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Solvent Extraction of Zinc from a Bioleaching Solution by Modification of D2EHPA: Optimization and Thermodynamic Studies

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Abstract

In this work, zinc extraction from an industrial leach solution was investigated by saponified di (2-ethylhexyl) phosphoric acid (D2EHPA). The solution obtained was from a bioleaching process of a low-grade lead-zinc sulfide ore that contained 50 g/L of zinc and 6.3 g/L of iron. The selective and high Zn(II) extraction yield were obtained by modification of D2EHPA in a proposed two-step process. Firstly, a significant amount of iron (87%) was removed as sodium-jarosite via precipitation from the pregnant leaching solution (PLS) prior to zinc extraction, and secondly, the effective parameters involved in zinc extraction including the contact time, saponification degree, type of saponifier, stirring speed, pH, temperature, D2EHPA concentration, and phase ratio (A:O) were investigated. The results obtained showed that 98.4% of zinc could be extracted under the optimum conditions, i.e. 20% D2EHPA, 15% saponification degree, 650 rpm, pH 2, and an A:O ratio of 1:1 at the ambient temperature (25 ± 2 °C) during 90 s; it was 25% higher than using non-saponified D2EHPA under the same conditions. Moreover, while one theoretical step was required for the complete extraction of zinc by saponified D2EHPA, the required number of steps using D2EHPA was about three. Therefore, the advantages of the process would be two-fold: reducing the number of extraction stages and no need for neutralizing the raffinate in every extraction stage.

1. Introduction

The conventional zinc processing method in the past decades consists of roasting, leaching, and electro-winning (RLE). However, various methods including solvent extraction (SX), ion exchange (IX), and chemical precipitation have been recently used for the purification of zinc from the leach solutions. Among these methods, the SX process is an effective technique used to extract various metals from the pregnant leaching solution (PLS) [1-5].

The high level of impurities leads to hydrogen uptake, zinc re-dissolution, and a lower efficiency during the subsequent electro-winning stage; therefore, purification would be crucial for the production of pure zinc [6]. The major impurities in the zinc solution consist of Fe, Ca, Cd, Mn, Co, and Ni, and the type of extractant used in the SX

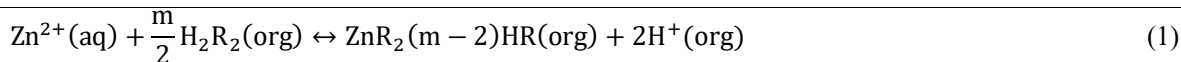
process entirely depends on the contaminants [7, 8].

Various extractants such as DEHPA and Ionquest 290 [9], di(2-ethylhexyl)phosphoric acid (D2EHPA) [10], mixture of Mextral V10 and Mextral 622H [11], HPMBP [12], β -diketone [13], ionic liquids [14], Aliquat 336-S [15], β -diketone, and Cyanex 923 or Lix 84I [16], Cyanex 272 [17], hydrophobic alkyl pyridyl ketoximes [18], and trialkyl amine and organic acids [19] have been used in the SX process for the concentration and purification of the leach solutions. Among the reagents, organophosphorus acids such as 2-ethylhexyl phosphoric acid-2-ethylhexyl ester (EHEHPA), bis-(2, 4, 4-trimethylpentyl) phosphinic acid (Cyanex 272), and D2EHPA have been widely used for solvent extraction and purification of zinc [7, 20-25]. The higher

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extraction rate, effective separation, safety, low maintenance, physical and chemical stabilities, and lower capital and operating costs have made D2EHPA one of the most common extractants in sulfate environments, especially at the pH range of

1-3 [7, 26]. The mechanism of zinc extraction by D2EHPA, which is often present in the dimeric form in kerosene, is cation exchange based on the following reaction [27]:



where HR represents D2EHPA, H_2R_2 is the dimer molecule of HR, and m shows the total number of HR molecules.

Many researchers have studied the use of D2EHPA for extraction of zinc from various aqueous solutions such as the ammonium oxalate, oxalic acid [28], sulfate [25, 27, 29], and phosphoric acid solutions [30], and the influence of the contact time parameters, phase ratio (O/A), equilibrium pH, and D2EHPA concentration on the extraction have been studied [30]. The synergistic separation of zinc and cadmium from sulfate-containing Ni, Co, and Cd has also been studied using a mixture of D2EHPA and TBP [31], and in another study, D2EHPA and Cyanex 272 have been used to extract zinc from a feed solution containing 10 g/L of nickel and 2 g/L of zinc, and 100% of zinc has been extracted using 0.5 M D2EHPA at pH 3.5 [32].

The recovery of zinc from a sulfate solution obtained from low-grade sulfide-oxide ore in the Bama Co., the second largest mining company in the central Iran, has been investigated by Asadi *et al.* using 80% D2EHPA, 20% Cyanex 272, and TBP. They found that a mixture of TBP with D2EHPA was almost ineffective, and the optimal concentrations of D2EHPA and Cyanex 272 were 0.5 mol/L and 0.035 mol/L, respectively [5]. In a research work carried out by Balesini *et al.*, zinc has been selectively extracted from a leach solution containing 25 g/L zinc, 20 mg/L cadmium, and 1.5 g/L nickel by D2EHPA in kerosene, and 98.8% zinc has been extracted under the optimum conditions of 40% D2EHPA concentration, pH of 2.5-3, and a 4:1 volumetric phase ratio (O:A) [33]. Zinc has been recovered from an industrial effluent by Pereira *et al.*, and the results obtained show that 98% of zinc could be extracted using three extraction steps at pH 2.5, D2EHPA = 20%, A:O = 1:1, and three stripping steps at O:A = 4:1 in a continuous mixer-settler. The final solution containing 125.7 g/L zinc has then been sent directly to the electro-winning process [34].

Based on the literature reviews, although D2EHPA was used by many researchers for the extraction of zinc, the cationic exchange

mechanism of acid extractants and releasing H^+ during removal restrict the zinc extraction from the aqueous solution. Therefore, in order to increase their effectiveness and avoid the increase in the solution acidity, they are required to be saponified using an acid/base reaction [35]. Saponification of D2EHPA is a process in which the H^+ ions are replaced by Na^+ and NH_4^+ through an acid-alkali reaction; so, the raffinate pH does not decrease during the SX process [23].

Common D2EHPA saponifiers include NaOH, NH_4OH , and Na_2CO_3 , which have been used in some research works [27, 36, 37]. Saponified D2EHPA has been used for zinc recovery from a low-grade sulfate solution by Jiang *et al.* The results obtained showed that 97% of zinc could be extracted in 10 minutes, at room temperature, a 1:1 phase ratio (A:O), the flow rate for both phases, 25 ml/min, 30% D2EHPA, and 60% saponification degree [38]. Nathsarma *et al.* have studied the separation of zinc and manganese from a sulfated solution using the sodium salt of the various extractants D2EHPA, PC88A, and Cyanex 272 in kerosene using 5%TBP as a modifier, in which the extraction of metal ions has increased with increase in the pH and the extractant concentration. The separation factor for Zn(II) and Mn(II) decreased with increase in the NaD2EHPA concentration from 0.03 to 0.06 M [39]. Solvent extraction of zinc from a solution of 18.7 g/L of zinc and 0.03 g/L of iron with 20% D2EHPA saponified as an extractant in kerosene has been performed by Long *et al.* The results obtained showed that 75% zinc could be extracted from zinc sulfate solution. Zinc ion was separated from ferric ion by a sulfuric acid solution (196 g/L) as a stripping agent, and 88.60% zinc and 1.76% of ferric ion were stripped [27].

