



Application of respon surface methodology for the determination of cadmium in sea waterby adsorptive stripping voltammety in the presence of calcon

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ABSTRACT

This paper describes an optimization method for rapid determination of cadmium in sea water by adsorptive stripping voltammety using response surface method. The influence of several parameters were studied : variations of calcon concentration, pH, accumulation potential and accumulation time. The design study was a central composite design with 4 factors / variables 3 levels and 31 treatment combinations. From the results of experiments and statistical evaluation (the results of 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 cadmium obtained optimum conditions are: concentration of calcon 0.47 mM, pH = 7.47, -0.59 Volt accumulation potential and accumulation time of 70.36 seconds with a maximum peak current value of cadmium 11.07 nA. At the optimum condition were obtained relative standard deviation of 0.41%, 98.91% recovery, the linear range up to 105 µg/L with a detection limit of 0.12 µg/L. The response surface method can be applied to the determination of cadmium in sea water rapid, effectively and efficiently.

Keywords: respon surface method, cadmium, adsorptive stripping voltammety

INTRODUCTION

Analysis of dangerous metals in the environment[1], better soil, rock and biological materials (Cu determination in blood samples[2]), foodstuffs and water (determination of Cu and Cd [3]) became the subject which occupies high priorities, and focused on the determination of toxic heavy metals which, when entered into the body of humans and animals for a long time so it can accumulate in vital organs. Unknown levels of the metal ions in the water and in the environment of materials is very small (trace) in the order of ng / kg to mg/kg, while the sample matrix (eg levels of salt in sea water) is quite large and is also tied up in a complex matrix ,

Existing methods for analysis of metal ions such methods Flame Atomic Absorption Spectrometry (FAAS), Graphite Furnace Atomic Absorption Spectrometry (GFAAS) and inductively coupled plasma atomic method of emissions spectrophotometry (ICP-AES). However, this method is costly for the operation, costs maintenance are quite expensive and less practical but it also can not measure the levels of metal ions are very small [4]. Although it has previously been carried out pre-concentration (concentration) to reduce or eliminate the salt content is high enough of a sample of sea water using solvent extraction method [5].

Therefore we need a sensitive and selective method for determining the levels of trace amounts of metal ions, namely the adsorptive stripping voltammety (AdSV). Adsorptive stripping voltammety method chosen as an alternative because it has many advantages such as: high salinity of the sea water does not interfere in the analysis, has a high sensitivity, low detection limit on a scale ug/L (ppb), the use of simple and convenient sample

preparation, analysis fast, inexpensive infrastructure [6-8]. In addition, with this method it is possible to study chemical species of heavy metals [1,9], which can not be done with other methods, this method can be performed for simultaneous determination of Cd, Cu and Pb in seawater using calcon as complexing [10]. Heavy metal toxicity is determined from chemical species [4,11]. Almost all methods of determining the metal in very small quantities requires considerable time on the stage of pre-concentration before measurement. On Stripping adsorptive voltammetry pre-concentration stage shorter time, generally less than 1 minute [12].

From the results of previous research, to find the optimum conditions (optimization) the determination of metal ions Cd, Cu, Pb and Zn [6,10] and metal ions Fe, Co, Ni and Cr [13] in both the singular and simultaneous 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 [14]. 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.

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 [14-15].

Adsorptive stripping voltammetry is a highly sensitive technique [9], the response obtained in the form of the peak current (I_p) 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 [16]. The research design used in this study, as a tool for optimization are: 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 using Response Surface Methodology.

The purpose of this study was to obtain the optimum condition of Cd, so it can be applied to the analysis of Cd in seawater. To achieve these objectives, required an optimization technique using analytical procedures that Response Surface Method (RSM) with a Central Composite Design (CCD) [17]. Some parameters to be studied, among others: variations calcon concentration, pH, accumulation potential and accumulation time.

EXPERIMENTAL SECTION

2.1. Apparatus

Apparatus used in this study were : 797 Metrohm Computrace with HMDE working electrode, reference electrode in the form of Ag/ AgCl / KCl, and a Pt electrode as the electrode support; 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. Reagents

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.

2.3. Procedures

Voltammeter into the vessel, put 10 ml of standard solution of Cd (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 the experimental design of the Central Composite Design in Table 1 below. From Table 1 the responses obtained in the form of the peak current of Cd metal ion.

