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Optimization of Trace Metal Ion Binding Properties of a Novel Schiff Base Using Response Surface Methodology

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In this study, solvent extraction technique combined with response surface methodology (RSM) applying Box-Behnken design was applied to study the uptake of metal ions from aqueous solutions using bis(2,2'-methylidene-phenol)diaminoethane (H₂BMPDE). The extractions were monitored based on the process variables of time, temperature and concentration of hydrochloric acid, metal ions and H₂BMPDE. The extraction efficiencies of metal ions by H₂BMPDE optimized using RSM models indicated the estimated extraction percentage of >99%. The predicted and experimental values under the same conditions showed less than 5% difference thereby making the Box-Behnken design approach an efficient, effective and reliable method for the uptake of metal ions from aqueous solution with H₂BMPDE by solvent extraction technique. The novel Schiff base (H₂BMPDE) synthesized was characterized using common physicochemical techniques of UV-Vis, FT-IR, elemental analysis, GC-MS and NMR spectral data. The result obtained indicated that the process could be applied in the removal of metal ions from environmental samples such as soil, industrial waste water and acid mine sites.

Keywords: Metal ions, Schiff base, RSM, Solvent extraction

INTRODUCTION

A Schiff base is a condensation product of aldehyde or ketone with an amine; Schiff bases are known to contain imine or azomethine (-C=N-) functional group. Many scientists are interested in research activities on this area because they can be tailored due to their structural flexibility and variability [1-3]. Bis(2,2'-methylidene-phenol)diaminoethane (H₂BMPDE), a Schiff base derived from the condensation of primary amine(ethane-1,2-diamine) and a ketone (2-hydroxybenzaldehyde), is of much research interest due to the structural variability, flexibility, modification of substituent, ease of synthesis and myriads of applications [4]. The ligand is a chelating tetradentate molecule with N₂O₂ donor properties observed in several studies to make metals in various oxidation states to achieve stability [5]. The reaction between H₂BMPDE and a metal

cation affords the formation of H₂BMPDE-metal complex usually coloured and are known to be important as models in many biological processes, in catalysis, in heavy metal removal, as photochromic and thermochromic agent, as antimicrobial agent and in the textile industries [3].

Solvent extraction also known as liquid-liquid extraction is a well-known technique applied for the preconcentration and separation of metals and in hydrometallurgical processing of raw and secondary materials [6]. This process is highly selective, of low energy cost, environmentally friendly, reliable and efficient especially when designing new liquid-liquid extraction plants if predictive modeling is sought [6]. Optimization of extraction analytical processes requires experimental designs that offer germane information extracted from minimal variable and low cost experiments and evaluating the relationship of interaction among the variables [3,7]. In response surface methodology (RSM) approach, Box-Behnken design, a symmetrical, evolving, multivariate and second-order polynomial design

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which predicts responses among variables through optimization of analytical technique, is applied [8-15]. Box-Behnken design (BBD) is more efficient and economical than other corresponding Central composite (CCD) and Doehlert designs and this informed the reason for its use in the optimization process.

Most optimization processes in chemistry using RSM focused on extraction of valuable materials from plant sources not until recently when Zhang and Liu [16] and Bilgin *et al.*, [3] applied the RSM in optimizing process conditions for the synthesis of iron-polysaccharide complex and N,N',N'',N''' -tetrasalicylidene-3,3',4,4'-tetraaminodiphenyl ether, respectively. From available literature, there is no research so far on the optimization and metal ion binding properties of H_2BMPDE Schiff base. Interestingly, efforts to develop an improved high affinity modified by de novo design or re-modification of existing scaffold metal ion binding organic materials is at the forefront of research [17]. Consequently, binding sites of this kind affords opportunity for developing novel catalytic species, regulating biological processes, stabilizing metal ions and developing biosensors for trace metal ion determination [17].

In this study, H_2BMPDE was synthesized by the condensation of ethane-1,2-diamine and 2-hydroxybenzaldehyde and characterized by elemental analysis, gas chromatography-mass spectrometry (GC-MS), Fourier transform infrared spectrophotometry (FT-IR), UV-Vis spectra and NMR data. The trace metal binding capacity of the Schiff base was studied in relation to the variables of time of extraction, temperature, metal ion, acid and H_2BMPDE concentrations with extraction solvent as trichloromethane. The study involving response surface methodology approach is a predictive simulation optimization process for getting optimum amounts of species sought for when the stated conditions are satisfied. Existing solvent extraction processes focused mainly on the specie extracted, the conditions of extraction and the mechanisms for extraction. As an extension of the existing work, the combinations of factors and prediction of favorable conditions for combination as well as the optimum conditions for maximum yield of the sought product was the major thrust of this work. These parameters are very important for industrial designs.

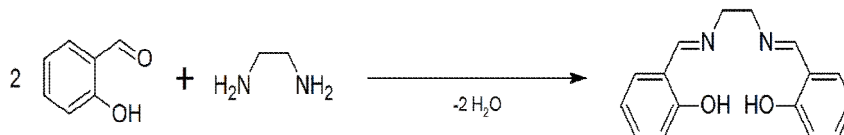
EXPERIMENTAL

Ethane-1,2-diamine and 2-hydroxybenzaldehyde were supplied by Merck chemicals. H_2BMPDE as described elsewhere was prepared by modified Takeshima procedure [18]. Other reagents (hydrochloric acid, trichloromethane, tetrachloromethane and ethanol) were commercially obtained and used as received. Melting point, equilibration and shaking, elemental analysis, GC-MS, UV-Vis, FT-IR and NMR spectra of H_2BMPDE were executed with electrothermal digital melting point apparatus (Labtech model AV1), rotary shaker (RF-12 Remi equipment), vario-elemental microcube ELIII, GC-MSQ2010 Plus (Shimadzu, Japan) coupled with gas chromatograph, UV-Vis spectrophotometer (model Genesis 10S), Perkin-Elmer FTIR-8400S Fourier transform infrared spectrophotometer in the range of $4000-400\text{cm}^{-1}$ in KBr pellets, Bruker Avance II 400 MHz spectrometers with $CDCl_3$ as solvent and tetramethylsilane as internal reference. Optimization of the process conditions was performed using design expert software version 8.0.7.1 (Stat-ease Inc., USA, 2011).

