

The Effect of Pressure and Temperature on Separation of Free Gadolinium(III) From Gd-DTPA Complex by Nanofiltration-Complexation Method

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ABSTRACT. Nowadays, the utilization of rare earth elements has been carried out widely in industry and medicine, one of them is gadolinium in Gd-DTPA complex is used as a contrast agent in a magnetic resonance imaging (MRI) diagnostic to increase the visual contrast between normal tissue and diseased. Although the stability of a given complex may be high enough, the complexation step couldnot have been completed, so there is possible to gadolinium(III) in the complex compound. Therefore, the function of that compounds should be dangerous because of the toxicity of gadolinium(III) in human body. So, it is necessary to separate free gadolinium(III) from Gd-DTPA complex by nanofiltration-complexation. The method of this study is complexing of Gd_2O_3 with DTPA ligand by reflux and separation of Gd-DTPA complex from gadolinium(III) with a nanofiltration membrane on the variation of pressures(2, 3, 4, 5, 6 bars) and temperature (25, 30, 35, 40 °C) and determined the flux and rejection. The results of this study are the higher of pressures and temperatures, permeation flux are increasing and ion rejections are decreasing and gave the free gadolinium(III) rejection until 86.26%.

1. INTRODUCTION

Rare earth elements (REE's) have been used increasingly in the field of industry. In the middle of 2008, about 120,000 tons of REE have been widely used in the some of industry sector, where 60% of them used in the field of chemical engineering, metalurgy, catalyst, glasses, catode tubes and fluorences. Meanwhile, about 40% of them used in the high technology materials fabrication, such as baterry alloy, ceramic, guns military, satellite system, and magnet [1]. Beside that, rare earth elements is also used as supporting materials such as in the medical field which is using gadolinium in Gd-DTPA complex form as contrasting agent in a magnetic resonace imaging (MRI) diagnostic equipment to increase visual contrast between normal and abnormal tissues [1,2].

The separation and purification of rare earth elements which has been done by scientists on the 18th - 19th centuries is the hardest challenge. Eventually, until the 20th century all of REEs had not been identified due to their similarity in physical and chemical characteristics [1,3]. The separation of REEs could be increase their purity actually involves liquid-liquid extraction method. This method is a great important due to its ability to produced highly purified lanthanides which commonly used in material fabrication, such as electronic, ceramic, optic, and catalyst. However, liquid-liquid extraction required additional solvent, which



is problem in a matter of environmental preservation [4]. Another method for REEs separation has been investigated. Solvent extraction with chelating agent di-n-dibutyldithiocarbamate (DBDTC) could attract gadolinium metal and formed gadolinium complex. However, only 20,8% purified gadolinium would be produced [2,4]. The separation of REEs has been accomplished by nanofiltration (NF) process with associating a metal-ion complexation step on charge organic membrane: effect of pH, pressure, flux, ionic strength, and temperature and gave 95% yields gadolinium [2]. Based on those previous research, the separation of REEs (gadolinium) will be achieve a great result by nanofiltration membrane process.

Among the different available separative methods (liqui-liquid extraction and solvent extraction), membran technology has many advantages such as high efficiency, no exchange phase, low energy, produce very few waste, and easy to operate. Nanofiltration (NF) is one of the most promising membran process to separate rare earth elements due to high permeability and permselectivity, suited for rejecting organics with weight molecular > 200 g/mol and metal ions with moderate pressure. Due to these characteristics, the NF process show a great interest for REE ion rejection [2,4]. The REE ion rejection by nanofiltration complexation can be explained by two mechanism. The first is the steric effect based on MWCO membrane which is related to pore size or pore radius of the membrane. The charge effect is the second mechanism which refers to electrostatic interactions between solute and charge surface membrane. Most membrane acquire an electric surface charge when brought into contact with an aqueous solution. Solutes having the same charge than the membrane are excluded, and solutes having the opposite charge can passed through it. Solutes having different valences can be separated based on the charge effect.

In this work, the rejection of free gadolinium(III) by nanofiltration process assisted by complexation using DTPA ligand was studied according to the pressure (2, 3, 4, 5, 6 bars) and temperature (25, 30, 35, 40 °C).

2. EXPERIMENT

Aqua miliqu, glacial acetic acid (p.a., 100%), buffer acetate buffer pH 5.8, diethylene triamine pentaacetic acid (p.a., Sigma Aldrich), gadolinium chloride hexahydrate (p.a., Sigma Aldrich), gadolinium oxide (p.a., Sigma Aldrich), sodium hydroxide (p.a.) and xylenol orange.

Device the reflux tool set, then as much as 5.4375 g Gd_2O_3 weighted, put into a 1000 mL reflux flask and added with 6.4902 g of DTPA. Then added 540.00 mL aqua miliqu to the mixture and then refluxed for 3 hours on the oil bath until the solution is clear and colorless. Allowed the solution to stand at room temperature. Furthermore, the pH of the solution is measured by a pH meter. If the solution is more acid, added 3 N sodium hydroxide gradually until reaching a pH of 7.0-7.5. Then the solution was filtered using filter paper [9].

