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To cite this article: N A Ismail *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **702** 012044

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Comparison of optimal solvent extraction stages between P204 and [A336][P204] for the separation of europium and gadolinium

N A Ismail¹, M Y Mohd Yunus^{1,2,*}, M A Abdul Aziz² and M A Abidin³

¹ Earth Resources and Sustainability Center, Universiti Malaysia Pahang, Lebuhraya Tun Razak 26300 Kuantan Pahang, Malaysia

² Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak 26300 Kuantan Pahang, Malaysia

³ Aras Kuasa Sdn. Bhd. Level 8, Menara Zenith, Jalan Putra Square 6, Putra Square 25200 Kuantan Pahang, Malaysia

*E-mail: yusri@ump.edu.my

Abstract. This study was designed to compare between the number of extraction stages required by 2-ethylhexyl phosphoric acid mono 2-ethylhexyl ester P204 and ionic liquid-based system of [A336][P204] in a cascade counter-current extraction process for the separation of europium (Eu) and gadolinium (Gd). Eu and Gd were chosen for this study as these metals are among the strenuous due to low availability in nature and small separation factor. The value of the separation factor (β) of both extractants, was obtained from the experimental work, while other process parameters were calculated using the counter-current model developed by Xu Guangxian. Extraction of Eu using [A336][P204] was found optimum at 3.5 M of nitric acid, with organic to aqueous (O/A) ratio of 9:1, while the optimum condition for P204 was determined at 3.0 M of hydrochloric acid and 9:1 of O/A ratio. The optimized β value for P204 was identified lower (β :2.38) compared to the condition for [A336][P204] (β :3.44). In order to obtain the optimal number of separation stages, the target purity and recovery rates were set to 99.9% and 90% respectively for both extractants. From the Xu model, the results show that [A336][P204] extractant requires at a minimum of four and two extraction and scrubbing stages respectively for maintaining the desired outputs. Meanwhile, P204 extractant needs to develop at least eight extraction stages as well as five scrubbing stages to produce the same production capacity. This finding generally suggests that [A336][P204] is favorable over P204 for the separation of europium and gadolinium particularly from the viewpoint of economic interest.

1. Introduction

Since the 1940s, the application of solvent extraction methods to separate rare earth (RE) has been studied in a laboratory and plant scale, primarily as a consequence of work created for the manufacturing of nuclear fuel. The extraction of liquid-liquid is a method of separation based on the distribution of a solution between two stages; aqueous and organic, which practically immiscible. The organic stage usually includes a diluent and an extractant that capable of complexing with the RE element and then forming more soluble compounds, i.e. showing higher affinity with the organic stage. Organophosphorus acids belong to a compound formation class and di-2-ethylhexylphosphoric acid (P204) is one of the examples. This extractant has been widely used since Peppard et al. [1] pioneering work for the discovery of the dimer for of RE-P204 metal complex. The use of P204 in RE separation



was discussed by Tianchi et al. [2], Qing et al. [3] and others. This extractant has been selected due to great separation factor among other extractant and environment-friendly properties as the extraction process is saponification-free.

A fresh category of advanced extractants based on ionic liquid, such as [methyltrioctylammonium][di-(2-ethylhexyl) phosphinate] ([A336][P227]) [4], [tricaprylmethylammonium][dihexyl diglycolamate], [A336][DHDGA] [5] and [trioctylmethylammonium][2,4,4-trimethylpentyl phosphinate] [A336/Cy272] [6] has been developed in the past few years. Most of these extractants are superior in term of extraction capabilities compared to common extractant in the market. Our earlier publication revealed that [A336][P204] provide synergistic impact towards La(III), Sm(III), and Y(III) compared to the P204 due to the presence of the dual-functional group [7]. This impact could considerably improve the extraction capabilities to extract RE while offering a greener separation path by eliminating the saponification process.

To recover a high purity RE from a solvent extraction technology, a multi-stage contact for the organic and aqueous phases using a mixer settler is often used. Also, to avoid coagulation, the aqueous liquid phase and the organic phase are injected in the opposite direction, known as the countercurrent process. The extraction process starts when the RE in the acidic medium (aqueous phase) is mixed with the extractant (organic phase) in a container until the mixture reaches an equilibrium point. In the settling stage, the mixture is then divided back into aqueous and organic phases, where some of the RE from the aqueous phase is now trapped in the organic phase, producing a complex of metal-extractants. The process of mixing, settling, and separating the organic and aqueous stages are repeated several times (1 to n times) until an adequate RE extraction purity and recovery value are achieved (Figure 1). Each cycle is counted as one extraction stage.

