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APPENDICES

Appendix A

Table A1 Determination results of interference species in tap water and waste water samples.

Interference	Tap water ($\mu\text{g}\cdot\text{L}^{-1}$)	Waste water ($\mu\text{g}\cdot\text{L}^{-1}$)	Method
Chloride (I) ion	56,400	129,000	Argentometry
Nickel (II) ion	-	305	ICP-AES
Zinc (II) ion	21	156	ICP-AES

Appendix B

Anodic stripping analysis of cadmium (II) and lead (II) ions by bismuth–carbon nanotube modified electrodes

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Abstract: Synthesized by polyol process, bismuth–carbon nanotube (Bi–CNT) composites have been developed as working electrodes for the determination of cadmium (II) and lead (II) ions at ppb level by means of anodic stripping voltammetry. Physical and electrochemical characterization of Bi–CNT composites were confirmed by X-ray diffraction technique and cyclic voltammetry, respectively. Various factors (e.g., bismuth concentration, deposition time, and deposition potential) influencing the detection of both metals were thoroughly investigated. Furthermore, in comparison with *in situ* bismuth film modified onto CNT electrodes, the Bi–CNT modified electrodes can yield larger stripping signals for cadmium (II) and lead (II) ions. According to these results, we have tried to optimize several experimental parameters to improve the ability of the Bi–CNT modified electrodes towards the determination of the metal ions in real samples.

Introduction

Anodic stripping voltammetry has been applied to the determination of a wide variety of trace metals [1–3]. Mercury electrodes in film and drop forms have been traditionally used for metal detection with high sensitivity and reproducibility [4]. However, due to the extreme toxicity of mercury and its salts employed for the electrode preparation, intensive researches have been attempted to investigate mercury-free electrodes. In 2000, bismuth film electrode was initially proposed as an alternative to the mercury electrodes [5] since its toxicity is negligible. Furthermore, the bismuth film electrode displayed comparable performance to mercury electrodes for the electrochemical analysis. Recently, Hwang *et al.* [6] reported that, owing to high electrical conductivity, high surface area, and good chemical stability of carbon nanotubes (CNTs), the bismuth film modified CNT electrode exhibited superior performance in comparison with the bismuth film electrodes modified on activated carbon, graphite, and glassy carbon electrode (GCE). Since typical bismuth film electrodes require additional step for film preparation by using the solution of bismuth (III) ions, it is sometimes inconvenient to utilize bismuth film electrodes in real sample analysis. Hence, in this work, a new and easy-to-prepare type of bismuth electrode, bismuth–CNT (Bi–CNT) composite modified electrode has been selected for the determination of cadmium (II) and lead (II) ions by means of square wave anodic stripping voltammetry (SWASV). Bi–CNT composites were simply synthesized by polyol

process [7], which uses a poly alcohol as a solvent and a reducing agent to produce bismuth particles deposited onto CNTs from the mixture of bismuth (III) ion solution and CNTs.

Methodology

1. Composite Preparation

Bi–CNT composites were prepared via the following procedure. Calculated bismuth (III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) was added into ethylene glycol to form a solution, followed by the addition of CNTs. Then, the BiNO_3 –CNT mixture was sonicated and heated for several hours. When the mixture was cooled down, its pH was adjusted with acidic solution. After that, the mixture was refluxed to settle the Bi–CNT which was subsequently filtered, washed, and dried. Additionally, the prepared Bi–CNT was characterized by X-ray diffraction (XRD) method (Bruker D8 ADVANCE, Germany).

2. Electrode Preparation

GCE modified with Bi–CNT composite or CNTs was used as a working electrode and prepared by the following protocol. Desired amount of Bi–CNT composite or CNTs was sonicated in a solvent to form a slurry. Then, the slurry was placed onto the surface of GCE and the solvent was left to evaporate at room temperature for 10 min.

