Synergistic Extraction of Cd, Cu and Ni with D2EHPA/TBP: Screening of Factors by Fractional Factorial Design

L. Y. Lee, N. Morad, N. Ismail, and M. Rafatullah

Abstract—This work aimed to determine the significant factors that provide great impacts on the efficiency of synergistic extraction of Cd, Cu and Ni from mixed synthetic aqueous solutions with mixture of extractants, di-(2-ethylhexyl) phosphoric acid (D2EHPA) and tributyl phosphate (TBP) by using two-level fractional factorial design. Six factors affecting the synergistic extraction consisted of mixing time (t), concentration of D2EHPA [D2EHPA], concentration of TBP [TBP], concentration of sodium sulphate [Na\textsubscript{2}SO\textsubscript{4}], equilibrium pH (pH\textsubscript{eq}) and organic to aqueous ratio (O:A) were examined. Results from the application of 2\textsuperscript{6} fractional factorial design showed that [D2EHPA], O:A and interaction of D2EHPA with TBP ([D2EHPA] \times [TBP]) have significantly influenced the extraction percentage (E\%) for Cd and Cu.

Index Terms—Synergistic extraction, heavy metal separation, liquid-liquid extraction, screening, fractional factorial design.

I. INTRODUCTION

The demand for recovery of precious metals from complex or low-grade ores, industrial waste and secondary sources is overwhelming due to the high prices of metals and the degradation of world’s metallic resources. Thus, techniques for removal of heavy metals from polluted waters must be able to retrieve valuable and high purity products and to comply the environmental regulations at the same time.

Cadmium is commonly extracted from metallurgical by-products in cadmium–rich dust, copper–cadmium slag and from the spent nickel–cadmium batteries [1]. Despite their toxicity, they are extensively used in diversified industries such as electroplating, batteries, pigments, synthetic chemicals, ceramics, metallurgical, electronics and other industries. Due to the similarities in physicochemical properties, separation of cadmium, copper and nickel are found to be complicated. Cu and Ni are found to be co-extracted with Cd [2], [3]. Thus, separation of divalent Cd, Cu and Ni from a mixed solution were considered in this study.

Liquid-liquid extraction (LLE) has been demonstrated to be one of the most commonly used techniques for the effective separation, removal and purification of aqueous media containing metallic ions, especially in treatment of metal-bearing liquid waste, hydrometallurgical industry and analytical waste. Among the various available techniques for heavy metal removal, LLE has been a well-established process for its cost efficiency, high selectivity and recovery, short reaction time and continuous operation with mild reaction condition [4]. In LLE process, metallic ions are retrieved based on their mass transfer rates and also the principle of solutes distribution ratio between two immiscible phases [5].

Di-(2-ethylhexyl) phosphoric acid (D2EHPA), one of the acid-based extractants is widely used as carrier in LLE for the extraction of several metals such as Cu\textsuperscript{2+} [6], Cd\textsuperscript{2+} [7], [8], Fe\textsuperscript{3+} [9], Mn\textsuperscript{2+} [10], [11], Ni\textsuperscript{2+} [12], Zn\textsuperscript{2+} [13]. Despite all the advantages of using D2EHPA, several issues must be addressed when working with D2EHPA. One of the issues to be considered is the poor metal selectivity due to the antagonistic effects of mono-(2-ethylhexyl) phosphoric acid (M2EHPA) as impurities after decomposition of D2EHPA [14], [15]. Single use of D2EHPA requires the usage of highly concentrated stripping solution due to the difficulties in dissolving certain heavy metals [16].

Tributyl phosphate (TBP) is known to be one of the major neutral extracting agent and effective organic phase modifier in numerous applications for extraction of several metals such as Cd\textsuperscript{2+} [17], Cu\textsuperscript{2+} [18], [19], Co\textsuperscript{2+} [4], [20], Fe\textsuperscript{3+} [21], Ni\textsuperscript{2+} [22], and Zn\textsuperscript{2+} [23]. Researchers agree that TBP enhances phase separation conditions when it is used as modifier [15]. However, the shortcoming of TBP is discovered when water is found to be transferred to the organic phase due to its hydrophilicity. High concentration of TBP (from 80 to 100 vol.%) is required to achieve a high percentage of extraction, is being the reason for high cost and not economically feasible compared with D2EHPA [24]. However, addition of TBP to the organic phase containing D2EHPA improves phase separation by modifying the extraction mechanism and promotes efficient separation of heavy metals by encouraging the extraction curves to shift apart [14].