2.3.1. Surface Response Design : Central Composite

Response Surface Methodology used 4 factors and 3 levels, level of each factor is coded -1, 0, and +1, with 2 replications. The numbers -1, 0, and +1 is a symbol (code) that indicates the value of the variable. -1 figures show

the value of the lowest vaiabel, +1 figures showed the highest variable values, and the number 0 indicates the value of the variable medium¹⁶. Factors/variables of this research design was the calcon concentration, pH, accumulation potential and accumulation time can be seen in Table 1.

Table 1. Experimental Design CCD of Cd

Experiment	Factor				Peak Current (Y)
	Calcon Concentration (X ₁)	pH (X ₂)	Potential (X ₃)	Time (X ₄)	
1	0.4	6	-0.7	50	2.96
2	0.4	6	-0.5	50	2.79
3	0.4	6	-0.7	90	6.32
4	0.4	6	-0.5	90	4.90
5	0.4	8	-0.7	50	2.67
6	0.4	8	-0.5	50	2.43
7	0.4	8	-0.7	90	6.17
8	0.4	8	-0.5	90	3.97
9	0.6	6	-0.7	50	6.73
10	0.6	6	-0.5	50	5.35
11	0.6	6	-0.7	90	5.59
12	0.6	6	-0.5	90	5.35
13	0.6	8	-0.7	50	1.23
14	0.6	8	-0.5	50	1.37
15	0.6	8	-0.7	90	1.44
16	0.6	8	-0.5	90	1.67
17	0.5	7	-0.6	70	10.81
18	0.5	7	-0.6	70	10.81
19	0.5	7	-0.6	70	10.82
20	0.5	7	-0.6	70	10.81
21	0.5	7	-0.6	70	10.82
22	0.5	7	-0.6	70	10.81
23	0.5	7	-0.6	70	10.81
24	0.34	7	-0.6	70	6.32
25	0.5	5.4	-0.6	70	9.30
26	0.5	7	-0.76	70	7.99
27	0.5	7	-0.6	38.1	9.80
28	0.66	7	-0.6	70	8.76
29	0.5	8.6	-0.6	70	7.32
30	0.5	7	-0.44	70	5.75
31	0.5	7	-0.6	101.9	8.42

RESULTS AND DISCUSSION

3.1. Analysis RSM Phase I of Cd Metal

The data processing at the trial stage I was done using software Minitab 16, can be seen in Table 2 the following results :

Table 2. Model Orde I regression coefficient

Term	Coef
Constant	4.91474
X ₁	-0.217500
X ₂	-1.19000
X ₃	-0.330000
X ₄	0.617500

Based on Table 1, a model derived from data analysis of Phase I was :

$$Y = 4.9147 - 0.2175X_1 - 1.1900X_2 - 0.3300X_3 + 0.6175 X_4$$

whereas the results of Analysis of Variance (ANOVA) phase I can be seen at Table 3.

Based on 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 free variable that significantly influence the response variable,

The hypothesis tested was:

$$H_0: \beta_i = 0,$$

$$H_1: \text{there } \beta_i \neq 0; i = 1,2,3,4$$

Based on Table 3, the test regression parameters simultaneously produce p-value of 0.587, 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_0 and conclude that none of the independent variables that significantly influence the response variable, so the first-order model can not be used.

Table 3. ANOVA Mode Orde 1

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regresi	4	31.258	31.258	7.814	0.73	0.587
Linear	4	31.258	31.258	7.814	0.73	0.587
X ₁	1	0.757	0.757	0.757	0.07	0.794
X ₂	1	22.658	22.658	22.658	2.11	0.168
X ₃	1	1.742	1.742	1.742	0.16	0.693
X ₄	1	6.101	6.101	6.101	0.57	0.463
Residu Error	14	149.989	149.989	10.499		
Lack of Fit	12	149.989	149.989	12.499		0.000
Pure Error	2	0.000	0.000	0.000		
Total	18	181.246				

3.2. Analysis RSM Phase II of Cd Metal

Model order I can not be used, then proceed with the second-order model by adding a quadratic effect and interaction. Results of a phase II data processing obtained (Table 4) the following results:

Table 4. Regression Coefficients in the Model Order II

Term	Coef
Constant	11.3336
X ₁	0.02881
X ₂	-1.03288
X ₃	-0.41775
X ₄	0.34901
X ₁ *X ₁	-1.89116
X ₂ *X ₂	-1.61899
X ₃ *X ₃	-2.12799
X ₄ *X ₄	-1.33622
X ₁ *X ₂	-0.97375
X ₁ *X ₃	0.17375
X ₁ *X ₄	-0.69625
X ₂ *X ₃	0.07125
X ₂ *X ₄	0.07625
X ₃ *X ₄	-0.12375

Based on Table4, the model obtained from the Phase II data analysis were :

$$\hat{y} = 11.3336 + 0.0288149X_1 - 1.03288X_2 - 0.417748X_3 + 0.349005X_4 - 1.89116X_1^2 - 1.61899X_2^2 - 2.12799X_3^2 - 1.33622X_4^2 - 0.973750X_1X_2 + 0.173750X_1X_3 - 0.696250X_1X_4 + 0.0712500X_2X_3 + 0.0762500X_2X_4 - 0.123750X_3X_4$$

Results of ANOVA phase II data were presented in Table 5.

