DETERMINATION OF MERCURY(II) USING ZINC/ ALUMINIUM LAYERED DOUBLE HYDROXIDE-3(4-HYDROXYPHENYL)PROPIONATE MODIFIED MULTI-WALLED CARBON NANOTUBE PASTE ELECTRODE

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UNIVERSITI PENDIDIKAN SULTAN IDRIS

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ABSTRACT

This study describes the preparation of chemically modified multi-walled carbon nanotube paste electrode with zinc/aluminium layered double hydroxide-3(4-hydroxyphenyl)propionate nanocomposite (Zn/Al-LDH-HPP) for determination of Hg(II) by cyclic voltammetry method. Experimental parameters influencing the voltammetric response including percentage of modifier, type of supporting electrolyte, pH and scan rate were examined and optimized. The results show that optimum conditions of the voltammetric response were obtained at 2.5% (w/w) of Zn/Al-LDH-HPP, 0.5 M potassium chloride, pH 5.0 and scan rate of 100 mV s^{-1}. A linear range was obtained within the concentration of 1.0×10^{-9} to 1.0×10^{-7} M Hg(II) and 1.0×10^{-7} to 1.0×10^{-3} M Hg(II) with the limit of detection 5.0×10^{-10} M Hg(II). The presence of 25-folds concentration of most metal ions did not interfere the anodic peak current except Zn(II). In conclusion, the proposed modified multi-walled carbon nanotube paste electrode showed a high sensitivity, good selectivity, repeatability and reproducibility, making it suitable for the determination of Hg(II) in marine animal samples, for instance, fish and shellfish.

PENENTUAN MERKURI(II) MENGGUNAKAN ELEKTROD PES NANOTIUB KARBON BERBILANG DINDING TERUBAH SUAI ZINK/ALUMINIUM LAPISAN BERGANDA HIDROKSIDA-3(4-HIDROKSIFENIL)PROPIONAT

ABSTRAK

Kajian ini menghuraikan penyediaan elektrod pes nanotiub karbon berbilang dinding terubah suai secara kimia dengan nanokomposit zink/aluminium lapisan berganda hidroksida-3(4-hidroksifenil)propionat (Zn/Al-LDH-HPP) bagi penentuan Hg(II) melalui kaedah voltammetri kitaran. Parameter kajian yang mempengaruhi gerak balas voltammetrik termasuk peratusan pengubah suai, jenis elektrolit penyokong, pH dan kadar imbasan telah dikaji dan dioptimumkan. Dapatan menunjukkan bahawa keadaan optimum gerak balas voltammetrik diperolehi pada 2.5% (w/w) Zn/Al-LDH-HPP, 0.5 M kalium klorida, pH 5.0 dan kadar imbasan 100 mV s^{-1}. Julat linear telah diperoleh di antara kepekatan 1.0 x 10^{-9} hingga 1.0 x 10^{-7} M Hg(II) dan 1.0 x 10^{-7} hingga 1.0 x 10^{-3} M Hg(II) dengan had pengesanan 5.0 x 10^{-10} M Hg(II). Kehadiran 25 kali ganda kepekatan kebanyakan ion logam tidak mengganggu arus puncak anodik kecuali Zn(II). Kesimpulannya, elektrod pes nanotiub karbon berbilang dinding terubah suai yang dicadangkan menunjukkan kepekaan yang tinggi, kepilihan yang baik, kebolehulangan dan kebolehhasilan, menjadikannya sesuai untuk penentuan Hg(II) dalam sampel hidupan laut, misalnya ikan dan kerang.

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LIST OF ABBREVIATIONS

ΔE_p	Difference in peak potential
AAS	Atomic absorption spectrometry
AdSV	Adsorptive stripping voltammetry
ASV	Anodic stripping voltammetry
CMCNTPE	Chemically modified carbon nanotube paste electrode
CMCPE	Chemically modified carbon paste electrode
CME	Chemically modified electrode
CNT	Carbon nanotube
CNTPE	Carbon nanotube paste electrode
CPE	Carbon paste electrode
CSV	Cathodic stripping voltammetry
CV	Cyclic voltammetry
CVAAS	Cold vapor atomic absorption spectrometry
DME	Dropping mercury electrode
DPASV	Differential pulse anodic stripping voltammetry
DPV	Differential pulse voltammetry
E^0	Formal reduction potential
E_{pa}	Anodic peak potential
E_{pc}	Cathodic peak potential
FTIR	Fourier transform infrared
GC	Glassy carbon
GCE	Glassy carbon electrode

HMDE	Hanging mercury drop electrode
I_{pa}	Anodic peak current
I_{pc}	Cathodic peak current
ISE	Ion-selective electrode
LDH	Layered double hydroxide
MWCNT	Multi-walled carbon nanotube
NPV	Normal pulse voltammetry
SEM	Scanning electron microscopy
SWCNT	Single-walled carbon nanotube
SWV	Square wave voltammetry
Zn/Al-LDH-HPP	Zinc/aluminium layered double hydroxide-3(4-hydroxyphenil)propionate

CHAPTER 1

INTRODUCTION

1.1 Elemental Mercury

Mercury is an element with the symbol Hg (from Greek: hydrargyrum) and known as quicksilver. Mercury is a metal with the atomic number 80 and atomic mass 200.59. It can be in the form of salts with two oxidation states Hg^{+} (mercurous) and Hg^{2+} (mercuric). Mercuric salts are more common than mercurous salts in the environment. Mercury with high purity is a dense, silvery white liquid with very low melting point of 234.321 K or -38.829 °C. Mercury occurs naturally in the earth's crust especially in the form of sulfides. The non-toxic red sulfide (cinnabar) is the common ore of the mercury and may contain up to 70% mercury.

Some inorganic mercury compounds are used in various fields. Mercury(II) chloride is used as a disinfectant in medicine and as a fungicide in agriculture. Calomel is used in medicine, in pyrotechnics and as a catalyst. Thiomersal is used as an antiseptic and antifungal agent in medicines and vaccines. Mercury is used as an antifouling agent in paints for ships, as a slimicide in paper production, as a component of pesticides and as bacterial agent in the making of amalgam dental fillings.

Mercury can be released into the environment by human activities such as mining, metal smelting, combustion of fossil fuels, waste disposal and industrial activities. Mercury can also be released into the environment by volcanoes and by natural evaporation from the ocean and land surfaces. Organic mercury compounds released into the environment are usually broken down to elemental mercury or mercuric compounds (Holmes, James, & Levy, 2009; Nordberg, Fowler, Nordberg, & Friberg, 2007; Virtanen, Rissanen, Voutilainen, & Tuomainen, 2007).

