

Voltammetric Study for Determination of Non-essential Metal Cd(II) in water samples (River and Sea) using *Eriochrome Blue Black R* as Complexing

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Abstract. The research on the determination of Cd(II) metal in river and seawater samples using the Adsorptive Cathodic Stripping Voltammetry (AdCSV) method has been done. In order to increase the sensitivity and selectivity of Cd(II) measurement, it is necessary to determine the optimum condition for the variation of potential ligand accumulation, accumulation time, pH and optimum ligand concentration. It is also determined the accuracy and precision of the method used by determining the value of the relative standard deviation (SDR), as well as the recovery value. The result obtained is chalcone as the optimum ligand, the optimum accumulation potential is -0.1 V, the optimum accumulation time is 60 seconds, the optimum solution pH is 6, and the optimum chalcone concentration is 0.5 mM. The relative standard deviation value is 4.27%, the recovery value is 98.31%. The application of the VSAd method to water sample results the concentration of Cu(II) metal in the sample of Bangek river, Indonesia is 4.778 g/L and seawater in Teluk Kabung, Indonesia is 5.189 g/L.

1 Introduction

It is widely recognized that cadmium is the most significant environmental pollutant which is highly toxic to the immune, nervous, gastro-intestinal and reproductive systems of animal and human [1]. In addition, the heavy metals are toxic and hazardous contaminants in the environment due to their non-biodegradability and its accumulation can cause a serious threat to living organism. For example, the accumulation of Cd (II) in the human body has a significant harmful effect on neurobehavioral development in children, increase blood pressure, kidney injury and anemia [2].

Since heavy metal ion is toxic and does not decompose naturally, it is crucial to use fast and sensitive analytical technique for heavy metal monitoring. In fact, heavy metal has been widely analyzed using various methods such as colorimetry [3], atomic absorption spectrometry (AAS) [4] atomic fluorescence spectrometry [5], Surface enhanced Raman spectrometry (SERS) [6] ion chromatography [7], extensively inductively coupled plasma optical emission spectrometry (ICP-OES) [8] and inductively coupled plasma mass spectrometry (ICP-MS) [9]. However, the above techniques have number of drawbacks such as difficult and expensive operations, and requires complicated instruments. This method is also not suitable for field analysis [10]. In doing so we need a simple, selective, sensitive, easy and relatively inexpensive method for the determination of Cd (II) metal.

The voltammetric method has a fast response, is very sensitive (can analyze at concentration of g/L), selective, not affected by measuring samples that have high salt

content, affordable, and this electrochemical technique has also been widely studied [10–12]. Based on previous research, the Adsorptive Cathodic Stripping Voltammetry (AdCSV), as a simple, fast and sensitive method of electro-analysis, has been confirmed as a good instrument for detecting small concentration of heavy metal ion from various clinical samples, environments, and industrial activities [13]. The AdCSV method uses complexes (ligands) to increase the selectivity of the analysis. In this study, 2-hidroxy-1-(2-hidroxy-1-naphtylazo) naphthalene-4-sulfonic acid sodium salt, also known as Eriochrome Blue Black R, were used as ligand.

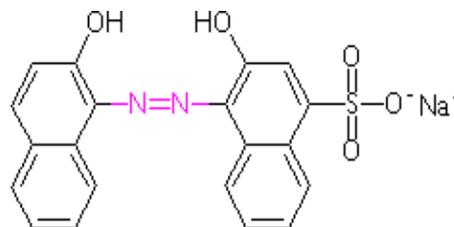


Figure 1. Structure of Eriochrome Blue Black R

This study aims to determine the optimum condition for deposition potential, deposition time, pH, concentration of supporting electrolyte (NH_4Cl), and ligand concentration in the determination of Cd(II) metal using the Adsorptive Cathodic Stripping Voltammetry (AdCSV) method.

2 Method

2.1 Tools and materials

Metrohm 797, 3 electrodes are used: hanging drop mercury electrode (HMDE) as working electrode, platinum metal as auxiliary electrode, and Ag/AgCl/KCl 3 M as reference electrode, a Metrohm 880 pH meter, analytical balance 756, and ordinary glassware as commonly used for laboratory. Standard solution of metal Cd(II) 1000 mg/L, eriochrome blue black R as metal ion Cd(II) complexing, NH₄Cl as supporting electrolyte, aquabides solvent and samples taken from the Bangek River and Teluk Kabung, Indonesia then added with HNO₃ 65% with a ratio of 1: 1000.