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 free variable (including quadratic and interaction effects) significantly affects the response variable.

The hypothesis tested was:

$$H_0: \beta_i = 0,$$

$$H_1: \text{there } \beta_i \neq 0; i = 1, 2, 3, \dots, k$$

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 $\alpha = 0.05$. Thus it was decided to reject H_0 and conclude that there was a free variable that significantly influence the response variable, so that the second-order model can be accepted.

Table 5. ANOVA Model Order II

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	295.894	295.894	21.135	8.79	0.000
Linear	4	29.542	29.542	7.385	3.07	0.047
X ₁	1	0.018	0.018	0.018	0.01	0.932
X ₂	1	23.106	23.106	23.106	9.61	0.007
X ₃	1	3.780	3.780	3.780	1.57	0.228
X ₄	1	2.638	2.638	2.638	1.10	0.310
Square	4	242.522	242.252	60.631	25.23	0.000
X ₁ *X ₁	1	78.209	59.923	59.923	24.93	0.000
X ₂ *X ₂	1	53.841	43.917	43.917	18.27	0.001
X ₃ *X ₃	1	80.557	75.871	75.871	31.57	0.000
X ₄ *X ₄	1	29.915	29.915	29.915	12.45	0.003
Interaction	6	23.830	23.830	3.972	1.65	0.197
X ₁ *X ₂	1	15.171	15.171	15.171	6.31	0.023
X ₁ *X ₃	1	0.483	0.483	0.483	0.20	0.660
X ₁ *X ₄	1	7.756	7.756	7.756	3.23	0.091
X ₂ *X ₃	1	0.081	0.081	0.081	0.03	0.856
X ₂ *X ₄	1	0.093	0.093	0.093	0.04	0.847
X ₃ *X ₄	1	0.245	0.245	0.245	0.10	0.754
Residual Error	16	38.456	38.456	2.404		
Lack of Fit	10	38.456	38.456	3.846		0.000
Pure Error	6	0.000	0.000	0.000		
Total	30	334.349				

3.3. Determination of Point Stasioner

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

$$b = \begin{bmatrix} 0.02881 \\ -1.03288 \\ -0.41775 \\ 0.34901 \end{bmatrix} \quad \text{dan} \quad B = \begin{bmatrix} -1.89116 & -0.97375 & 0.17375 & -0.69625 \\ -0.97375 & -1.61899 & 0.07250 & 0.07625 \\ 0.17375 & 0.07250 & -2.12799 & -0.12375 \\ -0.69625 & 0.07625 & -0.12375 & -1.33622 \end{bmatrix}$$

In order to obtain a stationary point as follows:

$$x_0 = -\frac{B^{-1}b}{2} = \begin{bmatrix} -0.250033 \\ 0.474385 \\ 0.092847 \\ 0.018159 \end{bmatrix}$$

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

Variable	Optimal value (with coding)	Optimal value (without coding)
X ₁ (calcon)	-0.25003	0.474997
X ₂ (pH)	0.474385	7.474385
X ₃ (Potential)	0.092847	-0.59072
X ₄ (Time)	0.018159	70.36318

