



Optimization Central Composite Design for the Simultaneous Determination of Cd(II) ion in Fruit and Vegetable Samples by Adsorptive Stripping Voltammetry

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ABSTRACT

This work describes a procedure for the simultaneous determination of cadmium in fruit and vegetable samples using adsorptive stripping voltammetry of complexes with calcon at a hanging mercury drop electrode (HMDE) has been optimized using central composite design (CCD). The selection of the experimental conditions was made using experimental of 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 central composite design, the determination of cadmium obtained optimum conditions were : calcon concentration 0.8435 mM, pH 8.0047, accumulation potential -0.6346 Volt and accumulation time 81.85 seconds with a maximum peak current 61.8146 nA. At the optimum condition were obtained relative standard deviation 0.84%, recovery 98.88%, the linear range up to 110 µg/L, limit of detection 1.009 µg/L and LOQ 3.363 µg/L. The procedure was successfully applied to the determination of cadmium in fruit and vegetable samples without prior treatment.

Keywords : simultaneous, cadmium, adsorptive stripping voltammetry, fruit and vegetable samples, central composite design.

INTRODUCTION

Cadmium is known to be a hazardous environmental pollutant with toxic effects. Adverse

effects of cadmium are produced not only because of its high toxicity in humans and animals, even at trace concentrations, but also due to bioaccumulation processes in almost all organs. The main target

organs affected by cadmium are lungs, kidney, bones and teeth.

The concentration of cadmium in various samples is low, so sensitive and selective methods for determination of cadmium in environmental samples are required. Sensitive methods for the determination of trace amounts of metal ions in natural samples have received much attention and many techniques have been employed.

Analysis of heavy metals at trace levels in fruit and vegetable samples are very important in the field of environmental analysis due to their important roles in life. For that, atomic absorption techniques have been usually used. However, they offer many difficulties due to insufficient detection limits and/or matrix interferences of real samples and a preconcentration step is often required¹⁻⁴.

The use of electroanalytical techniques is another alternative widely employed, specially the stripping voltammetry. These methods are well-established for trace metal analysis and adsorptive processes (AdSV) can further lower detection limits of stripping voltammetry to the picomolar concentration levels. In addition, these techniques are inexpensive, simple, quick and very useful for saline matrices like seawater and estuarine water samples and for speciation studies¹⁻⁶.

The previous study, to find optimization in the determination of trace metals Cd, Cu, Pb and Zn¹⁻³ and trace metals Fe, Co, Ni and Cr⁴ 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 parameter⁷. 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 techniques⁷⁻⁹.

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 performance⁷⁻¹¹. The RSM was done using Minitab.

Adsorptive stripping voltammetry is a highly sensitive technique¹², 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 results⁸⁻¹⁰. 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 cadmium, so it can be applied to the analysis of cadmium in fruit and vegetable samples. To achieve these objectives, required an optimization technique using analytical procedures that RSM with a CCD⁷⁻¹⁴. Some parameters were studied: variations of calcon concentration, pH, accumulation potential and accumulation time.

EXPERIMENTAL

Reagents were 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 auxiliary 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

Work Procedure

To the vessel voltammetry, put 10 mL of a mixture of standard solution of Cd (II), Cu(II), Pb (II) and Zn (II) 10 ug/L, added 0.2 mL and 0.2 mL of 0.1 M KCl calcon in 20 ml, this variable is set constant during the experiment. Calcon concentration, pH,

Tabel 1: Optimization Central Composite Design (CCD) for the Simultaneous Determination of Cd, Cu, Pb, and Zn using calcon

