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Optimization of Process Parameters using Response Surface Methodology for the Removal of Zinc (II) by Solvent Extraction

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***Abstract*—**A factorial design of experiments and a response surface methodology were implemented to investigate the liquid-liquid extraction process of zinc (II) from acetate medium using the 1-Butyl-imidazolium di(2-ethylhexyl) phosphate [BIm^+][$D2EHP^-$]. The optimization process of extraction parameters such as the initial pH effect (2.5, 4.5, and 6.6), ionic liquid concentration (1, 5.5, and 10 mM) and salt effect (0.01, 5, and 10 mM) was carried out using a three-level full factorial design (3^3). The results of the factorial design demonstrate that all these factors are statistically significant, including the square effects of pH and ionic liquid concentration. The results showed that the order of significance: IL concentration > salt effect > initial pH. Analysis of variance (ANOVA) showing high coefficient of determination (R^2 = 0.91) and low probability values ($P < 0.05$) signifies the validity of the predicted second-order quadratic model for Zn (II) extraction. The optimum conditions for the extraction of zinc (II) at the constant temperature (20 °C), initial Zn (II) concentration (1mM) and A/O ratio of unity were: initial pH (4.8), extractant concentration (9.9 mM), and NaCl concentration (8.2 mM). At the optimized condition, the metal ion could be quantitatively extracted.

***Keywords*—**Ionic liquid, response surface methodology, solvent extraction, zinc acetate.

I. Introduction

ZINC is a trace element essential for humans. It is essential for cell proliferation and differentiation, especially for the regulation of DNA synthesis and mitosis. On the molecular level, it is a structural constituent of a great number of proteins, including enzymes of cellular signaling pathway and transcription factors [1].

Zinc deficiency is associated with syndromes that cause short stature and dwarfism. It results in hypoplasia of the immune system, impaired immune response, poor wound healing, diminished T-cell dependent reactions, and attenuated chemotaxis by neutrophils and monocytes [2].

High concentrations of zinc affect the ecosystem and interrupt the activity of the soil as it negatively influences the activity of microorganisms and earthworms that are responsible for the decomposition of organic matter [3], [4]. Conventional methods for the removal of Zn (II) from wastewaters include chemical precipitation [5], solvent extraction [6]-[8], biosorption [9], adsorption [10], membrane separation processes [11], and so on.

In most previous studies [12], [13], optimization of solvent extraction process of metal ion involves changing one independent variable (pH, metal ion concentration, temperature, stirring time …). The factorial experimental design involves changing all variables from one experiment to the next. Thus, a lot of information can be taken with a minimum number of experiment trials [14]. The objective of the present study is to optimize liquid-liquid extraction of zinc (II) from aqueous acetate solution using [BIm^+][$D2EHP^-$] as ionic liquid in chloroform solvent. Experimental variables, such as the initial pH of solution, ionic liquid concentration and ionic strength, on the extraction yield were assessed and optimized with the aid of response surface methodology and experimental design. The effects of the various parameters will be studied by using a 3^3 full factorial design.

II. Experimental

A. Chemicals and Reagents

The synthesis of IL was performed using published procedure [15]. The chemical structure of IL used in the research is shown in Fig. 1.

All chemicals and reagents used in this work were reagent grade. Zinc acetate, di(2-ethylhexyl) phosphoric acid (D2EHPA), chloroform and hydrochloric acid were provided from Fluka. 1-(2-Pyridylazo)-2-naphthol (PAN), 1-Butyl-imidazole, chloride of sodium was purchased from Aldrich. The surfactant Tween 80 was acquired from Biochem chemopharma. Buffer solution at pH=9.0 was supplied from Riedel-Dehaen.

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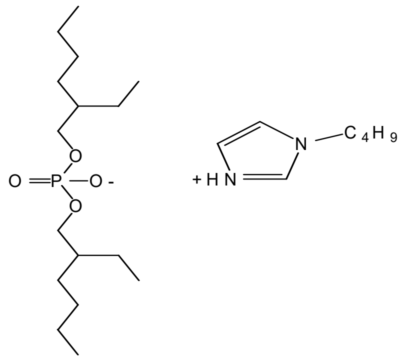

Fig. 1 Structure of 1-butyl-imidazolium di(2-ethylhexyl) phosphate

B. Apparatus

UV–visible absorption spectrophotometer; type Analytik Jena SPECORD 210 was used for the zinc (II) analysis. pH measurements were taken with a Consort C831 pH-meter using a combined electrode.