Thus, carrier synergism between two distinctive extractants, has brought clearly into focus due to the poor extraction efficiency of using one type of carrier. Synergism of the mixture of two different carriers will intensify the extraction capability rather than using the single extractive capability of one specific carrier [25], [26]. Several results from other researches which have proven that the synergism of the two carriers into membrane phase could improve the rate and selectivity of the metal ions transport. Synergism
was applied for better separation of Cd from Ni in sulfate media and co-extraction of Ni was restrained by synergistic effects of combined extractants such as Cyanex 471X (tri-isobutylphosphine sulphide) with TOPS 99 (an equivalent of di-(2-ethylhexyl) phosphoric acid) [27] and Cyanex 302 with D2EHPA [28].

Most of the stand-alone operation of a single metal extraction process tend to be unsuccessful in recovering all the possible precious materials present in complex wastewater. In fact, there are numerous valuable compounds that could be separated simultaneously. The existing simultaneous separation of several heavy metal ions only focused in laboratory scale and are not entirely intensive in covering vast applications. Presence of distinctive metal species with almost identical valence configurations in the same mixture permits the co-transport and it makes selective extraction a difficult challenge. Synergistic simultaneous LLE of Cd, Cu and Ni ions from the aqueous solution using a synergic mixture of D2EHPA-TBP system has not been reported yet. The aim of this work is to investigate the simultaneous separation of Cd, Cu, and Ni ions via binary mixtures of D2EHPA-TBP system from synthetic sulfate mixture of cadmium, copper and nickel.

To improve extraction efficiency, screening experiments which are normally conducted before optimization of significant factors. Screening experiment aims at determining significant factors that give large effects on an experimental response or responses [29]. Most researchers only conducted screening for the effect of single variable by changing its value while other variables remained constant. To study the effect of more variables (> 4), the number of runs that are likely to be performed in a complete factorial design often exceeds even for variables at only two levels each [30]. For example, a complete two-level factorial design of 5 factors requires 32 runs, 6 factors require 64 runs, 7 factors require 128 runs and so forth. In this work, fractional factorial design was used to screen a full factorial design partially by conducting fewer experiments without neglecting the response variation of each variables (main effect) and the interactions between variables. The importance of fractional factorial design is its resolution, that is its capability to distinguish the main effects and low-order interactions from one another [31]. A two-level fractional factorial design was used in the present work to screen a total of six factors with 32 runs for their effects.

II. MATERIALS AND METHODS

A. Chemicals and Reagents

Copper sulphate pentahydrate (CuSO₄·5H₂O) (≥99.6% purity), cadmium sulphate hydrate (CdSO₄·H₂O) (≥98% purity), nickel sulphate hexahydrate (NiSO₄·6H₂O) (≥98% purity) were obtained from Merck. The organic extractants used to extract the metal ion were an industrial-grade of organo-phosphoroc extractant, D2EHPA (≥95% purity) and a phosphorus-oxygen based solvating carrier, TBP (≥99% purity) from Merck. The dilution of organic extractant was performed using a commercial grade kerosene purchased from R&M.

Nitric acid (HNO₃) (≥65% purity), as well, sulfuric acid (H₂SO₄) (≥98% purity), hydrochloric acid (HCl) (≥35% purity), sodium hydroxide (NaOH) (≥99% purity) and sodium sulphate (Na₂SO₄) (≥99% purity) were purchased from Merck. Glassware were washed with phosphate free detergent and rinsed with distilled water before they were soaked in acid wash of 5% HNO₃ for at least 24 hours. De-ionized water was used for the preparation of all aqueous solutions and final rinsing of glassware. All chemicals and reagents were used as received in the experiments without further purification.

