



CHAPTER I

INTRODUCTION

1.1 Introduction

Nowadays, heavy metals such as mercury, cadmium, and lead are considered to be one of the main pollutants in air, soil, and natural water. They can cause damaging effects even at very low concentrations. Heavy metals can be taken into the human body via inhalation, ingestion, or skin absorption. They tend to accumulate in the food chain and, thus, in our bodies.

Commonly, the measurement of heavy metals at trace level are performed by the use of conventional analytical techniques such as flame atomic absorption spectroscopy (FAAS), graphite furnace atomic absorption spectroscopy (GFAAS), inductively coupled plasma-optical emission spectroscopy (ICP-OES), and inductively coupled plasma-mass spectrometry (ICP-MS). These techniques require skillful analysts as well as high acquisition and maintenance cost for routine operation. Hence, there have been needs of portable analytical systems for heavy metal detection. Electrochemical techniques, especially stripping analyses, satisfy many of the requirements for quantitative analysis of heavy metal ions because of the simple instrumentation and operation, affordable cost, high sensitivity and reproducibility, and low detection limit. Anodic stripping voltammetry (ASV), one of the stripping techniques, has been used for determining trace metal ions [1]. Initially, ASV makes use of an accumulation or preconcentration step at which the metal cations of interest are accumulated by reducing into a metallic form on a suitable working electrode. Then, this accumulation step is followed by the stripping step where the preconcentrated metals are electrochemically oxidized when the potential is scanned positively, causing metal removal from the electrode and the anodic current as an analytical signal. The initial preconcentration step enables us to determine extremely low concentrations of metal ions.

Hanging mercury drop electrode (HMDE) [2], dropping mercury electrode [3], and mercury film electrode (MFE) [4] have been traditional electrodes for performing

ASV since mercury possesses valuable properties for electroanalysis such as low background and noise, high hydrogen overpotential, excellent resolution and reproducibility, and ability to form amalgams with many heavy metals. However, the risks associated with the use, manipulation, and disposal of metallic mercury or mercury salts have led to the research for alternative electrodes with environmentally friendly quality. Several electrodes, *e.g.*, gold and iridium, were developed in order to substitute the use of mercury electrodes in stripping analysis [5-7], but none approached favorable properties of the mercury electrodes.

In 2000, bismuth-film-plated electrode (BiFE), prepared by depositing a thin film of bismuth on a carbon substrate, was introduced as an alternative electrode for metal analysis by ASV since it showed comparable performance with mercury film electrode in stripping analysis [8]. The performance characteristics of BiFE as its inherent low toxicity, insensitivity to oxygen, large anodic potential range, undistorted stripping peaks, and excellent signal resolution have made the bismuth electrode to be superior than the mercury electrode. These advantageous properties of bismuth are attributed to its ability to form “fuse” or “low temperature” alloys with heavy metals [9], facilitating the nucleation process during the accumulation of heavy metal ions and finally leading to the electrode with high sensitivity.

Carbon nanotube (CNT), one allotrope of carbon, has recently been used as BiFE support material which can improve the electrode sensitivity [10] due to its unique structural of nanometer size, high electrical conductivity, high surface area, and good chemical stability. Several synthetic methods, including sodium borohydride (NaBH_4) reduction [11], microwave synthesis method [12], and polyol process [13], can be utilized to prepare various metal–CNT composites which are metal particles supported on CNTs. Polyol process, one of the simple syntheses, uses poly alcohol as both a solvent and a reducing agent to produce metal nanoparticles deposited on CNTs from the mixture of metallic cation precursor and CNTs.

In this work, the attractive stripping voltammetric behavior of bismuth–CNT (Bi–CNT) composite modified electrode is described. This new and easy-to-prepare type of bismuth 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 with several bismuth-to-CNT ratios were simply synthesized by polyol process. Experiments conducted under identical conditions indicate that the stripping voltammetric performance of the resulting Bi–CNT composite modified

electrodes compared favorably with that of the bismuth film modified onto CNT electrodes. In addition, the application of the Bi–CNT composite modified electrodes towards water sample analysis are demonstrated.

1.2 Literature Review: Development of Bismuth Electrodes

The first bismuth electrodes are *in situ* bismuth film electrodes which were generated by simultaneously depositing the bismuth film and the metal cations via reduction onto the suitable substrates. Firstly, J. Wang's research group [8] introduced bismuth coated glassy carbon and carbon fiber electrodes for the measurement of microgram per liter levels of cadmium (II), lead (II), thallium (I), and zinc (II) ions in non-deaerated condition. The performance qualities of bismuth film electrodes as high sensitivity, well-defined stripping signals, and good resolution of the neighboring peaks were obtained. In the following year, they confirmed that the stripping performance of the bismuth electrodes was comparable to the mercury electrodes [14].

