NON-TOXIC ORGANIC DILUENTS FOR NICKEL (II) EXTRACTION FROM AQUEOUS SOLUTION: OPTIMIZATION BY RESPONSE SURFACE METHODOLOGY (RSM)

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Abstract - In order to promote a friendly environment for separation processes, the application of non-toxic diluents to nickel (II) extraction was investigated. Sunflower oil, soybean oil and rice bran oil were used as the diluents. Each non-toxic diluent was mixed with an extractant viz. Di-(2-Ethylhexyl) Phosphoric Acid (D2EHPA). Their utilization was operated by a Liquid-Liquid Extraction (LLE) system. The optimum conditions for the influencing parameters such as pH of aqueous solution and nickel (II) concentration were examined using Response Surface Methodology (RSM) based on Face-Central Composite Design (FCCD). Under optimum conditions as determined, the toxic diluent of kerosene was employed in the nickel (II) extraction system. Thereafter, the extraction efficiency of non-toxic diluents was compared with that of the toxic one. Results showed that the diluent of rice barn oil provided maximum percentage of nickel (II) extraction at 90.33 % under optimum conditions: namely, aqueous pH 4.64 and 5 ppm of nickel (II) concentration. Comparative results indicated that all the non-toxic diluents provided higher extraction percentages than that of the toxic diluent.

Keywords - Nickel (II), Non-toxic Diluents, Response Surface Methodology, Liquid-Liquid Extraction.

I. INTRODUCTION

Regarding commercial diluents, it is well known that they are typically inflammable, volatile, and toxic and have an adverse effect on human beings and the environment [1]. Thus, vegetable oil was chosen to replace toxic diluents because it is environmentally friendly and non-toxic [2]. Besides, vegetable oil was found to have special properties since it is non-volatile, low cost, renewable and biodegradable [3]. In addition, it is as efficient as many metal ion extractions such as copper, chromium and zinc [4]. Because of these advantages, the utilization of non-toxic diluents for metal ion extraction from aqueous solutions is interesting. In the manufacturing of spent catalyst and alloy scrap, nickel (Ni) is frequently used [5]. It is a toxic metal which can greatly affect the health of humans, thereby leading to skin allergies, lung fibrosis and respiratory tract cancer [6]. The treatment of water, therefore, containing nickel before discharge to the environment is important. Liquid-Liquid Extraction (LLE) is accepted as an effective method for metal ion extraction. LLE consists of two phases: an aqueous and organic phase. Accordingly, metal ions, in the aqueous phase, react with molecules of the extractant to form complexes [7]. The attractive points of LLE are as follows: easy operation, high performance and high purification of target ions [8]. Mathematical and statistical techniques, especially Response Surface Methodology (RSM) based on Face-Central Composite Design (FCCD) are benefits of the separation processes. Such technology can correctly predict optimal conditions of parameters which have an influence on metal ion extraction. Hence, the amount of experiments are reduced and results in saving time [9].

This work promotes the utilization of vegetable oils for nickel (II) extraction from an aqueous solution. Three vegetable oils i.e. sunflower oil, soybean oil and rice bran oil were selected as diluents. Further, a widely used extractant for metal ion extraction: namely, Di-(2-Ethylhexyl) Phosphoric Acid (D2EHPA) was employed [10]. All experiments were operated via the LLE system. The experiments were run following the conditions as predicted by FCCD with RSM. Optimum conditions, which provided the highest percentage of nickel (II) extraction, were determined. Subsequently, the extraction of nickel (II) using the toxic diluent of kerosene [1, 2, 11] was carried out under optimum conditions. Finally, the extraction percentage of each non-toxic diluent was compared with that of the toxic diluent.

II. DETAILS EXPERIMENTAL

2.1. Chemicals

Sunflower oil, rice bran oil and soybean oil were obtained from the local market in Thailand. Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, Panreac applichem ITW Reagent, ≥99% purity), di-2-ethylhexylphosphoric acid (D2EHPA, Merk, ≥95% purity), sodium hydroxide (NaOH, Loba Chemie, ≥99% purity), hydrochloric acid solution (HCl, Qrec, ≥37% purity) and kerosene (shell, ≥99% purity) were purchased. All chemicals were used without further purification. Aqueous solutions containing various concentrations of nickel (II) were prepared. Distilled water was used for all experiments.

2.2. Apparatus

Aqueous pH was measured by a pH meter (Mettler Toledo Seven Compact S220). A magnetic stirrer (VELP Scientifica F203A0450) was used to mix the aqueous and organic phases. Concentration of nickel (II) in aqueous solution was determined by an atomic absorption spectrophotometer (AAS, Varian model AA280FS) at a wavelength of 232.0 nm.