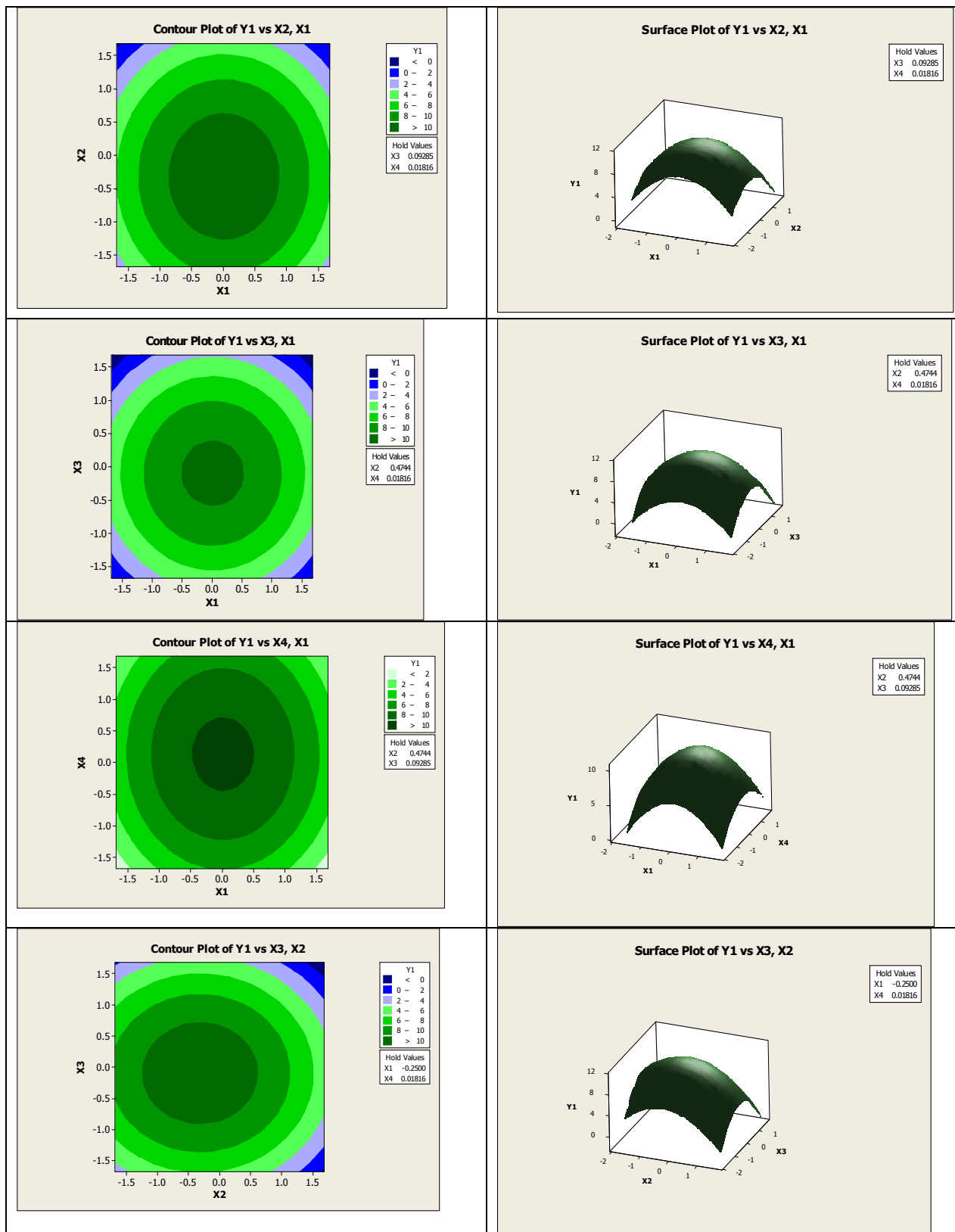
3.4 Characteristics of Response Surface Analysis.

To get an idea of the characteristics of the surface of the first response calculating eigen values(λ) of the matrix B and obtained :

$$\lambda = [-2.91919 \quad -2.13736 \quad -1.48877 \quad -0.42904]$$

Because all four eigenvalues 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 = 0.4749971, pH = 7.474385, potential = -0.59072 and time = 70.36318. The maximum value of the peak current is equal to 11.068 nA



