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RESPONSE SURFACE METHODOLOGY OF MULTI-FACTOR WITH ADSORPTIVE CATHODIC STRIPPING VOLTAMMETRY: DETERMINATION OF CHROMIUM(III) USING CALCEIN

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ABSTRACT

In this study, a multi-factor optimization method was developed to determine Cr(III) using calcein as a ligandwith adsorptive cathodic stripping voltammetry (AdCSV). The purpose of this study was to find sensitive and selective methods in determining Cr(III). For this reason, we need an analytical procedure optimization technique that is using the response surface methodology (RSM). The design of this study used 4 factors/variables, 5 levels/levels and 31 combinations of treatments. The first step of the factorial 2k design optimization is: code the highest level (+1.68), the lowest level (-1.68) and code (0) as the center point. The program used for processing statistical data is Minitab 17. Based on data analysis, the optimum conditions were obtained: calcein concentration 0.50 mM, pH = 4.94, potential accumulation -0.56 V and accumulation time 113.17 s. In this study also determined the relative standard deviation 0.90%, recovery 98.76% and limit of detection 1.24 ìg/L. This method showed good results after applying it to water samples (sea water, rivers, tap water and lake water) using standard addition methods.

KEY WORDS : A multi-factor optimization, Calsein, Adsorptive cathodicstripping voltammetry, Response surface methodology

INTRODUCTION

Chromium can contaminate water from anthropogenic sources such as tanning leather, industrial pigment production, metal coating industry around waters, and rinse water from domestic laundry. The toxicity of Cr (III) and Cr (VI) is very different, compared to Cr (III), Cr (VI) is more highly toxic (Korolczuk, 1999; Manova *et al.*, 2007). Cr (III) is useful for additions to plant and animal nutrition, glucose maintenance, fat and protein metabolism. Cr (III) is needed as a nutrient of 50-200 ug/day for adult humans. Cr (VI) is poisonous and carcinogenic to the human body, can cause lung cancer, skin allergies, asthma, and kidney disease. intracellular chrome can be increased because of the ability of Cr (VI) to migrate across cell membranes (Bobrowski *et al.*, 2009; Bobrowski *et al.*, 2004).

Cr (VI) is 10-100 times more toxic than Cr (III) compounds if both enter the body (Kanz and Salem, 1993). The chromium content in sea water is 0.1 - 0.5 μg/L and 0.3 - 0.6 μg/L in river water free from pollution. Cr (VI) in fresh water permissible levels are below 16 μg/L (Dyg *et al.*, 1994). Because of the very low concentration of chromium in alamaic waters, a very sensitive and selective method is needed to determine this.

Electrochemical techniques are a popular method for the determination of chromium metal, because the sample to be analyzed does not go through a treatment process first (Dominguez and Arcos, 2002). One alternative method is adsorptive cathodic stripping voltammetry (AdCSV) because it has many advantages, including applied to samples that have high salt content, has high sensitivity, is able to measure up to µg/L scale, the sample does not need treatment before measurement, faster measurement, measurement costs and infrastructure are not expensive (Deswati *et al.,* 2012; Deswati *et al*., 2013; Deswati *et al.,* 2015a; Deswati *et al.,* 2016a; Deswati *et al*., 2017a). this method, can determine other heavy metals that cannot be determined by other methods (Ensafi *et al.*, 2001; Zang and Huang, 2001).

Research has been carried out to optimize various metal ions such as Cd, Cu, Pb, Zn, Fe, Co, Ni, and Cr (Deswati *et al*., 2015c; Deswati, *et al.*, 2016c; Deswati *et al*., 2017b; Deswati *et al*., 2017c; Deswati *et al*., 2018a; Deswati *et al*., 2018b, Pardi, *et al*., 2017; Pardi *et al*., 2019) singly or simultaneously using the AdCSV method, using the optimization of one variable or factor.