3. Voltammetric Measurement

Stripping voltammetric measurements were performed without deaerating an analyte solution. At the preconcentration step, Bi–CNT modified electrode was usually held at -1.10 V in a solution of cadmium (II) and lead (II) ions for 120 s. After that, the voltammetry in a square wave mode was recorded with an anodic scan from -1.10 to $+0.30$ V. At the end, the electrode was cleaned at $+0.30$ V for 30 s. Note that all potentials are quoted with silver/silver chloride reference electrode.

For comparison, the electrochemical performance of *in situ* bismuth film modified CNT electrode was also observed. In a solution containing bismuth (III), cadmium (II), and lead (II) ions, the CNT modified GCE was set at the potential of -1.10 V to allow the formation of bismuth film and its alloys (BiCd and

BiPb). Similar to the Bi-CNT modified electrode, square wave voltammogram was then obtained prior to electrode cleaning.

Results and Discussion

1. XRD Characterization of Bi-CNT Composite

Bi-CNT composite and CNTs were confirmed by XRD investigation as shown in Fig. 1a and 1b, respectively. The diffraction peaks at $2\theta = 24.5^\circ$ correspond to the plane (002) of graphite [8], indicating the presence of CNTs. While the other diffraction peaks in Fig. 1a represent the planes of bismuth. This result exhibited the successful deposition of bismuth onto CNTs.

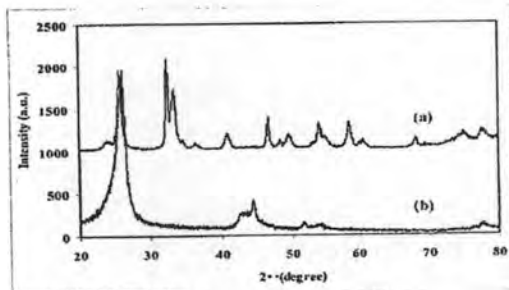


Figure 1 XRD patterns of (a) Bi-CNT composite and (b) CNTs.

2. Electrochemical Characterization of Bi-CNT Modified Electrode

Fig. 2 displays cyclic voltammogram of the GCE modified with Bi-CNT composite scanned in 0.1 M acetate buffer solution (pH 4.5) from +0.80 to -1.20 V and -1.20 to +0.80 V at the scan rate of 100 mVs^{-1} . The cathodic and anodic peaks of bismuth (III)-bismuth (0) redox couple [9] were observed with the

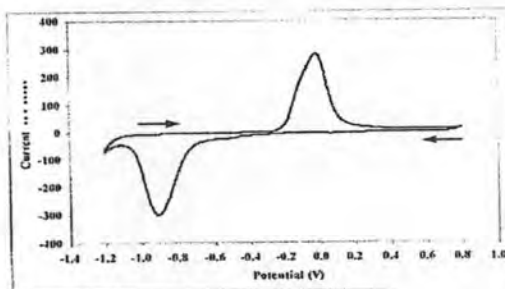


Figure 2 Cyclic voltammogram of 0.1 M acetate buffer solution (pH 4.5) recorded by the Bi-CNT modified GCE at the scan rate of 100 mVs^{-1} .

peak potentials of -0.89 and -0.08 V, respectively. This result not only confirmed that bismuth was successfully deposited on the surface of CNTs by our selected method, but revealed that the GCE modified with Bi-CNT could be fabricated.

3. Electrochemical Responses of In Situ Bismuth Film Modified CNT Electrode, CNT Electrode, and GCE towards Cadmium (II) and Lead (II) Ions

To understand the effect of bismuth film towards the determination of cadmium (II) and lead (II) ions by SWASV, the stripping voltammograms for $40 \mu\text{gL}^{-1}$ of these metal ions recorded with *in situ* bismuth film modified CNT electrode (Fig. 3a), CNT electrode (Fig. 3b), and bare GCE (Fig. 3c) were obtained. For the bismuth film modified electrode, the anodic peaks of cadmium (II), lead (II), and bismuth (III) ions appeared at the potentials of -0.86, -0.65, and -0.22 V, respectively, during the positive scan. On the contrary, only the tiny peak of cadmium (II) ions was observed at the bare CNT electrode and no peaks corresponding to the metal ions were found at GCE, implying that the presence of bismuth film is significant for the stripping analysis of the target metal ions. Our findings about the necessity of bismuth are in agreement with the results in earlier literatures [5,10].

