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Adsorptive Stripping Voltammetry for Determination of Cadmium in the presence of Cupferron on a Nafion-coated Bismuth Film Electrode

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The method for reliable determination of Cd(II) by square wave adsorptive cathodic stripping voltammetry was done. The technique involves an interfacial adsorption of Cd(II) as Cd-cupferron complex on a Nafion-coated bismuth film electrode and subsequent stripping from the electrode by square wave cathodic voltammetric and the reduction of Cd-cupferron complex. The optimum conditions of direct reduction of Cd(II) ions was observed by 0.1 M acetate buffer electrolyte (pH 4.0) containing with 0.04 mM cupferron and 0.4 mg L^{-1} Bi(III) of an accumulation potential at -300 mV versus Ag/AgCl and accumulation time 60 seconds. Under these optimum conditions, the linear concentration and detection limit (3σ) were found in the range of 3.0 to 40.0 μg L^{-1} and 0.38 μg L^{-1}, respectively. The relative standard deviation was 2.4% at the 5 μg L^{-1} (n=10). The procedure has been applied to the determination of Cd(II) in marine algae samples with satisfactory results.

Keywords: Nafion-coated bismuth film electrode; Cupferron; Cadmium; Adsorptive stripping voltammetry

1. INTRODUCTION

Cadmium is known to be hazardous environmental pollutant with toxic effects for the living organisms in aquatic ecosystems [1]. Adverse effects of cadmium are produced not only because of its high toxicity even at trace concentrations, but also due to bioaccumulation processes along the food chain [2]. The concentration of cadmium in food is usually found at the trace level and the matrix effect has interference to the analysis. Most of the sensitive and selective methods recently available such as ICP-MS, ICP-AES and GF-AAS are too expensive and are not practically applied in a developing country, i.e.Thailand [3]. Therefore, the analysis is often limited to laboratory level. Since reliable, low cost, quick and of course ultra sensitive analytical technique is a need of day. However, such requirements are greatly met with electrochemical methods.

Adsorptive cathodic striping voltammetry (AdCSV) techniques is one of the favorable method for trace analysis, because of low instrumentation, good selectivity, high sensitivity and good performance with different matrices. The techniques is based upon adsorptive accumulation of the metal ion complex with a suitable ligand at the electrode scanning in the negative direction. Several organic compounds such as oxine [4], xylenol orange [2,5], calcein blue [6], 2-mercaptobenzothiazole [7], 2-mercapto-5-phenil-amino-1,3,4-thiadia-zole [8], 2-acethylpyridine salicyloylhydrazone [9], ammonium-2-amino-cyclopente dithiocarboxylate [10], catechols [11], thymolphthalexone [12], luminol [13] and cupferron [14,15] have been used as complexing agents for the voltammetric determination of cadmium. The working electrodes all voltammetric methods apply mercury electrodes. The advantages of mercury based electrodes are numerous; easily prepared, sensitive and reproducible with fast and simple electrode kinetics. However, because of the toxicity of mercury, it is important to develop environmental friendly electrodes for stripping voltammetric determination of cadmium. Bismuth film electrodes (BiFE) have been successfully used in anodic stripping voltammetric analysis (ASV) [16,17] and adsorptive cathodic stripping voltammetry (AdCSV) [18-21]. Bismuth films can be deposited on different substrates such as, glassy carbon [16,22], carbon paste [23], carbon fiber [24,25], boron-doped diamond [26] and pencil-lead [27,28], showing excellent advantages with respect to mercury films. However, various surfactants in real samples can be adsorbed on the surface of BiFEs, which will result in serious interference and bad analytical performance [29]. The problem can usually be solved by using a protective Nafion layer [27, 30-34].

To our knowledge, the determination of cadmium using cupferron as complexing and adsorbing on a Nafion-coated bismuth film electrode has not been reported before. In this work a sensitive square wave adsorptive cathodic stripping voltammetric method is developed for the determination of cadmium in marine algae samples. The procedure is based on the reduction of the complex of the cadmium ion with cupferron after accumulation at the surface of a Nafion-coated bismuth film electrode plate *in situ*.

