

Full Paper

Application of Calcon as Complexing Agent for the Simultaneous Determination of Lead and Cadmium in Sea Water with Adsorptive Cathodic Stripping Voltammetry

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Abstract- In the present study, a selective method is presented for the simultaneous determination of lead and cadmium in sea water samples by adsorptive cathodic stripping voltammetry (AdCSV). In preliminary studies, it has been proven that the lead and cadmium react with Calcon, giving rise to the formation of these complexes. These complexes have adsorptive characteristics on hanging mercury drop electrode (HMDE) and can be reduced in a reduction step. In this study the optimum reaction parameters and conditions studies are investigated. The optimum conditions of the AdCSV-calcon method are KCl concentration 1 mol/L pH 5, calcon concentration 0.1 mmol/L, accumulation potential -0.2 V, accumulation time 60 s. RSD for lead and cadmium are (4.2 and 0.36)%, performed 10 replicates (n=10), recovery for lead and cadmium (99.87, and 99.39)%. The calibration graphs were linear in the concentration range of (10–160, and 10–190) ng/ml for lead and cadmium, respectively. The limit of detection of the method was 10 ng/mL for lead and cadmium are (0.02, and 0.05) ng/mL. The interference of some common ions was studied and it was concluded that application of this method for the determination of lead and cadmium in sea water samples led to satisfactory results.

Keywords- A selective method, (Pb and Cd), Sea water, Calcon, Adsorptive cathodic stripping voltammetry

1. INTRODUCTION

Heavy metals are elements having an atomic weight between 63.5 and 200.6, and the specific gravity is greater than 5.0. With the rapid development of industries such as metal plating facilities, mining operations, fertilizer industry, leather tanning, batteries, paper and pesticide industries, and so on, heavy metal liquids are directly or indirectly discharged into the environment, especially in developing countries. Unlike organic contaminants, heavy metals cannot biodegrade and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic [1].

Heavy metals such as lead and cadmium are toxic if absorbed into the body. When they are in numbers exceeding the threshold, they can lead to long-term health problems. Lead and cadmium accumulation can cause poisoning, cancer and brain damage [2].

Cadmium is known as harmful environmental pollutants with toxic effects on living organisms. The side effects of cadmium are not only because of their high toxicity even at small concentrations but also because of the bioaccumulation process along the food chain. Cadmium can stay accessible to living organisms, including microorganisms and microalgae, which are at the first stage of the food chain and involved in important biological processes [3]. Cadmium ions are readily absorbed by vegetables, as well as in animal-based foods, and are mainly distributed in the liver and kidneys. As research has been done the highest cadmium concentrations are found in rice, wheat, oysters, shellfish and animal rodent cortex [4].

Lead is a common metabolic toxin and can inhibit enzymes. This can damage nerve connections (especially in young children) and cause blood and brain disorders. Lead has the ability to replace calcium in bone to form sites for long-term [5]. Due to the increasing use of lead and cadmium in the industry and its harmful effects on human health, the development of new sensitive methods is needed to measure lead and cadmium metals [2]. The preliminary results of a total number of dietary results of 50 μg per day or less up to 150 μg per day [6].

The low concentrations of lead, and cadmium metals in water samples, food samples and biological samples required the development of new methods capable of measuring them in very small quantities. In some general procedures for the determination of small lead and cadmium concentrations, a pre-concentration step is needed before performing the determination. Most of the currently available sensitive and selective methods, such as ICP-AES, ICP-MS, GF-AAS, and NAA, are too expensive to use in the routine analysis [7]. However, this technique has several disadvantages: such as expensive equipment, difficult operation, expensive equipment maintenance costs, and require well-controlled experimental conditions. Therefore, electrochemical methods such as differential pulse polarography are used [2].

Adsorptive cathodic stripping voltammetry (AdCSV) for the determination of heavy metal ions, including lead and cadmium is one of the most profitable techniques. Some of the

advantages of AdCSV for metal analysis are high sensitivity and selectivity, relatively cheaper instrumentation, and the possibility of easy analysis of various samples without the need for prior separation. [2], AdCSV has demonstrated many advantages, including analytical speed, good selectivity and sensitivity, good performance with salt matrices such as river water and seawater, capable of simultaneous analysis.