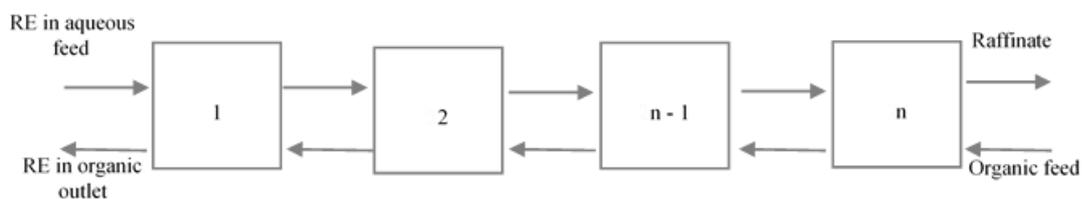


Figure 1. Schematic diagram of a counter-current extraction

This study evaluates the impact of two different extractants on the number of extraction and scrubbing stages needed for complete RE separation. An optimization study of P204 and [A336] [P204] in different parameters, such as type and concentration of acid, as well as organic to the aqueous ratio of the solution, was explored. In this study, the theory proposed by Xu Guangxian was used in calculating the theoretical stages required to separate Eu and Gd from their mixed solution. The least number of extraction and scrubbing stages is preferred as it reflects the cost and the efficiency of the overall extraction process.

2. Theoretical background

Figure 2 shows the simplified design procedure to calculate the number of extraction stage based on the counter-current theory developed by Guangxian Xu in 1978 [8]. Each stage of the design procedure is discussed in the following sections. This theory was established based on five assumptions;

1. The extractability sequence of the RE is represented by A, B, and C, in which A is the element or group with the highest extractability.
2. Since counter-current extraction is comprised of a multistage extraction process, the average separation factor is used due to the different distribution ratios in different stages.
3. The extraction factor is kept constant.
4. RE composition in the aqueous feed and the aqueous phase is assumed the same.
5. All extraction stages have a constant flow ratio.

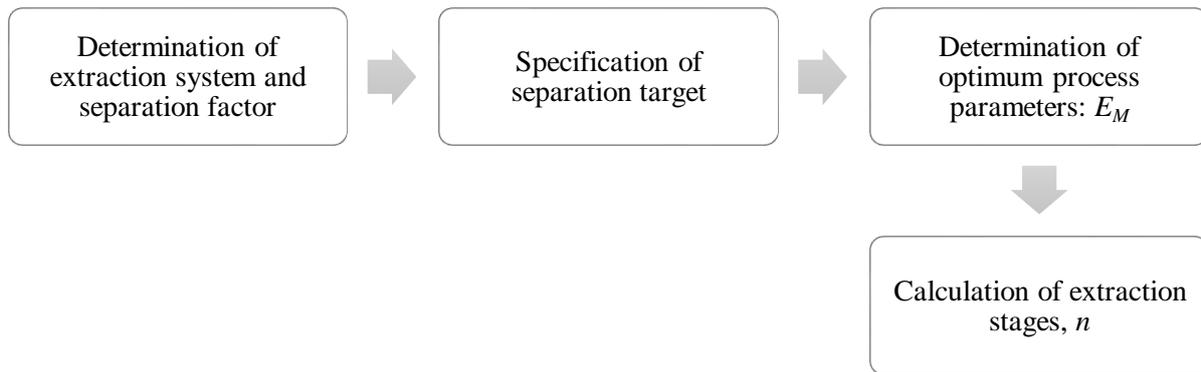


Figure 2. Simplified design procedure to calculate the number of extraction stage