Gold mining is one of the largest sources which contribute mercury contamination in the air, water and ground with various forms of mercury. Mercury pollution from gold mining tends to increase due to the high price of gold. Besides, secondary mercury pollution from other sources, for instance, fossil fuels, dental amalgams, fluorescent lighting and incineration of medical and municipal waste are decreasing due to elimination of mercury and environmental regulations (Kozin & Hansen, 2013).

The most form of mercury spreading in the oceans is Hg^{2+} ion (inorganic mercury). This ion then reacts with organic substances and anaerobic microorganisms to become organic mercury such as methylmercury and dimethylmercury, wherein both of them are known as toxic substances. Methylmercury and dimethylmercury easily dissolve in water and they are absorbed by microorganisms. These microorganisms are consumed by small fish, which in turn become food for larger fish. Mercury is also present in the meat of fowl and grazing animals, like sheep and cows. Both fish and meat are consumed by human, therefore mercury is able to enter in the human body and accumulate via this food chain (Kozin & Hansen, 2013).

All forms of mercury are harmful to mammalian species, including human. The level of the adverse effects caused by mercury depends on several factors like the time, the duration and the route of exposure (Nordberg et al., 2007). Hazard effects of mercury have been presented in the cardiovascular system, motor system, renal system, immune system, reproductive system, gastrointestinal system, liver, kidneys, and nervous system (Nordberg et al., 2007; Zahir, Rizwi, Haq, & Khan, 2005).

There are two cycles involved in the environmental transport and distribution of mercury. Figure 1.1 shows the cycles of the mercury in the environment. The first cycle is global scope which involves the atmospheric circulation of elemental mercury vapor from sources on land to the oceans. The second cycle is local scope which involves methylation of inorganic mercury particularly from anthropogenic sources (Boening, 2000). Metallic mercury (Hg^0) from hydrosphere (sea, rivers, lakes and ground water) and geosphere (soil) evaporates to the atmosphere and then returns to the Earth’s surface via the rainfall.

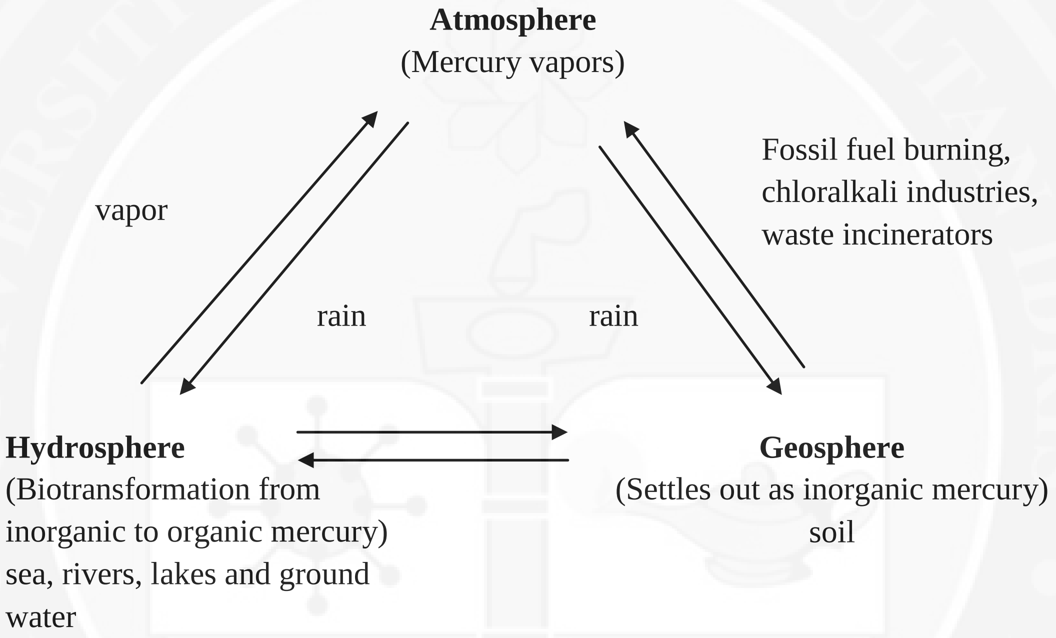

Figure 1.1. Cycles of the mercury in the environment.

1.2 Layered Double Hydroxide

Layered double hydroxide (LDH) is a group of synthetic two-dimensional nanostructured anionic clays (Li & Duan, 2006). It is called anionic clays because of its unusual properties of LDH exchange easily of interlayer anions. Hydrotalcite [$Mg_6Al_2(OH)_6CO_3{\cdot}4H_2O$] is one of the material group of LDH, which is naturally occurring in the environment, therefore LDH is known as hydrotalcite-like materials (Tonelli, Scavetta, & Giorgetti, 2013). The basic layer structure of a LDH is based on brucite [$Mg(OH)_2$], which consists of magnesium ions surrounded approximately octahedrally by six hydroxide ions, hence LDH is also known as brucite-like layer (Duan & Evans, 2006). Figure 1.2 shows the structure of a LDH.

The LDH can be fabricated by replacement of the divalent metal cations, coordinated octahedrally by hydroxyl groups in a brucite lattice, by trivalent metal cations, so that the layers obtain a positive charge then it is balanced by intercalation of organic or inorganic anions between the layers, and water molecule also usually occupy any free space in the interlayer area. The general formula of LDH is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} is divalent cations (such as Mg^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, or Zn^{2+}) and M^{3+} is trivalent cations (such as Al^{3+}, Cr^{3+}, Ga^{3+}, Mn^{3+} or Fe^{3+}); A is an interlayer anion (such as CO_3^{2-}, SO_4^{2-}, Cl^- or NO_3^-) or an organic species; the value of x is equal to the molar ratio of $M^{2+}/(M^{2+} + M^{3+})$ and is usually in the range of 0.2–0.33; m is the number of water molecules located in the interlayer region together with anions and n^- is charge on interlayer ion (Duan & Evans, 2006).

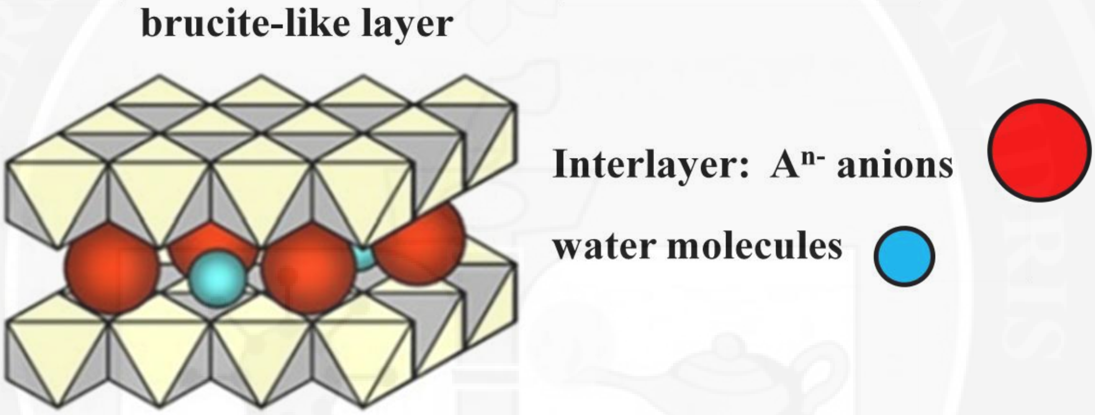

Figure 1.2. Structure of a LDH (Tonelli et al., 2013).