Increased sensitivity of the adsorption cathodic stripping voltammetric method can be done using a complex, several complexing agents have been studied to form complexes with Lead and cadmium ions in electrode hanging mercury drop electrode (HMDE) such as calcein [8-10], alizarin [11-13], oxine [14], luminol [2], mercapto-5-phenyl-amino-1,3,4-thiadiazole [15]. In this study used calcon as a complexing agent for the determination of lead and cadmium metals.

Calcon has a molecular formula $C_{20}H_{13}N_2NaO_5S$, with a relative molecular mass of 416.382 g/mol. Calcon has a free electron pair on carbonyl (C=O), so it can be used for complexing agents and very effectively forming complex compounds with metals.

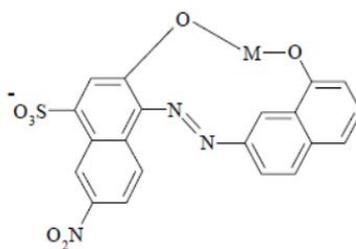


Fig. 1. Structure of Calcon-Metal

In this work, a sensitive adsorptive stripping voltammetric method is developed for the simultaneous determination of Lead and cadmium at trace levels in sea water samples. The procedure is based on the reduction of the complexes of those metal ions with calcon after accumulation at the surface of a hanging mercury drop electrode (HMDE).

2. EXPERIMENTAL DETAIL

2.1. Apparatus

Adsorptive cathodic stripping voltammetry (AdCSV) measurements were carried out with 797 AV Computrace (Metrohm, Switzerland) connected to a computer and controlled by VA Computrace 2.0 control software. A conventional three-electrode system was used in the hanging mercury drop electrode (HMDE) mode. pH values were measured on pH meter Griffin model 80 (Griffin and Loughbrough, England), analytical balance Mettler AE 200, (Toledo OH-USA), Biohit adjustable micropipettes and Brand adjustable micropipettes (Germany) were used to measure microlitre volumes of standard solutions and of all analyzed samples. A Labofuge 200 Heraeus Sepatech

2.2. Reagents

A lead and cadmium stock solution at 1000 mg/L was prepared and a calcon stock solution of 100 mM was prepared by dissolving the appropriate amount of calcon in ethanol in 25 ml volumetric flasks. These stock solutions were stored in the dark. Standard solutions of lower concentrations were prepared daily by diluting the stock solution with distilled water and ethanol. concentrated HNO₃ 65%, 0.01 mol/L acetate-acetic acid buffer (pH 2-6) and 0.01 mol/L phosphate buffer (pH 7-8), KCl prepared by using the Analytical Grade Merck Product, nitrogen gas, doubly distilled Water, Whatman filter paper used to filter samples in the form of seawater and added 1: 1000 HNO₃ 65%. The sample used is taken from Bungus Padang West Sumatra, Indonesia.

2.3. General procedure

Measurements were made using adsorptive cathodic stripping voltammetry (AdCSV) according to the following procedure: The supporting electrolyte solution (0.2 ml of KCl 0.12 mol/L) containing 0.2 mL of calcon 0.1 mmol/L was transferred into the electrochemical cell and purged with nitrogen for at least 300 s. The accumulation potential (-0.2 V vs. Ag/AgCl) was applied to a fresh mercury drop, while the solution was stirred for a period of 60 s. After 60 s of accumulation time, the stirring was stopped, and after equilibration for 10 s voltammograms were recorded from (-0.2 to -0.7)V with a potential scan rate of 200 mV/s and pulse amplitude of 50 mV. After the background voltammograms have been obtained, aliquots of the lead and cadmium standard solutions were introduced into the cell and then obtained solution was deoxygenated with nitrogen gas for 300 s. Then voltammograms were recorded according to the described procedure to give the sample peak current. After each scan was repeated three times with a new drop for each analyzed solution, the mean value was obtained. Lead and cadmium stripping peaks were registered at about (-0.339 and -0.532)V and their currents were used as a measure of lead and cadmium concentrations. All data were obtained at room temperature. Calibration graph was prepared for the peak current against lead and cadmium concentrations.