Stock solutions of iron(II), iron(III), Mn(II) and Cr(III) were made by dissolving $Fe_2(SO_4)_3$ (p.a), $Mn(CH_3COO)_2 \cdot 4H_2O$ (p.a), $Cr(NO_3)_3 \cdot 9H_2O$ (p.a) and $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (p.a) with distilled deionized water.

Synthesis of Bis(2,2'-methylidenephenol) diaminoethane (H_2BMPDE)

H_2BMPDE was synthesized according to the literature procedure by the modified Takeshima procedure [18]. Ethane-1,2-diamine and 2-hydroxybenzaldehyde were mixed in the mole ratio of 1:2 (Scheme 1) in a 500 cm^3 beaker and heated in a mantle. The crude product obtained after stirring for five minutes was recrystallized twice from carbon tetrachloride and dried [18]. Analytical yield: 64.45%, Melting point = $127 \pm 1\text{ }^\circ\text{C}$, electronic spectrum (DMF, nm, $\epsilon = \text{Mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$): 260 ($\epsilon = 3.0 \times 10^2$), 285 ($\epsilon = 3.6 \times 10^2$), 335 ($\epsilon = 4.7 \times 10^2$). Analytical calculated for $C_{16}H_{16}N_2O_2$: C, 71.64%; H, 5.97%; N, 10.44%. Found: C, 70.89%; H, 6.05%; N, 10.41%. FT-IR (KBr, cm^{-1}): 3401 cm^{-1} ν (-OH), 3042 cm^{-1} ν (=CH aromatic), 2913 cm^{-1} ν (-CH aliphatic), 1615 cm^{-1} ν (Imine-N=CH-), 1494, (aromatic-C=C-), 1416(N-C), 1285 cm^{-1} ν (phenol C-O); $^1\text{H NMR}$ ($CDCl_3$, δ , ppm): 7.4 (1H,



Scheme 1. Synthesis of H₂BMPDE

N=C(H); 6.5-7.11 (4H, ArH); 3.5 (4H, =NCH₂CH₂N=).
¹³C NMR (CDCl₃, d, ppm): 221.44 (bonded to phenolic oxygen); 152.65 (aromatic carbons); 48.69 (methylene carbon); GC-MS (m/z): calculated for [M+1]⁺ 268; found [M+1]⁺ 268.

Metal Extraction Procedure

Solvent extraction technique was applied to examine the extraction of H₂BMPDE-metal complexes from the aqueous media to the organic trichloromethane phase. The experiment was done by preparing aqueous solution of the metal-H₂BMPDE which was previously extracted into the trichloromethane layer with the aqueous phase containing the H₂BMPDE dissolved in ethanol. Pretest examination revealed the optimum conditions for the preparation and extraction to the hydrochloric acid concentration of 10⁻⁴ M, H₂BMPDE concentration of (1%) 1.86 × 10⁻² M, initial metal ion concentration of 2 mg l⁻¹ and temperature of 25 °C. The experiment was done by equilibrating and shaking in a mechanical shaker at 300 rpm with equal volumes of the organic trichloromethane and aqueous phases (made up of metal solution, acid solution and H₂BMPDE) in stoppered extraction bottles for 15 min at 30 °C. The solution containing the aqueous and organic components was transferred to a separatory funnel allowed standing and the aqueous phase separated from the organic components. The amount of metal ion left in the aqueous phase was determined spectrophotometrically as described elsewhere [19] while the mass balance result indicated the quantity of metal ion extracted into the organic phase. The amount (n) and extraction percentage (E%) of the metal ions extracted into the organic phase is calculated as shown in Eqs. (1) and (2), respectively;

$$n = \frac{(W_0 - W_e) m}{L} \quad (1)$$

$$\text{Extraction efficiency (\%)} = 100 \times \frac{W_0 - W_e}{W_e} \quad (2)$$

where W₀, W_e, m and L represents initial metal ion concentration (mg l⁻¹), equilibrium metal ion concentration (mg l⁻¹), volume of metal ion solutions (cm³), and mass of H₂BMPDE (g).

Response Surface Methodology

The response surface technique applying Box-behnken design matrix was applied to study the interaction and effects among the factors and their level of contributions and significance in the synthesis and extraction of metal complexes of H₂BMPDE. This method determines the needed best working conditions in a shorter time and detailed conditions of processes are provided. This was achieved through a designed experimental design applying Box-Behnken design of 46 steps of experiment consisting five factors and three levels. The experiment was performed in two replicates using 10 cm³ of H₂BMPDE solution, 10 cm³ of metal ion solution and 5 cm³ of HCl solution. The Box-Behnken design (BBD) following the design expert software version 8.0.7.1 (Stat-ease Inc., USA, 2011) was used to evaluate the effect of time, temperature, ligand, acid and metal concentrations on the synthesis and extraction of metal H₂BMPDE complexes.

RESULTS AND DISCUSSION

Characteristics of H₂BMPDE

H₂BMPDE was recrystallized in carbon tetrachloride to give bright yellow crystals with a yield percentage of 64.45% and melting point of 127 ± 1 °C. Elemental analysis, GC-MS, UV-Vis, FT-IR and NMR provided useful information for the formation of the ligand from the precursor compounds and the results obtained were satisfactory. Elemental analysis and GC-MS indicated

$[M+1]^+$ of the ligand as 268. In the ligand H₂BMPDE, the unavailability of amine proton signals is a confirmation of the condensation of the precursor compounds, ethane-1,2-diamine and 2-hydroxybenzaldehyde [3]. The ultraviolet visible spectra of H₂BMPDE indicated absorptions at 260, 285 and 335 nm representing $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and charge transfer transitions of the phenyl or imine ring, non-bonding electrons in the nitrogen and intraligand charge transfer transitions, respectively [20-21]. FT-IR of H₂BMPDE illustrated phenolic hydroxyl group with broad peak at 3401 cm⁻¹ and C=N stretching frequency at 1615 cm⁻¹ a confirmation that the ligand was actually made [3,22]. Absorption band at 1285 cm⁻¹ was assigned to phenol C-O group and characteristic band assignable to C=O and NH₂ present in the precursor compounds disappeared further, establishing that the ligand was actually synthesized [3,23-25]. The symmetrical nature of H₂BMPDE was shown by methyne proton, observed as a doublet at 3.5 ppm and azomethine proton as a quartet at 7.4 ppm [21]. The hydrogen of aromatic ring appeared at 7.11 ppm. The ¹³C NMR spectrum of H₂BMPDE shows phenolic carbon atom at 221.44 ppm, aromatic carbons at 152.65 ppm and methylene carbon at 48.69 ppm.