2.1. Determination of Extraction System and Separation Factor

It is important to experimentally optimize an SX system by determining its parameters, such as the type and concentration of acid, the organic to the aqueous ratio (O/A), and feed concentration. Once a suitable extraction system is determined, the distribution factor, D and separation factor, β are measured, as shown by equation (1) and equation (2). D can be calculated when the RE distribution between the organic and aqueous phases has achieved an equilibrium state,

$$D_A = \frac{[A]_{\text{org}}}{[A]_{\text{aq}}} \quad (1)$$

From the D , the separation factor, β can be measured. β is defined as the ratio of distribution between two adjacent rare earth metals (A and B) in the separation system,

$$\beta_{A/B} = \frac{D_A}{D_B} \quad (2)$$

2.2. Separation Target Specification

To calculate the number of extraction stages in one particular SX system, the mole fraction of metal A in the feed (f_A), the target purity of product A in the organic outlet ($P_{A(o)}$), and the target percentage of the product recovery of A (Y_A) must be determine beforehand. Based on the assumptions mentioned in Section 2, the REs are categorized based on their extractability in the SX system; A is the element/group of REs that are easily extracted, while B is the relatively difficult element/group to be extracted from the system. The f_A and f_B can be calculated using the following equation (3):

$$f_A = \frac{\text{Total mole of A}}{\text{Total mole of B}}, f_A + f_B = 1 \quad (3)$$

If A is the major product, then, the concentrating factor of A, a can be calculated using equation (4):

$$a = \frac{P_{A_{n+m}(o)} / (1 - P_{A_{n+m}(o)})}{f_A / f_B} \quad (4)$$

And the concentrating factor for B can be calculated using equation (5):

$$b = \frac{a - Y_a}{a(1 - Y_a)} \quad (5)$$

However, if the major product is B, then, the concentrating factor of B can be calculated using equation (6):

$$b = \frac{P_{B1(a)} / (1 - P_{B1(a)})}{f_B / f_A} \quad (6)$$

And the concentrating factor for A for the major product, B is calculated using equation (7):

$$a = \frac{b - Y_B}{b(1 - Y_B)} \quad (7)$$

The solute fraction in the organic and aqueous outlets can be calculated using equation (8), as follows

$$f'_A = \frac{f_A Y_A}{P_{A_{n+m(o)}}}, f'_B = \frac{f_B Y_B}{P_{B1(a)}}, f'_A + f'_B = 1 \quad (8)$$

2.3. Determination of Optimum Process Parameters

Next, the average extraction factors, E_M and E'_M , were measured from the optimum conditions based on either the SX system is the extraction or scrubbing controlled, as shown in table 1.

Table 1. Determining the extraction factor from the optimum conditions

If $f'_B > \frac{\sqrt{\beta}}{\sqrt{\beta+1}}$, the SX system is extraction controlled	If $f'_B < \frac{\sqrt{\beta}}{\sqrt{\beta+1}}$, the SX system is scrubbing controlled
$E_M = \frac{1}{\sqrt{\beta}}$ (9)	$E'_M = \sqrt{\beta}$ (11)
$E'_M = \frac{E_M f'_B}{E_M f'_A}$ (10)	$E_M = \frac{E'_M f'_A}{E'_M f'_B}$ (12)

2.4. Determination of the Number of Stages

If B is the major component in the feed and targeted as a high purity product at the aqueous outlet, the number of extraction stage, n can be calculated using the following equation (13):

$$n = \log b / \log \beta E_M \quad (13)$$

However, if the targeted end product is a high purity A, and A is the major component in the aqueous feed, then, equation (14) can be used:

$$n = \log b / \log \beta E_M + 2.303 \log \frac{P_{A(a)}^* - P_{A1(a)}}{P_{A(a)}^* - P_{A_n(a)}} \quad (14)$$

3. Experimental Method

3.1. Chemicals and Reagents

Aliquat 336, (<99% purity, [A336]Cl) and di-(2-ethylhexyl) phosphate (P204) were purchased from Sigma Aldrich (USA). Nitric acid (HNO₃), sulphuric acid (H₂SO₄), hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride (NaCl), and sodium nitrate (NaNO₃) were purchased from Fischer

Scientific. A stock solution consisting of Eu(III), and Gd(III) was prepared by dissolving their oxides (99.9%) in concentrated acid. The oxides are purchased from Sigma Aldrich (USA) All other chemicals used were of analytical grade.

3.2. Extraction Procedure

The [A336][P204] was prepared using the acid-base neutralization method, as described by Sun et al. (9). The extractant was dissolved in n-heptane for extraction. 5 mL of the aqueous phase containing RE(III) and 5 mL of the organic phase containing the extractant were mixed and shaken for 1 h at 200 rpm using a mechanical shaker, which was sufficient for equilibrium. The pH of the aqueous mixture was maintained at pH 1–2 using sodium salt (either NaCl or NaNO₃). The mixtures were then centrifuged for 5 min at 8,000 rpm to enhance the separation between the aqueous and organic layers. The separation factor was calculated for each extraction process.

