Respon surface methodology optimization for the determination of zinc in water sample by adsorptive stripping voltammetry

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ABSTRACT

A procedure for the determination of zinc in water sample by adsorptive stripping voltammetry using calcon as a complexing agent has been optimized. The influence of several parameters were studied : variations of calcon concentration, pH, accumulation potential and accumulation time. The design experiment was a central composite design with 4 factors/variables, 3 levels and 31 treatment combinations. From analysis of variance, it was decided to accept the second-order model and the independent variable, concluded that a significant effect on the response variable (peak current). Based on data analysis with response surface method, the determination of zinc obtained optimum conditions are : calcon concentration 0.62 mM, pH 7.85, accumulation potential -0.61 Volt and accumulation time 48.39 seconds with a maximum peak current 1008.44 nA. At the optimum condition were obtained relative standard deviation 2.5%, recovery 98 %, the linear range 0.2 - 105 µg/L, coefficient of correlation 0.966 with a detection limit of 1.21 µg/L. Finally, the method was succesfully applied to the determination of Zn(II) in water samples without prior treatment.

Keywords: zinc, adsorptive stripping voltammetry, water samples, respon surface method
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INTRODUCTION

The previous study, to find optimization in the determination of trace metals Cd, Cu, Pb and Zn [1, 2] and trace metals Fe, Co, Ni and Cr [3] in both individual and simultaneous by adsorptive stripping voltammetry (AdSV), carried out by observing the effect of one variable is changed, while the other variables are kept at a constant level. This optimization technique is called optimization of one variable or a factor at the current time.The main drawback of the results of the optimization of the factors that such optimization does not take into account the effect of the interaction between the variables studied. Therefore, this technique does not describe the full effect on the response parameter [4]. Another disadvantage of optimization of these factors is the increase in the number of trials required to do research, which leads to increased time and increased consumption of reagents and materials. To overcome this problem, an optimization technique of analytical procedures is by using multivariate statistical techniques [5].

The most relevant multivariate techniques used in analytical optimization is the Response Surface Method (RSM) with a Central Composite Design (CCD). RSM is a collection of mathematical and statistical techniques, which are used for modeling and analysis of problems in a response that is influenced by several variables, whose purpose is to optimize the response or optimize these variables to achieve the best system performance [4-6]. The RSM was done using Minitab.

Adsorptive stripping voltammetry is a highly sensitive technique [7], the response obtained in the form of the peak current (Ip) is influenced by variables (parameters) the following, namely: calcon concentration, pH , accumulation potential and accumulation time. Therefore it is very important to determine the optimization of these parameters,

which will affect the measurement of the peak flow in order to improve the quality of analytical results [8].The research design used in this study, as a tool for optimization was central composite design with 4 variables, 3 level/degree and 31 a combination of treatments. The first step of 2k factorial design optimization are: provide the code, where the value of the highest level (+1), the lowest level (-1) and code (0) as the center point. Programs for statistical data processing Minitab 16 using Response Surface Methodology.

The purpose of this study was to obtain the optimum condition of Zn, so it can be applied to the analysis of Zn in tap water. To achieve these objectives, required an optimization technique using analytical procedures that Response Surface Method (RSM) with a Central Composite Design (CCD) [4-6, 9]. Some parameters to be studied, among others: variations of calcon concentration, pH, accumulation potential and accumulation time.

EXPERIMENTAL SECTION

2.1. Material and Equipment
Reagents to be used in this study is a pure reagent, because stripping voltammetry is an ultra-sensitive method of analysis. The most important principle to remember is that an ultra-sensitive method of analysis, all chemicals must be pure (pa) and the equipment to be very clean and should be careful in its use. It aims to avoid or protect from contamination.

Voltammetric measurements were carried out using a Metrohm 797 VA. Electrode stand with a multimode electrode (MME) operating in the HMDE mode. An Ag/AgCl/KCl reference electrode and a platinum wire auxilary electrode were used. pH meter 80 models Griffin, Griffin & George Loughborough, England; and analytical balance Mettler AE 200, Toledo OH-USA; and glassware used in the laboratory.

2.2. Procedures
Voltammeter into the vessel, put 10 ml of standard solution of Zn(II) 10 ug/L, added 0.2 mL and 0.2 mL of 0.1 M KCl in 20 mL calcon, this variable is set constant during the experiment. Calcon concentration, pH, accumulation potential and accumulation time is set according to experimental design of the Central Composite Design, used 4 factors and 3 levels, level of each factor is coded -1, 0, and +1, with 2 replications. Factors/variables of experimental design were calcon concentration, pH, accumulation potential and accumulation time can be seen in Table 1.