Optimization Process

Solvent extraction technique where the mean results for 46 experiments providing different process conditions combination are illustrated in Table 1. Randomization of the process conditions order was done to avoid errors that may arise in the system. The experimental design showing the factor effects in relation with the response variables were evaluated using mathematical models showing their relevance and contributions to the entire process. Analysis of variance (ANOVA) was applied in the results of analysis and evaluation at 95% confidence level and is germane in process development and optimization of process conditions in analytical processes.

In ANOVA (Table 2), most of the main factors and combined interaction factors have p-values less than 0.05 indicating their significance at 95% confidence level. This means that they contribute to the model and are necessary for the formation and extraction of the compound whereas others with p-values greater than 0.05 are statistically insignificant, with no contribution, and should be excluded

from the model. The F-value, a measure of the model significance, was high for all the interactions illustrating the significance. The most significant factor, as shown by the high F-value, is acid concentration. High acid concentration impedes complexation as the ligand is degraded or metal complex formed is demetallated [5]. Similarly, to assess the relevance and significance of the models, any model with coefficient of determination (R^2) above 90% is significant, excellent and shows goodness of fit. From Table 3, the R^2 values, the standard deviation and coefficient of variation are presented. The R^2 value for all the metal ions was over 99%. The precision and reliability of the experiment, tested using the coefficient of variation (C.V), indicated the relatively low values of 1.90, 2.11, 1.99 and 2.08% for Fe(II), Fe(III), Cr(III) and Mn(II), respectively, showing a better reliability and precision.

The complexation of the various metal ions as a function of initial metal ion concentration was investigated at 25 °C and acid concentration of 1.0×10^{-4} M. A monotonous increase was observed in metal ion uptake as concentration increased consequent upon the concentration gradient driving force. The metal uptake increased to a concentration point of 20 µg with ligand concentration of 1.0% for which above this, more ligand is unavailable to occupy the co-ordination sites and as such a decrease was obtained.

The RSM based on Box-Behnken design (BBD) optimization of process conditions for Fe(II), Fe(III), Mn(II) and Cr(III) optimum extraction percentage at initial metal ions concentration of 20 µg, ligand concentration of 1.0%, acid concentration of 1.0×10^{-4} M and temperature of 25 °C was 81.75, 85.909, 70.612 and 69.615%, respectively. Higher uptake of Fe(II) and Fe(III) was observed for the Schiff base as a result of high complexing ability of the ligand H₂BMPDE toward the metal cations [26-28]. The presence of H⁺ is necessary for complexation and plays important role as without it there would be no complexation. At low concentration of acid (0.0001 M), metal uptake was high, but at high concentration (0.1-0.01 M), complexation was hindered as the ligand was degraded [5]. Thus, at decreased acid concentration, the metal ions uptake increased as a result of the dissociation of the hydroxyl group through which the metal ions co-ordinate. In other words, the decrease in the metal ions

Table 1. BBD Design Matrix and Experimental Results for Metal Ions-binding Properties of H₂BMPDE

F	S	coded	level			Of	F			F	F	F	F	F
			-1	0	+1									
Tm	X ₁		1.00	8.00	15.00									
A	X ₂		0.500	0.25	10 ⁻⁴									
Tp	X ₃		20.00	30.00	40.00									
M	X ₄		5.00	12.5	20.0									
L	X ₅		0.05	0.525	1.00									
Run	F		levels			actual				Pred				
	X ₁	X ₂	X ₃	X ₄	X ₅	Fe ²⁺	Fe ³⁺	Mn ²⁺	Cr ³⁺	Fe ²⁺	Fe ³⁺	Mn ²⁺	Cr ³⁺	
1	1.00	0.0001	30.00	12.50	0.525	43.39	55.0	29.66	41.86	43.60	55.26	30.16	41.43	
2	15.0	0.0001	30.00	12.50	0.525	40.95	65.00	33.22	41.62	41.22	64.95	33.06	41.35	
3	1.00	0.50	30.00	12.50	0.525	6.23	25.91	29.28	27.60	6.31	26.62	29.51	27.61	
4	15.0	0.50	30.00	12.50	0.525	8.63	15.89	32.95	27.95	8.78	16.29	32.53	28.12	
5	8.00	0.250	20.00	5.00	0.525	9.49	2.48	17.33	12.77	9.81	3.15	16.94	12.98	
6	8.00	0.250	40.00	5.00	0.525	6.38	19.39	12.97	5.69	6.56	19.62	13.14	5.33	
7	8.00	0.250	20.00	20.00	0.525	19.87	23.00	20.15	6.95	19.85	23.57	19.69	7.03	
8	8.00	0.250	40.00	20.00	0.525	6.55	1.91	16.50	17.07	6.38	2.05	16.60	16.58	
9	8.00	0.0001	30.00	12.50	0.05	44.07	66.08	28.63	35.46	44.20	66.62	29.22	35.75	
10	8.00	0.500	30.00	12.50	1.00	2.59	23.00	29.28	25.13	2.79	23.38	29.55	25.71	
11	8.00	0.0001	30.00	12.50	1.00	37.86	57.90	29.57	39.62	37.70	58.39	30.08	39.80	
12	8.00	0.500	30.00	12.50	0.525	9.11	24.00	28.38	22.32	9.20	24.33	28.57	22.78	
13	1.00	0.25	20.00	12.50	0.525	9.93	11.50	12.37	5.20	10.24	10.85	12.17	5.50	
14	15.0	0.25	20.00	12.50	0.525	10.86	12.00	15.64	8.78	10.97	12.55	16.06	9.10	
15	8.00	0.25	40.00	12.50	0.525	2.39	10.90	10.06	9.29	2.57	10.35	9.06	9.84	
16	8.00	0.25	40.00	12.50	0.525	1.94	7.35	11.46	6.10	1.92	8.00	11.68	6.66	
17	8.00	0.25	30.00	5.00	0.05	1.75	3.75	10.67	1.86	1.80	3.98	11.05	2.17	
18	8.00	0.25	30.00	20.00	0.05	7.49	8.81	14.43	4.18	7.53	9.07	14.33	4.20	
19	8.00	0.25	30.00	5.00	1.00	2.45	4.20	14.02	1.60	2.65	4.00	11.17	2.11	
20	8.00	0.25	30.00	20.00	1.00	6.58	1.94	55.78	5.16	6.77	1.76	14.09	5.38	

