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Experimental and DFT investigations on the supramolecular mechanism of Ni(II) extraction via D2EHPA blended 1-octanol extractant: Application of vegetable oils as diluents

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Abstract–This work presents the separation of trace Ni(II) from aqueous solution via liquid-liquid extraction. The application of vegetable oils (rice bran, soybean and sunflower oil) as alternative green solvents was evaluated. Results demonstrate that D2EHPA dissolved in rice bran oil provides the highest extraction of Ni(II), whereas D2EHPA dissolved in kerosene reveals much lower performance. Furthermore, extraction of Ni(II) dramatically increases when the binary system of D2EHPA/1-octanol is applied, suggesting the occurrence of synergism having the synergistic coefficient=3.580. Under optimum conditions, extraction and stripping of Ni(II) achieved 99.70% and 88.00%, complying with the wastewater discharge limit in Thailand. Herein, a novel approach involving supramolecular mechanisms via density functional theory in a binary system of D2EHPA/1-octanol is first reported. Results show that intermolecular hydrogen bonds play an important role in supramolecular complexing. Fourier transform infrared spectrometer is analyzed to verify the functional groups in which the reactions occur. Significant numeric results are as follows: $k_{extraction}=0.134\ s^{-1}$, $k_{stripping}=0.038\ s^{-1}$, $\Delta H^{o}=72.759$ kJ/mol and $\Delta S^{o}=0.268$ kJ/mol·K.

Keywords: Nickel, Green Solvent, D2EHPA, 1-Octanol, Synergistic Extraction

INTRODUCTION

Ni(II) is a very toxic metal that can cause a variety of health problems, such as dermatitis, cardiovascular disease, asthma, lung fibrosis and respiratory tract cancer [1]. Although Ni(II) is hazardous, it is frequently used in the manufacturing of alloy steel, batteries, electroplating, electronic circuits, hydrogenated catalysts and military equipment [2,3]. The concentration of Ni(II) discharged into the aquatic environment must follow the regulatory discharge limit. According to the Ministry of Industry (Thailand), the permissible concentration of Ni(II) in industrial wastewater is <1.000 mg/L [4].

In the field of metal separation and purification, the liquid-liquid extraction (LLE) process is widely applied due to its outstanding capability, such as high efficiency, low power consumption and simple operation [5-7]. In general, commercial solvents, e.g., kerosene and toluene used in such a process, are harmful and volatile. Such solvents affect both the environment and one's health, inducing headaches, dizziness and lightheadedness progressing to unconsciousness, seizures and death. Exposure to volatile solvents fosters irritation in the eye, nose and throat [8]. Therefore, global development of extraction processes into green growth has drawn much attention from researchers [9]. Vegetable oils, being biodegradable, economical, inflammable, non-toxic, non-volatile as well as renewable, are considered to be the best alternatives to replace traditional solvents [10,11]. Therefore, the utilization of various green solvents in the extraction of metals needs to be explored.

In Table 1, the extraction of Ni(II) using different extractants and organic solvents via the LLE process is reported. Results achieved are proof of their high efficiency. However, usage of green solvents, except for palm oil, is still found to be quite sparse. To counter such limitations, the application of many green solvents for Ni(II) extraction must be further investigated.

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Table 1. Extraction of Ni(II) via the LLE process

Concentration of Ni(II) (mg/L)	Extractant	Organic solvent	%Extraction	Ref.
5,048.000	VERSATIC10+LIX63+TBP	Petroleum naphtha	99.60	[25]
5,000.000	D2EHPA+LIX63	Palm oil	83.00	[26]
4,360.000	[Bmim][PF_6]	Dithizone	95.00	[27]
2,800.000	LIX63+VERSATIC10+NONYL-4PC	Petroleum naphtha	>90.00	[28]
2,000.000	D2EHPA+CYANEX272	Kerosene	90.00	[29]
1,174.000	LIX984N	Kerosene	93.00	[30]
500.000	D2EHPA+1-Octanol	Palm oil	90.00	[17]
200.000	LIX63+VERSATIC10	Petroleum naphtha	>99.00	[31]
10.000-100.000	D2EHPA+TBP	Palm oil	95.60	[32]
5.000 (±0.300)	D2EHPA+1-Octanol	Rice bran oil	>99.00	This work

In the transfer of metals, from the aqueous phase to the organic phase, extractants have an important role to play. Effective extractants must have characteristics of high selectivity towards targeted metal ions, i.e., chemical and thermal stability, moderate viscosity and low surface tension [12]. For the extraction of metal ions, D2EHPA is duly utilized owing to its high efficiency [13]. D2EHPA is inexpensive and exhibits excellent extraction of various metal ions [14, 15]. For the extraction of Ni(II), D2EHPA is often used by mixing with other extractants. Such mixtures can result in synergistic extraction displaying greater efficiency than when a single extractant is used: synergism ensures the cooperation of all extractants to transport metal ions into the organic phase [16]. For instance, the synergistic green binary system of D2EHPA+1-octanol has been conducted using palm oil as a diluent, demonstrating that up to 90.00% of Ni(II) can be extracted from wastewater [17]. Nevertheless, the use of palm oil is acknowledged to be a major contributor to global warming [18]. In consideration of this, the applicability of other green solvents is necessary and therefore encourages interest in the extraction of Ni(II).

As for the control, design, improvement, operation and optimization of the extraction process, studies regarding chemical reactions and thermodynamics are essential. A better understanding of molecular interactions is required to obtain the best solvent, which can provide optimum distribution in the extraction system [19]. Yu et al. [20] stated that molecular interactions are key issues in the application of extraction for the industry. Greater knowledge, therefore, of extraction mechanisms and interactions of substances is needed for the successful implementation of green solvents [21]. Ni(II) extraction applying D2EHPA+1-octanol at a molecular level has not been studied before and it is important for further development.

Density functional theory (DFT) is one of the most important theoretical methods enabling greater understanding of molecular chemistry [22,23]. Due to their high accuracy, both the Becke three-parameter hybrid (B3LYP) and Lee-Yang-Parr correlation functional method combined with the LANL2DZ effective core potential double zeta basis set have been widely applied for analysis of molecular structures, thermodynamic properties and interactions [24].

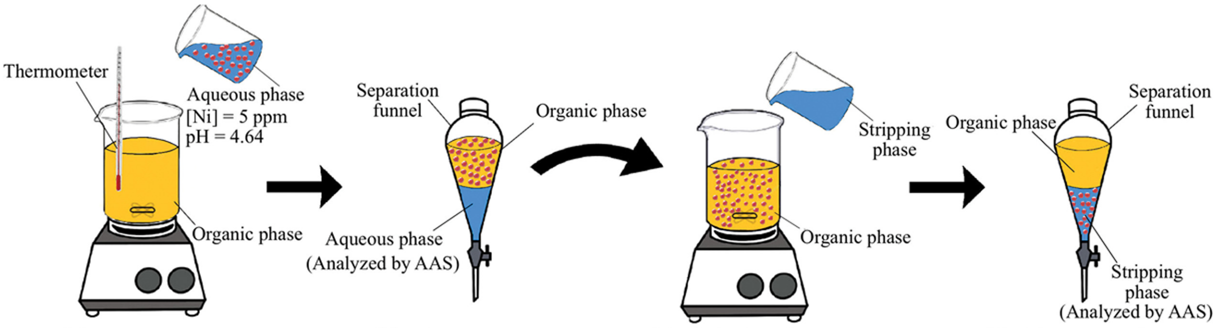
Herein, the extraction and back extraction (stripping) of trace Ni(II) via LLE using green solvents was evaluated. The investigation employed pure and synergistic extractants: D2EHPA and 1-octanol. Response surface methodology (RSM) was also applied to obtain the best results for extraction of Ni(II) using selected green solvents. Supramolecular mechanisms in a binary system between D2EHPA+1-octanol system are first addressed in detail via DFT. However, investigation into the supramolecular mechanisms of these synergistic extractants for Ni(II) extraction is still lacking. Further, calculated infrared vibrational frequencies are provided and compared with the experimental ones. Finally, kinetics, thermodynamics as well as the mechanisms of extraction are examined.

1. Materials and Reagents

To synthesize wastewater during the aqueous phase, a standard solution (1,000 ppm) of Ni(II) was utilized (Panreac, Spain). To adjust the pH of the aqueous phase, the following were used, i.e., NaOH: sodium hydroxide, 99.00% purity (Loba Chemie, India) and HCl: hydrochloric acid, 37.00% purity (Qrec, New Zealand). Extractants employed were D2EHPA: Di-(2-ethylhexyl)phosphoric acid, 95.00% purity (Merck, Germany), and 1-octanol: 99.00% purity (Panrea, Spain). Types of solvents investigated included kerosene (Shell, Thailand), rice bran oil (Thai Edible Oil Co., Ltd., Thailand), soybean oil (Thai Vegetable Oil Public Co., Ltd., Thailand) and sunflower oil obtained from the local market in Thailand (Thanakorn Vegetable Oil Products Co., Ltd., Thailand). Four types of strippant solutions were investigated, i.e., HCl: 37.00% purity (Loba Chemie, India), CH_4N_2S: thiourea, 99.00% purity (Loba Chemie, India), H_2SO_4: sulfuric acid, 98.00% purity (Merck, Germany) and HNO_3: nitric acid, 65.00% purity (Merck, Germany). For all experiments, distilled water was used.

2. Apparatus

The pH of aqueous solutions was determined using a pH meter (EuTech Instruments, pH 700). Both temperature and stirring speed were controlled using a digital hotplate stirrer (Stuart UC152D). The accuracy of temperature was confirmed by mercury thermometer (±274.15 K). Atomic absorption spectrometer (AAS: Varian Model, AA280FS) was employed to determine the concentration of Ni(II). Density and viscosity of materials used and their organic solutions were measured by density meter (DMA, 4,500 M) and viscometer (Brookfield, LVDV2T). Fourier-transform infrared spectroscopy (FTIR: Nicolet, iS5) was utilized to analyze the functional groups of organic solutions, before and after extraction.



(a) Extraction (b) Phase separation (c) Stripping phase (d) Phase separation

Fig. 1. Process of extraction and stripping of Ni(II) using LLE.

3. Procedure

In Fig. 1, synthetic wastewater (aqueous phase) having 5.000 (±0.300) mg/L Ni(II) was prepared by diluting the Ni standard solution (Product Code: 313187) in distilled water. The pH of aqueous solution was 4.64 (±0.01). Koonsang et al. [33] observed that these conditions proved to be most suitable; the experiment was carried out mixing synthetic wastewater along with D2EHPA at volume ratio 1 : 1 and stirring at 400 rpm for 90 min. The operating volume was 20 ml (aqueous phase) and 20 ml (organic phase). The concentration of D2EHPA was studied in the range of 0.30 to 0.90 M. Subsequently, the mixture was transferred to a separation funnel in order to separate the aqueous and organic phases, which were then collected after the phase separation. Aqueous samples where kept to be analyzed by using AAS for Ni(II) determination. In the case of the synergistic solutions, the concentration of 1-octanol was varied from 0.30 to 1.90 M and D2EHPA was varied from 0.3-1.2 M. Thereafter, the organic phase was undertaken to strip Ni(II) using an aqueous strippant. The stirring process was followed using the same procedure as previously : volume ratio 1 : 1, stirring speed at 400 rpm during 90 min [24,33]. Meanwhile, applying FTIR, the organic samples were removed to analyze the functional groups of the organic solutions. Accordingly, the calculated infrared vibrational frequencies were carried out using the DFT method. The experiment was repeated three times.

During the process of LLE, the percentage of extraction and stripping was calculated using Eqs. (1) and (2):

$$\%\ \mathrm{Extraction} = \frac{C_{Ni(II),\ Initial} - C_{Ni(II),\ Final}}{C_{Ni(II),\ Initial}} \times 100 \qquad (1)$$

where $C_{Ni(II), Initial}$ and $C_{Ni(II), Final}$ are the initial and final concentrations of Ni(II) in aqueous solutions, respectively.

$$\%\ \mathrm{Stripping} = \frac{C_{Ni(II),\ stripping}}{C_{Ni(II),\ organic}} \times 100 \qquad (2)$$

where $C_{Ni(II), stripping}$ is the concentration of Ni(II) in the stripping phase after stripping and is the concentration of Ni(II) in the organic phase after extraction.

Both the distribution ratio (D) and synergistic coefficient (S.C.) were determined as follows:

$$D = \frac{C_{Ni(II),\ org.}}{C_{Ni(II),\ aq.}} \qquad (3)$$

$$\mathrm{S.C.} = \frac{D_{mixture}}{D_{1\text{-}octanal} + D_{D2EHPA}} \qquad (4)$$

where $C_{Ni(II), org.}$ and $C_{Ni(II), aq.}$ refer to the concentration of Ni(II) in both organic and aqueous solutions after extraction. D_{D2EHPA}, $D_{1\text{-}octanol}$ and $D_{mixture}$ are the distribution ratios of Ni(II) extraction using D2EHPA, 1-octanol, as well as the mixture of D2EHPA and 1-octanol, respectively.

