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Optimization of nickel removal using liquid–liquid extraction and response surface methodology

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ABSTRACT

The nickel extraction efficiency by means of liquid–liquid extraction (LLE) method was studied using response surface methodology; six parameters were identified as influential factors on nickel removal efficiency as the response. However, on screening experiments, only two factors were selected: pH and di-(2-ethylhexyl) phosphoric acid (D2EHPA) concentration. Face-centered composite design (FCCD) was applied in order to determine the optimum conditions for nickel removal by LLE. The results of FCCD showed that a second-order model described the relationship between the factors and nickel removal properly. Results showed that the optimum conditions are pH 1.1 and D2EHPA concentration 0.2 M, where 95.57% of nickel removal was achieved.

Keywords: Response surface methodology; Liquid–liquid extraction; Di-(2-ethylhexyl) phosphoric acid (D2EHPA); Face-centered composite design

1. Introduction

Water pollution by heavy metals is one of the most serious and important issues in wastewater treatment, which has been studied for many years and by many researchers [1–8].

Exposure to heavy metals has straight and serious consequences of toxicity for human health. It causes serious and somber health disorders such as headache, nausea, vomiting, depression, lethargy, neurologic signs such as seizures and ataxia, increased thirst, kidney damage, renal disorder, Itai-Itai, chronic asthma, coughing [9].

Nickel and its compounds are widely used in nickel plating and in the manufacture of alloys along with iron, copper, aluminum, zinc, etc. due to their high strength and resistance to corrosion in many media [10]. As a consequence of nickel's wide industrial applications, it has become an important contaminant in the environment as it is a toxic and carcinogenic heavy metal. Upon exposure to human beings, nickel has the potential to produce various pathologic effects such as skin allergies, lung fibrosis, respiratory tract cancer [11]. There is a growing need to remove and recover nickel and its compounds from the industrial wastewater. Conventional techniques used to remove nickel from aqueous solutions include ultrafiltration membranes, cation exchange, electrochemical removal, adsorption, biosorption, electrocoagulation, and electroflocculation [12–18].

Recently, separation techniques such as solvent extraction or liquid–liquid extraction (LLE), liquid membrane have been widely used in the separation of heavy metals from aqueous solutions [19]. LLE is a process where a solute can distribute itself in a certain ratio between immiscible solvents, and extraction process depends on the mass transfer rate of solute [20]. A few

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advantages of LLE are (a) high throughput, (b) ease of operation, and (c) high purification [21]. Researchers have studied the few parameters affecting the extraction efficiency, such as equilibrium pH (pH_{eq}), mixing time, extractant concentration, salt concentration, and organic-to-aqueous-phase ratio (O/A) [22–26]. Most of them used univariate method, where only one factor was studied at a time. This method might not reach the actual optimum operational conditions [27].

In order to overcome this problem, the present study utilizes experimental design methods—face-centered composite design (FCCD) and response surface methodology (RSM) to investigate the combination of parameters for the best Ni(II) extraction from aqueous solutions. The advantages of multivariate design methods include simultaneous study of several control variables, low cost, and being easy and faster to implement [28]. RSM is a collection of mathematical and statistical techniques. It is a useful tool for developing, improving, and optimizing a process. It can also be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions [29]. There are three main steps in RSM: design and experiments, response surface modeling through regression, and optimization [30]. To our knowledge, there has not been any study on the use of statistical methods to optimize the process parameters of Ni(II) extraction by cooking oil-based organic solvents. In the present study, optimization of parameters such as pH_{eq}, tri-n-butyl phosphate (TBP) (phase modifier) concentration, di-(2-ethylhexyl) phosphoric acid (D2EHPA) (extractant) concentration, O/A ratio, and shaking time was carried out to enhance the percentage extraction (%E) of Ni(II) using RSM FCCD.