Table 1. Experimental Design CCD of Zinc

Run	Factor				Peak current (Y)
	Calcon Concentration (X_1)	pH (X_2)	Accumulation Potential (X_3)	Accumulation time (X_4)	
1	0.6	6	-0.7	30	182.21
2	0.6	6	-0.5	30	204.90
3	0.6	6	-0.7	70	161.10
4	0.6	6	-0.5	70	215.55
5	0.6	8	-0.7	30	687.84
6	0.6	8	-0.5	30	675.90
7	0.6	8	-0.7	70	678.52
8	0.6	8	-0.5	70	625.44
9	0.8	6	-0.7	30	220.07
10	0.8	6	-0.5	30	236.43
11	0.8	6	-0.7	70	194.57
12	0.8	6	-0.5	70	246.37
13	0.8	8	-0.7	30	276.84
14	0.8	8	-0.5	30	291.08
15	0.8	8	-0.7	70	259.01
16	0.8	8	-0.5	70	323.89
17	0.7	7	-0.6	50	898.46
18	0.7	7	-0.6	50	898.34
19	0,7	7	-0.6	50	898.26
20	0.7	7	-0.6	50	898.32
21	0.7	7	-0.6	50	898.30
22	0.7	7	-0.6	50	898.31
23	0.7	7	-0.6	50	898.32
24	0.54	7	-0.6	50	873.32
25	0.7	5.4	-0.6	50	821.24
26	0.7	7	-0.76	50	887.13
27	0.7	7	-0.6	18.1	791.15
28	0.86	7	-0.6	50	675.41
29	0.7	8.6	-0.6	50	724.54
30	0.7	7	-0.44	50	775.15
31	0.7	7	-0.6	81.9	681.12

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RESULTS AND DISCUSSION

3.1. Optimization of Zinc Using One Variable.

The optimization by observing the effect of one variable in the determination of trace metal Zn in the presence of calcon has been done [1]. The optimum condition as follow: calcon concentration 0.7 mM, accumulation potential -0.6 V, pH 7, accumulation time 50 seconds. At the optimum conditions, the relative standard deviation was obtained with 8 replicates (n = 8) measurements standard solution Zn(II) 10µg/L was 0.86%, respectively.

This technique does not describe the full effect on the response parameters and optimization of these factors is the increase in the number of trials required to do research, which leads to increased time and increased consumption of reagents and materials. Therefore to overcome this problem, an optimization technique of analytical procedures is by using Respon Surface Methodology.

3.2. Optimization of Zinc Using RSM (Respon Surface Methodology)
3.2.1. Analysis of RSM First-Order Model of Zinc

The data processing was done using software Minitab 16, and the resuls can be seen in Table 2 the following :

Table. 2. Model Orde I regression coefficient

Term	Coef
Constant	430.252
X1	-86.450
X2	134.833
X3	9.963
X4	-4.426

Based on Table 2, regression equation of first-order model was :

$\hat{y} = 430.252 - 86.450x_1 + 134.833x_2 + 9.963x_3 - 4.426x_4$

Where x_1 = calcon concentration (µg/L), x_2 = pH, x_3 = accumulation potential (µg/L), x_4 = accumulation time (seconds), and $\hat{y}$ = peak current (nA).

whereas the results of Analysis of Variance (ANOVA) of first-order model can be seen at Table 3.

Table 3. ANOVA of First-Order Model of Zinc

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	4	412356	412356	103089	1.51	0.253
Linear	4	412356	412356	103089	1.51	0.253
X1	1	119578	119578	119578	1.75	0.207
X2	1	290877	290877	290877	4.26	0.058
X3	1	1588	1588	1588	0.02	0.881
X4	1	313	313	313	0.00	0.947
Residual Error	14	956921	956921	68352		
Lack-of-Fit	12	956921	956921	79743	7869419.43	0.000
Pure Error	2	0	0	0		
Total	18	1369277				

Table 3 test procedure used to determine whether first-order models can be used or not. This hypothesis test was used to test the significance of regression models, which test whether there was a independent variable that significantly influence the response/dependent variable,

The hypothesis tested was: H_O: $\beta i = 0$,
H_1: there $\beta i \neq 0$; i = 1,2,3,4