3.3. Calculating the Extraction Stages

Based on the value of the separation factor, the number of extraction stages was calculated in Microsoft Office Professional Plus Excel 2013 as described in the counter-current theory. For this study, the recovery was set to 90%, whereas the purity was fixed at 99.99%.

4. Results and Discussion

4.1. System Optimization and Determining the Separation Factor

To determine the optimum condition based on the value of the separation factor, Eu and Gd were separated from their mixed solution. The results are shown in figure 3 and figure 4. The outcome of the Eu and Gd separation on different acid medium, HNO₃ and HCl are shown in figure 3 and expressed as *D* versus concentration. For both acidic media, the separation is higher using [A336][P204] as the extractant compared to the P204. In the separation using the HCl, the effect of the acid was evident in lower acid concentration. Once the acid concentration exceeds 3.0 M, the distribution for both acids was quite similar. The order of the distribution coefficient are as follows; [A336][P204] in HNO₃ > P204 in HNO₃ > [A336][P204] in HCl > P204 in HCl. Guo et al. reported a similar result showing a high separation of RE(III) in the nitrate medium compared to the chloride medium when [A336][P204] was used as an extractant (10).

Sun et al. [9] suggested that neutral dissociation is the primary extraction mechanism for [A336][P204] in the HNO₃ medium [11]. They reported that the distribution percentage of Eu(III) was 11 times greater in HNO₃ than in HCl ($D_{HNO_3} = 21.7$, $D_{HCl} = 1.97$). However, in this research, when the same extractant was used, the largest distribution ratio for HNO₃ compared with HCl was only 0.7 times greater. The changes in the extraction capabilities in a different medium were due to the property of the anion in the system (NO₃⁻, Cl⁻, and SO₄²⁻), which regulate the stability and selectivity of the extractant in the system [10]. While it can be verified that HNO₃ is the best extraction medium for this study, the detailed mechanism is not fully understood.

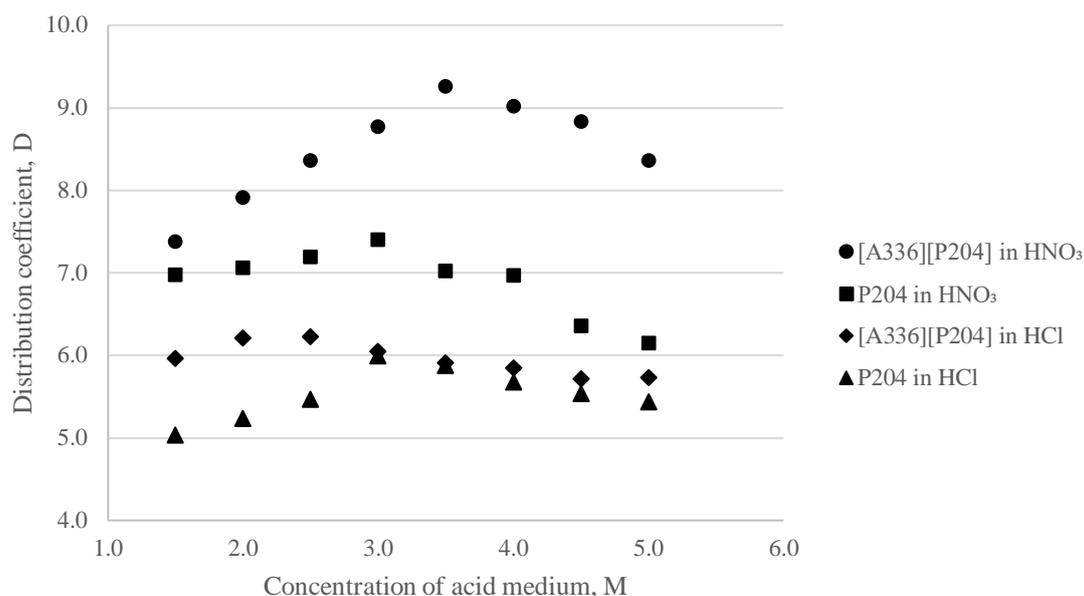


Figure 3. Effect of acid concentration on the distribution coefficient of Eu and Gd

