

Differential pulse anodic stripping voltammetry for the detection of Cd²⁺ and Pb²⁺ in sediment samples using BI/RGO modified glassy carbon electrode

¹S. Meenakshi, ²M. Merlin, K.Pandian*

¹*Department of Inorganic Chemistry, University of Madras, Guindy Campus, Chennai-600025

²Department of Chemistry, Jeppiaar Engineering College, Chennai-600119.

Corresponding Author: E.Mail: drmerchem@gmail.com

ABSTRACT

We have demonstrated an anodic stripping pulse voltammetry method for simultaneous detection of Cd²⁺ and Pb²⁺ present in sediment samples using bismuth deposited graphene film electrode. The surface modification was accomplished by electrochemical deposition of Bi/rGO by potential scanning between the predetermined potential ranges from 0 to -2.0 V vs Ag/AgCl_{sat}. The calibration plots were constructed by peak current values against concentration of Cd²⁺ and Pb²⁺. The detection limit was found to be 0.025 nM and 0.012 nM for Cd²⁺ and Pb²⁺, respectively.

Key words: Differential pulse stripping voltammetry, graphene oxide, cadmium, lead and sediment samples.

INTRODUCTION

Heavy metals are toxic and hazardous pollutants in environment due to their non-biodegradability and persistence, which can cause serious threat to living organisms. For example, the accumulation of Pb or Cd ion in human body exhibits severe deleterious effects on neurobehavioral development in kids, increases blood pressure, and causes kidney injury and anemia. The development of a sufficiently simple, sensitive, selective and reproducible analytical method for their determination at trace levels is necessary. Many conventional methods such as atomic absorption spectrometry, atomic fluorescence spectrometry and inductively coupled plasma mass spectroscopy were utilized for determination of heavy metals. However, these methods have some limitations like tedious sample preparation procedure, high cost and serious interference effect. Electrochemical stripping voltammetry has been widely used as a powerful technique for determination of trace metal ions attributable to its distinctive ability to pre-concentrate target metal ions throughout the accumulation step and a lower detection limit. Various graphite electrodes were used for anodic stripping voltammetry (ASV) to measure concentration of trace elements. The attractive stripping behavior of bismuth modified electrodes is recent interest as the ability of bismuth to form a 'fusible' alloy with trace heavy metals during pre-concentration step. However, it has been shown that within the presence of Pb ion, peak currents of Cd ion decreased by half, as compared to individual Cd ion analysis. Since the environmental sample contains several metal species sensitivity detection is a concern, bismuth deposited graphene modified electrode is selected.

In this study, bismuth deposited graphene oxide (Bi/rGO) based electrode was fabricated for simultaneous determination of Pb²⁺ and Cd²⁺ by differential pulse stripping voltammetry from predeposited bismuth modified graphene electrochemically. An enhanced sensitivity and lower detection limit can be achieved by this method.

MATERIALS AND METHODS

Chemicals: All chemicals were received from commercial sources. Deionized water was used for the preparation of all electrolytes and stock solutions. All the experiments were performed at nitrogen atmosphere.

Instrumental method: Voltammetric measurements were carried out with a Gamry model 330 Electrochemical Analyzer USA. A three electrode system was completed by a bismuth deposited graphene modified GCE as a working electrode, platinum wire as an auxiliary electrode and Ag/AgCl electrode as a reference electrode. All solutions were deoxygenated with high-purity nitrogen for 5 min prior to each experiment and kept under nitrogen atmosphere during the measurements.

Electrode Modification procedure: The electrodeposition of bismuth onto the graphene oxide was accomplished by using a cyclic voltammetry method. Briefly, graphene oxide was electrodeposited by potential range at 0 to -2.0 V vs. Ag/AgCl for 10 cycles in 0.1 M sodium nitrate and 0.1 M acetic acid (pH 4.5) as a supporting electrolyte containing 500 µg/l bismuth nitrate and graphene oxide (100 mg/ml) under nitrogen gas atmosphere. The modified electrode subsequently characterized by using cyclic voltammetry (CV) and differential pulse stripping voltammetry (DPSV).