Table 1. Continued

21	8.00	0.001	20.00	12.50	0.525	67.27	67.22	13.63	46.44	67.05	66.92	55.96	46.56
22	8.00	0.500	20.00	12.50	0.525	0.58	37.06	11.26	28.65	0.085	36.74	14.05	28.55
23	8.00	0.0001	40.00	12.50	0.525	26.50	73.16	51.75	42.99	26.59	72.88	11.19	43.03
24	8.00	0.500	40.00	12.50	0.525	24.01	26.04	9.61	34.16	23.82	25.74	51.90	33.98
25	1.00	0.25	30.00	5.00	0.525	4.66	0.37	15.53	4.99	4.41	0.62	10.09	5.33
26	15.0	0.25	30.00	5.00	0.525	3.76	3.00	15.63	6.11	3.14	2.57	16.05	6.19
27	1.00	0.25	30.00	20.00	0.525	7.82	3.81	15.67	8.55	8.03	4.32	16.20	8.63
28	15.0	0.25	30.00	20.00	0.525	9.53	1.89	15.58	8.36	9.38	1.72	16.15	8.19
29	8.00	0.25	30.00	12.50	0.05	9.61	22.70	10.24	4.45	9.65	22.09	10.42	4.12
30	8.00	0.25	30.00	12.50	0.05	0.04	7.53	10.43	3.56	0.048	7.23	10.50	3.63
31	8.00	0.25	20.00	12.50	1.00	8.50	6.00	14.03	3.83	8.46	6.11	13.88	3.24
32	8.00	0.25	40.00	12.50	1.00	1.41	15.51	7.16	5.82	1.34	15.93	6.91	5.63
33	1.00	0.25	30.00	12.50	0.05	0.88	5.02	4.89	0.95	0.50	4.87	4.20	0.44
34	15.0	0.25	30.00	12.50	0.05	0.27	5.22	13.47	0.93	0.38	4.86	12.78	0.51
35	1.00	0.25	30.00	12.50	1.00	0.73	1.92	10.21	1.20	0.38	1.54	9.76	0.86
36	15.0	0.25	30.00	12.50	1.00	0.44	1.50	7.55	1.48	0.59	0.91	7.10	1.22
37	8.00	0.0001	30.00	5.00	0.525	30.57	61.02	33.11	44.59	30.56	60.78	32.08	44.29
38	8.00	0.500	30.00	5.00	0.525	22.78	23.19	36.53	28.54	22.92	22.68	35.85	27.74
39	8.00	0.0001	30.00	20.00	0.525	62.83	63.18	40.07	43.54	62.71	62.75	39.54	43.92
40	8.00	0.500	30.00	20.00	0.525	0.59	24.24	34.77	33.54	0.62	23.55	34.59	33.41
41	8.00	0.250	30.00	12.50	0.525	19.09	53.73	70.55	60.90	0.62	53.65	70.61	60.78
42	8.00	0.250	30.00	12.50	0.525	19.00	54.00	71.00	61.00	19.15	53.65	70.61	60.78
43	8.00	0.250	30.00	12.50	0.525	19.50	53.00	70.00	60.20	19.15	53.65	70.61	60.78
44	8.00	0.250	30.00	12.50	0.525	19.08	53.71	71.56	60.70	19.15	53.65	70.61	60.78
45	8.00	0.250	30.00	12.50	0.525	19.10	53.73	71.00	60.70	19.15	53.65	70.61	60.78
46	8.00	0.250	30.00	12.50	0.525	19.10	53.70	70.55	61.00	19.15	53.65	70.61	60.78

Legend: T_m = time (min), A = acid concentration (M), T_p = temperature (°C), M = metal concentration (M), L = ligand concentration (M), F = factors, S = symbols.

Table 2. The ANOVA for RSM Quadratic Model Ion Binding Properties Showing P and F Values

Model	Fe(II)		Fe(III)		Mn(II)		Cr(III)	
	F	P	F	P	F	P	F	P
Model	7589.93	<0.0001	4127.49	<0.0001	3033.88	<0.0001	4620.48	<0.0001
X ₁	0.097	0.7582	1.35	0.2563	111.31	<0.0001	0.85	0.3662
X ₂	62226.46	<0.0001	19327.22	<0.0001	4.45	0.0450	3473.72	<0.0001
X ₃	3579.02	<0.0001	82.20	<0.0001	151.38	<0.0001	17.17	0.0003
X ₄	1242.94	<0.0001	26.17	<0.0001	122.50	<0.0001	133.28	<0.0001
X ₅	0.12	0.7368	171.64	<0.0001	0.048	0.8287	6.03	0.0213
X ₁ X ₂	74.95	<0.0001	324.04	<0.0001	0.00096	0.9226	0.41	0.5263
X ₁ X ₃	6.11	0.0206	13.25	0.0012	2.78	0.1077	54.37	<0.0001
X ₁ X ₄	21.79	<0.0001	16.78	0.0004	28.75	<0.0001	2.04	0.1660
X ₁ X ₅	0.33	0.5722	0.31	0.5822	100.57	<0.0001	0.11	0.7466
X ₂ X ₃	13187.00	<0.0001	232.55	<0.0001	5436.58	<0.0001	95.23	<0.0001
X ₂ X ₄	9485.75	<0.0001	1.00	0.3278	60.53	<0.0001	43.42	<0.0001
X ₂ X ₅	518.48	<0.0001	68.13	<0.0001	2.70	0.1132	57.63	<0.0001
X ₃ X ₄	333.52	<0.0001	1167.19	<0.0001	0.40	0.5322	350.93	<0.0001
X ₃ X ₅	19.68	0.0002	492.48	<0.0001	39.68	<0.0001	9.84	0.0043
X ₄ X ₅	8.29	0.0080	43.34	<0.0001	0.11	0.7441	1.82	0.1889
X ₁ ²	8194.13	<0.0001	19818.52	<0.0001	25167.63	<0.0001	329940.58	<0.0001
X ₂ ²	23151.46	<0.0001	5247.26	<0.0001	2352.44	<0.0001	173.85	<0.0001
X ₃ ²	1928.53	<0.0001	7879.92	<0.0001	21984.36	<0.0001	25480.81	<0.0001
X ₄ ²	2104.72	<0.0001	17415.63	<0.0001	18630.51	<0.0001	26912.78	<0.0001
X ₅ ²	11433.39	<0.0001	16391.10	<0.0001	28558.63	<0.0001	41934.60	<0.0001

uptake at high acid concentration could be attributed to the lower dissociation extent of the hydroxyl group with the protonation of the lone nitrogen pair on the imine molecule [28].