2.2 Work procedures

2.2.1 Variation of deposition potential

Put standard solution of 10 g/L Cd(II) metal into a voltammeter vessel 10 mL, added 0.2 mL NH₄Cl 0.1 M supporting electrolyte, added 0.2 mL of complexing eriochrome blue black R 1mM, adjusted pH to 5, 60 seconds of time deposition, and the deposition potential was set -0.1 V to -1.0 V then the measurement was taken with a voltammeter.

2.2.2 Variation of deposition time

Put standard solution of 10 g/L Cd(II) metal into a voltammeter vessel 10 mL, added 0.2 mL NH₄Cl 0.1 M supporting electrolyte, added 0.2 mL of complexing eriochrome blue black R 1 mM, adjusted pH to 5, -0.3 V deposition potential, and the deposition time was set from 30 seconds to 100 seconds. Next, measurement was made using a voltammeter.

2.2.3 pH Variation

Put standard solution of Cd(II) 10 g/L metal into a voltammeter vessel 10 mL, added supporting electrolyte 0.2 mL NH₄Cl 0.1 M, added 0.2 mL complexing eriochrome blue black R 1 mM, set deposition time for 60 seconds, the deposition potential is -0.3 V, and the pH is adjusted from 2 to pH 8. Next the measurement was made using a voltammeter.

2.2.4 Variation of NH₄Cl. concentration

Inserted standard solution of Cd(II) 10 g/L metal into a voltammeter vessel 10 mL, added 0.2 mL of complexing eriochrome blue black R 1 mM, set deposition time for 60 seconds, deposition potential -0.3 V, pH 4, and adjusted supporting electrolyte NH₄Cl 0.01 M to 0.1 M. Next, measurement was made with a voltammeter.

2.2.5 Variation of concentration of eriochrome blue black R

Put standard solution of Cd(II) 10 g/L metal into a voltammeter vessel 10 mL, added supporting electrolyte 0.2 mL NH₄Cl 0.05 M, set deposition time for 60 seconds, deposition potential -0.3 V, pH 4, and set the complexing eriochrome blue black R 0.1mM to 1mM. Next, measurement was made with a voltammeter.

2.3 Sample measurement

Put the sample into voltammeter vessel 10 mL, added supporting electrolyte 0.2 mL NH₄Cl 0.05M, added complexing 0.2 mL eriochrome blue black R 0.5 mM. The deposition time was set to 60 seconds, the deposition potential was -0.3 V, pH 4 then measured with a voltammeter. Measurement was carried out using the standard addition method.

Table 1. Voltammeter Set for Measurement of Standard Solution of Cd(II) metal 10 g/L

Parameter	Measurement Set
working electrode	HMDE
Drop Size	7
Method	DP
Nitrogen gas bubble time	300 s
Equilibrium time	5 s
Amplitude	0.05 V
Initial Potential	-0.3 V
Final Potential	-1.0 V
Peak Potential	-0.56 V

2.4 Determination of the Relative Standard Deviation

Put standard solution of Cd(II) 10 g/L into a voltammeter vessel 10 ml, added supporting electrolyte 0.2 mL NH₄Cl 0.05M, added complexing 0.2 mL eriochrome blue black R 0.5 mM. The deposition time was set to 60 seconds, the deposition potential was -0.3 V, pH 4 then measured with a voltammeter. Measurement was carried out using the standard addition method.

$$SDR = \frac{S}{x} \times 100 \%$$

$$S = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}}$$

Description :

\bar{S} = Standard deviation

\bar{x} = mean/average

2.5 Recovery Determination

Recovery determination is done by using a sample that is added to standard solution with certain

concentration. The recovery percentage was obtained by comparing the concentration of the added sample with a number of standard and sample concentrations. % recovery is calculated by the formula:

$$\% \text{Recovery} = B / (A+C) \times 100\%$$

Note: B = Sample concentration after added
 A = Sample concentration
 C = Concentration added

3 Result and Discussion

3.1 Optimum Measurement Condition

The determination of cadmium by AdCSV was carried out in this study. Five optimum measurement conditions were investigated: accumulation potential, accumulation time, pH, supporting electrolyte concentration, and complexing concentration.

3.2 Potential Accumulation

The relationship between accumulation potential and peak current was determined in the range of -0.3 to -0.8 V. The result can be seen in Figure 2.