4. Experimental Design

RSM along with face-central composite design (FCCD): Minitab 18 software trial version: Minitab Inc., State College, PA, USA was applied to find the most suitable solvent having the highest efficiency for extraction of Ni(II). Two parameters involving the concentration of D2EHPA (X_1) and extraction time (X_2) were investigated. As listed in Table 2, each parameter was coded into three levels:

Table 2. FCCD levels for the experimental conditions of two parameters

Parameters	Code	Level		
		−1	0	+1
D2EHPA concentration (M)	X_1	0.30	0.60	0.90
Extraction time (min)	X_2	30	60	90

Table 3. Experimental designs of thirteen runs for Ni(II) extraction

Run	Level		Experimental condition	
	X_1	X_2	X_1	X_2
1	−1	+1	0.30	90
2	0	0	0.60	60
3	0	0	0.60	60
4	+1	−1	0.90	30
5	+1	+1	0.90	90
6	−1	0	0.30	60
7	0	0	0.60	60
8	0	0	0.60	60
9	−1	−1	0.30	30
10	0	−1	0.60	30
11	0	0	0.60	60
12	+1	0	0.90	60
13	0	+1	0.60	90

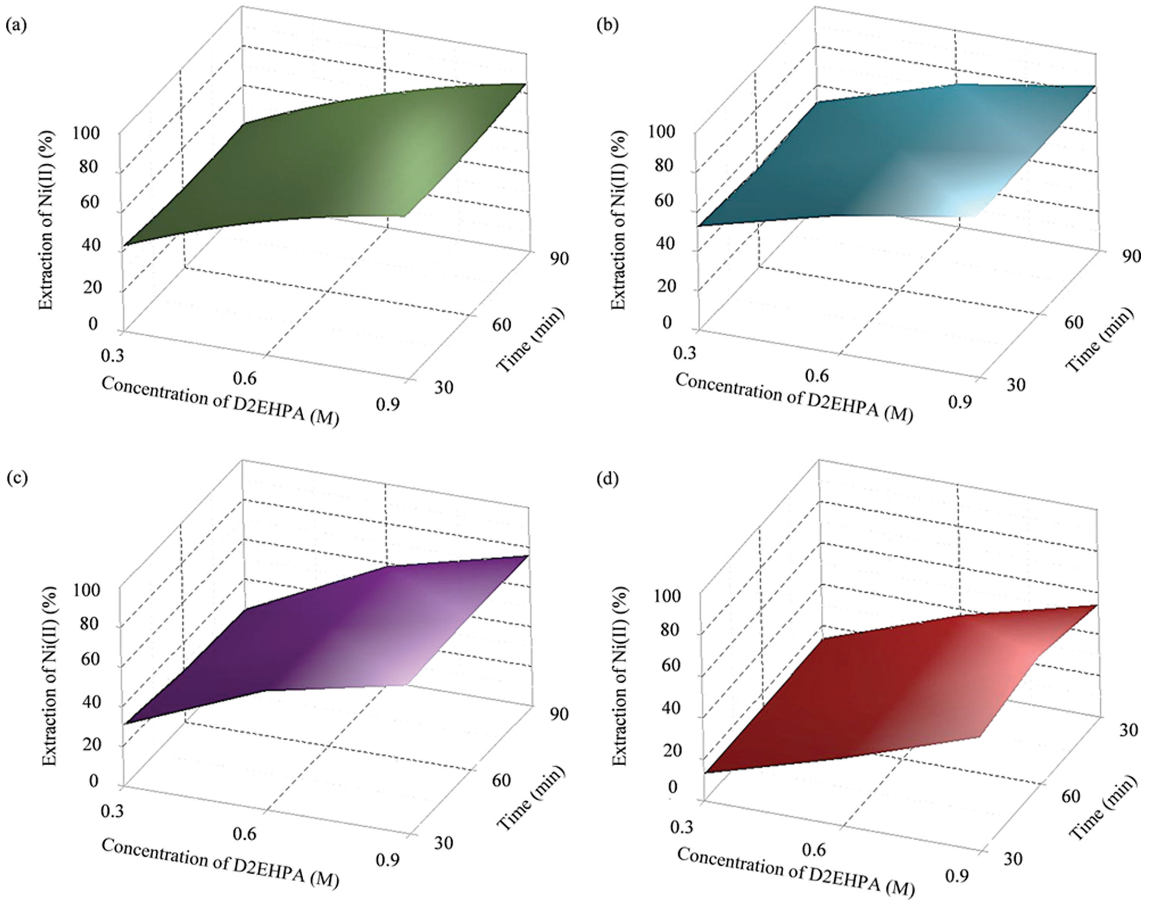


Fig. 2. Percentage of extraction of Ni(II) against extraction time and concentration of D2EHPA dissolved in various solvents: (a) rice bran oil (b) soybean oil (c) sunflower oil and (d) kerosene.

−1, 0 and +1. In Table 3, eight experimental runs with five repetitions, at the center level, are provided in random order. Results of all runs were analyzed via the Minitab program in order to generate a second-order polynomial equation. The general form of the equation is as follows [35]:

$$Y=\beta_0+\sum_{j=1}^{k}\beta_j X_j+\sum_{j=1}^{k}\beta_{jj}X_j^2+\sum\sum_{i<j}\beta_{ij}X_iX_j \quad (5)$$

where Y is the calculated value. β_0, β_j, β_{jj} and β_{ij} are the regression coefficients for intercept, linear, quadratic and interaction coefficients, respectively. X_i and X_j are the coded independent variables, k is the number of independent variables (k=2). i and j are equal to 1 or 2, respectively.

Subsequently, the generated equation was used to predict the percentage of Ni(II) extraction. These values were then compared with the percentage of Ni(II) extraction obtained from the experiments. The validity of the equation was evaluated by the coefficient of determination (R^2). In addition, the variables of the equation were analyzed using analysis of variance (ANOVA). The relevant significance of each source in the equation was identified by F- and P-values: a higher F-value and lower P-value (<0.05) indicates greater significance [36]. Graphical and numerical analyses are also presented. Optimum conditions for the extraction of Ni(II) using various solvents were achieved via these analyses.

It is noted that both individual and composite desirability assess how well a combination of variables satisfies the goals defined for the responses. Individual desirability (d) evaluates how the settings optimize a single response, while composite desirability ($\mathcal{D}$) evaluates how the settings optimize a set of responses overall. Desirability has a range of zero to one, where one represents the ideal case and zero indicates that one or more responses are outside their acceptable limits [71].

The concentration of D2EHPA was carried out in the range of 0.05-1.50 M. At higher concentration, D2EHPA>1.00 M had no effect on the percentage of extraction since extractability reached almost maximum [17,26,60]. Therefore, the range of D2EHPA concentration between 0.30-0.90 M was selected (Fig. 2). As for reaction time, previous works conducted the experiment for 30-120 min. However, when reaction time increased further (t>60 min), extraction percentages were found to be the same [25,32]. Therefore, 30-90 min of operating time was chosen.

5. Computational Calculations

DFT was employed for all calculations in this work; starting geometries were created in cartesian coordinates. For optimization processes, B3LYP was used along with the LANL2DZ effective core potential double zeta basis set [55]. As regards both optimization and frequency calculation processes, the effect of solvents was taken into account using the CPCM solvation model, which added the

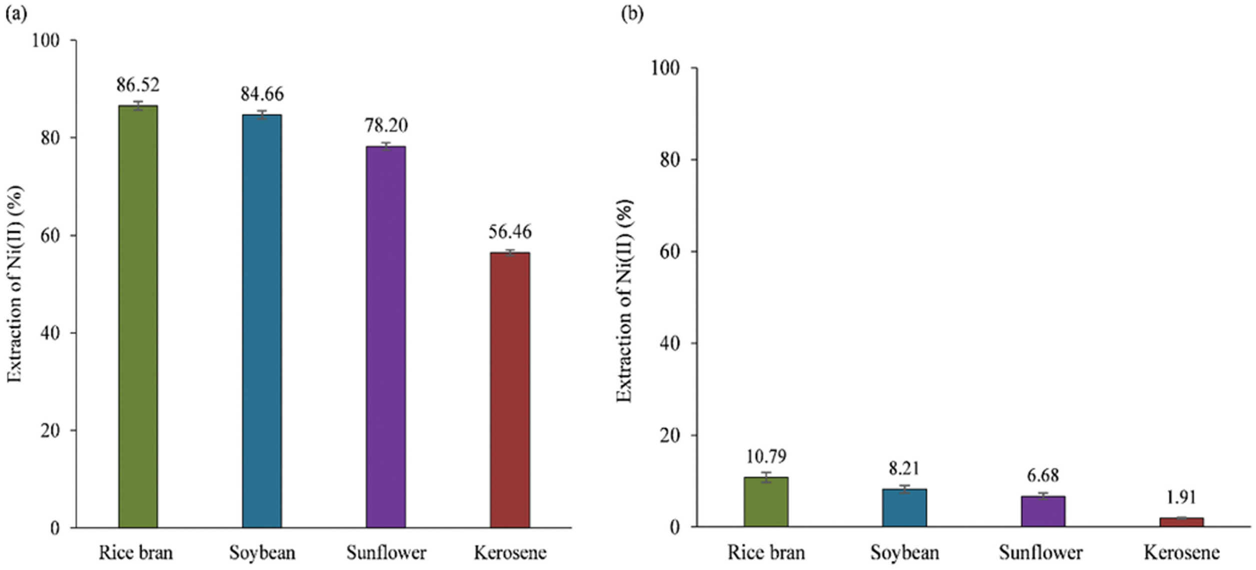


Fig. 3. Percentage of Ni(II) extraction using (a) different solvents under conditions: [D2EHPA]=0.90 M, temperature of extraction=298.15 K and extraction time=90 min, and (b) different pure solvents at 298.15 K and extraction time=90 min.

dielectric constant and refractive index of rice bran oil into the CPCM solvation model. Thermodynamic properties were calculated for each mechanism pathway. Hence, the thermodynamic data obtained from DFT were calculated at molecular-level 298 K and P=0 atm. A series of experiments was carried out for both pure and binary systems as follows [35,36].

RESULTS AND DISCUSSION

1. Effect of Types of Green Solvents for Ni(II) Extraction

Three selected vegetable oils, rice bran, soybean and sunflower oil, were used as alternative green solvents and compared with kerosene. In Fig. 2, the effect of D2EHPA concentration, dissolved in various solvents against time, on the percentage of extraction of Ni(II) is demonstrated. It is seen that the concentration of D2EHPA greatly impacted on the percentage of extraction of Ni(II). Thus, D2EHPA played a significant role in the extraction of Ni(II) for all solvents used. When the concentration of D2EHPA increased from 0.30 to 0.60 M, percentages of Ni(II) extraction increased considerably. In contrast, when the concentration of D2EHPA increased from 0.60 to 0.90 M, extraction percentages increased only slightly, almost reaching equilibrium. As for kerosene, when the D2EHPA concentration increased to 0.90 M, the percentage of extraction continued to increase. On account of the increase in concentration of D2EHPA, a higher number of D2EHPA molecules are seen to arise, increasing the binding of Ni(II) molecules [14,37]. Moreover, for all solvents used, percentages of extraction of Ni(II) increased along with extraction time; longer reaction time allowed the reaction to reach extraction equilibrium. In the case of kerosene, small differences in extraction rate between 60 and 90 min were observed due to extended extraction time, which increased the probability of oxidation, epimerization, and degradation of bioactive compounds. Prolonged extraction time, therefore, may not be appropriate for all kinds of nutraceutical compounds [70].

Considering the efficiency of extraction of Ni(II) using D2EHPA dissolved in various solvents at optimum conditions, 0.90 M D2EHPA and 90 min of extraction time (Fig. 3(a)), the percentages of Ni(II) extraction decreased in the order: rice bran oil>soybean oil>sunflower oil>kerosene. Such an outcome is thought to be the effect of oleic acid in the solvent as the trend of extraction corresponded with the trend of the content of oleic acid in vegetable oil. The content (%) of oleic acid in the rice bran, soybean and sunflower oil proved to be 38.40-42.50%, 18.00-23.00% and 14.00-39.40%, respectively [39-41]. To verify these results, the extraction of Ni(II) using pure solvents was investigated (Fig. 3(b)). Thus, it was found that the trend of extraction using pure solvents was similar to that using D2EHPA dissolved in solvents. The percentages of Ni(II) extraction using pure solvents decreased in the same order: rice bran oil>soybean oil>sunflower oil, since vegetable oils have a variety of fatty acids in their structure, i.e., oleic acid at different quantities.