Based on Table 3, the test regression parameters simultaneously produce p-value of 0.253, meaning that the p-value is greater than the significance level used in the amount of $\alpha = 0.05$. Thus it was decided not to reject H_O and conclude that none of the independent variables that significantly influence the response variable, so the first-order model can not be used

3.2.2. Analysis RSM Second-Order Model of Zinc

First-order model can not be used, then proceed with the second-order model by using a quadratic effect

and interaction. Results of second-order model data processing obtained (Table 4) the following results:

Table 4. Regression Coefficients in the Second-Order Model

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Term          Coef
Constant   966.188
X1         -47.107
X2          54.755
X3          -0.795
X4          -7.024
X1*X1      -49.309
X2*X2      -49.493
X3*X3      -42.216
X4*X4      -54.085
X1*X2      -36.464
X1*X3        2.986
X1*X4        1.539
X2*X3       -2.898
X2*X4       -0.415
X3*X4        1.694
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Based on Table 4, the model regression equation :

$\hat{y} = 966.188 - 47.107x_1 + 54.755x_2 - 0.795x_3 - 7.024x_4 - 49.309x_1^2 - 49.493x_2^2 - 42.216x_3^2 - 54.085x_4^2 - 36.464x_1x_2 + 2.986x_1x_3 + 1.539x_1x_4 - 2.898x_2x_3 - 0.415x_2x_4 - 1.694x_3x_4$

Where x_1 = calcon concentration (µg/L), x_2 = pH, x_3 = accumulation potential (µg/L), x_4 = accumulation time (seconds), and $\hat{y}$ = peak current (nA).

Results of ANOVA second-order model data were presented in Table 5.

Table 5. ANOVA of Second-Order Model

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	1989022	1989022	142073	3.97	0.005
Linear	4	322740	322740	80685	2.25	0.109
X1	1	135973	135973	135973	3.80	0.069
X2	1	183704	183704	183704	5.13	0.038
X3	1	39	39	39	0.00	0.974
X4	1	3023	3023	3023	0.08	0.775
Square	4	1493100	1493100	373275	10.42	0.000
X1*X1	1	435962	326058	326058	9.10	0.008
X2*X2	1	395847	328500	328500	9.17	0.008
X3*X3	1	269006	238995	238995	6.67	0.020
X4*X4	1	392286	392286	392286	10.95	0.004
Interaction	6	173182	173182	28864	0.81	0.580
X1*X2	1	170272	170272	170272	4.75	0.045
X1*X3	1	1142	1142	1142	0.03	0.861
X1*X4	1	303	303	303	0.01	0.928
X2*X3	1	1076	1076	1076	0.03	0.865
X2*X4	1	22	22	22	0.00	0.981
X3*X4	1	368	368	368	0.01	0.921
Residual Error	16	573055	573055	35816		
Lack-of-Fit	10	573055	573055	57305	14693709.29	0.000
Pure Error	6	0	0	0		
Total	30	2562077				

The hypothesis tested was: H_O: $\beta i = 0$,
H_1: there $\beta i \neq 0$; i = 1,2,3, ..., k

Based on Table 5 test procedure against the second-order model. This hypothesis test was used to test the significance of regression models, which test whether there is a independent variable (including quadratic and interaction effects) significantly affects the response variable.

Based on Table 5, test regression parameters simultaneously produce p-value of 0.000, meaning that the p-value obtained is smaller than the significance level used in the amount of a = 0.05. Thus it was decided to reject H_O and conclude that there was a independent variable that significantly influence the response variable, so that the second-order model can be accepted.

Based on the regression coefficient values in Table 3 can be arranged matrix b and B as follows:

$$b = \begin{bmatrix} -47.107 \\ 54.755 \\ -0.795 \\ -7.024 \end{bmatrix} \quad dan \quad B = \begin{bmatrix} -49.3090 & -18.2320 & 1.493 & 0.7695 \\ -18.2320 & -49.4930 & -1.449 & -0.2075 \\ 1.4930 & -1.4490 & -42.216 & 0.8470 \\ 0.7695 & -0.2075 & 0.847 & -54.0850 \end{bmatrix}$$

In order to obtain a stationary point as follows:

$$x_0 = -\frac{B^{-1}b}{2} = \begin{bmatrix} -0.794622 \\ 0.848214 \\ -0.068248 \\ -0.080563 \end{bmatrix}$$