The LDH has a lot of physical and chemical properties which are astonishingly similar to those of clay minerals, such as the layer structure, the widely chemical compositions (due to modifiable isomorphous substitution of metallic cations), the modifiable layer charge density, the ion-exchange properties, the reactive interlayer area and the colloidal properties. These properties make LDH known as clay-like (Bergaya, Theng, & Lagaly, 2006).

The LDH has great interest for academic and industrial due to its several potential applications. One of the noteworthy properties of LDH is that the interlayer anions can be exchanged easily with numerous organic and inorganic charged compounds (Rives, 2001). LDH can be used for removal of harmful anions from liquid (Abdolmohammad-Zadeh, Rezvani, Sadeghi, & Zorufi, 2011; Goha, Lim, Banas, & Dong, 2010; Violante, Pucci, Cozzolino, Zhu, & Pigna, 2009) owing to the permanent positive charge, the high capacity of anion-exchange, the large surface area, the good thermal stability and the water-resistant structure (Tonelli et al., 2013). Mixed cation oxides, which are formed after thermal decomposition of LDH, can be used as catalysts (Basile et al., 2009) for a wide range of catalytic processes. The interlayer of LDH can act as a two-dimensional matrix for diverse chemical reactions (Rives, 2001). LDH also shows its potential as materials for several practical applications in pharmaceutics (Hoyo, 2007; Perioli et al., 2011; Trikeriotis & Ghanotakis, 2007), photochemistry (Musumeci et al., 2010; Shi, Wei, Evans, & Duan, 2010), polymer additives (Manzi-Nshuti et al., 2009) and electrochemistry (Yang et al., 2013; Yin, Cui, Ai, Fan, & Zhu, 2010). This is owing to its high versatility, easily modified properties and low cost, which make it feasible to create materials designed to execute definite requirements (Duan & Evans, 2006).

Recently, inorganic materials, like zeolites, clays and microporous, are widely applied in modified electrodes besides organic polymers. Inorganic materials have better stability, tolerance to high temperatures and oxidizing conditions, and chemical inertness, compare to organic polymers, therefore they are interesting as replacements of organic polymers (Duan & Evans, 2006). LDH clay-like is one of the inorganic materials that has been used as modifier in the electrode, known as chemically modified electrode (CME). Numerous studies have shown that LDH is a good material for construction of sensor based on CME (Guo, Zhang, Evans, & Duan, 2010; Mousty, 2010; Mousty, Vieille, & Cosnier, 2006). CME confines the analyte to a small amount close to the electrode surface during the preconcentration step, so that the low level of analyte can be measured. CME is greatly applied to electroanalysis because it has electrocatalytic properties that enhance the sensitivity and selectivity of the measurement (Tonelli et al., 2013).

Several types of electrodes modified with LDH show electrocatalytic activity. Biosphenol A was oxidized at glassy carbon electrode modified with Mg-Al-CO_3 LDH (Yin et al., 2010) and at glassy carbon electrode modified with Mg-Al LDH that functionalized with sodium dodecyl sulfonate (Yin et al., 2011). A nanomaterial Mg-Fe-Ni LDH, prepared by coprecipitation, is employed for immobilization of glucose oxidase on glassy carbon electrode. This CME shows good electrochemical performances with regard to the determination of glucose, like fast response, high sensitivity with low detection limit, wide range of linear concentration and long-time stability (Xu et al., 2011). A gold electrode modified with Zn-Al LDH by spreading a colloidal suspension to get a film on the surface of electrode. LDH prepared by coprecipitation and subsequent hydrothermal reaction. The CME has a good selectivity for determination of iodate towards its reduction, and it was studied in the amperometric determination of iodate in iodized table salt and kelp (Li et al., 2009).

1.3 Electrochemical Sensors

Electrochemistry is one of the chemistry sections focused with the interaction between electricity and chemistry, specifically in the measurements of electrical quantities (current, potential or charge) and their correlation to chemical parameters. Electrochemical processes occur at the electrode and solution interface. It involves the charge transfer from the electrode to another phase (solid or liquid). While this transfer process, chemical changes occur at the electrodes and the charge conducts through the bulk of the sample. Electrochemical measurements have been widely used for analytical purposes, for instance, in the industrial, environmental and medical applications (Janata, 2009; Wang, 2006).

Electrochemical methods can be categorized as steady-state and nonsteady-state methods. The steady-state just needs simple electronic devices, but tends to interfere from other electrochemically active compounds which are present in the sample and sometimes gives less sensitivity. In a steady-state method (such as potentiometry), the stable limiting current is measured at a fixed potential. On the other hand, the nonsteady-state methods depend on the potential electrode and the measurement of the current produced in response to the applied potential. The nonsteady-state methods are included in the class of voltammetric methods (Banica, 2012).

Electroanalytical techniques can be distinguished based on their type of electrical signal used for the measurements. The two main types of electroanalytical measurements are potentiometric and potentiostatic. Both types require at least two electrodes as conductors and electrolyte solution which are called as electrochemical cell. Thus, the electrode surface is a junction between an electronic conductor and an ionic conductor. One of the two electrodes acts as working electrode which gives responds to the analytes. The second one acts as the reference electrode which is of constant potential. Electrochemical cells can be classified as electrolytic when they consume electricity from external source. Besides, electrochemical cells can also be classified as galvanic when they are used to produce electrical energy (Wang, 2006).

Controlled-potential (potentiostatic) techniques involve the study of charge transfer processes at the electrode-solution interface, and are based on dynamic (non-zero-current) situations, like voltammetry. In these techniques, the electrode potential is used to produce the electron transfer reaction, and the current resulted from this process can be measured. The process enables chemical species to get electron (reduction) or lose electron (oxidation). Any chemical species which are electroactive, namely, that can be reduced or oxidized, can be measured by potentiostatic techniques (Wang, 2006).

It is important to ensure that reduction and oxidation reaction fulfilled reversible process. An electrochemical cell can be categorized as chemically reversible when reversing the current through the cell reverses the cell reaction without appearance of the side product or new reactions. In the contrary, it is categorized as chemically irreversible when reversing the current renders the different electrode reactions and yields new side products (Zoski, 2007).

