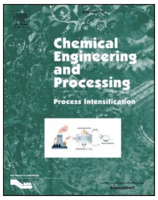
Chemical Engineering & Processing: Process Intensification 176 (2022) 108976

Contents lists available at ScienceDirect

Chemical Engineering and Processing - Process Intensification

journal homepage: www.elsevier.com/locate/cep



# Potential use of synergist D2EHPA/Cyanex 302 in kerosene system for reactive extraction: Zinc recovery and organic phase regeneration

Norul Fatiha Mohamed Noah [a,b], Norasikin Othman [a,b,*], Izzat Naim Shamsul Kahar [a], Sazmin Sufi Suliman [a]

[a] School of Chemical & Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia
[b] Centre of Lipids Engineering and Applied Research (CLEAR), Ibnu Sina Institute for Scientific and Industrial Research (ISI-SIR), Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

## ARTICLE INFO

*Keywords:*
Reactive extraction
D2EHPA-Cyanex 302 system
Zinc
Synergistic extractant
Regeneration
Intensification

## ABSTRACT

The extraction of Zn(II) from aqueous solution was studied using extractants mixture in organic base kerosene by reactive extraction. The extraction process was conducted by evaluating some base and synergistic extractants, followed by back-extraction using several types of stripping agents. Around 99% of zinc extraction was achieved at pH 9 using 9 mM D2EHPA as a base and 1 mM Cyanex 302 as a synergistic extractant with a synergistic coefficient of 2.9. Such findings proof to the intensification of reactive extraction compared to the single system. So, the mixture system produced synergistic and productive extraction with minimum use of extractants. The reaction between Cyanex 302-D2EHPA and Zn was studied, and its stoichiometry, as well as the possible structure of Zn(II)-extractant complexes in the extract phase, were investigated. FTIR and the slope analysis method both produced similar findings that $Zn{\bullet}A_2{\bullet}2HB$ is the zinc form complex with 2 mol D2EHPA (HA) and 2 mol Cyanex 302 (HB) extracted species. Meanwhile, the back-extraction revealed that 0.45 M acidic thiourea is the most effective stripping agent, which achieved almost 100% stripping efficiency. For recycling, the organic phase can be recycled/reused successfully up to 4 times with almost 100% stripping performance.

## 1. Introduction

Rapid world industrialization significantly impacted natural water reservoir pollution due to the enormous discharge of heavy metals in various industrial wastewater [1]. One of the significant elements that contribute to water pollution is zinc. Table 1 shows the various zinc concentrations in secondary waste of metallurgical industries. Recycling Zn is vital and beneficial in order to save the environment and operating costs because it will consume less energy than primary metal production and so helps to save natural resources [2].

A variety of pyrometallurgical and hydrometallurgical methods were implemented in removing zinc from waste liquor [3]. Roasting, for example, is a pyrometallurgical process with several drawbacks such as high consumption of energy and a large amount of residue produced [4]. Currently, hydrometallurgical processes account for almost 80–85% of the zinc production in the world [5]. Precipitation of metal ions in the wastewater as hydroxides is considered as one of the most conventional and economical methods, but the method needs to be stopped due to the high production of heavy metal sludge or slime during the process, which is considered a secondary environmental pollutant [6]. Recently, selective extraction of Zn has been extensively researched [4,7,8], and reactive extraction is a clean hydrometallurgical separation technology that is widely employed [9,10]. Reactive extraction can be defined as a classical analytical technique in investigating the content of various organic and inorganic species. It is the most beneficial method compared to other options as the operation can process a high volume of wastewater to be treated. In this method, the use of a carrier or an extractant is required, depending on the targeted metals. Several extractants have been studied regarding their effectiveness for Zn extraction, such as di-(2-ethylhexyl) phosphoric acid (D2EHPA) [11,12], tri-n-butyl phosphate (TBP) [13], and Cyanex 302 [14]. However, as reported, the separation factors decreased as the pH decreased. It has been reported that TBP provides an efficient extractant for Zn(II) extraction [15]. However, a considerable amount of TBP used is required to obtain an excellent extraction performance, which, in terms of cost, is not comparable with D2EHPA [16]. In addition, the hydrophilicity of TBP

---

* Corresponding author.
*E-mail address:* norasikin@cheme.utm.my (N. Othman).

https://doi.org/10.1016/j.cep.2022.108976
Received 14 February 2022; Received in revised form 16 April 2022; Accepted 11 May 2022

**Table 1**
Concentration of zinc present in industrial wastewater.

| Waste | Metal | Concentration | References |
|---|---|---|---|
| Zinc leaching filter cakes | $ZnCl_2$ | 6.5 (wt %) | [3] |
| Scrubber | ZnO | 18.4 ppm | [4] |
| Contaminated aquatic environments | Zn | 3.25-99.25 ppm | [5][6] |
| Flux skimming (after the wet galvanizing process) | Zn | 5.6 (wt %) | [2] |
| | $ZnCl_2$ | 48.1 (wt %) | |
| | ZnO | 27.4 (wt %) | |
| | Zn | 81 (wt %) | |

resulting in the transport of a significant quantity of water to the organic phase. Thus, it should be emphasized as a major drawback [15]. Organophosphorus compounds containing the phosphoryl group (P=O) such as D2EHPA have been widely used for extraction of zinc from various aqueous solutions at pH range of 1-3. Meanwhile, the use of Cyanex 302 increased the extraction of Zn in the pH range of 6-8.5 [17]. The substitution of sulfur in organophosphorus acids gives different properties to the extractant molecules, as predicted by the Hard-Soft Acid-Base (HSAB) principle. The donor atoms of common bases have electronegativities increasing in the order: $S < Br < N < Cl < O < F$. Reagents containing sulfur donor atoms are therefore expected to be strong extractants for soft metal ions such as Zinc and Nickel [18]. In addition, low hydrophilicity of Cyanex 302 (less oxygen atom) is a major advantage compare to TBP and D2EHPA. However, $pK_a$ of 5.63 for Cyanex 302 indicates that it may be inactive for the extraction of metal at lower pH conditions.

Process intensification generally converts conventional chemical processes into more cost-effective, productive, and environmentally friendly processes [19]. The branch of reactive extraction, which is synergistic extraction, can be employed to enhance the extraction performance, as well as improve the stability of the extracted complexes. Nathsarma and Devi [20] performed the separation and extraction of Zn and manganese (Mn) from a sulfate solution using several extractants such as Cyanex 272, PC88A, and D2EHPA in kerosene. It is found that Zn extraction could be performed at a lower pH compared to Mn [20]. Meanwhile, from the extraction perspective, synergism can be described as having the greater capability of extraction due to the use of extractant mixture compared to the individual capabilities of extractants [21].

Alamdari et al. [22] observed that commercially used D2EHPA usually consists of a small impurity concentration of M2EHPA, which influences solvent-extraction circuits when D2EHPA decomposes and yields an undesirable antagonistic effect toward metal extraction. The addition of TBP as a co-extractant together with D2EHPA helps to increase the separation efficiency and the phase separation of cadmium and Zn. When Cyanex 302 is added to D2EHPA as a co-extractant, the synergistic effect helps to improve the extraction capacity of Zn and Mn. Thus, the use of Cyanex 302 improved the extraction of Zn and Mn [17]. Synergistic effects of D2EHPA/Cyanex 302 in kerosene system were investigated by Darvishi et al. [23] to extract nickel dan cobalt. Synergistic effects were also reported by mixing amine and organophosphorus acid. For instance, Wachter et al. [38] investigated the synergic and antagonistic effect of a mixture of amines and phosphoric acid in the extraction of metals.

In order to determine a suitable extractant(s), it is very advantageous to investigate the reactive extraction mechanism, the stoichiometry of extractants, the identification of new bond formation such as the interaction between extractants and metal ions, or the interaction between extractants in the synergistic system and others. Formerly, researchers have explained the reactive extraction mechanism by focusing on the stoichiometry of extractants [23,24]. The equilibrium slope method is widely employed to determine metal-extractant complexes stoichiometry in the organic phase [24]. Through this method, only the equation of reaction stoichiometry can be described whereas the properties of new bond formation in the organic phase are disregarded. Fourier Transform Infrared (FTIR) spectroscopy was employed to overcome the limitation of previous approaches. This technique offers an alternative to identifying chemical bonds such as covalent bonds and functional groups in organic or inorganic compounds [25].

Although the extraction of Zn by mixed extractants has been the subject of many papers, there are gaps in knowledge that require attention. All the aforementioned studies did not consider the possible polymerization structure and different ratios of organic phase compositions. Moreover, once synergism extractant is achieved, regeneration of the organic phase for reusing should be considered. Therefore, the focus of this paper is to investigate more deeply the behaviour of different organic phase compositions for the extraction of zinc from the aqueous solution. This study involves an analytical investigation to determine the relative proportions of different organic phase compositions that comprise the base and synergistic extractants. Then, the results were used to determine the possible polymerization structure where both qualitative and quantitative studies were applied. For the qualitative analysis, FTIR tests were carried out on individual extractant and extractants mixtures in order to identify newly formed bonds and the structure of the complex formation in the organic phase. Concerning the quantitative studies, the method of slope analysis was used. A complementary study was performed to investigate the most effective stripping agent of Zn from Zn-loaded extractant mixture and the strip structure was also determined. In the last subsection, the regeneration and recycling capacity of synergism D2EHPA-Cyanex 302 mixture after extraction and stripping process was studied in detailed. Therefore, synergism among several extractants is one of the approaches that can be utilised for intensifying reactive extraction process since it can synergize the reaction while reducing chemical consumption.