Len *et al.* have studied the extraction of copper and zinc from bioleaching solutions from a low-grade sulfide ore with LIX984 and D2EHPA, respectively. After copper extraction with LIX984, zinc was recovered by 30% saponified D2EHPA, and the extraction rate obtained was about 98% [29].

Considering the fact that the Bama co. aims to extract zinc by the bioleaching process followed by

solvent extraction in the near future due to the low-grade ore and some operational and economic issues, the aim of this work is to assess the effects of different parameters on the solvent extraction of zinc from an industrial bioleaching solution obtained from this low-grade sulfide ore. Besides that, the modification of D2EHPA has been extensively studied in order to obtain high zinc extraction yields in fewer steps.

2. Experimental

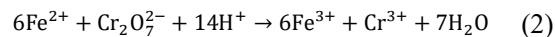
2.1. Materials and Chemicals

The pregnant leach solution (PLS) was obtained from a large-scale continuous bioleaching system including three 50 L stirred bioreactors in series at the Goushfil mine (Isfahan, Iran), which was adopted for leaching a low-grade bulk flotation concentrate. The bioleaching operations were carried out at a 15% (w/w) solid content using a mixed culture of moderately thermophile bacteria at pH 1.8 for 15 days continuously, in which 83% of zinc was recovered. The PLS solution was sent for A.A.S (ContrAA700 model), and it contained 50 g/L of zinc.

The iron concentration was determined by the titration method, and it was about 6.3 g/L. For the titration, a mixture of sulfuric acid 98% (Merck Co., Germany), phosphoric acid 85% (Merck Co., Germany), and hydrochloric acid (37%, Merck Co., Germany) were used. The other reagents such as $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, HgCl_2 , potassium dichromate 0.01 M ($\text{K}_2\text{Cr}_2\text{O}_7$) standard solution, and barium diphenylamine sulphonate ($\text{C}_{24}\text{H}_{20}\text{BaN}_2\text{O}_6\text{S}_2$) were all of analytical grade and purchased from the Merck Co. (Germany).

For the determination of iron concentration in solution, 30 mL of the bioleaching solution was transferred into a 150-mL beaker, and the solution temperature was fixed close to the boiling point with the help of a hot plate. 10 mL of HCl was added to the solution, and then the tin chloride solution was added dropwise until the solution became colorless. Afterward, 8 mL of mercury chloride was added to the mixture, and it was cooled to create a white precipitation. 30 mL of a mixture of acids and 5-6 drops of barium diphenylamine sulphonate were added, and the mixture was titrated quickly with the potassium dichromate 0.01 M solution. The endpoint of the titration was determined by changing the color of the solution into purple. Considering the consumption volume of potassium dichromate and stoichiometric coefficients in Equation 2, the total

iron concentration was obtained from Equation 3 [40].



$$C_1V_1 = 6C_2V_2 \quad (3)$$

where C_1 and V_1 are the concentration and the volume of the solution with unknown iron concentration, respectively, and C_2 and V_2 are the concentration of potassium dichromate (0.01 M) and the volume of potassium dichromate.

The organic phase in the SX experiments consisted of a mixture of the D2EHPA extractant (Merck Co., Germany) as an extractant, kerosene (Tehran Oil Refinery, Iran) as a diluent, and 1-decanol (Merck Co., Germany) as a modifier at certain ratios. The pH value was adjusted by adding sulfuric acid (H_2SO_4 , 98%) and sodium hydroxide (NaOH , 97%), supplied from the Merck Co. (Germany).

2.2. Apparatus and experimental procedure

2.2.1. Iron removal by jarosite precipitation

Iron is the major impurity in the zinc and copper production industries, and it can dissolve along with these metals, and reduces both the extraction capacity and the selectivity. Therefore, the iron content should be significantly reduced before solvent extraction of zinc by precipitation as hydroxide, jarosite, hematite or goethite.

For iron removal from the sulfate solution as a jarosite compound, a certain amount of NH_4OH or NaOH or NH_3 was added dropwise to 300 mL of the sulfate solution at 95 °C and pH 1.5 to form ammonium-jarosite or sodium-jarosite, which could be removed through solid-liquid filtration [41]. The solution was stirred for 3.5–4 h at 500 rpm, during which the parameters such as the time, volume of solution, temperature, and pH were regularly monitored. Finally, the concentrations of both ferric and ferrous iron in the leaching solution were determined by the titration method, and consequently, the removal percentage was calculated by mass balance (Equation 4). The precipitation was also sent to a mineralogical laboratory for XRD analysis (Asenware AW-DX300).

$$\text{Fe removal (\%)} = \frac{[\text{Fe}]_i - [\text{Fe}]_f}{[\text{Fe}]_i} \times 100 \quad (4)$$

where $[\text{Fe}]_i$ and $[\text{Fe}]_f$ are the initial and final concentrations of iron in the solution, respectively. All experiments were repeated at least for each condition, and the mean was used.

2.3. Saponification of D2EHPA and zinc extraction

The organophosphorous extractants such as D2EHPA have been widely used for metal extraction due to their high extraction efficiency. This acid extractant is usually presented as the form of hydrogen-bonded dimer (H_2A_2) in the non-polar diluents and extract zinc based on the cation exchange mechanism and pH of the aqueous solution; therefore, reduces due to H^+ ion release during extraction, which may consequently affect the metal ion extraction. Thus these extractants should be saponified by an acid/base neutralization reaction. After the hydrogen bonds in the dimer molecules are broken and the alkali metal cations (NaA) are formed, water-in-oil micro-emulsions in an organic phase can easily form using the saponified extractants, and as a result, both the separation efficiency and the extraction selectivity may change [35]. Saponification of the extractant is determined by the titration method with NaOH, and the mass of NaOH should first be calculated based on the stoichiometric ratio. After vigorous mixing of the mixture for 20 min, the organic extractant would be saponified.

For batch SX experiments, an equal volume of the aqueous phase containing 2500 mg/L of zinc and 30 mg/L of iron and organic phases (25 mL per each phase) is poured into a 100-mL beaker and mixed by a magnetic stirrer for a certain time at the ambient temperature. The organic phase was a mixture of 20% (v/v) D2EHPA, 79% (v/v) kerosene, and 1% (v/v) 1-decanol.

The effective parameters such as the pH, concentration of extractant, contact time, saponification degree, stirring speed, temperature, A:O, and saponifier were investigated on the solvent extraction process as the one-factor-at-a-time (OFAT) method. The temperature was kept constant at $25 \pm 2^\circ C$ for all experiments, except for those designed for studying the effect of temperature. The pH of the solution was measured at the beginning and end of each experiment using a pH-meter (pH 310 model, Eutech). The separation time of both phases was considered to be one min. At the end of each experiment, the zinc concentration in the aqueous phase was determined by AAS (ContrAA700 model), and the concentrations of the elements in the organic phase were determined based on the mass balance calculations. The zinc distribution coefficient and extraction percentage were calculated using Eqs. 5 and 6.

$$D_{Zn} = \frac{[Zn]_{org}}{[Zn]_{aq}} \quad (5)$$

$$E_{Zn} = \frac{D_{Zn}}{D_{Zn} + V_a/V_o} \times 100 \quad (6)$$

where D_{Zn} is the distribution coefficient of Zn, and $[Zn]_{org}$ and $[Zn]_{aq}$ are the zinc concentrations in the organic and aqueous phases. E_{Zn} shows the extraction percentage of zinc and V_a/V_o used for the aqueous to organic volumetric phase ratio.

