

# 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 [ $\text{Na}_2\text{SO}_4$ ], equilibrium pH ( $\text{pH}_{\text{eq}}$ ) and organic to aqueous ratio (O:A) were examined. Results from the application of  $2^{6-1}$  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  $\text{Cu}^{2+}$  [6],  $\text{Cd}^{2+}$  [7], [8],  $\text{Fe}^{3+}$  [9],  $\text{Mn}^{2+}$  [10], [11],  $\text{Ni}^{2+}$  [12],  $\text{Zn}^{2+}$  [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  $\text{Cd}^{2+}$  [17],  $\text{Cu}^{2+}$  [18], [19],  $\text{Co}^{2+}$  [4], [20],  $\text{Fe}^{3+}$  [21],  $\text{Ni}^{2+}$  [22], and  $\text{Zn}^{2+}$  [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

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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 binary 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 require 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

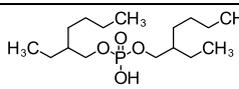
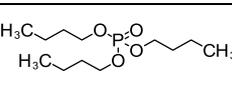
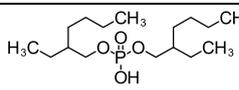
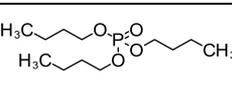
Copper sulphate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) ( $\geq 99.6\%$  purity), cadmium sulphate hydrate ( $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ ) ( $\geq 98\%$  purity), nickel sulphate hexahydrate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ) ( $\geq 98\%$  purity) were obtained from Merck. The organic extractants used to extract the metal ion were an industrial-grade of organo-phosphoric extractant, D2EHPA ( $\geq 95\%$  purity) and a phosphorus-oxygen based solvating carrier, TBP ( $\geq 99\%$  purity) from Merck. The dilution of organic extractant was

performed using a commercial grade kerosene purchased from R&M.

Nitric acid ( $\text{HNO}_3$ ) ( $\geq 65\%$  purity), as well, sulfuric acid ( $\text{H}_2\text{SO}_4$ ) ( $\geq 98\%$  purity), hydrochloric acid ( $\text{HCl}$ ) ( $\geq 35\%$  purity), sodium hydroxide ( $\text{NaOH}$ ) ( $\geq 99\%$  purity) and sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) ( $\geq 99\%$  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%  $\text{HNO}_3$  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.

TABLE I: PROPERTIES OF EXTRACTANTS USED

Properties	D2EHPA	TBP
Structural formula		
Molecular formula	$\text{C}_{16}\text{H}_{35}\text{O}_4\text{P}$	$\text{C}_{12}\text{H}_{27}\text{O}_4\text{P}$
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		
Molecular formula	$\text{C}_{16}\text{H}_{35}\text{O}_4\text{P}$	$\text{C}_{12}\text{H}_{27}\text{O}_4\text{P}$
Molar mass (g/mol)	322.43	266.31
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Physical state (room temperature)	Liquid	Liquid
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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  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  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,  $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  in distilled water loaded with (200 and 250mM)  $\text{Na}_2\text{SO}_4$ . 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  $\text{pH}_{\text{eq}}$  (4 and 4.5) with  $\text{H}_2\text{SO}_4$  or  $\text{NaOH}$ . 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 analysis to determine the concentrations of metal contents,  $[M_{\text{aq}}]$  of  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ , respectively with FAAS after appropriate dilution. The recommended flame conditions of FAAS for Cd, Cu, and Ni were wavelengths of 228.8 nm, 324.8 nm and 232.0 nm respectively [32].

The experiments were carried out in duplicate or triplicate for each run with standard error was found to be less than 1%. The percentage of extraction (E%) of metal (Cd, Cu and Ni) ions were calculated using (1).

