Full Paper

Adsorptive Stripping Voltammetry for the Simultaneous Determination of Cd, Cu, Cr, and Pb in Water Samples using Fluorexon: an Optimization Single Factor

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Abstract- Optimization single factor for the simultaneous determination of Cd, Cu, Cr, and Pb in water samples by adsorptive stripping voltammetry (AdSV) has been investigated. In preliminary studies, it has been proven that the Cd, Cu, Cr, and Pb react with fluorexon, giving rise to the formation of these complexes. Variable factors that affect the response were studied: fluorexon concentration, pH, potential accumulation and time accumulation. The optimum conditions of the AdSV-fluorexon method were: fluorexon concentration 0.6 mmol/L, pH 6, potential accumulation -0.7 V, and time accumulation 70 s. The relative standard deviations (RSD) were (0.46; 0.11; 2.39, and 0.90)% for ten replicates(n=10) measurements of 10 µg/L, recovery were (99.11; 99.88; 98.12, and 98.76)%, the linear calibration graph were (10.0-100.0) µg/L, the limit of detection (LOD) were (0.590; 1.794; 1.235, and 1.595) µg/L for Cd, Cu, Cr, and Pb. This procedure was successfully applied for the simultaneous determination of Cd, Cu, Cr, and Pb in the water (sea water, tap water, lake water and river water) with standard addition method.

Keywords- Heavy metals, Adsorptive stripping voltammetry, Fluorexon, Optimization single factor

1. INTRODUCTION

The negative impact of the industrialization process is the entry of heavy metals into aquatic environments and has become a global issue as metals are indestructible and have toxic effects on living organisms especially at high concentrations. The industrial waste is the result of the activities of petroleum refining, battery manufacturing, tannery, mining, pesticides, among others: Cd, Zn, Cu, Ni, Pb, Hg and Cr are often found [1,2]. The first dissolved in water, then adsorbed, and finally accumulated on the bed sediments acting as sinks [3].

Analytical techniques commonly used in the determination of heavy metals: polarography, FAAS with detection limit μg/L, ICP-MS with a detection limit of 0.01 μg/L, and AdSV with a detection limit of 0.1 μg/L [4,5]. AdSV is chosen as an alternative method because it has many advantages including high salt content from seawater not disturbing in the analysis, high sensitivity, low detection limit on μg/L scale (ppb), easy use and easy sample preparation, rapid analysis, inexpensive infrastructure [6-10]. In addition, by this method, it is possible to study the chemical specimens of heavy metals [11,12], which can not be done by other methods. Almost all methods of determining metals in very small quantities require considerable time in the pre-concentration stage before measurement, while in AdSV, the pre-concentration phase is shorter, less than 1 minute [13].

Selection of ligands is the most important component in the method of AdSV because the selectivity, sensitivity, and accuracy of the method one of them is determined by the complex used. The method development of the AdSV is characterized by the selective and sensitive models of the metal ions and the optimization technique [4,5].

Based on the description previously described, then in this study developed a method that is selective for the simultaneous determination of Cd, Cu, Cr, and Pb using fluorexon. Selection of fluorexon as a selective compound has been reported [14] on the determination of Cd, Cu, Cr, and Pb, not jet reported. AdSV is one of the most sensitive techniques [14], the peak currents (Ip) is strongly influenced by the following variables: the concentration of the complexing agent, pH, potential accumulation, and time accumulation. It is therefore very important to determine the optimum of these parameters, which will affect the quality of the analysis [15].

AdSV is a part of the electrode or suspended mercury electrode (HMDE), followed by the reduction of the metal complex of adsorbed on the surface of the working electrode by providing a reduction potential rapidly. This method consists of four steps: the formation of complexes between metals and complex reduction and current measurement with anode or cathode potential scans [13].