In the kinetic studies, 5 mL of samples were taken from the mixture at certain time intervals (30, 60, 90, 180, 300, 420, and 600 s), while the other conditions were kept constant ($25 \pm 2^\circ C$, 600 rpm stirring speed, pH_i 2, 20% D2EHPA in kerosene, 1% decanol, A:O = 1:1, and NaOH as a saponifier). The immiscible phases were then separated using a decanting funnel and analyzed for the zinc content. The organic phase was also sent to the Fourier transform-infrared (FT-IR) spectroscopy analysis (Tensor27 model, Germany) in order to determine the functional groups and support the justification of the changes.

The viscosity (cP) of the organic phase was measured by the Ostwald method [42]. In this method, the viscosity of the unknown solution is calculated by comparing the unknown solution with distilled water whose density (ρ_1) and viscosity (μ_1) are known at a certain temperature (Equation 7):

$$\frac{\mu_1}{\mu_2} = \frac{\rho_1 t_1}{\rho_2 t_2} \quad (7)$$

where t_1 is the time that distilled water passes through certain distances in the capillary tube, and ρ_2 and t_2 are the density and time for the unknown solution, which were calculated the same way as water. The density was calculated using Equation 8. m_p and m'_p are, respectively, the weights of the pycnometer when it is filled and empty, and V_p is the pycnometer volume.

$$\rho_2 = \frac{m_p - m'_p}{V_p} \quad (8)$$

3. Results and Discussion

3.1. Characterization of feed solution

The leaching solution obtained from the bioleaching process contained 50 g/L of zinc and 6.3 g/L of iron; thus before the extraction of zinc, iron must be removed due to the high contamination of the final zinc product in the downstream process as well as the high extractant

consumption. The iron removal process, described in part 2.2.1, was used, and the concentration of iron in the bioleaching solution reached 830 mg/L, indicating that 86.83% of iron was precipitated as natrojarosite ($\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$). At the same

time, no significant change was observed in the concentration of zinc (Table 1). The precipitate was also sent for XRD analysis, which confirmed that the solid was entirely composed of jarosite (Figure 1).

Table 1. Concentrations of elements in the bioleaching solution before and after the removal of iron in the jarosite precipitation method.

Elements	Zn	Fe	Pb	Cu	Na	S	Mg	Ag	Sb	As	Ca
Concentrations before precipitation (mg/L)	50×10^3	6300	3.32	163	161	8794.8	933	0.16	5.16	47	665
Concentrations after precipitation (mg/L)	50×10^3	830	0.21	189	2642	9633.6	1159	0.09	4.24	35	754

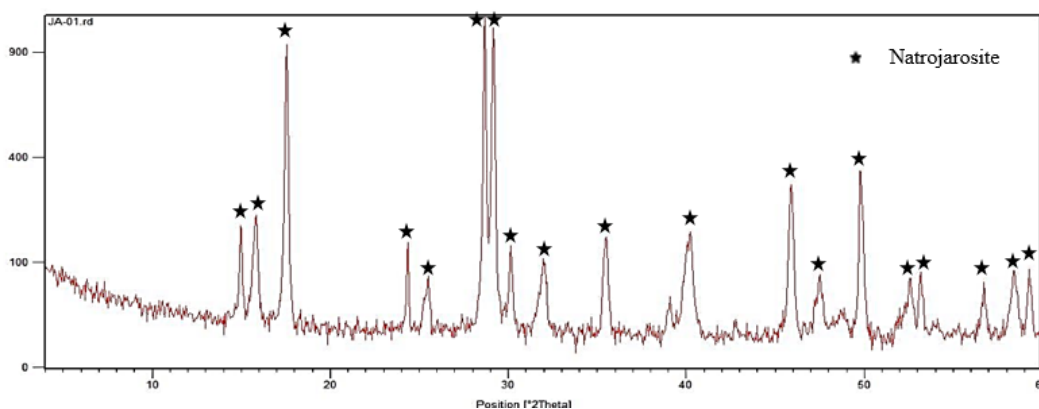


Figure 1. XRD pattern for iron precipitation from the Bama PLS solution.

However, since the industrial bio heap process aims to achieve 2-3 g/L of zinc and 30 mg/L of iron, the solution, after jarosite precipitation, was diluted before use for solvent extraction (Zn:2588 ppm and Fe:30 ppm).

3.2. Influence of different parameters on solvent extraction of zinc by saponified D2EHPA

The aqueous solution was used for the SX experiments after iron removal in which the concentrations of zinc and iron were about 2588 mg/L and 30 mg/L, respectively. According to the previous studies and preliminary tests, the levels for the parameters such as the contact time, saponification degree, stirring speed, pH, temperature, D2EHPA concentration, phase ratio (A:O), and saponifier type were determined, and the results obtained were discussed.

3.2.1. Effect of saponification of extractant on zinc recovery

As mentioned earlier, D2EHPA is one of the acidic extractants that release H^+ ions during

extraction, reduce zinc extraction, and increase the acidity of the solution. Therefore, the extractant is required to be saponified before use for the extraction process. Hence, the effect of a saponification degree was considered as crucial factor that must be studied.

The different saponification percentages (0%, 5%, 15%, 25%, and 40%) were investigated at various time intervals (30 s, 60 s, 90 s, 180 s, 300 s, 420 s, and 600 s). Experiments were performed at 25 ± 2 °C, 200 mL volume, 600 rpm stirring speed, pH_i 2, 20% D2EHPA in kerosene, 1% decanol, A:O = 1:1, and NaOH as a saponifier. It was observed that although by increasing the contact time up to 90 s the metal ion extraction rate increased considerably, the metal extraction then remained unchanged (Figure 2). The high extraction rate ($\approx 99\%$) within 90 s indicates that the extraction kinetics are relatively fast. It also showed that only 77.94% of zinc could be recovered using non-saponified D2EHPA, 21 % less than using saponified D2EHPA; thus saponification had a positive effect on the zinc extraction.

Increasing the saponification degree from 5% to 25% improved the extraction, and it reached 99.88% after 60 s from the beginning of the test. The excess amount of saponifier, 40% saponification degree, dramatically decreased the efficiency due to the higher viscosity of the organic phase at this level (Table 2), which caused difficulties for phase mixing, and consequently, reduced the effective surface area and mass transfer. pH_f also increased drastically at a 40% saponification degree (Table 2); some research works have confirmed that as the degree of saponification increases, the equilibrium pH of the aqueous phase also increases [43, 44]. Based on the above observation, the optimum conditions were chosen at a 15% saponification degree and 90 s, in which zinc extraction was obtained by about 98.87%. The saponification degree of 25% was not considered as an optimal condition since there was a negligible difference between 15 % and 25%; however, the color of raffinate changed significantly in the latter.