Current measurement can be carried out by three-electrode cells. The cell consists of working electrode, reference electrode and auxiliary (counter) electrode, wherein these electrodes, they are immersed in the analyte solution. The working electrode is the electrode where the cell reaction takes place. The reference electrode supplies a stable and reproducible potential. The potential of the working electrode is always measured relatively to the reference potential. The counter electrode, together with the working electrode, serves circuit over which current is either applied or measured. An inert conducting material is usually chosen as counter electrode, for instance, platinum wire or graphite rod (Wang, 2006; Zoski, 2007).

Electrochemical sensors in the electrochemical techniques are served as a generator of electrical signals with numerous advantages, such as low cost, time saving, low energy consumption, high sensitivity, good selectivity, wide linear range, portable, ease of data read-out and ease of operation (Janegitz et al., 2011; Kempegowda & Malingappa, 2012; Yuan, Peng, Song, & Gong, 2013). Moreover, electrochemical sensor allows to simultaneous detection of multiple analytes (Khalid, 2013).

1.4 Reference Electrode

In an electrochemical cell of electrochemical measurements, one of the electrodes is required to keep a constant potential which is called reference electrode. Reference electrode function to control the potential of a working electrode in voltammetry, and so as in the measurement of an indicator electrode in potentiometry. The standard hydrogen electrode is a basic reference element in electrochemical devices that is difficult to handle (Scholz, 2010). As a result, secondary reference electrodes are mostly chosen in most experiments. There are several criteria that must be fulfilled by a secondary reference electrode, namely, it should be chemically and electrochemically reversible, the potential must remain effectively constant when a small current passes through the electrode and return to its original value after such small current flow, and the thermal coefficient of potential should be small (Scholz, 2010; Wang, 2006).

Proper experimental design must be considered in choosing a suitable reference electrode for an electrochemical measurement, i.e., it must avoid incompatible species present in the electrolyte from reacting with the reference electrode materials. For example, an ionic species with poor solubility can precipitate in the frit, clogging the reference electrode, and as a consequence increasing the junction potential. Furthermore, species which are in the electrochemical cell may interfere with the performance of a reference electrode by poisoning the controlling reduction-oxidation (redox) process, or increase the solubility of the reference couple (Zoski, 2007).

The silver/silver chloride (Ag/AgCl) reference electrode is commonly used owing to its simplicity, low cost, reproducibility of the potential and nontoxic components (i.e. free of mercury). The simplicity of the Ag/AgCl reference electrode, i.e., it can be produced in a very small size, gives itself to microfabrication as well as incorporation into sensors. A silver wire is coated with silver chloride, which can be accomplished electrochemically or thermally. The fabrication of a commercially available Ag/AgCl electrode is analogous to the calomel electrode. The electrolyte solution used in the Ag/AgCl electrode is usually a potassium chloride solution (mostly saturated or 3 M), and only seldom sodium or lithium chloride (Scholz, 2010).

1.5 Supporting Electrolyte

Electrochemical measurements are usually performed in a medium that consists of solvent and a supporting electrolyte that are mobile and can support current flow (Zoski, 2007). Choosing of solvent is based on the solubility of the analyte and its redox activity, and solvent properties, like the electrical conductivity, electrochemical activity and chemical reactivity. The solvent should not react with the analyte (or products) and should not undergo electrochemical reactions over a wide potential range (Wang, 2006). The supporting electrolytes chosen for use in electrochemical measurements are usually strong electrolyte, may be an inorganic salt, a mineral acid, or a buffer (Zoski, 2007). When water is used as a solvent, potassium chloride, potassium nitrate, ammonium chloride, sodium hydroxide, or hydrochloric acid can be employed as supporting electrolyte. Tetraalkylammonium salts are often employed in organic media. When a pH control is necessary, buffer systems can be used as supporting electrolyte, such as acetate, phosphate, or citrate. In the voltammetric measurements, the composition of the supporting electrolyte can influence the selectivity. Highly purified reagents are proper for preparation of the supporting electrolytes. The supporting electrolyte should not be easily oxidized or reduced to avoid potential contamination or background contributions (Wang, 2006).

Supporting electrolytes are needed especially in controlled-potential experiments to diminish the resistance of the solution, reduce electromigration effects, and keep a constant ionic strength (Wang, 2006). At the electrodes always occur the productions or the consumptions of ions during electrochemical reaction, and the supporting electrolyte provides the pathway for the flowing ions between and among electrodes for maintenance of charge balance (Zoski, 2007).

1.6 Cyclic Voltammetry

Cyclic voltammetry (CV), as one of the electrochemical methods, is seldom used for quantitative purpose, but is essentially used to gain qualitative information about electrochemical reactions in various conditions, such as the thermodynamics of redox processes, the reaction intermediates, the stability of reaction products, the kinetics of heterogeneous electron transfer reactions, the coupled chemical reactions and the adsorption processes (Settle, 1997; Wang, 2006). In addition, by CV, complex chemical systems such as electrodes modified with film or particulate deposits can be studied quantitatively (Scholz, 2010).

In organic and inorganic chemistry, cyclic voltammetry is commonly used as the first experiment for investigation of a system with electroactive species. The CV extends a quick location of redox (reduction-oxidation) potentials of the electroactive species, and appropriate evaluation of the effect of media on the redox process (Skoog, Holler, & Crouch, 2007; Wang, 2006). For instance, CV has been used to study the behavior of the modified electrodes (Bianchini, Curulli, Pasquali, & Zane, 2014; Pourbeyram, 2014; Sharifi, Salimi, Shams, Noorbakhsh, & Amini, 2014; Yang et al., 2014; Zhang et al., 2014).

Electrochemical cell is normally used in the experiment to record cyclic voltammograms. Electrochemical cell in the CV requires three electrodes, namely, reference electrode, auxiliary (counter) electrode and working electrode. All of these electrodes are immersed in the solution and are connected to a potentiostat. The reference electrode that is commonly used is aqueous Ag/AgCl, which can simply be made in the laboratory or can be obtained commercially. The counter electrode should be non-reactive material, such as platinum wire. The function of the potentiostat is to control the potential difference between the reference and the working electrode by minimizing IR (ohmic) drop (Scholz, 2010).

A triangular waveform is used in CV that consists of scanning linearly the potential of a stationary working electrode (Wang, 2006). A scan that runs to more positive potentials is called a forward scan, and a scan that runs to more negative potentials is called a reverse scan (Skoog et al., 2007). Single or multiple cycles can be chosen depending on the necessary information. Measuring the resulting current from the applied potential by potentiostat, occurs when the potential is sweep. The plot of resulting current and potential is called a cyclic voltammogram (Wang, 2006). In cyclic voltammogram, a forward scan is the anodic side, and a reverse scan is the cathodic side (Böckris, Reddy, & Gamboa-Aldeco, 2002).