Based on of previous research, it has been reported by various scientists as well as simultaneously with AdSV. The simultaneous determination of Cu and Cd using 2,2-dichlosalicylic acid [16], simultaneous determination of Pb and Cd with morin [17],

simultaneous determination of Cu and Cd levels of ultra traces [18], simultaneous determination of Cu, Cd, and Pb with calcon [19], determination of Zn with calcon [20], simultaneous determination of Pb and Cd at the level of trace in natural waters by red pyrogalol [21], simultaneous determination of Cu, Pb, Cd, Ni, Co and Zn in bioethanol fuel samples with mixtures of multiple adsorptive volatile stripping stripometers and multi-variance regression [22], simultaneous determination of Cu, Pb, Cd and Zn with alizarin [23-25] and the simultaneous determination of Pb, Cd, and Zn using clioquinol [26]. A very sensitive determination for Cu traces in a food sample with 1,10 phenanthroline [27], and the determination of Cu in the ultra-trace level in food samples with thiosemicarbazide [28]. The use of catalyst stripping (Ti) by adsorptive catalytic stripping volatile stripping [14]. In this study was used AdSV for the simultaneous determination of Cd, Cu, Cr, and Pb in the presence of fluorexon.
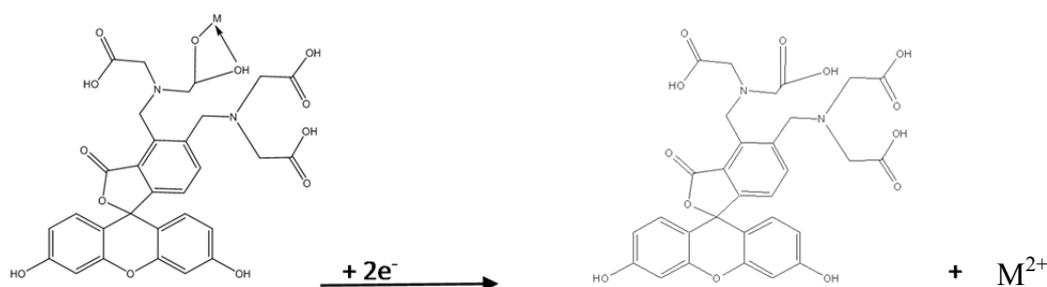
Fig .1. Mechanism of the electrochemical reduction process for complex Fluorexon-metal complex

The use of fluorexon (Fig. 1) as a precursor has been reported [29] for the simultaneous determination of Cu, Pb, and Cd by AdSV, further the determination of Cd, Cu, Pb, and Zn individuals in a sample of fruits [30-31].

Santos-Echeandia has reported the direct determination of Co, Cu, Fe, Ni, and V simultaneously with adsorptive cathodic stripping voltammetry using a mixture of ligand (dimethyl glioksim and chatechol) [32]. AdSV has been used for the determination of Fe and Al in environmental samples by using the Solochrome violet RS (SVRS) compound, acetate buffer pH 4.5 supporting electrolyte [33]. Furthermore, Kenji and Nakaya have reported comparisons of the method of determining Cr in seawater and its species [34].

2. EXPERIMENTAL

2.1. Instruments and Materials

The instruments used in this study include analytical balance Mettler AE 200, Toledo OH-USA, pH meter model 80 Griffin, 797 Computrance from Metrohm HMDE as working

electrode, Ag/AgCl KCl 3M Refrensi electrode and Pt as auxiliary electrode and glassware used in the laboratory.

Various chemicals were purchased from Merck and the aqueous solution of Cd, Cu, Cr, and Pb 1000 mg/L were prepared by using analytical grade Merck product. The ingredients used in this study were: HNO_3, NaOH, HCl, KCl, acetate buffer, fluorexon, NH_4OH, buffer ammonia, nitrogen gas, doubly distilled water, buffer pH 4, 7 and 10 and Whatman 42 filter paper. The samples used are water from sea water, tap water, river water and Maninjau lake water.

2.2. Work procedures

The aims of this study were to get the optimum condition of the simultaneous determination of Cd, Cu, Cr and Pb ions by AdSV. The procedure was used in this research according to the reported previously [19].