2.3. Procedure

The aqueous phase was prepared by dissolving $Ni(NO_3)_2$•$6H_2O$in distilled water.The pH of aqueous solution was adjusted using NaOH or HCl solution. The mixed solutions of D2EHPA (30 % (v/v)) with each vegetable oil or kerosene were used as the organic phases. Thereafter, the aqueous and organic solutions were added into a glass bottle at a volume ratio of 1:1. They were stirred at 400 rpm for 1 hr. The mixture was left all night in order for both phases to be separated. An aqueous sample was taken using a small syringe and further analyzed by AAS. The percentage of nickel (II) extraction was calculated as in Eq. (1):

$$\%\text{Extraction} = \left(\frac{[\text{Ni}]_{\text{int.}} - [\text{Ni}]_{\text{fin.}}}{[\text{Ni}]_{\text{int.}}}\right) \times 100 \quad (1)$$

where $[Ni]_{int.}$ and $[Ni]_{fin.}$ are the initial and final concentration of Ni (II) in aqueous phase, respectively.

2.4. Experimental design

In Table 1, following the experimental design by FCCD with RSM, the conditions of the independent parameters viz. aqueous pH (X_1) and Ni (II) concentration (X_2) are presented. Their experiments were designed to be completed in thirteen runs and listed, as shown in Table 2. The extraction result (%Extraction) for each run was used to generate a second-order polynomial model. This model predicted the extraction percentage under optimum conditions. In this section, all experiments were operated using only the diluent of sunflower oil.The general form of the second-order polynomial equation is as in Eq. (2):

$$Y = \beta_0 + \sum_{t=1}^{k} \beta_1 X_1 + \sum_{t=1}^{k} \beta_2 X_2 + \cdots + \sum \sum i < j + \varepsilon \quad (2)$$

where Y is the predicted value, β_0, β_j, β_{jj}, β_{ij} are the intercept, linear, quadratic and interaction coefficients, respectively, X_i, X_j are coded independent parameters, k is the number of independent parameters (k = 3), i, j = 1, 2 or 3 and ε is the error.

From the model, the relationship between the independent parameters were analyzed by the variance (ANOVA) and identified using the F-test and t-test based on 95% of confidence level. As for the t-test, it was presented by p-value that should be less than 0.05. Optimal conditions were obtained by graphical and numerical analyses. Lastly, the fitting quality was evaluated by the coefficient of determination (R^2) [12].

Parameter	Code	Level		
		-1	0	+1
pH of aqueous solution	X_1	2.0	3.5	5.0
Ni (II) concentration	X_2	5.0	65.0	125.0

Table 1 - FCCD levels for the experimental conditions of the two independent parameters.

Run	Level		Experimental condition		%Extraction	
	X_1	X_2	X_1	X_2	Experimental	Predicted
1	-1	1	2.00	125.00	2.43	0.00
2	0	0	3.50	65.00	65.82	64.91
3	0	0	3.50	65.00	65.86	64.91
4	1	-1	5.00	5.00	84.36	86.31
5	1	1	5.00	125.00	50.08	45.45
6	-1	0	2.00	65.00	9.56	11.32
7	0	0	3.50	65.00	65.80	64.01
8	0	0	3.50	65.00	65.84	64.91
9	-1	-1	2.00	5.00	12.08	14.47
10	0	-1	3.50	5.00	78.89	74.22
11	0	0	3.50	65.00	65.81	64.91
12	1	0	5.00	65.00	68.62	70.85
13	0	1	3.50	125.00	37.00	45.66

Table 2 - Experimental design of thirteen runs for the Ni (II) extraction via LLE and %Extraction of predicted and experimental values.

III. RESULTS AND DISCUSSION

3.1. Statistical analysis

In Eq. (3) below, the second-order polynomial equation, as generated by the software, is presented. From the equation, the extraction percentage of Ni (II) was predicted by replacing the values of aqueous pH (X_1) and Ni (II) concentration (X_2).

$$\%\text{Extraction} = -140.200 + 98.420X_1 + 0.181X_2 - 10.590X_1X_1 - 0.001X_2X_2 - 0.068X_1X_2 \quad (3)$$

In Table 3, the relationship between the independent parameters, as shown in Eq. (3), was analyzed by the variance (ANOVA). The equation term, which displayed the p-value less than 0.05, was considered as significant [8]. From the table, the significant terms were as follows: model, linear (X_1 and X_2), square (X_1X_1 and X_2X_2) and 2-way interaction (X_1X_2). In addition, all equation terms showed F-values more than 3.97. This indicated the reliability of Eq. (3) [13].

Source	Sum of square	DF	Mean square	F-value	p-value
Model	8,923.82	5	1,784.76	79.22	0.00
Linear	6,566.57	2	3,283.29	145.73	0.00
Square	2,205.53	2	1,102.76	48.95	0.00
2-Way reaction	151.72	1	151.72	6.73	0.04
Total	9,081.52	12			

Table 3 - The variance (ANOVA) analysis of the second-order polynomial equation for Ni (II) extraction.