The characteristics and structural formula of the extractant D2EHPA and TBP are presented in Table I.

| Properties | D2EHPA | TBP |
|------------|--------|-----|
| Structural formula | ![D2EHPA](image) | ![TBP](image) |
| Molecular formula | C₈H₁₃O₂P | C₁₂H₁₆O₆P |
| Molar mass (g/mol) | 322.43 | 266.31 |
| Boiling point (°C) | 393 | 289 |
| Physical state (room temperature) | Liquid | Liquid |
| Density (g/mL) | 0.9758 | 0.9727 |
| Appearance | Odorless yellow liquid | Odorless colorless liquid |

| Properties | D2EHPA | TBP |
|------------|--------|-----|
| Structural formula | ![D2EHPA](image) | ![TBP](image) |
| Molecular formula | C₈H₁₃O₂P | C₁₂H₁₆O₆P |
| Molar mass (g/mol) | 322.43 | 266.31 |
| Boiling point (°C) | 393 | 289 |
| Physical state (room temperature) | Liquid | Liquid |
| Density (g/mL) | 0.9758 | 0.9727 |
| Appearance | Odorless yellow liquid | Odorless colorless liquid |

B. Equipment

Digital overhead stirrer (IKA, RW 20) was used to mix the aqueous and organic phases and a pH meter (Hach, Sension+) was used to measure the pH of aqueous phase before and after extraction. Metal concentration of Cd²⁺, Cu²⁺ and Ni²⁺ in the aqueous phase after extraction was measured separately with a flame atomic absorption spectrophotometer (FAAS) (Perkin Elmer, AA-400).

C. Preparation of Aqueous and Organic Phases

Mixed working solutions containing a fixed initial metal
concentration, $[M_i]$ of Cd, Cu and Ni respectively were used. The working solutions were prepared by dissolving appropriate amount of suitable salts, CdSO$_4$·H$_2$O, CuSO$_4$·5H$_2$O and NiSO$_4$·6H$_2$O in distilled water loaded with (200 and 250mM) Na$_2$SO$_4$. Organic phases were prepared with varying concentrations of D2EHPA (50mM and 100mM) and TBP (50mM and 100mM) in kerosene as diluent.

D. Liquid-Liquid Extraction of Cd, Cu and Ni

Extraction experiments were carried out by mixing 20 mL of the organic phase with an aqueous phase containing three metal ions at O/A ratio of 1 and 1.5 in Erlenmeyer flasks. The flasks were stirred with overhead stirrers at 100 rpm for 5 and 10 minutes. The mixtures were left to separate for 5 minutes. pH of aqueous sample at the lower phase was measured and adjusted to desired pH$_{aq}$ (4 and 4.5) with H$_2$SO$_4$ or NaOH. The mixture was then mixed and allowed to separate for 5 minutes until the desired pH was obtained. After that, the mixtures of aqueous and organic phases were left to separate in a separating funnel.

After 10 minutes of phase disengagement, the aqueous samples were taken from the lower phase of the separated funnel, filtered through filter paper. Samples were taken for feed phase after extraction (ppm).

The percentage of extraction (E%) of metal (Cd, Cu and Ni) ions were calculated using (1).

$$E\% = \frac{[M_i] - [M_{aq}]}{[M_i]} \times 100 \quad (1)$$

where, $[M_i]$ is the initial metal concentration in aqueous feed phase (ppm) and $[M_{aq}]$ is the metal concentration in aqueous feed phase after extraction (ppm).

E. Design of Experiment

Fractional factorial design was used to determine the parameters that significantly affect the metal ions extraction. The novelty and contribution of this work is taken into consideration and the specific range for each variable is selected based on literature review. 2$^{6-1}$ fractional factorial design was employed to assess six process variables, namely mixing time (t), D2EHPA concentration [D2EHPA], TBP concentration [TBP], concentration of sodium sulphate [Na$_2$SO$_4$], equilibrium pH (pH$_{eq}$) and organic to aqueous ratio (O:A) for their effects on response (E%). Factors and levels described in Table II where the limits of the experimental region for each factor was identified from the preliminary works[12, 30]. The low and high levels of these parameters are coded as -1 and +1, respectively. Other factors such as operating temperature (28±1°C), mixing rate (100 rpm), initial concentration of metal ions $[M_i]$ (100 ppm), diluent type (kerosene) were fixed at specific values based on literature review [19]. A total of 32 experimental runs were conducted for each metal. Minitab software was used to evaluate the statistical significance of each individual factor and their combinations at 5% significance level.