Cyclic voltammogram has important parameters, such as the cathodic peak potential (E_{pc}), the anodic peak potential (E_{pa}), the cathodic peak current (I_{pc}) and the anodic peak current (I_{pa}) (Skoog et al., 2007). Cyclic voltammogram that is shown in Figure 1.3 depicts the reversible of the redox process with two peaks, the first one is the anodic peak (corresponding to the oxidation of analyte) and the second one is the cathodic peak (corresponding to the reduction of analyte) (Eggins, 2002).

The redox process is represented by Equation 1.1, where O is the oxidized species, R is the reduced form and n is the number of electrons transferred. The reaction from the left to the right is a reduction, and in the opposite direction is an oxidation. The process which involves an electron transfer of the analyte species at the electrode surface is called faradic process, and the corresponding current is called faradic (Švancara, Kalcher, Walcarius, & Vytřas, 2012).

$$O + ne^- \leftrightharpoons R \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.1)$$

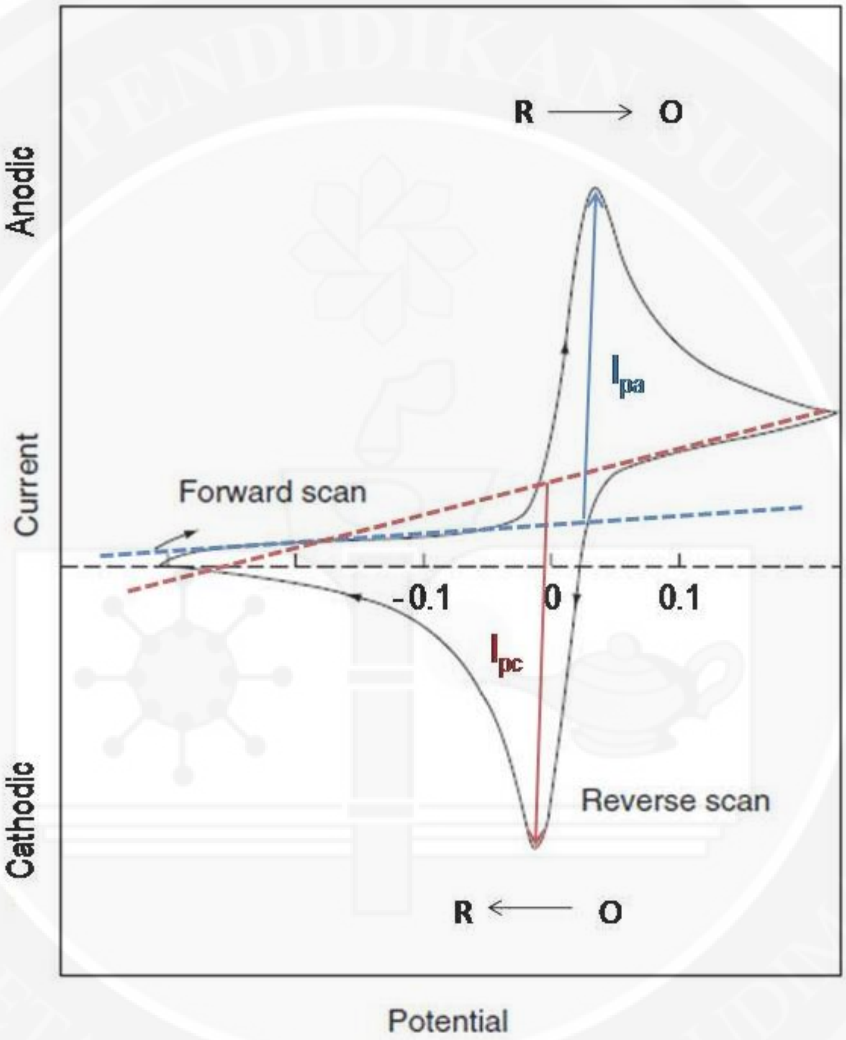

Figure 1.3. Cyclic voltammogram for a reversible redox process (Wang, 2006).

For a reversible process in CV, the formal reduction potential (E^0) is given by Equation 1.2. The difference in peak potential (ΔE_p) of reversible process is given by Equation 1.3, where n is the number of electrons involved in the half-reaction (Settle, 1997). The value of ΔE_p can be used to determine the amount of electrons transferred, where a fast one-electron process shows a ΔE_p of about 59 mV (Wang, 2006).

$$E^0 = \frac{E_{pc} + E_{pa}}{2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1.2)}$$

$$\Delta E_p = |E_{pa} - E_{pc}| = \frac{0.0592}{n}\ \text{V} \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1.3)}$$

The peak current of a reversible process is given by the Randles–Sevcik equation (Equation 1.4), where I_p is the peak current (A), A is the electrode area (cm^2), D is the diffusion coefficient (cm^2/s), c is the concentration (mol/cm^3) and v is the scan rate (V/s) (Skoog et al., 2007). Thus, the current is directly proportional to concentration and increases with the square root of the scan rate. Dependence of the current on the scan rate indicates that electrode reaction is controlled by mass transport. Values of the current peaks are gained by extrapolating the preceding baseline current (Wang, 2006).

$$I_p = 2.686 \times 10^5 n^{3/2} A c D^{1/2} v^{1/2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1.4)}$$

If the irreversible process occurs, the E_{pc} and the E_{pa} will be widely separated, therefore the ΔE_p is more than 0.056/n. The irreversible process shows a sluggish electron exchange. Furthermore, totally irreversible process can be investigated from the different or distorted peak shape, and indicates the further reaction of the initially formed reduction product (Eggins, 2002). Intermediate situation between reversible and irreversible is called quasi-reversible which the current is controlled by the charge transfer and mass transport. Cyclic voltammogram of a quasi-reversible process shows a larger separation in peak potentials compared to a reversible process (Wang, 2006).

1.7 Working Electrode

Working electrode is the electrode where the electrochemical process takes place. In voltammetry, the potential of the working electrode is controlled versus a reference electrode using a potentiostat. So that, the current can flows among the working and auxiliary electrodes, and none of the current flows through the reference electrode (Scholz, 2010).

Material of the working electrode has an influence in gaining a good performance of the voltammetric measurement. The working electrode should provide a reproducible response, therefore the redox behavior of the analyte and the background current over the potential area must be considered. Several materials have been applied as working electrode for electrochemical analysis, such as mercury, carbon and noble metals (especially platinum and gold) (Wang, 2006).