## 2. Methodology

### 2.1. Reagents

The reactive extraction reagents used in the experiment are di-(2-ethylhexyl) phosphoric acid (D2EHPA, 97% purity, Sigma-Aldrich), diisooctylthio phosphinic acid (Cyanex 302, 95% purity, Sigma-Aldrich), triethanolamine (TEA, 99% purity, Merck), and tributyl phosphate (TBP, 99% purity, Acros Organics). Kerosene (Sigma-Aldrich) was used as a diluent in the experiment and Zn solution (100 ppm) was prepared by dissolving $ZnCl_2$ (Sigma-Aldrich, 99%) in distilled water. In the experiments, pH was adjusted between 1 to 9. Hydrochloric acid (98% pure) and sodium hydroxide, from Merck, Germany, were used as pH modifiers. All chemicals were used without further purification.

### 2.2. Reactive Extraction

#### 2.2.1. Zinc Extraction using single extractant

The use of an extractant in the extraction process was varies for a single extractant and a mixture of extractants. The extraction process was conducted by adding an equivalent amount of 10 mL 0.01 M organic solution (extractant in kerosene) to the feed phase (Zn solution) and agitated via a mechanical shaker for 18 h at 320 rpm to reach equilibrium. After the extraction, the mixture was poured into a separation funnel and left for 5–10 min to separate aqueous and organic loaded phases. The aqueous and organic phases were separated via gravity settling. Sequentially, the treated Zn in the aqueous phase was analyzed for Zn concentration using atomic absorption spectroscopy (AAS). The extractant with the highest extraction efficiency was chosen as a base extractant and noted as Ext1 and Ext2.

#### 2.2.2. Zinc Extraction using synergist extractant

To formulate the synergistic formulation, the mixture of the chosen base extractant and potential synergistic extractant was tested in the extraction of Zn. The combination of the base and synergistic extractant is tabulated in Table 2. 10 mL of organic phase containing equal volume of base extractant and synergistic extractant (5 mL, 0.01 M) were mixed. Similarly, the extraction process and Zn concentration measurement were conducted based on the procedures as mentioned earlier. The synergistic extractant effect on the extraction percentage and synergistic coefficient was determined. The combination of extractants that provided a high extraction percentage and synergistic coefficient was selected for further study. The stoichiometry of the reaction between Zn and extractants was obtained and FTIR analysis was performed to study the extraction mechanism.

#### *2.2.3. Stripping process*

In the stripping part, the loaded organic phase from the extraction process was stripped to recover the solute for the recovery process. A mixture of 10 mL of organic loaded Zn from the extraction process and 10 mL of stripping agent solutions were placed in a mechanical shaker for Zn extraction at 320 rpm for 18 h. Upon completion, the aqueous stripping phase and organic phase was separated in a separating funnel in 5–10 min. The aqueous stripping phase or recovery phase was used to determine Zn ion concentration using AAS. All experiments were conducted at ambient temperature (25 ± 1 °C). The experiments were carried out in triplicates with fewer than 5% standard deviations. Fig. 1 shows flowchart for reactive extraction process.

### *2.3. Data Analysis*

The percentage of Zn extracted from the feed phase was obtained using Eq. (1):

$$\text{Extraction }(\%) = \frac{[C]_{in.aq} - [C]_{fi.aq}}{[C]_{in.aq}} \times 100\% \tag{1}$$

Where $[C]_{in.aq}$ is the concentration of Zn in the aqueous phase (ppm) before extraction and $[C]_{fi.aq}$ is the concentration of Zn after extraction.

The distribution ratio of Zn ion in which the ratio of Zn ion concentration being transported to the organic phase from the aqueous feed phase is represented in Eq. (2):

$$\text{Distribution ratio} = \frac{[C]_{org}}{[C]_{aq}} \tag{2}$$

Where $[C]_{org}$ is the concentration of Zn ion in the organic phase and $[C]_{aq}$ is the concentration of Zn ion in the aqueous phase.

Eq. (3) was used to determine the synergistic coefficient of extractants:

$$\text{Synergistic coefficient, R} = \frac{D_{mix}}{D_{extractant} + D_{synergist}} \tag{3}$$

Where $D_{mix}$ is the mixed extractants (base and synergist) distribution ratio, whereas $D_{extractant}$ and $D_{synergist}$ are the individual distribution ratios of the base and synergistic extractants, respectively.

The percentage of the stripping phase was determined using Eq. (4):

$$\text{Stripping }(\%) = \frac{C_s}{C_{org}} \tag{4}$$

**Table 2**
Combination of the base and synergist extractant.

| Base extractant | Synergist extractant |
|---|---|
| Ext1 | TEA |
| | TBP |
| | D2EHPA |
| | Cyanex 302 |
| Ext2 | TEA |
| | TBP |
| | D2EHPA |
| | Cyanex 302 |

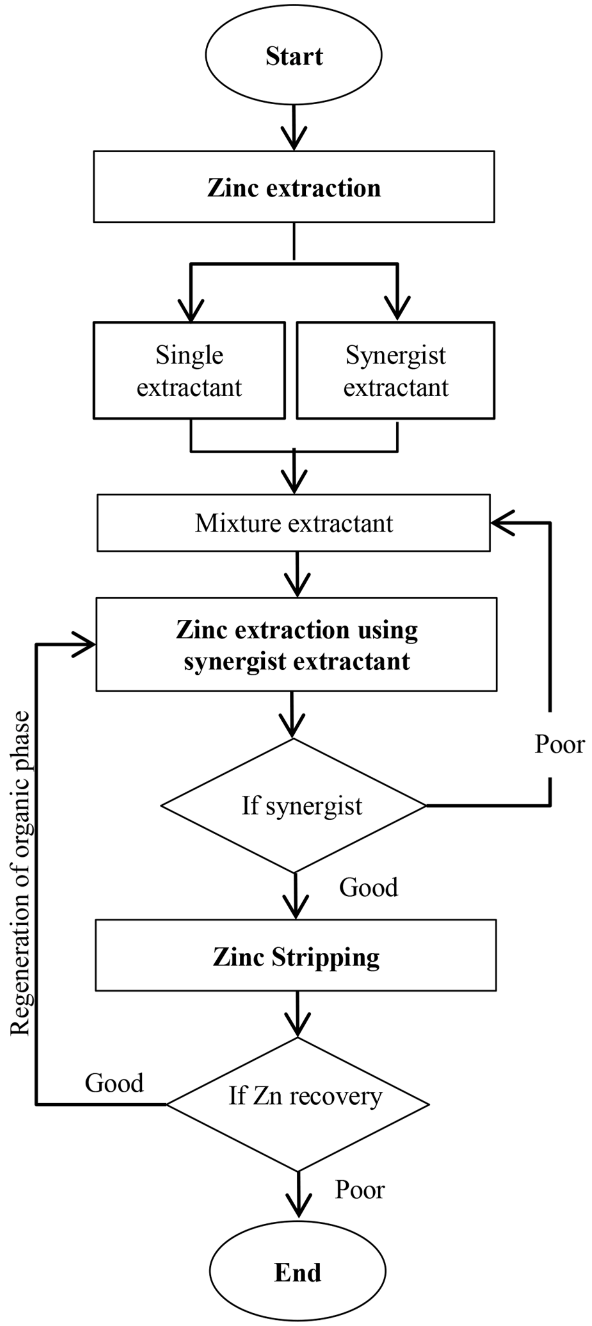


**Fig. 1.** Flow chart for reactive extraction process.

Where $C_s$ and $C_{org}$ represent the Zn concentration in the aqueous and organic phase after the stripping process (ppm), respectively.

## 3. Results and discussion

### *3.1. Selection of base and synergistic extractants*

Four types of extractants (Cyanex 302, D2EHPA, TEA, and TBP) were utilized to extract Zn as shown in Table 3. The distribution ratio and extraction performance of Zn increased by an order of magnitude: TBP < TEA < Cyanex 302 < D2EHPA. This result illustrates that the acidic extractant D2EHPA and Cyanex 302 have shown the capability of removing Zn molecules from the feed phase. This is due to the pH of the initial feed solution (4.9) that provides the lower proton concentration, hence resulting in higher metal extraction. Such behaviour is typical for

**Table 3**
Effect of distinct types of base extractant (Experimental conditions: [Zn(II) = 100ppm, [Extractant] = 0.01M, Agitation speed = 320rpm, Duration = 18h, Diluent = kerosene, Treat ratio = 1:1, Temperature = 26±1°C).

| Extractant | Distribution ratio, D | Extraction (%) |
|---|---|---|
| Cyanex 302 | 1.13 | 52 |
| D2EHPA | 1.78 | 64 |
| TEA | 0.15 | 13 |
| TBP | 0 | 0 |

the extraction of metal cations by cationic extractants of D2EHPA and Cyanex 302. These findings are in accordance with previous research by Darvishi et al. [26] which achieved high Zn extraction using single D2EHPA and Cyanex 302. Due to the presence of oxygen atoms connecting to the alkyl radicals and the phosphorus atom, D2EHPA (phosphoric acid) possessed a stronger acidic character and has a higher affinity for Zn extraction compared to Cyanex 302 (phosphinic acid). Meanwhile, the TEA show low extraction efficiency (13%) with distribution ratio, D=0.15 and TBP as a solvating extractant provide no extraction. This result might be because TEA and TBP are most suitable to extract neutral or anionic compounds and the speciation of Zn in the aqueous phase at high chloride concentrations and low pH, such as $ZnCl_4^{2-}$ and $ZnCl_3^-$. This result is comparable with the research by Randazzo et al. who observed high extraction of $ZnCl_4^{2-}$ using TBP as an extractant. As the Zn ion exists as cationic $Zn^{2+}$ in the solution, the extraction efficiency decreases [27]. To further the study for the organic formulation, D2EHPA and Cyanex 302 were employed as the base extractants and noted as Ext1 and Ext2 respectively.