2. EXPERIMENTAL PART

2.1 Reagents

All solutions were prepared by using deionized water. The standard solutions of Cd(II) was prepared from 1000 μg/mL standard solution (HPS, USA) by diluting with deionize water. A 0.1 mol L^{-1} of cupferron (Aldrin, Germany) was prepared by dissolving the appropriate amount of the solid compound in deionized water. Nafion, 5% w/v solution in a mixture of lower aliphatic alcohols and water, was purchased from Aldrich (Aldrin, Germany). An acetate buffer solutions (pH 3.6-5.6) were prepared by mixing different amounts of CH_3COOH (Merck, Germany) 1.0 M, and CH_3COONa (Merck, Germany) 1.0 M in a 100.0 ml volumetric flask. A stock Hg(II) solution was prepared from $HgCl_2$ (Merck, Germany) dissolved in 0.1 M HCl. Desired standard solutions of Cu(II), Pb(II), Bi(III), Zn(II) (HPS, USA), Ca(II), Mg(II) and Fe(III) (Merck, Germany) were prepared by accurate dilution of their standard stock solutions (each, 1,000 μg/mL) by deionized water. A 10% $NH_4H_2PO_4$ matrix modifier (Perkin-Elmer, USA) and nitric acid concentrated 65% HNO_3 (Merck, Germany).

2.2 Instruments

Square wave voltammetric measurements were performed with PalmSens instrument connected to PC (PalmSens BV, The Netherlands), using a miniaturized cell with three electrodes. A three electrodes system, including a glassy carbon electrode (2 millimeter diameter) served as a working electrode for study electrochemical behavior (Metrohm, Switzerland), a double junction Ag/AgCl (3 M KCl) (Metrohm, Switzerland) and a platinum wire (Metrohm, Switzerland) were employed as reference and auxiliary electrodes, respectively. An AAnalyst™ 800 Atomic Absorption Spectrometer (Perkin-Elmer, USA) with longitudinal Zeeman background correction was used for the GFAAS measurements of cadmium in the digested samples. An Anton Paar Microwave Oven (Perkin-Elmer, USA) was used for the microwave-assisted digestion. The pH value was measured using Metrohm pH meter model 827 pH lab (Metrohm, Switzerland). All glassware and storage bottles were soaked overnight in 10% (v/v) HNO_3, followed by thorough rinsing with deionized water before using.

2.3 Sample preparation and digestion

All the marine algae samples were washed with deionized water to remove salts, and oven dried at 55±5 ^oC for 24 h. A 0.2 g of each dehydrated marine algae samples were accurately weighed and transferred into Teflon high pressure microwave digestion vessel. A 5.0 mL of 65% nitric acid was added into each vessel, then digestion with microwave system, the heating program was: 1 min at 250 W, 2 min at 0 W, 5 min at 250 W, 5 min at 400 W, 5 min at 600 W. After the digestion completed, the solution was transferred to a volumetric flask and diluted to 25.0 mL with deionized water.

2.4 Preparation of the Nafion-coated electrode

Prior to Nafion coating, the glassy carbon electrode was polished with a 0.05 μm alumina in aqueous slurry, rinsed with ethanol and deionized water. The Nafion coating was made by applying 5 μL of a solution of 1.5% Nafion in ethanol place on the surface of the glassy carbon electrode with a micropipette and solvents was then allowed to evaporate at room temperature for 10 min. Then the Nafion membrane was treated with a jet of warm air about 1 min and left to cool at room temperature. This heat treatment has been shown to improve the stability of the Nafion membrane [35]. The bismuth film was then deposited on the Nafion-coated glassy carbon electrode according to an *in situ* procedure.