Figure 4 explores on the effect of different O/A phase ratios on the separation of Eu and Gd. As displayed on the previous graph, since both [A336][P204] and P204 showed greater separation capabilities in the nitrate medium, the effect of O/A phase ratio was studied in their preferred medium. The trend showed increasing distribution coefficient with higher organic content for both extractants. The larger volume of organic compared to aqueous, increase the possibility of the metal to move and complex with the extractant in the organic medium. A similar finding was also discovered by other researchers [12] and [3]. Based on figure 3 and figure 4, the best condition for Eu and Gd separation using [A336][P204] (β : 3.44) would be in HNO₃, with O/A ratio of 9:1. Meanwhile, HCl and O/A ratio of 9:1 would be the best condition for Eu separation using P204 (β : 2.38).

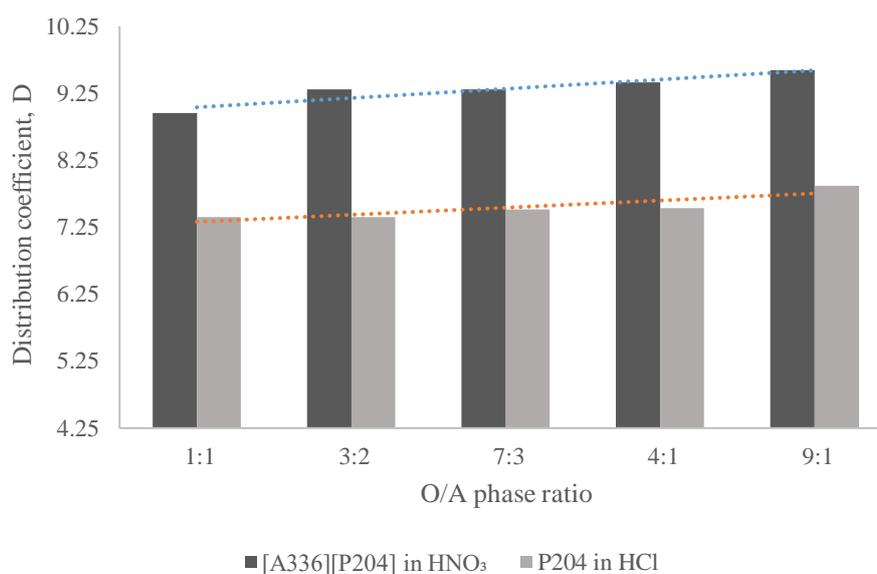


Figure 4. Effect of O/A phase ratio on the separation of Eu and Gd mixed solution

4.2. Extraction Stages of P204 and [A336][P204]

Two extractants, a common extractant, P204, and a synthesized bifunctional ionic liquid, [A336][P204], were chosen to compare and evaluate the effectiveness for Eu and Gd separation. The optimum condition for both extractants was explored and the value of β was determined. The amount of the theoretical extraction and scrubbing stages were calculated based on the experimental information as shown in table 2. [A336][P204] needed four complete extraction stages and two scrubbing stages, to separate Eu with 99.99% purity and 90% recovery, while P204 needed eight extraction stages and five scrubbing stages. Both processes were extraction controlled and the schematic diagrams are as in figure 5.