The optimization of one factor has the disadvantage that the interaction effect between the variables studied is not taken into account. so this optimization is not able to describe all the variables specified. One factor optimization can increase the number of research samples so that time increases, reagents and materials will be used up a lot. because of this multi-factor optimization is used (Bezerra *et al*., 2008; Espada-Bellido *et al*., 2009).

The parameters that will affect the measurement of peak currents to improve the quality of the analysis results of the determination of the metal Cr (III) are crucial. Response Surface Methodology (RSM) with coding, where the highest level value (+1.68), lowest level (-1.68) and code (0) as the center point, 4 variables, 5 levels/degrees, and 31 treatment combinations are used in this study . Minitab 17 is used for statistical data processing as a first step in optimization of factorial 2k (Bezerra *et al*., 2008; Espada-Bellido *et al*., 2009; Dewi *et al.*, 2013).

The studies using RSM has been carried out such as determination of Al content in salt samples using the Adsoprtif stripping voltammetry (AdSV) method (Yilmaz *et al.,* 2013), determination of In (III) with the AdSV method (Phaollicci *et al*., 2004), optimization of Cu, Pb, Cd , Ni, Co, and Zn with the AdSV method. PB in water by the AdSV method (Espada-Bellido *et al.*, 2009), determination of cadmium and zinc in water by AdSV Deswati *et al.,* 2016b), determination of Zn by AdSV (Deswati *et al*., 2016c).

EXPERIMENTAL

Chemicals and Reagents

Cr(III) 1000 mg/L (E. Merck), $CH_3COONa.3H_2O$ (E. Merck), CH_3COOH 100% (E. Merck), $NH_4Cl.3H_2O$ (E. Merck) , NH_4OH 100% (E. Merck), double distilled water, 65% HNO_3 (E. Merck), KCl (E. Merck).

Equipment and Instrumentation

The instrument used in this study was 797 Metrohm Computrace (*Switzerland*), HMDE (working electrode), Ag/AgCl/KCl (reference electrode), Pt (supporting electrode), *914 pH/Conductometer (Metrohm, Switzerland)*, and Analytical Balance ME204T/00, Cole-Parmer (UK), and glassware used in the laboratory.

Work procedures

10 mL Cr (III) 10 µg/L, calcein, and 0.2 mL KCl 0.1 M were included in the voltammeter vessel, during constant variable experiments. The variables determined include calcium concentration, pH, deposition potential, and deposition time, arranged according to Table 1.

Research design

The research design was RSM with 4 factors and 5 levels, each - each factor was coded -1.68, 0 and +1.68 with 2 replications. Score of -1.68 indicates the lowest variable value, +1.68 digits shows the highest variable value, and the number 0 indicates the value of the medium variable. The factors that influenced the results of the study were calcine concentration ($C_{calcein}$), pH, accumulation potential (P_{acc}), and accumulation time (t_{acc}), then RSM analysis was performed using Minitab 17.

Detection Method

Determination of relative standard deviation (RSD), limit of detection (LOD), linear range LR (LR) and recovery, the procedure has been carried out by previous researchers (Edgar *et al*., 2012; Herrero *et al*., 2014).

RESULTS AND DISCUSSION

One Factor Optimization

Optimization of 1 factor was carried out to determine the effect of $C_{calsein}$, pH, P_{acc}, and t_{acc} on peak currents, with the following results: 0.5 M $C_{calcein}$, pH 5, P_{acc} -0.6 V, t_{acc} 60 s (Deswati 2017). This 1-factor optimization technique has not yet described the full effect of response parameters, due to an increase in the number of experimental samples, thus increasing the time of research, and adding chemical reagents. Optimization techniques using RSM are needed to overcome this problem.

Multi-Factor Optimization

1st order model analysis

Based on RSM processing with Minitab 17, the first order model is obtained as follows:

$y_4 = 70.34 - 1.69\, x_1 - 1.88\, x_2 - 3.01\, x_3 - 0.77\, x_4$

Furthermore, a variety of 1st order model analysis is carried out (Table 2).