Table 4 shows the composition of pure rice bran oil, sunflower oil, soybean oil and kerosene. A fatty acid is comprised of carboxylic acid and an aliphatic chain. Fatty acids have an even number of carbon atoms and polar carboxyl groups. When dissolved in water, a hydrogen ion is transferred from the -COOH group to a water molecule [71]. Besides, -COOH can dissociate to hydrogen-bond acceptor protons [34]. Coordination of -COOH with a metal cation usually proceeds via deprotonation of the ligand and formation of a charge neutral complex, allowing hydrogen ions to support D2EHPA for the extraction of Ni(II) [36,37]. The extraction of metal using carboxylic acids has been a subject of much research [9]. Kerosene, in contrast, consists of aliphatic and aromatic hydrocarbons as well as sulfur, and has been reported to have no effect on Ni(II) extraction [42,43]. Halim et al. [9] reported a study whereby oleic acid was used to extract (Cu(II)) having two positive charges, the same as Ni(II), providing the high extraction percentage of 94.00%. However, in the process of extracting Ni(II) with D2EHPA in all

Table 4. The composition of solvents and their standard content

Type of green solvents	Composition (%standard amount)				
	Oleic acid	Linoleic acid	Palmitic acid	Stearic acid	Linolenic acid
Rice bran oil [39]	38.40-42.50	34.40-39.10	15.00-21.50	1.90-2.90	1.10-2.20
Soybean oil [40]	18.00-23.00	51.00-55.00	10.00	4.00	7.00-10.00
Sunflower oil [41]	14.00-39.40	48.30-74.00	5.00-7.60	2.70-6.20	0.00-0.30
	Aliphatics	Mono-aromatics	Di-aromatics	Tri-aromatics	Sulphered
Kerosene [44]	82.00	16.00	1.90	0.00	0.10

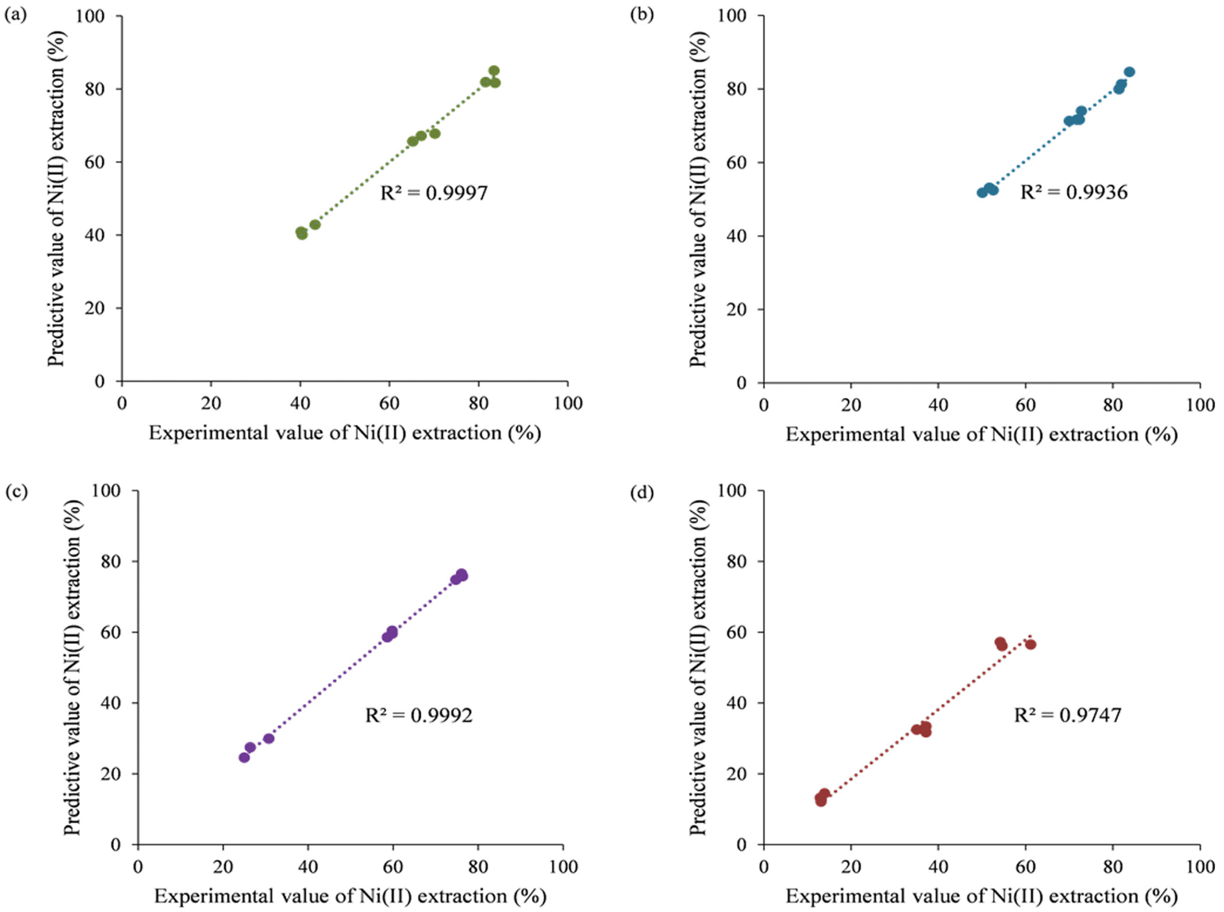


Fig. 4. Validity of the second-order polynomial equations for various solvents: (a) rice bran oil (b) soybean oil (c) sunflower oil and (d) kerosene.

vegetables oils, the structure of D2EHPA, being dimer, resulted in the high steric hindrance of the organophosphorus acids, which do not favor hydrogen bonds and can destabilize the aggregates with all vegetables oils [38].

Second-order polynomial equations for predicting the percentage of extraction for Ni(II) in each solvent are expressed as follows:

Rice bran oil:

$$\%\ \text{Extraction}=16.460+3.753X_1-0.312X_2-0.048X_1X_1+0.002X_2X_2+0.004X_1X_2 \quad (6)$$

Soybean oil:

$$\%\ \text{Extraction}=22.900+3.454X_1-0.054X_2-0.052X_1X_1+0.002X_2X_2+0.003X_1X_2 \quad (7)$$

Sunflower oil:

$$\%\ \text{Extraction}=-12.430+5.259X_1-0.125X_2-0.080X_1X_1-0.002X_2X_2+0.006X_1X_2 \quad (8)$$

Kerosene:

$$\%\ \text{Extraction}=-3.780+1.267X_1+0.037X_2+0.024X_1X_1-0.001X_2X_2-0.001X_1X_2 \quad (9)$$

As shown in Fig. 4, the validity of the second-order polynomial equations was verified by the experimental results. All second-order polynomial equations confirmed R-squared values >0.95, which demonstrated the high accuracy of the equations. In Table 5, ANOVA results are reported. According to the analyses of variance, significance levels proved to be 0.05. D2EHPA concentration

Table 5. ANOVA results for the second-order polynomial equations of Ni(II) extraction via LLE

Source	Degree of freedom	Sum of squares	Mean square	F-value	P-value
Rice bran oil					
Model	**5**	**2,667.160**	**533.430**	**256.940**	**0.000***
Linear	**2**	**2,597.010**	**1,298.510**	**625.460**	**0.000***
X_1	1	2,596.460	2,596.460	1,250.660	0.000*
X_2	1	0.550	0.550	0.260	0.623
Square	**2**	**63.860**	**31.930**	**15.380**	**0.003***
X_1X_1	1	63.850	63.850	30.760	0.001*
X_2X_2	1	8.830	8.830	4.250	0.078
2-Way interaction	**1**	**6.290**	**6.290**	**3.030**	**0.125**
X_1X_2	1	6.290	6.290	3.030	0.125
Error	**7**	**14.530**	**2.080**		
Lack of fit	3	14.530	4.840		
Pure error	4	0.000	0.000		
Total	**12**	**2,681.690**			
Soybean oil					
Model	**5**	**1,524.370**	**304.870**	**392.500**	**0.000***
Linear	**2**	**1,437.490**	**718.750**	**925.340**	**0.000***
X_1	1	1,434.310	1,434.310	1,846.580	0.000*
X_2	1	3.180	3.180	4.090	0.083
Square	**2**	**84.260**	**42.130**	**54.240**	**0.000***
X_1X_1	1	73.960	73.960	95.220	0.000*
X_2X_2	1	0.100	0.100	0.120	0.736
2-Way interaction	**1**	**2.620**	**2.620**	**3.370**	**0.109**
X_1X_2	1	2.620	2.620	3.370	0.111
Error	**7**	**5.440**	**0.780**		
Lack of fit	3	5.440	1.810		
Pure error	4	0.000	0.000		
Total	**12**	**1,529.800**			
Sunflower oil					
Model	**5**	**3,734.940**	**746.990**	**1,841.430**	**0.000***
Linear	**2**	**3,512.820**	**1,756.410**	**4,329.790**	**0.000***
X_1	1	3,507.670	3,507.670	8,646.900	0.000*
X_2	1	5.150	5.150	12.690	0.009*
Square	**2**	**209.630**	**104.810**	**258.380**	**0.000***
X_1X_1	1	176.140	176.140	434.220	0.000*
X_2X_2	1	0.090	0.090	0.210	0.658
2-Way interaction	**1**	**12.500**	**12.500**	**30.810**	**0.001***
X_1X_2	1	12.500	12.500	30.810	0.001*
Error	**7**	**2.840**	**0.410**		
Lack of fit	3	2.840	0.950		
Pure error	4	0.000	0.000		
Total	**12**	**3,737.780**			

was found to be significant for all solvents used (P-value<0.05). However, extraction time was only significant for the use of sunflower oil as solvent (P value<0.05).

In Fig. 5, optimum conditions for the extraction of Ni(II) for each solvent using the response optimizer program are shown. Results indicate the satisfaction of the responses using the values of composite desirability ($\mathscr{D}$). For $\mathscr{D}$ values between 0 and 1, 0 denotes the result is completely dissatisfied, but 1 indicates the result is completely satisfied [47]. It is seen that $\mathscr{D}$ values for all solvents are equal to 1. As summarized in Table 6, under optimum conditions, percentages of extraction and prediction obtained from the experiment were compared. Small differences were found (between 0.80 and 2.50% deviations), confirming the reliability of RSM combined with FCCD [35]. As rice bran oil provided the highest ex-

Table 5. Continued

Source	Degree of freedom	Sum of squares	Mean square	F-value	P-value
		Kerosene			
Model	**5**	**2,839.970**	**567.990**	**77.520**	**0.000***
Linear	**2**	**2,820.380**	**1,410.200**	**192.470**	**0.000***
X_1	1	2,815.800	2,815.800	384.310	0.000*
X_2	1	4.580	4.580	0.620	0.455
Square	**2**	**19.210**	**9.610**	**1.310**	**0.328**
X_1X_1	1	15.940	15.940	2.180	0.184
X_2X_2	1	0.020	0.020	0.000	0.957
2-Way interaction	**1**	**0.380**	**0.380**	**0.050**	**0.827**
X_1X_2	1	0.380	0.380	0.050	0.827
Error	**7**	**51.290**	**7.330**		
Lack of fit	3	51.290	17.100		
Pure error	4	0.000	0.000		
Total	**12**	**2,891.260**			

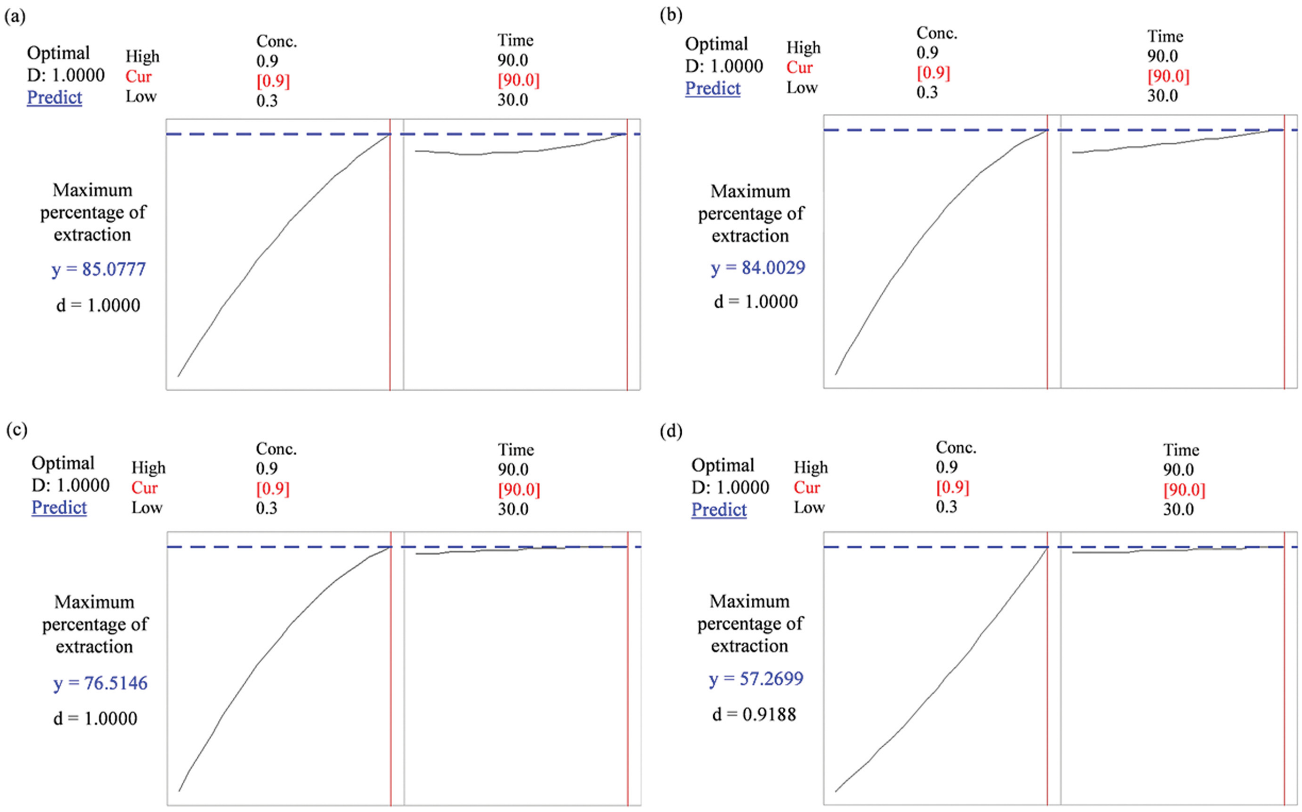


Fig. 5. Plots of response optimization for Ni(II) extraction using various solvents: (a) rice bran oil (b) soybean oil (c) sunflower oil and (d) kerosene.

