CHAPTER III

EXPERIMENTAL

3.1 Instruments and Apparatus

3.1.1 Electrochemical Instruments

The instruments and apparatus for electrochemical measurement are shown in Table 3.1.

Table 3.1 List of electrochemical instruments and apparatus

Instrument	Model	Company (Country)
1. potentiostat/galvanostat	μAutolab III	Eco Chemie B.V. (The Netherlands)
2. working electrode		
2.1 glassy carbon (GC)		BAS (Japan)
3. reference electrode		
3.1 silver/silver chloride (Ag/AgCl) electrode		BAS (Japan)
4. counter electrode		
4.1 home-made platinum wire		
5. other apparatus		
5.1 home-made glass cell		
5.2 alumina micropolish 0.3 μm		Buehler (USA)
5.3 alumina micropolish 1.0 μm		Buehler (USA)
5.4 home-made salt-bridge		
5.5 stir bar		

Instrument	Model	Company (Country)
5.6 magnetic stirrer		Metrohm (The Netherlands)

3.1.2 Other Characterization Instruments

All instruments for characterization are given in Table 3.2.

Table 3.2 List of instruments for characterization

Instrument	Model	Company (Country)
1. Fourier transform infrared (IR) spectrometer	Spectrum One	Perkin Elmer (USA)
2. transmission electron microscope (TEM)	JEM-2100	JEOL (Japan)
3. X-ray diffraction (XRD) instrument	DMAX 2200	Rigaku (Japan)
4. energy dispersive X-ray fluorescence (EDXRF) spectrometer	ED-2000	Oxford (USA)

3.2 Chemicals

In this research, the chemicals used are AR grade and summarized in Table 3.3. All solutions were prepared by milli-Q water.

Table 3.3 List of chemicals

Chemical	Supplier (Country)
1. multi-walled carbon nanotube 99%, MWCNT*	Chang Mai University (Thailand)
2. ethylene glycol, $HO(CH_2)_2OH$	Merck (Germany)
3. sodium hydroxide, $NaOH$	Merck (Germany)
4. hydrochloric acid, HCl	Merck (Germany)
5. sulfuric acid, H_2SO_4	Merck (Germany)
6. nitric acid, HNO_3	Merck (Germany)
7. acetic acid, CH_3COOH	Carlo Erba (Italy)
8. sodium acetate, CH_3COONa	Fluka (Switzerland)
9. Nafion solution	Wako (Japan)
10. bismuth (III) nitrate pentahydrate, $Bi(NO_3)_2 \cdot 5H_2O$	Fluka (Germany)
11. cadmium (II) ion standard solution	BDH Chemicals (UK)
12. lead (II) ion standard solution	BDH Chemicals (UK)

* MWCNT will be represented as CNT in the remaining sections.

3.3 Chemical Preparation

The following section explains procedures for the preparation of chemical solutions employed in this work.

3.3.1 Solutions for The Preparation of Bismuth–CNT (Bi–CNT) Composites

3.3.1.1 0.5 M Hydrochloric Acid

2.07 mL of concentrated HCl was diluted to 50 mL by milli-Q water.

3.3.1.2 Mixtures of Bismuth (III) Ions and CNTs

To synthesize Bi–CNT composites, the mixtures of bismuth (III) ions and CNTs were prepared by mixing $Bi(NO_3)_2{\cdot}5H_2O$ with CNTs at various mole ratios. Then, the mixtures were dissolved in $HO(CH_2)_2OH$ solution.

3.3.2 Electrolyte Solution

3.3.2.1 0.1 M Acetate Buffer Solution

0.1 M acetate buffer solution was prepared by combining 0.1 M CH_3COOH (2.86 mL of CH_3COOH in 500 mL of milli-Q water) and 0.1 M CH_3COONa (4.10 g of CH_3COONa in 500 mL of milli-Q water) prior to the fine pH adjustment of the solution mixture to 4.5 using pH meter.

3.3.3 Solution for Electrochemical Measurements

3.3.3.1 100 ppm Cadmium (II) Ions (Stock Solution)

1.00 mL of 1,000 ppm cadmium (II) ion standard solution was diluted to 10.00 mL by 0.1 M acetate buffer solution (pH 4.5).