Sample preparation procedure: 100 mg of finely powdered core samples was taken in a Teflon beaker. Initially 3 ml of conc. HF and then 1 ml conc. HNO₃ was added. The sample was digested by placing on a hot plate at 100°C. Finally the wet samples were dispersed in 1M HNO₃ and then made up to 100 ml.

RESULTS AND DISCUSSION

Electrochemical deposition of Bi deposited rGO/GCE: A variety of modified electrode systems have been reported on simultaneous electrochemical detection of Cd^{2+} and Pb^{2+} present in water and sediment samples. Here, we demonstrate to use bismuth deposited reduced graphene oxide modified GCE for simultaneous determination of both Cd^{2+} and Pb^{2+} in sediment samples. The electrochemical performance has been evaluated for the determination of Cd^{2+} and Pb^{2+} in mg L^{-1} concentration ranges using cyclic voltammetry and DPSV methods. Figure 1 shows the cyclic voltammogram of Bi/rGO/GCE in the presence of 0.1 M acetate buffer solution (pH 4.5) at a scan rate 50 mV/s.

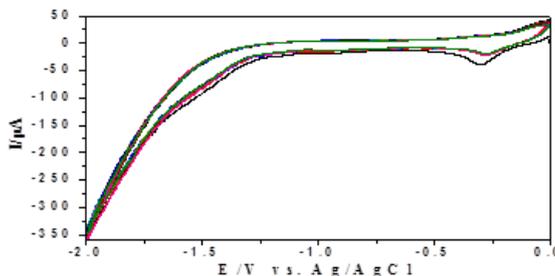


Fig. 1. Cyclic voltammogram of bismuth deposited graphene oxide modified GCE in 0.1 M acetate buffer (pH 4.5) at a scan 50 mV/s

To deposit GO on GCE, the potential scanning between 0 to -2.0 V vs Ag/AgCl in presence of 100 mg/ml GO. For the simultaneous deposition of Bi deposited rGO, the same potential range was used in presence of 100 mg/ml of GO and 1mM $\text{Bi}(\text{NO}_3)_3$ in acetate buffer medium (pH 4.5). A small peak at 0.2 is due to the reduction of bismuth on graphene oxide surface. The decrease of peak current values was noted in the subsequent cycles. The decreasing of peak current is due to the deposition of graphene oxide on GCE.

Simultaneous determination of Pb (II) and Cd (II): Figure 2A shows DPSV of Cd^{2+} and Pb^{2+} in 0.1M acetate buffer (pH 4.5) as the supporting electrolyte medium using Bi/rGO modified glassy carbon electrode.

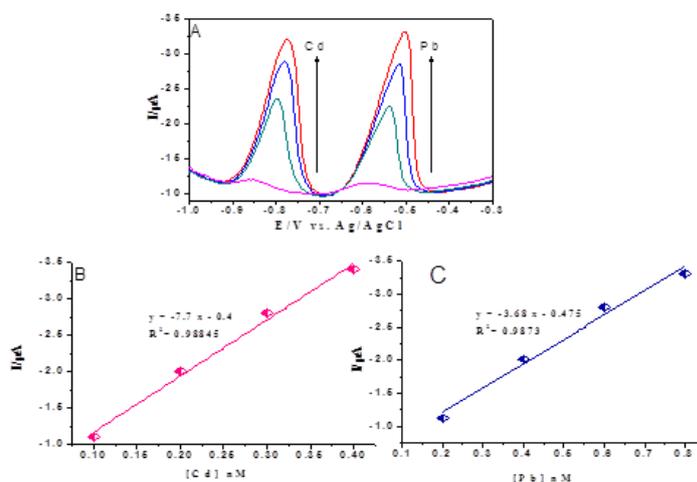


Fig. 2.A) Differential pulse stripping voltammogram for different concentrations of Cd^{2+} and Pb^{2+} at the rGO/Bi/GCE in 0.1 M acetate buffer (pH 4.5). at a scan of 50 mV/s. B) Linear plot of peak current vs. concentration. (B) and (C) the corresponding calibration curves of Cd^{2+} and Pb^{2+} , respectively