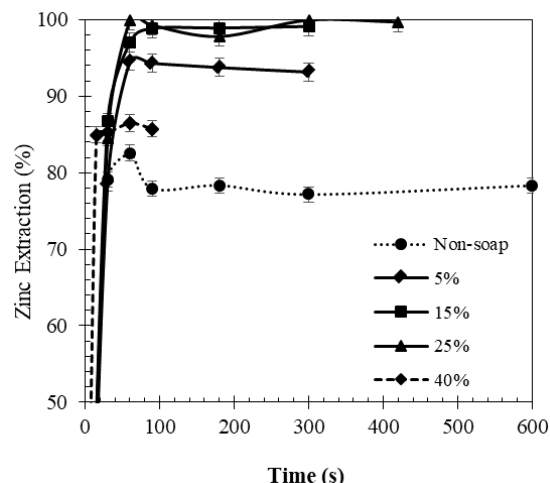


Figure 2. Effect of saponification degree on solvent extraction of zinc with D2EHPA at different times (25 ± 2 °C, pH_i 2, 20% D2EHPA in kerosene, 1% decanol, A: O=1:1, saponifier NaOH, and zinc concentration of 2588 mg/L).

Table 2. Chemical and physical characteristics of the aqueous phase at different saponification degrees.

No.	Saponification degree (%)	Time (S)	D	pH_i	pH_f	Viscosity (cP)	Zinc extraction (%)
1	0	30	3.78	2	1.98	Nd.	79.08
2	0	60	4.74	2	1.98	Nd.	82.57
3	0	90	3.53	2	1.98	Nd.	77.94
4	0	180	3.62	2	1.98	Nd.	78.34
5	0	300	3.38	2	1.98	Nd.	77.16
6	0	600	3.61	2	1.98	Nd.	78.32
7	5	30	3.66	2	2.10	1.85	78.54
8	5	60	17.28	2	2.10	1.85	94.53
9	5	90	16.55	2	2.10	1.80	94.30
10	5	180	15.01	2	2.10	1.85	93.76
11	5	300	13.61	2	2.10	1.85	93.16
12	15	30	6.51	2	2.30	1.89	86.68
13	15	60	32.38	2	2.30	1.89	97.00
14	15	90	87.57	2	2.30	1.89	98.87
15	15	180	92.50	2	2.30	1.89	98.93
16	15	300	114.07	2	2.30	1.89	99.13
17	25	30	5.48	2	2.30	1.90	84.56
18	25	60	861.95	2	2.30	1.90	99.88
19	25	90	132.82	2	2.30	1.90	99.25
20	25	180	44.72	2	2.30	1.90	97.81
21	25	300	2784.79	2	2.30	1.90	99.96
22	25	420	328.72	2	2.30	1.90	99.70
23	40	15	5.64	2	5.00	2.12	84.95
24	40	30	5.77	2	5.00	2.12	85.23
25	40	60	6.39	2	5.00	2.12	86.46
26	40	90	6.01	2	5.00	2.12	85.74

3.2.2. Effect of stirring speed

An appropriate mixing of the immiscible phases is a crucial factor in the SX process, which lowers the speed and causes a smaller contact area, while an excessive shear can lead to a higher entrainment of the organic phase in the raffinate and

consequently the organic phase loss [45, 46]. The effect of the stirring speed was studied at the five different levels of 100 rpm, 250 rpm, 400 rpm, 650 rpm, and 800 rpm, while the other conditions including a temperature of 25 ± 2 °C, 90 s, pH_i 2, 20% D2EHPA in kerosene, 1% decanol, 15%

saponification, A:O = 1:1, and the saponifier NaOH were kept constant.

The results in Figure 3 demonstrate that increasing the stirring speed in the range of 100-650 rpm increase the extraction efficiency from 53.36% to 98.42%, and the highest yield (99.11%) is obtained at 800 rpm. There was no significant change in the extraction rate as the stirrer speed increased from 650 rpm to 800 rpm. Therefore, 650 rpm was chosen as the optimal stirring speed in order to avoid entrainment or/and entrapment and difficult phase separation.

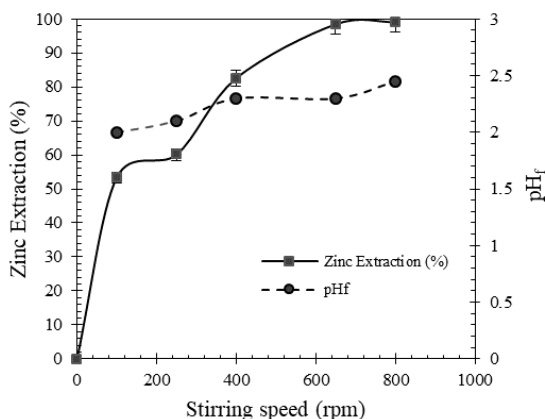


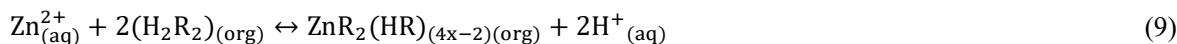
Figure 3. Effect of stirring speed on the solvent extraction (25 ± 2 °C, time of 90 s, pH_i 2, 20% D2EHPA in kerosene, 1% decanol, 15% saponification degree, A:O 1:1, NaOH saponifier, and zinc concentration of 2588 mg/L).

3.2.3. Effect of feed solution pH on zinc extraction

The metal ion extraction by an acidic extractant is strongly influenced by the pH of the aqueous phase due to the release of hydrogen ions (H⁺) during the metal cation exchange [41, 47]. The influence of pH_i on zinc extraction at the four different levels of 1, 1.5, 2, and 2.5 was studied, while the other parameters were kept constant (25 ± 2 °C, 90 s, 650 rpm, 20% D2EHPA in kerosene, 1% decanol, 15% saponification degree, A:O=1:1, and NaOH as the saponifier). The pH levels were selected based on the previous studies, which reported that D2EHPA could act as a selective solvent for zinc in the studied rang [20, 25, 27, 29, 33]. Note that some precipitation occurred at pH 3; thus the pH range was limited to 1-2.5.

The effect of the initial pH on the zinc recovery (Figure 4a) showed that the zinc extraction increased dramatically from 28.17% to 98.42% increase in the pH_i from 1 to 2. In contrast, at a higher pH_i (≥ 2.5), a negligible change was observed in the zinc recovery. These results obtained were in agreement with the previous studies [25, 27, 29, 33]; hence, the next experiments were performed at pH_i 2.

Generally, based on the following chemical reaction (Equation 9), decreasing the H⁺ ion concentration (or increasing the pH) is expected to increase the extraction rate.



The cationic acid extractants (HA) often exist in the form of dimers, and can react with metal ions. If x = 1, then K_{ex} will be in equilibrium as follows:

$$K_{\text{ex}} = \frac{[\text{ZnR}_2(\text{HR})_2]_{\text{org}} \cdot [\text{H}^+]_{\text{aq}}^2}{[\text{Zn}^{2+}]_{\text{aq}} \cdot [(\text{H}_2\text{R}_2)]_{\text{org}}^2} \quad (10)$$

According to the above equation, it can be written that:

$$\log \left[\frac{[\text{ZnR}_2(\text{HR})_2]_{\text{org}}}{[\text{Zn}^{2+}]_{\text{aq}}} \right] = \log K_{\text{ex}} + 2 \log [(\text{H}_2\text{R}_2)]_{\text{org}} - 2 \log [\text{H}^+] \quad (11)$$

The distribution coefficient (D) for zinc extraction can be expressed as follows:

$$D_{\text{Zn}} = \frac{[\text{ZnR}_2(\text{HR})_2]_{\text{org}}}{[\text{Zn}^{2+}]_{\text{aq}}} \quad (12)$$

and so it can be written as:

$$\log(D_{\text{Zn}}) = \log K_{\text{ex}} + 2 \log [(\text{H}_2\text{R}_2)]_{\text{org}} + 2 \text{pH} \quad (13)$$

According to Equation 13, the changes in log(D_{Zn}) versus pH at a constant concentration of D2EHPA should be linear with a slope ≈2. As shown in Figure 4b, the slope of a line obtained from log(D_{Zn}) versus pH changes at 20% D2EHPA is 1.966, close to 2. This indicates that the reaction under this condition applies to this process.