3.3.3.2 100 ppm Lead (II) Ions (Stock Solution)

1.00 mL of 1,000 ppm lead (II) ion standard solution was diluted to10.00 mL by 0.1 M acetate buffer solution (pH 4.5).

3.3.3.3 100 ppm Bismuth (III) Ions (Stock Solution)

1.00 mL of 1,000 ppm bismuth (III) ion standard solution was diluted to 10.00 mL with 0.1 M acetate buffer solution (pH 4.5).

3.3.3.4 0.5 M Nitric Acid

3.49 mL of concentrated HNO_3 was diluted to 100 mL by milli-Q water.

3.3.4 Sample Preparation

Waste water samples were collected in polypropylene bottles from one of the aluminium factories in Bangkok. In order to preserve the sample, 1.00 mL of concentrated HNO_3 was added into each of 1.00-L waste water sample prior to sample filtration. After that, 10.00 mL of sample was pipetted into an electrochemical cell and the volume was made up to 20.00 mL by 10.00 mL of 0.1 M acetate buffer solution (pH 4.5). Tap water samples were collected in polypropylene bottles from local laboratory. A total of 10.00 mL tap water were taken in order to guarantee the representative of the samples. These collected samples were acidified with HNO_3, stored in a freezer, and analyzed in similar way to waste water, but without the filtering procedure.

3.4 Experimental Procedures

In this section, it mainly consists of experimental procedures for purification and modification of CNTs, synthesis of Bi–CNT composites, morphological studies of CNTs and Bi–CNT composites, electrode preparation, electrochemical characterization of the modified electrodes, and the determination of cadmium (II) and lead (II) ions by the modified electrodes.

3.4.1 Purification and Modification of CNTs [45]

In order to remove any impurity and to functionalize CNTs with active groups such as carboxylic acid, CNTs were dispersed into mixed concentrated HNO_3 and H_2SO_4, and subjected to ultrasonication for several hours. Then, the CNT mixture was diluted with milli-Q water, filtered, washed, and dried. The information of functional groups attached on modified CNT was provided by Fourier transform infrared (FTIR) spectrometer.

3.4.2 Synthesis of Bi–CNT Composites [46]

Bi–CNT composites or bismuth particles supported on CNTs were prepared via the following procedure. Appropriate amount bismuth precursor, $Bi(NO_3)_3 \cdot 5H_2O$, was mixed with CNTs and dissolved in $HO(CH_2)_2OH$ solution to form a bismuth (III) ion–CNT mixture. After this step, the pH of the mixture was adjusted to above 7 with NaOH solution. The mixture was ultrasonically treated to ensure that the modified CNTs was uniformly dispersed in the solution mixture. Then, the mixture was heated to 160-180°C in an oil bath and maintained at this temperature range for several hours to complete the reduction of metal precursors. When the mixture was cooled, its pH was adjusted with 0.5 M HCl solution. After that, the mixture was refluxed to settle the Bi–CNT composite, which was subsequently filtered, washed, and dried.

3.4.3 Morphological Studies of CNTs and Bi–CNT Composites

The morphological and structural information of CNTs and Bi–CNT composites were obtained by TEM, XRD instrument, and EDXRF spectrometer.

3.4.4 Preparation of Electrodes

3.4.4.1 Glassy Carbon (GC) Electrode

GC electrode was polished with 1.0 and 0.3 μm alumina slurries, respectively, until a mirror-like electrode surface was obtained. Then, the electrode was rinsed with milli-Q water and dried prior to use.

3.4.4.2 CNT Modified Glassy Carbon (CNT/GC) Electrode

Milligram amount of CNTs was sonicated in Nafion solution to form slurry. Then, the slurry was cast on the surface of GC electrode and allowed to dry at room temperature to generate CNT/GC electrode. This electrode was used as a base or substrate for preparing *in situ* bismuth film electrode.