D2EHPA, which is a cation extractant, extracts metal ion (nickel in current study) by a cation exchange reaction between metal ion (from the aqueous phase) and H^+ (from D2EHPA in the organic phase) [31]. The process of solute transport from aqueous phase to organic phase has been widely studied [32]. When a solute is introduced into a system containing two immiscible liquids, it will distribute itself in the two phases, according to its solubility; according to Chang et al. [31] in a similar study on copper removal, the extraction efficiency of an organic phase without a carrier (extractant) is very low.

2. Materials, equipment, and methods

2.1. Materials and equipment

Refined palm cooking oil (100% purity) manufactured by Delima Oil Products Sdn. Bhd. was used. Nickel sulfate ($NiSO_4 \cdot 6H_2O$) (R&M Chemicals, 98% purity), D2EHPA (Acros Organic, 97% purity), TBP (97% purity), hydrochloric acid (HCl) (98% purity), sodium hydroxide (NaOH) (99% purity), and sodium sulfate (Na_2SO_4) (Merck, 98% purity) were used as received. An orbital shaker (WiseShake, SHO-2O) was used to mix the aqueous and organic phases, while a pH meter (HACH) was used for pH measurement of aqueous phase before and after extraction. The concentration of Ni in the aqueous phase after extraction was measured with a flame atomic absorption spectrophotometer (Perkin Elmer AANALYST 100) at a wavelength of 232 nm.

2.2. Preparation of aqueous and organic phases

Aqueous solutions containing 10–100 mg/L of various initial Ni concentrations were prepared by dissolving specific amounts of $NiSO_4 \cdot 6H_2O$ in distilled water loaded with 50 mM Na_2SO_4. Na_2SO_4 was used as an inner salt in order to break down the formed emulsion during the extraction process and was prepared by dissolving 7.101 g of Na_2SO_4 in 1 L of sample [26]. The organic phases were prepared by loading palm cooking oil with 0.01–0.04 M TBP and various concentrations of D2EHPA (0.002–0.22 M). The pH of the aqueous solution was adjusted to the desired value by adding dilute HCl or NaOH before equilibration.

2.3. Extraction procedures

One hundred milliliters of aqueous solutions of various initial nickel concentrations were prepared and were mixed with same volume of organic phase containing a range of D2EHPA and TBP (as shown in Table 1). pH was measured before and after each run, and organic and aqueous phases in different ratios were mixed in an orbital shaker and settled down in separation funnels for half an hour at room temperature. Then, the samples were taken by a syringe (after filtration and dilution) in order to measure nickel concentration using atomic adsorption spectrophotometer. The %E (removal efficiency) of nickel was calculated according to the following equation:

$$\%E = \left\{1 - \frac{[\mathrm{Ni}]_{\mathrm{final}}}{[\mathrm{Ni}]_{\mathrm{initial}}}\right\} \times 100. \quad (1)$$

More than 100 preliminary runs, including four different designs of experiment and five factors (each factor two levels), were carried out in order to find the best condition for optimization process. Table 1 shows the studied factors and their related ranges.

Table 1
Studied factors and their related ranges

Factor	Range
Initial nickel concentration (mg/L)	10–100
pH	1–6
Shaking time (min)	10–30
A/O ratio	1–4
TBP concentration (M)	0.01–0.04
D2EHPA concentration (M)	0.002–0.22

After studying all preliminary experiments, gathering and analyzing the basic data, it is found that the most effective factors among those studied are pH and D2EHPA, and therefore, the optimization was focused to find the best pH value and D2EHPA for nickel removal through LLE.

2.4. Face-centered composite design

FCCD was used to study the effect of two factors, namely pH (x_1) and [D2EHPA] (x_2), in order to determine the optimum conditions for nickel removal from aqueous solutions. Based on preliminary studies and experiments, the low and high levels of these two factors were 1 and 5 for pH and 0.1 and 0.2 mg/L for D2EHPA concentration. Based on 13 runs, a model was developed to optimize the process by finding the best operating condition for maximum nickel (response) removal.