Table 2 shows, Hypothesis Testing of first order models can be used or not, testing the significance of the regression model whether there are significant independent variables on the response variable. The equation is as follows:

H_0: $\beta i = 0$,

H1: there is $\beta i \neq 0$; i = 1,2,3,4

The p value was 0.788 for the simultaneous regression parameter test, p> significance level (α = 0.05). H0 is not pinned and concluded that there are no independent variables that have a significant effect on the response variable, this states the use of the first order model cannot be used.

Analysis of the 2nd order model

Because the 1st order model cannot be used, it is followed by the 2nd order model which is by adding quadratic influences and interactions. The results of processing RSM with Minitab 17 obtained the following results:

$y = 80.10 - 1.69\, X_1 - 1.88X_2 - 3.01X_3 - 0.77X_4 + 12.27X_1^2 - 6.89X_2^2 - 9.69X_3^2 + 10.70X_4^2 - 1.36X_1X_2 +$

Table 1. RSM design for determination of Cr(III)

Run	Factor				Response(Ip)
	$C_{calcein}$ (mM)	pH	P_{acc}(V)	t_{acc}(s)	
1	0.4	4	-0.7	40	28.14
2	0.4	4	-0.5	40	73.73
3	0.4	4	-0.7	80	38.14
4	0.4	4	-0.5	80	74.06
5	0.4	6	-0.7	40	71.73333
6	0.4	6	-0.5	40	61.50667
7	0.4	6	-0.7	80	40.12333
8	0.4	6	-0.5	80	67.44333
9	0.6	4	-0.7	40	27.82667
10	0.6	4	-0.5	40	77.88
11	0.6	4	-0.7	80	48.88333
12	0.6	4	-0.5	80	77.21667
13	0.6	6	-0.7	40	86.77333
14	0.6	6	-0.5	40	61.69667
15	0.6	6	-0.7	80	34.86
16	0.6	6	-0.5	80	66.93
17	0.5	5	-0.6	60	105.09
18	0.5	5	-0.6	60	105.1433
19	0.5	5	-0.6	60	105.29
20	0.5	5	-0.6	60	104.8867
21	0.5	5	-0.6	60	105.37
22	0.5	5	-0.6	60	105.47
23	0.5	5	-0.6	60	105.4033
24	0.34	5	-0.6	60	105.15
25	0.5	3.4	-0.6	60	99.32667
26	0.5	5	-0.76	60	92.58333
27	0.5	5	-0.6	29.1	90.09667
28	0.66	5	-0.6	60	94.47
29	0.5	6.6	-0.6	60	100.5067
30	0.5	5	-0.44	60	98.59333
31	0.5	5	-0.6	91.9	98.99

$0.07X_1X_3 + 5.18X_1X_4 - 0.20X_2X_3 + 6.84X_2X_4 + 5.44X_3X_4$

and then the results of the analysis of the variety of order 2 models can be seen in Table 3.

Table 3 shows the testing procedure for the 2nd order model. This hypothesis test is used to test whether there is a significant independent variable on the response variable.

The hypothesis is:

H_0: βi = 0,

H_1: there is βi ≠ 0; i = 1, 2, 3, ..., k

Table 3 shows the regression parameters test simultaneously, p-value 0.066 (p < level of significance), α = 0.05. H0 is rejected and there are significant independent variables on the response variable (2nd order model is acceptable).