C. Extraction Experiments and Analytical Procedure

All the experiments were carried out at room temperature (20±1 °C). Equal volumes (5 cm^3) of the aqueous phase containing desired concentrations of zinc (II) and organic phase containing ionic liquid in chloroform solvent, were placed in 50 cm^3 glass-stoppered flasks, and agitated with a magnetic stirrer at 300 rpm for 15 minutes which was sufficient to achieve equilibrium in preliminary experiments. The initial pH of the aqueous solution (pHi) was adjusted by adding small amounts of HCl or NaOH. After the separation of the two phases, the zinc ion concentrations in the aqueous phase were spectrophotometrically determined using 1-(2-Pyridylazo)-2-naphthol as a chromogenic reagent in Tween 80 micellar solution at pH 9.0 [16]. The absorbance of PAN–Zn (II) complex was measured at 553 nm. The extraction efficiency (E) of zinc (II) was calculated by using (1).

$$E(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where C_i and C_e are the initial concentration and equilibrium concentration of Zn (II), respectively.

D. Experimental Design

Response surface methodology (RSM) is an empirical statistical technique employed for multiple regression analysis by using quantitative data obtained from properly designed experiments to solve multivariate equations simultaneously [17]. In order to optimize the extraction of Zn (II) by IL according to three variables, namely the initial pH (X1), IL concentration (X2) and NaCl concentration (X3), in suitable parameter ranges, the factorial of the type 33 has been applied. Three variation levels for each parameter were considered as summarized in Table I. All the experiments were carried out in duplicates using a 1 mM zinc solution.

TABLE I
CODIFICATION AND LEVELS OF THE THREE INDEPENDENT VARIABLES CONSIDERED FOR THE EXTRACTION OF ZINC (II)

Variable	Range and Levels		
	Low (−1)	Medium (0)	High (+1)
pHi, X_1	2.5	4.5	6.6
[IL], X_2 (mM)	1	5.5	10
[Na Cl], X_3 (mM)	0.01	5.0	10

TABLE II
EXPERIMENTAL DATA

Run	Factor levels			Response function
	X_1	X_2	X_3	(E%)
1	-1	-1	-1	15.52
2	-1	-1	0	25.50
3	-1	-1	+1	41.50
4	-1	0	-1	26.90
5	-1	0	0	53.61
6	-1	0	+1	70.88
7	-1	+1	-1	57.85
8	-1	+1	0	82.33
9	-1	+1	+1	91.98
10	0	-1	-1	31.93
11	0	-1	0	58.40
12	0	-1	+1	84.09
13	0	0	-1	69.10
14	0	0	0	90.89
15	0	0	+1	91.54
16	0	+1	-1	77.33
17	0	+1	0	90.66
18	0	+1	+1	85.99
19	+1	-1	-1	23.20
20	+1	-1	0	43.26
21	+1	-1	+1	48.23
22	+1	0	-1	74.28
23	+1	0	0	80.12
24	+1	0	+1	81.26
25	+1	+1	-1	79.51
26	+1	+1	0	97.21
27	+1	+1	+1	96.60
(28, 29, 30) [a]	0	0	0	90.36 90.44 90.98

a = Three additional tests at the central point (0, 0, 0) for the calculation of the Student and Fisher's tests.

The experimental data were analyzed by the response surface method using the software Statgraphics Centurion XVI. 27 experiments were carried out to investigate the experimental domain; three experiments were added to investigate the performance in the center of the experimental domain and to estimate the model validity, reproducibility and experimental error. The experiment design was given in Table II along with experimental data and predicted responses. The extraction efficiency (E) of Zn (II) was chosen as experimental response. Each experimental response Y, can be described by a second order model for predicting the response in all experimental regions from the following equation [18]:

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=2}^{n} \beta_{ij} X_i X_j \quad (2)$$

where *Y is* the predicted response, β_0 is a constant, β_i, β_{ii}, and β_{ij} are the coefficients estimated from regression and they represent the linear, quadratic, and cross products of variables on response.