3. Results and discussion

Two variables, pH and [D2EHPA], are considered to play a major role in Ni removal. The results of 13 runs in FCCD on two variables with one response (nickel removal) are shown in Table 2, including the input variables (pH and [D2EHPA]) and the observed and predicted values. It shows that the proposed FCCD is suitable for predicting nickel removal, revealing an accurate prediction of nickel removal. RSM was used to evaluate the effect of pH and [D2EHPA]. RSM is a statistical method that has been used in the design and analysis of experiments in order to optimize a response (output variables) which is influenced by several independent variables (input variables). The advantage of RSM is that the interaction and interference of various independent variables can be analyzed and investigated simultaneously. This method consists of series of tests, called runs, in which changes are made in the input variables in order to identify the sources of changes in the output response [33]. Then, a model that describes the behavior of Ni removal is built in order to optimize the process by finding the best settings of pH and [D2EHPA] that maximize the Ni removal.

A second-order model was chosen to fit the data:

$$y = \beta_0 + \sum_{i=1}^{2} \beta_i x_i + \sum_{i=1}^{2} \beta_{ii} x_i^2 + \sum \sum_{i<j} \beta_{ij} x_i x_j, \tag{2}$$

where $\beta_0, \beta_i, \beta_{ii}$, and β_{ij} are regression coefficients and x_i are the coded variables.

The second-order model for nickel removal in terms of coded variable is given by the following equation:

Table 2
Input variables pH and [D2EHPA] and the observed and predicted values

Input variables		Ni removal (*E*%)	
pH	[D2EHPA]	Observed	Predicted
1	0.1	92	91
5	0.1	90	90
1	0.2	96	95
5	0.2	89	89
1	0.15	90	91
5	0.15	88	87
3	0.1	92	92
3	0.2	94	94
3	0.15	91	90
3	0.15	91	90
3	0.15	90	90
3	0.15	91	90
3	0.15	91	90

$$\%\text{Ni removal} = +90.72 - 1.83x_1 + 0.83x_2 - 1.53x_1^2 + 2.47x_2^2 - 1.25x_1x_2. \tag{3}$$

A positive sign for the regression coefficient in the fitted model indicates the ability of the factor to increase the response, while the negative sign indicated the ability of a factor to decrease the response.

The second-order regression model obtained for Ni removal is satisfactory since the value of the coefficient of determination (R^2) is high and close to 1. The value of R^2 for %Ni removal model is 0.94.

The results of analysis of variance (ANOVA) for nickel removal are given in Table 3. The ANOVA revealed that a second-order model adequately fitted the experimental data. The linear and quadratic effects of pH (x_1) and [D2EHPA] (x_2) were significant (p-values < 0.05). The relative contribution of each factor to nickel removal was directly measured by the regression coefficient in the fitted model in Eq. (1). A positive sign for the regression coefficient in the fitted model indicates the ability of the factor to increase nickel removal, while the negative sign indicates the ability of a factor to decrease nickel removal. Furthermore, the interaction between pH and [D2EHPA] was significant as well. This interaction could be due to the fact that metal in organic and aqueous phases reacts as a function of equilibrium pH and extractant concentration, based on the following equation:

$$M^{n+}_{\text{aq}} + \overline{n\text{RH}} \leftrightarrow \overline{\text{MR}_n} + n\text{H}^+. \tag{4}$$

Extraction process using D2EHPA or other acidic extractants that possess ionizable hydrogen atoms that can be replaced by metal ions can be regarded as the following reaction [34–36]:

$$\text{Ni}^{2+} + \left(\frac{2+n}{n}\right)\overline{(\text{RH})_2} \leftrightarrow \overline{\text{NiR}_2(\text{RH})_{(2+n)/n}} + 2\text{H}^+. \tag{5}$$

RH represents the D2EHPA dimers, and the overbar refers to the organic phase.