Determination of stationary points

Regression coefficient (Table 3), the following b and B matrices are arranged as follows:

$$b = \begin{bmatrix} -1.68939 \\ -1.88468 \\ -3.01269 \\ -0.77095 \end{bmatrix}$$

and

$$B = \begin{bmatrix} -12.2686 & -0.68164 & 0.01857 & 2.5878 \\ -0.6816 & -6.88859 & -0.09814 & 3.4188 \\ 0.0186 & -0.09814 & -9.69359 & 2.7186 \\ 2.5878 & 3.41882 & 2.71861 & -10.6986 \end{bmatrix}$$

Table 2. Results of Analysis of variance of 1st order model

Analysis of Variance Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	4	123.07	30.7687	0.43	0.788
Linear	4	123.07	30.7687	0.43	0.788
X1	1	21.85	21.8491	0.30	0.587
X2	1	27.19	27.1924	0.38	0.544
X3	1	69.48	69.4833	0.96	0.335
X4	1	4.55	4.5501	0.06	0.804
Error	26	1874.25	72.0864		
Lack-of-Fit	20	1871.21	93.5604	184.78	0.000
Pure Error	6	3.04	0.5063		
Total	30	1997.32			

Table 3. Results of Analysis of Order Model 2

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	14	1315.47	93.962	2.20	0.066
Linear	4	123.07	30.769	0.72	0.589
X1	1	21.85	21.849	0.51	0.484
X2	1	27.19	27.192	0.64	0.436
X3	1	69.48	69.483	1.63	0.220
X4	1	4.55	4.550	0.11	0.748
Square	4	982.50	245.624	5.76	0.005
X1*X1	1	315.08	315.082	7.39	0.015
X2*X2	1	99.33	99.333	2.33	0.146
X3*X3	1	196.70	196.699	4.62	0.047
X4*X4	1	239.60	239.600	5.62	0.031
2-Way Interaction	6	209.90	34.983	0.82	0.570
X1*X2	1	3.72	3.715	0.09	0.772
X1*X3	1	0.00	0.003	0.00	0.994
X1*X4	1	53.55	53.546	1.26	0.279
X2*X3	1	0.08	0.077	0.00	0.967
X2*X4	1	93.46	93.461	2.19	0.158
X3*X4	1	59.10	59.098	1.39	0.256
Error	16	681.85	42.616		
Lack-of-Fit	10	678.81	67.881	134.06	0.000
Pure Error	6	3.04	0.506		
Total	30	1997.32			

So that the stationary point is obtained as follows:

$$x_0 = -\frac{B^{-1}b}{2} = \begin{bmatrix} -0.095046 \\ -0.213287 \\ -0.203596 \\ -0.178913 \end{bmatrix}$$

so, at the stationary point the response solution obtained as follows:

$$\hat{y} = \hat{\beta}_0 + \frac{1}{2} x_0^{'} b = 80.1048 + 0.6569 = 80.7617$$

stationary points can form initial values (true values), the results are shown in Table 4.

Table 4. Results of optimum conditions of metal Cr(III) by RSM

Variable	Optimal value (encoded)	Optimal value (not encoded)
X_1 (kons kalsein)	-0.095046	0,590495
X_2(pH)	-0.213287	5.78671
X_3 (Potensial)	-0.203596	-0,720360
X_4 (Waktu)	-0.178913	66.4217

Analysis of Response Surface Characteristics.

Calculate the eigenvalue (l) from matrix B to get a picture of the response surface characteristics, and the following equation:

$$\lambda = -15.6952 \quad -11.1233 \quad -8.3392 \quad -4.3916$$

The shape of the response surface becomes maximum (all four negative eigenvalues). this can be seen from the contour plot and the response surface plot. Stationary points, contour plots and response surfaces can be made as shown in Figure 1.

Contour plot and response surface at the stationary point

The shape of the contour and the surface of the maximum response By making a constant of two of the four factors used (Figure 1).