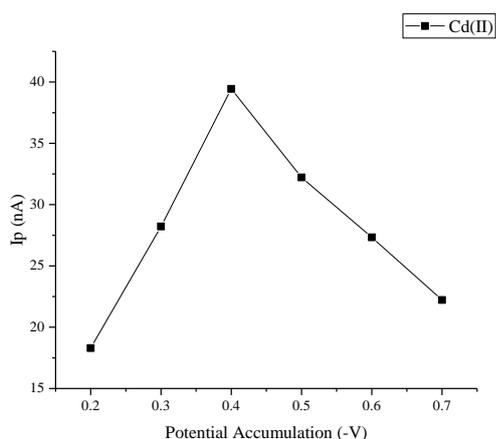


Figure 2. Accumulation potential curve (-V) Vs peak current (Ip) Measurement condition: standard solution of Cd(II) 0.01 ppm; deposition time 60 seconds, pH 8; NH₄Cl 0.1 M, chalcone 0.12 mM

The accumulation potential is the potency when analyte is deposited on working electrode. In the curve above, it can be seen that for each variation of the accumulated potential tested gives a different peak current value. At the accumulation potential of -0.3 V to -0.5 V the curve drops significantly. In the potential range of -0.6 to -0.7 V the curve rises and then falls at -0.8 V. This indicates that the analyte complex deposition process on the surface of the working electrode reaches maximum at -0.7 V. Potential accumulation -0.7 V is used in the next determination.

3.3 Accumulation Time

The relationship between accumulation time and peak current was also determined by varying the time 0, 20, 40, 60, 80, 100 seconds. The result can be seen in Figure 3.

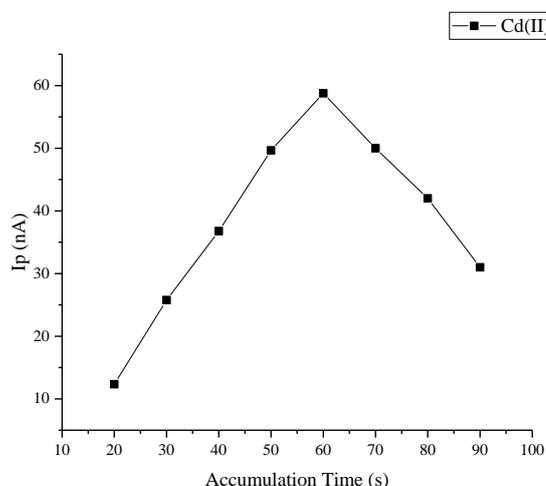


Figure 3. Accumulation time curve (seconds) Vs peak current (Ip) Measurement condition: standard solution of Cd(II) 0.01 ppm; deposition potential -0.7 V; pH 8; NH₄Cl 0.1 M, chalcone 0.12 mM

The accumulation time is the time at which the analyte is deposited on the working electrode. The longer the accumulation time, the stronger the analyte is deposited on the electrode. According to the theory, the longer the accumulation time, the more analyte will be deposited on the electrode. At 0 and 20 seconds, no peak current is obtained. It is possible that there is no analyte deposited on the working electrode. However, at 60 seconds the optimum time for analyte absorption is obtained at the electrode. After 60 seconds there is a decrease in the peak current value. This is possible because the longer the accumulation time, the more analyte is deposited on the working electrode and saturates the electrode. Therefore when stripping, not all analyte is released, so the resulting current is also smaller.

3.4 pH Variation

The relationship between pH and peak current was determined by varying the pH 5, 6, 7, 8, 9. The result can be seen in Figure 4.

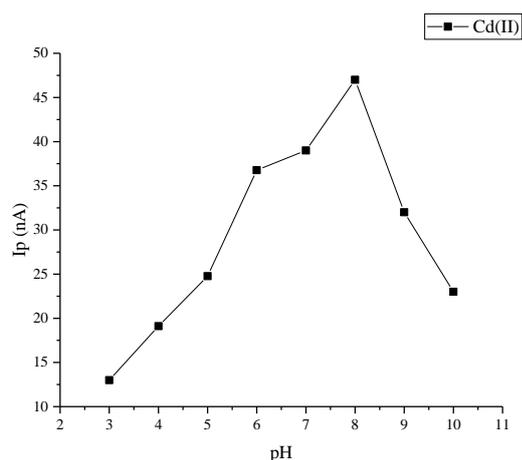


Figure 4. Curve of pH Vs peak current (I_p) Measurement condition: standard solution of Cd(II) 0.01 ppm; deposition potential -0.7 V; deposition time 60 seconds; NH_4Cl 0.1 M, chalcone 0.12 mM

The pH affects the stable complex that will form between metal and ligand. Otherwise, the analyte is not completely deposited on the electrode. According to the graph it can be seen that the pH decreased from pH 5 to pH 9, but at pH 7 there is a slight deviation in the form of increase in peak current. This is because at this pH, metals and ligands form a large ionic association. The solution still contains H^+ at below optimum pH, which can compete with metal ion to form complexes. Meanwhile, at above the optimum pH there is an excess of OH^- in the solution which will break down the metal ligand complex so that the adsorption to the electrode will be reduced and the current will be reduced.