Thus, the solution in response to the stationary point is obtained as follows:

$$\hat{y} = \hat{\beta}_0 + \frac{1}{2}x_0'b = 966.188 + 1/2 \begin{bmatrix} -0,794622 & 0.848214 & -0.068248 & -0.080563 \end{bmatrix} \begin{bmatrix} -47.107 \\ 54.755 \\ -0.795 \\ -7.024 \end{bmatrix} = 10$$

Furthermore, the stationary point can be restored to the true value, acquired conditions that provide the optimal solution (Table 6) was as follows:

Table 6. Optimal Value of Zinc

Variable	Optimal value (with coding)	Optimal value (without coding)
X_1	-0.794622	0.620538
X_2	0.848214	7.84821
X_3	-0.068248	-0.606825
X_4	-0.080563	48.3887

Where x_1 = calcon concentration (µg/L), x_2 = pH, x_3 = accumulation potential (µg/L), and x_4 = accumulation time (seconds).

To get an idea of the characteristics of the surface of the response calculating eigen values (λ) of the matrix B and obtained :
$$\lambda = [\ -67.6448\ -54.1467\ -42.5513\ -30.7602]$$

Because all four eigen values is negative, then the surface shape is the maximum response. It can be seen plot contour and response surface plot. By making constans two of the four factors were observed at a stationary point, then it may be possible to plot contour and response surface as shown in Figure 1.

Based on data analysis with response surface method, it is concluded that the peak flow will reach its maximum value at the time of calcon concentration 0.62 mM, pH = 7.85, accumulation potential -0.61 Volt and accumulation time 48.39 seconds with a maximum peak current value of zinc 1008.44 nA.
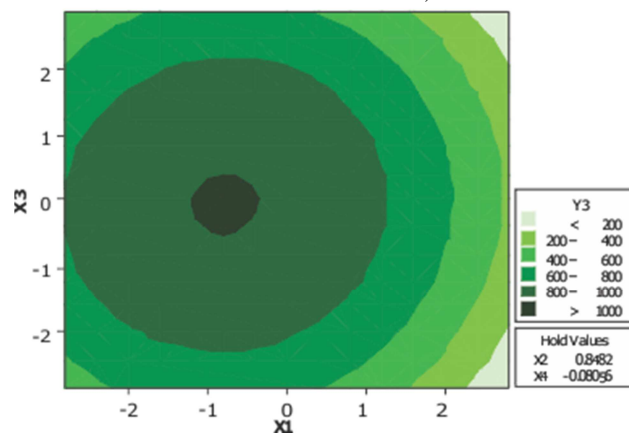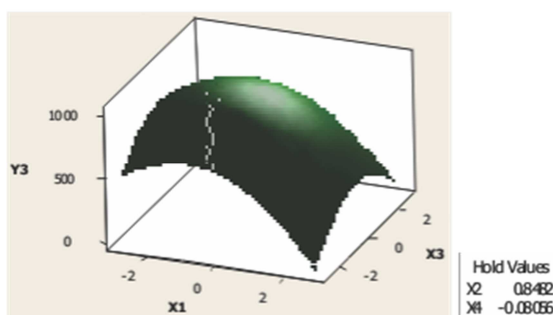
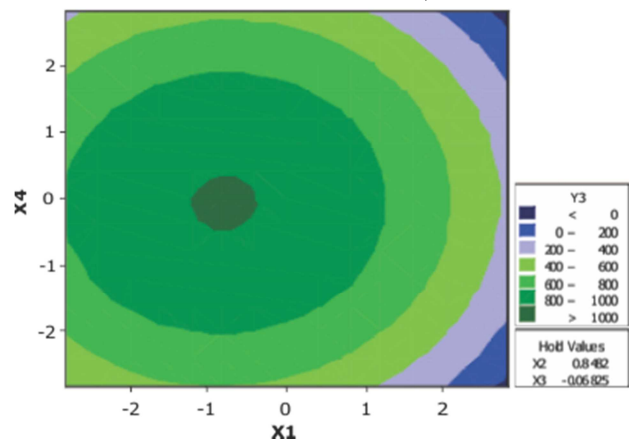Contour Plot Y3 vs X2, X1
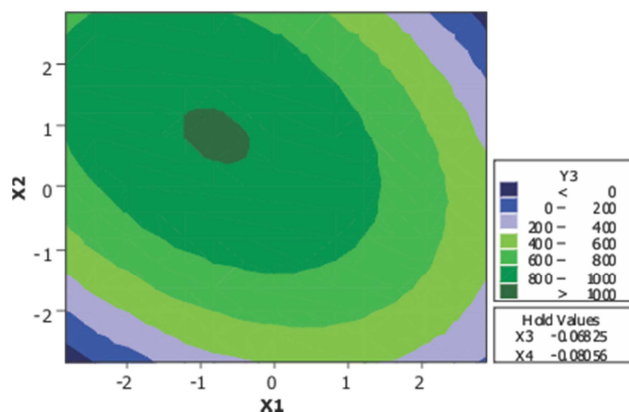
Surface Plot of Y3 vs X2, X1
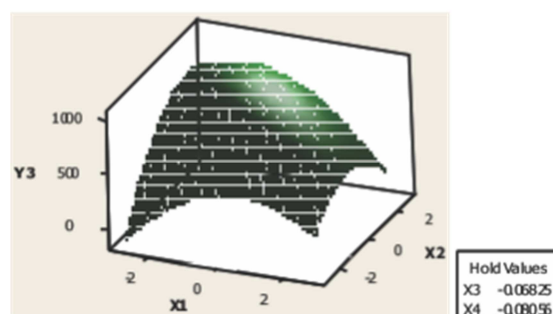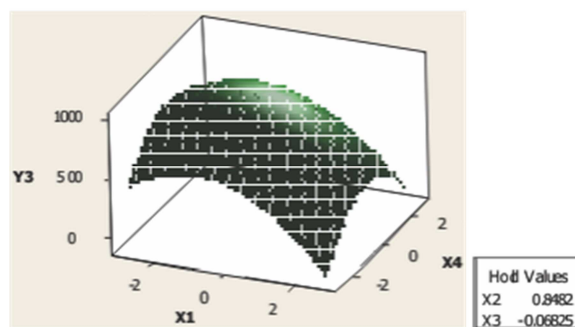