III. RESULTS AND DISCUSSION

To reduce the unexpected variability in the observed response, the experimental sequence (Std Order) was randomized and all the experiments were conducted under the same conditions in one block of measurements. Tables III, IV and V show the design matrices used in the 2$^{6-1}$ fractional factorial design, along with the screening of various operating parameters affecting the extractions for Cd, Cu and Ni.
respectively, measured with average E% from triplicate tests in each run. The average E% of Cd and Cu were found within a similar range from 37.95 to 94.92 (Table III) and 38.76 to 93.06 (Table IV) respectively whereas, the average E% of Ni was found to range from 0.21 to 11.96 (Table V). Unlike Cd and Cu, the extraction of Ni was found to be negligible with low E%.

The significant effect of each factor on E% of Cd, Cu and Ni was evaluated by normal probability plots of standardized effects and Pareto charts at 5% significance level using the Minitab software. Normal probability plot of effects shows the estimates of main effects of the factors and their interaction between factors. Insignificant effects are normally distributed with mean zero and variance and they fall along a straight line in the plot. On contrary, significant effects are outliers that are away from the straight line and they have non-zero means. The bigger the significant effects, the further away they are from the straight line.

Pareto charts of standardized effects are used to verify the results acquired from the normal probability plot of effects. Vertical line in the Pareto chart represents the minimum statistically significant effect magnitude for 5% significance level with the value of 2.228, while the horizontal columns represent the degree of significance for each effect. Effect or interaction that surpasses the vertical line is considered significant.

### TABLE V: DESIGN MATRIX FOR 2^4-1 FRACTIONAL FACTORIAL DESIGN AND AVERAGE E% OF NICKEL

| Std Order | Run Order | Variables | A | B | C | D | E | F | Avg E% |
|-----------|-----------|-----------|---|---|---|---|---|---|--------|
| 16        | 1         | 10        | 100| 100| 250| 1  | 4  | 4.5   | 81.05  |
| 14        | 2         | 10        | 50 | 50 | 250| 1.5| 4  | 4.5   | 90.30  |
| 3         | 3         | 5         | 100| 50 | 200| 1  | 4  | 4    | 74.95  |
| 17        | 4         | 5         | 50 | 50 | 200| 1  | 4  | 4    | 42.96  |
| 29        | 6         | 5         | 50 | 50 | 250| 1.5| 4  | 4    | 58.86  |
| 23        | 7         | 5         | 100| 100| 250| 1.5| 4  | 4    | 79.18  |
| 13        | 8         | 5         | 50 | 50 | 250| 1  | 4  | 4    | 45.28  |
| 11        | 9         | 5         | 100| 50 | 250| 1  | 4  | 4    | 72.75  |
| 14        | 10        | 10        | 50 | 100| 250| 1  | 4  | 4    | 74.96  |
| 9         | 11        | 5         | 50 | 50 | 250| 1  | 4  | 4    | 38.76  |
| 19        | 12        | 5         | 100| 50 | 250| 1.5| 4  | 4    | 78.12  |
| 24        | 13        | 10        | 100| 100| 250| 1  | 4  | 4    | 81.6   |
| 22        | 14        | 10        | 50 | 100| 200| 1.5| 4  | 4    | 50.48  |
| 28        | 15        | 10        | 100| 50 | 250| 1.5| 4  | 4    | 84.28  |
| 25        | 16        | 5         | 50 | 50 | 250| 1.5| 4  | 4    | 45.55  |
| 8         | 17        | 10        | 100| 100| 200| 1  | 4  | 4    | 70.44  |
| 16        | 18        | 10        | 100| 50 | 250| 1  | 4  | 4    | 53.73  |
| 12        | 19        | 10        | 100| 50 | 250| 1  | 4  | 4    | 93.06  |
| 26        | 20        | 10        | 50 | 50 | 250| 1.5| 4  | 4    | 53.16  |
| 32        | 21        | 10        | 100| 100| 250| 1.5| 4  | 4    | 83.89  |
| 17        | 22        | 5         | 50 | 50 | 200| 1.5| 4  | 4    | 79.79  |
| 18        | 23        | 10        | 50 | 50 | 200| 1  | 4  | 4    | 71.74  |
| 2         | 24        | 10        | 50 | 50 | 200| 1  | 4  | 4    | 40.13  |
| 15        | 25        | 5         | 100| 100| 250| 1  | 4  | 4    | 83.06  |
| 20        | 26        | 10        | 100| 50 | 250| 1.5| 4  | 4    | 71.21  |
| 10        | 27        | 10        | 50 | 100| 250| 1  | 4  | 4    | 50.00  |
| 5         | 28        | 5         | 50 | 50 | 200| 1  | 4  | 4    | 73.03  |
| 31        | 29        | 5         | 100| 100| 200| 1.5| 4  | 4    | 69.98  |
| 7         | 30        | 5         | 100| 100| 200| 1  | 4  | 4    | 62.71  |
| 30        | 31        | 10        | 50 | 100| 200| 1.5| 4  | 4    | 71.34  |
| 21        | 32        | 5         | 50 | 100| 200| 1.5| 4  | 4    | 85.74  |