The extraction mechanism of the metal ions from aqueous acid solutions using the tetradentate Schiff base at the acid concentration of 10⁻¹ to 10⁻⁴ M is suggested to

proceed by anion association route with the protonation of the ligand at high acid concentration (10⁻⁴ M) which could ligate as neutral molecule with the metal cations as shown in Eqs. (3)-(5) [28];

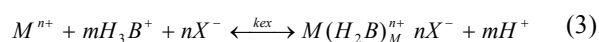


Table 3. Regression Models for Metal Ion Binding Properties of H₂BMPDE (Performed at Coded Units)

Metal ion	R ²	Adj R ²	C.V (%)	Mean	S.D	Regression equation
Fe(II)	0.9998	0.9997	1.90	14.70	0.28	Yield = 19.15 + 0.022X ₁ - 17.43X ₂ - 4.18X ₃ + 2.46X ₄ + 0.024X ₅ + 1.21X ₁ X ₂ - 0.33X ₁ X ₃ + 0.65X ₁ X ₄ + 0.080X ₁ X ₅ + 16.05X ₂ X ₃ - 13.61X ₂ X ₄ + 3.18X ₂ X ₅ - 2.55X ₃ X ₄ + 0.62X ₃ X ₅ - 0.040X ₄ X ₅ - 8.57X ₁ ² + 14.40 X ₂ ² - 4.16 X ₃ ² - 4.34 X ₄ ² - 10.12 X ₅ ²
Fe(III)	0.9997	0.9995	2.11	26.34	0.56	Yield = 53.65 - 0.16X ₁ - 19.33X ₂ - 1.26X ₃ + 0.71X ₄ - 1.82X ₅ - 5.00X ₁ X ₂ - 1.01X ₁ X ₃ - 1.14X ₁ X ₄ - 0.15X ₁ X ₅ - 4.24X ₂ X ₃ - 0.28X ₂ X ₄ + 2.29X ₂ X ₅ - 9.50X ₃ X ₄ + 6.17X ₃ X ₅ - 1.83X ₄ X ₅ - 26.50X ₁ ² + 13.64 X ₂ ² - 16.71X ₃ ² - 24.84X ₄ ² - 24.10X ₅ ²
Mn(II)	0.9996	0.9993	2.08	27.00	0.56	Yield = 70.61 + 1.48X ₁ - 0.30X ₂ - 1.72X ₃ + 1.55X ₄ - 0.031X ₅ + 0.028X ₁ X ₂ - 0.47 X ₁ X ₃ - 1.50X ₁ X ₄ - 2.81X ₁ X ₅ + 20.66X ₂ X ₃ - 2.18X ₂ X ₄ - 0.46X ₂ X ₅ + 0.18X ₃ X ₄ - 1.76X ₃ X ₅ - 0.093X ₄ X ₅ - 30.09X ₁ ² - 9.20X ₂ ² - 28.13X ₃ ² - 25.89X ₄ ² - 32.06X ₅ ²
Cr(III)	0.9997	0.9995	1.99	23.12	0.46	Yield = 60.78 + 0.11X ₁ - 6.76X ₂ + 0.48X ₃ + 1.32X ₄ + 0.28X ₅ + 0.15X ₁ X ₂ - 1.69X ₁ X ₃ - 0.33X ₁ X ₄ + 0.075X ₁ X ₅ + 2.24X ₂ X ₃ + 1.51X ₂ X ₄ - 1.74X ₂ X ₅ + 4.30X ₃ X ₄ + 0.72X ₃ X ₅ + 0.31X ₄ X ₅ - 28.20X ₁ ² + 2.05X ₂ ² - 24.81X ₃ ² - 25.49X ₄ ² - 31.82X ₅ ²

$$k_{ex} = \frac{[M(H_2B)_M^{n+} \cdot nX^-][H^+]^m}{[M^{n+}][H_3B^+]^m[X^-]^n} \quad (4)$$

where

X = Cl⁻, ClO₄⁻, NO₃⁻, or HSO₄⁻, M = metal cation and D = Distribution ratio

$$\log D = M \log[H_2B] + n \log[X^-] + m \log K_1 + \log k_{ex} \quad (5)$$

The dissociation is highly acid dependent, and increase in acid concentration lowers dissociation while decrease in acid strength increases dissociation and then metal uptake [29-30]. Dissociation processes from thermodynamic point of view entails dissociation of binding sites of decreased affinity for metal ions. Thus, at low acid concentration, dissociation is slow and metal ions are strongly bound. This observation may not hold for all processes especially when an asymmetric ligand is involved. Extraction of metal ions