Table 6. Experimental and predicted percentages of Ni(II) extraction under optimum conditions

Organic solvent	Model desirability	Response optimization		% Extraction		% Deviation
		[D2EHPA] (M)	Extraction time (min)	Experiment	Prediction	
Rice bran oil	1.0000	0.90	90	86.50	85.10	1.70
Soybean oil	1.0000	0.90	90	84.70	84.00	0.80
Sunflower oil	1.0000	0.90	90	78.20	76.30	2.50
Kerosene	0.9188	0.90	90	56.50	57.30	1.40

Table 7. Densities and viscosities of pure organic materials

Material	Density (g/mL)		% Deviation	Viscosity (mPa·s) at T=298.15 K		% Deviation	Viscosity (mPa·s) at T=313.15 K
	Measurement	Literature		Measurement	Literature		Literature
Rice bran	0.9135	0.9160-0.9210 [39]	0.3-0.8	60.6430	59.3000 [42]	2.3	39.8000 [46]
Soybean	0.9117	0.9140-0.9180 [40]	0.3-0.7	39.6030	36.8000 [43]	7.6	23.2000 [46]
Sunflower	0.9131	0.9150-0.9190 [41]	0.2-0.6	48.8740	48.7000 [42]	0.4	32.3000 [46]
Kerosene	0.7862	0.8090 [45]	2.8	1.1650	1.0674 [44]	9.1	0.8800 [44]

Note: % Deviation is calculated by $\frac{\text{Literature value} - \text{Measurement value}}{\text{Literature value}} \times 100$.

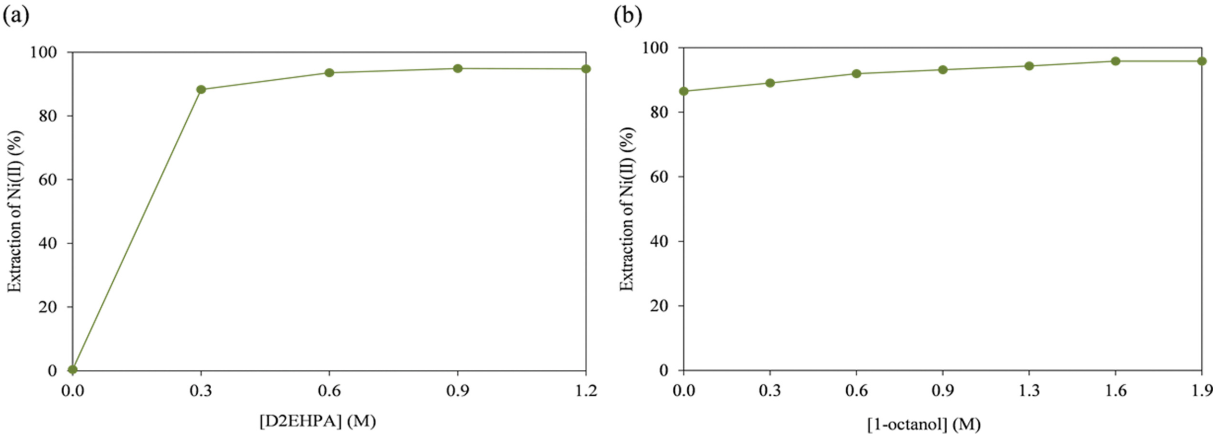


Fig. 6. Percentage of Ni(II) extraction using rice bran oil as solvent, temperature of extraction=298.15 K and extraction time=90 min: (a) using 1.60 M 1-octanol applying various concentrations of D2EHPA as the synergistic extractant, and (b) using 0.90 M D2EHPA applying various concentrations of 1-octanol as the synergistic extractant.

traction of Ni(II), it was used for further investigation.

2. Analysis of Solvents for Ni(II) Extraction

In the process of extraction, the organic phase has a significant role to play. In Table 7, the density and viscosity of the pure organic solvents are shown. It is seen that the densities of green solvents are similar. When the density and polarity of the organic phase is different from the aqueous phase, the mixture of organic and aqueous phase becomes heterogeneous [48]. In fact, density difference around 0.100 g/mL is able to ensure the phase separation of both organic and aqueous phases [46]. The differences in density of such solutions mean that the mixture of these solutions is not homogeneous. When the solution is placed in a separation funnel, separation between the organic and aqueous phase can be clearly observed in a short time, The viscosity of pure organic solvents decreased in the order: rice bran oil>sunflower oil>soybean oil>kerosene, respectively. In the process of metal ion extraction, viscosity can affect molecular diffusion. During stirring, when the viscosity of an organic solution is too high, it can result in crud appearing at the interface of the two phases [51]. Results demonstrate that rice bran oil proved to be the most effective solvent; no crud was observed during the experiment even though it had demonstrated the highest viscosity. It is noted that the extraction behavior of metals is affected by various factors such as solubility, molecular structure, intermolecular links and temperature [50]. In Table 7, the viscosity of the mixed solutions decreases as temperature increases; increasing temperature can improve diffusion and increase extraction efficiency [54].

3. Effect of concentration of the Synergistic Extractant

In Fig. 6(a), percentages of Ni(II) extraction using 1.60 M 1-octanol, applying various concentrations of D2EHPA, are presented. It is observed that when concentration of D2EHPA increased, percentage of extraction increased, reaching a maximum of 94.87% at 0.90 M D2EHPA. When concentration of D2EHPA was higher than 0.90 M, the percentage of extraction remained constant. Therefore, 0.90 M D2EHPA was employed for further study. In Fig. 6(b), percentage of extraction of Ni(II) using 0.90 M D2EHPA mixed with 1-octanol at various concentrations is illustrated, demonstrating that when concentration of 1-octanol increased, percentage of extraction increased. It is noted that 1-octanol helps to destroy the dimer structure of D2EHPA, enhancing the ability of D2EHPA to form a complex species with Ni ions [53]. These outcomes are in accordance with Le Chatelier's principle whereby an increase in reactant concentration results in higher extraction efficiency [54]. The percentage of extraction of Ni(II) reached maximum value when concentration of 1-octanol hit 1.60 M. Therefore, 0.90 M D2EHPA and 1.60 M 1-octanol were applied for further investigation.

4. Effect of the Synergistic Extractant on Ni(II) Extraction

To enhance the efficiency of Ni(II) extraction, synergistic extraction was investigated by adding 1-octanol in D2EHPA dissolved in rice bran oil. Rice bran oil was found to be the best solvent observed from the previous experiment. In Table 8, it is seen that the

Table 8. Distribution ratio and synergistic coefficient of Ni(II) extraction using the mixture of D2EHPA and 1-octanol dissolved in rice bran oil

Extractant	%Extraction	Distribution ratio, D
1.60 M 1-octanol	0.38	0.004
0.90 M D2EHPA	86.52	6.417
0.90 M D2EHPA+1.60 M 1-octanol	94.87	23.013

percentage of Ni(II) extraction significantly increased when the mixture of D2EHPA and 1-octanol was used. Such an outcome is considered to be due to the synergistic effect. To confirm such an effect, the distribution ratio of each extractant was determined via Eq. (3). Calculating the synergistic coefficient (S.C.) using Eq. (4) together with the distribution ratios in Table 8, S.C. was found to be 3.580. Note that an S.C. value >1.000 confirms the synergistic effect of Ni(II) extraction using D2EHPA mixed with 1-octanol [52]. This result probably arose because the polar property of 1-octanol is able to disperse in both aqueous and organic phases, ensuring sufficient contact between the aqueous and organic phases. In addition, 1-octanol aids in the destruction of the dimer structures of D2EHPA for the cation exchange process with Ni(II), thus increasing the extraction of D2EHPA [53].

5. The Supramolecular Mechanism of Ni(II) Extraction via DFT

DFT was employed for all calculations in this work. A series of experiments was carried out for both pure and binary systems whereby the optimized geometrical parameters contributed significantly to identify the structural chemistry of complex formations [72]. The strength of a chemical bond is directly proportional to the amount of energy required to break it. Therefore, bond energy is inversely proportional to bond length; longer bonds have lower bond energies as follows [73].

5-1. Pure D2EHPA as an Extractant

The extraction mechanism of Ni(II) using D2EHPA as an extractant can be written, accordingly [60]:

$$\mathrm{Ni}^{2+}_{aq.}+2(\mathrm{RH})_{2,\,org.}\rightarrow \mathrm{Ni}(\mathrm{R-HR})_{2,\,org.}+2\mathrm{H}^{+}_{aq.} \tag{10}$$

where Ni^{2+} and Ni(R−HR) represent the divalent Ni(II) ions and the complex molecules of Ni(II)-D2EHPA, respectively. H^+ is the proton, the abbreviation aq. represents the aqueous phase and org. represents to the organic phase.

As regards the molecules of D2EHPA, they were considered in the form of dimerization, as shown in Eq. (11) [59-61]:

$$2(\mathrm{RH})_{org.}\rightarrow(\mathrm{RH})_{2,\,org.} \tag{11}$$

where RH and $(RH)_2$ are the monomer and dimer of D2EHPA, respectively.

The optimum extraction mechanism of Ni(II) with pure D2EHPA was carried out. First, a square bi-pyramidal structure of Ni(II)hexahydrate occurred via a coordinated covalent bond between Ni(II); six water molecules reacted with a dimer of D2EHPA, $(RH)_2$. In the aqueous solution, Ni^{2+} combined with water ligands to form the complex Ni(II)hexahydrate. The coordinate covalent bond lengths between Ni^{2+} and the oxygen atoms in the water ligands were found to be approximately 1.81 Å. Subsequently, the dimer of D2EHPA formed via two hydrogen bonds in the position of the phosphoric acid groups for each monomer, reaching hydrogen bond distances of 1.41 and 1.42 Å, respectively. When Ni(II)hexahydrate was added to the D2EHPA dimers in the rice bran oil green solvent, the bond between Ni^{2+} and six water ligands was destroyed: in each D2EHPA dimer, one hydrogen bond was destroyed and one proton of each D2EHPA dimer was lost. Next, Ni^{2+} synchronized with two D2EHPA dimers to form the complex $(Ni(R\text{-}HR)_2)$. Thus, the orientation in the linear molecular structure of $Ni(R\text{-}HR)_2$, having the bond angle of $Dimer_1$-Ni^{2+}-$Dimer_2$ close to 180 degree, seized up. The two coordinated bond lengths between Ni^{2+} and D2EHPA dimers proved to be 1.94 Å. The calculated thermodynamic properties indicated that extraction reaction is endothermic, attaining the standard enthalpy change of 699.12 kJ/mol and the standard Gibb's free energy change of 1,027.37 kJ/mol, respectively. In Fig. 7, the optimized geometries of the reaction mechanism for the extraction of Ni(II), using D2EHPA in the green solvent rice bran oil are depicted.

The results obtained from B3LYP/LANL2DZ calculations were found to be in agreement with previous research. Sulaiman et al. [60], for instance, reported that the dimers of D2EHPA interacted with Ni(II) ions via cationic exchange. Two protons from the O-H group were released into the aqueous phase. Simultaneously, Ni(II) replaced the released protons and bonded with two oxygens of dimers to form a complex molecule in the organic phase.