**A. Screening of Factors Affecting E% of Cd**

Based on the analysis in Fig. 1, significant effects that emerge from the normal probability plot are the main effects of B ([D2EHPA]) and E (O:A), and the BC ([D2EHPA] × [TBP]) interaction. The sequence of the significant main and interaction effects with respect to decreasing of influence on the extraction of Cd was found to be B > E > BC.
From the Pareto chart in Fig. 2, the sequence of the significant main and interaction effects with respect to decreasing of influence on E% of Cd coincided with the results obtained from the normal probability plot of standardized effects, that is B > E > BC.

There are outliers other than B, E and BC in the Pareto charts that are not highlighted. This is due to the use of resolution VI [31] in the fractional factorial design whereby, B and E were aliased with ACDEF and ABCDF, respectively, and BC with ADEF. These outliers were formed by the effects of three-factor and higher interactions whereby, they are usually negligible [33]. It could be concluded that B, E, and BC were the only significant factors present.

Synergism between carriers (BC) is also an important effect to be focused on. This result is in line with the work of Fatmehsari et al. [15], which also demonstrated the importance of the interaction between D2EHPA and TBP. The results of Fourier Transform Infrared Spectroscopy analysis showed that the P=O vibration band for TBP in the D2EHPA-TBP mixture has affected the P=O vibration band of D2EHPA by lowering the wavenumber. Due to the bonding of P=O groups by H2O, synergistic shifts occurred after the formation of new bonds in the D2EHPA-TBP mixture and therefore, some extractant molecules are polymerized through hydrogen bonds. [14].

B. Screening of Factors Affecting E% of Cu

The estimates of main effects of the factors that affect E% of Cu and their interactions were also examined using normal probability plot (Fig. 3) and Pareto chart of standardized effects (Fig. 4). The sequence of significant main and interaction effects on the E% of Cu is B > E > BC, which is similar with the E% of Cd. The current findings had proven that Cd and Cu ions were co-extracted simultaneously since they approach closely to each other at a close range of pH variation of 4 to 4.5. Besides, a different behaviour in the interaction between parameters was found as compared with other authors, whereby most authors reported that [D2EHPA] and pH_eq were the significant effects for the extraction of Cu [30] and Ni [12] since D2EHPA is a pH-dependent extractant.

C. Screening of Factors Affecting E% of Ni

Based on the normal probability plot (Fig. 5) and Pareto chart of standardized effects (Fig. 6), it can be concluded that A (mixing time) is the only important effect for the extraction of Ni. Meanwhile, the interactions between the rest of the main effects were relatively weak. This result is consistent with the finding by Gega and Otrembska [34] who reported the E% of Ni ions was not affected by the concentration of D2EHPA. This is also suggested that Ni ions stay in the feed phase. Competitive transportation exists in the presence of combinatorial separation of several heavy metal ions. The existence of another metal reduces the overall separation of heavy metals as compared to the separation of individual
metal [35]. The present work showed that the extraction rate of Ni was much lower than those of the other two elements. The preferential transportation of Cd²⁺ and Cu²⁺ over Ni²⁺ can be elucidated by the difference in their electronic configurations. Electronic configurations of Cd, Cu and Ni are [Kr] 4d¹⁰5s², [Ar] 3d¹⁰4s¹ and [Ar] 3d⁴4s², respectively and their atomic numbers are 48, 29 and 28 respectively.