3.5 Variation of NH_4Cl Concentration

The relationship between the concentration of NH_4Cl and the peak current was determined in the range of 0.02 M to 0.2 M. The result can be seen in Figure 5.

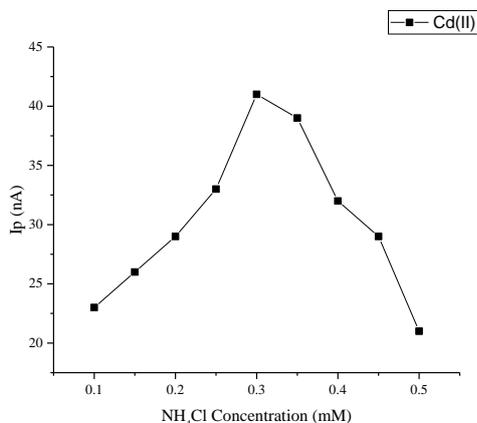


Figure 5. NH_4Cl concentration curve Vs peak current (I_p) Measurement conditions: standard solution of Cd(II) 0.01 ppm; deposition potential -0.7 V; deposition time 60 seconds; pH 7; 0.12 mM chalcone.

NH_4Cl functions as a medium, amplifies the current that will be formed, increases the selectivity of analyte deposition and as a protector of the analyte being

analyzed. It can be seen in the graph that in the concentration range of 0.02 to 0.1 M the current fluctuations occur. It reaches a maximum at a concentration of 0.12 M. It is possible at a concentration of 0.12 M NH_4Cl can deliver anlyte to the electrode optimally. Meanwhile, at higher concentration, the peak current decreases.

3.6 Variation of Concentration of Chalcone

The correlation between complexing concentration and peak current was determined in the concentration range of 0.02 mM to 0.22 mM. The result can be seen in Figure 6.

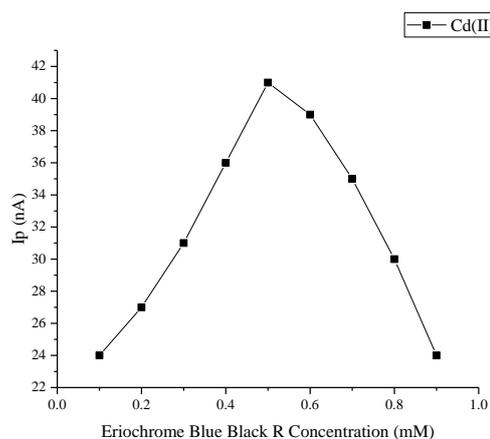


Figure 6. Chalcone concentration curve Vs peak current (I_p) Measurement condition: standard solution of Cd(II) 0.01 ppm; deposition potential -0.7 V; deposition time 60 seconds; pH 7; NH_4Cl 0.12 M

The complexing concentration of 0.12 mM gives the optimum peak current. At lower complexing concentration there is no complete complex between metal and complexing so the current obtained is still small. At optimal concentrations the metal and complex have been fully complexed to provide optimal current. At higher concentrations it is possible to compete between complexes as ligands in bonding with metal ion so the current decrease. In addition, it is possible to form a thick layer on the electrode to prevent the transfer of electrons [14,15].

3.7 Relative Standard Deviation (SDR)

Relative standard deviation (SDR) is used to see the accuracy of a method under the same operating condition in a short time interval. Determination of the relative standard deviation was carried out at a concentration of 0.01 ppm Cd(II) solution with 8 repetitions ($n = 8$). The results can be seen in Table 2:

Table 2. Measurement Result of Standard Solution Cd(II) 0.01 ppm

Repetition	Peak Current (nA)
1	14.37
2	16.09
3	16.09
4	16.04
5	16.03
6	16.28
7	17.00
8	16.23
Average	16.02
Standard Deviation	0.74
SDR	4.61%

From Table 2 above, the average peak current is 16.02 nA, with a standard deviation of 0.74. Meanwhile, the relative standard deviation of the adsorptive stripping voltammetry method for 0.01 ppm Cd (II) standard solution was 4.61%. The smaller the SDR value, the higher the accuracy of the method. It can be concluded that this method is quite precise.