G. Kefala *et al.* [15] reported the simultaneous determination of cadmium (II), lead (II), and zinc (II) ions at the low ppb levels by SWASV using *in situ* plated bismuth film on glassy carbon electrodes. These film electrodes were successfully applied to trace measurements of lead (II) and zinc (II) ions in tap water and human hair. Moreover, the results were in satisfactory agreement with atomic absorption spectroscopic (AAS) observation.

A. Charalambous *et al.* [16] studied to the utility of *in situ* bismuth film modified glassy carbon electrodes for quantitative measurements of indium (III) ions in the presence of other metal cations (cadmium (II) and lead (II) ions) by SWASV. Using the optimized choice of the associated chemical and instrumental conditions, the bismuth film electrodes provided better separation between cadmium and indium signals than the mercury film ones.

Besides glassy carbon electrode which has been the most common substrate for bismuth film plating, carbon paste and graphite can be used as electrode supports for bismuth film in stripping voltammetry because they are inexpensive and easy to be modified as well as they can offer readily renewable surfaces.

D. Demetriades *et al.* [17] reported the utility of inexpensive and disposable pencil-lead graphite as a substrate for *in situ* bismuth film electrode to determine trace

cadmium (II), lead (II), and zinc (II) ions by SWASV. In comparison with mercury film electrode, the sensitivity of the pencil-lead bismuth film electrode for lead (II) and cadmium (II) ions was comparable whereas the mercury film electrode offered a higher sensitivity than the pencil-lead bismuth film electrode for zinc (II) ions since it produced a lower background current at more negative potentials. The detection limits of the pencil-lead bismuth film electrode were 0.3 ppb for cadmium (II) ions and 0.4 ppb for lead (II) and zinc (II) ions, but these values could be further decreased with the use of Nafion-covered pencil-lead bismuth film electrode.

L. Baldrianova *et al.* [18] fabricated a new type of carbon paste minielectrodes (CPmEs) as substrates for the *in situ* bismuth film electrodes (BiF-CPmEs) that were used in the determination of metal ions by SWASV. CPmEs were prepared by heat shrinking the end of plastic micropipette tips and filling them with carbon paste. BiF-CPmEs gave lower detection limits than carbon microdisc electrodes for metal ion detection in unbuffered and unstirred samples due to the combination of near-microelectrode behavior with high mass transfer rate and high electroactive surface area of carbon paste.

L. Cao *et al.* [19] developed an effective method to prepare the bismuth film electrodes for trace analysis of cadmium (II) and lead (II) ions by the use of zeolite doped carbon paste electrode (ZDCPE). The results exhibited that, after proper optimization of the experimental conditions, the *in situ* bismuth film modified ZDCPE (BiF-ZDCPE) was suitable for the quantification of both metal ions with satisfied sensitivity and reproducibility. Furthermore, the prepared electrodes were successfully utilized to determine cadmium (II) and lead (II) ions in real samples and the results were in agreement with those of AAS.

Several researchers attempted to use permselective polymeric materials for the modification of bismuth film electrodes in order to decrease the adsorption of interferences on the electrode surfaces. The examples of using various polymers as modifiers are:

G. Kefala *et al.* [20] investigated the polymer coated bismuth electrodes plated *in situ* for the simultaneous on-line determination of cadmium (II), lead (II), and zinc (II) ions by SWASV in the sequential injection analysis (SIA) mode. Polymeric Nafion was used to coat on the glassy carbon electrode. This electrode demonstrated that applying a permselective Nafion film on the flow-through bismuth film electrode

conferred significant improvement in terms of sensitivity, tolerance to surfactants, and electrode stability.

W. W. Zhu *et al.* [21] used an *in situ* bismuth/polyaniline film electrode for simultaneous measurement of lead (II) and cadmium (II) ions at ppb level by means of ASV. Compared with the bismuth film and the polyaniline film electrodes, this bismuth/polyaniline film electrode had better electrochemical activity, more stable, and higher sensitivity. These results confirmed that polyaniline film can improve the activity of bismuth particles on the glassy carbon electrode for determining the metal ions.

H. Xu *et al.* [22] developed a Nafion coated bismuth film electrode (NCBiFE) plated *in situ* to determine lead (II), cadmium (II), and zinc (II) ions by differential pulse ASV (DPASV) and investigated the application of *in situ* NCBiFE to heavy metal analyses in vegetable samples. Nafion film on NCBiFE can significantly improve sensitivity and long-term stability of the electrode.