| Run | Factor | | | | Peak current (nA) | | | |
|-----|---------------------------|------|----------------------------|-----------------------|-------------------|--------|--------|--------|
| | Calcon concentration (mM) | pH | Potential accumulation (V) | Time accumulation (s) | Cd | Cu | Pb | Zn |
| 1 | 0.6 | 5 | -0.7 | 40 | 21.75 | 129.74 | 52.22 | 57.58 |
| 2 | 0.6 | 5 | -0.5 | 40 | 12.17 | 174.41 | 54.45 | 57.16 |
| 3 | 0.6 | 5 | -0.7 | 80 | 37.35 | 178.61 | 105.90 | 43.44 |
| 4 | 0.6 | 5 | -0.5 | 80 | 11.61 | 176.06 | 104.21 | 49.35 |
| 5 | 0.6 | 7 | -0.7 | 40 | 16.36 | 266.66 | 40.21 | 87.60 |
| 6 | 0.6 | 7 | -0.5 | 40 | 9.56 | 284.95 | 44.71 | 92.37 |
| 7 | 0.6 | 7 | -0.7 | 80 | 23.61 | 269.02 | 38.17 | 77.73 |
| 8 | 0.6 | 7 | -0.5 | 80 | 9.45 | 251.44 | 75.64 | 84.67 |
| 9 | 0.8 | 5 | -0.7 | 40 | 25.11 | 180.35 | 41.40 | 61.13 |
| 10 | 0.8 | 5 | -0.5 | 40 | 13.12 | 182.27 | 38.77 | 54.13 |
| 11 | 0.8 | 5 | -0.7 | 80 | 48.71 | 191.26 | 79.17 | 54.13 |
| 12 | 0.8 | 5 | -0.5 | 80 | 10.05 | 176.11 | 57.54 | 46.14 |
| 13 | 0.8 | 7 | -0.7 | 40 | 92.35 | 295.00 | 39.16 | 83.35 |
| 14 | 0.8 | 7 | -0.5 | 40 | 62.63 | 293.86 | 37.28 | 92.71 |
| 15 | 0.8 | 7 | -0.7 | 80 | 101.69 | 313.50 | 40.20 | 90.03 |
| 16 | 0.8 | 7 | -0.5 | 80 | 70.97 | 276.99 | 39.19 | 105.80 |
| 17 | 0.7 | 6 | -0.6 | 60 | 104.33 | 221.07 | 80.86 | 101.49 |
| 18 | 0.7 | 6 | -0.6 | 60 | 100.35 | 231.13 | 81.85 | 104.32 |
| 19 | 0.7 | 6 | -0.6 | 60 | 105.21 | 232.14 | 80.86 | 105.29 |
| 20 | 0.7 | 6 | -0.6 | 60 | 104.12 | 223.12 | 79.36 | 103.41 |
| 21 | 0.7 | 6 | -0.6 | 60 | 103.13 | 222.07 | 83.14 | 103.43 |
| 22 | 0.7 | 6 | -0.6 | 60 | 102.23 | 221.32 | 81.26 | 102.21 |
| 23 | 0.7 | 6 | -0.6 | 60 | 104.12 | 222.04 | 81.26 | 101.21 |
| 24 | 0.532 | 6 | -0.6 | 60 | 15.61 | 204.06 | 86.38 | 98.24 |
| 25 | 0.7 | 4.32 | -0.6 | 60 | 19.67 | 201.89 | 74.87 | 92.89 |
| 26 | 0.7 | 6 | -0.768 | 60 | 28.48 | 169.23 | 69.04 | 84.43 |
| 27 | 0.7 | 6 | -0.6 | 26,4 | 12.25 | 123.32 | 33.70 | 88.11 |
| 28 | 0.868 | 6 | -0.6 | 60 | 39.90 | 118.98 | 45.76 | 84.98 |
| 29 | 0.7 | 7.68 | -0.6 | 60 | 78.77 | 117.77 | 69.87 | 97.65 |
| 30 | 0.7 | 6 | -0.432 | 60 | 7.35 | 226.99 | 46.84 | 99.76 |
| 31 | 0.7 | 6 | -0.6 | 93,6 | 12.72 | 186.71 | 87.97 | 83.61 |

potential accumulation and time accumulation is set according to the experimental design of the Central Composite Design (CCD) in Table 1. From Table 1 was obtained peak current response of Cd, Cu, Pb and Zn ions.

Experimental design

The CCD system is an effective model and used for sequential experimentation which provides information for testing 'the goodness of fit' and does not require unusual large number of design points thereby reducing the overall cost associated with the experiment. A four-factor central composite design (CCD) obtained by using Minitab 16 was applied. The four factors considered to affect the peak current were calcon concentration, pH, potential accumulation and time accumulation. The level and ranges chosen for the factors are shown in Table 2.

Sample Preparation

Vegetable samples were used in this study are: cauliflower, cabbage, eggplant and broccoli, while the fruit samples are used : apples, bananas kepok, melon and dragon fruit.