2.5 Analytical procedure

The three electrodes was immersed in an electrochemical cell containing the 0.1 M acetate buffer (pH 4.0), 0.04 mM cupferron and 0.4 mg L^{-1} Bi(III). An initial accumulation potential (-0.3 V vs. Ag/AgCl) was applied to the Nafion-coated glassy carbon electrode for 60 s and then the cathodic stripping voltammogram were recorded from -0.6 V to -1.1 V in square wave mode, for which the scan rate is 5 mV s^{-1}, the pulse amplitude is 100 mV and modulation frequency is 25 Hz each scan was repeated five times. Prior to the next cycle, a 30 s conditioning step at +0.3 V was used to remove the target metals and bismuth [32]. The cadmium concentrations in the samples were determined by the standard addition method. All measurements were carried out at room temperature and it was not deaeration of the electrolyte solutions. The results will be compared with ones of graphite furnace atomic absorption spectrometry (GFAAS) at a wavelength of 228.8 nm.

3. RESULTS AND DISCUSSION

Preliminary experiments were carried out to identify the general features which characterize the behavior of Cd(II)-cupferron systems on a Nafion-coated bismuth film electrode. Figure 1 illustrates the influence of cupferron on the cathodic stripping behavior of cadmium on the Nafion-coated bismuth film electrode (NCBiFE) in acetate buffer, following an initial accumulation for 60 s. No peak response was obtained for the blank solution (Fig. 1(a)), as well as when cupferron alone was added to the blank solution (Fig. 1(b)).

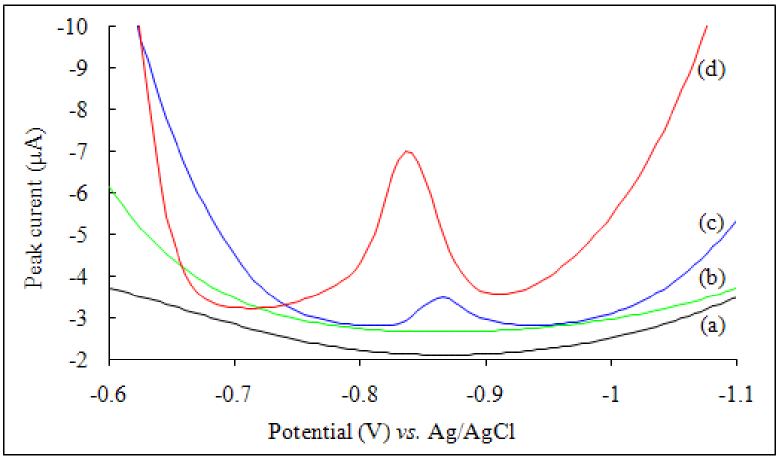

Figure 1. Cathodic stripping voltammograms demonstrating the influence of cupferron on the reduction of Cd(II) on the NCBiFE. (a) blank solution consisting of 0.1 mol L^{-1} acetate buffer (pH 4.0), 0.4 mg L^{-1} BI(III); (b) solution (a) with 0.04 mM cupferron; (c) solution (a) with 25 μg L^{-1} Cd(II); (d) solution (a) with 25 μg L^{-1} Cd(II) and 0.04 mM cupferron. Conditions: E_{acc} -0.3 V; t_{acc} 60 s; E_{pulse} 100 mV; E_{step} 5 mV; frequency 25 Hz.

However, when cadmium alone was added to the blank (Fig. 1(c)), a small peak due to the reduction of Cd(II) at -0.821 V was obtained. The addition of small amount of cupferron to the cadmium solution resulted in a considerable enhancement of the cathodic peak (Fig. 1(d)), a high well-defined peak. The enhancement of the cathodic peak by cupferron clearly indicates that the accumulation of cadmium as the Cd-cupferron complex onto the electrode surface is involved. Compared with NCBiFE, the electrochemical signal on NCBiFE in the presence of cupferron was improved about two times and the Cd(II) peak was shift to more positive value about 30 mV. This phenomenon can be concluded that the Cd-cupferron complex was adsorbed on the surface of electrode.