3. RESULTS AND DISCUSSION

Addition of the complex can increase the selectivity of the measurement as well as lower the detection limit. Choosing the right compiler is necessary to obtain optimal results. The detection limit was decreased by increasing the concentration of the adsorbed analyte on the electrode surface [37]. FIG. 2 is a fluorexon voltammogram without the addition of Cu, Pb, Cd, and Cr: (a) metals showing no peak current in potential reactions of the half-reaction reactions, so as not to interfere with the measurement. Cu, Pb, Cd, and Cr metals of 10 µg/L each produce a small peak current (b). The addition of fluorexon indicates an increasingly high voltammogram (c). This shows that fluorexone can increase the selectivity of the measurement, so the detection limit of the method will also decrease.
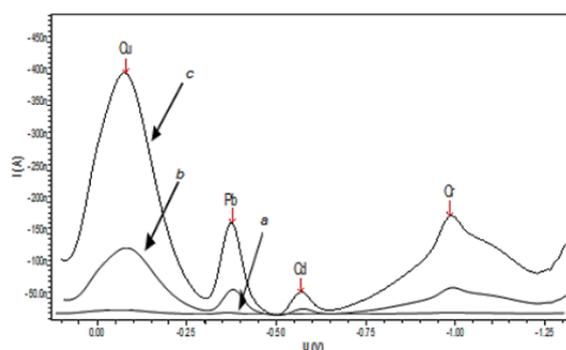
Fig. 2. Adsorptive stripping voltammetry scan of Cu, Pb, Cd and Cr in the presence of fluoreexon. 10 mL Mixture 10 µg/L; 0.2 mL of fluorexon 0.6 mM; 0.2 mL KCl 0.1 M; potential accumulation of -0.7 V; time accumulation 70s; pH 6

3.1. Effects of Fluorexon Concentration

In this research, determination of the correlation between fluorexon concentration with peak current to mixed standard solution of Cd, Cu, Cr, and Pb 10 μg/L with potential accumulation -0,7 V, time accumulation 60 s, pH adjusted 6. Variation of fluorexon concentration in 20 mL of test solution between (0.1-0.9) mM. The results can be seen in Fig. 3.
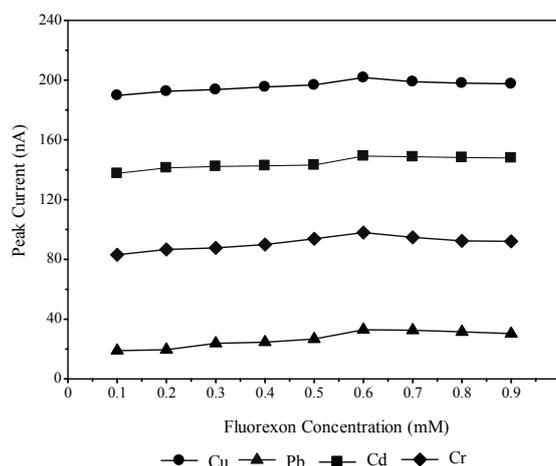
Fig. 3. The relation curve of fluorexon concentration to the peak current (Ip) ion metals simultaneously, conditions: 10 mL of standard solution mixed 10 μg/L 0.2 mL fluorexon; KCl 0.1 M; time 60 s; potential -0.7 V; pH 6

Fig. 3 shows that the peak current increases with increasing fluorexon concentration up to 0.6 mM. The highest peak current is Cu followed by Cd, Cr, and Pb. This is because the formation of complexes between Cu and fluorexon is more stable than other metal ions, wherein this simultaneous condition, each metal ion competes to form a complex with fluorexon. At concentrations of fluorexon above 0.6 mM, there is a decrease of peak current. This is due to competition between the complexing agent to be adsorbed on the electrode surface at the deposition stage (preconcentration) and forming a complex with metal ions [19]. The peak current generated due to the reduction of the metal- complexing agent is adsorbed on the surface of the working electrode at the stripping stage. The peak current produced depends on the concentration of fluorexon used, the higher the concentration of fluorexon provided the more difficult the metal - complexing agent is reduced so that the peak current is getting smaller.

The higher fluorexon concentration of 0.6 mM of the resulting peak current decreases as a consequence of the full surface coverage of the electrode. The optimum 0.6 mM fluorexon concentration was selected for further experiments.