III. Results and Discussion

Analysis of variance (ANOVA) was performed to characterize the coefficients of the quadratic form of (2). The quality of the fit of quadratic model was determined from correlation coefficient (R^2) value. The significance and adequacy of the model was assessed from the F-ratio (Fisher variation ratio), probability value (P-value), and the value of adequate precision [19]. The ANOVA table (Table III) shows the analysis of variance model for the extraction efficiency (E) of zinc (II) using ionic liquid. In this case, five effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level. The effect of linear coefficients (X_1, X_2, X_3) on Zn (II) extraction were significant ($P<0.05$). The square effects of initial pH (X_1^2) and ionic liquid concentration (X_2^2) were also found to be statistically significant at 95% confidence level. However, the other interaction effects were not significant since P-values were greater than 0.05.

TABLE III
Statistical Parameters for 3^3 Design

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
X_1:pH	1379.88	1	1379.88	16.66	0.0006 ^{b}
X_2:[IL]	8356.23	1	8356.23	100.86	0.0000 ^{b}
X_3:[NaCl]	3106.03	1	3106.03	37.49	0.0000 ^{b}
X_1^2	1787.34	1	1787.34	21.57	0.0002 ^{b}
$X_1 X_2$	6.73501	1	6.73501	0.08	0.7786
$X_1 X_3$	251.992	1	251.992	3.04	0.0973
X_2^2	587.111	1	587.111	7.09	0.0154 ^{b}
$X_2 X_3$	156.169	1	156.169	1.89	0.1858
X_3^2	288.508	1	288.508	3.48	0.0775
$X_1 X_2 X_3$	32.361	1	32.361	0.39	0.5394
Total error	1574.09	19	82.8466		
Total (corr.)	18413.5	29			

$R^2 = 91.4515$ %, $R^2_{adj} = 86.9522$ %, b= significant variable

The coefficient of determination is about 0.91 indicating that the model is significant and explains about 91% of the total variation. The coefficient of determination adjusted (R^2_{adj}), which is more suitable for comparing models with different numbers of independent variables, is 86.95%. The values of regression coefficients obtained are given in Table IV. The Pareto chart (Fig. 2) gives the relative importance of the individual and interaction effects, it contains a bar for each effect, sorted from most significant to least significant. A vertical line is drawn at the location of the 0.05 critical value for Student's t. These results confirmed that the individual effect of the initial pH of aqueous phase, IL concentration, and effect of NaCl concentration were very significant and have net positive effects on zinc extraction, further, the square effects of pH and concentration of ionic liquid have net negative effects on zinc removal. The results show that significance effect upon extraction efficiency have the control factors: IL concentration, salt effect, initial pH. The same control factors and in the same order has a significant effect upon process efficiency.

The coefficients that were not significant were removed from the general polynomial (2). Consequently, a simplified polynomial model that describes the zinc (II) extraction by ionic liquid can thus be expressed using (3):

$$Y = 87.179 + 8.756X_1 + 21.546X_2 + 13.136X_3 - 16.145X_1^2 - 9.253X_2^2 \quad (3)$$

TABLE IV
Values of Model Coefficients

Coefficient	*Estimate*
β_0	87.179
β_1	8.756
β_2	21.546
β_3	13.136
β_{11}	-16.145
β_{12}	0.749
β_{13}	-4.583
β_{22}	-9.253
β_{23}	-3.608
β_{33}	-6.486
β_{123}	-2.011