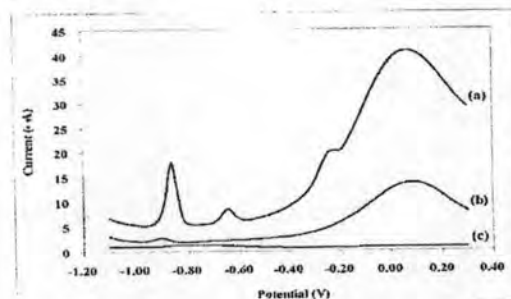


Figure 3 SWASV signals obtained from (a) *in situ* bismuth film modified CNT electrode, (b) CNT electrode, and (c) GCE for 0.1 M acetate buffer solution (pH 4.5) containing $40 \mu\text{gL}^{-1}$ of cadmium (II) and lead (II) ions with the deposition potential of -1.10 V, the deposition time of 120 s, and the scan rate of 7.5 mVs^{-1} .

4. Optimization of Deposition Conditions for In Situ Bismuth Film Modified CNT Electrode

For stripping voltammetric analysis by *in situ* bismuth film modified CNT electrode, the influence of bismuth (III) ion concentration on the peak currents of cadmium (II) and lead (II) ions are shown in Fig. 4. Bismuth (III) ion concentration was investigated in the range of 250 to $2,000 \mu\text{gL}^{-1}$ for a solution containing $25 \mu\text{gL}^{-1}$ of cadmium (II) and lead (II) ions. Similar to previous work [10], the concentration of bismuth (III)

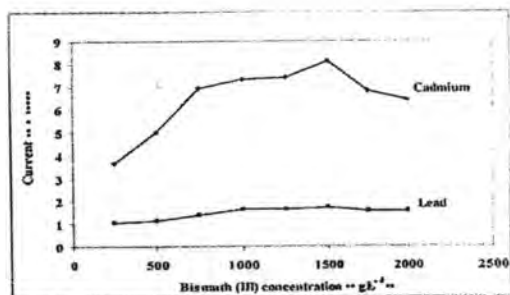


Figure 4 Effect of bismuth (III) ion concentration on the peak currents of $25 \mu\text{gL}^{-1}$ cadmium (II) and lead (II) ions recorded with *in situ* bismuth film modified CNT electrode in 0.1 M acetate buffer solution (pH 4.5) by SWASV using the deposition potential of -1.10 V , the deposition time of 120 s, and the scan rate of 7.5 mVs^{-1} .

ions controlled the thickness of the bismuth film, but it did not affect the peak positions of both heavy metal ions. A bismuth (III) ion concentration of $1,500 \mu\text{gL}^{-1}$ was used for subsequent analytical work by the *in situ* bismuth film electrode since this concentration provided the highest peak currents for both heavy metal ions.

To obtain better stripping signals for cadmium (II) and lead (II) ions, the effect of the deposition potential

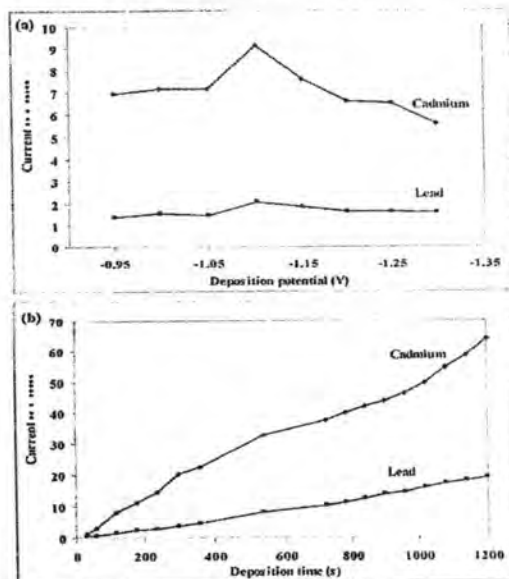


Figure 5 Effects of (a) the deposition potential and (b) the deposition time on the stripping peak currents of cadmium (II) and lead (II) ions recorded with *in situ* bismuth film modified CNT electrode by SWASV.

was probed in the range from -0.95 to -1.30 V and the result is given in Fig. 5a. Since the peak currents of both heavy metal ions had the maximum values when the deposition potential of -1.10 V was used, this deposition potential was then chosen throughout the work.