3.2. Effects of pH

The reaction between metal ions Cd, Cu, Cr, and Pb with fluorexon as the compound is affected by the pH condition of the solution [37]. In AdSV, at the preconcentration stage occurs complex reaction between metal ions with complexing agent, then the complex is formed is adsorbed on the surface of the working electrode. The reaction process is described in reaction (a)

$$M^{n+} + nL \leftrightarrows MLn(diss) + n\,H^+ \qquad\qquad (a)$$
$$MLn(diss) \rightarrow MLn(ads)$$

The stripping stage, given the potentially more rapidly negative potential, so that the complex between the adsorbed metal-complexing agent in the reduced electrode forms M^0 and nL^- like reaction (b). The reaction is as follows:

$$MLn(ads) + ne^- \rightarrow M^0 + nL^- \qquad\qquad (b)$$

When the reduction reaction occurs (b) the peak current is measured which is proportional to the concentration of the analyte in solution. pH the solution may affect the formation of complexes between Cd, Cu, Cr, and Pb ions with fluorexon at stage deposition (preconcentration).
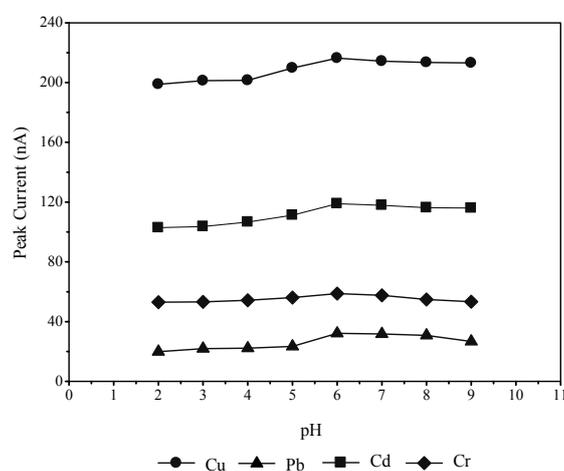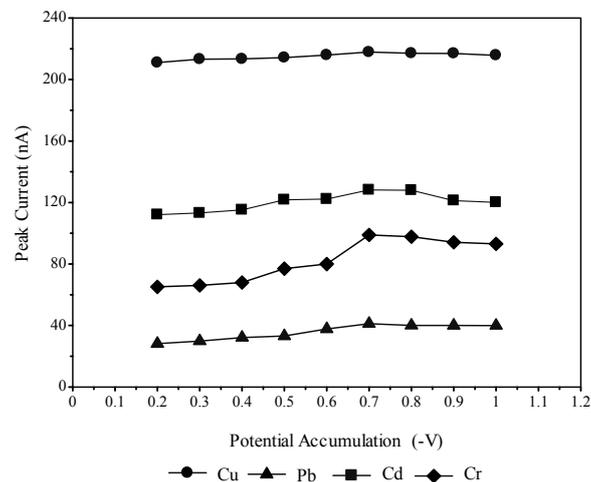

Fig. 4. The curve of pH relationship to the peak current (Ip) of metal ions simultaneously, conditions: 10 mL mixture 10 µg/L; 0.2 mL of fluorexon 0.6 mM; 0.2 mL KCl 0.1 M; time 60 s; potential accumulation -0.7 V

Appropriate pH conditions are expected to be more complex (Cd, Cu, Cr, and Pb) - fluorexon occurring on the electrode surface resulting in optimum peak current at the measurement.

The research determines the relation between pH of the solution with peak current to standard solution mix of Cd, Cu, Cr, and Pb 10 µg/L with potential accumulation -0,7 V, time accumulation 60 s with 0.1 µm of fluorexon concentration (optimum fluorexon concentration). The pH variations performed in 20 mL of the test solution are from a range of pH (2- 9). The results can be seen in Fig. 4.

The deposition phase (preconcentration) forms a complex between Cd, Cu, Cr, and Pb ions with fluorexon, where the complex stability formed from each of the metal ions is affected by the pH solution. Inappropriate pH conditions, more complex (Cd, Cu, Cr, and Pb) - fluorexon are expected to occur on the surface of the electrode resulting in optimum peak current at the measurement.