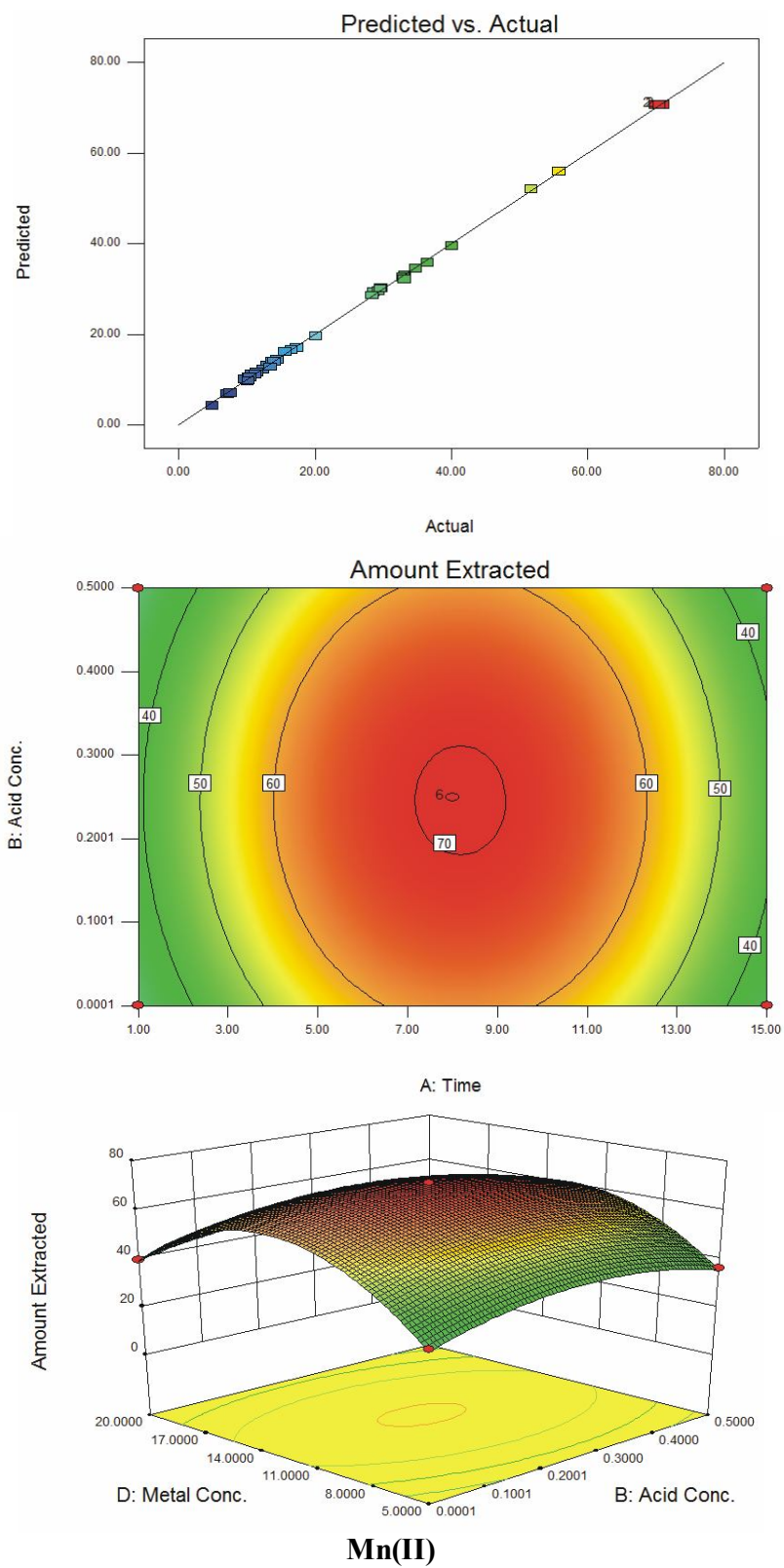
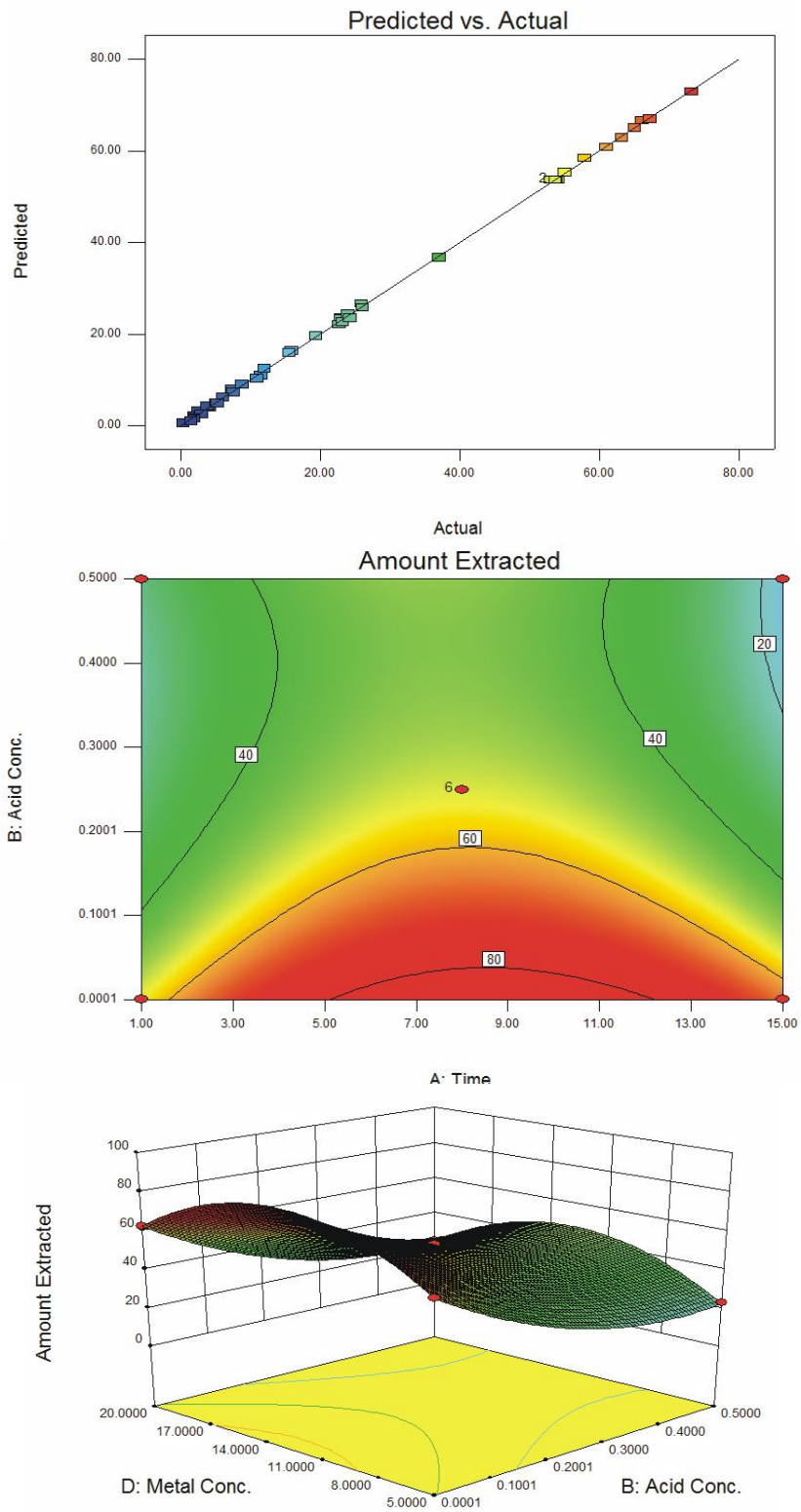
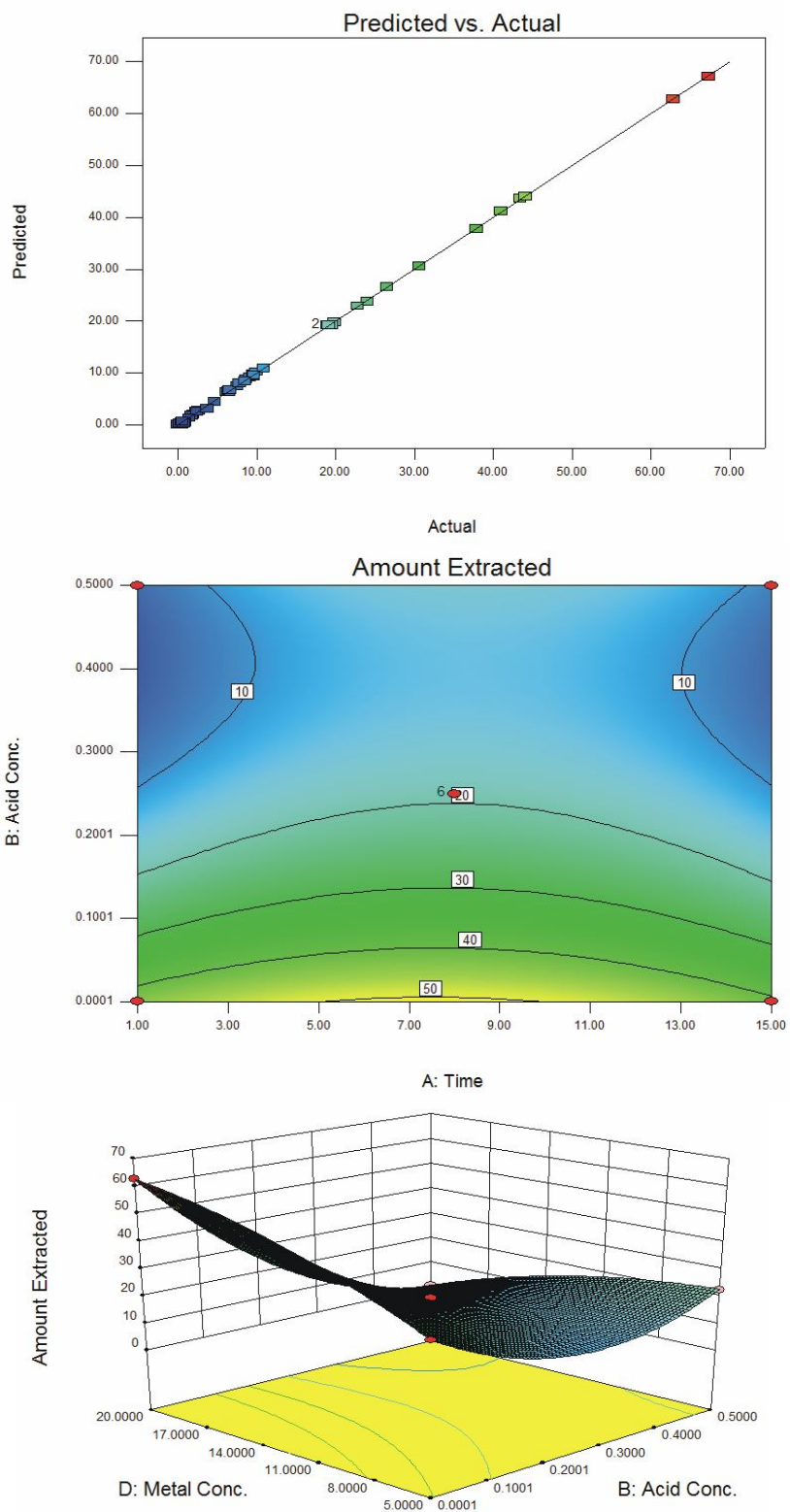