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

where,  $[M_i]$  is the initial metal concentration in aqueous feed phase (ppm) and  $[M_{\text{aq}}]$  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 [ $\text{Na}_2\text{SO}_4$ ], equilibrium pH ( $\text{pH}_{\text{eq}}$ ) 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 ( $28 \pm 1^\circ\text{C}$ ), 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

TABLE II: PARAMETERS AND LEVELS APPLIED IN  $2^{6-1}$  FRACTIONAL FACTORIAL DESIGN

Factors	Symbols	Units	Levels	
			High (+1)	Low (-1)
$t$	A	Min	10	5
[D2EHPA]	B	mM	100	50
[TBP]	C	mM	100	50
[ $\text{Na}_2\text{SO}_4$ ]	D	mM	250	200
O:A	E	-	1.5	1
$\text{pH}_{\text{eq}}$	F	-	4.5	4

TABLE III: DESIGN MATRIX FOR  $2^{6-1}$  FRACTIONAL FACTORIAL DESIGN AND AVERAGE E% OF CADMIUM

Std Order	Run Order	Variables						Avg E%
		A	B	C	D	E	F	
3	1	5	100	50	200	1	4.5	85.78
27	2	5	100	50	250	1.5	4.5	93.36
6	3	10	50	100	200	1	4	52.47
4	4	10	100	50	200	1	4	81.24
1	5	5	50	50	200	1	4	47.02
29	6	5	50	100	250	1.5	4.5	67.23
23	7	5	100	100	200	1.5	4.5	85.92
13	8	5	50	100	250	1	4	53.58
11	9	5	100	50	250	1	4	83.13
14	10	10	50	100	250	1	4.5	80.12
9	11	5	50	50	250	1	4.5	45.27
19	12	5	100	50	200	1.5	4	84.43
24	13	10	100	100	200	1.5	4	86.30
22	14	10	50	100	200	1.5	4.5	56.57
28	15	10	100	50	250	1.5	4	92.87
25	16	5	50	50	250	1.5	4	52.79
8	17	10	100	100	200	1	4.5	78.32
16	18	10	100	100	250	1	4	65.91
12	19	10	100	50	250	1	4.5	94.92
26	20	10	50	50	250	1.5	4.5	61.52
32	21	10	100	100	250	1.5	4.5	90.44
17	22	5	50	50	200	1.5	4.5	81.17
18	23	10	50	50	200	1.5	4	74.32
2	24	10	50	50	200	1	4.5	37.95
15	25	5	100	100	250	1	4.5	89.14
20	26	10	100	50	200	1.5	4.5	79.73
10	27	10	50	50	250	1	4	56.76
5	28	5	50	100	200	1	4.5	75.99
31	29	5	100	100	250	1.5	4	80.36
7	30	5	100	100	200	1	4	72.49
30	31	10	50	100	250	1.5	4	77.29
21	32	5	50	100	200	1.5	4	87.97

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%.

TABLE IV: DESIGN MATRIX FOR 2<sup>6-1</sup> FRACTIONAL FACTORIAL DESIGN AND AVERAGE E% OF COPPER

Std Order	Run Order	Variables						Avg E%
		A	B	C	D	E	F	
3	1	5	100	50	200	1	4.5	81.05
27	2	5	100	50	250	1.5	4.5	90.30
6	3	10	50	100	200	1	4	49.46
4	4	10	100	50	200	1	4	74.95
1	5	5	50	50	200	1	4	42.96
29	6	5	50	100	250	1.5	4.5	58.86
23	7	5	100	100	200	1.5	4.5	79.18
13	8	5	50	100	250	1	4	45.28
11	9	5	100	50	250	1	4	72.75
14	10	10	50	100	250	1	4.5	74.96
9	11	5	50	50	250	1	4.5	38.76
19	12	5	100	50	200	1.5	4	78.12
24	13	10	100	100	200	1.5	4	81.6
22	14	10	50	100	200	1.5	4.5	50.48
28	15	10	100	50	250	1.5	4	84.28
25	16	5	50	50	250	1.5	4	45.55
8	17	10	100	100	200	1	4.5	70.44
16	18	10	100	100	250	1	4	53.73
12	19	10	100	50	250	1	4.5	93.06
26	20	10	50	50	250	1.5	4.5	53.16
32	21	10	100	100	250	1.5	4.5	83.89
17	22	5	50	50	200	1.5	4.5	79.79
18	23	10	50	50	200	1.5	4	71.74
2	24	10	50	50	200	1	4.5	40.13
15	25	5	100	100	250	1	4.5	83.06
20	26	10	100	50	200	1.5	4.5	71.21
10	27	10	50	50	250	1	4	50.00
5	28	5	50	100	200	1	4.5	73.03
31	29	5	100	100	250	1.5	4	69.98
7	30	5	100	100	200	1	4	62.71
30	31	10	50	100	250	1.5	4	71.34
21	32	5	50	100	200	1.5	4	85.74