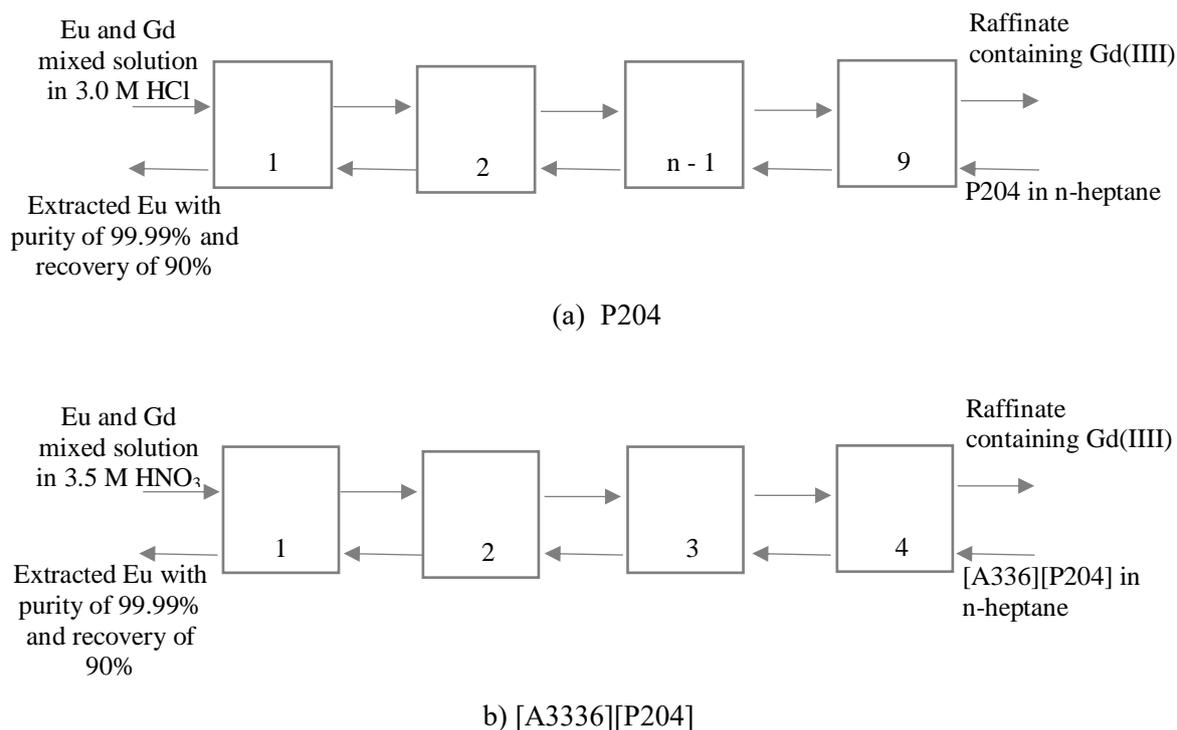


Figure 5. Countercurrent process of Eu and Gd separation by (a) P204 (b) [A336][P204]

5. Conclusion

This study focuses on the model development of the countercurrent process for Eu and Gd by P204 and [A336][P204]. The modelling was based on the Counter-current Theory and the least number of extraction and scrubbing stages were preferred. Under the optimized condition of 3.0 M of HCl and 9:1 of O/A, the β for the separation of Eu and Gd using P204 was 2.38. For [A336][P204], the β was 3.44, under the optimized condition of 3.5 M of HNO₃ and 9:1 of O/A. The [A336][P204] was proved to have higher separation capabilities based on the value of the β . The total number of extraction and scrubbing stages was calculated based on the information from the experimental work. P204 required a total of thirteen stages (eight stages for extraction and five stages for scrubbing) to extract Eu from Gd with 99.99% purity and 90% recovery, while [A336][P204] required only six stages (four for extraction and two for scrubbing). To conclude, the [A336][P204] offered better separation capacities, thus reducing the number of extraction stages required.

Table 2. Simplified theoretical output for Eu and Gd separation using P204 and [A336][P204] as the extractants

		Extractant	P204	[A336][P204]
STEP 1	System condition	Medium	3.0 M HCl	3.5 M HNO ₃
		O/A phase ratio	9:1	9:1
		Group A	Eu	Eu
	Group B	Gd	Gd	
	Separation Factor	$\beta_{Eu/Gd}$	2.38	3.44
STEP 2	Mole fraction in feed solution	f_A	0.36	0.37
		f'_A	0.32	0.32
		f_B	0.64	0.63
		f'_B	0.68	0.68
	Target purity of the product	P_A	0.9999	0.9999
		P_B	0.0001	0.0001
	Percentage of the product recovery	Y_A	0.90	0.90
		Y_B	0.1	0.1
Concentrating factor	a	17,776	17,025	
	b	9.999	9.999	
STEP 3	Average extraction factor	E_M	0.65 (extraction controlled)	0.54 (extraction controlled)
STEP 4	Number of extraction stage	n	≈ 8 stages	≈ 4 stages
	Number of scrubbing stage	m	≈ 5 stages	≈ 2 stages

Acknowledgement

The research was supported by the Universiti Malaysia Pahang under the Internal Grant Scheme RDU 160339 and RDU 190160.

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