Vegetable and fruit samples before the specified metal content of Cd are determined once the water content, then wet destruction with the addition of nitric acid and perchloric acid pa. Each sample weighed 0.5000 grams carefully dried and crushed, put in a flask digestion/kjeldahl flask. Furthermore, wet destruction with the addition of 5 mL of concentrated nitric acid and 0.5 mL of concentrated perchloric acid, shaken and left overnight. Onwards, heated at block digester started with a temperature of 100°C, after the yellow steam discharged elevated temperature up to 200 °C.

Destruction ended when already out of white vapor and liquid in the flask remained about 0.5 mL, cooled and diluted with double destillation and matched into a 50 mL volume, shaken until homogeneous and left overnight and filtered with Whatman paper 41. The clear solution is ready determined metal content Cd with Voltammeter tools and Atomic Absorption Spectrophotometer. Determining the optimum conditions used in this study was the procedures that have been developed prior research team¹⁻². The data processing is done with the help of software Minitab 16.

RESULTS AND DISCUSSION

Optimization of Cadmium Using One Variable

The optimization of one variable in the simultaneous determination of trace metal cadmium in the presence of calcon has been done¹⁻³. The optimum condition as follow: calcon concentration 0.6 mM, pH 6, accumulation potential -0.6 V, accumulation time 60 seconds. 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 Central Composite Design (CCD).

Optimization of Cadmium Using CCD

Analysis of CCD First-Order Model of Copper

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

Table 2: Level CCD variables for parameters independent (free) of a mixture of metal ions (Cd, Cu, Pb and Zn)

| Factor | | Level (Cd, Cu, Pb, Zn) | | |
|----------------------------|----|------------------------|------|------|
| | | -1 | 0 | +1 |
| Calcon concentration (mM) | C | 0,6 | 0,7 | 0,8 |
| pH | pH | 5 | 6 | 7 |
| Accumulation Potensial (V) | E | -0,7 | -0,6 | -0,5 |
| Accumulation time (s) | T | 40 | 60 | 80 |

Source : level 0 taken from previous research [1]

Table 3: Model Orde I regression coefficient

| Term | Coef |
|----------|---------|
| Constant | 46,125 |
| X1 | 17,673 |
| X2 | 12,922 |
| X3 | -10,461 |
| X4 | 3,774 |

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

$$Y = 46,125 + 17,673 X_1 + 12,922 X_2 - 10,461 X_3 + 3,774 X_4$$

Where X_1 = calcon concentration (mM), X_2 = pH, X_3 = accumulation potential (Volt), X_4 = accumulation time (seconds), and v = peak current (nA), whereas the results of Analysis of Variance (ANOVA) of first-order model can be seen at Table 3.

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.

Table 4: ANOVA of First-Order Model of Copper

| Source | DF | Seq SS | Adj SS | Adj MS | F | P |
|----------------|----|---------|---------|---------|--------|-------|
| Regression | 4 | 9647,8 | 9647,8 | 2411,94 | 2,08 | 0,138 |
| Linear | 4 | 9647,8 | 9647,8 | 2411,94 | 2,08 | 0,138 |
| X1 | 1 | 4997,4 | 4997,4 | 4997,43 | 4,31 | 0,057 |
| X2 | 1 | 2671,6 | 2671,6 | 2671,60 | 2,31 | 0,151 |
| X3 | 1 | 1750,8 | 1750,8 | 1750,79 | 1,51 | 0,239 |
| X4 | 1 | 227,9 | 227,9 | 227,93 | 0,20 | 0,664 |
| Residual Error | 14 | 16214,7 | 16214,7 | 1158,19 | | |
| Lack-of-Fit | 12 | 16201,3 | 16201,3 | 1350,11 | 201,34 | 0,005 |
| Pure Error | 2 | 13,4 | 13,4 | 6,71 | | |
| Total | 18 | 25862,5 | | | | |