In order to enhance the process performance, a synergistic extraction process consisting of a mixture of base extractants with other extractants with the same concentration were investigated, and the result is demonstrated in Fig. 2. The result shows that the mixture of D2EHPA-Cyanex 302 can separate Zn better than other extractants mixtures used in this study. The combination of D2EHPA-Cyanex 302 increased the Zn extraction from 64 to 72%. This is due to the addition of Cyanex 302 to D2EHPA change the dimeric D2EHPA to monomers by breaking the hydrogen bonds of D2EHPA-dimers and forming complex structures of Cyanex302-D2EHPA as illustrated in Eq. 5. These structures increase the HA groups of the D2EHPA in the extraction process, which increase the amount of extraction [28]. In addition, the presence of sulphur donor atoms (soft base) in Cyanex 302-D2EHPA complexes makes it an effective synergist extractant for zinc (soft metals ion). In terms of the phase medium, the stronger acidic Cyanex 302 can reduce the pKa value of D2EHPA for the maximum extraction of Zn from acidic aqueous solution [29]. A similar finding was presented by Sulaiman et al. [30] in the synergistic extraction of hexavalent chromium [Cr(VI)] using Cyanex 272 and Cyanex 302. The synergism effect resulted in a high Cr(VI) extraction from acidic feed solution owing to the stronger acidic Cyanex 302 that reduced the pKa value of Cyanex 272.

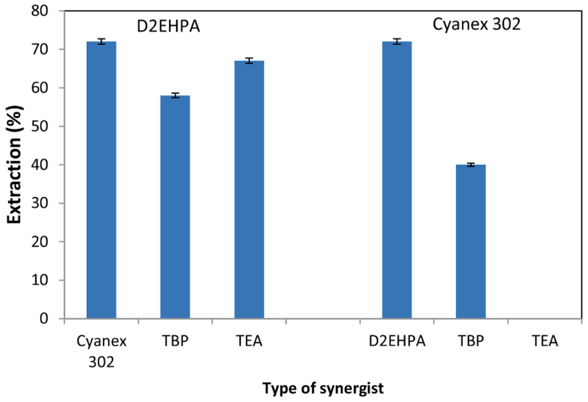


**Fig. 2.** Effect of different types of synergist extractant on zinc extraction. Experimental conditions: [Zn(II) = 100 ppm, [Mix Extractant] = 0.01M, Agitation speed = 320rpm, Duration = 18h, Diluent = kerosene, Treat ratio = 1:1, Temperature = 26±1°C).

$$(HA)_2 + (HB)_2 \rightarrow 2H^+ + [A_2.2HB]^{2-} \qquad (5)$$

There was no significant effect of D2EHPA toward synergistic system with TBP (58%) and TEA (67%) as illustrated in Fig. 2. The addition of TBP and TEA shows insignificant extraction performance compare to 64% zinc extraction using single D2EHPA. This antagonism effect of TBP and TEA is due to low acidic conditions to form the $ZnCl_2$ complex in the solution. Therefore, Zn is maintained in cationic formed [31]. As a result, the addition of TBP and TEA as a modifier or co-extractant could prevent the extraction of Zn.

In order to access the synergism of the system, the value R and D as Eq. 2 and 3 respectively, were evaluated. The synergism of the extraction process was assessed in terms of the synergistic coefficient (R). The value of $R > 1$ indicates synergism whereas the value of $R < 1$ represents antagonism [32]. Notably, the synergistic effect exists when the mixture distribution ratio is higher than the total distribution ratio of a single extractant (Eq. 3). Therefore, R>1 signify that the loading of extracted zinc into the organic phase increased with synergist extractant. Meanwhile, having R<1 means the extractant combination provides no synergistic effect towards zinc extraction. The R values for the different mixtures of base and synergistic extractant are presented in Table 4. The results show that synergism was observed with the use of D2EHPA and Cyanex 302 as the base and synergist extractant, respectively, indicating that the equal molar of 5 mM D2EHPA-Cyanex 302 system is more efficient in extracting Zn than the individual extractants of D2EHPA and Cyanex 302. This is due to increase the HA groups of the D2EHPA as discussed above. This finding is in line with Darvishi et al. for the extraction of Mn [26]. In addition, synergism of D2EHPA-Cyanex 302 extractants indicates intensification of reactive extraction process.

Meanwhile, based on the distribution ratio and R, the mixed extractant of D2EHPA-Cyanex 302 provided high values of D=2.8 and R=1.08. While, the other D and R values for D2EHPA-TBP, D2EHPA-TEA, Cyanex 302-TBP, and Cyanex 302-TEA mixtures were lower, thus suggesting the antagonism effect. The results and their interpretation are consistent with previous findings for cationic Zn.

### 3.2. *FTIR Spectroscopy Analysis*

FTIR measurements were performed to clarify the existence of interactions in the organic phase between the mixtures of D2EHPA-Cyanex 302 with Zn. Kerosene was employed as an organic phase/diluent in this reactive extraction process. Fig. 3 shows the FTIR spectra of pure D2EHPA and Cyanex 302, and the combination of D2EHPA-Cyanex 302 before and after Zn extraction. A previous study on the analysis of FTIR for the reactive extraction using the D2EHPA and Cyanex 302 system revealed that there was no interaction between kerosene and both extractants [21].

#### 3.2.1. *Single D2EHPA and Cyanex 302*

Fig. 3 illustrates the characteristic vibrational bands for single D2EHPA (green line), where P=O, P-O-H, and OH are identified at 1150,

**Table 4**
The value of R at a different base and synergistic enhancement factor

| Base extractants | Synergist Extractants | D | R |
|---|---|---|---|
| D2EHPA | Cyanex 302 | 2.80 | 1.08 |
| | TBP | 1.38 | 0.85 |
| | TEA | 2.03 | 0.97 |
| Cyanex 302 | D2EHPA | 2.80 | 1.08 |
| | TBP | 0.76 | 0.94 |
| | TEA | 0.02 | 0.02 |

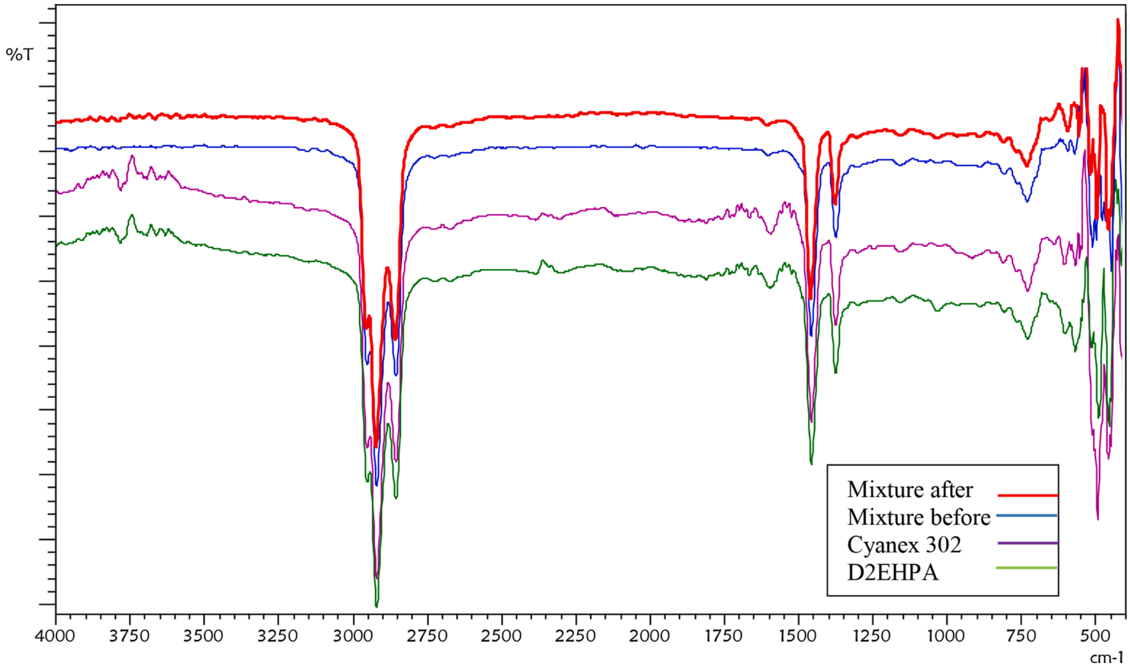


**Fig. 3.** FTIR spectra of single organic D2EHPA and Cyanex 302 solutions, mixture D2EHPA/Cyanex 302 extractant before and after the zinc extraction.

1033, and 3600 cm$^{-1}$, respectively. Meanwhile, the peak around 493 cm$^{-1}$ for the FTIR spectra of Cyanex 302 (purple line) is allocated to the P=S species. In accordance with Cyanex 302 structure, phosphorous (P) on one side is bonded to two alkoxy groups. Meanwhile, P on another side is double bonded to a sulfur atom and one hydroxyl group (OH). Additional distinctive vibration bands for Cyanex 302, for instance, P-OH and P-C stretch vibration, are identified as strong absorption bands at 3600 cm$^{-1}$ and 1033 cm$^{-1}$, respectively. For both single D2EHPA and Cyanex 302, the bands matching C-H stretching vibration present at 2920 and 2854 cm$^{-1}$, respectively. Meanwhile, the deformation of the C-H vibration band has occurred at the frequencies of 1458 cm$^{-1}$ and 1375 cm$^{-1}$. These are several bands that confirmed the occurrence of several $CH_3$ groups on a carbon atom. The FTIR spectra of organic D2EHPA and Cyanex 302 solutions are quite similar to those found by other researchers [23,14].

### 3.2.2. D2EHPA-Cyanex 302 Mixture

Looking at Fig. 3, the FTIR spectra of O-H characteristics vibrational peak at 3600 cm$^{-1}$ disappeared for the synergistic extractants. This phenomenon reveals that the D2EHPA dimer dissociates into two monomeric D2EHPA molecules in the presence of Cyanex 302, where the dissociation increases the capacity of D2EHPA. The existence of the O-H peak in D2EHPA exhibits the hydrogen bonds between each two D2EHPA molecules known as dimeric D2EHPA. Compared to dimeric D2EHPA, its dissociation enhanced the extraction efficiency due to the increment of D2EHPA capacity.