3. RESULTS AND DISCUSSION

Preliminary experiments were performed to identify the general features which characterize the behaviour of Pb-and Cd-Calcon systems on mercury drop electrode. Fig. 2 shows cathodic stripping differential pulse voltammograms of the Pb-and Cd-Calcon systems at pH 5.0 (acetate buffer), after accumulation at -0.2 V for 60 s on a HMDE. The metal ions in supporting electrolyte solutions showed small peak currents in the absence of Calcon (Curve a).

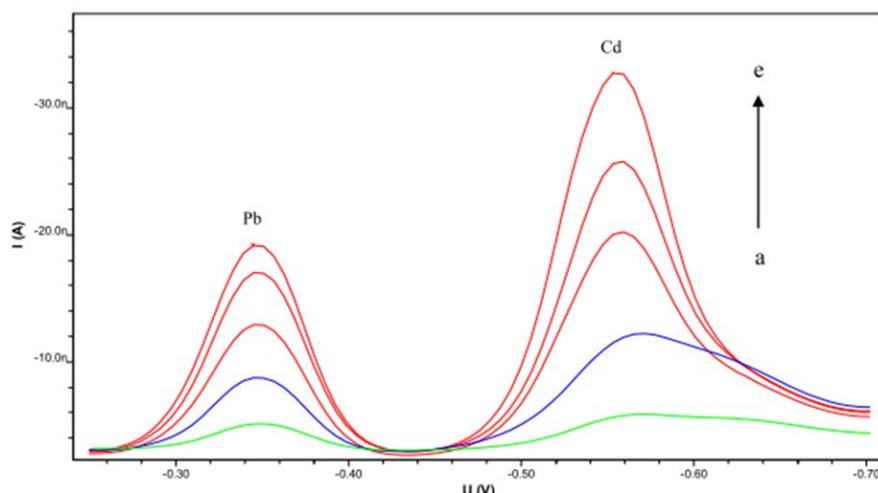


Fig. 2. Adsorptive cathodic stripping voltammetry for (Pb and Cd)-Calcon system. (a) Adsorptive cathodic stripping voltammograms in a solution containing Pb and Cd without Calcon; (b) 1,0 ng/ml (Pb and Cd) added 0.1 mmol/L Calcon; (c) 10 ng/ml (Pb and Cd) added 0.1 mmol/L Calcon; (d) 20 ng/ml (Pb and Cd) added 0.1 mmol/L Calcon; (e) 30 ng/ml (Pb and Cd) added 0.1 mmol/L Calcon, respectively, at optimal conditions: 0.10 mmol KCl, pH 5, deposition potential -0.2 V, deposition time 60 s and the scan rate of 200 mV/s

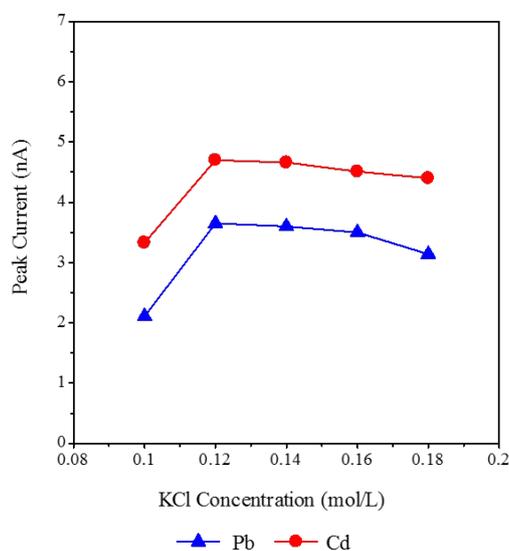


Fig. 3. Effect of supporting electrolyte concentration on the peak currents respectively, at optimal conditions: 0.10 mmol/L Calcon, pH 5, deposition potential -0.2 V, deposition time 60 s and the scan rate of 200 mV/s

Curve a shows the voltammograms of a solution containing 1 ng/mL of lead and cadmium in the absence of calcon under similar conditions. The sample solution containing the metal ions with calcon shows two peaks (curve b) at (-0.339 and -0.532)V that correspond

to the reduction of lead and cadmium complexes with calcon in pH of 5.0 (Fig. 2). The concentration of lead and cadmium enhanced ie (10; 20; 30)ng/mL showed peak current lead and cadmium also increased (curve c to e). For the best sensitivity in the simultaneous determination of lead and cadmium the influence of different parameters such as, supporting electrolyte concentration (KCl), pH, complexing agent concentration (calcon), deposition time and deposition potential.