Table 5: Regression Coefficients in the Second-Order Model

| Term | Coef |
|----------|----------|
| Constant | 96,2949 |
| X1 | 14,9424 |
| X2 | 14,1358 |
| X3 | -9,3687 |
| X4 | 2,8248 |
| X1*X1 | -16,7662 |
| X2*X2 | -9,1791 |
| X3*X3 | -20,2443 |
| X4*X4 | -22,1637 |
| X1*X2 | 15,9094 |
| X1*X3 | -3,4256 |
| X1*X4 | 1,0019 |
| X2*X3 | 0,2856 |
| X2*X4 | -0,6719 |
| X3*X4 | -3,1994 |

Ho: $\beta_i = 0$,
H1: $\beta_i \neq 0$; $i = 1,2,3,4$

Based on Table 3, the test regression parameters simultaneously produce p-value of 0.138, 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 Ho and conclude that none of the independent variables that significantly influence the response variable, so the first-order model can not be used

Analysis CCD Second-Order Model of Copper

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:

Based on Table 4, the model regression equation :

$$Y = 96,2949 + 14,9424 X_1 + 14,1358 X_2 - 9,3687 X_3 + 2,8248 X_4 - 16,7662 X_1^2 - 9,1791 X_2^2 - 20,2443 X_3^2 - 22,1637 X_4^2 + 15,9094 X_1 X_2 - 3,4256 X_1 X_3 + 1,0019 X_1 X_4 + 0,2856 X_2 X_3 - 0,6719 X_2 X_4 - 3,1994 X_3 X_4$$

Where X_1 = calcon concentration (mM), X_2 = pH, X_3 = accumulation potential (Volt), X_4 = accumulation time (seconds), and v = peak current (nA). Results of ANOVA second-order model data were presented in Table 5.

Ho: $\beta_i = 0$,

H1: $\beta_i \neq 0$; $i = 1, 2, 3, \dots, k$

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. 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 Ho 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:

$$b = \begin{bmatrix} 14,9424 \\ 14,1358 \\ -9,3687 \\ 2,8248 \end{bmatrix} \text{ dan } B = \begin{bmatrix} -16,7662 & 7,95469 & -1,7128 & 0,5009 \\ 7,9547 & -9,17908 & 0,1428 & -0,3359 \\ -1,7128 & 0,14281 & -20,2443 & -1,5997 \\ 0,5009 & -0,33594 & -1,5997 & -22,1637 \end{bmatrix}$$

In order to obtain a stationary point as follows:

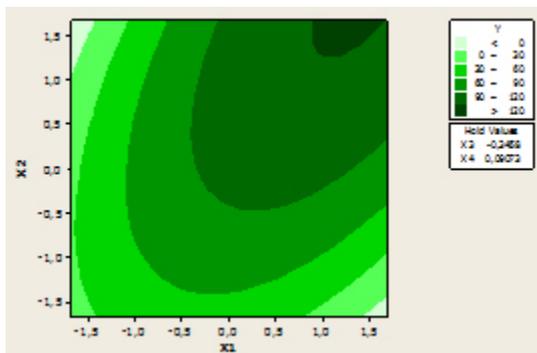
$$x_0 = -\frac{B^{-1}b}{2} = \begin{bmatrix} 1,43476 \\ 2,00468 \\ -0,34581 \\ 0,09073 \end{bmatrix}$$