In addition, as can be observed, the P=S bond stretching vibration at 493 cm$^{-1}$ in the organic phase is separated into two distinct characteristic vibrations for phosphoryl groups. As a result, the phosphoryl group has been separated into two peaks with the same intensity at 500 and 479 cm$^{-1}$, referring to P=S in the single organic Cyanex 302 solution and P=S in the resulting complex produced from the reaction of D2EHPA and Cyanex 302, respectively. The C-H stretching peaks that occurred from 1375 to 2920 cm$^{-1}$ are fairly identical in the FTIR spectrum for all samples.

The FTIR spectrum of the D2EHPA-Cyanex 302 extractant mixture also illustrates that the peak of the phosphoryl group does not change. It can be seen that the positions of the P=O stretching vibration in both D2EHPA and the D2EHPA-Cyanex 302 extractant mixture are similar (i.e., 1150 cm$^{-1}$). The FTIR spectra characteristics vibrational peak positions for Cyanex 302, D2EHPA, their mixture, and the Zn-loaded organic phase are given in Table 5.

On the other hand, the FTIR spectra of a D2EHPA-Cyanex 302 extractant mixture loaded with Zn shows that the P=S bond stretching vibration at 479 and 500 cm$^{-1}$ in the organic phase-shifted to 493 cm$^{-1}$. The shift is due to the high attraction of the oxygen atom of P=O functional groups of organic solvent molecules for O-H hydrogen bonding of Cyanex 302 with the oxygen atom of P=O of D2EHPA. The shifting of peak position indicates the changes in a substance's bonding. Therefore, it can be concluded that the effect of D2EHPA as an extractant is stronger than Cyanex 302 in the mixture of D2EHPA-Cyanex 302. Only the characteristic vibrational band of Cyanex 302 (P=S) is affected by Zn interaction, while the vibration of D2EHPA (P=O) is unaffected. Fig. 4 shows that the P=S stretching vibration present at the frequency of 480-560 cm$^{-1}$ is absent in the former spectrum but exists in the latter spectrum. The presence of this stretching vibration indicates that the extraction reaction occurred owing to the extracted Zn containing Cyanex 302 in its complexes.

### 3.3. Effect of Mixed Extractant Concentrations

In order to obtain a high extraction performance, a proper amount of base and synergist extractants should be employed since each extractant

**Table 5**
The FTIR spectra characteristics vibrational peak positions for Cyanex 302, D2EHPA, their mixture and zinc loaded organic phase

| Corresponding bond | Cynex 302 | D2EHPA | Cyanex 302 mixed D2EHPA | Zinc loaded mixture of Cyanex 302/ D2EHPA |
|---|---|---|---|---|
| -OH | 3600 | 3600 | - | - |
| -C-H | 2920/ 2854 | 2920/ 2854 | 2920/2854 | 2920/2854 |
| -$CH_2$ | 1458/ 1375 | 1458/ 1375 | 1458/1375 | 1458/1375 |
| P=S | 493 | - | 479/500 | 493 |
| P=O | - | 1150 | 1150 | 1150 |
| P-O-C | - | 1033 | 1033 | 1033 |
| P-R | 1033 | - | 1033 | 1033 |

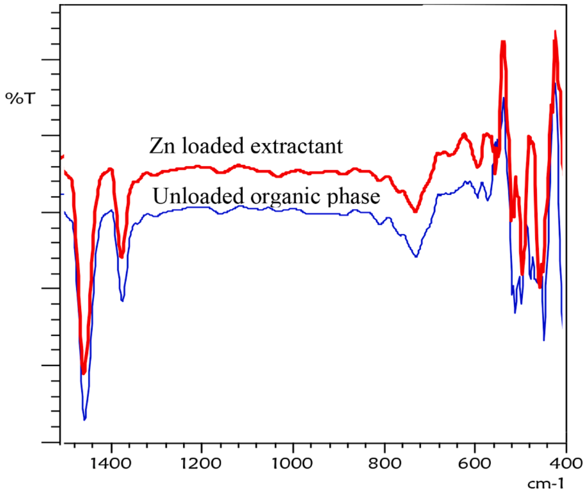


**Fig. 4.** FT-IR spectra of mixture extractant before (unloaded organic) and after (Zn loaded) the zinc extraction took place.

functions differently during Zn extraction. The extraction efficiency of Zn using D2EHPA-Cyanex 302 extractants mixture was investigated by varying the individual extractant concentration, as tabulated in Table 6. The concentration of D2EHPA was fixed, whereas the Cyanex 302 concentration was varied from 1 to 9 mM and vice versa.

The findings demonstrate that at a lower Cyanex 302 concentration (1 mM), the extraction of Zn increased as D2EHPA concentration increased up to 9 mM. The increase of extraction percentage (54.69% to 78.63%) is likely to be related to the forward shifting reaction based on Le Châtelier's principle when a higher amount of extractants were used [33]. Meanwhile, the extraction increased slightly with a further increase of D2EHPA concentration beyond 5 mM at higher concentrations of Cyanex 302 (7–9 mM), from 78.05% to 80.82% and 80.33% to 83.07%. This is because Cyanex 302 as a synergist was added in excess to the system, which may hinder Zn extraction. Furthermore, a small amount of Cyanex 302, which is relatively expensive compared to D2EHPA, is favourable for reducing the reagent cost. This finding is consistent with Darvishi et al. who stated Cyanex extractants are relatively expensive to be utilized commercially even though they provide good separation of nickel and cobalt [23]. The values of synergistic coefficient (R) were calculated and summarized in Table 7. The results indicate that the highest value of R (2.9) was obtained using 9 mM D2EHPA and 1 mM Cyanex 302. Through this synergism, eventhought the concentration of the based extractant of D2EHPA was reduced by 10% form 10 to 9 mM, the extraction performance become more effective. This indicates that current synergism system is able to minimize the consumption of chemicals. It can be inferred that the prospect of synergism has intensify the reactive extraction.

At fixed 9 mM D2EHPA, the R decreased from 2.9 to 2.1 with the addition of Cyanex 302. This result indicates that the synergistic extraction system with higher than 1 mM Cyanex 302 is insignificant. D2EHPA is well known to be fully protonated over the pH range studied ($pK_a = 1.35$) [34]. Meanwhile the $pK_a$ of 5.63 for Cyanex 302 [35] indicates that it may be inactive for the extraction of metal at lower pH conditions. In general, compounds dissociate at pH levels higher than their pKa value. Thus, the existence of non-protonated Cyanex 302 molecules at lower pH conditions occupied the aqueous-organic interface, thereby resisting Zn extraction since only D2EHPA acts as an extractant at such conditions.

**Table 6**
Influence of D2EHPA/Cyanex 302 concentration on extraction efficiency of zinc (experimental condition: agitation speed: 320 rpm; extraction time: 18 h)

| | [D2EHPA] (mM) | | | |
|---|---|---|---|---|
| [Cyanex 302] (mM) | 1 | 5 | 7 | 9 |
| **1** | 54.69 | 65.61 | 72.00 | 78.23 |
| **5** | 50.60 | 70.20 | 78.66 | 80.54 |
| **7** | 61.66 | 78.05 | 78.95 | 80.82 |
| **9** | 66.93 | 80.33 | 81.06 | 83.07 |

**Table 7**
Influence of base and synergist extractant concentration on synergistic coefficient.

| | [D2EHPA] (mM) | | | |
|---|---|---|---|---|
| [Cyanex 302] (mM) | 1 | **5** | **7** | 9 |
| **1** | 1.8 | 0.9 | 0.8 | 2.9 |
| **5** | 0.8 | 0.9 | 1.1 | 2.3 |
| **7** | 1.2 | 1.2 | 0.9 | 2.1 |
| **9** | 1.2 | 1.3 | 0.1 | 2.1 |

### *3.4. Determination of the Zn(II) organic complexes stoichiometry*

The method of slope analysis is extensively utilized to investigate the stoichiometry of reactive extraction equilibrium [36]. From the FTIR analysis, it is apparent there exists an interaction between the Zn ion and phosphoryl group of the extractant. In addition, the interaction via hydrogen bonding between Cyanex 302 and D2EHPA also can be observed. This outcome is in accordance with Wilson et al. [37] who specified that the extraction of $M^{2+}$ cation of the base metals by the mixture of commercial reagents of phosphoric, phosphonic, and phosphinic acids usually gives complexes with 4:1 of ligand:metal stoichiometry, $[M(L)_2(LH)_2]$. Therefore, the possible reactive extraction mechanism between Zn and acidic extractants mixture is illustrated in Eq. (6):

$$Zn^{2+}(aq) + n(HA)_2(org) + m(HB)_2(org) \rightarrow ZnA_{2n}.m(HB)_2(org) + 2nH^+(aq) \tag{6}$$

Where n and m are stoichiometric constants. To find the values of the constants of reactive extraction reaction stoichiometry by the method of slope analysis [21], the extraction reaction equilibrium constant $K_{ex}$ is defined in Eq. (7):

$$K_{ex} = \frac{[H^+]^{2n}_{aq} \cdot \left[ZnA_{2n}.m(HB)_2\right]_{org}}{Zn^{2+}{}_{aq} \cdot \left[(HA)_2\right]^n_{org} \cdot \left[(HB)_2\right]^m_{org}} \tag{7}$$

By substituting distribution ratio, D into Eq. (7), Eq. (8) is obtained:

$$D_{mix} = K_{ex} \frac{\left[(HA)_2\right]^n_{org} \cdot \left[(HB)_2\right]^m_{org}}{[H^+]^{2n}_{aq}} \tag{8}$$

Where $D_{mix}$ is the concentration ratio of Zn ion being transported to the organic phase from the aqueous feed phase using D2EHPA-Cyanex 302 extractants mixture. By performing the logarithm of Eq. (7), Eq. (8) can be obtained:

$$\log D_{mix} = \log K_{ex} + n\log\left[(HA)_2\right]_{org} + m\log\left[(HB)_2\right]_{org} + 2npH \tag{9}$$