According to Chang et al. [31], n (the number of molecules of D2EHPA engaged in the reaction), in most cases, has a value of 2 when aliphatic organic solvents are used [37,38]:

$$\text{Ni}^{2+} + 2\overline{(\text{RH})_2} \leftrightarrow \overline{\text{NiR}_2(\text{RH})_2} + 2\text{H}^+. \tag{6}$$

Considering the distribution coefficient as total analytical concentration of metal in organic to aqueous phases, then

$$D = \frac{\overline{[\text{Ni}]}}{[\text{Ni}]}. \tag{7}$$

Considering that the aqueous complexations of Ni^{2+} and Cl^- are not taken into account and only a single species of the type $\text{NiR}_2(\text{RH})_2$ is formed in the organic phase, then

$$D = \frac{[\overline{\text{NiR}_2(\text{RH})_2}]}{[\text{Ni}^{2+}]}. \tag{8}$$

The equilibrium constant (K) for reaction (6) is

$$K = \frac{[\overline{\text{NiR}_n}][\text{H}^+]^n}{[\text{Ni}^{n+}_{\text{aq}}][\overline{\text{RH}}]^n}, \tag{9}$$

Table 3
ANOVA results for Ni removal

SOV	SS	DF	MS	F-value	P-value
Model	48.52	5	9.70	21.39	<0.004
X_1	20.17	1	20.17	44.46	<0.0003
X_2	4.17	1	4.17	9.19	<0.0191
X_1^2	6.50	1	6.50	14.34	<0.0068
X_2^2	16.79	1	16.79	37.01	<0.0005
X_1X_2	6.25	1	6.25	13.78	<0.0075
Residual	3.18	7	0.45		
Lack of fit	2.38	3	0.79	3.96	0.1085
Pure error	0.8	4	0.20		
Total	51.69	12			

Note: SOV: source of variation; SS: sum of squares; DF: degrees of freedom; and MS: means of SS.

$$D = K \cdot \frac{[\overline{\mathrm{RH}}]^n}{[\mathrm{H}^+]^n}, \tag{10}$$

$$\log D = \log K + n \log[\overline{\mathrm{RH}}] + n\,\mathrm{pH}. \tag{11}$$

This equation shows how distribution coefficient is a function of pH, and consequently, the observed significant interaction of pH and [D2EHPA] could be due to this function.

It should be mentioned that according to the literature, insignificant metal uptake occurs at a lower pH (pH 1–2) and high metal acceptance occurs at a higher pH (3.5–5) [39]. Furthermore, the characteristics of used extractant have a crucial role in LLE process. D2EHPA, which belongs to phosphoric acid type of acidic extraction agents ($R^1 = R^2 = C_4H_9CH(C_2H_5)CH_2O$–), shows chemical stability, low aqueous solubility, and good loading and stripping characteristics [34].

The significant interaction between pH and [D2EHPA] could be due to the existence of H^+ ion released according to the above reaction and consequently lead to a very slight increase in final pH [40]. These results are in agreement with the findings of Devi et al. [41] where it was found that the separation factor was pH sensitive and was highest, showing that the sodium salt of the phosphinic acid (NaD2EHPA) is the best extractant for metal separation. However, if the level of [D2EHPA] is higher than certain level of interaction, the increase in the concentration of D2EHPA resulted in higher metal extractions, independently of the pH level investigated. It occurs due to the higher amount of free D2EHPA [42]. According to Chang et al. [31], the interaction between pH and nickel removal could be due to the release of H^+ in the reaction of aqueous phase with D2EHPA (represented as RH) as shown in the following equation:

$$\mathrm{Ni}^{2+} + 2\overline{(\mathrm{RH})_2} \leftrightarrow \overline{\mathrm{NiR}_2(\mathrm{RH})_2} + 2\mathrm{H}^+. \tag{12}$$

Maximum Ni removal can be achieved at pH between 1 and 1.13 and [D2EHPA] at 0.2 M.

According to Juang and Huang [37] on solvent extraction mechanistic analysis and in a membrane module, it was found that metal ion spreads into the very fine layer of aqueous phase of the aqueous–organic interface, and it reacts with D2EHPA to form complex. The formed complex thereafter moves to the bulk of the organic phase and leaves space for free D2EHPA to form more complexes with metal ion. The highest extraction efficiency was achieved at 0.2 M of D2EHPA. However, the effect of [D2EHPA] is closely related to the effect of pH of the aqueous phase and the interaction between these two factors, which is an important factor that determines the extraction efficiency and optimum condition.