It can be seen (Fig. 4) that the peak current height is affected by the pH condition of the solution of each of the metal ions. The pH range is (2-5), the increase of the non-significant peak currents mainly for Cr and Pb. Mean variation of pH of the solution does not affect the stability of the Cr, and Pb complexes with fluorexon so that the peak current measurements can be ranged. The pH conditions of the solution also affect the complex stability that is formed, will also affect the concentration of the analyte that is deposited on the working electrode as well as the resulting peak current [4,36]. At pH 6.0 found the peak current of Cd, Cu, Cr, and Pb with maximum value. pH 6.0 was selected as the optimum pH for further research (Fig. 4). The decline in response to Cd, Cu, Cr, and Pb is due to the competitive formation of the metal hydroxide [6-10].

Fig. 5. The potential accumulation relationship curve to the peak current (Ip) of the metal ion simultaneously, condition: 10 mL mixture of 10 µg/L; 0.2 mL of fluorexon 0.6 mM; 0.2 mL KCl 0.1 M; time accumulation 60 s; pH 6
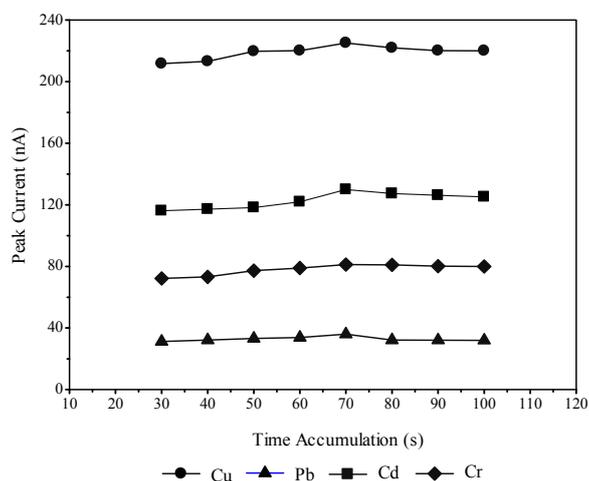
3.3. Effects of Potential Accumulation

The effect of the potential accumulation on the stripping-top currents of (Cd, Cu, Cr, and Pb)-fluorexon complexes are simultaneously studied in the potential range (-0.1 to -1.0) V. Fig. 5 can be seen, in the potential range (-0.1 to -0.7) V the peak current generated for each of these metal ions increases, where the increase of peak current is not significantly different for Cu ions. This shows the process of deposition (accumulation) of the analyte on the working electrode more and more so that the peak current generated also increased. The highest produced peak current is Cu> Cd > Cr> Pb ions, in the potential range (-0.8 to -1.0)V down the curve.

At potential accumulation -0.7 V, the resulting peak current for the metal ion mixture tested is maximum, indicating that the process of deposition of the analyte complex at the maximum working electrode occurs at that potential and the sensitivity of the method occurs at that potential [37]. For the next measurement, -0.7 V used as the optimum potential accumulation for the simultaneous determination of Cd, Cu, Cr, and Pb.

3.4. Effects of Time Accumulation

The time accumulation is the time at which the analyte is accumulated or deposited on the working electrode surface (HMDE). Deposition time affects the accumulation stage (preconcentration). At the preconcentration stage, the time accumulation is used to increase the sensitivity and lower the detection limit [6,7,37].

Fig. 6. The time accumulation relationship curve to the peak current (Ip) of metal ions simultaneously, condition: 10 mL Mixture 10 μg/L; 0.2 mL of fluorexon 0.6 mM; 0.2 mL KCl 0.1 M; potential accumulation of -0.7 V; pH 6

The length of time accumulation of Cd, Cu, Cr, and Pb affects the complex stability formed on the electrode surface.

In this study, determination of the relationship between the time accumulation with the peak current tested, by varying the time accumulation in the range (20-100) s. The results can be seen in Fig. 6.