During the extraction, the alkali metal ions are exchanged and entered the aqueous phase. In addition, H₂O in the organic phase is usually transferred to the aqueous phase, which leads to increasing the final pH.

For understanding the difference between the saponified and non-saponified solvents, it is important to know that the aqueous solution pH should be kept at a suitable range in order to reach high extraction efficiencies.

The solution pH decreases after extraction using non-saponified D2EHPA, which restrains the

extraction process due to increasing the H^+ concentration in the aqueous phase. However, saponification with NaOH improves both the extraction efficiency and the distribution coefficient.

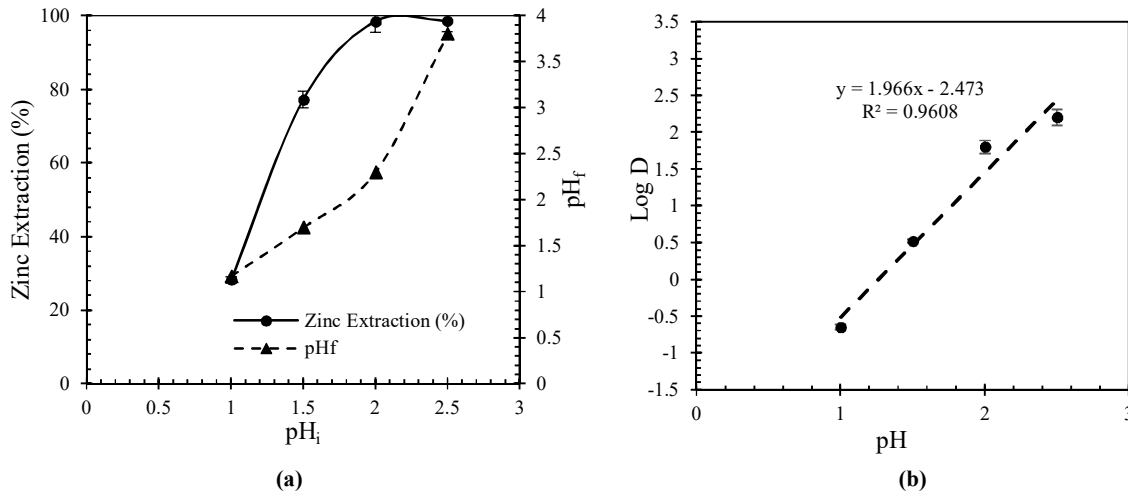


Figure 4. (a) Effect of pH of feed solution on zinc solvent extraction and (b) Log (D_{Zn}) versus pH in condition of D2EHPA 20% (v/v) (temperature $25 \pm 2^\circ C$, time of 90 s, 650 rpm stirring speed, 20% D2EHPA in kerosene, 1% decanol, 15% saponification degree, A:O = 1:1, NaOH saponifier, and zinc concentration of 2588 mg).

3.2.4. Effect of extractant mass fraction

The influence of the extractant concentration on the zinc extraction from PLS containing 2588 mg/L of Zn and 30 mg/L of Fe was studied at four different levels of the D2EHPA concentrations of 5%, 10%, 15%, and 20% diluted in kerosene. The levels were selected according to the industrial

concerns and the stoichiometric ratio of D2EHPA in the dimeric form and zinc ions in the chemical reaction. The results illustrated in Figure 5a show that the zinc extraction enhance by about 33.35% when the volumetric percentages of D2EHPA increase from 5% to 20% and E_{Zn} reaches 98.42% at 20% D2EHPA.

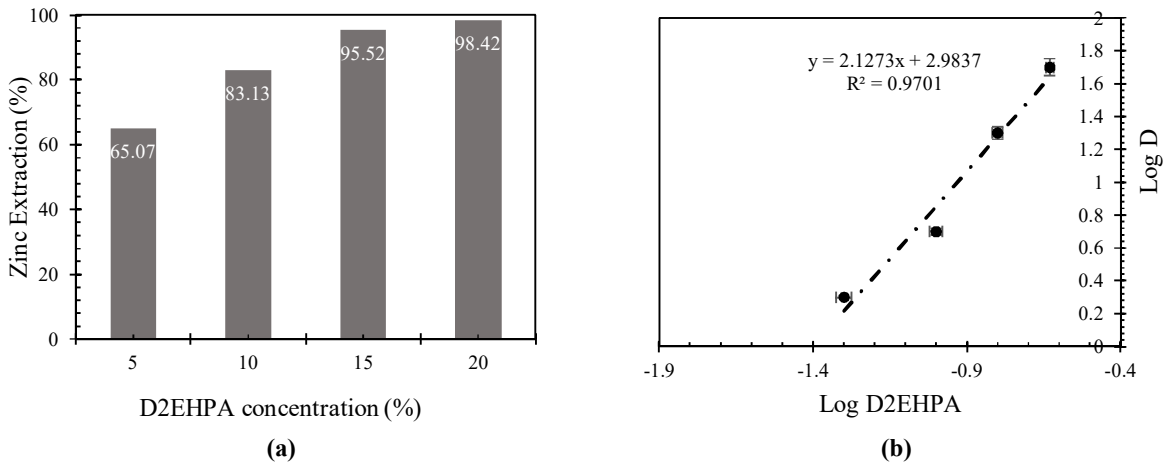


Figure 5. (a) Effect of extractant concentration on zinc solvent extraction and (b) Log (D_{Zn}) versus D2EHPA concentrations at pH 2 (pH_i 2, time of 90 s, 650 rpm, 1% decanol, 15% saponification, A:O = 1:1, NaOH saponifier, and zinc concentration of 2588 mg/L).

According to Equation 14, the distribution coefficient (D) and the extraction percentage increase at a higher initial extractant concentration (C_0) due to the increase in the free extractants participating in the extraction reaction [41, 48].

$$\log D = \log K_1 + n \log [(C_0) - (M^{++})]_s \quad (14)$$

where K_1 is the equilibrium constant, n is the number of moles of the extractant, and M^{++} is the initial concentration of the metal ion. $\log(D_{Zn})$ versus different concentrations of D2EHPA at an optimal solution pH was illustrated in Figure 5b. Based on Equation 13, the plot should be linear with a slope of about 2; however, the obtained slope in this study was equal to 2.1, which indicates that this reaction can apply to the process understudied conditions.

Since the extractant consumption is a critical factor and imposes high costs on the SX process, it is important to use less D2EHPA; thus zinc extraction at a lower D2EHPA concentration and a longer contact time was also considered. Therefore, two experiments were performed with 10% D2EHPA at 300 s and 15% D2EHPA at 180 s, and the recoveries of zinc were obtained at about 74% and 90%, respectively, which were lower than that of 20% D2EHPA in 90 s. Therefore, the 20% D2EHPA concentration was used as the

appropriate volumetric percentage for the next experiments.