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 resembles 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<sup>6-1</sup> FRACTIONAL FACTORIAL DESIGN AND AVERAGE E% OF NICKEL

Std Order	Run Order	Variables						Avg E%
		A	B	C	D	E	F	
16	1	10	100	100	250	1	4	4.44
14	2	10	50	100	250	1	4.5	4.17
3	3	5	100	50	200	1	4.5	7.33
17	4	5	50	50	200	1.5	4.5	7.11
31	5	5	100	100	250	1.5	4	2.09
28	6	10	100	50	250	1.5	4	11.15
30	7	10	50	100	250	1.5	4	4.97
24	8	10	100	100	200	1.5	4	7.24
25	9	5	50	50	250	1.5	4	0.21
21	10	5	50	100	200	1.5	4	3.32
15	11	5	100	100	250	1	4.5	4.31
23	12	5	100	100	200	1.5	4.5	3.32
6	13	10	50	100	200	1	4	5.28
11	14	5	100	50	250	1	4	2.19
20	15	10	100	50	200	1.5	4.5	7.76
27	16	5	100	50	250	1.5	4.5	5.89
5	17	5	50	100	200	1	4.5	4.95
9	18	5	50	50	250	1	4.5	1.86
12	19	10	100	50	250	1	4.5	7.90
29	20	5	50	100	250	1.5	4.5	4.31
26	21	10	50	50	250	1.5	4.5	2.72
19	22	5	100	50	200	1.5	4	4.82
4	23	10	100	50	200	1	4	3.19
1	24	5	50	50	200	1	4	2.48
18	25	10	50	50	200	1.5	4	2.48
32	26	10	100	100	250	1.5	4.5	2.36
2	27	10	50	50	200	1	4.5	6.58
10	28	10	50	50	250	1	4	3.68
13	29	5	50	100	250	1	4	1.44
7	30	5	100	100	200	1	4	2.67
8	31	10	100	100	200	1	4.5	11.96
22	32	10	50	100	200	1.5	4.5	4.82

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.

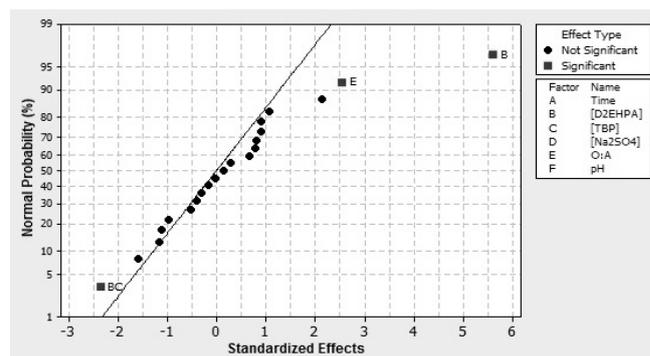


Fig. 1. Normal probability plot of standardized effects for E% of Cd.

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  $B > E > BC$ .

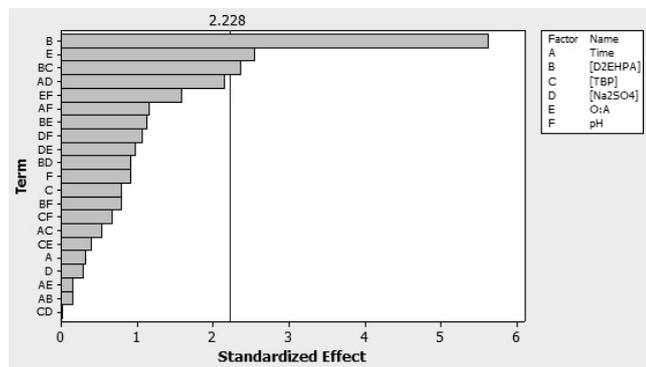


Fig. 2. Pareto chart of standardized effects for E% of Cd.