Contour Plot Y3 vs X3, X1

Surface Plot of Y3 vs X3, X1
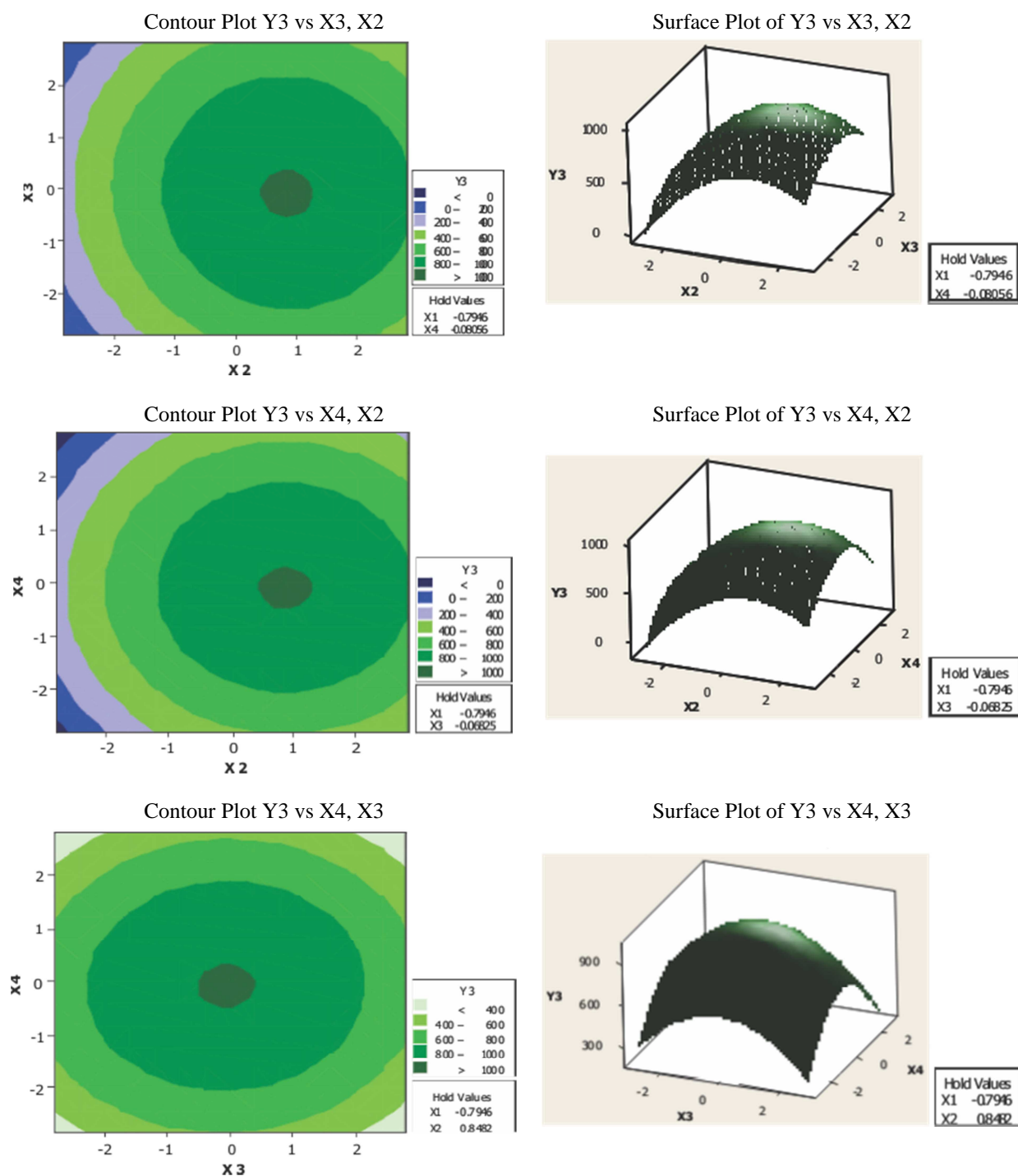

Contour Plot Y3 vs X4, X1

Surface Plot of Y3 vs X4, X1

Contour Plot Y3 vs X3, X2

Surface Plot of Y3 vs X3, X2

Contour Plot Y3 vs X4, X2

Surface Plot of Y3 vs X4, X2

Contour Plot Y3 vs X4, X3

Surface Plot of Y3 vs X4, X3

Figure 1. Contour and surface plot of Zn metal

3.3. Parameter Analytical overview

At optimal conditions a linear relationship between the peak current of Zn-calcon complex with a concentration of Zn(ll) obtained calcon concentration 0.62 mM, pH = 7.85, accumulation potential -0.61 Volt and accumulation time 48.39 seconds with a maximum peak current 1008.44 nA. This method has been successfully applied to a sample of fresh water in which were obtained relative standard deviation 2.5 %, recovery 98 %, the linear range 0.2 - 105 µg/L, coefficient of correlation 0.966 with a detection limit 1.21 µg/L. More information can be seen in the Table 7 and 8

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Table 7. Overview of Analytical Parameters

Parameters	Zn
Tap water sample	33.504 µg/L
RSD	2.5 %
Recovery	98 %
Linier range	0.2 - 105 µg/L
R^2	0.966
LOD	1.21 µg/L

Table 8. Fixed Variable for adsorptive stripping voltammetry procedure

Parameters	Zn
working electrode HMDE	HMDE
stirrer speed	2000 rpm
drop size	4
mode	DP
purge time	300 s
deposition potential	-0.98 V
deposition time	81.85 s
equilibration time	5 s
pulse amplitude	0.05005 V