Furthermore, the deposition time for the stripping analysis of cadmium (II) and lead (II) ions were changed from 30 to 1,200 s and its effect towards the stripping currents are demonstrated in Fig. 5b. The peak currents of both heavy metal ions increased proportionally with the deposition time. Thus, the whole range of 30 to 1,200 s could be effectively used as the deposition time; however, 120-s deposition time was selected in this work to obtain rapid and efficient analysis.

For the purpose of direct comparison, these optimized deposition conditions for *in situ* bismuth film electrode were applied to the Bi-CNT modified GCE in subsequent investigation.

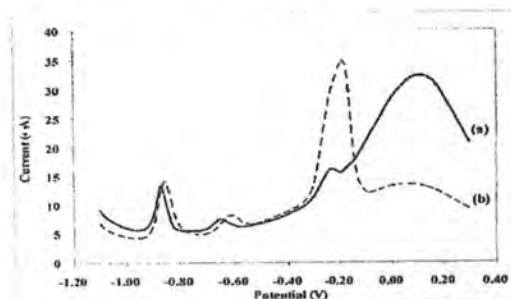


Figure 6 SWASV signals obtained from (a) *in situ* bismuth film modified CNT electrode and (b) Bi-CNT modified GCE for 0.1 M acetate buffer solution (pH 4.5) containing $25 \mu\text{gL}^{-1}$ of cadmium (II) and lead (II) ions with the deposition potential of -1.10 V , the deposition time of 120 s, and the scan rate of 7.5 mVs^{-1} .

5. Electrochemical Performance Comparison between *In Situ* Bismuth Film Modified CNT Electrode and Bi-CNT Modified Electrode

Fig. 6 displays typical anodic stripping voltammograms for $25 \mu\text{gL}^{-1}$ of cadmium (II) and lead (II) ions obtained from (a) *in situ* bismuth film modified CNT electrode and (b) Bi-CNT modified GCE. The peak potentials of cadmium (II) and lead (II) ions were approximately the same at these electrodes. With 120-s deposition at -1.10 V , well-defined and sharp stripping peaks were observed at both electrodes. For cadmium (II) ion, the peak currents of $7.80 \mu\text{A}$ and $10.19 \mu\text{A}$ were obtained from *in situ* bismuth film modified CNT electrode and Bi-CNT modified GCE, respectively. For the stripping peak current of lead (II) ion, the bismuth film modified electrode gave $0.37 \mu\text{A}$ whereas the Bi-CNT modified electrode led to $1.94 \mu\text{A}$. Our results have shown that, compared to the *in situ* bismuth film modified CNT electrode, the Bi-

CNT modified GCE yielded slightly larger stripping signals for these heavy metal ions. Therefore, due to simpler preparation and better electrochemical performance, we have tried to optimize various experimental parameters to improve the ability of the Bi-CNT modified GCE towards metal determination.

Conclusions

In this research, the Bi-CNT composites were synthesized by polyol process. XRD and voltammetric results confirmed the deposition of bismuth onto CNTs and the successful fabrication of Bi-CNT modified GCEs. For the determination of cadmium (II) and lead (II) ions at low $\mu\text{g L}^{-1}$ levels using SWASV, the Bi-CNT modified electrodes exhibited more attractive voltammetric response than the *in situ* bismuth film modified CNT electrodes. Currently, we are trying to optimize several experimental parameters to improve the ability of the Bi-CNT modified electrodes towards the determination of the heavy metal ions in real samples.

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1. **Pikroh, N.;** and Vanalabhpatana, P. Anodic stripping analysis of cadmium (II) and lead (II) ions by bismuth-carbon nanotube modified electrodes. **Science Journal Ubonratchathani University** 1 (2010): 5-8.