3.1 Effect of supporting electrolyte and pH

In difference type of buffer were investigated as supporting electrolyte such as acetate, phosphate and borate. It was found that the acetate buffer gave the sharper peak and much enhanced peak currents. The influence of pH value of the used buffer solution on the cathodic stripping peak current of Cd(II) was also investigated in the range of 3.6 to 4.4 (Fig. 2). It was found that at pH 4.0 the peak current of cadmium was at maximum value, the reduction of peak current were decreasing both at lower and higher pH values due to the protonation of coordination sited of the ligand and the hydrolysis of the Cd(II), respectively [15]. Thus, pH 4.0 of acetate buffer solution was used for further experiments.

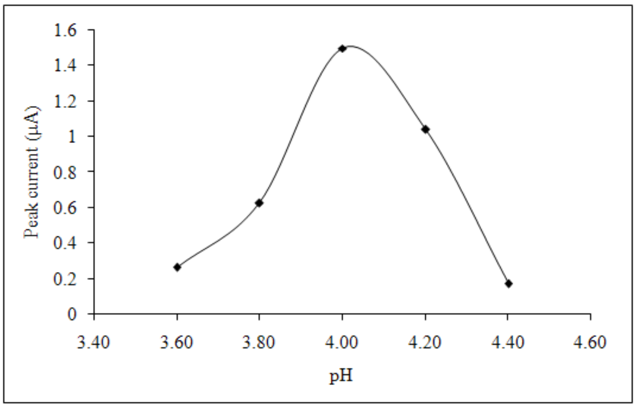

Figure 2. Effect of pH on the peak current of 50 µg L^{-1} Cd(II). Conditions: 0.5 mg L^{-1} Bi(III); 0.02 mM cupferron; E_{acc} -0.4 V; t_{acc} 60 s; E_{pulse} 80 mV; E_{step} 5 mV s^{-1}; frequency 25 Hz.

3.2 Effect of Nafion concentration

The effect of Nafion concentration on the sensitivity of cadmium analysis procedure was investigated in a range from 0.5 to 2% (Fig. 3). The experimental results were shown that the cathodic stripping peak current of Cd-cupferron increasing Nafion concentration increased from 0.5 to 1.5%(w/v). Indeed, at very thin or very thick polymer films, the stripped species were able to diffuse away from electrode due to incomplete coating or cracks, respectively [36]. Thus, a Nafion concentration of 1.5% was selected as the optimum condition in the further experiments.

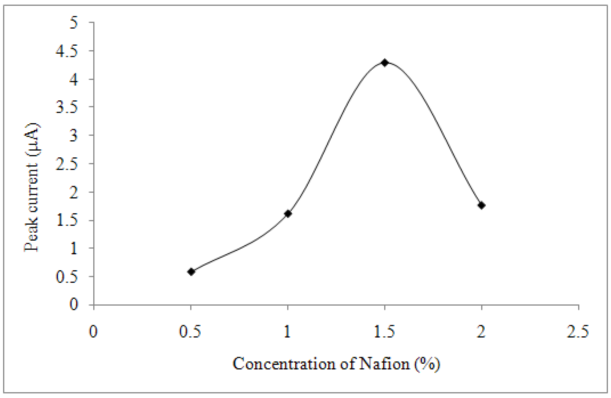

Figure 3. Effect of Nafion concentration on the peak current of 50 μg L^{-1} Cd(II). Conditions: 50 μg L^{-1} Cd(II); 0.1 M acetate buffer pH 4.0; other conditions similar as Fig. 2.