This study, the effect of the time accumulation on the peak current generated for the mixture of standard solutions of Cd, Cu, Cr, and Pb ions in simultaneous conditions, the results can be seen in Fig. 6. Theoretically, long time accumulation, more accumulated analytes on the surface of the working electrode so that the peak current generated is greater [37]. The length of time accumulation of Cd, Cu, Cr, and Pb affects the complex stability formed on the electrode surface. The effect of the time accumulation on peak currents from Cd, Cu, Cr, and Pb is studied in the range of (30-100) s. Initially, the peak current increases as a function with increasing time accumulation of up to 60 s. Prior research, higher than expected fluorexon concentrations may Pb to inhibition of complexing agent adsorption with competitive coverage with free complexing agent.

In the adsorption process, the peak current dependence on the time accumulation is limited by the saturation of the electrode, resulting in a current reaching a maximum value at a 60 s time accumulation as shown in Fig. 6. The time deposition 60 s is chosen as the optimum time accumulation used for further research, as it combines good sensitivity and relatively short analysis times [4,5].

3.5. Determination of relative standard deviation (RSD)

The RSD is used to see the accuracy of this method under the same operating conditions [35,36]. The determination of the RSD was performed on the optimum conditions obtained above, with ten replications (n=10) measurements of standard solutions of each Cd, Cu, Cr, and Pb 10 μg/L, the results can be seen in Table 1.

Table 1. Measurement of a Standard Solution Mixture of Cd, Cu, Cr, and Pb 10 μg/L

| Replicates	Peak current (nA)			
	Cd(II)	Cu(II)	Cr(III)	Pb(II)
1	112.17	217.18	98.29	41.17
2	112.88	217.65	98.77	42.08
3	113.26	216.77	98.12	41.67
4	113.09	216.98	99.01	41.76
5	113.21	217.09	98.12	41.22
6	113.42	217.24	98.17	41.23
7	112.98	217.21	98.31	42
8	112.09	217	97.98	41.09
9	112.32	217.12	91.02	41.22
10	112.14	217.32	98.31	41.76
Mean	112.756	217.156	97.61	41.52
SD	0.52	0.23	2.34	0.37
RSD	0.46	0.11	2.39	0.90

Table 1 shows the results of measurement of the relative standard deviation values of each of the metal ions Cd, Cu, Cr, and Pb were: (0.46; 0.11; 2.39, and 0.90)%. According to the AOAC method, the relative standard deviation (RSD) value is less than 8% at a concentration of 10 μg/L. That means this method has a high degree of precision because the RSD obtained for each metal is smaller than 8.

3.6. Determination of Recovery

Recovery is used to determine the accuracy of this method. A number of known standard solutions of concentration are added to the sample and then compared with the sample and standard concentrations added. In this study used seawater taken from Bungus Padang to determine recovery. The results of recovery of Cd, Cu, Cr, and Pb by AdSV under optimum conditions were (99.11; 99.88; 98.76; and 99,79)%. According to the AOAC method[38], the percent recovery for 50 μg/L solution is in the range of (70-110)%. That is, this method has a high accuracy.

3.7. Determination of Linear Concentration and Limit of Detection (LOD)

The linear concentration for analysis of Cd, Cu, Cr, and Pb in AdSV was studied to know the range of concentration which gives a linear relationship between the peak current height and the concentration of the metal ions.
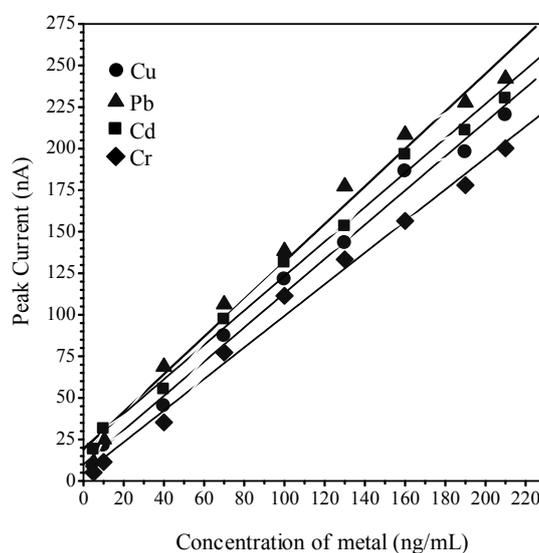
Fig. 7. Calibration graph for (Cu, Pb, Cd and Cr) in the presence of 0.2 mL of fluorexon 0.6 mM; 0.2 mL KCl 0.1 M; potential accumulation of -0.7 V; time accumulation 70 s; pH 6