5-2. The Binary System of Synergistic Extraction: D2EHPA Mixed with 1-Octanol

To enhance the extraction efficiency of Ni(II), synergistic extraction was carried out. Thus, adding 1-octanol to D2EHPA dimers dissolved in rice bran oil, the reaction of the synergistic extraction can be expressed as:

$$(\mathrm{RH})_{2,\,org.}+(\mathrm{R'-OH})_{org.}\rightarrow(\mathrm{RH-HOR'})_{org.}+\mathrm{RH}_{org.} \tag{12}$$

where (R′−OH) denotes the molecule of 1-octanol. (RH−HOR′)

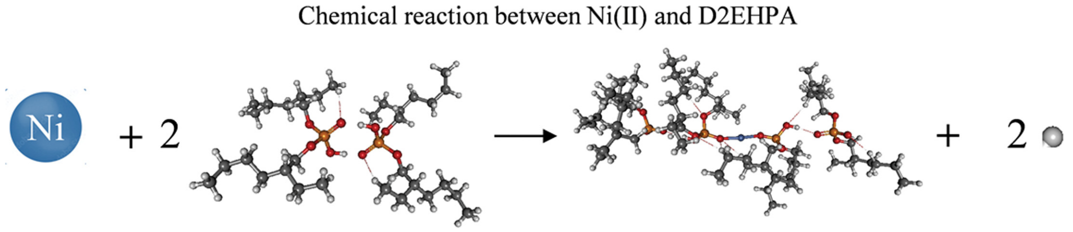


Fig. 7. Schema of B3LYP/LANL2DZ optimum geometry of the reaction mechanism for the extraction of Ni(II), using D2EHPA in the rice bran oil (blue=Ni atom, red=O atoms, orange=P atoms, white=H atoms and black=C).

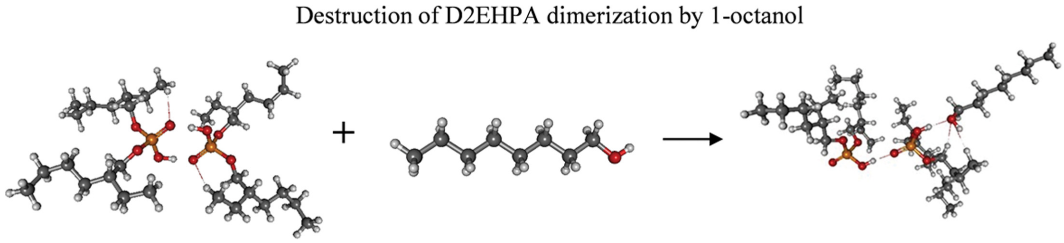


Fig. 8. Schema of B3LYP/LANL2DZ optimum geometries of the binary system between D2EHPA mixed with 1-octanol in rice bran oil (red=O atoms, orange=P atoms, white=H atoms and black=C).

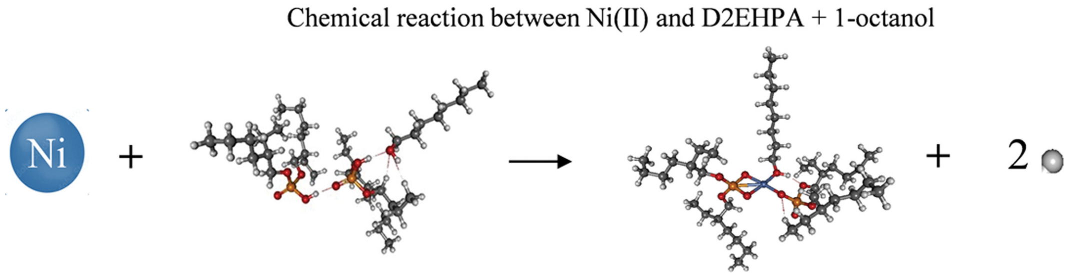


Fig. 9. Schema of B3LYP/LANL2DZ optimum geometry of Ni(II) extraction using the binary system of D2EHPA mixed with 1-octanol in rice bran oil (blue=Ni atom, red=O atoms, orange=P atoms, white=H atoms and black=C).

is the complex molecule of 1-octanol and D2EHPA monomer.

Consequently, the extraction mechanism of Ni(II) using the binary system as extractants is given [60]:

$$\begin{aligned}&\mathrm{Ni}^{2+}_{aq.}+\mathrm{m(R'-OH)}_{org.}+\mathrm{n(RH)}_{2,\,org.}\\&\quad\rightarrow\mathrm{Ni}\bullet(\mathrm{R}_{2n})\bullet(\mathrm{R'-OH})_{m,\,org.}+2\mathrm{n(H^+)}_{aq.}\end{aligned}\tag{13}$$

where $\mathrm{Ni}\bullet(\mathrm{R}_{2n})\bullet(\mathrm{R'–OH})_{m,org.}$ is the complex molecule of Ni(II), D2EHPA and 1-octanol in the organic phase.

To evaluate the supramolecular mechanism of the binary system via the DFT based B3LYP/LANL2DZ level of theory, the mechanism can be carried out in two steps:

Step 1: As illustrated in Fig. 8, the complex $\mathrm{(RH)_2}\bullet\mathrm{(R'–OH)}$ is formed when 1-octanol reacts with the dimer of D2EHPA in the rice bran oil. When adding 1-octanol, the hydrogen bond between the two phosphoric groups in D2EHPA dimer is broken. Thereafter, two new hydrogen bonds with the oxygen atom in the hydroxyl group of 1-octanol are generated. Thus, intermolecular hydrogen bonds play an important role in supramolecular complexing. Hydrogen bond distances in the supramolecular complex are found to be 1.81, 1.82, and 2.70 Å, respectively. This step proved to be an endothermic reaction achieving 312.16 kJ/mol of standard enthalpy change and the standard Gibb's free energy change of 556.35 kJ/mol, respectively.

Step 2: In Fig. 9, Ni(II) extraction with the supramolecular complex $\mathrm{(RH)_2}\bullet\mathrm{(R'–OH)}$ is given. It is seen that the hydrogen bond between the two phosphoric acids of D2EHPA dimer in the supramolecular $\mathrm{(RH)_2}\bullet\mathrm{(R'–OH)}$ are broken, losing two protons. Subsequently, the complex $\mathrm{Ni}\bullet\mathrm{(R_2)}\bullet\mathrm{(R'–OH)}$ is formed. Thus, the coordinated covalent bond lengths between Ni^{2+} and oxygen atom in the ligands were found to be 1.86, 1.89, 1.95 and 1.95 Å, respectively. The two protons as by-products were abstracted. Such a step turned out to be exothermic with the standard enthalpy change of –972.81 kJ/mol and the standard Gibb's free energy change of –1,207.52 kJ/mol, respectively.

6. Stoichiometric Determination

The equilibrium constant of extraction reaction in Eq. (13), K_{eq}, can be defined as:

$$K_{eq}=\frac{[\mathrm{Ni}\bullet(\mathrm{R}_{2n})\bullet(\mathrm{R'-OH})_m][\mathrm{H}^+]^{2n}}{[\mathrm{Ni}^{2+}][(\mathrm{R'-OH})]^m[(\mathrm{RH})_2]^n}\tag{14}$$

where $[\mathrm{Ni}\bullet(\mathrm{R}_{2n})\bullet(\mathrm{R'–OH})_m]$ refers to the concentration of Ni(II) ions in the organic phase and $[\mathrm{Ni}^{2+}]$ refers to the concentration of Ni(II) ions in the aqueous phase. $[(\mathrm{RH})_2]$ refers to the concentration of the dimer of D2EHPA and $[(\mathrm{R'–OH})]$ refers to the concentration of 1-octanol.

In addition, the distribution ratio of extraction of Ni(II) ions (D) can be expressed as:

$$\mathrm{D}=\frac{[\mathrm{Ni}\bullet(\mathrm{R}_{2n})\bullet(\mathrm{R'-OH})_m]}{[\mathrm{Ni}^{2+}]}\tag{15}$$

The relationship between the distribution ratio and the equilibrium constant (K_{eq}) can be described as:

$$K_{eq}=\frac{\mathrm{D}[\mathrm{H}^+]^{2n}}{[(\mathrm{R'-OH})]^m[(\mathrm{RH})_2]^n}\tag{16}$$

where m is obtained by taking the logarithm of Eq. (16) yielding Eq. (17), plotting log D versus $\log[(\mathrm{R'–OH})]$ while fixing the concentration of D2EHPA, $[(\mathrm{RH})_2]$:

$$\log\mathrm{D}=\log\frac{K_{eq}[(\mathrm{RH})_2]^n}{[\mathrm{H}^+]^{2n}}+\mathrm{m}\log[(\mathrm{R'-OH})]\tag{17}$$

where n is determined by taking the logarithm of Eq. (16), obtaining Eq. (18), plotting logD versus $\log[(\mathrm{RH})_2]$ while fixing the con-

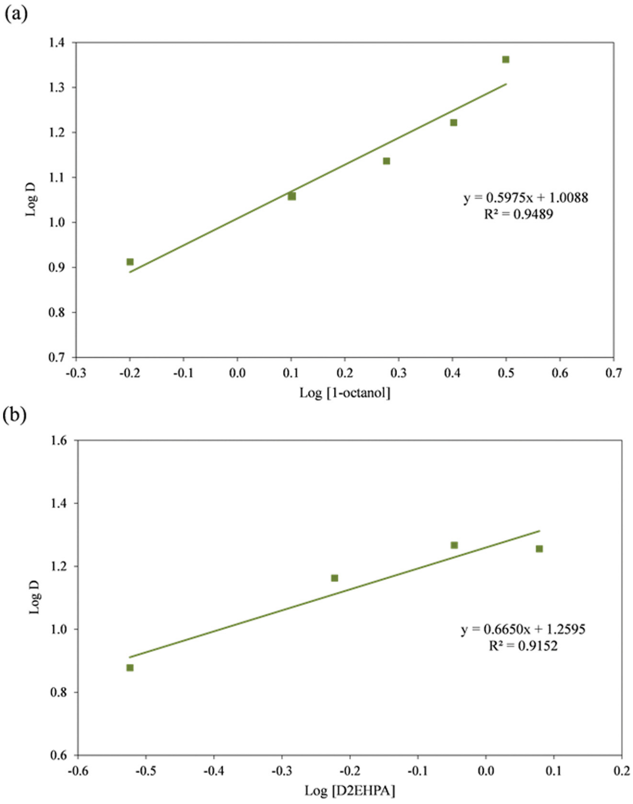


Fig. 10. Log [D] vs log [extractant] of synergistic extraction of Ni(II) in rice bran oil: (a) log [D] vs log [1-octanol], [D2EHPA]= 0.90 M, and (b) log [D] vs log [D2EHPA], [1-octanol]=1.60 M, temperature=313.15 K and extraction time=90 min.

centration of 1-octanol, [(R′–OH)]:

$$\log D=\log\frac{K_{eq}[(R'-OH)]^{m}}{[H^{+}]^{2n}}+n\log[(RH)_2] \tag{18}$$

The stoichiometric number of the extraction reaction was estimated via the slope analysis method [29]. Thus, as seen in Fig. 10(a), the slope from plotting log [D] vs log [1-octanol] and fixing the concentration of D2EHPA at 0.90 M yielded the stoichiometric coefficient (m=0.598), for the complex Ni-D2EHPA$_n$-1-octanol$_m$. Likewise, in Fig. 10(b), plotting log [D] vs log [D2EHPA] and fixing the concentration of 1-octanol at 1.60 M provided the stoichiometric coefficient (n=0.665). These values indicate that approximately one mole of D2EHPA plus 1-octanol took part in the extraction reaction; when rounded up, the values equal 1. Rounding up the stoichiometric coefficients to a value of 1 has been reported in many studies [72,73]. Thus, the experimental stoichiometric numbers were found to be in agreement with DFT calculations. Sulaiman et al. [60] confirmed that both the m molecule of 1-octanol (R′–OH) and n molecule of D2EHPA ((RH)$_2$) equaled one and reacted with one molecule of Ni(II). Hence, Eq. (13) can be expressed as:

$$\begin{aligned}&Ni^{2+}_{aq.}+(R'-OH)_{org.}+(RH)_{2,\,org.}\\&\quad\rightarrow Ni\bullet(R_2)\bullet(R'-OH)_{org.}+2(H^{+})_{aq.}\end{aligned} \tag{19}$$

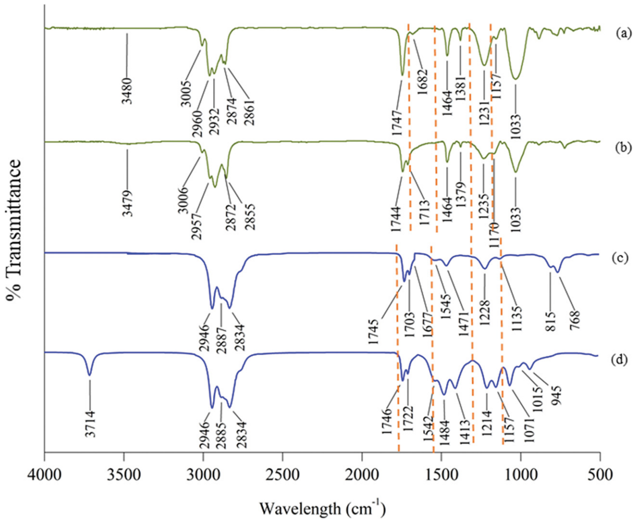


Fig. 11. FTIR spectra of Ni(II) extraction using D2EHPA as extractant. Experimental spectra: (a) before and (b) after extraction; calculated spectra: (c) before and (d) after extraction.

