DBDTC ligand is shown in Table 4.

Based on scale up result of DBDTC synthesis by using experimental design optimization parameters, the maximum scale up can be done up to 20-fold times, which can be seen from the results of small precision and high recovery. Increasing the scale of synthesis will be affected to the longer reaction and dry time.

Table 4. Scale Up Synthesis Result of DBDTC on Optimum Parameter from Design Experiment

No	Scale (fold times)	Vial + Ligand (g)	Vial (g)	Ligand (g)	Yield (%)	Precision (%)
1	1	94.1203	89.8525	4.2678	85.36	0.95
2	5	117.6894	97.1284	20.5610	82.24	4.12
3	10	129.4202	89.6944	39.7258	79.45	1.22
4	20	175.745	95.3481	80.0264	80.03	1.25

IV. CONCLUSION

1. Based on DBDTC ligand synthesis optimization procedure with experimental design, the scale of synthesis test can be done up to 20-fold times with recovered 80, 03% and the synthesis precision is 1.25%.
2. The optimum parameter of Gd-DBDTC complex synthesis by using experimental design are: pH extraction = 6, mol ratio of Gd and DBDTC= 1: 4 and extraction time = 60 minutes. The Gd-DBDTC yield is 76.52%.

ACKNOWLEDGMENT

The authors would like to thank to the Padjadjaran University for the Internal and Output Grants (Fundamental Research Unpad / RFU) which has provided funding of this research, as well as in the Chemical Laboratory of Analytical and Separation, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Padjadjaran University Bandung for giving a place for research implementation.

REFERENCES

1. S. B. Castor and J. B. Hedrick. “Rare Earth Elements.” *Industrial minerals and rocks*, pp. 769-792, 2006.
2. N. Haque, A. Hughes, S. Lim and C. Vernon. “Rare Earth Elements: Overview of Mining, Mineralogy, Uses,Sustainability and Environmental Impact.” *Resources*, vol. 3, no. 4, pp. 614-635, 2014.
3. M. A. Zulfikar, A. Sulaeman, and H. Setiyanto. “Transport and Separation of Some Rare Earth Elements (REEs) Through Stripping Hollow Fiber Supported Liquid Membrane (SHFSLM) with Di-di-(2ethylhexyl) Phosphoric acid and Trybutylphosphate as a Carriers.” *Australian Journal of Basic and Applied Sciences*, pp. 525-531, 2014.
4. D. C. Onwudiwe, and P. A. Ajibade. “Synthesis and characterization of metal complexes of N-alkyl-N-phenyl dithiocarbamates.” *Polyhedron*. Vol. 29, no. 5, pp. 1431– 1436, 2010.
5. N. Iljas, D. Hendrati, and V. Srigati. “Separation and determination of gadolinium and cerium metals from monazite of Bangka Island by extraction following UV/visible spectroscopy using di-n-buthyldithiocarbamate as complex formation agent.” In *Proc. Int. Semin. Chem,* pp. 93-99, 2008.
6. M. Kincl, S. Turk, and F. Vrecer. “Application of Experimental Desain Methodology in Developmentand Optimization of Drug Release Method.” *International Journal of Pharmaceutics*, vol. 291, no. 2, pp. 39-49, 2005.
7. D. Hendrati, E. S. Purnamasari, S. Effendi and S. Wyantuti. “Pemantapan Proses Sintesis Ligan Dibutilditiokarbamat (DBDTK) Sebagai Pengekstrak Logam Tanah Jarang Berdasarkan Desain Eksperimen.” *ALCHEMY Jurnal Penelitian Kimia*, vol. 14, no. 2, pp. 219-235, 2018.
8. D. C. Montgomery. *Desingn and Analyses of Experiment.* New York: John Wiley & Sons, 2012.