Amount of 500.00 mL of Gd-DTPA complex solution diluted with aqua miliqu until 3000.00 mL in the dilution flask. A certain amount of aqua miliqu passed into the membrane and nanofiltration process is run for 60 minutes until the membrane reached a stable condition, and then permeates were collected and the flux values were calculated. A solution of Gd-DTPA complex which acts as the feed solution is passed through the membrane and carried out the separation process of Gd-DTPA complex solution at pressure of 2, 3, 4, 5, and 6 bar and temperature of 25, 30, 35, 40 °C for 135 minutes with cross-flow system. Permeate was collected, and then permeate fluxes were calculated for each variation of pressure and temperature by using the formula $J_v = V / (A.t)$. The concentration of free gadolinium(III) in the feed and permeate determined by using a visible spectrophotometer and the rejections of free gadolinium(III) were calculated by using the formula $R = (1 - C_p / C_f) \times 100\%$.

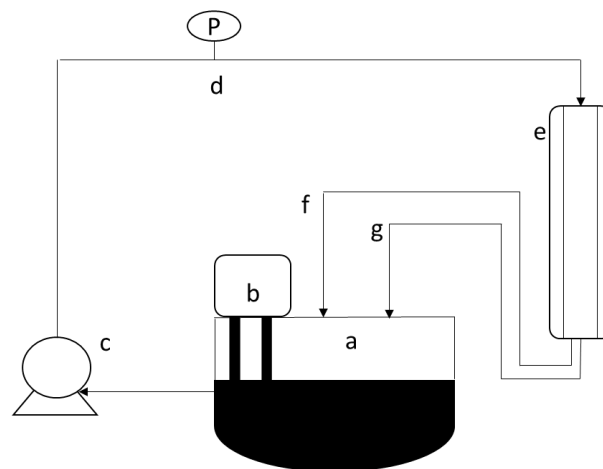


Figure 1. Schematic flow diagram of membrane system: (a) feed tank, (b) heat exchanger, (c) pump, (d) pressure gauge, (e) nanofiltration membrane, (f) permeate, (g) retentate

3. RESULT AND DISCUSSION

An optimum condition of membrane performance is generally expressed by the permeation flux and rejection of free gadolinium(III) in the feed solution. The higher the value of fluxes and rejections, the membrane has a better performance. But in fact, in a separation process by nanofiltration membrane discovered a phenomenon that the membrane flux is inversely proportional to its rejection. If the membrane flux was increased, the rejection will decrease, and vice versa. If the membrane flux was decreased then rejection will increase. In this study, an optimum conditions of membrane will be obtained by influenced of several parameters, such as the effects of pressure and temperature.

a. Effect of Pressure

Figure 2 shows the effect of pressure on the permeation fluxes and free gadolinium(III) rejections. In that figure, it can be seen the flux values at a pressure of 2, 3, 4, 5, and 6 bars respectively 237.530 L / m².h, 371.061 L / m².h, 523.100 L / m².h, 700.930 L / m². h, and 864.552 L / m².h. The higher of applied pressure, the permeation fluxes increase linearly. This is consistent with the driving force on the membrane operation, where the higher of pressure can make the propulsion that given to the feed solution across the membrane getting bigger so those chemical species that contained in the feed solution will be quickly moving into the membrane pores and out as permeates. In addition, the higher pressure caused by high feed diffusion rate. The high diffusion rate may causing interactions between a feed solution to the membrane surface occurred faster thus the speed of the feed solution to through the membrane pores getting bigger, hard to resist the membrane feed solution and a lot of free gadolinium(III) which can diffuse through the membrane.

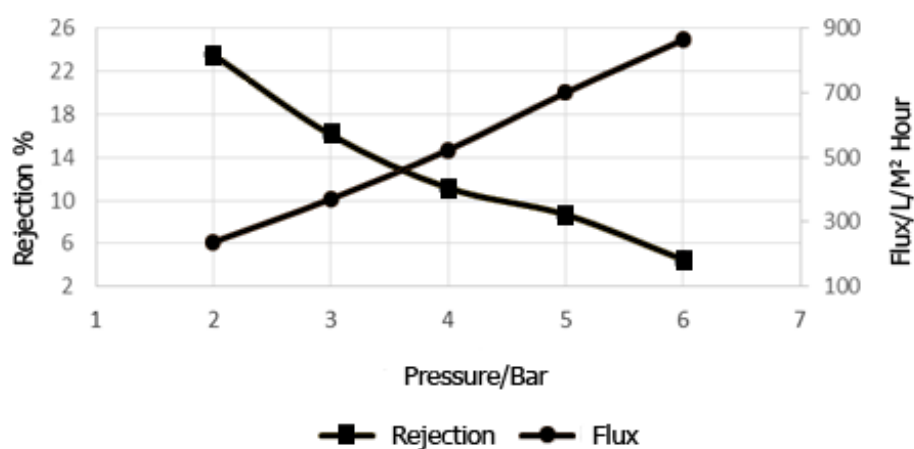


Figure 2. The effect of pressure on permeation fluxes and free gadolinium(III) rejections