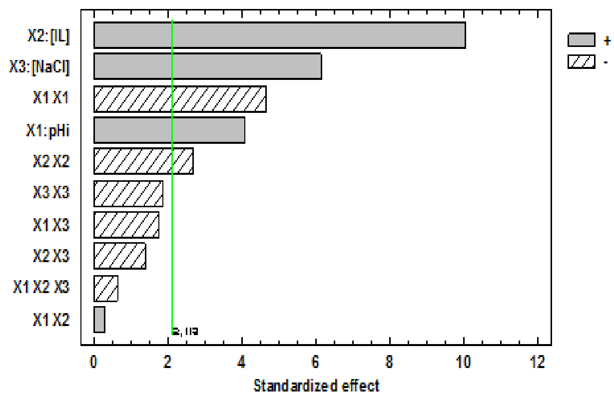

Fig. 2 Pareto chart of standardized effects on the removal efficiency for Zn (II)

The visualization optimization of the predicted model equation can be obtained by the 3D surface response plot. These plots confirm the results discussed previously. The responses of surfaces curves give the interactions of variables and also determine the optimal level variables for maximum response. Tracing response surfaces for significant interactions between two variables based on the extraction yield of the Zn (II), is presented in Figs. 3 (a)-(c). The responses were mapped against two experimental factors, while the other factors are held constant at its central level. Therefore, the zinc ion could be quantitatively removed from aqueous acetate medium at optimal conditions: initial pH 4.8, extractant concentration of 9.9 mM and NaCl concentration of 8.2 mM.

IV. Conclusion

The factorial design of experiments for batch extraction of the zinc ion using 1-butyl imidazolium di(2-ethylhexyl) phosphate as ionic liquid was studied. The effects of three factors; initial pH, ionic liquid concentration and ionic strength on efficiency of extraction were identified. The statistical analysis confirmed that (3) gave a reasonably good fit with an R^2 value of 0.91. All independent factors as well as the square effects of pH and concentration of ionic liquid were found to have significant effect on zinc (II) extraction. The best performance for Zn (II) extraction (100% of metal ion removed) was obtained with 9.9 mM of IL at initial pH 4.8 in the presence of NaCl 8.2 mM. This study showed that factorial experimental design approach is an excellent tool and could successfully be used to develop empirical equation for the prediction and understanding of Zn (II) extraction efficiency.

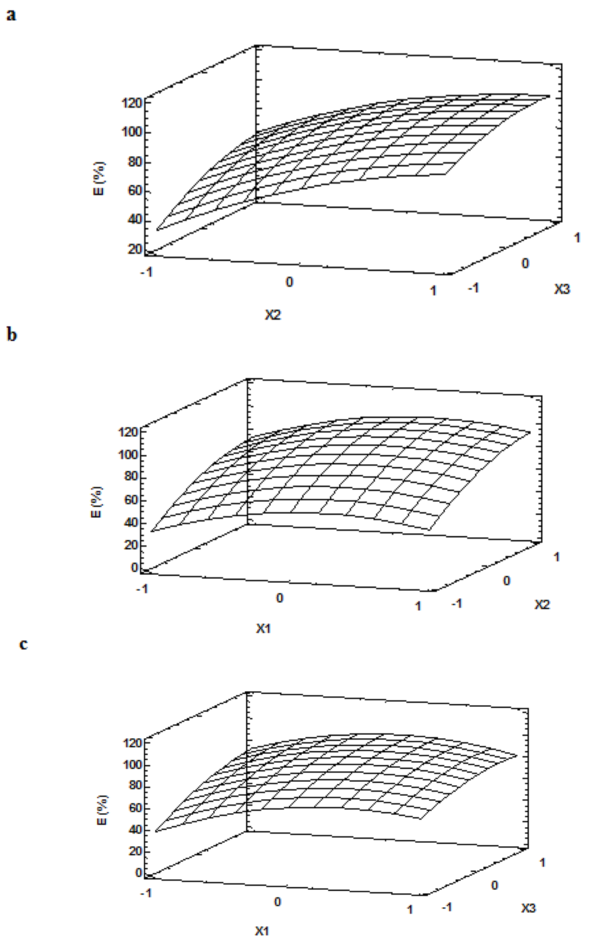

Fig. 3 3D representations of the extraction efficiency of Zn (II) at fixed: (a) pHi=4.5, (b) [NaCl]=5mM, (c) [IL]=5.5mM

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