Eq. (6) can validate the synergistic reactive extraction mechanism by Eq. (9). At constant pH and constant Cyanex 302 concentration (7 mM), the plot of the log $D_{mix}$ against log $[HA]_{org}$ gives straight lines. As shown in Fig. 5, the slopes of the graph log $D_{mix}$ vs. log $[HA]_{org}$ give a value of 0.968, indicating that one molecule of D2EHPA is required for Zn(II) extraction ($n = 1$). The same method was repeated to determine the number of Cyanex 302 molecules. Log $D_{mix}$ versus log $[HB]_{org}$ was plotted with all other parameters held constant. Based on Fig. 6, the slope of 1.008 was obtained, suggesting that one molecule of Cyanex 302 reacts with Zn during the extraction process ($m = 1$). Considering the FTIR analysis and method of slope analysis results, the reaction equation of Zn with the synergistic mixtures of D2EHPA-Cyanex 302 can be expressed in Eq. (10):

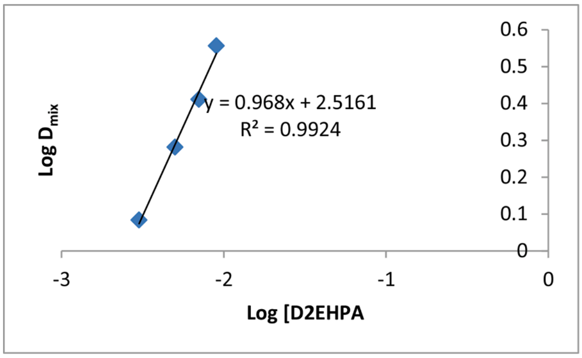


**Fig. 5.** Stoichiometry of zinc extraction equilibrium using D2EHPA.

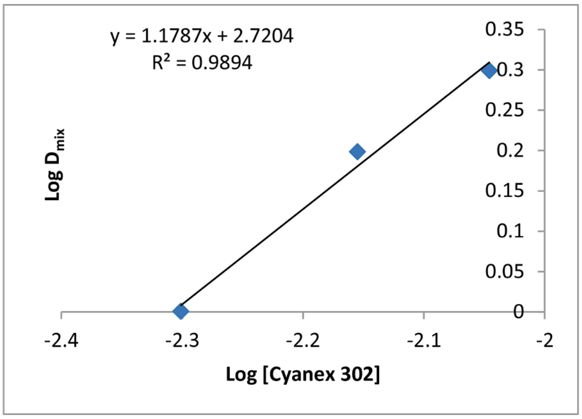


**Fig. 6.** Stoichiometry of zinc extraction equilibrium using Cyanex 302.

$$Zn^{2+}(aq) + (HA)_2(org) + (HB)_2(org) \rightarrow Zn.A_2.2HB(org) + 2H^{+}(aq) \quad (10)$$

Fig. 7 demonstrates the proposed polymerization structure of the Zn with the synergistic mixtures of D2EHPA-Cyanex 302 complex, Zn•A$_2$•2HB. It is obvious that Cyanex 302 functions better as a modifier than as an extractant for Zn. Meanwhile, D2EHPA is a key component as an extractant in the extraction of Zn.

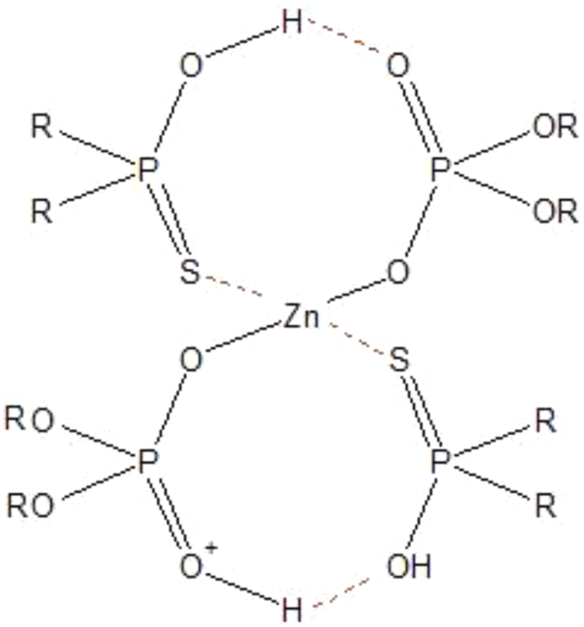


**Fig. 7.** The proposed structure of the Zn with the D2EHPA-Cyanex 302 complex.

### 3.5. Kinetics of Zinc Extraction

Extraction time, plays an important role in obtaining optimal extraction efficiency. Fig. 8 shows the extraction efficiency of Zn at extraction time variation from 1 to 60 minutes. The finding indicates that with an increment of extraction time to 5 min, the extraction performance improved up to 78%. As the extraction time is extended, the percentage of Zn extraction becomes almost plateau, indicating that the extraction equilibrium was attained. This result signifies that the equilibrium extraction time was reached after 5 min of the extraction process. The mixture of D2EHPA-Cyanex 302 demonstrated improved extraction kinetic than the single D2EHPA extraction, as discussed in Section 3.1, wherein only 64% of Zn extraction performance was achieved.

The kinetics of Zn extraction during the synergistic reactive extraction system can be determined by Eq. (11):

$$ln\frac{(Zn)_i}{(Zn)_f} = kt \quad (11)$$

Where k designates the constant extraction rate, whereas $(Zn)_i$ is the concentration of Zn in the aqueous feed phase at the initial state and $(Zn)_f$ signify Zn concentration at time t. The graph of $ln\frac{(Zn)_i}{(Zn)_f}$ versus t is presented in Fig. 9. The linear slope, indicates that the extraction of Zn using a mixture of D2EHPA-Cyanex 302 extractants follows the first-order reaction kinetics with a k value of 0.3667 min$^{-1}$. The extraction kinetics of zinc with D2EHPA have been explored by several authors and result in range 3–7 min$^{-1}$ [38]. It can be deduced that the kinetics of Zn extraction is very fast and synergism extractant has intensify the reactive extraction.

### 3.6. Effect of stripping agent

A stripping agent is vital in the back-extraction of Zn for recovery purposes. Several stripping agents were investigated for the back-extraction of Zn from the loaded organic phase. The stripping agents (e.g., hydrochloric acid (HCl), sulfuric acid ($H_2SO_4$), nitric acid ($HNO_3$), thiourea, and acidic thiourea) were used with an aqueous/organic ratio of 1:1. The results presented in Fig. 10 show that the stripping percentage of Zn increased in the following order: thiourea ($S = 6\%$) < HCl ($S = 64\%$) < $HNO_3$ ($S = 69\%$) < $H_2SO_4$ ($S = 72\%$) < acidic thiourea ($S = 78\%$). The lower stripping recorded using thiourea alone as a stripping agent is due to the low rate of ligand displacement, leading to the inefficiency of thiourea for the back-extraction of Zn complexes. Meanwhile, compared to a single acidic stripping agent and thiourea, the

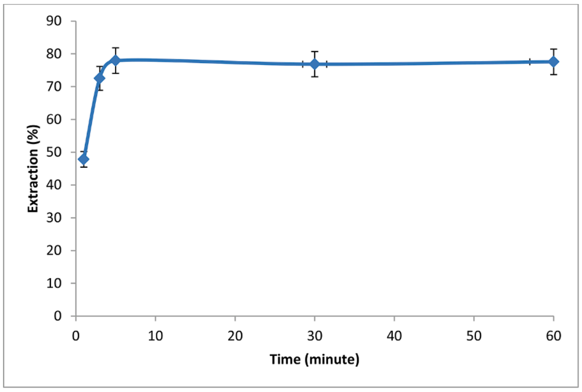


**Fig. 8.** Effect of extraction time on the extraction of zinc using synergistic D2EHPA/Cyanex 302 mixture (experimental condition: agitation speed: 320 rpm; D2EHPA: 9 mM; Cyanex 302: 1 mM).

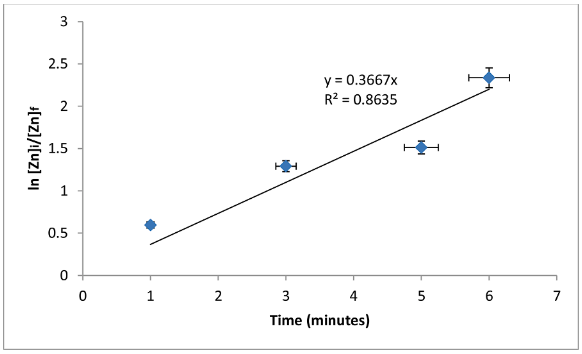


**Fig. 9.** Kinetic of Zn extraction zinc using synergistic D2EHPA/Cyanex 302 mixture (experimental condition: agitation speed: 320 rpm; D2EHPA: 9 mM; Cyanex 302: 1 mM).