F. Torma *et al.* [23] demonstrated the advantageous properties of the Nafion/2,2'-bipyridyl/bismuth composite film coated on glassy carbon electrode for the determination of trace zinc (II), lead (II), and cadmium (II) ions. The electrode was prepared by applying a drop of a coating solution containing Nafion and 2,2'-bipyridyl onto the surface of glassy carbon electrode. Then, the bismuth film was *in situ* plated with the target metal ions on the Nafion/2,2'-bipyridyl coated surface. It was clear that Nafion film enhanced the mechanical stability of the bismuth film and the electrode resistance to any interferences while the sensitivity and selectivity of the stripping responses were improved by the neutral 2,2'-bipyridyl chelating agent.

Y. Wu and co-workers [24] used *in situ* bismuth/poly(*p*-aminobenzene sulfonic acid) film electrode for the determination of lead (II), cadmium (II), and zinc (II) ions. Experimental results suggested that the polymer on the prepared electrode can protect the bismuth surface against abrasion or adsorption of surface active agents and enhance the sensitivity of bismuth for quantitative measurements of heavy metal ions.

However, the *in situ* bismuth plating method has serious limitations due to the sensitivity towards pH of the sample solution and interfering species. Hence, the *ex situ* bismuth plating method was used to decrease these weaknesses of the *in situ* bismuth film electrode.

A. Krolicka *et al.* [25] investigated the performance for the determination of lead (II), cadmium (II), and zinc (II) ions by bismuth film plated carbon paste

electrodes (BiFCPEs). The results confirmed that the *ex situ* BiFCPE exhibited significantly better analytical performance for cadmium (II) and lead (II) ions than the *in situ* BiFCPE whereas the sensitivity for zinc (II) ions was approximately the same for the two electrodes.

M. Yang *et al.* [26] employed the bismuth film electrode for the quantification of cadmium (II) and zinc (II) ions inherent in metallothionein protein. The *ex situ* bismuth film electrode showed excellent performance for the quantification of both metal ions in metallothionein. At pH 2-5.5, two well-defined anodic stripping peaks corresponding to the cadmium (II) and zinc (II) ions disassociated from metallothionein were produced and the peaks were more concise than those obtained at mercury electrode.

Nevertheless, bismuth film electrodes need an additional washing or plating step. In order to overcome the above disadvantage of the bismuth film electrodes, many researchers have developed bismuth modified electrodes that can be directly applied to analyze metal ions without a film plating.

R. Pauliukaite *et al.* [27] used carbon paste electrodes modified with bismuth (III) oxide (Bi_2O_3) for the determination of cadmium (II) and lead (II) ions in drinking water, mineral water, and urine. In comparison with the unmodified carbon paste electrode, the Bi_2O_3 electrode yielded larger stripping signals for both metal ions. The lowest concentration that could be determined by the prepared Bi_2O_3 electrode was 5 ppb for cadmium (II) and lead (II) ions.

S. B. Hocevar *et al.* [28] presented the bismuth-powder modified carbon paste electrodes (Bi-CPEs) for the detection of trace heavy metals by means of ASV. These modified electrodes were prepared by homogenizing bismuth powder with graphite powder and silicon oil. The significant properties of Bi-CPEs involve with non-toxic character, simple preparation, and fast surface renewal. Moreover, these electrodes did not require the additional step of preparing pre-plated bismuth film or the undesirable introduction of bismuth ions into the analyte solution. The Bi-CPEs demonstrated superior electrochemical performances in comparison with the bare carbon paste electrode, the *in situ* bismuth film on carbon paste electrode, and the bismuth paste electrode.

G. J. Lee *et al.* [29] fabricated the bismuth nanopowder electrode for trace analysis of cadmium (II) and lead (II) ions in conjunction with ASV. The bismuth nanopowder had been synthesized by the levitational gas condensation method. After

that, the nanopowder was coated onto the conductive carbon layer which was pasted onto the flexible polymer film by the screen printing method. This new bismuth nanopowder electrode was proven to be highly sensitive and reliable for the determination of both metal ions. Moreover, the detection limit of lead (II) ions is lower than the previously reported values for bismuth film electrodes.

C. Kokkinos *et al.* [30] proposed a novel type of bismuth electrode for stripping voltammetry based on sputtering a silicon substrate with a thin bismuth film. Not only the sputtered bismuth film electrodes were successfully applied to determine lead (II), cadmium (II), and nickel (III) ions, but they were also employed in the semi-disposable mode for at least 15-20 stripping cycles without apparent deterioration of their performance. Subsequently, this research group proposed the lithographically fabricated bismuth-sputtered disposable electrodes [31]. The new bismuth electrodes exhibited significant advantages compared to their electroplated counterparts, *i.e.*, the experimental procedure was simplified, the waste was reduced, and a conductive substrate was not necessary. Additionally, this modified electrode could be used for at least 15-20 repetitive measurements without loss of sensitivity.