Furthermore, the coefficient of determination (R^2), as confirmed by Fig.1, was used to determine the precision of Eq. (3). Its value 0.9839 demonstrated the good fitting between the experimental and predicted values.

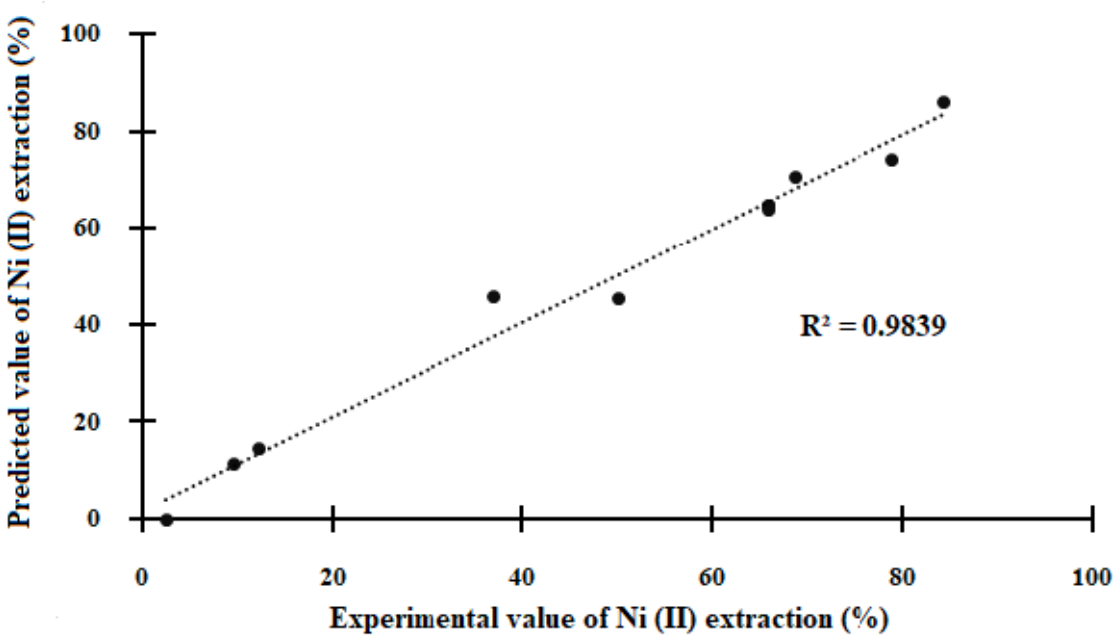


Fig 1. Fitting quality between experimental and predicted values.

3.2. Optimization analysis

In Fig. 2, the response optimization for Ni (II) extraction was plotted using the Response Optimizer of the Minitab Software V.18. A maximum percentage of 87.92% was predicted under optimum conditions: namely,aqueous pH 4.64 and Ni (II) concentration 5.0 ppm. In Table 4, under optimum conditions, the predicted and experimental values of the extraction percentages are reported. It is noted that both percentages showed good agreement with the error of 2.42%, thus proving the reliability of FCCD with RSM.

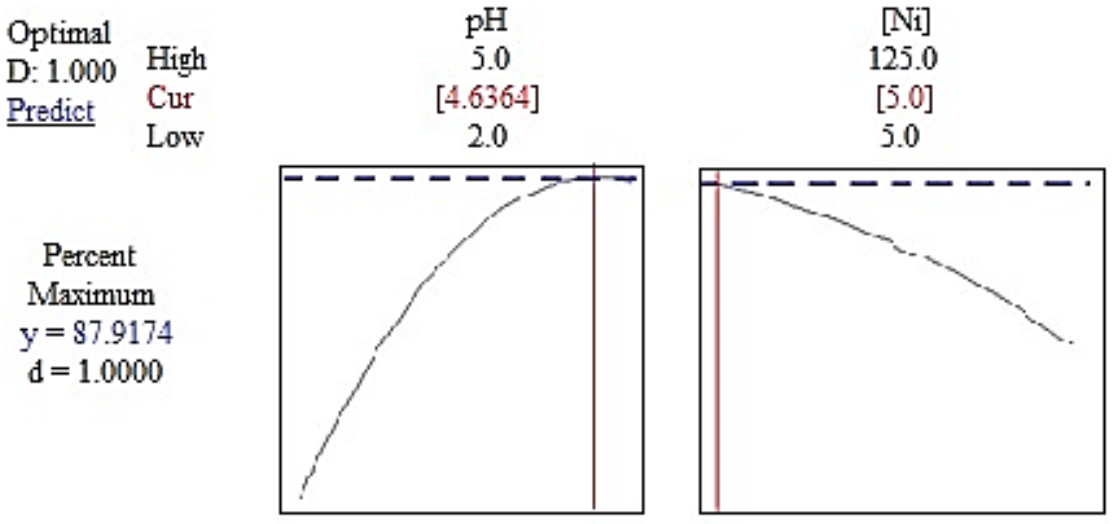


Fig. 2. Plot of response optimization for Ni (II) extraction.