A number of criteria must be noted in the selection of the material for working electrode. Firstly, the electrode should provide an appropriate potential window for the relevant electrochemical reaction. Secondly, the electrode material must allow the chemical reaction occurs as low an over potential as possible. Thirdly, the electrode material has the possibility of the surface modification to build up the sensing layer. The potential range where the electrode can be polarized is called the working window of the electrode. Only in the working window, the measurement can be performed (Banica, 2012).

1.7.1 Mercury Electrode

Mercury may be considered as an ideal electrode material. It displays a very negative electrode potential in the potential scan because of high over potential for releasing hydrogen. There are several physical and chemical properties that represent the excellence of mercury as an electrode, including, it is liquid at room temperature, it can be easily purified, its surface is smooth and may be continuously renewed, it has a high interfacial tension, its surface is hydrophobic and it forms amalgams with a wide range of heavy metals (Bagotsky, 2006; Kozin & Hansen, 2013; Scholz, 2010). On the other hand, there are disadvantages in the usage mercury as working electrode. The mercury must be very pure by six-time distillation. The mercury vapors are toxic. Moreover, after using the mercury electrode, it must be recovered and recycled (Rouessac & Rouessac, 2007).

Several types of mercury electrode that are commonly used include the dropping mercury electrode (DME) and the hanging mercury drop electrode (HMDE). DME is the traditional mercury electrode, i.e., a drop which is periodically produced and dispatched at the tip of a glass capillary that is immersed in an electrolyte solution. Mercury flows from a reservoir through a capillary and forms drops due to its high interfacial tension. The surface which is clean and continually renewed is the important advantage of the DME (Scholz, 2010). Besides, it is difficult to control the drop time outside the range of 0.5-10 seconds (Bard & Faulkner, 2001).

HMDE is the mercury electrode which the drop time can be controlled in the wide range either by manual or by electronic control. In the HMDE, stationary mercury drops are displaced from a reservoir through a vertical capillary. The mercury reservoir must be totally filled with mercury and free of air (Scholz, 2010; Wang, 2006). The HMDE is mostly used for stripping and cyclic voltammetry (Dar, Brahman, Tiwari, & Pitre, 2012; Giannakopoulos, Deligiannakis, & Salahas, 2012; Koniari & Avranas, 2011; Nagles, Arancibia, & Ríos, 2012; Rodrigues et al., 2011). Modern HMDE allows controlling the mercury drop (time and size) electronically by a solenoid-activated valve, which gives improvement of reproducibility and stability (Wang, 2006).

1.7.2 Metal Electrode

Gold and platinum are good materials for electrode fabrication due to their chemical stability. Metal electrodes display fast electron transfer kinetics for a lot of redox systems, and they have a wide anodic potential window. In the contrary, cathodic potential window is limited owing to the low hydrogen overvoltage. The existence of surface oxides or adsorbed hydrogen layers can affect the electrode reaction kinetics and mechanism for definite redox systems; as a result this can cause variability in the electrochemical measurement. Gold electrode is better than platinum electrode because it is more inert than platinum electrode. Therefore gold electrode is more resistant from the formation of stable oxide films or surface contamination. Metal electrodes are commonly used for stripping measurement of trace metals (Wang, 2006; Zoski, 2007).

Platinum electrode is suitable for studying various adsorption processes in electrochemical measurement (Attard et al., 2013; Ensafi, Allafchian, Saraji, & Farajmand, 2012; Gilman, 2013; Gilman, 2014; Masuda, Sonsudin, Singh, Naohara, & Uosaki, 2013). It has a surface which is very stable and reproducible (Bagotsky, 2006). Besides, platinum is not an ideally inert electrode in all media. Therefore, testing of the background current and determination the limits of the working window in the electrolyte (without analyte) are important before measurement of the analyte sample is done. Before the measurement, the surface of platinum electrode should be electrochemically cleaned by polarizing the electrode with cyclic voltammetry or square wave voltammetry. This polarizing process works in the potential range from the formation of the oxide layer to the potential of evolution of hydrogen (Scholz, 2010).

Gold electrode, like platinum electrode, also forms stable oxide layer on the anodic polarization before oxygen evolution. This stable oxide layer can be totally reduced to the bare metal during the cathodic sweep. Nevertheless, the existence of chloride and cyanide anions can easily cause corrosion at the gold electrode (Scholz, 2010). Gold electrode has been widely used in the electrochemical measurements to determine of trace metals (Bernalte, Sánchez, & Gil, 2011; Daud, Yusof, & Nor 2013;

Daud, Yusof, & Tee, 2011; Giacomino, Abollino, Malandrino, & Mentasti, 2008; Korolczuk & Rutyna, 2008; Okçu, Ertaş, & Ertaş, 2008; Wei, Yang, Chen, Gao, & Li, 2014).

1.7.3 Glassy Carbon Electrode

Glassy carbon (GC), also called vitreous carbon, is one of the carbon electrode that is mostly used in electrochemical analysis (Fink & Mandler, 2010; Fu et al., 2011; Fu et al., 2012; Gong, Zhou, Song, & Zhang, 2010; Radhi, Tan, Ab Rahman, & Kassim, 2010; Xu et al., 2008; Yi, 2003). GC is available as rods, disks or plates, which is hard and microstructurally isotropic. It is impermeable to gases and liquids with slightly lower electrical and thermal conductivity (Zoski, 2007).

Popularity of the GC usage as working electrode is due to its excellent electrical and mechanical properties, wide range of potential window, chemical inertness (solvent resistance) and relatively reproducible (Wang, 2006). The surface of GC is gradually deactivated when exposed to the atmosphere or when used in the electrochemical measurement. Hence, pretreatment is important to activate and to reproduce the surface of GC. This polishing will enhance its analytical performance. Polishing provide a new surface by cleaning and removing the memory effect. Mechanical polishing by alumina particles is the common method to activate the GC surface. After mechanical polishing, the surface should be rinsed with deionized water before use, because the remnants of alumina particle will be remained on the surface and influence the electrochemical properties. For the best result, the electrode must be used immediately after the polishing (Wang, 2006; Zoski, 2007).

1.7.4 Carbon Fiber Electrode

Carbon fiber is grown in the electroanalysis as microelectrodes (with diameters 5–30 μm) (Wang, 2006). Pitch and lignin are some of starting materials for manufacturing of carbon fiber electrode. Each material will possess different chemical compositions (Zoski, 2007). Carbon fiber is produced as high-strength composites by high-temperature pyrolysis of polymer textiles or via catalytic chemical vapor deposition. Different fabrication processes will produce different carbon fiber microstructures (Wang, 2006). If the pyrolysis temperature increases, the fiber will enrich with carbon and the microstructure becomes more graphitized (Zoski, 2007). They can be categorized into three modulus types, namely, low, medium and high. The high modulus type is the most suitable for electrochemical analysis due to low porosity and well-ordered graphite-like structure. Several electrode pretreatments can be employed to improve electron transfer performance, such as mild and strong electrochemical activations, and heat treatment (Wang, 2006).