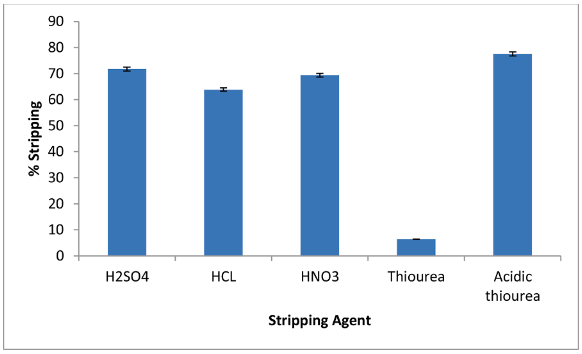


**Fig. 10.** Effect of stripping agent types on the stripping of zinc (experimental condition: feed: loaded organic phase (zinc/D2EHPA/Cyanex 302); extraction time: 18 h; agitation speed: 320 rpm; [stripping agent]: 0.1 M).

capacity of thiourea to achieve an outstanding result depends on its protonation behaviour, where the mixture of thiourea and $H_2SO_4$ (acidic thiourea) provided the highest percentage of Zn stripping of 78%. This finding can be attributed to the fact that thiourea is protonated in an acidic medium (Eq. 12). The protons bind to the sulfide atoms that favour the metal ions' interaction with nitrogen atoms [39]. This mixture offers contribution towards intensification of reactive extraction process since $H_2SO_4$ helps dissolving the thiourea properly as well as avoiding the precipitation. Such condition increases the substitution reaction of thiourea with the sulphate ion from the zinc loaded mixture system, thus enhancing stripping behaviour. This reaction agrees with Akretche et al. who asserted that thiourea has the ability to extract metals in acidic media [40]. Consequently, at the end of the reactive extraction process, a metal-free D2EHPA-Cyanex 302 stream is obtained and ready to be used for subsequent Zn extraction from aqueous solutions. Further stripping studies were carried out using acidic thiourea.

$$SC(NH_2)_2 + H_2SO_4 \leftrightarrow HSC(NH_2)_2{}^+ + HSO_4{}^- \tag{12}$$

### 3.7. Effect of stripping agent concentration

To enrich the Zn recovery in the strip solution, studies were carried out by varying acidic thiourea concentrations from 0.1 to 0.45 M as shown in Fig. 11. The finding shows that insufficient concentration of thiourea (0.1 M) in the stripping phase resulted in poor stripping efficiency. It is due to the insufficient stripping agent to strip Zn from its complexes in the organic phase into the stripping phase. Further increase of acidic thiourea concentration was increased the Zn stripping from 77% to 99%. This is due to the increased production of thiourea cation, resulting in the increment of protonated thiourea that reacts with Zn complexes. This condition increases the capacity of Zn ion to be stripped into the stripping phase, hence enhancing stripping performance. Similar findings have been observed by Mokhtari and Pourabdollah [41], where increasing the stripping agent concentration leads to more efficient stripping of metals.

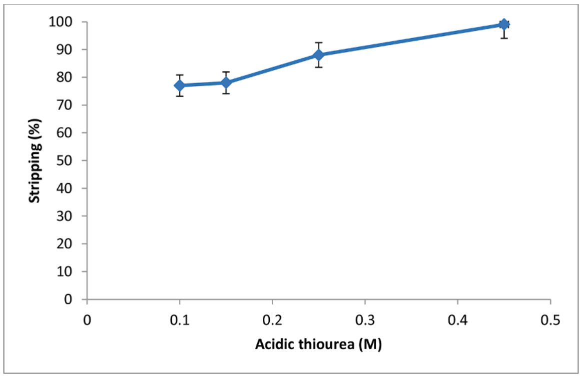


**Fig. 11.** Effect of stripping agent concentration on the stripping of zinc (Experimental conditions: [Zn] = 88 ppm; A/O = 1:1; extraction time = 18 hrs; agitation speed = 320 rpm; T = ± 26°C; diluent = Kerosene).

By assuming that all the thiourea in $H_2SO_4$ presented in the system reacted with Zn complex, the mechanism of solute stripping was examined by constructing a graph of log D versus log [acidic thiourea], as demonstrated in Fig. 12. The plot provides a straight line with a positive slope, m of 2.22, which is near 2.0. Therefore, the ratio of Zn-extractant complexes to thiourea in $H_2SO_4$ solution was determined as 1:2. Hence, two moles of acidic thiourea react with one mole of Zn-carrier complex during the stripping process as shown in Eq. 13. Meanwhile, the possible structure for di(thiourea)zinc(II) sulfate is shown in Fig. 13.

$$\begin{aligned} &Zn\cdot A_2\cdot B_{2(org)} + 2\left[(NH_2)_2HCS\right]^+{}_{(aq)} + SO_{4(aq)}^{2-} + 2H^+{}_{(aq)} \\ &\rightarrow ZnSO_4\left[CS(NH_2)_2\right]_{2(aq)} + (HA)_{2(org)} + (HB)_{2(org)} \end{aligned} \tag{13}$$

Where $[(NH_2)_2HCS]^+$ is acidic thiourea in the aqueous phase.

### 3.8. Effect of pH

The effect of pH on the extraction efficiency of Zn ions is shown in Table 8. As observed, the increase in pH (lower proton concentration) results in higher zinc extraction. Results show that insignificant metal uptake occurs at a pH of 1. These results are likely to be related to at high chloride concentrations and low pH, Zn exists as anionic compounds such as $ZnCl_4^{2-}$ and $ZnCl_3^-$ which is not extractable by D2EHPA-Cyanex 302 system [27]. On the other hand, although Zn exists as a cationic compound at pH 3, low extraction efficiency was observed due to the

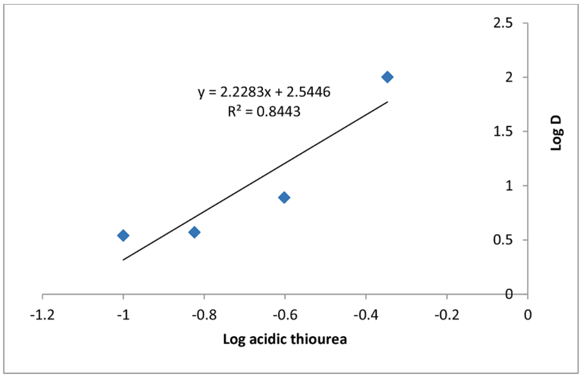


**Fig. 12.** stoichiometric plots for the stripping equilibrium of zinc using acidic thiourea as stripping agent.

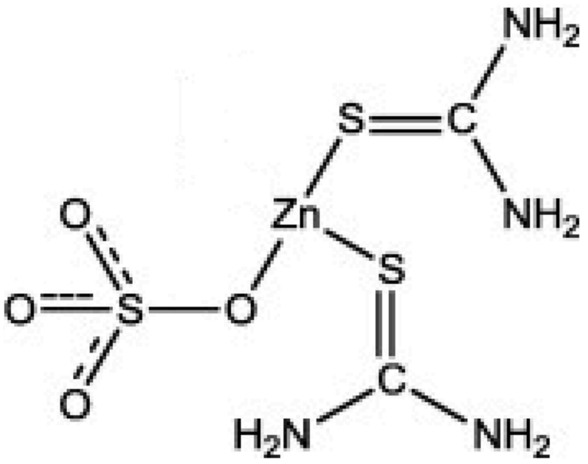


**Fig. 13.** The possible structure of the stripped complex.

protonation of D2EHPA-Cyanex 302 [42]. Hence, the high $H^+$ concentration competes with Zn to react with organic matter.

It was observed that extraction of zinc increased with pH, and was completely extracted into the organic phase at equilibrium pH of 5 as shown in Table 8. During extraction of metals using acidic extractants, the extraction is governed by the cation exchange reaction in which the protons ($H^+$) are released, causing the decrease in pH equilibrium. Meanwhile, an increase in pH leads to a decrease in the $H^+$ concentration in the solution. Therefore, the competition between zinc and protons to react with D2EHPA-Cyanex 302 in organic solution decreased and the extraction efficiency increased [43]. This trend has also been observed by Katoozi and Anari [44].

### 3.9. *Regeneration and recycling of organic phase*

Organic phase regeneration is one of the main advantages of reactive extraction [30]. A process for extraction and stripping of Zn from chloride solutions by D2EHPA-Cyanex 302 was shown in Fig. 14. All experiments on the regeneration and recycling of organic phase were conducted under the optimum condition in the extraction and stripping process. The stripped organic phase was used for the regeneration of the extraction and stripping process.

Six extraction and stripping cycles were carried out at the same experimental conditions, and the recovery of each stage was calculated from the amount of Zn extracted into the organic phase at each particular cycle. The obtained results are shown in Table 9. The extraction and stripping percentage of Zn was unchanged up to four cycles, indicating that the regeneration and recycling capacity of the organic phase was obtained in the present study. The results show that at cycle 5, the stripping process diminishes Zn's extraction from the Zn-loaded organic phase where only 78% of Zn was striped.

This is supported by FTIR analysis comparison between cycle 4 and 5 of organic loaded, as shown in Fig. 15. In comparison to the first four cycle of FTIR in organic loaded, after 5 cycle of regeneration, O-H vibration band were appeared at 3400 $cm^{-1}$. The existence of the O-H peak in D2EHPA exhibits the hydrogen bonds of dimeric D2EHPA. Therefore, the pKa value decreased due to attractive inductive effects. The lower the value of pKa, the stronger the bonding of zinc with the D2EHPA-Cyanex 302 (ligand) makes the stripping of zinc is hard to detach. Similar observation was made by Sulaiman et al. [45] who stated that the stronger the acid, the greater its ability to donate its protons. Hence, the liquid organic phase will accumulate with unstripped Zn. As can be seen at cycle 6, the contaminated organic phase will disturb the Zn extraction from the feed phase during recycling where only 72% of Zn was extracted. Current result is more effective compare to previous work by Xu et al. [46] which on the 2nd extraction-stripping-washing process, the extraction performance already decreases. Therefore, this synergists system proof that the intensification effect for synergism of extraction and the regeneration of the organic phase.