Table 6: ANOVA of Second-Order Model

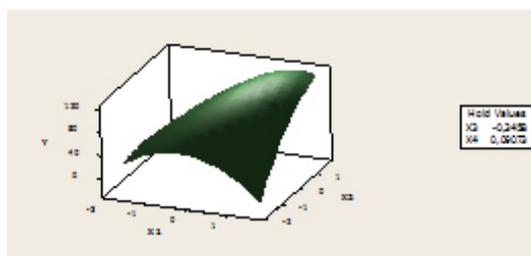
| Source | DF | Seq SS | Adj SS | Adj MS | F | P |
|----------------|----|---------|---------|---------|--------|-------|
| Regression | 14 | 39993,3 | 39993,3 | 2856,66 | 8,12 | 0,000 |
| Linear | 4 | 11237,3 | 11237,3 | 2809,33 | 7,99 | 0,001 |
| X1 | 1 | 4835,7 | 4835,7 | 4835,74 | 13,75 | 0,002 |
| X2 | 1 | 4327,8 | 4327,8 | 4327,76 | 12,31 | 0,003 |
| X3 | 1 | 1901,0 | 1901,0 | 1901,02 | 5,41 | 0,034 |
| X4 | 1 | 172,8 | 172,8 | 172,82 | 0,49 | 0,493 |
| Square | 4 | 24330,1 | 24330,1 | 6082,51 | 17,30 | 0,000 |
| X1*X1 | 1 | 6365,1 | 4709,9 | 4709,87 | 13,39 | 0,002 |
| X2*X2 | 1 | 2131,9 | 1411,7 | 1411,68 | 4,01 | 0,062 |
| X3*X3 | 1 | 7602,6 | 6866,6 | 6866,65 | 19,53 | 0,000 |
| X4*X4 | 1 | 8230,4 | 8230,4 | 8230,39 | 23,41 | 0,000 |
| Interaction | 6 | 4425,9 | 4425,9 | 737,64 | 2,10 | 0,111 |
| X1*X2 | 1 | 4049,7 | 4049,7 | 4049,73 | 11,52 | 0,004 |
| X1*X3 | 1 | 187,8 | 187,8 | 187,76 | 0,53 | 0,476 |
| X1*X4 | 1 | 16,1 | 16,1 | 16,06 | 0,05 | 0,833 |
| X2*X3 | 1 | 1,3 | 1,3 | 1,31 | 0,00 | 0,952 |
| X2*X4 | 1 | 7,2 | 7,2 | 7,22 | 0,02 | 0,888 |
| X3*X4 | 1 | 163,8 | 163,8 | 163,78 | 0,47 | 0,505 |
| Residual Error | 16 | 5626,4 | 5626,4 | 351,65 | | |
| Lack-of-Fit | 10 | 5610,5 | 5610,5 | 561,05 | 211,60 | 0,000 |
| Pure Error | 6 | 15,9 | 15,9 | 2,65 | | |
| Total | 30 | 45619,6 | | | | |