In optimum condition, the linear relationship between the peak current with the concentration of each ion Cd, Cu, Cr, and Pb is obtained. To verify the linear relationship

between the peak current and the concentration of the four metals, the four calibration curves were plotted under optimum conditions.

The calibration equation, obtained by the quadratic method is $I_p=3.936C+161.2$ ($r^2=0.986$) for the determination of Cd, $I_p=4.327C+303.6$ ($r^2=0.988$) for Cu $I_p=1.5667C+78.881$($r^2=0.9416$) for Cr, and $I_p=5,012C+146$ ($r^2=0.988$) for Pb, where C is the metal ion concentration µg/L and Ip is the current peak (nA). Stripping peaks during the (Cd, Cu, Cr, and Pb) - fluorexon complexes and were found to be directly proportional to the (10 - 100.0)% concentration for Cd, Cu and Pb, while (10-80.0)µg/L for Cr.

The detection limit is calculated from three times the standard deviation of the blank solution divided by the slope ($3\sigma/B$) under the optimum conditions obtained respectively (0,590; 1,794; 1,235 and 1,595) µg/L for Cd, Cu, Cr, and Pb.

3.8. Effects of Interference of Cations and Other Anions

The effects of the addition of other cations and anions in the analysis of Cd, Cu, Cr, and Pb were studied in order to determine the selectivity of the working electrode employed. The cation and anion of the agent used in the selectivity test can be seen in Table 2.

Table 2. Interference tolerance of ions in the determination of Cd, Cu, Cr, and Pb 10 µg/L

Ions	Tolerance limit (mg/L)			
	Cu	**Pb**	**Cd**	**Cr**
Na^+, Al^+, Ca^+, Li^+, K^+, Ba^{2+}, , Co^{2+}, Ni^{2+}, Cl^-, F^-, Br^-, SO_4^{2-}, I^-	10	10	10	10
Cu^{2+}	-	10	1	10
Pb^{2+}	10	-	10	10
Cd^{2+}	10	10	-	10
Zn^{2+}	1	1	10	10
Fe^{3+}	1	1	1	1
Cr^{+3}	10	10	10	-

Other metallic disturbances to the determination of Cd, Cu, Cr, and Pb by AdSV were investigated by addition of other ions into a solution containing 10.0 mg/L of the metal using the optimum conditions. Based on the results of the study, it was found that most of the foreign ions did not interfere with the determination of Cd, Cu, Cr, and Pb. The tolerance limit for the selectivity method for the determination of Cd, Cu, Cr, and Pb on the interference of other ions was 10 mg/L.

3.9. Application method

To evaluate the validity of the methods used for the analysis of real samples, the proposed procedure is applied to various samples including water samples from seawater, tap water, river water and lake water. The concentrations of Cd, Cu, Cr, and Pb in the sample can be seen in Table 3 determined by standard addition methods using recommended procedures under optimal conditions.

Table 3. Determination of Cd, Cu, Cr, and Pb in water samples by AdSV

Sample	Calcon (µg/L)				Fluorexon (µg/L)			
	Cu	**Pb**	**Cd**	**Cr**	**Cu**	**Pb**	**Cd**	**Cr**
Sea water	0.017	0.001	0.013	0.062	0.271	0.127	0.045	112.21
Tap water	0.034	0.031	0.152	0.034	0.117	0.004	0.010	17.28
Maninjau lake Water	0.260	0.090	0.010	80.67	0.275	0.011	0.015	92.69
River Water	nd	Nd	nd	0.010	0.119	0.007	0.034	Nd