7. FTIR Spectroscopy Analysis

To understand the mechanisms that occurred, the experimental FTIR spectra of pure D2EHPA and binary system of D2EHPA+1-octanol dissolved in rice bran oil, before and after extractions of Ni(II) were studied. In comparison, the calculated infrared vibrational frequencies were carried out using the DFT method.

7-1. Pure D2EHPA as an Extractant

In Fig. 11, the experimental wavenumbers obtained from FTIR spectroscopy as well as the calculated vibrational frequencies of Ni(II) coordinated D2EHPA ligands are observed. Results show that the functional group O-H at 1,682 cm^{-1} (before extraction, Fig. 11(a)) obviously shifted to 1,713 cm^{-1} (after extraction, Fig. 11(b)) [61,62]. The functional group P=O at 1,231 cm^{-1} (before extraction, Fig. 11(a)) slightly shifted to 1,235 cm^{-1} (after extraction, Fig. 11(b)) [59,60].

In comparison, the calculated vibrational frequencies at 1,677 cm^{-1} (before extraction, Fig. 11(c)) shifted to 1,722 cm^{-1} and are attributed to O-H (after extraction, Fig. 11(d)) [67]. The peak of the functional group P=O at 1,228 cm^{-1} (before extraction, Fig. 11(c)) shifted to 1,214 cm^{-1} (after extraction, Fig. 11(d)) [63]. Hence, it was found that the calculated IR spectra were in good agreement with the corresponding experimental spectra. Both shifted peaks indicate that complex Ni(II) coordinated D2EHPA ligands formed [63].

7-2. The Binary System of the Synergistic Extraction between D2EHPA Mixed 1-Octanol

Before extraction:

In Fig. S7, the experimental FTIR results of both the pure and binary system extractants are presented. The peak at 3,345 cm^{-1}, which corresponded to the O-H group of 1-octanol, revealed the dissociation of dimer into monomers after bonding with D2EHPA, indicating that the molecule of 1-octanol destroyed the dimer of D2EHPA [68]. This outcome occurred in the same way as in Fig. 12(c) whereby the peak at 3,882 cm^{-1}, from the O-H group of 1-octanol, appeared after 1-octanol was added to D2EHPA.

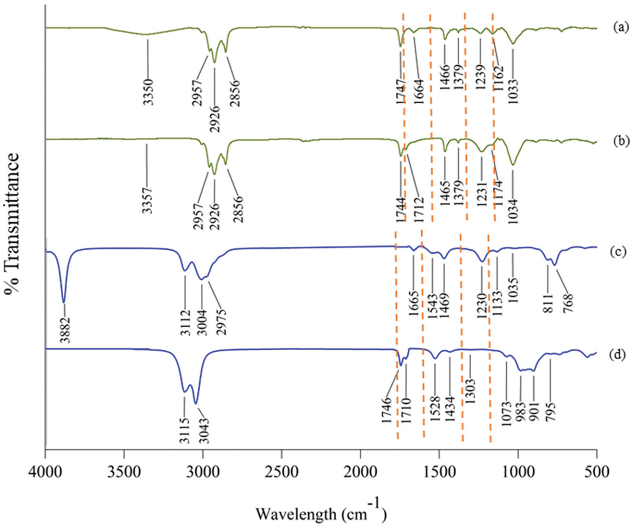


Fig. 12. FTIR spectra of Ni(II) extraction using synergistic extractant (D2EHPA+1-octanol. Experimental spectra: (a) before and (b) after extraction; calculated spectra: (c) before and (d) after extraction.

After extraction:

In Figs. 12(a) and (b), the experiment wavenumbers obtained via FTIR spectroscopy of Ni(II) coordinated D2EHPA+1-octanol ligands are observed, before and after extraction, respectively. Results depict that the functional group O-H at 1,664 cm^{-1} shifted to 1,712 cm^{-1} and the functional group P=O at 1,239 cm^{-1} slightly shifted to 1,231 cm^{-1} [65,66].

On the other hand, in Figs. 12(c) and (d), the calculated vibrational frequencies of the functional group O-H at 1,665 cm^{-1} shifted to 1,710 cm^{-1}. Meanwhile, the functional group P=O at 1,230 cm^{-1} shifted to 1,303 cm^{-1}. Results show that the calculated IR spectra were in good agreement with the corresponding experimental spectra, as shown in Table S2. Thus, it can be implied that both O-H and P=O groups of D2EHPA and D2EHPA+1-octanol interacted with Ni(II) [64]. Results correspond with the general action of acidic extractants, which exchange protons when bonding with metal ions [63].

8. Effect of Temperature on the Synergistic Extraction of Ni(II)

In Fig. 13(a), the effect of temperature on the extraction of Ni(II) is presented. It was found that when temperature increased from 303.15 to 333.15 K, the percentage of extraction increased. The rise in temperature lowered the viscosity of the rice bran oil, enhancing the diffusion of Ni(II) from the aqueous phase to the organic phase. Wongsawa et al. [24], utilizing sunflower oil, reached a similar outcome: namely, when extraction temperature increased, extraction of mercury ions increased. Optimal temperature was observed to be 313.15 K whereby percentage of extraction reached approximately 100%.

9. Effect of Extraction Time on the Synergistic Extraction of Ni(II)

In Fig. 13(b), the percentages of extraction of Ni(II) with respect to extraction time are shown. Thus, it was found that extraction percentage increased as extraction time increased. Within 20 min, percentage of Ni(II) extraction reached maximum (99.70%). Sulaiman et al. [26] reported a similar trend whereby the synergistic extraction of Ni ions using a mixture of chelating and organophosphorus carriers was carried out; within 20 min, extraction reached equilibrium. Therefore, an interval of 20 min was chosen for the extraction of Ni(II) to ensure that extraction reached equilibrium.

10. Effect of Stripping Agents

The type of stripping agent is a significant factor in determining the efficiency of the back extraction of Ni(II) ions from the organic phase. To investigate the most suitable stripping agent for Ni(II) ions, the concentrations of D2EHPA and 1-octanol were fixed at 0.90 M and 1.60 M, respectively. In general, inorganic acids and thiourea can strip metal ions from the organic phase. Thus, for the stripping of Ni(II) ions, this work compared the efficiency of sulfuric acid, nitric acid, hydrochloric acid as well as the mixture of

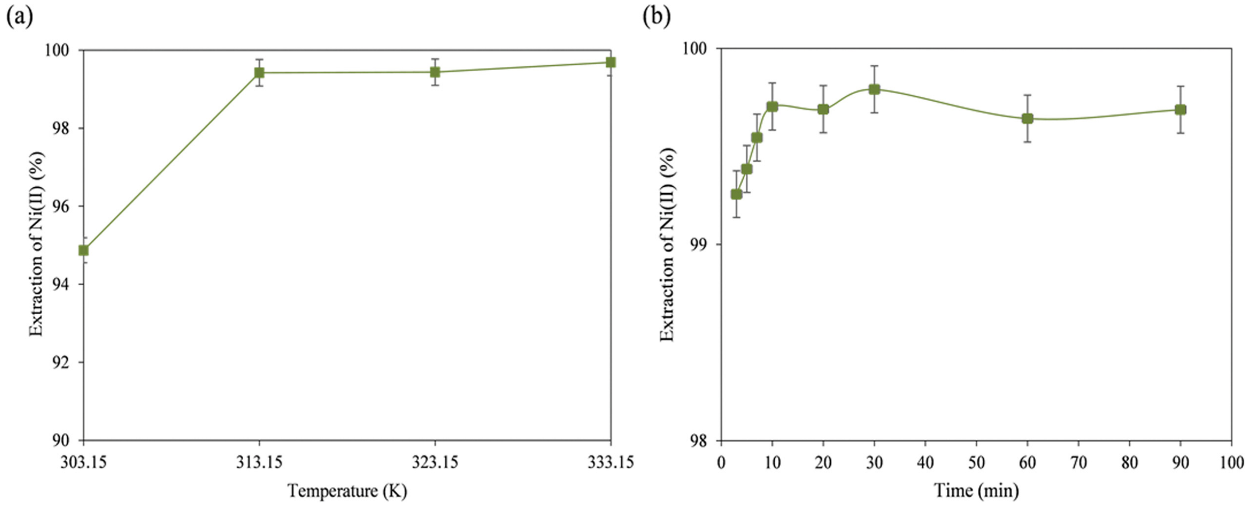


Fig. 13. Percentage of extraction of Ni(II): (a) versus temperature employing rice bran oil as solvent; [D2EHPA]=0.90 M, [1-octanol]=1.60 M and extraction time=90 min, and (b) versus time using rice bran oil as solvent, [D2EHPA]=0.90 M, [1-octanol]=1.60 M and temperature of extraction=313.15 K.

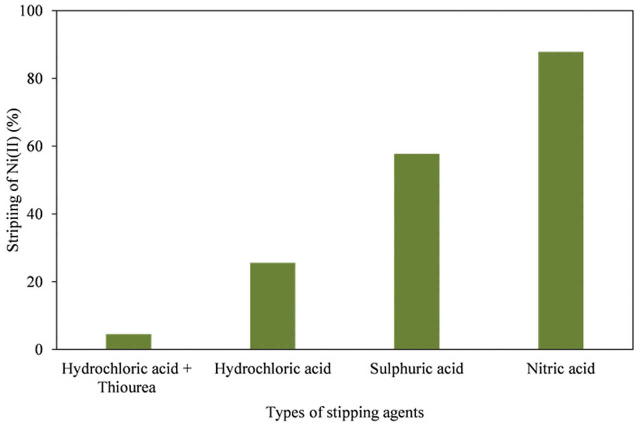


Fig. 14. Effect of stripping agents (1.00 M each) on the stripping of Ni(II): organic solvent=rice bran oil, [D2EHPA]=0.90 M, [1-octanol]=1.60 M, temperature of stripping=298.15 K and stripping time=90 min.

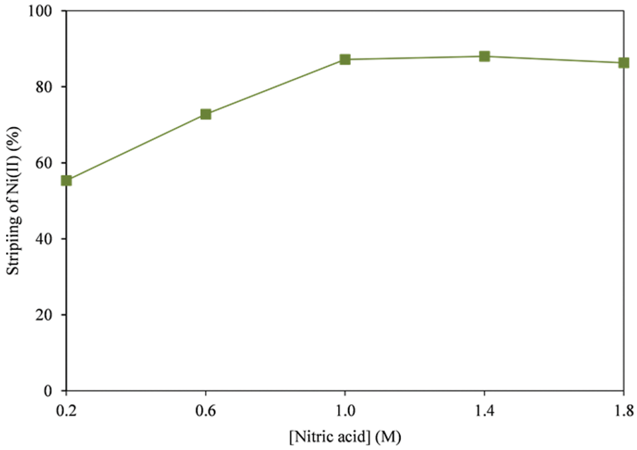


Fig. 15. Effect of concentration of nitric acid on the stripping of Ni(II) ions: organic solvent=rice bran oil, extractant=0.90 M [D2EHPA]=1.60 M [1-octanol], temperature of stripping=298.15 K and stripping time=90 min.

hydrochloric acid and thiourea. As shown in Fig. 14, results found that nitric acid was best for stripping Ni(II). Ni(II) proved to be more soluble in nitric acid than hydrochloric and sulfuric acid; organic solution tends to decompose when using hydrochloric acid, sulfuric acid [69] and thiourea as stripping solution [54], causing the efficiency of stripping to reduce. Therefore, nitric acid was recommended for the stripping of Ni(II).

11. Effect of Stripping Concentration

By varying the concentration of nitric acid from 0.20 to 1.80 M, the effect of stripping concentration was investigated. In Fig. 15, results are depicted. It is seen that when the concentration of nitric acid is in the range: 0.20-1.00 M, stripping percentage of Ni(II) ions linearly increased. After that, the percentage of stripping of Ni(II) ions remained constant. Maximum percentage of stripping of Ni(II) ions was found to be 88.00% at 1.00 M of nitric acid.

12. Stripping Mechanism via DFT Optimization

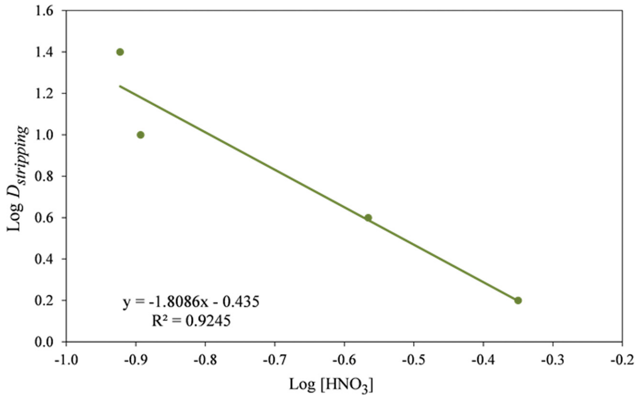


Fig. 16. Log [HNO_3] vs log $D_{stripping}$ of stripping of Ni(II): green solvent=rice bran oil, extractant=0.90 M [D2EHPA]+1.60 M [1-octanol], temperature of stripping=298.15 K and stripping time=90 min.