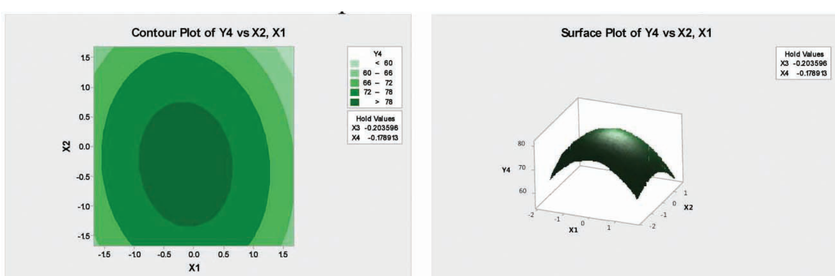
RSM Application for determining Cr(III)

From the RSM analysis, optimum multi-factor conditions are obtained, including: peak flow 113.172; $C_{calcein}$ 0.5005 µg/L; pH 4.9377; P_{acc} -0.5608 V and t_{acc} 60.5687 s, then the optimum condition was applied to determine Cr(III) metal in the water sample (Table 5). From the water sample, RSD value was 0.90 %, recovery of 98.76% andLOD 1.24 µg/L.

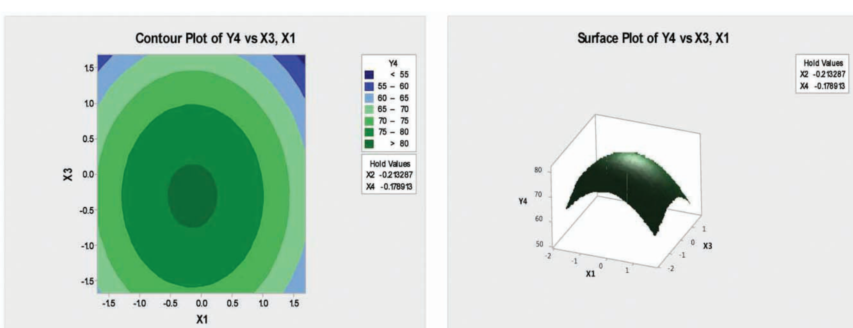
Table 5. Determination of Cr (III) Metals in water samples

Sample	**Cr (III) (µg/L)**
Sea water	112.21
Tap water	17.28
Maninjau Lake Water	92.69

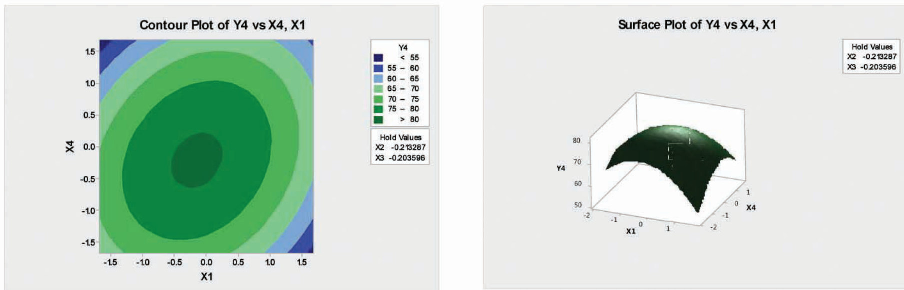
Plot Contour and Surface Response at Conditions X_3 and X_4 at the Stationary point



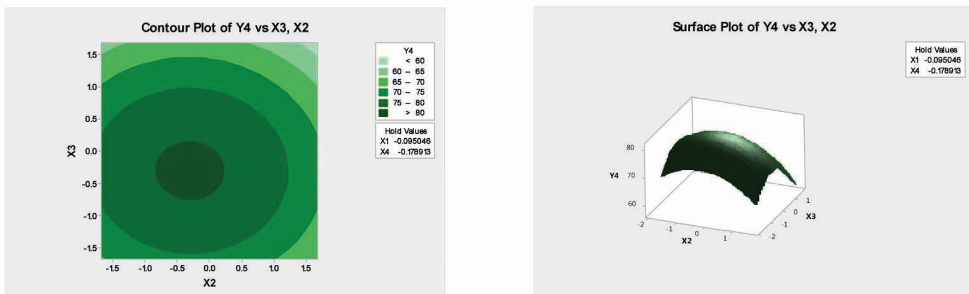
Plot Contour and Surface Response at Conditions X_2 and X_4 at the Stationary point