3.3 Effect of cupferron concentration

The influence of increasing concentration of cupferron on the cathodic stripping peak heights of cadmium at pH 4.0 in 0.1 M acetate buffer at a accumulation potential -0.4 V for 60 s on a NCBiFE was investigated in the range of 0.0 to 0.3 mM and is shown in Figure. 4(A). At lower cupferron concentrations, the cadmium peak height increased with increasing ligand concentration and reached the maximum value for cupferron concentrations in the range 0.0 to 0.1 mM. The presence of higher cupferron concentration level over 0.1mM (0.1 mM to 0.3 mM) caused leveling off of the cathodic stripping peak height. At cupferron concentrations higher than 0.04 mM, the peak current of cadmium increased more considerably, but the peak current of acetate buffer decreased and peak position of acetate at -0.486 V became shift to more cathodic potential (Fig 4(B)). This phenomenon was possibly due to ligand competition by the acetate on the electrode surface. Under the experimental conditions, the optimum concentration of cupferron resulting in the best sensitivity for the cadmium peak at 0.04 mM was used for all following works.

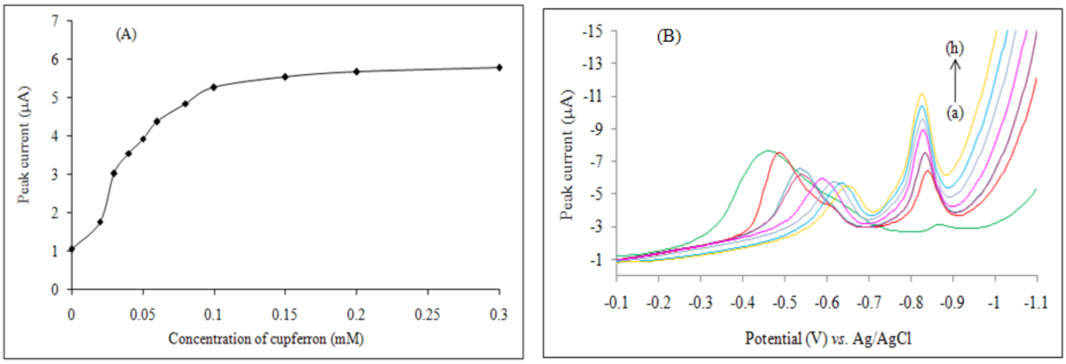

Figure 4. Effect of cupferron concentration on the peak current of 50 μg L^{-1} Cd(II) in 0.1 M acetate buffer pH 4.0, (A) 0-0.3 mM cupferron, (B) various concentration cupferron; (a)-(h) 0, 0.04, 0.06, 0.08, 0.1, 0.15, 0.2 and 0.3 mM, respectively. Other conditions similar as Fig. 2.

3.4 Effect of accumulation potential

The effect of varying accumulation potential on the cathodic stripping peak current of cadmium was studied in the range from -0.1 to -0.8 V at a accumulation time of 60 s, and the results were shown in Figure 5. It was found that the peak current was rather high with changing potentials from -0.1 to -0.3 V, probably due to the increased accumulation of the complex on the electrode surface [37]. The peak current slightly decreased at potentials more negative than -0.3 V. An accumulation potential of -0.3 V gave the base sensitivity and was used for further determinations.

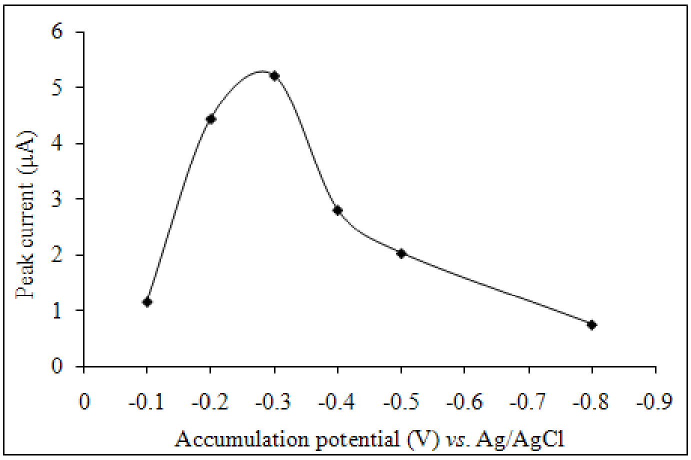

Figure 5. Effect of accumulation potential on the peak current of 50 μgL^{-1} Cd(II). Conditions: 0.1 M acetate buffer (pH 4.0); 0.4 mg L^{-1} BI(III); 0.04 mM cupferron; t_{acc} 60 s; E_{pulse} 80 mV; E_{step} 5 mV; frequency 25 Hz.