The composition of the species formed in the extraction of Ni in organic phase containing D2EHPA is $NiR_2(RH)_4$. It should be noted that during the formation of single species of $NiR_2(RH)_4$, aqueous complexations of Ni^{2+} and CI^- are not taken into account.

The three-dimensional response surface plot for Ni removal is given in Fig. 1, which shows the effect of

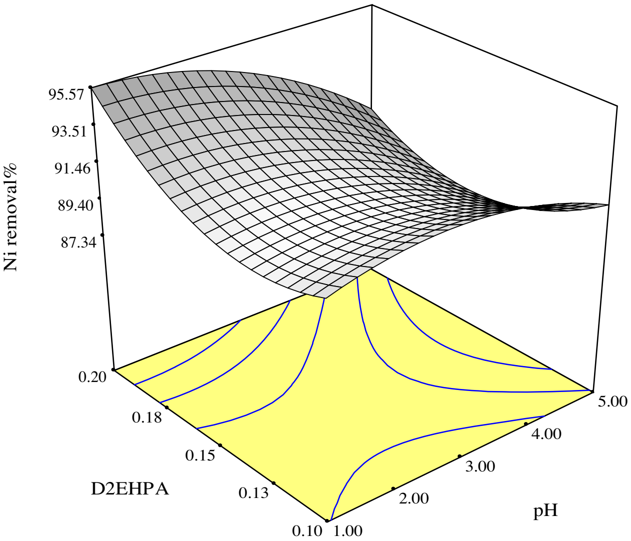

Fig. 1. Three-dimensional response surface for nickel removal as a function of pH and [D2EHPA].

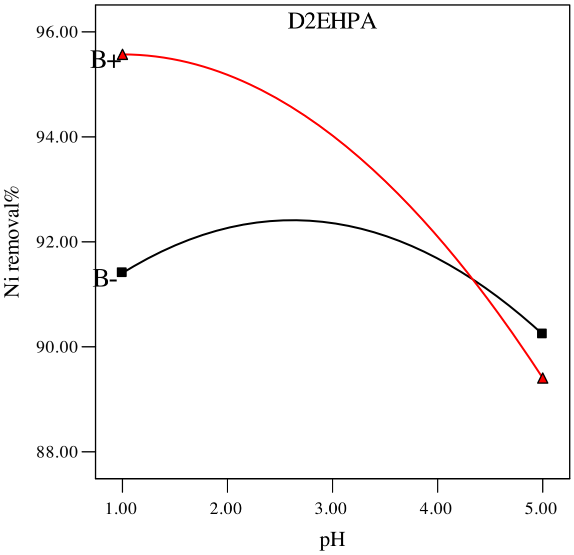

Fig. 2. Interaction effect between pH and [D2EHPA].

pH and [D2EHPA] on Ni removal. It can be seen that nickel removal exhibited a clear surface, it suggests that the optimum condition for maximum nickel removal is well defined and inside the design boundary. Interaction plot between pH and [D2EHPA] is given in Fig. 2. B− shows the effect of pH, and B+ shows the effect of [D2EHPA]; the interception occurred at a high level of pH and a low level of [D2EHPA] clearly reveals the interaction between these two factors.

4. Conclusion

Two main factors (pH and D2EHPA concentration) were selected among total six different factors (including TBP concentration, aqueous-to-organic-phase ratio, etc.) in order to evaluate the effectiveness of nickel in LLE. A FCCD was used for the optimization of operating conditions, and results showed a significant effect in a second-order model, in which the linear effect and quadratic effect of pH and D2EHPA concentration played the major role. Furthermore, the interaction between pH and [D2EHPA] was significant as well. Results showed that in the optimum condition, where pH 1.1 and D2EHPA concentration 0.2 M, 95.57% of nickel removal was achieved.

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