start potential	-0. 7V
end potential	-1.3 V
voltage step	0.005951 V
voltage step time	0.5 s
sweep rate	0.0119 V/s
peak potential	-1 V

3.4. Interference studies

Possible interference by other metals with the adsorptive stripping voltammetry of zinc was investigated by the addition of the interfering ion to the solution containing 10.0 mg/L of this metal using the optimized conditions. The results of this study are summarised in Table 9. Based on the results, it were found that most of the foreign ions did not interfere for zinc determination.

Table 9. Tolerance ratio of interfering ions in the determination of 10 µg/L of Zn

Ions	Tolerance limit Zn (mg/L)
Cu^{2+}, Pb^{2+}, Cd^{2+} Al^+, Ca^+, Li^+, K^+, Ba^{2+}, Cr^{+3}, Cl^-, F^-, Br^-, SO_4^{2-}, I^-, Ni^{2+}, Co^{2+} $\cdot Fe^{3+}$, Na^+	10

CONCLUSION

Based on data analysis with response surface method, the determination of zinc obtained optimum conditions, namely: calcon concentration of 0.62 mM, pH 7.85, accumulation potential -0.61 Volt and accumulation time 48.39 seconds with a maximum peak current value of zinc 1008.44 nA. The response surface method can be applied to the determination of zinc in water sample quickly, effectively and efficiently. At the optimum condition were obtained relative standard deviation 2.5%, recovery 98 %, the linear range 0.2 - 105 µg/L, coefficient of correlation 0.966 with a detection limit of 1.21 µg/L.

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