IV. CONCLUSION

Presence of various metal ions in an aqueous media allows co-transport whereby they can also be transported based on their chemical attractions with the chosen carrier. Distinctive metal species with identical valence configurations may present in the same mixture and it makes selective extraction a difficult challenge. The synergistic extraction of multiple divalent metal ions from a mixed (Cd-Cu-Ni) synthetic sulfate solution in a D2EHPA-TBP-kerosene system has been studied. Screening of six factors (r, [D2EHPA], [TBP], [Na₂SO₄], O:A and pH₃₀) affecting the extraction of Cd, Cu and Ni using a 2⁶-1 fractional factorial design, reveals only [D2EHPA], O:A and the interaction of ([D2EHPA]×[TBP]) are influential statistically. The obtained experimental results had proven the possibility of using synergism of D2EHPA with TBP to selectively separate two types of metals (Cd and Cu) with high extractability up to 94.92% and leave behind the least extracted metal ions (Ni) in the system. Another revelation of the present work is the advantage of fractional factorial design, which has the capability to evaluate the effect of many variables with a minimum number of experiments, and as well as to prove the feasibility of simultaneous extraction of multiple heavy metals. The results of this study could lead to the optimization of the process conditions based on the most significant factors which would enable an effective separation of multiple heavy metals in the wastewater to the maximum extent in the future work.

REFERENCES

[1] E. Bidari, M. Irannejad, and M. Gharabaghi, “Solvent extraction recovery and separation of cadmium and copper from sulphate solution,” Journal of Environmental Chemical Engineering, vol. 1, pp. 1269-1274, 2006.

[2] C. A. Nogueira and F. Delmas, “New flowsheet for the recovery of cadmium, cobalt and nickel from spent Ni-Cd batteries by solvent extraction,” Hydrometallurgy, vol. 52, pp. 267-287, 1999.

[3] L. Gotfrayd and M. Cox, “The selective recovery of cadmium(II) from sulfate solutions by a counter-current extraction-Stripping process using a mixture of diisopropylsalicylic acid and Cyanex® 471X,” Hydrometallurgy, vol. 81, pp. 226-233, 2006.

[4] R. Torkaman, M. Asadolahzadeh, M. Torab-Mostaedi, and M. G. Maraghehi, “Reactive extraction of cobalt sulfate solution with D2EHPA/TBP extractants in the pilot plant Oldshude–Rushion column,” Chemical Engineering Research and Design, vol. 120, pp. 58-68, 2017.

[5] V. S. Kislík, “Chemistry of metal solvent extraction.” Solvent Extraction, Amsterdam: Elsevier, 2012, ch. 3, pp. 113-156.

[6] S. H. Chang, T. T. Teng, and N. Ismail, “Extraction of Cu(II) from aqueous solutions by vegetable oil-based organic solvents,” J. Hazard Mater, vol. 181, pp. 868-72, 2010.

[7] M. K. Jha, V. Kumar, J. Jeong, and J. C. Lee, “Review on solvent extraction of cadmium from various solutions,” Hydrometallurgy, vol. 111-112, pp. 1-9, 2012.

[8] V. Kumar, M. Kumar, M. K. Jha, J. Jeong, and J. C. Lee, “Solvent extraction of cadmium from sulfate solution with di(2-ethylhexyl) phosphoric acid diluted in kerosene,” Hydrometallurgy, vol. 96, pp. 230-234, 2009.

[9] Y. Jin, Y. Ma, Y. Weng, X. Jia, and J. Li, “Solvent extraction of Fe⁺ from the hydrochloric acid route phosphoric acid by D2EHPA in kerosene,” Journal of Industrial and Engineering Chemistry, vol. 20, pp. 3446-3452, 2014.

[10] C. S. Sousa Junior, M. Nascimento, I. O. C. Masson, and O. G. C. Cunha, “Equilibrium study for manganese extraction in sulfate media with D2EHPA in IsoparAF (17/21),” Hydrometallurgy, vol. 103, pp. 114-117, 2010.

[11] R. Pérez-Garibay, J. Martínez-Jiménez, A. Uribe-Salas, and A. Martínez-Luévano, “Comparative study between D2EHPA and Cyanex 272 as extractants of Mn(II) from a leached liquor produced by reductive leaching of a pyrolusite ore with SO₃,” Engineering, vol. 04, pp. 526-531, 2012.