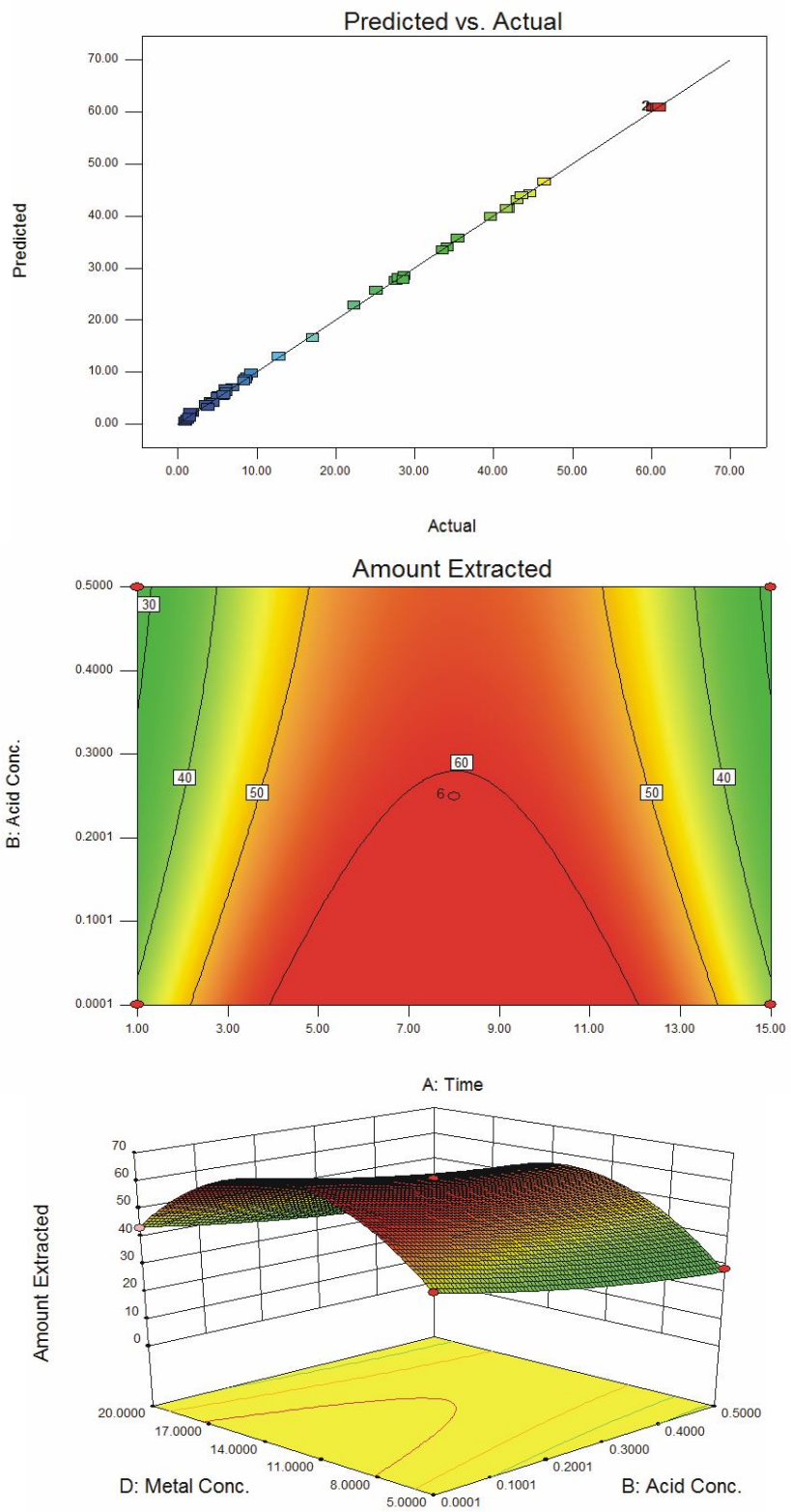
Fig. 1. Response surface plots and predicted *versus* extracted (%) at the optimized levels.