R. O. Kadara and co-workers [32] employed bulk Bi_2O_3 -modified screen-printed carbon electrodes for metal ion detection. The electrodes were fabricated by mixing Bi_2O_3 with graphite-carbon ink and then printing the mixture onto the surface of the screen-printed carbon electrode. Although, the analytical performances of the Bi_2O_3 modified electrode was lower than the *in situ* bismuth film screen-printed carbon electrode, it did not require the addition of bismuth (III) ions to the analyte solution in order to generate bismuth film.

G. H. Hwang *et al.* [33] examined the use of bismuth-carbon (Bi-C) composite electrode for the determination of trace amounts of cadmium (II) and lead (II) ions. Prepared by mixing bismuth powder and carbon powder with turpeneol containing 5% ethyl cellulose, the Bi-C composite paste was screen-printed on the alumina plate. Comparing the Bi-C composite electrode with the *in situ* plated bismuth film electrode, the Bi-C composite electrode exhibited superior performance due to its larger surface area, but its conductivity was lower.

Lately, CNT, one allotrope of carbon with two-dimensional graphite sheets rolled into a tube, has been proposed to be an electrode material support due to its cylindrical nanostructure with high surface area as well as unique mechanical and electrical properties. There has been recent work revealing that, compared with other

substrates, CNT is a better support for the electrodes used in the determination of trace heavy metal ions. Many researchers used CNTs as substrates of bismuth electrodes, for example:

G. Liu *et al.* [34] used nanoelectrode arrays containing CNTs for ultrasensitive voltammetric detection of metal ions. An epoxy layer that was used to seal CNTs helped reduce the current leakage and eliminate the electrode capacitance, leading to the nanoelectrode arrays with low background current. The CNT nanoelectrode arrays coated with *in situ* bismuth film were used successfully for voltammetric detection of trace cadmium (II) and lead (II) ions at the sub-ppb level and the detection limit obtained was much lower than that of glassy carbon electrode.

G. H. Hwang's research group [10] employed the bismuth film modified CNT electrode for the determination of trace lead (II), cadmium (II), and zinc (II) ions by SWASV. Using *in situ* plating method, the bismuth film was coated onto the screen-printed CNT electrode. In comparison with the bismuth film electrodes modified on activated carbon, graphite, and glassy carbon electrode, the bismuth film modified CNT electrode exhibited superior performance because CNTs had more active sites than other carbon materials. In addition, the bismuth film modified CNT electrode was successfully applied to the quantification of trace metals in real samples.

H. Xu *et al.* [35] developed bismuth/CNT–Nafion composite electrode for the stripping analysis of trace lead (II) and cadmium (II) ions. The bismuth film was plated *in situ* onto the CNT–Nafion substrate. Electrochemical results suggested that the synergistic effect of CNT and bismuth film improved the sensitivity and reproducibility for the detection of lead (II) and cadmium (II) ions. Moreover, the prepared electrodes were successfully applied to determine these two metal ions in real sample and the results agreed well with those of AAS.

Up to present, CNTs have been only used as substrates of bismuth film electrodes. There have been no reports regarding the use of CNT composite with bismuth for the voltammetric detection of trace metals. This work reports Bi–CNT composite modified electrode as a new and easy-to-prepare type of bismuth electrode. That can be directly applied to analyze metal ions without a film plating step.

1.3 Objectives and Scopes of The Thesis

This research aims are to develop and fabricate Bi–CNT composite modified electrodes for the determination of cadmium (II) and lead (II) ions at ppb level by means of SWASV. Several experimental parameters have been optimized to improve the ability of the Bi–CNT composite modified electrodes towards the determination of the both metal ions. The thesis is divided into four parts. For the first part, the preparation of Bi–CNT composites via polyol process is demonstrated. The second part presents the electrochemical characterization of the Bi–CNT composites by cyclic voltammetry and the morphological information of the composites by X-ray diffraction (XRD) method, energy dispersive X-ray fluorescence (EDXRF) spectroscopy, and transmission electron microscopy (TEM). In the third part, the performance of the Bi–CNT composite modified electrode and that of *in situ* bismuth film modified onto CNT electrode for the determination of both metal ions are compared. Finally, the determination of cadmium (II) and lead (II) ions in water samples is displayed in the fourth part.