**Table 8**
Effect of pH on the extraction of zinc using synergistic D2EHPA-Cyanex 302 mixture (experimental condition: agitation speed: 320 rpm; D2EHPA: 9 mM; Cyanex 302: 1 mM).

| pH initial | pH equilibrium | % Extraction |
|---|---|---|
| 1 | 0.96 | 0 |
| 3 | 2.05 | 46 |
| 5 | 3.13 | 82 |
| 7 | 6.05 | 85 |
| 9 | 5 | 99 |

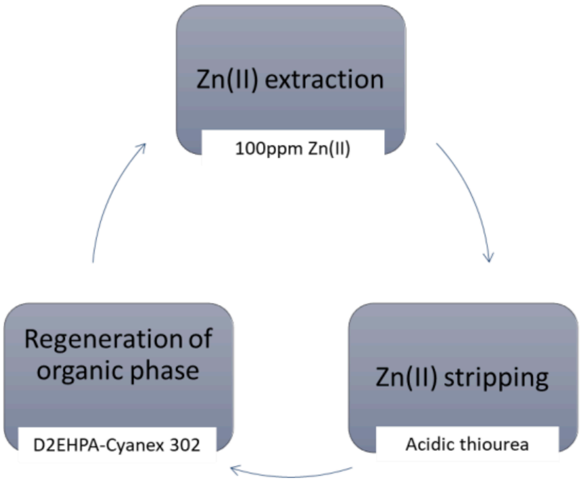


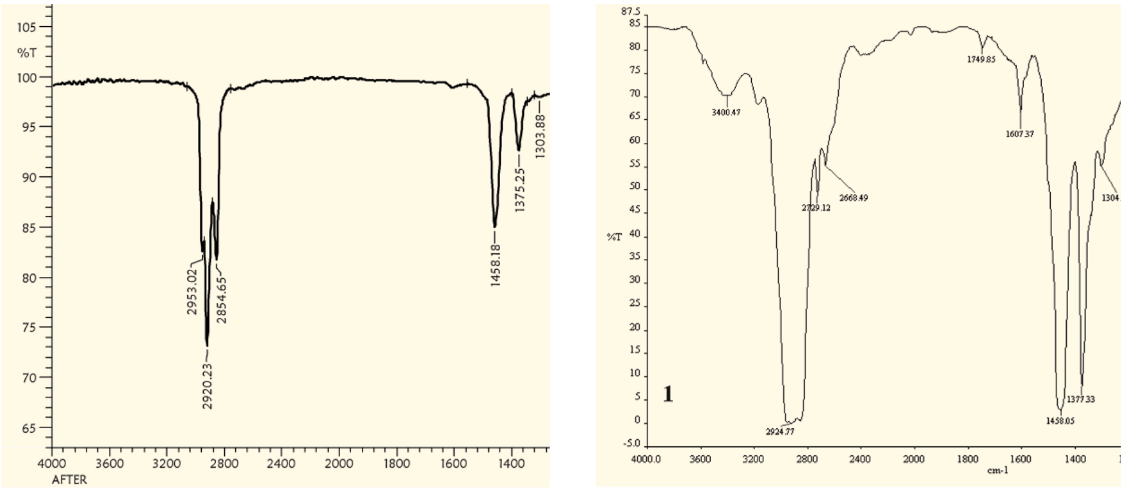
**Fig. 14.** A schematic process of extraction and stripping of Zn (II) from chloride solutions by D2EHPA-Cyanex 302 mixture.

**Table 9**
Regeneration and recycling capacity of D2EHPA-Cyanex 302 mixture.

| No. of run | Extraction (%) | Stripping (%) |
|---|---|---|
| 1 | 98 | 99 |
| 2 | 99 | 99 |
| 3 | 99 | 99 |
| 4 | 99 | 99 |
| 5 | 99 | 78 |
| 6 | 72 | 63 |

## 4. Prospect of extractive extraction synergism

Synergism of extractants formulation for organic and inorganic extractions has become a new perspective employed in the reactive extraction. Several benefits can be observed through synergism, including reducing the total concentration used and the fast reaction process. Based on this study, throughout the synergistic extraction of Zn, there is a huge difference in terms of the extraction efficiency, where a mixture of 9 mM D2EHPA and 1 mM Cyanex 302 (a total of 0.01 M) achieved almost 100% of Zn extraction compared to 52% for a single extractant of 0.01 M Cyanex 302 and 64% extraction for 0.01 M D2EHPA. Therefore, the amount of the extractants used can be reduced and the process becomes more sustainable due to less chemical used. Additionally, a synergistic system can achieve equilibrium within a shorter time.



Cycle 4

Cycle 5

**Fig. 15.** FT-IR spectra of organic loaded for cycle 4 and 5

## 5. Conclusions

The behaviour of different organic phase compositions for the extraction of zinc from the aqueous solution was studied in term of synergism and extraction performance. The discussion contained the synergism interaction, its probable polymerization structure, and distinct ratios of organic phase compositions. Almost 99% of zinc was extracted using synergist mixture of of 9 mM D2EHPA and 1 mM Cyanex 302. It is found that the effect of D2EHPA is more significant in the extraction process and Cyanex 302 was acting as a modifier or synergistic extractant. The possible extracted Zn structure is $Zn\bullet A_2\bullet 2HB$. Meanwhile, acidic thiourea was selected as a stripping agent with a stripping performance of 99%. The extracted species is likely to be di(thiourea)zinc(II) sulfate, $ZnSO_4[CS(NH_2)_2]$. The extraction and stripping percentages of Zn was consistent in a good performance up to four cycles. The limitation of this system for real waste application is a regeneration of organic phase due to impurities and should be considered for further study. It is expected this synergist reactive reaction can reduce the chemical use and increase the extraction performance.

## CRediT authorship contribution statement

**Norul Fatiha Mohamed Noah:** Conceptualization, Methodology, Writing – original draft, Formal analysis. **Norasikin Othman:** Supervision, Validation, Data curation, Formal analysis, Writing – review & editing. **Izzat Naim Shamsul Kahar:** Writing – review & editing. **Sazmin Sufi Suliman:** Writing – review & editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgement

The grant from Professional Development Research University (PDRU) (Q.J130000.21A2.05E51) is acknowledged for making this research possible. This research was also funded by the Research University Grant from Universiti Teknologi Malaysia (UTM) (Q. J130000.4551.00N02).

## References

[1] S. Imdad, R.K. Dohare, A critical review on heavy metals removal using ionic liquid membranes from the industrial wastewater, Chem. Eng. Process. - Process Intensif. 173 (2022), 108812, https://doi.org/10.1016/J.CEP.2022.108812.

[2] M.K. Jha, V. Kumar, R.J. Singh, Review of hydrometallurgical recovery of zinc from industrial wastes, Resour. Conserv. Recycl. 33 (2001) 1–22, https://doi.org/10.1016/S0921-3449(00)00095-1.

[3] H. Yan, L.Y. Chai, B. Peng, M. Li, N. Peng, D.K. Hou, A novel method to recover zinc and iron from zinc leaching residue, Miner. Eng. 55 (2014) 103–110, https://doi.org/10.1016/j.mineng.2013.09.015.

[4] M. Bartkowska, M. Regel-Rosocka, J. Szymanowski, Extraction of zinc(II), iron(III) and iron(II) with binary mixtures containing tributyl phosphate and di(2-ethylhexyl)phosphoric acid or cyanex 302, Physicochem. Probl. Miner. Process. 36 (2002) 217–224. http://www.journalssystem.com/ppmp/Extraction-of-zinc-II-iron-III-and-iron-II-with-binary-mixtures-containing-tributyl,79544,0,2.html.

[5] W. Liu, L. Lü, Y. Lu, X. Hu, B. Liang, Removal of chloride from simulated acidic wastewater in the zinc production, Chinese J. Chem. Eng. 27 (2019) 1037–1043, https://doi.org/10.1016/J.CJCHE.2018.06.025.

[6] V. Eyupoglu, R.A. Kumbasar, Extraction of Ni(II) from spent Cr-Ni electroplating bath solutions using LIX 63 and 2BDA as carriers by emulsion liquid membrane technique, J. Ind. Eng. Chem. 21 (2015) 303–310, https://doi.org/10.1016/j.jiec.2014.02.037.

[7] S.I. El Dessouky, Y.A. El-Nadi, I.M. Ahmed, E.A. Saad, J.A. Daoud, Solvent extraction separation of Zn(II), Fe(II), Fe(III) and Cd(II) using tributylphosphate and CYANEX 921 in kerosene from chloride medium, Chem. Eng. Process. Process Intensif. 47 (2008) 177–183, https://doi.org/10.1016/j.cep.2007.03.002.

[8] M.K. Sinha, S.K. Sahu, P. Meshram, B.D. Pandey, Solvent extraction and separation of zinc and iron from spent pickle liquor, Hydrometallurgy 147-148 (2014) 103–111, https://doi.org/10.1016/J.HYDROMET.2014.05.006.

[9] T. Hosseini, N. Mostoufi, M. Daneshpayeh, F. Rashchi, Modeling and optimization of synergistic effect of Cyanex 302 and D2EHPA on separation of zinc and manganese, Hydrometallurgy 105 (2011) 277–283, https://doi.org/10.1016/J.HYDROMET.2010.10.015.

[10] Y. Wang, Y. He, S. Yin, H. Long, S. Li, Research on extraction of zinc from spent pickling solution using Aliquat 336, Hydrometallurgy 193 (2020), 105322, https://doi.org/10.1016/J.HYDROMET.2020.105322.

[11] xxx Recovery of Zn(II), Mn(II) and Co(II) from the zinc plant residue using the solvent extraction with CYANEX 302 and D2EHPA/TBP: Stoichiometry and structural studies - ScienceDirect, (n.d.). https://www-sciencedirect-com.ezproxy.utm.my/science/article/pii/S0892687521001734 (accessed May 30, 2021).

[12] S. Aghazadeh, M. Gharabaghi, Z. Shafaei, Thermodynamical and catalytic aspects of zinc separation from aqueous solution, Chinese J. Chem. Eng. 26 (2018) 2455–2460, https://doi.org/10.1016/J.CJCHE.2018.07.022.

[13] S. Hussaini, A.M. Tita, S. Kursunoglu, S. Top, Z.T. Ichlas, U. Kar, M. Kaya, Pb-Zn recovery from a malic leach solution of a carbonate type ore flotation tailing by precipitation and solvent extraction, Sep. Purif. Technol. 272 (2021), 118963, https://doi.org/10.1016/j.seppur.2021.118963.

[14] O.S.M. Kani, A. Azizitorghabeh, F. Rashchi, Recovery of Zn(II), Mn(II) and Co(II) from the zinc plant residue using the solvent extraction with CYANEX 302 and D2EHPA/TBP: Stoichiometry and structural studies, Miner. Eng. 169 (2021), 106944, https://doi.org/10.1016/j.mineng.2021.106944.