Aqueous pH	Ni (II) concentration	Predicted (%Extraction)	Experimental (%Extraction)	Error (%)
4.64	5.00	87.92	85.79	2.42

Table 4 - The predicted and experimental percentages of Ni (II) extraction under optimum conditions.

3.3. Effect of diluent types on Ni (II) extraction

In Fig 3, four diluents are classified into two groups: namely, non-toxic (sunflower oil, soybean oil and rice bran oil) and toxic (kerosene). Their effects on the extraction of Ni (II) are presented. Rice bran oil provided the highest extraction. In addition, all non-toxic diluents resulted in higher percentages of Ni (II) extraction than that of the toxic diluent. This is because vegetable oil is composed of free fatty acids which can transform into acidic protons (H^+) for cationic exchange between nickel ions (Ni^{2+}) in aqueous solution [3]. Rice bran oil was found to have free fatty acids more than those of the other diluents [14].

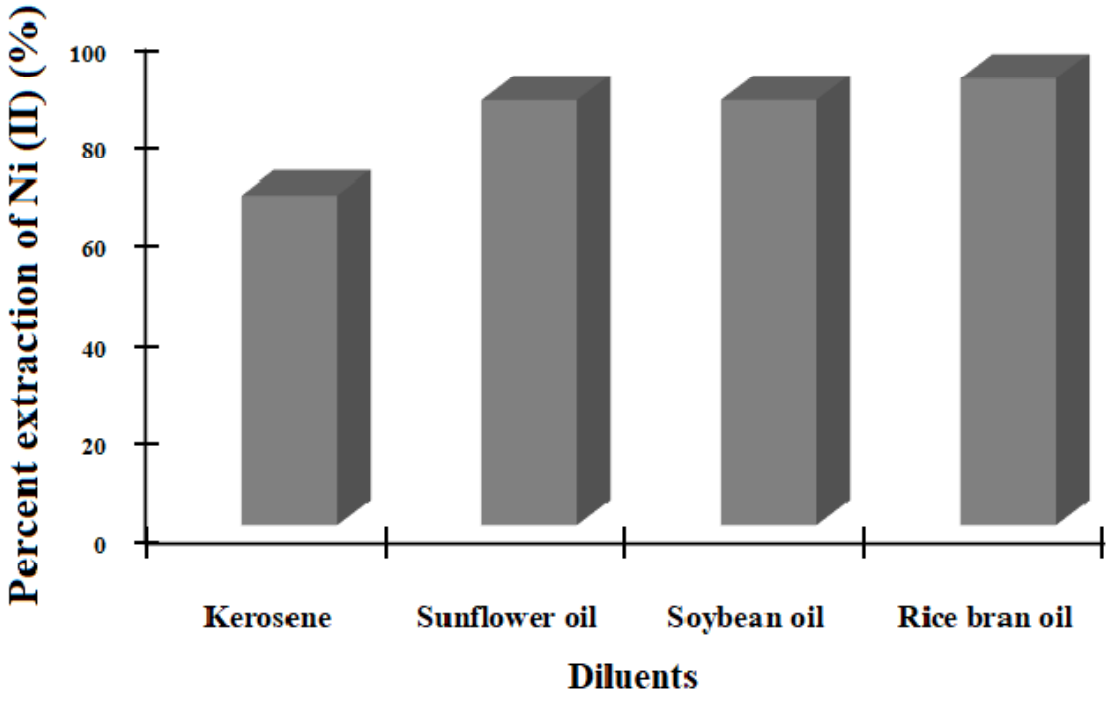


Fig. 3. Percent extraction of Ni (II) using toxic and non-toxic diluents.

IV. CONCLUSIONS

In this work, both non-toxic and toxic diluents for Ni (II) extraction were studied. It was noted that FCCD with RSM proved to be most reliable for optimization analysis. Thus, using the non-toxic diluents, extraction efficiency (more than 86%) was achieved under optimum conditions:aqueous pH 4.64 and Ni (II) concentration 5.0 ppm; volume ratio between the aqueous and organic phases was 1:1, stirring rate 400 rpm, extraction time 1 hr. and D2EHPA concentration 30 % (v/v). All non-toxic diluents showed higher extraction percentages than that of the toxic diluent. Especially, the diluent of rice bran oil provided the highest extraction percentage at 90.33%. Hence, it can be observed that in the Ni (II) extraction process, the non-toxic diluents can successfully replace the toxic diluent.

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