[12] A. Talebi, T. T. Teng, A. F. M. Alkarkhi, I. Norli, and L. W. Low, “Optimization of nickel removal using liquid–liquid extraction and response surface methodology,” Desalination and Water Treatment, vol. 47, pp. 334-340, 2012.

[13] A. Jafari, H. Abdollahi, M. Gharabaghi, and A. A. Balestini, “Solvent extraction of zinc from synthetic Zn-Cd-Mn chloride solution using D2EHPA: Optimization and thermodynamic studies,” Separation and Purification Technology, vol. 197, pp. 210-219, 2018.

[14] E. K. Alamdari, D. Moradkhani, D. Darvishi, M. Askari, and D. Behnini, “Synergistic effect of MEHPA on co-extraction of zinc and cadmium with D2EHPA,” Minerals Engineering, vol. 17, pp. 89-92, 2004.

[15] D. H. Fatmehsari, D. Darvishi, S. Etemadi, A. R. E. Hollagh, E. K. Alamdari, and A. A. Salardini, “Interaction between TBP and D2EHPA during Zn, Cd, Mn, Cu and Ni solvent extraction: A thermodynamic and empirical approach,” Hydrometallurgy, vol. 98, pp. 143-147, 2009.

[16] T. Hirato, Z.-C. Wu, Y. Yamada, and H. Majima, “Improvement of the stripping characteristics of Fe(III) utilizing a mixture of di-(2-ethylhexyl) phosphoric acid and tri-n-butyl phosphate,” Hydrometallurgy, vol. 28, pp. 81-93, 1992.

[17] H. G. Nowier, N. El-Said, and H. F. Aly, “Carrier-mediated transport of toxic elements through liquid membranes: Transport of Cd(II) from high salinity chloride medium through supported liquid membrane containing TBP/cyclohexane,” Journal of Membrane Science, vol. 177, pp. 41-47, 2000.

[18] A. Datta, D. Datta, and A. Chandra, “Separation and recovery of copper from aqueous solutions using tri-n-butyl phosphate in benzene,” Journal of Molecular Liquids, vol. 221, pp. 139-148, 2016.

[19] A. Ghosh, D. Datta, H. Ushu, H. S. Banumath, and S. Kumar, “Separation of copper ion (Cu²⁺) from aqueous solution using tri-n-butyl phosphate and di-2-ethylhexyl phosphoric acid as extractants,” Journal of Molecular Liquids, vol. 258, pp. 147-154, 2018.

[20] P. Amani, J. Asadi, E. Momhammad, S. Akhgar, and M. Esmaati, “Cooperative influence of D2EHPA and TBP on the reactive extraction of cobalt from sulfuric acid leach solution in a horizontal semi-industrial column,” Journal of Environmental Chemical Engineering, vol. 5, pp. 4716-4727, 2017.

[21] Y. Ma, X. Wang, M. Wu, C. Jiang, X. Xiang, and X. Zhang, “Separation of V(IV) and Fe(III) from the acid leach solution of stone coal by D2EHPA/TBP,” Hydrometallurgy, vol. 153, pp. 38-45, 2015.

[22] L. Y. Wang and M. S. Lee, “Recovery of Co(II) and Ni(II) from chloride leach solution of nickel laterite ore by solvent extraction with a mixture of Cyanex 301 and TBP,” Journal of Molecular Liquids, vol. 240, pp. 345-350, 2017.

[23] E. Vahidi, F. Rashchi, and D. Moradkhani, “Recovery of zinc from an industrial zinc leach residue by solvent extraction using D2EHPA,” Minerals Engineering, vol. 22, pp. 204-206, 2009.

[24] K. K. Sahu and R. P. Das, “Synergistic extraction of iron(III) at higher concentrations in D2EHPA-TBP mixed solvent systems,” Metallurgical and Materials Transactions B, vol. 28, pp. 181-189, 1997.

[25] M. Aguilar and J. L. Cortina, Solvent Extraction and Liquid Membranes: Fundamentals and Applications in New Materials, CRC Press, 2008.

[26] R. N. R. Sulaiman and N. Othman, “Solvent extraction of nickel ions from electrolless nickel plating wastewater using synergistic green binary mixture of D2EHPA-octanol system,” Journal of Environmental Chemical Engineering, vol. 6, pp. 1814-1820, 2018.