The reaction of stripping of Ni(II) using nitric acid from previous research has been expressed as [17]:

$$\mathrm{Ni}\cdot(\mathrm{R}_2)\cdot(\mathrm{R'-OH})_{org.}+2\mathrm{HNO}_{3\ aq.}$$
$$\rightarrow \mathrm{Ni(NO_3)}_{2,\ aq.}+\mathrm{RH-HOR'}_{org.}+\mathrm{RH}_{org.} \tag{20}$$

where $Ni(NO_3)_2$ denotes the Ni(II)-nitrate complex, resulting from the stripping reaction.

The equilibrium constant of stripping ($K_{eq,\,stripping}$) can be defined as:

$$K_{eq,\ stripping}=\frac{[\mathrm{Ni(NO_3)_2}][\mathrm{RH-HOR'}][\mathrm{RH}]}{[\mathrm{Ni}\bullet(\mathrm{R}_2)\bullet(\mathrm{R'-OH})][\mathrm{HNO_3}]^2} \tag{21}$$

In addition, the distribution ratio of stripping ($D_{stripping}$) can be described as:

$$D_{stripping}=\frac{[\mathrm{Ni(NO_3)_2}]}{[\mathrm{Ni}\bullet(\mathrm{R}_2)\bullet(\mathrm{R'-OH})]} \tag{22}$$

The relationship between the distribution ratio and the equilibrium constant of stripping becomes:

$$K_{eq,\ stripping}=\frac{D_{stripping}[\mathrm{RH-HOR'}][\mathrm{RH}]}{[\mathrm{HNO_3}]^2} \tag{23}$$

Taking the logarithmic of Eq. (23) obtains:

$$\log D_{stripping}=2\log[\mathrm{HNO_3}]+\log\frac{K_{eq,\ stripping}}{[\mathrm{RH-HOR'}][\mathrm{RH}]} \tag{24}$$

The stoichiometric coefficient can be determined by plotting Log $D_{stripping}$ versus Log [HNO_3] [17], as shown in Fig. 16.

In Fig. 16, the slope of plotting $D_{stripping}$ versus Log [HNO_3] yielded the stoichiometric coefficient (1.809), suggesting that one mole of Ni • (R_2) • (R′–OH) reacts with two moles of nitric acid. Sulaiman et al. [17] confirmed such a result. In Fig. 17, DFT calculations reach the same outcome.

In Fig. 17, DFT along with B3LYP/LANL2DZ level of theory was conducted to examine the stripping mechanism. Thus, it was found that nitric acid donated protons to the D2EHPA ligands and combined with Ni(II), resulting in the breaking of covalent bonds in the complex molecule between Ni(II) and the ligands of

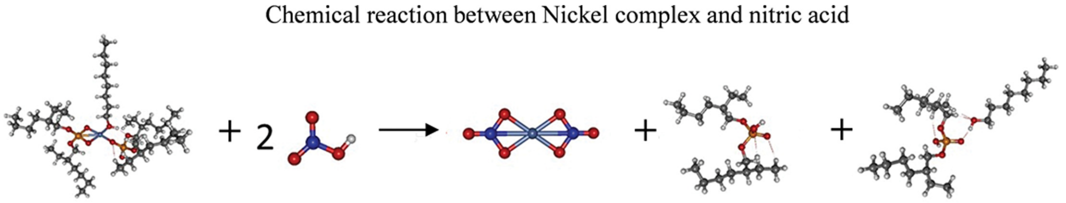


Fig. 17. Optimum stripping reaction of Ni(II) via B3LYP/LANL2DZ of nitric acid (blue=N atom, red=O atoms, orange=P atoms, white=H atoms).

Table 9. Integral plots and rate constants for zero, first and second-order reactions for Ni(II) extraction using the mixture of D2EHPA and 1-octanol dissolved in rice bran oil [24]

Reaction order	Rate law	Unit of k_{Ni}	Integral plot	Rate constant (k)		R-squared	
				Extraction	Stripping	Extraction	Stripping
n=0	$-r_{Ni}=k_{Ni}$	$\{k_{Ni}\}$=mol/L·s	$C_{Ni,\,t}$ and t	0.003	0.037	0.992	0.899
n=1	$-r_{Ni}=k_{Ni}C_{Ni}$	$\{k_{Ni}\}=s^{-1}$	$\mathrm{Ln}\frac{C_{Ni,\,Initial}}{C_{Ni,\,t}}$ and t	0.134	0.038	0.993	0.957
n=2	$-r_{Ni}=k_{Ni}C_{Ni}^2$	$\{k_{Ni}\}$=L/mol·s	$\frac{1}{C_{Ni,\,t}}$ and t	5.992	0.036	0.963	0.914

D2EHPA and 1-octanol. Consequently, the oxygen atom of two moles of nitric acid formed a new connection with Ni(II), yielding the products: $Ni(NO_3)_2$, RH and RH-HOR′. The coordinated bond distances between Ni^{2+} and oxygen atom of the nitric ligands proved to be 1.94 Å. The mechanism in this step was an endothermic process having the standard enthalpy change of 22.46 kJ/mol and the standard Gibb's free energy change of 18.36 kJ/mol, respectively.

13. Kinetics of the Synergistic Extraction and Stripping of Ni(II)

The reaction orders of extraction and stripping of Ni(II) were ascertained via the integral plots of Ni(II) concentration. Reaction rate constants were calculated via the slope analysis method. All values can be seen in Table 9. In Fig. 18(a), the highest R-squared (R^2) value of the reaction order and rate constant for Ni(II) extraction, using the synergistic extraction, was found to be of first-order: 0.1338 s^{-1}. In Figs. S1-S3, the rate constants for both zero-order and second-order proved to be 0.0032 and 5.9918, respectively. Regarding HNO_3 used in the stripping system, its graphs of zero, first and second-order reactions were determined and also displayed in Figs. S4-S6. In Fig. 18(b), the highest R-squared (R^2) value of the reaction order and rate constant for Ni(II) stripping, using HNO_3, was found to be of first-order: 0.0383. The rate constants for Ni(II) stripping of zero-order and second-order were found to be 0.0365 and 0.0363, respectively. Regarding rice bran oil used in the extraction system, its graphs of zero, first and second-order reactions were evaluated and displayed, as in the Supplementary material.

In general, first-order reaction means that the rate of reaction depends on concentration of only one reactant. In this work, the reaction rate of Ni(II) extraction is based on the concentration of one extractant because the concentration of Ni(II) is fixed at 5.000 mg/L for all studies; Ni(II) stripping reaction depends on strippant concentration only. In this work, the reaction rate of Ni(II) stripping is based on the concentration of HNO_3. In Table 9, results listing zero, one and second-order reactions as well as results for

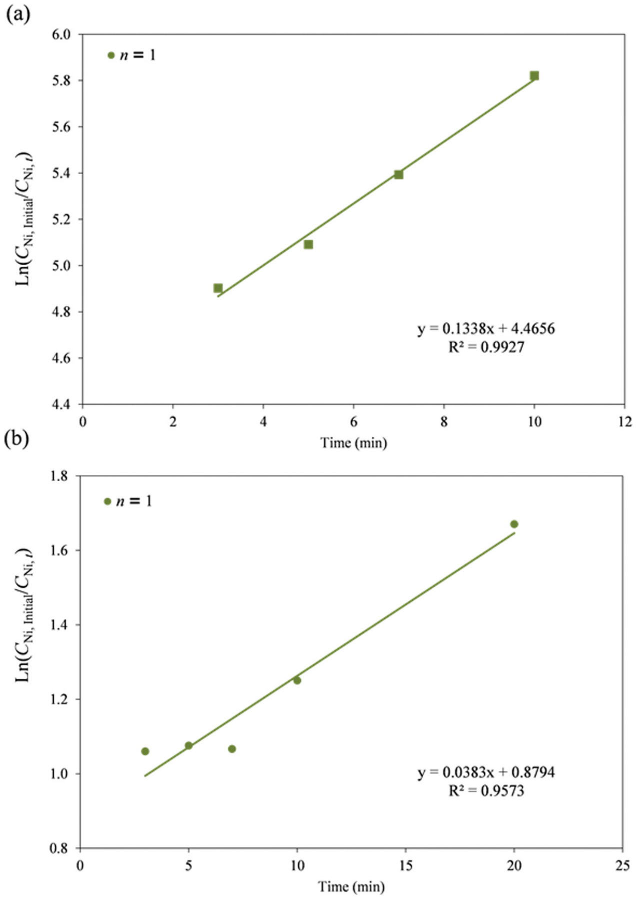


Fig. 18. First-order reaction and rate constants: (a) synergistic extraction of Ni(II), organic solvent=rice bran oil, extractant=0.90 M [D2EHPA]+1.60 M [1-octanol], temperature of extraction=313.15 K and extraction time=90 min, and (b) stripping of Ni(II), strippant=1.00 M [HNO_3], temperature of stripping=298.15 K and stripping time=90 min.

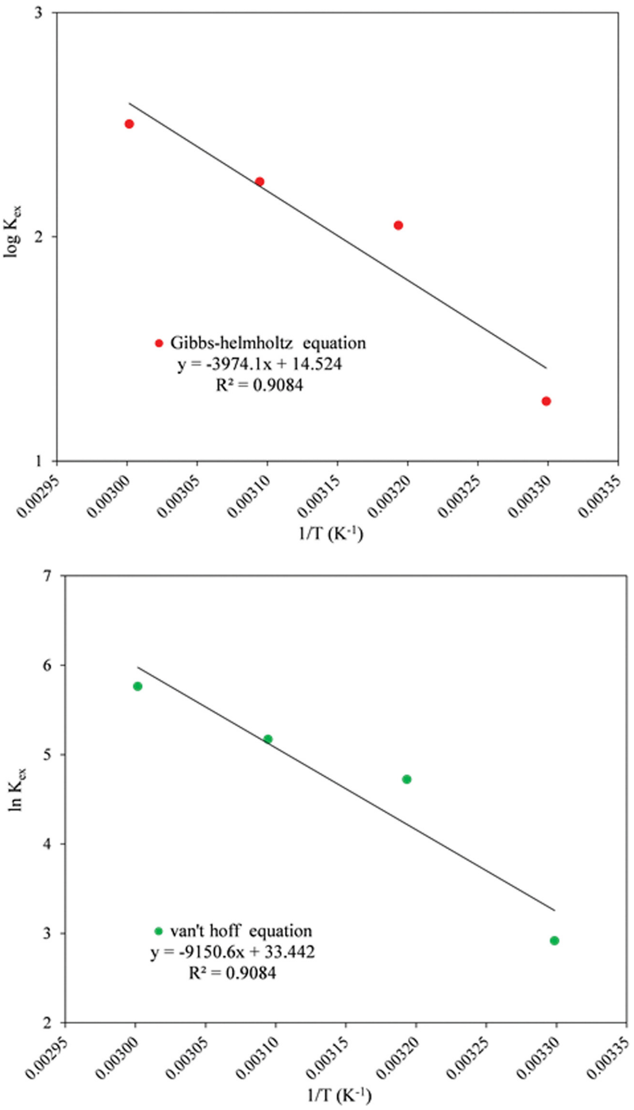


Fig. 19. Linear plots following the Gibbs-Helmholtz and van't Hoff equations using the experimental data: solvent=rice bran oil, the extractant=0.90 M [D2EHPA]+1.60 M [1-octanol], and extraction time=90 min.

extraction and stripping are found.

14. Thermodynamics of the Synergistic Extraction of Ni(II)

The values of ΔH^o, ΔS^o and ΔG^o for the extraction reaction of Ni(II) in the temperature range of 303.15-333.15 K can be determined, using the equations of Gibbs-Helmholtz and van't Hoff, as follows [24]:

Table 10. Values of K_{eq} in the temperature range 303.150 to 333.150 K

T (K)	303.150	313.150	323.150	333.150
K_{eq}	18.500	112.520	176.150	318.790

Gibbs-Helmholtz equation:

$$\log K_{eq} = -\frac{\Delta H^o}{2.303RT} + \frac{\Delta S^o}{2.303RT} \tag{25}$$

$$\Delta G^o = -2.303RT\log K_{eq} \tag{26}$$

van't Hoff equation:

$$\log K_{eq} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{RT} \tag{27}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{28}$$

As shown in Fig. 19, Gibbs-Helmholtz and van't Hoff equations, ΔH^o and ΔS^o of Ni(II) extraction were obtained via the plots of log K_{eq} as in Eq. (14) versus 1/T, using data in Table 10. In Table 11, all values obtained are listed. Results of both the Gibbs-Helmholtz and van't Hoff equations were found to be similar. The positive ΔH^o value indicated that the reaction of the synergistic extraction was endothermic and required energy during the process of extraction. The positive value of ΔS^o indicated that the relationship between Ni(II) and D2EHPA was slightly abnormal during the Ni(II) extraction process. Furthermore, the negative ΔG^o value reveals that Ni(II) extraction reaction can occur naturally at any temperature, ranging from 303.15 to 333.15 K [70].