Deposition potential was optimized at -1.1 V for 100s to pre-concentrate of both Pb^{2+} and Cd^{2+} present in the buffer solution under constant stirring to enrich the deposition of metal ions at the electrode surface. After a short equilibration time, the deposited ions were quantified by performing anodic stripping pulse voltammetry experiment in the same reaction medium. The same experiment was repeated many times using different concentration of the added Cd and Pb ions. For the each addition of Cd and Pb ions, a freshly prepared Bi/rGO/GCE was used. The resulting peak current values were recorded and quantified separately Cd and Pb ions. A linear calibration graph was obtained for both Cd and Pb ions concentration against peak current values. The corresponding calibration plots are shown in Fig. 2B and 2C.

Figure 2 depicts the stripping response of Bi/rGO/GCE without any interference while simultaneously increasing concentrations of both metal ions from 0.01 mM to 0.1 mM. Results show that the stripping peak current increased linearly with concentration in the ranging from 0.1×10^{-7} M to 4×10^{-7} M. In the case of Cd^{2+} (Fig. 2B), the linear regression equation is $y = -7.7x - 0.47$ with the correlation coefficient of 0.98848 (R^2) and sensitivity of

0.025 nM. On the other hand Pb^{2+} (Fig. 2C), the linear regression equation is $y = -3.68x - 0.475$ with the correlation coefficient of 0.9873 (R^2) and sensitivity of 0.012 nM. Repetitive measurements of Cd^{2+} and Pb^{2+} with different concentrations (in the linear range) showed good reproducibility with the relative standard deviations less than 4.1% and 3.9%, respectively ($n = 10$). Lower detection limits for both target metal ions could be expected by prolonging the detection time.

Selective detection of Pb^{2+} in presence of Cd^{2+} : For the selective detection of individual Cd and Pb ions present in the samples, the standard addition method was carried out. In this method by keeping the concentration of Cd ion is constant and then subsequent addition of a known concentration of Pb ion (Fig. 3A). There is a linear graph is obtained over the concentration ranging from 1×10^{-8} to 7×10^{-7} M using RGO/Bi/GCE. The correlation coefficient of Pb (II) was found to be 0.99012 with a detection limit of 0.2 nM (Fig. 3B).