3.1. Effect of supporting electrolyte

This research is done to determine the relationship between supporting electrolyte concentration with peak current. Supporting electrolyte used is KCl (0.1-0.18) mol/L. The results can be seen in Fig. 3. KCl serves as a supporting electrolyte, it plays a role in controlling potential during measurement, eliminating electromigration effects, and maintaining ionic strength so that the resulting current does not vary. In addition, this supportive electrolyte solution also plays a role in improving the analytical deposition effectiveness analyzed [16].

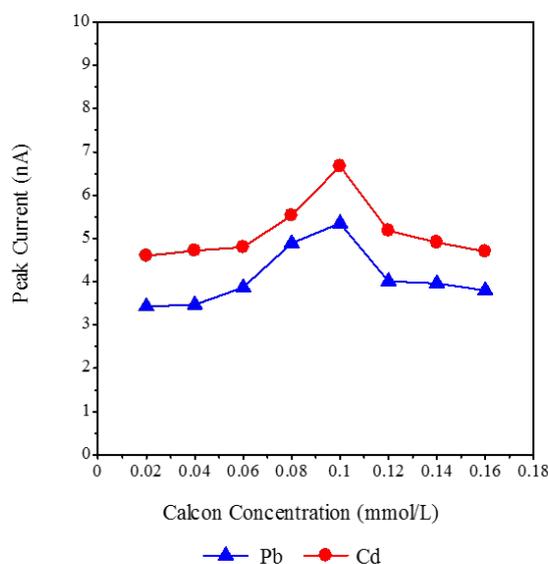


Fig. 4. Effect of calcon concentration on the peak currents respectively, at optimal conditions: 0.10 mol/L KCl, pH 5, deposition potential -0.2 V, deposition time 60 s and scan rate of 200 mV/s

Fig. 3 shows the concentration range of (0.1-0.12) mol/L. The peak current increases, but in the range (0.12-0.18) mol/L there is a peak current decrease so that the concentration of KCl 0.12 mol/L is chosen as the optimum concentration and used for the research next.

3.2. Effect of Calcon concentration

Determination of the relationship between calcon concentration with peak current (I_p) was done on concentration variations (0.02; 0.04; 0.06; 0.08; 0.1; 0.12; 0.14, and 0.16) mmol/L. The results can be seen in Fig. 4.

Calcon serves as a complex that will form complexes with metal. Calcon acts as a Lewis base that donates a lone electron pair to a carbonyl (C=O) metal ion. The stability of the complex will determine the amount of analyte deposited on the surface of the working electrode. A stable complex with metal ions will produce high peak currents [17-19].

Fig. 4 shows peak current increases in the concentration range (0.02-0.1)mmol/L. The concentration range of (0.12-0.16)mmol/L decreased the peak current. Based on the above curve, 0.1 mmol/L calcon concentration was chosen as the optimum condition in determining calcon concentration and used for further research.

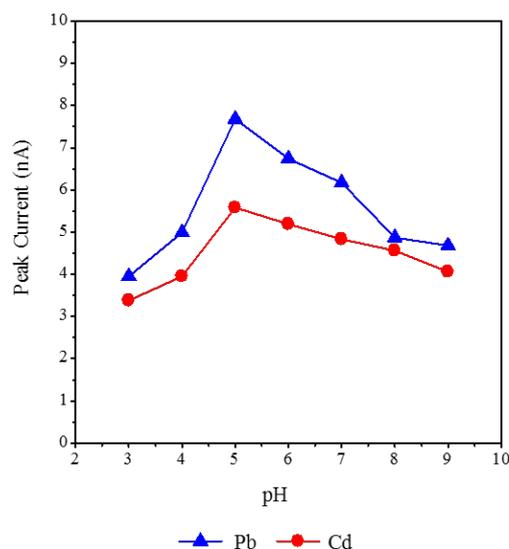


Fig. 5. Effect of pH on the peak currents respectively, at optimal conditions: 0.10 mol/L KCl; 0.10 mmol/L calcon; deposition potential -0.2 V, deposition time 60 s and scan rate of 200 mV/s

3.3. Effect of pH

pH is a very important parameter because it deals with the formation of complex compounds between calcon with lead and cadmium [16]. pH plays a role in improving the complex stability that is formed. Optimization of pH determination was done in the pH range (3-9). The results can be seen in Fig. 5.

pH (3-5) a significant rise in current (Fig. 5). This shows more and more complexes accumulating on the electrode surface. pH (5-9) complexes that accumulate on the working

electrode is decreasing so there is decrease peak current. Based on the above curve, the optimum pH obtained is 5 and used for further research.