Note: nd=not detected

From Table 3, it can be seen the comparison of determination methods of Cd, Cu, Cr, and Pb with AdSV by using calcon and fluorexon as a complexing agent. The results show the proposed method using Fluorexon as a compound gives a sensitive and satisfying result.
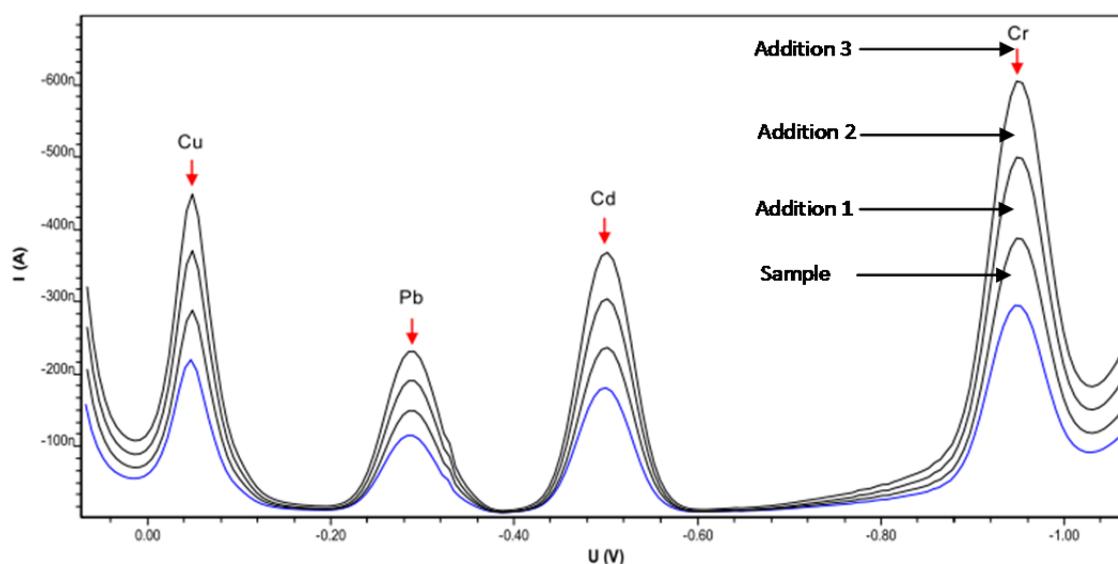
Fig. 8. Voltammogram of Cu, Pb, Cd, and Cr inTap water sample in the presence of 0.2 mL of fluorexon 0.6 mM; 0.2 mL KCl 0.1 M; deposition potential of -700 mV; deposition time 70 s; pH 6

Table 4. Comparison of detection limits (LOD) determination of Cd, Cu, Pb and Zn results previous research with the results of the research found

Method	LOD (µg/L)				Ref.
	Cd	Cu	Pb	Zn	
AdSV (clioquinol)	0.06	-	0.10	0.06	[26]
AdCSV (multivariate analysis)	0.28	0.051	0.026	-	[39]
AdSV (multivariate analysis)	0.036	0.02	0,61	0.47	[22]
DPASV (microwave digestion)	1.0	2.0	0.5	0.5	[40]
DP-AdCSV (alizarin)	0.005	-	0.008	0.001	[24]
AdSV (calcon)	7.12	5.37	1.02	3.21	[20]
AdSV (calcein)	6.37	1.28	0.42	1.24	[30]
AdSV	0.59	1.79	1.2	-	This work

4. CONCLUSION

The optimum conditions of the AdSV- fluorexon method are KCl concentration 1 mol/L, pH 6, fluorexon concentration 0.6 mmol/L, potential accumulation -0.7 V, time accumulation 70s. The RSD were (0.46; 0.11; 2.39, and 0.90)%, recovery were (99.11; 99.88; 98.12, and 98.76)%, the linear calibration graph were (10.0-100.0) µg/L, the LOD were (0.590; 1.794; 1.235, and 1.595) µg/L for Cd, Cu, Cr, and Pb. This procedure was successfully applied for the simultaneous determination of Cd, Cu, Cr, and Pb in samples: water (seawater tap water, lake water, and river water), by standard addition method with satisfying.

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