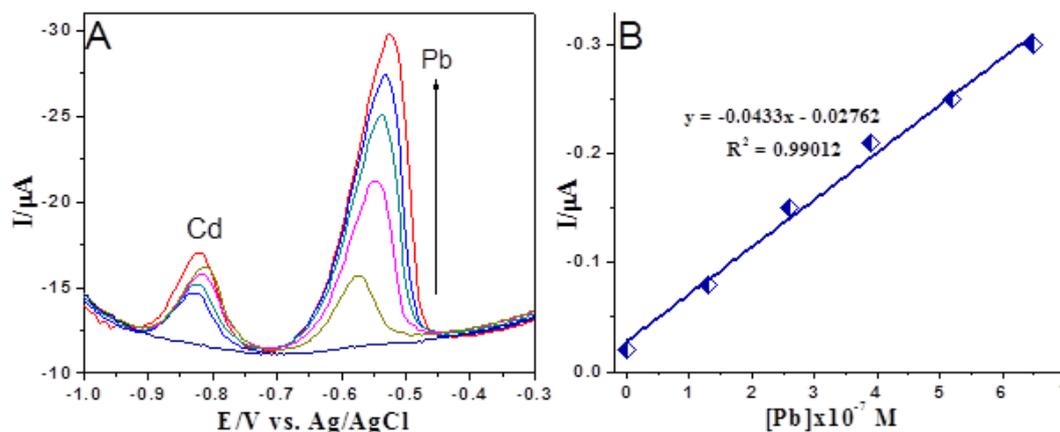


Fig. 3.A) DPSV of graphene oxide deposited bismuth nitrate modified GCE in different concentration of Pb^{2+} in 0.1 M acetate buffer (pH 4.5) at a scan of 50 mV/s. B) Linear plot of peak current vs. concentration

Selective Detection of Cd^{2+} in presence of Pb^{2+}

Figure 4A shows DPSV of Cd^{2+} and Pb^{2+} in 0.1 M acetate buffer at pH 4.5 as the supporting electrolyte medium using Bi/rGO/GCE. Deposition potential was optimized at -1.1 V for 100 s to pre-concentrate Cd^{2+} in presence of Pb^{2+} . The resulting calibration plots of Cd^{2+} is shown in Fig. 4B. The calibration plot exhibits a linear relationship over the concentration ranges from 0.1×10^{-7} M to 6.6×10^{-7} M using Bi/rGO/GCE. The correlation coefficient of Cd (II) was found to be 0.9975 and the calculated detection limit was 0.1 nM.

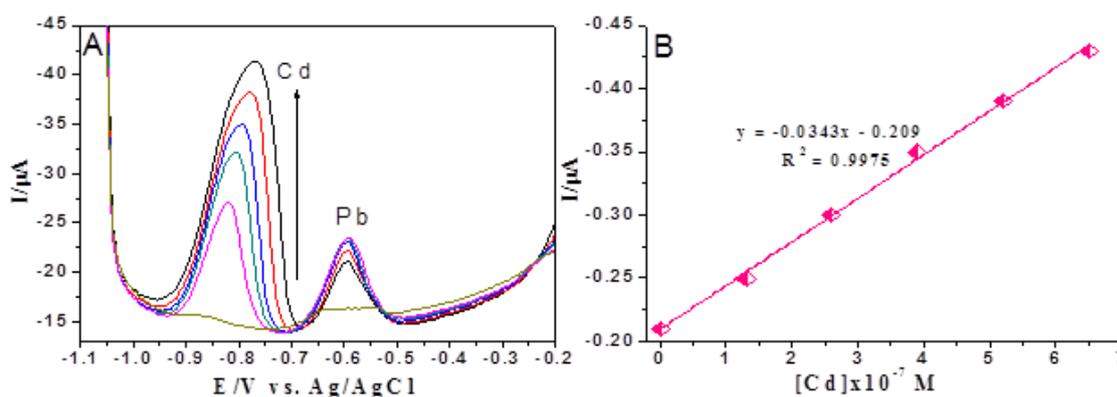


Fig.4. A) Differential pulse stripping voltammetry of graphene oxide deposited bismuth nitrate modified GCE in different concentration of Cd^{2+} in 0.1 M acetate buffer (pH 4.5) at a scan of 50 mV/s. B) Linear plot of peak current vs. concentration

CONCLUSION

Hence the present method can be exploited for the detection of both simultaneous and individual elemental concentration of metal pollutants like Cd^{2+} and Pb^{2+} present in sediment samples. Calibration plots for the simultaneous determination of Cd^{2+} and Pb^{2+} at the developed rGO/Bi/GCE were obtained by differential pulse stripping voltammetry under the optimal conditions described above. It can be seen that Bi/rGO/GCE possesses

improved or comparable performance for the simultaneous determination of Cd²⁺ and Pb²⁺, nevertheless the present modified electrodes system are inexpensive and easy to be fabricated.

ACKNOWLEDGEMENT: The authors are grateful to UGC-CPEPA programme, New Delhi for providing financial assistance to carry out a part of the work.

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