3.4. Effect of deposition potential

Deposition potential is done from the accumulated potential of (-0.1 to -0.8)V. The result can be seen in Fig. 6.

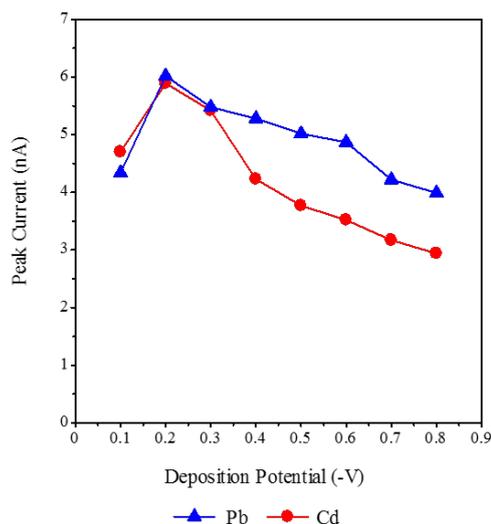


Fig. 6. Effect of deposition potential on the peak currents. respectively, at optimal conditions: 0.10 mol/L KCl; 0.10 mmol/L calcon; pH 5; deposition time 60 s and scan rate of 200 mV/s

Deposition potential is a potential at the time the analyte is accumulated or deposited on the surface of the working electrode [16]. Fig. 6 shows the peak current increases with increasing potential to a more negative potential (-0.1 to -0.2)V. When the potential exchange of (-0.3 to -0.8)V peak current decreases. This shows the lead and cadmium deposited on the surface of the most electrode at a potential of -0.2 V. Thus, the potential -0.7 V is chosen as the optimum deposition potential of the measurement and is used for further research.

3.5. Effect of Deposition Time

Deposition time is the time at which the analyte is deposited on the surface of the mercury electrode [16]. Deposition time is determined in the range of (30-120)s. The measurement results can be seen in Fig. 7.

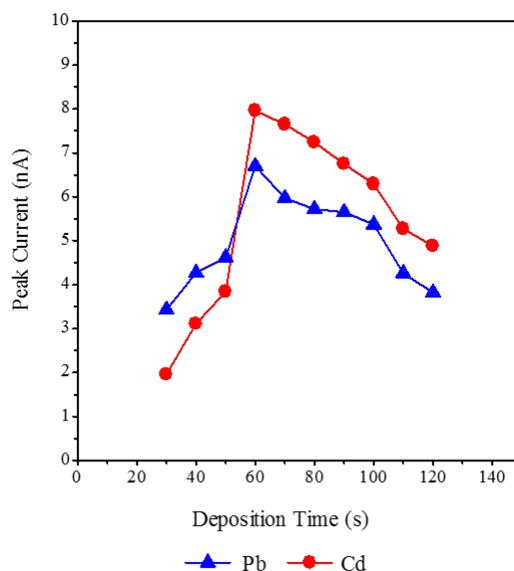


Fig. 7. Effect of deposition time on the peak currents. respectively, at optimal conditions: 0.10 mol/L KCl; 0.10 mmol/L calcon; deposition potential -0.2 V; pH 5 and scan rate of 200 mV/s

Fig. 7 shows the effect of deposition time on peak current with the presence of calcon as a complexing agent. Peak current increases from deposition time (30–60)s. Theoretically, the longer the accumulated time the more the analyte is deposited onto the surface of the mercury electrode so that when stripping is generated a large current. However after deposition time 60 s peak current decreases. This is because there is saturation on the surface of the electrode, so that at the time of stripping not all analytes detached from the surface of the electrode resulting in a small generated current [16]. Thus, the optimum deposition time obtained is 60 s and used for further research.