3.5 Effect of accumulation time

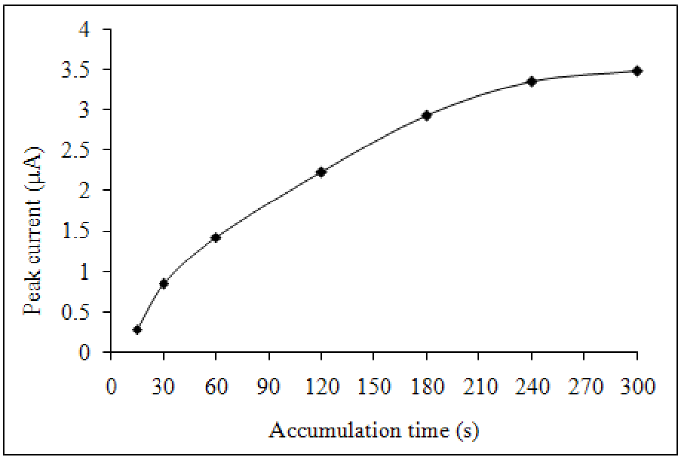

Figure 6. Effect of accumulation time on the peak current of 50 μgL^{-1} Cd(II). Other conditions as in Fig. 5.

The effect of the accumulation time on the stripping peak currents of Cd(II) was studied in the range from 15 to 300 s as illustrate in Figure 6. The peak current increased nearly with increasing accumulation time until the saturation surface concentration is gradually reached. As is expected for adsorption processes, the dependence of the peak current on the accumulation time is limited by the saturation of the electrode [38] and the thickness of the bismuth film also increased [30]. Thus, accumulation time of 60 s was used throughout the remaining experiments, as it gave good sensitivity and relatively short analysis time.

3.6 Effect of square wave parameters

In order to obtain well-defined square wave adsorptive cathodic stripping voltammetry (SWAdCSV) response to the signal of Cd(II) in the presence of 0.04 mM cupferron, 0.1 M acetate buffer pH 4.0, following accumulation on the Nafion-caoted bismuth film electrode (NCBiFE) at -0.3 V for 60 s, the square wave parameters investigated were the step potential, the square wave amplitude and the frequency. The reduction of peak current increased of all the increased parameters. However, when the frequency was higher than 30 Hz, the peak of Cd-cupferron complex did not shaped. The increasing of the potential step did not enhance significantly the peak height of Cd(II) despite of the dramatic increasing in the effective scan rate, as similar as in according with earlier report [39]. The best conditions for quantitative measurement of cadmium concentration were then selected at 25 Hz frequency, 5 mV s^{-1} potential step with 100 mV square wave amplitude.

3.7 Analytical figure of merit

3.7.1 Analytical performance

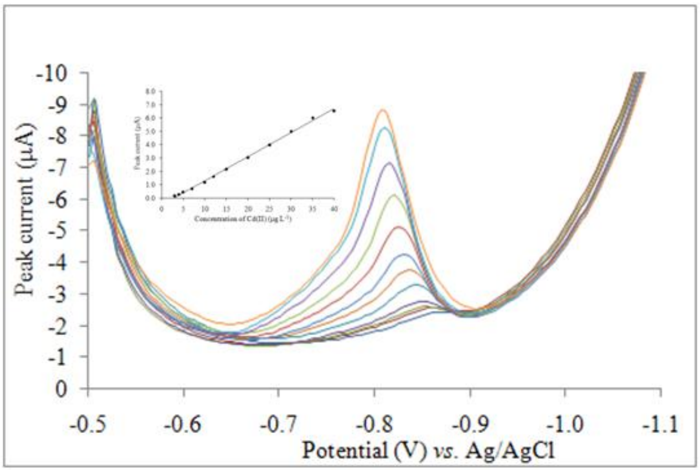

Figure 7. Adsorptive stripping voltamograms and calibration curve for increasing concentration of Cd(II) with NCBiFE. Conditions similar as Fig. 1.