The rejections of free gadolinium(III) at a pressure of 2, 3, 4, 5, and 6 bars respectively 23.56%; 16.12%; 11.16%; 8.68% and 4.49%. In this study, the percentages of rejection explained the ability of membrane to be able to reject the free gadolinium(III) across the membrane pores. In Figure 2 it can be seen that the rejections of free gadolinium(III) are decreasing with the higher pressure. It happened because the more species of free gadolinium(III) which passed through the membrane pores due to the propulsion on the feed solution is greater so that those smaller particle (in this case free gadolinium(III)) can passed through the membrane, while Gd-DTPA complex which have larger size will be retained. So, the membrane's ability to reject free gadolinium(III) are decreasing. 6 bar pressure is the most optimum pressure on the separation of free gadolinium(III) from Gd-DTPA complex because it produced the smallest rejection about 4.49%. In this study, the decreasing rejections did not indicate the concentration polarization on the membrane.

b. Effect of Temperature

Figure 3 shows the permeation fluxes as a function of a feed temperature. The permeate flux values at 25, 30, 35, and 40 ° C respectively 782.268 L/m².h, 847.458 L/m².h, 995.022 L/m².h, and 1129.938 L/m².h. In Figure 3 it can be seen that the higher of feed temperature, the permeation fluxes are increasing. This is due to the higher temperature causes the viscosity solution is decreasing [12]. The higher temperature causes the distance between the particles in the feed solution increasingly stretched so that the friction force getting smaller, consequently viscosity solution is decreasing. Decreasing viscosity solution may causing the speed of the particles (in this case free gadolinium(III)) to pass through the membrane pores become larger thus permeation fluxes are increasing.

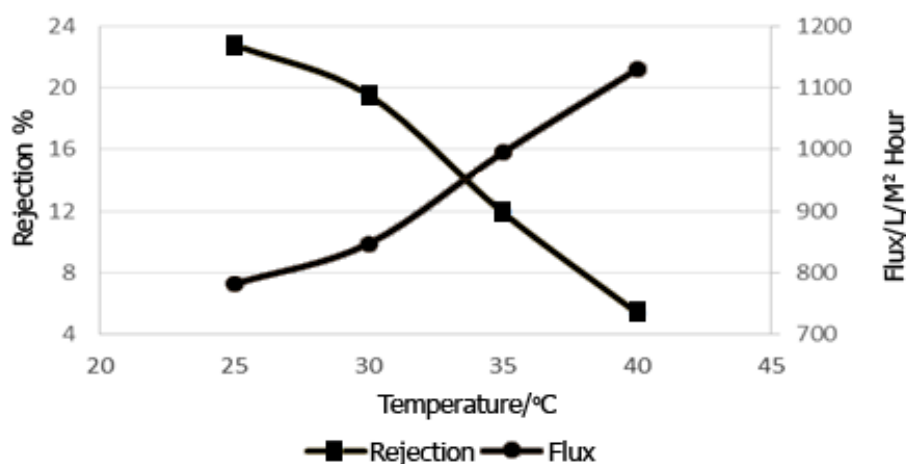


Figure 3. The effect of feed temperature on permeation fluxes and free gadolinium(III) rejections

Rejections of free gadolinium(III) at temperature of 25, 30, 35 and 40°C, respectively 22.79%; 19.53%; 11.93% and 5.42%. Figure 3 shows that the higher of feed temperature, the rejection of free gadolinium(III) are decreasing. It happened due to the pore size of the membrane getting bigger so that the more free gadolinium(III) in the feed solution that passed through the membrane pores and out as permeates thus the rejection of free gadolinium(III) are decreasing. 45°C is an optimum temperature for separation of free gadolinium(III) from Gd-DTPA complex because it produces the lowest rejection about 5.42%.

4. CONCLUSION

The higher of applied pressure and feed temperature cause permeation fluxes are increasing and free gadolinium(III) rejections are decreasing. An optimum condition for separation of free gadolinium(III) from Gd-DTPA complex have been done at pressure 6 bar and temperature 40°C where the rejection values are about 4.49% and 5.42%.

REFERENCES

- [1] Chitry F, Pellet-Rostaing S, Gozzi, C, & Lemaire M 2001 *Journal of Separation Science and Technology* **36** 605
- [2] Sorin A, Favre-Reguillon A, Pellet-Rostaing S, Sbair M, Szymczyk A, Fievet P, & Lemaire M 2005 *Journal of Membrane Science* **267** 41
- [3] Murthy Z V P, and Choudhary A 2011 *Journal of rare earths* **29** 297
- [4] Choi S, Yun Z, Hong S and Ahn K 2001 *Desalination* **133** 53