3.6. Relative Standard Deviation (RSD)

Relative standard deviation (RSD) is used to see the accuracy of a method under the same operating conditions in a not too long time interval. The determination of RSD was performed at 10 $\mu\text{g/L}$ lead and cadmium solution concentration with 10 replicates ($n=10$). The measurement conditions are set based on the optimum conditions that have been obtained, namely; deposition potential -0.2 V; deposition time 60 s; KCl concentration 0.12 mol/L; calcon concentration 0.1 mmol/L; and pH of solution 5. The results can be seen in Table 1.

Table 1. Standard Measurement Results of 10 µg/L lead and cadmium

Replicates	Peak current (nA)	
	Pb	Cd
1	7.33	8.22
2	7.47	8.31
3	7.89	8.28
4	7.55	8.3
5	7.34	8.31
6	7.88	8.29
7	7.05	8.25
8	7.67	8.33
9	7.99	8.29
10	7.98	8.3
Average	7.615	8.288
SD	0.320425	0.031903
RSD	4.2%	0.36%

Table 1 shows the average peak current values for lead and cadmium are 7.615 nA and 8.288 nA, respectively. The RSD obtained for the determination of both metals was 4.2% for lead and 0.36% for cadmium respectively. Based on the AOAC method, a good RSD value for a solution with a concentration of 10 ng/mL is small from 6% [20]. That is, this method has a high degree of accuracy because RSD is obtained for each small metal of 6%.

Table 2. Result of the determination of Pb and Cd in sea water with AdCSV-Calcon method

Sample	Added (µg/L)		Found (µg/L)		Recovery (%)	
	Pb	Cd	Pb	Cd	Pb	Cd
Karolina Beach	0	0	177.37±0.12	62.52±0.09	-	-
	5	5	183.22±0.12	67.11±0.12	100.47	99.39
	10	10	187.12±0.12	71.02±0.12	99.87	97.93
Teluk Buo	0	0	73.92±0.05	17.99±0.12	-	-
	5	5	77.97±0.12	23.34±0.12	98.80	101.52
	10	10	84.01±0.12	27.11±0.12	100.11	96.86
Labuan China	0	0	231.77±0.15	102.67±0.14	-	-
	5	5	236.78±0.12	106.45±0.12	100.04	98.87
	10	10	240.23±0.12	112.45±0.12	99.36	99.80

Determination of Pb and Cd in sea water sample (n=5), mean ±SD

3.7. Application and recovery

Determination of recovery value aims to determine the accuracy and accuracy of a method. This recovery is determined by adding a certain amount of standard solution of a certain concentration into one of the already known samples of concentration by addition method. In this research, the recovery value is examined by sea water sample at Bungus Padang, Karolin Beach, Teluk Buo, and Labuan China West Sumatera, Indonesia. Recovery was performed by adding 2 mL standard lead and cadmium solution (5; 10) $\mu\text{g/L}$ to 8 mL sea water sample. The results of this recovery can be seen in Table 2.

Table 2 shows recovery of lead and cadmium with AdCSV-Calcon. Based on the recovery results obtained when compared with the AOAC standard, the recovery value of the solution with a good concentration of 10 ng/mL was in the range (70 - 120)% [20]. That is, this method has good accuracy.