Under the optimum conditions and after 60 s accumulation time, the linear relationship between the cathodic peak current of Cd-cupferron complex and concentration of cadmium ion, the linear concentration range was 3.0 to 40.0 µg L^{-1} (Fig. 7). The limit of detection (LOD) estimated according to Grabarczyk and Koper [40] as three time the standard deviation for low Cd(II) concentration, and it was found to be 0.38 μg L^{-1} for 60 s at a accumulation time. The detection limit of the present sensor was lower than those obtained with Nafion modified bismuth film electrodes [39, 41-42]. The reproducibility of method was checked by successive measurements (n = 10) of 5 μg L^{-1} Cd(II) after 60 s accumulation time, the relative standard deviation (RSD) was 2.4%.

3.7.2 Interference studies

The possible interferences by other metals with the cathodic adsorptive stripping voltammetric determination of cadmium was studied by addition of the interfering ion to a solution containing 25 μg L^{-1} of Cd(II) of these metals using the optimum experiment. (the criterion for interference was a ±5% error in the peak current of Cd). Tolerance levels of foreign ions in the determination of Cd(II) were 50 μg L^{-1} of Cu(II); 20 μg L^{-1} of Pb(II); 10 μg L^{-1} of Zn(II) and 5 μg L^{-1} of Cd(II), Mg(II), Hg(II), Fe(III).

3.8 Analysis of marine algae samples

The developed method was applied to determination of cadmium in marine algae. In this work, the method of standard addition was selected for quantification of cadmium under the optimized, in order to eliminate the matrix effect. The contents of cadmium calculated in marine algae were 0.223±0.21 to 0.388±0.54 μg g^{-1} (SWAdCSV) and 0.169 to 0.472 μg g^{-1} (GFAAS). The analytical results for cadmium obtained by the proposed method were in good agreement with those obtained by graphite furnace atomic absorption spectrometry.

4. CONCLUSIONS

The present study demonstrates that the adsorptive stripping analysis of cadmium ion in the presence of cupferron on a Nafion-coated bismuth film electrode plate *in situ* is an excellent method, the method is high sensitivity, fast and simple operate for the determination of Cd(II) in marine algae sample at μg L^{-1} concentration levels. The Nafion-coated bismuth film electrode can serve as disposable, environmentally friendly sensors for a trace metal analysis by AdCSV.

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References

1. T. R. Crompton, *Toxicants in the Aqueous Ecosystem*, Wiley, Chinchester (1997).
2. A. A. Ensafi, T. Khayamian, A. Benvidi and E. Mirmomtaz, *Anal. Chim. Acta*, 561 (2006) 225.