a. Contour and surface plot on conditions X3 and X4 in the stationary point

Contour Plot of Y4 vs X2, X1

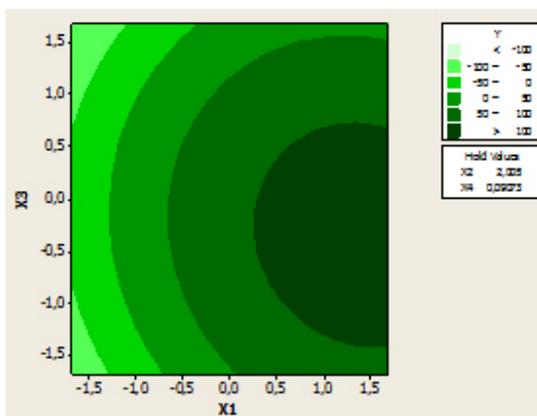


Surface Plot of Y4 vs X2, X1

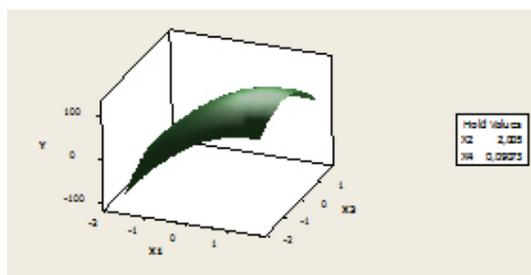


b. Contour and surface plot on conditions X2 and X3 in the stationary point

Contour Plot of Y4 vs X3, X1

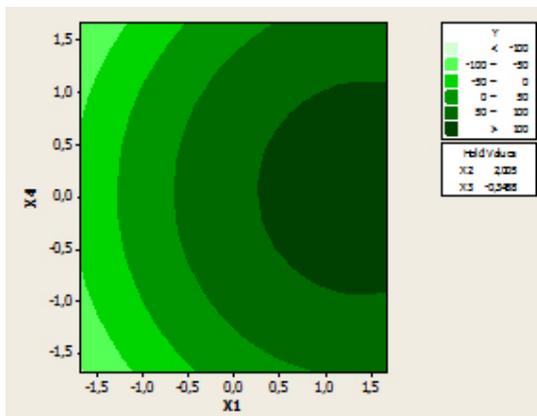


Surface Plot of Y4 vs X2, X1

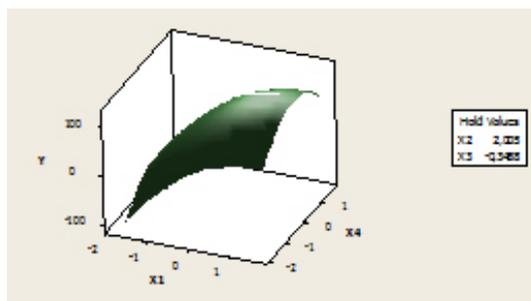


c. Contour and surface plot on conditions X2 and X3 in the stationary point

Contour Plot of Y4 vs X4, X1

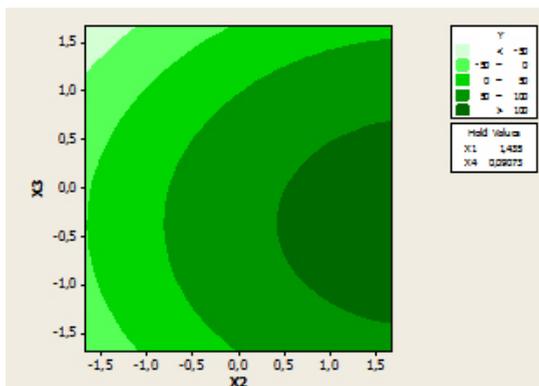


Surface Plot of Y4 vs X2, X1

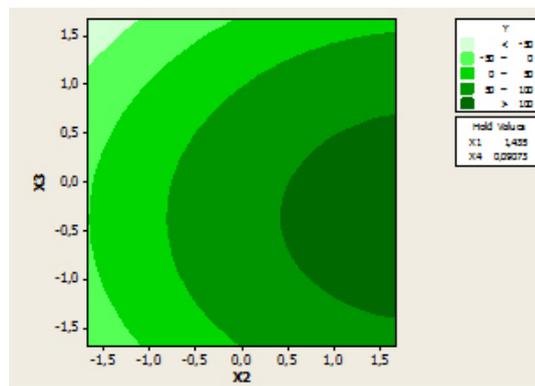


d. Contour and surface plot on conditions X1 and X4 in the stationary point

Contour Plot of Y4 vs X3, X2

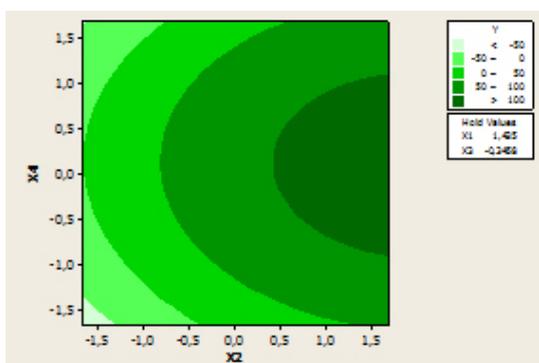


Surface Plot of Y4 vs X3, X2

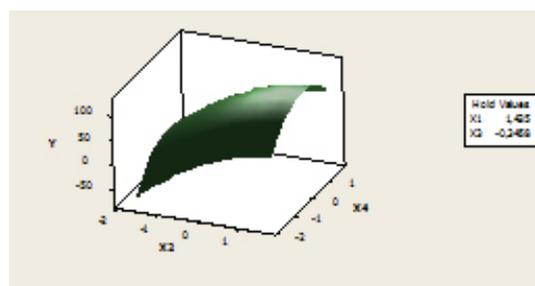


e. Contour and surface plot on conditions X1 and X3 in the stationary point

Contour Plot of Y4 vs X3, X2

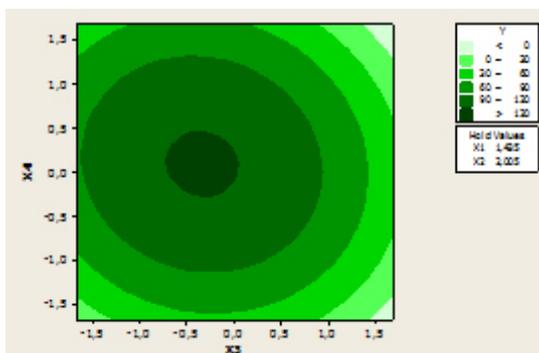


Surface Plot of Y4 vs X4, X2



f. Contour and surface plot on conditions X3 and X4 in the stationary point

Contour Plot of Y4 vs X4, X3



Surface Plot of Y4 vs X4, X3

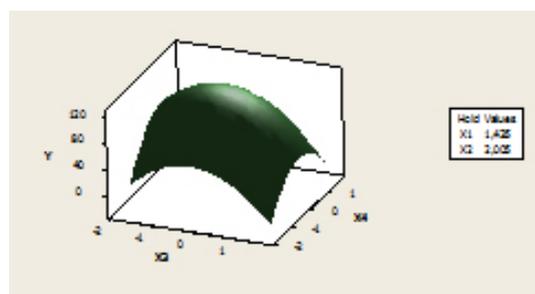


Fig. 1: Contour and surface plot of cadmium

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

$$\hat{y} = \hat{\beta}_0 + \frac{1}{2} x_0' b = 96,2949 + 294926, = 122,931$$

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

Table 7: Optimal Value of cadmium

| Variable | Optimal value (with coding) | Optimal value (without coding) |
|----------|-----------------------------|--------------------------------|
| X1 | 1,43476 | 0,8435 |
| X2 | 2,00468 | 8,0047 |
| X3 | -0,34581 | -0,6346 |
| X4 | 0,09073 | 61,8146 |

Where X_1 = calcon concentration (mM), X_2 = pH, X_3 = accumulation potential (Volt), 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 :

$$\lambda = [-23,1582 \quad -22,5219 \quad -18,5531 \quad -4,1201]$$

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 CCD, it is concluded that the peak flow will reach its maximum value at the time of calcon concentration 0.8435 mM, pH 8.0047, accumulation potential -0.6346 Volt and accumulation time 81.85 seconds with a maximum peak current value of cadmium 61.8146 nA.