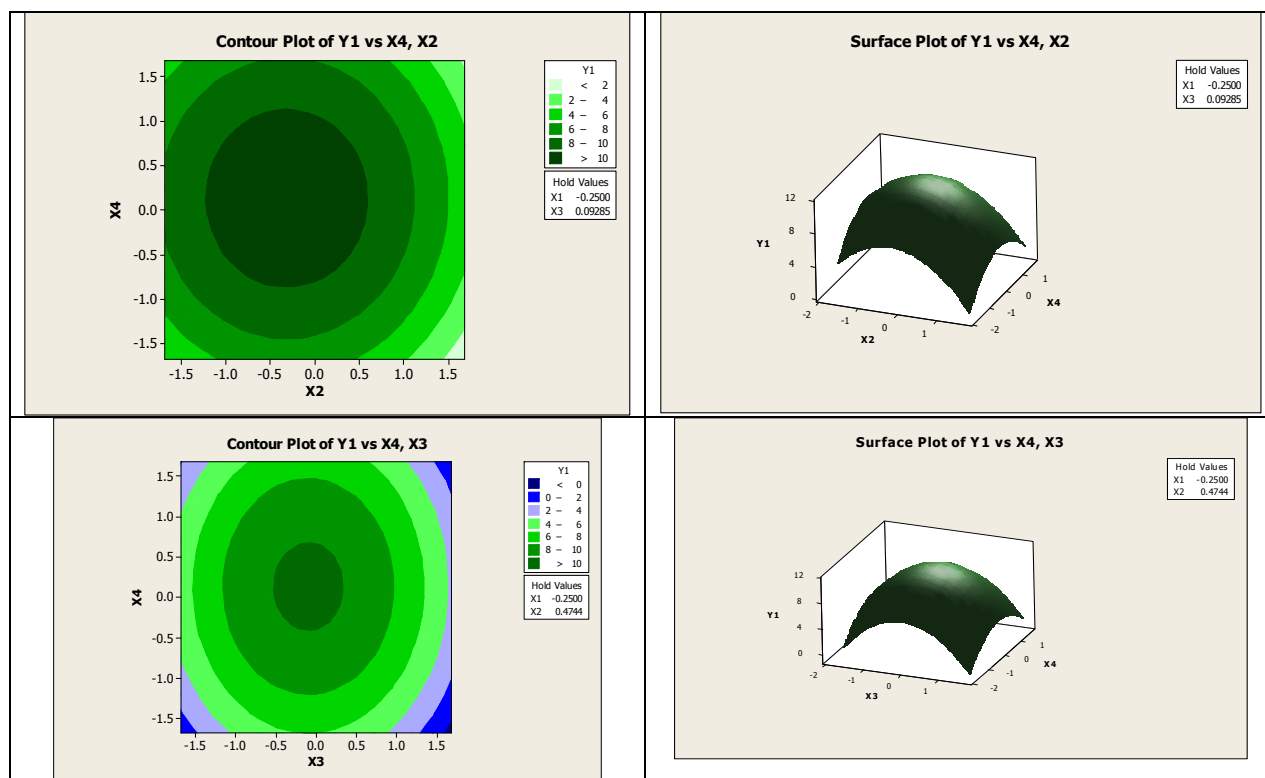


Figure 1. Contour and surface plot of Cd metal

3.5. Parameter Analytical overview

At optimal conditions a linear relationship between the peak current of Cd-calcon complex with a concentration of Cd(II) obtained in the range from 0.2 to 135 g/L with a time of 70.36 seconds with the press; $y = 0.879x + 0.457$ with a correlation coefficient (r) = 0.971. Limit of detection (LOD) calculated from three times the standard deviation of the blank divided by the slope of the curve (3 SD/B) obtained by 0.1213 $\mu\text{g/L}$. The relative standard deviation values obtained 0.413% of ten times ($n = 10$) measurement of Cd(II) with recovery (recovery) 98.91%. This method has been successfully applied to a sample of sea water in which the concentration of Cd(II) are: 333.35 g/L. More information can be seen in the Table 7 and 8.

Table 7. Overview of Analytical Parameters

Parameter	Cd
Sea water sample	333.347 $\mu\text{g/L}$
RSD	0.4130 %
Recovery	98.913 %
Linear range	105 $\mu\text{g/L}$
R^2	0.971
LOD	0.1213 $\mu\text{g/L}$

Table 8. Fixed Variable for adsorptive stripping voltammetry procedure

Parameters	Cd
Working Electrode	HMDE
Stirrer Speed	2000 rpm
Drop Size	4
Mode	DP
Purge Time	300 s
Deposition Potential	-0.591 V
Deposition Time	70.363 s
Equilibration Time	5 s
Pulse Amplitude	0.05005 V
Start Potential	-0.45 V
End Potential	-0.67 V
Voltage Step	0.005951 V
Voltage Step Time	0.5 s
Sweep Rate	0.0119 V/s
Peak Potential	-0.56 V

CONCLUSION

Based on data analysis with response surface method, the determination of cadmium obtained optimum conditions, namely: calcon concentration of 0.47 mM, pH = 7.47, -0.59 Volt accumulation potential and accumulation time of 70.36 seconds with a maximum peak current value of cadmium 11.07 nA. On condition optimum obtained value relative standard deviation of 0.41%, 98.91% recovery, the linear range up to 105 g/L with a detection limit of 0.12 mg/L. The response surface method can be applied to the determination of cadmium in sea water quickly, effectively and efficiently.

Acknowledgment

The author would like to thank to Ministry of Research, Technology dan Higher Education, which has funded this study, in accordance with the Agreement on Implementation of Research Grant Number: 030 / SP2H / PL / DITLITABMAS / II / 2015, dated February 5, 2015.

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