[27] B. R. Reddy, S. V. Rao, and D. N. Priya, “Selective separation and recovery of divalent Cd and Ni from sulphate solutions with mixtures of TOPS 99 and Cyanex 471 X.” Separation and Purification Technology, vol. 59, pp. 214-220, 2008.
A. Babakhani, F. Rashchi, A. Zakeri, and E. Vahidi, “Selective separation of nickel and cadmium from sulfate solutions of spent nickel–cadmium batteries using mixtures of D2EHPA and Cyanex 302,” *Journal of Power Sources*, vol. 247, pp. 127-133, 2014.

D. C. Montgomery, G. C. Runger, and N. F. Hubele, *Engineering Statistics*, 5 ed. United States of America: John Wiley & Sons Inc., 2010.

S. H. Chang, T. T. Teng, and N. Ismail, “Screening of factors influencing Cu(II) extraction by soybean oil-based organic solvents using fractional factorial design,” *J. Environ Manage*, vol. 92, pp. 2580-2585, 2011.

R. H. Myers and D. C. Montgomery, *Response Surface Methodology: Process and Product Optimization Using Designed Experiments*, 2nd ed. New York: John Wiley and Sons, 2002.

E. W. Rice, L. Bridgewater, A. P. H. Association, A. W. W. Association, and W. E. Federation, *Standard Methods for the Examination of Water and Wastewater*, 22 ed. American Public Health Association, 2012.

T. Lundstedt, E. Seifert, L. Abramo, B. Thelin, A. Nystrom, J. Pettersen, and R. Bergman, “Experimental design and optimization,” *Chemometrics and Intelligent Laboratory Systems*, pp. 3-40, 1998.

J. Gega and P. Otrembska, “Separation of Ni(II) and Cd(II) Ions with Supported Liquid Membranes (SLM) using D2EHPA as a Carrier,” *Separation Science and Technology*, vol. 49, pp. 1756-1760, 2014.

K. K. Bhatluri, M. S. Manna, P. Saha, and A. K. Ghoshal, “Supported liquid membrane-based simultaneous separation of cadmium and lead from wastewater,” *Journal of Membrane Science*, vol. 459, pp. 256-263, 2014.

Lai Yee Lee was born in August 1990. She obtained a bachelor of science in environmental science and technology from University Putra Malaysia (UPM), Malaysia in 2014. She is currently pursuing her Ph.D. in environmental technology, in School of Industrial Technology, University Sains Malaysia (USM), Malaysia. Her research interest are liquid-liquid extraction and liquid membrane technology for metals extraction.

Norhashimah Morad was born in May 1964. She earned a bachelor of science in chemical engineering from University Missouri, Columbia in 1985. She joined in the School of Industrial Technology in University Sains Malaysia (USM), Malaysia as a tutor in 1988 and pursued her Ph.D. in control engineering at the University of Sheffield, United Kingdom under the Commonwealth Scholarship. She is currently a professor in the environmental technology division, USM, Malaysia. Her research interest are intelligent systems in manufacturing, optimization using genetic algorithms, life cycle assessment (LCA), phytoremediation and new methods and materials in biological and chemical wastewater treatment.

Norli Ismail was born in September 1971. She obtained a bachelor of science in environmental science from University in Putra Malaysia in 1995. She earned a master of science in chemical process, School of Industrial Technology from University Sains Malaysia (USM), Malaysia in 1999 and a doctor of philosophy in environmental technology, USM, Malaysia in 2003. She is currently a professor in the environmental technology division, USM, Malaysia. Her research interest is water, wastewater, solid waste treatment technology and management.

Mohd Rafatullah is presently working as a senior lecturer of environmental technology in the School of Industrial Technology, University Sains Malaysia (USM), Malaysia. He joined USM in the year 2008 as a post-doctoral fellow. He earned a Ph.D. in environmental chemistry (2007), master of science in analytical chemistry (2003) and bachelor of science in chemistry (2001) from Aligarh Muslim University, India. His research interest is in the areas of environmental pollutants and their safe removal, water and wastewater treatment, adsorption and ion-exchange, adsorption potential of oil palm products and by-products, instrumental methods of analysis, thermodynamic and kinetic studies, and activated carbons and its electrochemical properties.