Fe(III)
Fig. 1. Continued.



Fe(II)
Fig. 1. Continued.



Cr(III)

Fig. 1. Continued.

with asymmetric ligands may lead to aggregation of ions at high acid concentration due to the presence of proton switchable ligand co-ordination sites [30]. Similarly, variation of solvents, possibly using tetrachloromethane in lieu of trichloromethane, has notable influence on metal ion extracted. The studies performed [30] have demonstrated that low solvent polarity and water solubility are likely responsible for small extent of metal ions partitioning in extraction of metal ions.

Comparison between the experimental values and the predicted results, shown in Table 1, gave results that were consistent at same conditions and difference less than 5%. The R^2_{adj} value, illustrating the agreement between the experimental values and the predicted results for Fe(II), Fe(III), Mn(II) and Cr(III) (Table 3, Fig. 1), was 99.97, 99.95, 99.93 and 99.95%, respectively, indicating that the BBD optimization process is an efficient, effective and suitable model for metal uptake through solvent extraction.

Examples of response surface plots illustrating the five process conditions on the amount of H₂BMPDE formed which shows a clearer understanding of the interaction effects of the variables are shown in Fig. 1. Since the most significant factor is acid concentration, Fig. 1 shows the predicted and percentage extraction of the metal ions as a function of metal ions and acid concentration at 10⁻⁴ M. As expected, at high acid concentration, monotonous decrease was observed due to ligand degradation or demetallation [5]. The study showed that the novel Schiff base can effectively and efficiently uptake the metal ions under study in aqueous solution in the following decreasing order: Fe(III) (85.909%), Fe(II) (81.757%), Mn(II) (70.612%) and Cr(III) (69.615%). The values showed that Fe(III) was the best extracted metal cation indicating a more stable complex. An increased electronegativity difference between the ligand donor atom and metal atom imparts strong covalent character and increased complex compound stability [3,29-30] as hard donor acids form stronger and more stable inner sphere complexes with oxygen donors.

The metal ions (Fe(III), Mn(II), Fe(II) and Cr(III)) are the hard acid donors except Fe(II) which is a borderline acid donor. The observed similarity between the binding capacity of Fe(III) and Fe(II) could be as a result of similar small ionic radius and polarizability of high spin 6-co-ordinated octahedral Fe(III) ion (ionic radius = 78.5 pm)

and 6-co-ordinated octahedral Fe(II) ion (ionic radius = 75 pm) [30]. The little dissimilarity observed in metal ions binding capacity of Fe(III) and Mn(II), and in Fe(III) and Cr(III), even though they belong to hard acid donors could be attributed to differences in macro ionic charge and also the extent of electrostatic attraction and co-ordination sites present. Thus, the co-ordination of metal ions to H₂BMPDE upon deprotonation at pH 4 suggests chelation of metal ions and predominance of inner sphere complexation. Even though the authors correlated not the extraction models with co-ordination number of metals, results indicate the formation of 6-co-ordinated inner sphere complexes.

CONCLUSIONS

The study presented the synthesis and characterization of H₂BMPDE as a metal ion chelator or extractant. The Schiff bis base was made by condensation reaction of ethane-1,2-diamine and 2-hydroxybenzaldehyde and characterized using UV-Vis, GC-MS, FT-IR and NMR. The optimum conditions for liquid-liquid extraction method for the variables of time, acid concentration, ligand concentration, temperature and metal concentration was determined using RSM approach. The extraction of the metal ions studied from trichloromethane increased in the order Cr(III) → Mn(II) → Fe(II) → Fe(III). Fe(III) was the best extracted metal cation and formed a stoichiometrically more stable complex than other cations. Acid concentrations (10⁻⁴ M) was the most effective medium for metal ion uptake as electrons are available at the N and O donor atoms of the ligand where co-ordination occurs. The predicted and experimental values from the model showed less than 5% difference thereby making the Box-Behnken design approach an efficient, effective and reliable method for the removal of metal ions from aqueous solution with H₂BMPDE by solvent extraction technique.

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