CONCLUSION

It is evident that vegetable oils, rice bran, soybean and sunflower oil, are seen to be promising green solvents. Extraction of Ni(II) using D2EHPA dissolved in all green solvents proved to be higher than when dissolved in kerosene. Maximum percentage of Ni(II) extraction (99.70%) was obtained when a mixture of D2EHPA (0.90 M) and 1-octanol (1.60 M) was used as the synergistic extractant dissolved in rice bran oil at pH of 4.64, extraction temperature of 313.15 K, and extraction time of 90 min. Moreover, the extraction mechanism of Ni(II) using the synergistic extractant D2EHPA+1-octanol was found to involve cationic exchange between hydrogen and Ni(II) ions. As for stripping, the optimum stripping of Ni(II), 88.00%, was observed when 1.00 M HNO_3 was used as stripping solution. Both extraction and stripping reactions were of first-order. Considering the effectiveness of the green solvents investigated in this work, rice bran oil is highly recommended as a

Table 11. Thermodynamic parameters of synergistic extraction using rice bran oil as solvent, [D2EHPA]=0.90 M, [1-octanol]=1.60 M, and extraction time=90 min

Equation	ΔH^o (kJ/mol)	ΔS^o (kJ/mol·K)	ΔG^o (kJ/mol)			
			Temperature (K)			
			303.150	313.150	323.150	333.150
Gibbs-Helmholtz	72.759	0.268	−7.355	−13.401	−13.896	−15.970
van't Hoff	72.757	0.263	−6.865	−9.491	−12.1187	−14.744

valid alternative for further Ni(II) extraction. Besides, DFT optimization indicated that intermolecular hydrogen bonds play an important role in the supramolecular complexing of the synergistic extraction between D2EHPA and blended 1-octanol.

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The protection of intellectual property has been cautiously considered and rigorously follow the regulations of our institutions. Hence, there are no problems as regards publication and public time.

RESEARCH ETHICS

The sources of all references, figures and tables, as shown in the manuscript are listed below. There are no copies of information and figures. In addition, the funding organizations and the supporting laboratory have been acknowledged in the sections of Acknowledgments and Funding.

AUTHORSHIP

The authors as presented in the manuscript understand and fulfill the ICMJE criteria. They have created and carefully checked the manuscript, figures and tables by themselves. The order of their names has been already approved by them.

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Watcharapong Ampronpong did research (searching information, conducting experiment and analyzing experimental results). Sira Suren and Vanee Mohdee checked the results as well as proofread the scientific content. Kreangkrai Maneeintr and Tatchanok Prapasawat were project administrators and supported analytical instruments. Sanong Ekgasit also supported analytical support. Wikorn Punyain supported theoretical calculations, writing review and editing. Dr. Ura Pancharoen undertook overall supervision of the review.

DECLARATION OF COMPETING INTEREST

The authors declare no known competing financial interests or personal relationships that can influence the work reported in this manuscript.

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Experimental and DFT investigations on the supramolecular mechanism of Ni(II) extraction via D2EHPA blended 1-octanol extractant: Application of vegetable oils as diluents

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1. Reaction Orders and Rate Constants of Ni(II) Extraction by D2EHPA+1-Octanol Extractants and Stripping by HNO_3

According to each organic solvents used in the systems of Ni(II) extraction, its integral plots of zero, first and second-order reactions are presented in Figs. S1-S3 and Figs. S4-S6 for D2EHPA+1-octanol extractants and stripping by HNO_3, respectively.

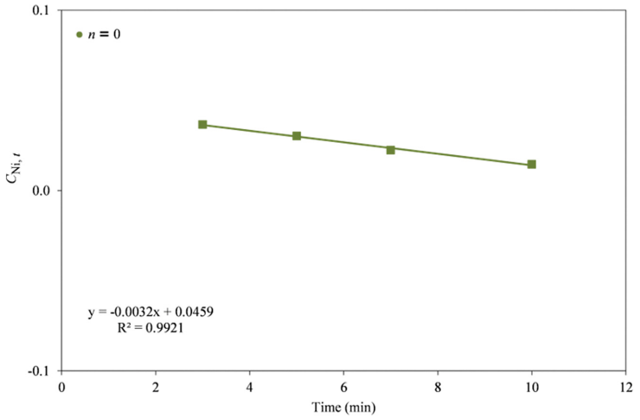

Fig. S1. Zero-order reaction and rate constants of synergistic extraction of Ni(II), organic solvent=rice bran oil, extractant=0.90 M [D2EHPA]+1.60 M [1-octanol], temperature of extraction=313.15 K and extraction time=90 min.

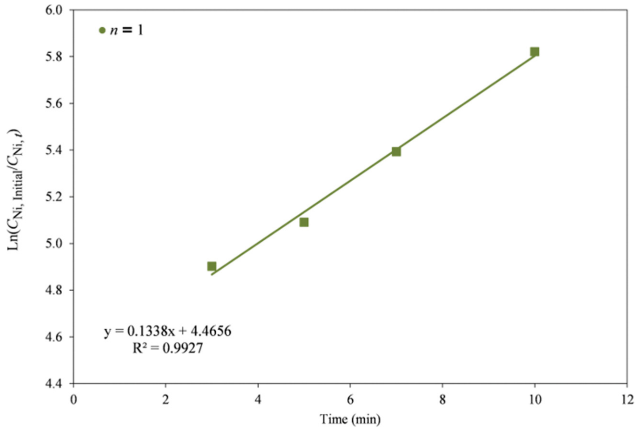

Fig. S2. First-order reaction and rate constants of synergistic extraction of Ni(II), organic solvent=rice bran oil, extractant=0.90 M [D2EHPA]+1.60 M [1-octanol], temperature of extraction=313.15 K and extraction time=90 min.

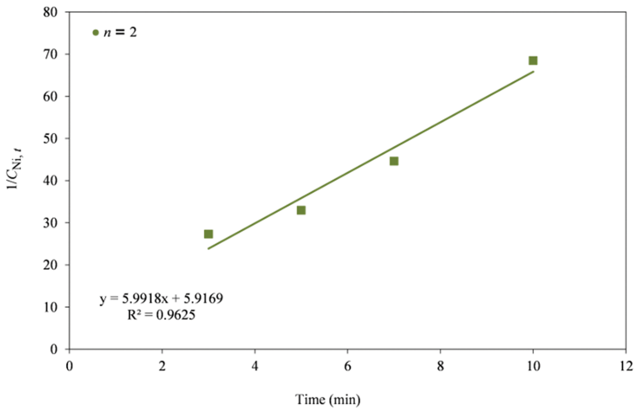

Fig. S3. Second-order reaction and rate constants of synergistic extraction of Ni(II), organic solvent=rice bran oil, extractant=0.90 M [D2EHPA]+1.60 M [1-octanol], temperature of extraction=313.15 K and extraction time=90 min.

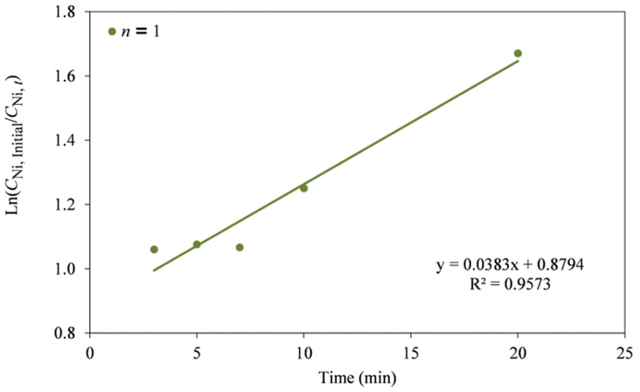

Fig. S5. Frist-order reaction and rate constant of stripping of Ni(II): strippant=1.00 M [HNO_3], temperature of stripping=298.15 K and stripping time=90 min.

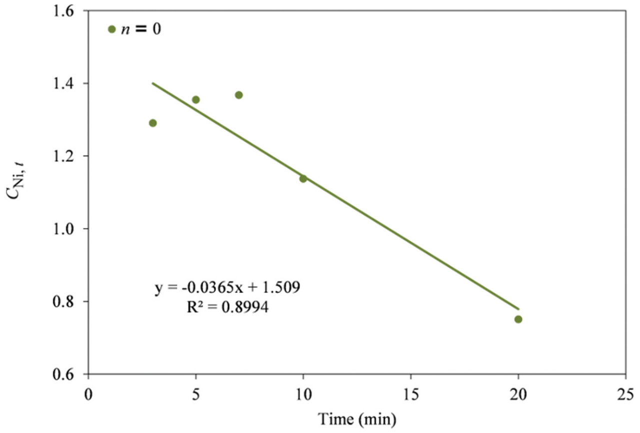

Fig. S4. Zero-order reaction and rate constant of stripping of Ni(II): strippant=1.00 M [HNO_3], temperature of stripping=298.15 K and stripping time=90 min.

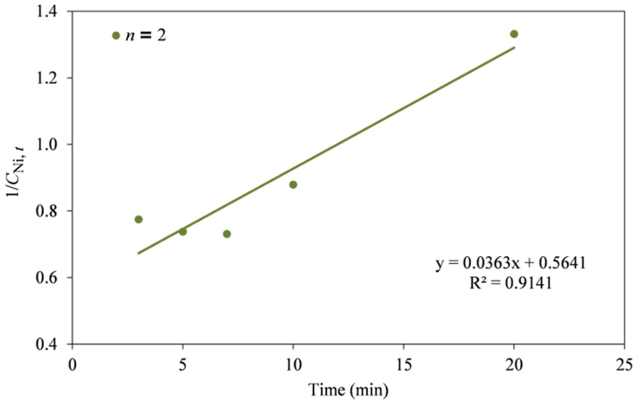

Fig. S6. Second-order reaction and rate constant of stripping of Ni(II): strippant=1.00 M [HNO_3], temperature of stripping=298.15 K and stripping time=90 min.

Table S1. Discharged concentration of Ni(II) in each source.

Source	Concentration of Ni(II) (mg/L)	Reference
Wastewater treatment plant in Tuscaloosa, Alabama.	5.400	[1]
Waste Water on Bentonite Clay from Jeddah, Saudi Arabia	5.000-30.000	[2]
Electroplating Industrial Liquid Waste	2.140	[3]
Raw and treated waste water from 20 industrial e.g.		
- iron and steel manufacturing	1.700-7.800	[4]
- battery manufacturing	6.700	
- nonferrous metal manufacturing	14.000	
- porcelain enameling	19.000	
- raw wastewater were inorganic chemicals manufacturing	20.000	

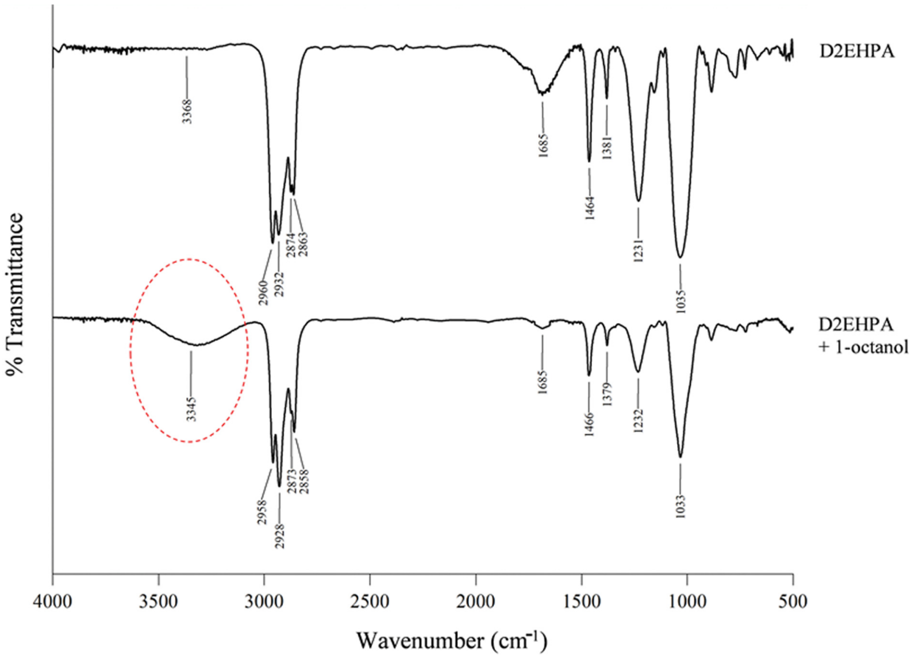

Fig. S7. FTIR spectra of D2EHPA as well as the mixture of D2EHPA and 1-octanol before Ni(II) extraction.

Table S2. FTIR spectroscopy from the calculated IR spectra and experimental spectra of pure D2EHPA and binary system

System	Functional group of O-H (cm^{-1})		Functional group of P=O (cm^{-1})	
	Before extraction	After extraction	Before extraction	After extraction
Pure D2EHPA				
- Experimental	1,682	1,713	1,231	1,235
- Calculated from DFT	1,677	1,722	1,288	1,214
D2EHPA+1-octanol				
- Experimental	1,664	1,712	1,239	1,231
- Calculated from DFT	1,665	1,710	1,230	1,303

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