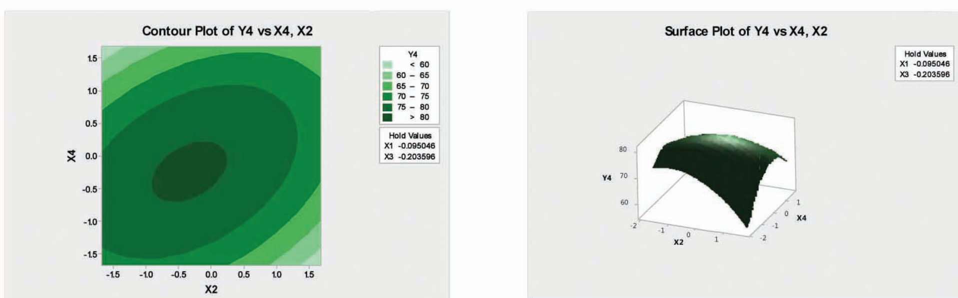
Plot Contour and Surface Response at Conditions X_2 and X_3 at the Stationary point



Plot Contour and Surface Response at Conditions X_1 and X_4 at the Stationary point



Plot Contour and Surface Response at Conditions X_1 and X_3 at the Stationary point



Plot Contour and Surface Response at Conditions X_1 and X_2 at the Stationary point

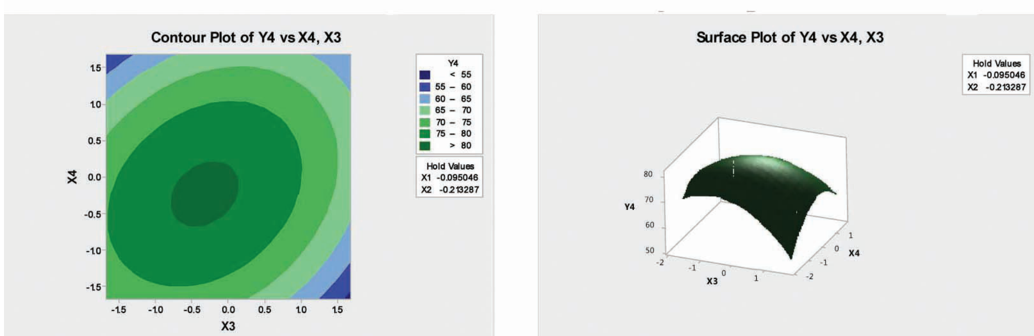


Fig. 1. Contour Plots and Response Surfaces at Stationary Points

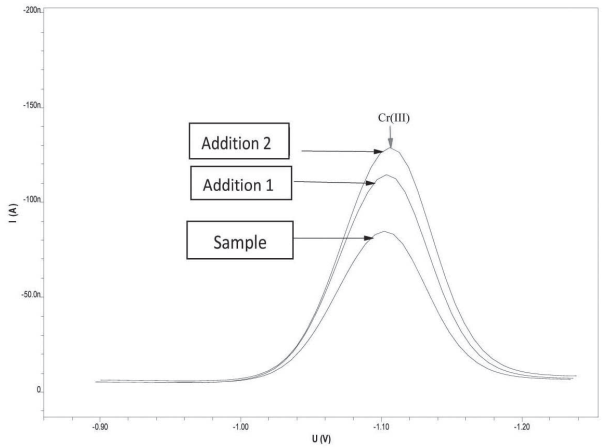


Fig. 2. Cr(III) metal voltammogram in Lake Maninjau water samples

CONCLUSION

From the results of this study, it can be concluded that this method has been successfully applied to water samples, such as seawater, rivers, tap water, and lake water. Based on data analysis with the surface response method, the peak current is 80.7617; calcein concentration 0.590495 μg/L; pH 5.78671; the accumulated potential of -0.721104 V and accumulated time of 66.4217 s. In this study also determined the relative standard deviation value of 0.90%, recovery of 98.76% and the detection limit of 1.24 μg/L.

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