Table 8: Determination of Cd using Adsorptive stripping voltammetry (AdSV) and Atomic absorption spectroscopy (AAS)

| Sample | Cd (mg/L) | |
|---|-----------|-------|
| | AdSV | AAS |
| Broccoli (<i>Brassica oleracea var. Italica</i>) | 3,340 | 0,926 |
| Cauliflower (<i>Brassica oleracea var. botrytis</i>) | 3,086 | 0,994 |
| Eggplant (<i>Salanim melongena</i>) | 2,357 | 1,080 |
| Cabbage (<i>Brassica juncea L</i>) | 5,761 | 1,126 |
| Apple (<i>Malus sieversii</i>) | 1,887 | 1.012 |
| Banana kepok (<i>Musa acuminata L</i>) | 6,591 | 0,824 |
| Dragon fruit (<i>Hylocereus undatus</i>) | 2,671 | 0,936 |
| Melon (<i>Cucumis melo L</i>) | 4,318 | 0,839 |

Contour and surface plot of cadmium at stationary point

By making constant two of the four factors used, then it can be shown that the shape and surface contour is the maximum response. The following will be presented contour plot and the surface on every possible pair of factors used.

Analysis of Real Samples

To evaluate the validity of the proposed method for real sample analysis, the proposed procedure was applied to various fruit and vegetable samples. The cadmium contents of fruit and vegetable samples were determined by standard addition method using the recommended procedure under optimum conditions. The results in Tables 7 show that the method is good results with relative standard deviation of 0.84%, recovery 98.884%, the linear range up to 110 $\mu\text{g/L}$, limit of detection 1.009 $\mu\text{g/L}$ and LOQ 3.363 $\mu\text{g/L}$. Also, as it can be seen, the assay results for all the fruit and vegetable samples were in good agreement with the values that were obtained by standard atomic absorption spectroscopy.

CONCLUSION

Based on data analysis with central composite design, the simultaneous determination

of cadmium obtained optimum conditions, namely: calcon concentration 0.8435 mM, pH 8.0047, accumulation potential -0.6346 Volt and accumulation time 81.85 seconds with a maximum peak current value of cadmium 61.8146 nA. The method has a very excellent with relative standard deviation of 0.84%, recovery 98.884%, the linear range up to 110 µg/L, limit of detection 1.009 µg/L and LOQ 3.363 µg/L. The central composite design can be applied to the determination of cadmium in fruit and vegetable samples quickly, effectively and efficiently.

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