3. J. Jakmunee, S. Suteerapataranon, Y. Vaneesorn and K. Grudpan, *Anal. Sci*, 17 (2001) i399.
4. A. M. Beltagi and M. M. Ghoneim. *J Appl Electrochem*, 39 (2009) 627.
5. A. A. Ensafi, A. Benvidi and T. Khayamian, *Anal. Lett.*, 37 (2004) 449.
6. K. Yokoi, M. Mizumachi and T. Koide, *Anal. Sci.*, 11 (1995) 257.
7. S. Abbasi, K. Khodarahmiyan and F. Abbasi, *Food Chemistry*, 128 (2011) 254.
8. P. Suciu, M. Vega and L. Roman, *J. Pharm. Biomed. Anal.*, 23 (2000) 99.
9. J. A. Jurado-González, M. D. Galindo-Riaño and M. Garcıa-Vargas, *Anal. Chim. Acta*, 487 (2003) 229.
10. A. A. Ensafi and K. Zarei, *Talanta*, 52 (2000) 435.
11. J. Limson and T. Nyokong, *Anal. Chim. Acta*, 344 (1997) 87.
12. A. Babaei, M. Babazadeh and E. Shams, *Electroanalysis*, 19 (2007) 978.
13. S. Abbasi, A. Bahiraei and F. Abbasai, *Food Chemistry*, 129 (2011) 1274.
14. M. Grabarczyk and A. Koper, *Electroanalysis*, 24 (2012) 33.
15. S. Abbasi, A. Farmany and S. S. Mortazavi, *Electroanalysis*, 22 (2010) 2884.
16. J. Wang, J. Lu, S. B. Hocevar, P. A. M. Farias and B. Ogorevc, *Anal. Chem*, 72 (2000) 3218.
17. G. Kefala, A. Economou and M. Sofoniou, *Talanta*, 68 (2006) 1013.
18. J. Wang and J. M. Lu, *Electrochem. Commun*, 2 (2000) 390.
19. A. Krolicka, A. Bobrowski, K. Kalcher, J. Mocak, I. Svancara and K. Vytras, *Electroanalysis*, 15 (2003) 1859.
20. M. Morfobos, A. Economou and A. Voulgaropoulos, *Anal. Chim. Acta*, 519 (2004) 57.
21. E.A. Hutton, J.T. van Elteren, B. Ogorevc and M. R. Smyth, *Talanta*, 63 (2004) 849.
22. G. Kefala, A. Economou, A. Voulgaropoulos and M. Sofoniou, *Talanta*, 61 (2003) 603.
23. G-U. Flechsig, M. Kienbaum and P. GrYndler, *Electrochem. Commun*, 7 (2005) 1091.
24. E. A. Hutton, S. B. Hocevar and B. Ogorevc, *Anal. Chim. Acta*, 537 (2005) 285.
25. S. B. Hocevar, B. Ogorevc , J. Wang and B. Pihlar, *Electroanalysis*, 14 (2002) 1707.
26. C. E. Banks, J. Kruusma, R. R. Moore, P. Tomcık, J. Peters, J. Davis, S. Komorsky-Lovric and R. G. Compton, *Talanta*, 65 (2005) 423.
27. D. Demetriades, A. Economou and A. Voulgaropoulos, *Anal. Chim. Acta*, 519 (2005) 167.
28. V. Rehacek, I. Hotovy, M. Vojs and F. Mika, *Microsyst Technol.*, 14 (2008) 491.
29. A. Economou and P. R. Fielden, *Analyst*, 128 (2003) 205.
30. G. Kefala, A. Economou and A. Voulgaropoulos, *Analyst*, 129 (2004) 1082.
31. C. Gouveia-Caridade, R. Pauliukaite and C. M. A. Brett, *Electroanalysis*, 18 (2006) 854.
32. H. Xu, L. Zeng, D. Huang, Y. Xian and L. Jin, *Food Chem*, 109 (2008) 834.
33. G. Kefala and A. Economou, *Anal. Chim. Acta.*, 576 (2006) 283.
34. D. Li, J. Jia and J. Wang, *Microchim Acta*, 169 (2010) 221.
35. B. Hoyer and N. Jensen, *Talanta*, 41 (1994) 449.
36. B. Hoyer, T. M. Florence and G. E. Batley, *Anal. Chem.*, 59 (1987) 1608.
37. A. Safavi and E. Shams, *Anal. Chim. Acta.*, 385 (1999) 265.
38. M. B. Gholivand and A. A. Romiani, *Anal. Chim. Acta.*, 571 (2006) 99.
39. H. Li, J. Li, Z. Yang, Q. Xu, C. Hou, J. Peng and X. Hu, *J. Hazard. Mater.*,191 (2011) 26.
40. M. Grabarczyk and A. Koper, *Electroanalysis*, 22 (2010) 1.
41. Y. Wang, Z. Liu, G. Yao, P. Zhu, X. Hu, Q. Xu and C. Yang, *Talanta*, 80 (2010) 1959.
42. G. Kefala and A. Economou, *Anal. Chim. Acta*, 576 (2006) 283.