3.2.5. Thermodynamic study of zinc extraction

Extraction with organic solvents is generally rapid at the ambient temperature, and results in a low equilibrium time. The process of metal ions extraction from aqueous solutions is usually slightly exothermic and the distribution ratio decreases by increasing the temperature, while the kinetic of extraction increases under this condition [26, 41]. The effect of temperature on the extraction of zinc at the three different temperatures of 25 °C, 35 °C, and 45 °C from an aqueous solution with 2588 mg/L zinc concentration was investigated. The results obtained showed that increasing the temperature from 25 °C to 45 °C had no significant effect on the zinc extraction, and the extraction percentage changed slightly from 98.42% to 99.33% (Figure 6a). Several studies also confirm these results [5, 26, 33]. Therefore, considering the energy consumption and the loss of aqueous and organic phases due to partial evaporation, 25 °C was chosen as an optimum value. There was no change in pH_f at different temperatures, and it remained constant at 2.4; also the color of the raffinate phase was almost similar.

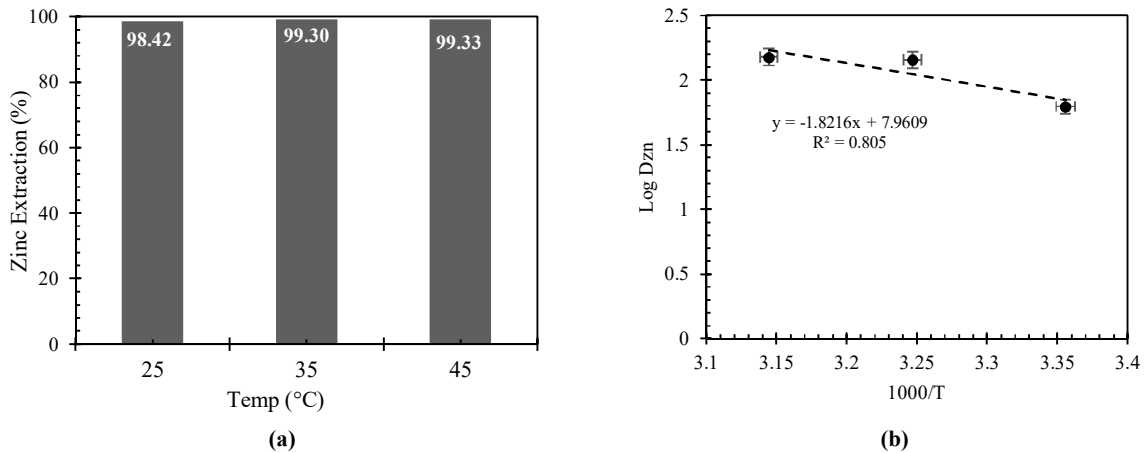


Figure 6. (a) Effect of temperature on zinc extraction and (b) $\log(D_{Zn})$ versus $1000/T$ (pH_i 2, time of 90 s, 650 rpm, 20% D2EHPA in kerosene, 1% decanol, 15% saponification degree, A:O = 1:1, NaOH saponifier, and zinc concentration of 2588 mg/L).

According to Equation 13 and the Gibbs-Helmholtz Equation:

$$\log K_{ex} = \frac{-\Delta H^0}{2.303RT} + \frac{\Delta S^0}{2.303R} \quad (15)$$

$$\log(D_{Zn}) = \frac{-\Delta H^0}{2.303RT} + \frac{\Delta S^0}{2.303R} + 2 \log[H_2R_2]_{eq} + 2pH \quad (16)$$

Based on Equation 16, the slope of the graph of $\log(D_{Zn})$ versus $1000/T$ will be equal to $\frac{-\Delta H^\circ}{2.303R}$. The linear relationship between $\log(D_{Zn})$ and $1000/T$ is presented in Figure 6b, and ΔH° is calculated as follows:

$$\frac{-\Delta H^\circ}{2.303R} = -1.82$$

$$\Delta H^\circ = 34.85 \text{ kJ} \cdot \text{mol}^{-1}$$

Considering the positive value of ΔH° , it can be concluded that zinc extraction by D2EHPA is an endothermic process, which is in agreement with the previous studies [5, 26, 44]. The entropy can be calculated from the intercept of the graph; however, the equilibrium concentration of the extractant in the system, $[H_2A_2]_{eq}$, is required to be obtained by the difference of the initial extractant concentration and the amount of extractant that forms an organometallic compound:

$$[H_2A_2]_{eq} = [H_2A_2]_{in} - [Zn^{2+}] =$$

$$0.6 - 0.039 = 0.56$$

Therefore, the entropy can be calculated as follows:

$$pH = 2$$

$$7.96 = \frac{\Delta S^\circ}{2.303R} + 2\log(0.56) + 2(2)$$

$$\Delta S^\circ = 85.47 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

The entropy change for the extraction of zinc is positive, which means an increase in disorder. Also the Gibbs free energy (ΔG°) can be calculated at 298 K using Equation 17.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (17)$$

$$\Delta G^\circ = 9.38 \text{ kJ} \cdot \text{mol}^{-1}$$

According to the data presented in Table 3, it can be concluded that the extraction of zinc by D2EHPA is a non-spontaneous process at all the studied temperatures (25 °C, 35 °C, and 45 °C).

Table 3. Thermodynamic parameters (ΔH , ΔS , and ΔG) for the zinc extraction with D2EHPA.

Log Kex	ΔH (kJ.mol ⁻¹)	ΔS (J.K ⁻¹ .mol ⁻¹)	ΔG (kJ.mol ⁻¹)		
			298 °K	308 °K	318°K
4.46	34.85	85.47	9.38	8.53	7.67

3.2.6. Effect of volumetric phase ratio (A:O)

The aqueous to organic volumetric phase ratio plays an important role in the extraction process. Although theoretically a high phase ratio (A/O) is considered as a special privilege for the industry, sometimes the use of low organic phase values is undesirable due to a higher entrainment and solvent loss; however, the high ratio of the organic phase to the aqueous phase may also impose higher costs on the process.

The effect of the A:O phase ratio at six levels of 10:1, 5:1, 3:1, 1:1, 1:3, and 1:5 was investigated. As expected, with decrease in the organic phase volume, zinc extraction significantly decreased (Figure 7) from 100% in 1:5 to 29.8% in 10:1 when saponified D2EHPA was used, and decreased from 93.1% in 1:5 to 20.2% in 10:1 for non-saponified D2EHPA. According to the results obtained, no remarkable change occurs in zinc extraction with higher A:O ratios (such as 1:3 and 1:5), and the 1:1 ratio can be selected as an optimum ratio.

The McCabe-Thiele plot was used in order to find the number of stages of the theory of complete extraction of zinc at a constant pH and an A:O ratio under the continuous conditions (Figure 8). The

distribution isotherm curve obtained at optimum extraction conditions (25 ± 2 °C, pH; 2, 650 rpm, 20% D2EHPA, 15% saponification degree, 90 s) at the A:O ratios ranged from 1:5 to 10:1. For saponified D2EHPA and A:O = 1:1 as the operating line, one step is required to extract zinc completely (≈99%) from the aqueous solution and reach the maximum concentration in the organic phase (and 40 mg/L in raffinate) under the counter-current flow (Figure 8a), and for the non-saponified D2EHPA (A:O = 1:1), three extraction steps are required (Figure 8b).

In order to compare the effect of the saponification extraction on the number of stages required for the complete extraction, some experiments were designed with non-saponified D2EHPA at the A:O ratios of 10:1, 5:1, 3:1, 1:1, 1:3, and 1:5. It was observed that the extraction rate and the zinc recovery were strongly affected by an increase in the phase ratio (A:O) and they were decreased from 93% at A:O = 1:5 to 20.2% at A:O = 10:1 (Figure 7). For the non-saponified D2EHPA, three extraction steps are required, in which zinc is extracted almost entirely from the aqueous solution under the counter-current flow (Figure 8b).