3.4.4.3 Bi–CNT Composite Modified Glassy Carbon (Bi–CNT/GC) Electrode

Milligram amount of Bi–CNT composite was sonicated in Nafion solution to form composite slurry. Then, the slurry was placed on the surface of GC electrode and allowed to dry at room temperature for several minutes to generate Bi–CNT/GC electrode.

3.4.5 Electrochemical Characterization of The Modified Electrodes

3.4.5.1 Electrochemical Set-up

Electrochemical cell for cyclic voltammetric experiment is shown in Fig. 3.1. Working electrode (WE) was either CNT/GC or Bi–CNT/GC electrode. Counter electrode (CE) and reference electrode (RE) were Pt wire and Ag/AgCl electrode, respectively. WE, CE, and RE were contained in a glass cell containing analyte solution and these three electrodes were connected with the μAutolab III potentiostatic system. Electrochemical cell with the electrodes was housed in a faradaic cage to reduce electronic noise.

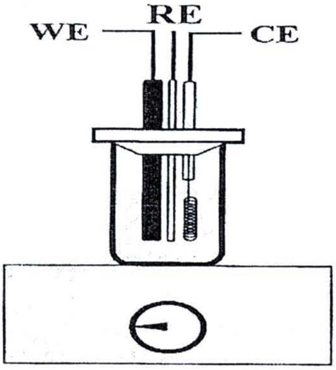

Figure 3.1 Electrochemical cell for cyclic voltammetry.

3.4.5.2 Measurement of Background Current

Cyclic voltammograms of the modified electrodes (CNT/GC and Bi–CNT/GC electrodes) were obtained in the solution of 0.1 M acetate buffer which served as a supporting electrolyte. The responses of different electrodes were detected with the scan rate of 100 $mV \cdot s^{-1}$. These cyclic voltammograms were employed to reveal the characteristic features of the modified electrodes.

3.4.6 Determination of Cadmium (II) and Lead (II) Ions by The Modified Electrodes

Analytical performances of CNT/GC and Bi–CNT/GC electrodes for the determination of cadmium (II) and lead (II) ions were investigated by square wave anodic stripping voltammetry (SWASV) at room temperature.

3.4.6.1 Electrochemical Set-up

Electrochemical set-up for SWASV experiment is displayed in Fig. 3.2. Similar set-up with cyclic voltammetric measurement was used, except that a magnetic bar was present in this case. SWASV measurements were performed under stirring condition in 20.00 mL of the sample solution.

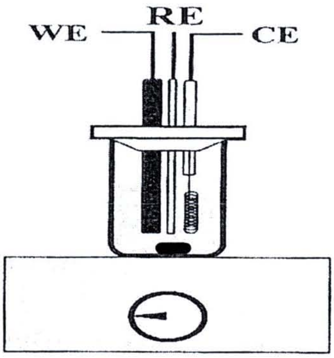

Figure 3.2 Electrochemical cell for SWASV.

3.4.6.2 Stripping Analysis by *In Situ* Bismuth Film on CNT Modified Glassy Carbon (*In Situ* BiF/CNT/GC) Electrode

Stripping voltammetric measurements were performed without deaerating an analyte solution. At the preconcentration step, immersed into a mixed solution of bismuth (III), cadmium (II) and lead (II) ions, CNT/GC electrode was initially held at –0.95 to –1.30 V under the magnetic bar stirring for a carefully defined period of time. After 10-s rest period, the voltammogram in a square wave mode was recorded with an anodic scan from the initial potential to +0.30 V. At the end, the electrode was cleaned using chronoamperometric mode at +0.30 V for 30 s under stirring solution.

3.4.6.3 Stripping Analysis by Bi–CNT Composite Modified Glassy Carbon (Bi–CNT/GC) Electrode

Stripping voltammetric measurements were performed without deaerating an analyte solution. Initially, Bi–CNT/GC electrode was placed into a solution of cadmium (II) and lead (II) ions and was usually set at the deposition potential for a certain period of time under stirring condition, followed by 10-s equilibrium period. Similar to the *in situ* BiF/CNT/GC electrode, square wave voltammogram was then obtained prior to electrode cleaning.