[15] A. Grzeszczyk, M. Regel-Rosocka, Extraction of zinc(II), iron(II) and iron(III) from chloride media with dibutylbutylphosphonate, Hydrometallurgy 86 (2007) 72–79, https://doi.org/10.1016/j.hydromet.2006.11.005.

[16] K.K. Sahu, R.P. Das, Synergistic extraction of iron(III) at higher concentrations in D2EHPA-TBP mixed solvent systems, Metall. Mater. Trans. B. 28 (1997) 181–189, https://doi.org/10.1007/s11663-997-0083-6.

[17] T. Hosseini, F. Rashchi, E. Vahidi, N. Mostoufi, Investigating the Synergistic Effect of D2EHPA and Cyanex 302 on Zinc and Manganese Separation, Sep. Sci. Technol. 45 (2010) 1158–1164, https://doi.org/10.1080/01496391003727908.

[18] Y. Liu, H.S. Jeon, M.S. Lee, Solvent Extraction of Pr and Nd from Chloride Solution by Mixtures of Acidic Extractants and LIX 63, 54 (2016). 10.3365/KJMM.2016.54.8.592.

[19] H. Wang, A. Mustaffar, A.N. Phan, V. Zivkovic, D. Reay, R. Law, K. Boodhoo, A review of process intensification applied to solids handling, Chem. Eng. Process. Process Intensif. 118 (2017) 78–107, https://doi.org/10.1016/J.CEP.2017.04.007.

[20] K.C. Nathsarma, N. Devi, Separation of Zn(II) and Mn(II) from sulphate solutions using sodium salts of D2EHPA, PC88A and Cyanex 272, Hydrometallurgy (2006), https://doi.org/10.1016/j.hydromet.2006.05.004.

[21] A. Azizitorghabeh, F. Rashchi, A. Babakhani, Stoichiometry and structural studies of Fe(III) and Zn(II) solvent extraction using D2EHPA/TBP, Sep. Purif. Technol. 171 (2016) 197–205, https://doi.org/10.1016/j.seppur.2016.07.037.

[22] E. Alamdari, D. Moradkhani, D. Darvishi, M. Askari, D. Behnian, Synergistic effect of MEHPA on co-extraction of zinc and cadmium with DEHPA, Miner. Eng. - Min. ENG. 17 (2004) 89–92, https://doi.org/10.1016/j.mineng.2003.10.003.

[23] D. Darvishi, D.F. Haghshenas, E.K. Alamdari, S.K. Sadrnezhaad, M. Halali, Synergistic effect of Cyanex 272 and Cyanex 302 on separation of cobalt and nickel by D2EHPA, Hydrometallurgy 77 (2005) 227–238, https://doi.org/10.1016/j.hydromet.2005.02.002.

[24] M.B. Mansur, S.D.F. Rocha, F.S. Magalhães, J. dos S. Benedetto, Selective extraction of zinc(II) over iron(II) from spent hydrochloric acid pickling effluents by liquid-liquid extraction, J. Hazard. Mater. 150 (2008) 669–678, https://doi.org/10.1016/j.jhazmat.2007.05.019.

[25] S.H. Chang, T.T. Teng, N. Ismail, Efficiency, stoichiometry and structural studies of Cu(II) removal from aqueous solutions using di-2-ethylhexylphosphoric acid and tributylphosphate diluted in soybean oil, Chem. Eng. J. 166 (2011) 249–255, https://doi.org/10.1016/j.cej.2010.10.069.

[26] D. Darvishi, D.F. Haghshenas, E.K. Alamdari, S.K. Sadrnezhaad, Extraction of ZN, MN and CO from ZN-MN-CO-CD-NI containing solution using D2EHPA, Cyanex® 272 and Cyanex® 302, Int. J. Eng. Trans. B Appl. 24 (2011) 183–192.

[27] S. Randazzo, V. Caruso, D. Ciavardelli, G. Micale, M. Morreale, Recovery of zinc from spent pickling solutions by liquid-liquid extraction using tbp, Desalin. Water Treat. 157 (2019) 110–117, https://doi.org/10.5004/dwt.2019.24111.

[28] V. Iv, Synthesis of Di-(2-ethylhexyl) Phosphoric Acid (D2EHPA)-Tributyl Phosphate (TBP) Impregnated Resin and Application in Adsorption of Vanadium (IV), (2018) 1-12. 10.3390/min8050206.

[29] R.N.R. Sulaiman, N.F.M. Noah, N. Othman, N. Jusoh, M.B. Rosly, Synergetic formulation of Cyanex 272/Cyanex 302 for hexavalent chromium removal from electroplating wastewater, Korean J. Chem. Eng. 38 (2021) 514–522, https://doi.org/10.1007/s11814-020-0702-3.

[30] R.N.R. Sulaiman, N.F.M. Noah, N. Othman, N. Jusoh, M.B. Rosly, Synergetic formulation of Cyanex 272/Cyanex 302 for hexavalent chromium removal from electroplating wastewater, Korean J. Chem. Eng. 38 (2021) 514–522, https://doi.org/10.1007/s11814-020-0702-3.

[31] F.S. Hoseinian, B. Rezai, M. Safari, D. Deglon, E. Kowsari, Separation of nickel and zinc from aqueous solution using triethylenetetramine, Hydrometallurgy 202 (2021), 105609, https://doi.org/10.1016/j.hydromet.2021.105609.

[32] L. Guo, J. Guo, W. Zhu, X. Jiang, Optimized synchronous extraction process of tea polyphenols and polysaccharides from Huaguoshan Yunwu tea and their antioxidant activities, Food Bioprod. Process. 100 (2016) 303–310, https://doi.org/10.1016/j.fbp.2016.08.001.

[33] N. Jusoh, M.B. Rosly, N. Othman, H.A. Rahman, N.F.M. Noah, R.N.R. Sulaiman, Selective extraction and recovery of polyphenols from palm oil mill sterilization condensate using emulsion liquid membrane process, Environ. Sci. Pollut. Res. (2020), https://doi.org/10.1007/s11356-020-07972-5.

[34] R.K. Biswas, R.A. Banu, M.N. Islam, Some physico-chemical properties of D2EHPA Part 2. Distribution, dimerization and acid dissociation constants in n-hexane/1 M (Na+,H+)SO42- system, interfacial adsorption and excess properties, Hydrometallurgy 69 (2003) 157–168, https://doi.org/10.1016/S0304-386X(02)00212-8.

[35] R.K. Biswas, M.A. Habib, H.P. Singha, Colorimetric estimation and some physicochemical properties of purified Cyanex 272, Hydrometallurgy 76 (2005) 97–104, https://doi.org/10.1016/j.hydromet.2004.09.005.

[36] H.A. Rahman, N. Jusoh, N. Othman, M.B. Rosly, R.N.R. Sulaiman, N.F.M. Noah, Green formulation for synthetic dye extraction using synergistic mixture of acid-base extractant, Sep. Purif. Technol. 209 (2019) 293–300, https://doi.org/10.1016/j.seppur.2018.07.053.

[37] A.M. Wilson, P.J. Bailey, P.A. Tasker, J.R. Turkington, R.A. Grant, J.B. Love, Solvent extraction: the coordination chemistry behind extractive metallurgy, Chem Soc Rev 43 (2014) 123–134, https://doi.org/10.1039/c3cs60275c.

[38] B. Wachter, H. Bart, T. Moosbrugger, R. Marr, Reactive liquid-liquid test system Zn/Di (2-ethyl hexyl) phosphoric acid/n-Dodecane. Equilibrium and kinetics, Chem. Eng. \& Technol. 16 (1993) 413–421.

[39] N. Othman, H. Mat, M. Goto, Separation of silver from photographic wastes by emulsion liquid membrane system, J. Memb. Sci. 282 (2006) 171–177, https://doi.org/10.1016/j.memsci.2006.05.020.

[40] D.-E. Akretche, A. Gherrou, H. Kerdjoudj, Electrodialysis of solutions obtained by elution of cyanide complexes from anionic exchange resin by means of acidic thiourea, Hydrometallurgy 46 (1997) 287–301, https://doi.org/10.1016/S0304-386X(97)00026-1.

[41] B. Mokhtari, K. Pourabdollah, Nano-assisted extraction of alkali metals using emulsion liquid membranes, Acta Chim. Slov. (2013), https://doi.org/10.1007/s11814-012-0085-1.

[42] T. Asadi, A. Azizi, J. chun Lee, M. Jahani, Solvent extraction of zinc from sulphate leaching solution of a sulphide-oxide sample using D2EHPA and Cyanex 272, J. Dispers. Sci. Technol. 39 (2018) 1328–1334, https://doi.org/10.1080/01932691.2017.1402338.

[43] F. Soltani, H. Darabi, R. Aram, M. Ghadiri, Leaching and solvent extraction purification of zinc from Mehdiabad complex oxide ore, Sci. Rep. 11 (2021) 1–11, https://doi.org/10.1038/s41598-021-81141-7.

[44] E. Katoozi, Z. Anari, Statistical optimization of extraction column parameters for the zinc (ll) solvent extraction by D2EHPA in a continuous mode, Miner. Eng. 174 (2021), 107255, https://doi.org/10.1016/J.MINENG.2021.107255.

[45] R.N.R. Sulaiman, N. Othman, N. Jusoh, N.F.M. Noah, R. Rashid, S.M. Saufi, Intensification reactive recovery of tetravalent platinum from spent catalyst via synergism of TBP/Cyanex 302 system, Chem. Eng. Process. - Process Intensif. 168 (2021), https://doi.org/10.1016/j.cep.2021.108581.

[46] C. Xu, J. Zhou, S. Yin, Y. Wang, L. Zhang, S. Hu, X. Li, S. Li, Solvent extraction and separation of zinc-iron from spent pickling solution with tri-n-octylamine, Sep. Purif. Technol. 278 (2021), 119579, https://doi.org/10.1016/J.SEPPUR.2021.119579.