The important advantage of carbon fiber electrode is its small size which gives a good performance in the anodic measurements in several microenvironments (Wang, 2006). Moreover, it has a faster response time and a low background current owing to the smaller exposed area (Zoski, 2007).

1.7.5 Carbon Paste Electrode

Carbon paste electrode (CPE) has been reported as an electrode with very low background current in the electrochemical measurements (Švancara et al., 2012). Fabrication of CPE is by mixing graphite powder with a binder (pasting liquid), and packed in insulator holder (Banica, 2012). Electronic conductivity is gained from the contact between analytes and graphite microparticles, whilst the binder ensures the compactness of the mixture (Scholz, 2010). Graphite is the most commonly used for preparations of CPEs, but other carbonaceous materials can also be used, such as activated carbon, glassy carbon powder, carbon nanofibers, fullerenes, ordered mesoporous carbon and carbon nanotubes (Švancara et al., 2012).

Beside the graphite powder, the binder also has an important role in the preparation of CPE which influences the properties of the resulting paste. The most commonly used as binder materials is mineral oils. Mineral oils, such as nujol and paraffin oil, is chosen because it fulfills the important criteria, including chemically inert, nonvolatile, insulating, water-immiscible and forming fine paste mixture (Švancara, Vytřas, Barek, & Zima, 2001). Reactivity of the electrode is greatly influenced by paste composition. Increasing amount of mineral oil will decrease the electron transfer rates (Wang, 2006).

CPE is one of the great electrodes in the electrochemistry since it is low cost, its surface can be easily renewed by simple polishing and the electrode material is easy to regenerate (Banica, 2012; Švancara et al., 2012; Wang, 2006). In comparison to the other conventional solid carbon electrodes such as glassy carbon, CPE shows better properties, involving the graphite powder which has randomly exposed edge and basal plane which electrochemically reactive, CPE has a wide potential window and an efficient mass transport of electroactive species due to radial diffusion of carbon particles (McCreery, 2008).

1.8 Carbon Nanotube

Recent years, carbon nanotube (CNT), as an allotrope of carbon, has a great attention in the group of nanomaterials due to its unique geometric, mechanical, electronic and chemical properties (Wang, 2006). CNT is a graphene sheet rolled into a cylinder, therefore the carbon atoms in the nanotube are all sp^2 hybridized (Tuantranont, 2013). CNTs can be categorized into two classes: single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT). SWCNT is formed by one cylindrical graphite sheet, while MWCNT is formed by collection of SWCNTs with different diameters (Zhang, Ju, & Wang, 2008). They have a high aspect ratio (the ratio of longer dimension to shorter dimension), so they are categorized as one-dimensional nanomaterials (Khanna, 2012). MWCNT is a conductor material with electrical conductivity better than metal, whereas the electronic property of SWCNT can be like metal or semiconductor depending on the tube diameter and chirality (Tuantranont, 2013). MWCNT has a great tensile strength and breaking strain due to the covalent sp^2 bonds between the carbon atoms which are stronger than the sp^3 bonds in diamonds, as a result it is much stronger than steel. Interactions between nanoparticles of CNTs involve Van der Waals forces that yield a rope-like structure (Khanna, 2012).

The CNT is popular in the electrochemical study, especially in the usage as electrode material due to its properties which include good electronic conductivity, rapid electron transfer kinetics, high sensitivity and low limit of detection. Electrochemical sensors based on CNT offer fast response owing to the signal enhancement provided by low overvoltage, large surface area and rapid electrode kinetics. Moreover, CNT is proper for electrode material because it is small, straight and strong, and it also has a good chemical stability (Campbell & Compton, 2010; Gao, Guo, Liu, & Huang, 2012; Hernández-Santos, González-García, & García, 2002; Jacobs, Peairs, & Venton, 2010; Vashist, Zheng, Al-Rubeaan, Luong, & Sheu, 2011; Wanekaya, 2011; Yáñez-Sedeño, Pingarrón, Riu, & Rius, 2010).

There are three ways to construct CNT as an electrode, namely, it can be made like carbon paste electrode, can be attached to an electrode surface and can be fabricated into a microelectrode (Zoski, 2007). It is suitable to make CNT as carbon nanotube paste electrode (CNTPE) using some binders such as mineral oil, Teflon, or ionic liquids, because it has low solubility in most common solvents (Yáñez-Sedeño et al., 2010). According to the high surface area of CNT, it is possible to make a stable and robust paste electrode by adding high amounts of mineral oil, which is not possible when applied in the preparation of conventional CPE using graphite powder because the CPE will leak into the solution (Merkoçi et al., 2005). CNTPE retains the properties of conventional CPE such as low background current, can be incorporated with other substances, easy preparation and rapid renewal of the surface (Devnani & Satsangee, 2013; Rivas et al., 2009; Rubianes & Rivas, 2003).

1.9 Chemically Modified Electrode

The term chemically modified electrode (CME) is usually understood as a coating by a conducting or semiconducting material that changes the properties of the interface such as electrochemical and optical. Modification of the electrode surfaces is intended to improve the electrochemical function from the conventional electrode including selectivity, sensitivity, chemical and electrochemical stability (Martín-Yerga, González-García, & Costa-García, 2013; Zoski, 2007). Especially for modification of the carbon electrode surface, it will provide an electrode which is more reproducible, not readily degradable due to surface oxidation reactions and less prone to fouling by impurity adsorption (Bard, Stratmann, & Schäfer, 2007).

The surface of CPEs can be easily incorporated with chemical modifiers (such as solid or molecular catalysts or enzymes), and then called chemically modified carbon paste electrode (CMCPEs). One of the techniques to modify the electrode is by mixing the modifier together with graphite and binder (Švancara et al., 2001; Wang, 2006). The used modifier depends on the redox reaction mechanism (Scholz, 2010). Recently, the types of modifier from organic materials for CPEs have been reported, including polyvinylimidazole (Yildiz, Oztekin, Orbay, & Senkal, 2014), coconut shell (Rajawat, Kumar, & Satsangee, 2014), sodium dodecyl sulfate (Thomas et al., 2014) and maize tassel (Moyo, Okonkwo & Agyei, 2014), and also from inorganic materials, such as copper doped natural montmorillonite (Abbaci, Azzouz, & Bouznit, 2014), ZnO nanoparticle (Seifie-Makrani, Sajjadi, Younesi, & Bagheri, 2014) and Pt-ZrO_2 (electrodiposition of Pt nanoparticles on the ZrO_2 nanoparticles) (Gholivand & Mohammadi-Behzad, 2014).