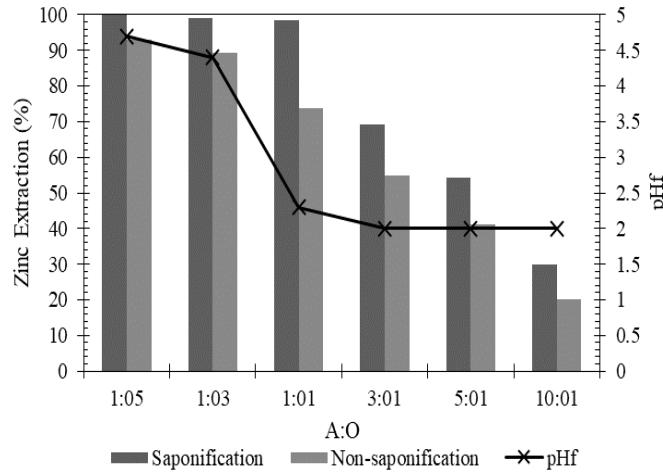
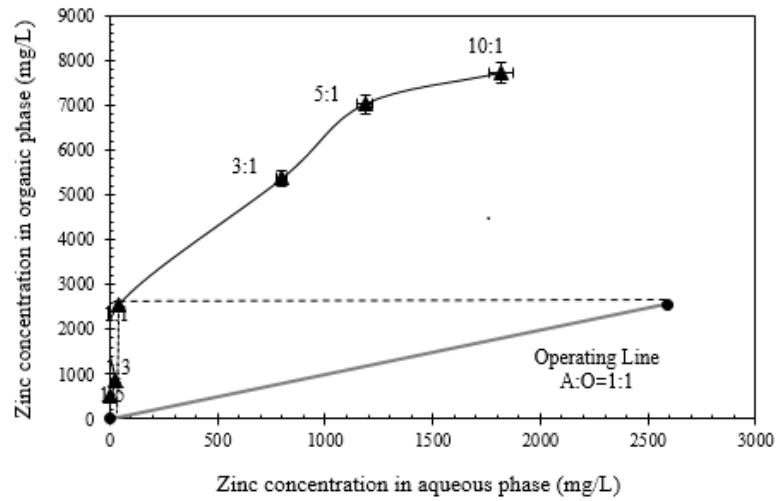
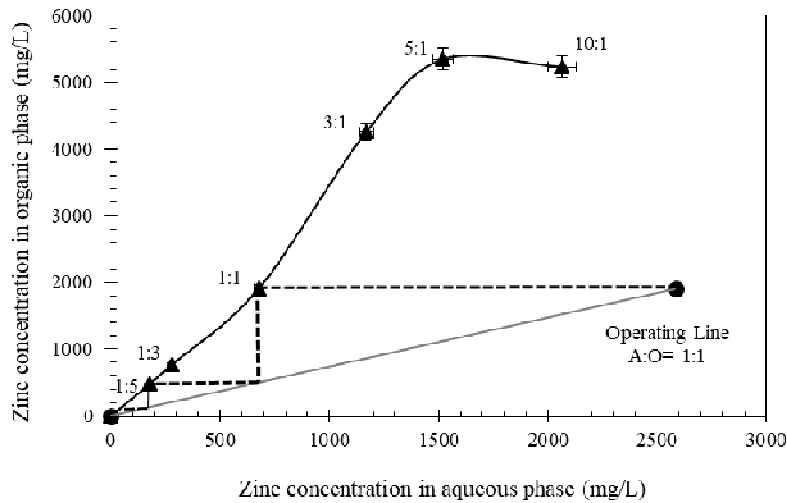


Figure 7. Ratio of the A:O volumetric phase ratio in the extraction of zinc (temperature of 25 ± 2 °C, time of 90 s, pH_i 2, stirring speed of 650 rpm, 20% D2EHPA in kerosene, 1% decanol, 15% saponification degree, NaOH saponifier, and zinc concentration of 2588 mg/L).



(a)



(b)

Figure 8. McCabe–Thiele diagram for extraction of zinc in the (a) saponified D2EHPA and (b) non-saponified D2EHPA.

3.2.7. Effect of saponifier type on extraction

Saponification is a process in which Na^+ ions or NH_4^+ ions replace H^+ ions through an acid-alkali reaction. In the extraction process, sodium ions exchange with the metal ions, which accelerates the extraction reaction in an alkaline medium [38]. The common saponifiers including NaOH, KOH, K_2CO_3 , and Na_2SO_4 were studied, while the other conditions were kept constant (temperature of 25 ± 2 °C, 90 s, pH_i 2, stirring speed of 650 rpm, 20% D2EHPA in kerosene, 1% decanol, 15% saponification degree, A:O of 1:1, and zinc

concentration of 2588 mg/L). It can be seen in Figure 9 that the efficiency of extraction changes in the following order: NaOH (98.42%) > KOH (96.3%) > Na_2SO_4 (88.3%) > K_2CO_3 (60.2%). According to Sun *et al.*, the use of NaOH and KOH form smaller micro-emulsions and create a higher contact area, which may increase zinc extraction [23]. The observations showed that as K_2CO_3 was used for saponification of the extractant, the color of raffinate changed quickly to milky-white and the pH_f reached nearly 6 (Figure 9), which could affect the process.

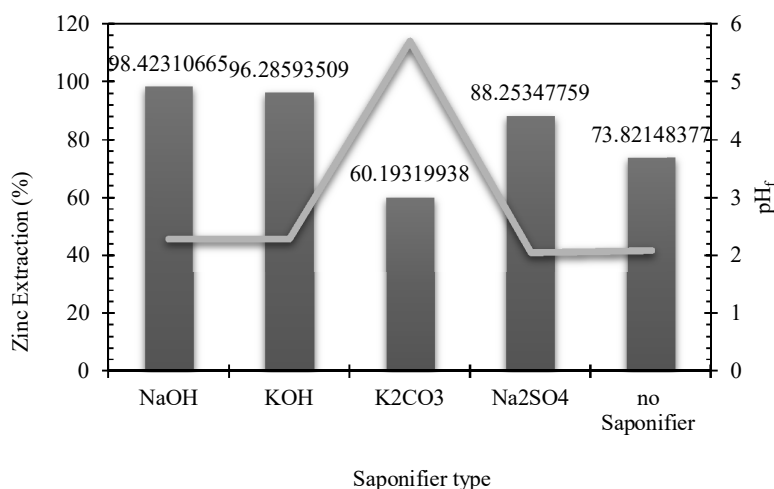


Figure 9. Effect of saponifier type on zinc extraction (temperature of 25 ± 2 °C, time of 90 s, pH_i 2, stirring speed of 650 rpm, 20% D2EHPA in kerosene, 1% decanol, 15% saponification degree, A:O = 1:1, and zinc concentration of 2588 mg/L).

3.4. Optimal conditions for zinc solvent extraction by saponified D2EHPA

According to the results obtained from the solvent extraction experiments, the optimal recovery obtained at 25 ± 2 °C, pH_i 2, 650 rpm, 20% D2EHPA, A:O = 1:1, 15% saponification degree, 90 s, and NaOH as a saponifier, in which 98.42% of zinc was extracted. The McCabe-Thiele diagram also confirmed that the complete extraction of zinc could be achieved at one theoretical stage at A: O = 1:1.