3.8 Application On Sample

The application of this method in determining cadmium was carried out on water samples from the Bangek River and Teluk Kabung seawater using the optimum measurement condition that has been obtained: accumulation potential -0.7 V, deposition time 60 seconds, pH 7, NH₄Cl 0 concentration .12 M and chalcone concentration 0.12 mM. Sample measurement was carried out using the standard addition method.

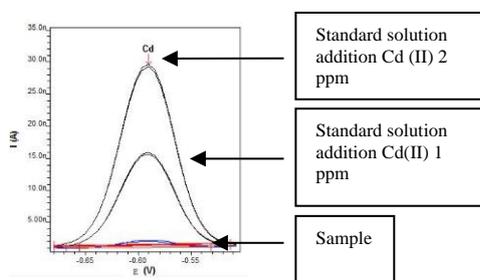


Figure 7. Voltammogram of Teluk Kabung seawater samples using the standard addition method

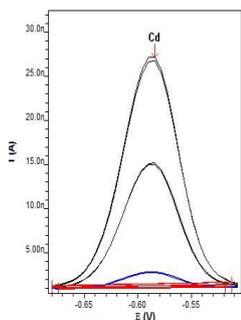


Figure 8. Voltammogram of Bangek River water sample with standard addition method.

Figures 7 and 8 show the voltammograms for measuring samples of estuary and lower pits using the standard addition method on a Metrohm 797 Computrace voltameter. From the figures, it can be seen that the peak current of the sample increased with the addition of 1 ppm cadmium standard solution twice. This proves that the sample contains cadmium.

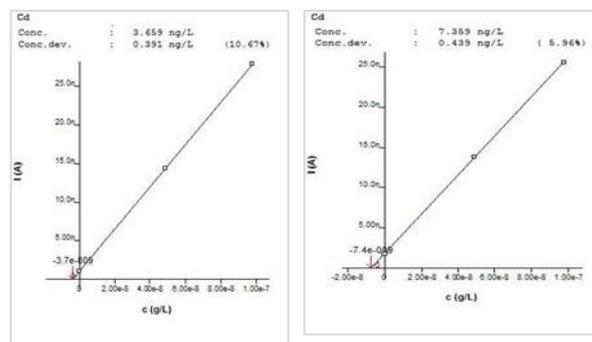


Figure 9. Standard addition curve for water samples from Bangek River and Teluk Kabung.

The concentration of Bangek River water sample and Teluk Kabung seawater sample obtained from the two standard addition curves above were 7.359 ng/L and 3.659 ng/L. The peak currents obtained are not much different, which are 1.76 nA for the Bangek River sample and 1.04 nA for the Teluk Kabung sample. The cadmium content in the Teluk Kabung sample is lower than the Bangek River sample. This is assumed because the Bangek River water contains various contaminant compounds originating from the community waste. There is interference with contaminant compounds in the form of detergent or surface active compounds contained in the river. This will cause the process of accumulation of cadmium-calcon on the surface of the working electrode to be disrupted because the working electrode has been filled with these interference compounds. As result it affects the peak current obtained.

3.9 Recovery

In order to determine the level of accuracy of this method, it is necessary to determine the recovery value by comparing the concentration of the sample obtained with the concentration of the analyte in the sample that has been added. The recovery was carried out by measuring the sample with a known concentration of 10 mL which was then added using a standard solution of Cd(II) 2, 4 and 6 ng/L. The result can be seen in Table 3:

Table 3. Cd(II) Recovery Results

N o	Concentration added (ng/L)	Sample concentration (ng/L)	Concentration after added (ng/L)	Recovery (%)
1	2	3.659	5.160	91.18
2	4	3.659	7.359	96.08
3	6	3.659	10.613	109.87
Amount				297.13
Average				99.04

From Table 3 it can be seen that the recovery value obtained is 99.04%. The recovery value in this study is quite good because it is close to 100%.

4 Conclusion

From this study it can be concluded that the accumulation potential of -0.7 V, accumulation time of 60 seconds, pH 7, 0.12 M NH_4Cl concentration, and 0.12 mM chalcone concentration were used as the optimum conditions for determining cadmium by voltammetry adhesive stripping. The application of the AdSV method to determine the concentration of cadmium in water samples from the Bangek River and Teluk Kabung seawater, Indonesia was 7.359 ng/L and 3,659 ng/L with a recovery value of 99.04%.

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