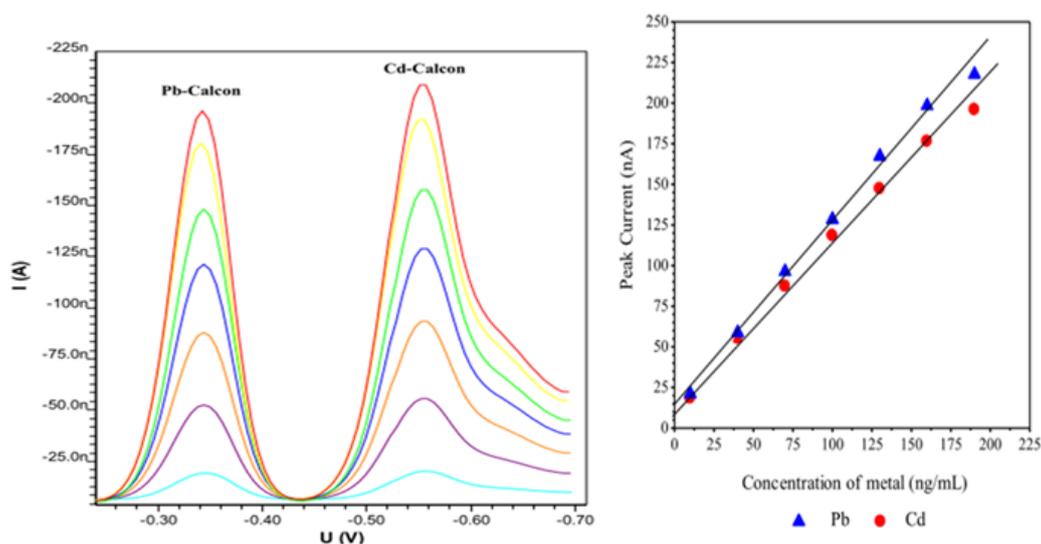


Fig.8. voltammograms for AdCSV in the solutions with different concentrations (from bottom to top, 10; 40; 70; 100; 130; 160; 190)ng/mL of Pb and Cd Conditions: pH 5; deposition potential, -0.2 V vs. Ag/AgCl; deposition time 60 s; Calcon concentration 0.1 mmol/L; 0.1 mol/L KCl; Scan potential from $(-0.02$ to $-0.7)$ V

3.8. Linear range, detection limit, and precision

Under the optimised conditions, a linear range between the reduction peak current of the lead and cadmium-Calcon and the concentrations of lead and cadmium was obtained. To verify the linear range between peak currents and metal concentrations, seven calibration graphs (Fig. 8) were constructed under optimum conditions and after 60 s accumulation time. The calibration graphs were performed for lead and cadmium separately and in the presence of 10 ng/mL, respectively. The result of this study (correlation coefficient 0.993 for lead and

0.994 for cadmium) indicated that in all cases the current concentration relationships were linear in the concentration range of (10–160 and 10–190)ng/ml for lead and cadmium, respectively. The limit of detection (3σ) [21] of (0.02 and 0.05)ng/ml were obtained for copper and cadmium, respectively. Ten successive measurements of 10 ng/mL (copper and cadmium) are obtained RSD (4.2 and 0.36)% respectively. The sensitivity was the slope of the calibration curve of copper and cadmium (1.119 and 0.994) for lead and cadmium, respectively.

3.9. Interference study

Possible interference of other species in the adsorptive stripping voltammetric determination of lead and cadmium were studied by addition of the interfering ion to a solution containing 10 ng/ml of lead and cadmium, using the optimised conditions (the criterion for interference was a 5% error in the peak heights of Pb and Cd). The results of this study are summarised in Table 3. It was found that most of the foreign ions did not interfere for lead and cadmium determination.

Table 3. Interferences study for lead and cadmium determination

Species	Tolerance limit	
	Pb (mg/L)	Cd (mg/L)
Na ⁺ , Al ³⁺ , Ca ²⁺ , Li ⁺ , K ⁺ , Ba ²⁺ , Cr ⁺³ , Co ²⁺ , Ni ²⁺ , Cl ⁻ , F ⁻ , Br ⁻ , SO ₄ ²⁻ , I ⁻	100	100
Cu ²⁺	10	100
Pb ²⁺	-	10
Cd ²⁺	10	-
Zn ²⁺	100	10
Fe ³⁺	10	10

4. CONCLUSION

The optimum conditions of the AdCSV-calcon method are : pH 5, calcon concentration 0.1 mmol/L, accumulation potential -0.2 V, accumulation time 60 s. Relative standard deviation (RSD) for lead, and cadmium are (4.2, and 0.36)%, recovery for lead and cadmium (99.87, and 99.39)%, the calibration graphs were linear for lead and cadmium (10–160 and 10–190)ng/ml, the limit of detection of the method was 10 ng/mL for lead and cadmium are (0.02, and 0.05)ng/mL. This study demonstrates that the application of calcon in the adsorptive cathodic stripping voltammetry of lead and cadmium is an excellent method with high sensitivity, selectivity, simplicity, and speed for the determination of trace amounts of these two metal ions in sea water samples.

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