### 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.

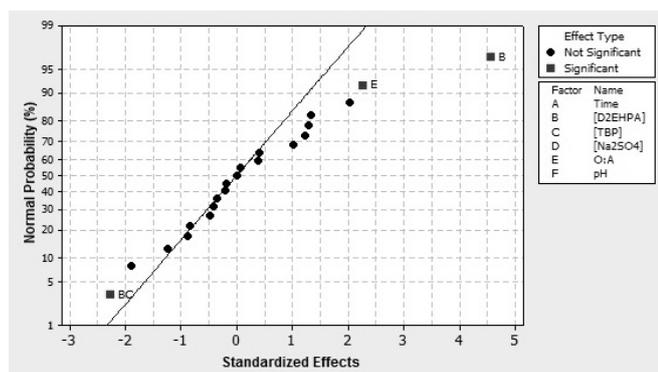


Fig. 3. Normal probability plot of standardized effects for E% of Cu.

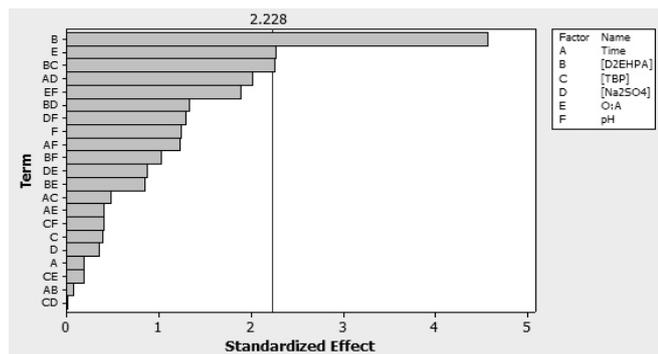


Fig. 4. Pareto chart of standardized effects for E% of Cu.

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 H<sub>2</sub>O, 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].

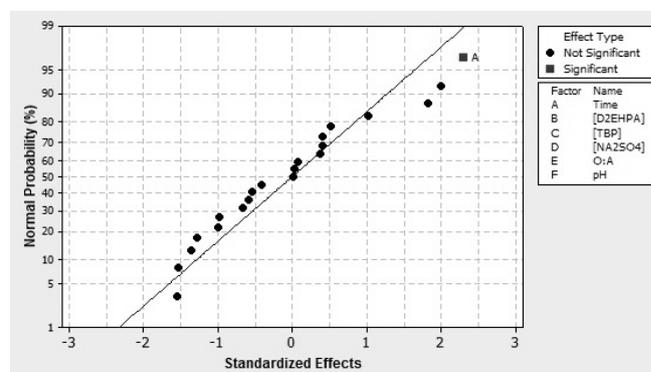


Fig. 5. Normal probability plot of standardized effects for E% of Ni.

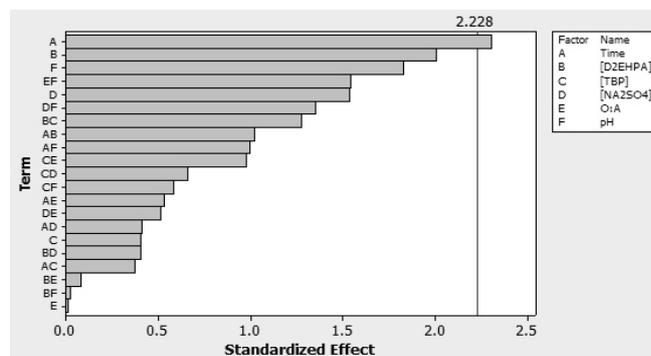


Fig. 6. Pareto chart of standardized effects for E% of Ni.

### 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 Otremska [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  $Cd^{2+}$  and  $Cu^{2+}$  over  $Ni^{2+}$  can be elucidated by the difference in their electronic configurations. Electronic configurations of Cd, Cu and Ni are  $[Kr] 4d^{10}5s^2$ ,  $[Ar] 3d^{10}4s^1$  and  $[Ar] 3d^84s^2$ , 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 ( $t$ , [D2EHPA], [TBP],  $[Na_2SO_4]$ , O:A and  $pH_{eq}$ ) affecting the extraction of Cd, Cu and Ni using a  $2^{6-1}$  fractional factorial design, reveals only [D2EHPA], O:A and the interaction of  $([D2EHPA] \times [TBP])$  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.

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