4. FT-IR spectrometry analysis of organic phase

Fourier transform-infrared (FT-IR) spectroscopy is a method most commonly used in order to identify a functional group and to study the mechanism of metal extraction by D2EHPA [26, 49, 50]. In this work, a fresh, loaded, and stripped organic phase was sent for analysis to confirm the

extraction of zinc by saponified D2EHPA and its stripping. Figure 10a shows the FT-IR spectrum for the fresh saponified organic phase before contacting PLS. A specific peak at 1683.57 cm^{-1} may correspond to the vibration peak of water [51]. According to Figure 10, the peaks at 1033 cm^{-1} and 1229 cm^{-1} are for the vibration bonds of P-O-H and P=O, respectively, which are in agreement with similar research works [26, 52, 53]. The peaks at 1379 cm^{-1} and 1462 cm^{-1} are attributed to the CH_2 and CH_3 deformation vibration bonds, respectively, which indicate the presence of D2EHPA. The water peak can be observed at 1673 cm^{-1} . The tensile vibrations in the region of $3000\text{--}2800 \text{ cm}^{-1}$ are related to the C-H stretch bonds [54, 55]. The Zn-O compound appearing at 521.58 cm^{-1} in Figure 10b confirm the extraction of zinc by saponified D2EHPA, and it is obvious that zinc could completely strip from the organic phase by sulfuric acid.

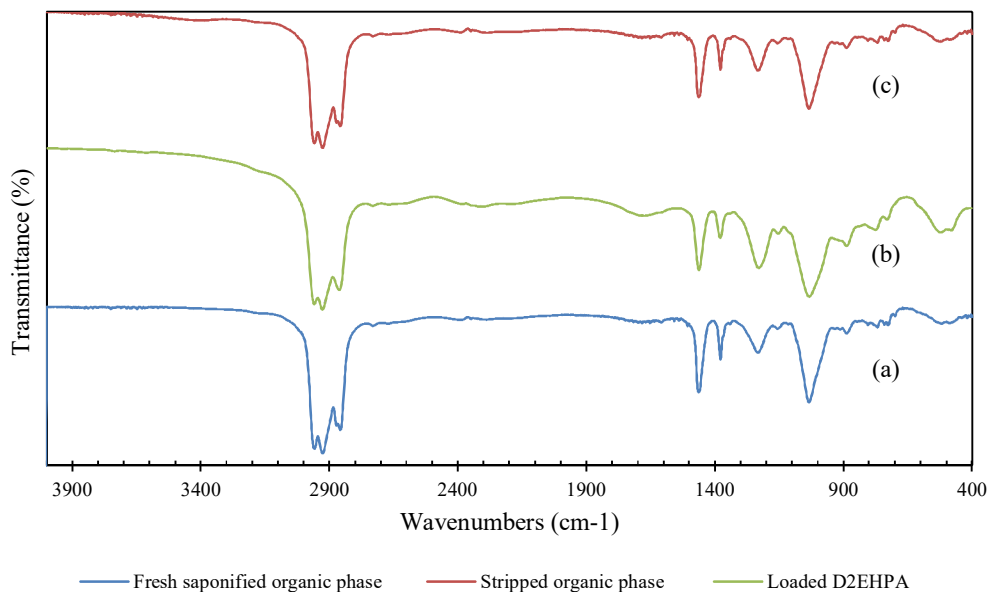


Figure 10. FT-IR spectra for (a) fresh saponified organic phase; (b) loaded organic phase; and (c) stripped organic phase at optimum conditions.

5. Conclusions

Based on the results of zinc recovery from the low-grade lead/zinc sulfidic ore bioleached solution by saponified D2EHPA, as an extractant, the following conclusions can be drawn:

- Due to the negative effect of the high concentration of iron in PLS (6.3 g/L) on zinc extraction, 86.83% of iron was first removed as the jarosite compound, and the iron content reached 30 mg/L in the SX feed solution.
- The effect of saponification of extractant on zinc extraction was studied in details, and it was proved that increasing the saponification degree up to 25% would be beneficial. In contrast, a higher percentage increased the viscosity of the solution, and consequently, led to a lower extraction. The extraction efficiency of more than 98.5% was achieved at 15% saponification degree during 90 s.
- The effects of the extraction conditions on the zinc separation such as the stirring speed (100- 800 rpm), pH (1-2.5), temperature (25-45 °C), D2EHPA concentration (5-20%), and A:O (10:1-1:5) were investigated. More than 98% of zinc was recovered from the bioleaching solution under the optimum conditions (20% D2EHPA, 15% saponification degree with NaOH, contact time of 90 s, stirring speed of 650 rpm, temperature of 25 ± 2 °C, and A:O = 1:1).
- Although increasing the pH value had a significant effect on zinc extraction due to the cation exchange mechanism of acidic extractant, it

reached a maximum value of 98.4% at pH 2; the effect of temperature was negligible, and the best results were obtained at the ambient temperature.

- The results obtained revealed that by increasing the concentration of the available saponified D2EHPA, the distribution coefficient and thus the extraction efficiency increased. Among the common saponifiers (NaOH, KOH, Na₂CO₃, and K₂CO₃), a higher zinc extraction was obtained by NaOH.
- Using the McCabe-Thiele diagram, it was found that one theoretical step was necessary for the complete extraction of zinc by saponified D2EHPA, while at least three stages was required to be apply using non-saponified D2EHPA under the same conditions.

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Conflicts of Interest

The authors declare no conflict of interests.

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استخراج حلال روی از محلول بیو-لیچینگ با اصلاح D2EHPA: بهینه سازی و مطالعات ترمودینامیکی

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چکیده:

در این مقاله، استخراج روی از محلول لیچ حاصل از فرآیند بیولچینگ کانسنگ سولفیدی سرب-روی با عیار پایین حاوی ۵۰ g/L و ۶/۳ g/L آهن توسط D2EHPA صابونی شده بررسی شد. نتایج نشان داد که استخراج انتخابی روی (II) با اصلاح D2EHPA در یک فرآیند دو مرحله‌ای امکان پذیر می باشد. در مرحله اول، قبل از استخراج روی مقدار قابل توجهی آهن (۸۷ درصد) به صورت سدیم-جاروسیت از PLS حذف شد و در مرحله دوم، پارامترهای موثر بر استخراج روی از جمله زمان تماس، درجه صابونی‌کردن، نوع صابونی‌کننده، سرعت هم زدن، pH، دما، غلظت D2EHPA و نسبت فاز (A:O) بررسی شد. نتایج نشان داد که ۹۸/۴ درصد روی در شرایط بهینه، ۲۰ درصد D2EHPA، ۱۵ درصد درجه صابونی‌کردن، $\text{pH} = 2.65$ rpm و نسبت A:O ۱:۱ در دمای محیط ($25 \pm 2^\circ\text{C}$) طی ۹۰ ثانیه استخراج می شود که این مقدار ۲۵ درصد بالاتر از زمانی است که از D2EHPA غیر صابونی استفاده شده بود. علاوه بر این، در حالی که یک مرحله تئوری برای استخراج کامل روی توسط D2EHPA صابونی شده مورد نیاز بود، تعداد مراحل مورد نیاز با استفاده از D2EHPA حدود سه مرحله بدست آمد. بنابراین، کاهش تعداد مراحل استخراج و عدم نیاز به خنثی کردن رفینیت در هر مرحله استخراج از مزیت های این مطالعه می باشد.

کلمات کلیدی: استخراج روی؛ D2EHPA؛ صابون کردن؛ ترمودینامیک.