The CMCPEs have been applied in the determination of organic and inorganic compounds by electrochemical analysis. Catalase enzyme-Au nanoparticles modified CPE has been used to determine hydrogen peroxide (Sistani et al., 2014). CPE modified with poly-beryllon II by electropolymerization method which is selective for determination of pyrocatechol and hydroquinone (Zhou, Tang, Dang, Chai, & Zhang, 2014). Boehmite nanoparticles are mixed with graphite powder and paraffin oil for constructing CMCPE which is sensitive to determine nanomolar piroxicam (Gholivand, Malekzadeh, & Derakhshan, 2014). Using differential pulse anodic stripping voltammetry, CPE modified by TiO_2 nanoparticles and 1,2-bis-[o-aminophenyl thio] ethane ligand has been successfully used to determine cadmium(II) in tap water, Livergol herbal medicine and garden soil aqueous samples (Ramezani, Ghobadi, & Bideh, 2014).

In addition, the same way with CPEs, CNTPEs can also be incorporated with chemical modifiers, then called chemically modified carbon nanotube paste electrode (CMCNTPEs). There are two types of CMCNTPEs, the first one is the modifying agent (M) attached to the surface (M/CNTPE) and the second one is the modifier embedded into the carbon paste bulk (M-CNTPE) (Švancara, 2012). Different modifiers have been employed in the CNTPEs for the voltammetric measurements. CNTPE modified with crosslinked chitosan and glutaraldehyde has been successfully applied to determine lead(II) in natural water using square wave adsorptive stripping voltammetry (Vicentini et al., 2014). Zinc phosphate modified multi-walled CNTPE is low cost electrode for captopril determination in the commercial tablet excipients and biological samples (Janegitz et al, 2014).

Solid modifier (M) which is added to carbon paste will appear on the surface electrode at the certain surface concentration (M_{surf}), and reacts with the analyte (A). This reaction can be described as shown in Equation 1.5, where the subscripts sol is the solution and the subscripts surf is the electrode surface (Švancara et al., 2012).

$$A_{sol} + M_{surf} \leftrightarrow AM_{surf} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ \ (1.5)$$

1.10 Problem Statement

Mercury is known as a substance which is reactive, volatile and soluble in water and living tissues. A human can be contaminated with mercury via respiratory or food chain. If human body is contaminated to mercury, it will be accumulated due to the persistent character of mercury in the living organisms. As the consequence, the human will be risked to get many diseases, such as birth defects, brain and nerve damage, skin rash, neurological damage and mental disabilities. Therefore, mercury is highly toxic even at low levels.

Cold vapor technique is commonly used to determine mercury in the sample. This technique is complicated, expensive and time consuming. The sample must be reduced first using a reducing agent to convert mercuric ions to elemental mercury. Then it is converted to the gas phase by bubbling air through the solution using nitrogen or argon.

An electrochemical technique is needed to solve this problem because it offers simple determination of mercury by direct measurement (without reduced the mercuric ions) to the sample, so it only needs a short time. Besides, this technique has a high sensitivity which is the important thing to determine mercury at low levels. Moreover, this technique has other advantages, such as good selectivity, low cost, ease of data read-out and simple to operate.

1.11 Objectives of Study

The aim of this study is to develop an electrochemical sensor using MWCNT as a paste electrode incorporated with Zn/Al layered double hydroxide-3(4-hydroxyphenil)propionate (Zn/Al-LDH-HPP) nanocomposite as a modifier for the cyclic voltammetric determination of Hg(II).

The objectives of this study are:

1. To investigate the potential of Zn/Al-LDH-HPP modified CNTPE as a selective and sensitive electrode to determine Hg(II) by cyclic voltammetry.
2. To study the optimum experimental conditions to determine Hg(II) using Zn/Al-LDH-HPP modified CNTPE.
3. To apply Zn/Al-LDH-HPP modified CNTPE to determine Hg(II) in real samples.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Mercury is widely distributed in the environment and can exist as elemental mercury (Hg^0), inorganic (Hg^+ and Hg^{2+}) and organic mercury (methylmercury and ethylmercury) (Lemos & dos Santos, 2014) and it is highly toxic even at low levels because of its reactivity, volatility and solubility in water and living tissues (Wiener, Krabbenhoft, Heinz, & Scheuhammer, 2003). Moreover, mercury is able to accumulate in the human body via the food chain owing to accumulative and persistent character of mercury in the living organisms (Pourreza & Ghanemi, 2009). This may pose health risk for human includes birth defects, brain and nerve damage, skin rash (Afkhami, Madrakian, et al., 2012), neurological damage (Zhang, Wang, Zhang, Sun, & Zhang, 2009) and mental disabilities (Clarkson, Magos, & Myers, 2003).

Due to the toxicity and bioaccumulation of mercury, analytical techniques that are sensitive and reliable to determine mercury content in the environmental samples are of great importance. Nowadays the available methods for low levels determination of mercury are complicated, too costly and time consuming (Fu et al., 2012), like inductively coupled plasma mass spectrometry (Iwashita et al., 2007; Kenduzler, Ates, Arslan, McHenry, & Tchounwou, 2012; Pyhtilä et al., 2012), cold vapor atomic absorption spectrometry (Bansal, Vaughan, Boullemant, & Leong, 2014; Londonio, Fujiwara, Rebagliati, Gómez, & Smichowski, 2012; Martinis, Bertón, Olsina, Altamirano, & Wuilloud, 2009; Zhang & Adeloju, 2008), gas chromatography (Nevado, Martín-Doimeadios, Bernardo, & Moreno, 2005) and atomic fluorescence spectrometry (Leopold, Foulkes, & Worsfold, 2009; Zhang, Su, Chu, & Yang, 2010).

On the contrary, electrochemical techniques offer advantages owing to the fact that instrumentations possess high sensitivity, good selectivity, time effectivity, low cost, ease of data read-out and simple to operate. Amongst the electrochemical techniques recently used to determine mercury are potentiometry (Ghanei-Motlagh, Fayazi, & Taher, 2014; Naushad, Rangreez, & Alothman, 2014), cyclic voltammetry (Giannetti, Moreira, Bonilla, Almeida, & Rabóczkay, 2006; Niu, Ding, Chen, Zhao, & Lan, 2011), differential pulse voltammetry (Tchinda, Ngameni, & Walcarius, 2007; Wu et al., 2010), square wave voltammetry (Martín-Yerga, González-García, & Costa-García, 2012; Safavi & Farjami, 2011) , anodic stripping voltammetry (Dal Borgo, Jovanovski, & Hocevar, 2013), square wave anodic stripping voltammetry

(Bernalte, Marín Sánchez, & Pinilla Gil, 2012; Locatelli & Melucci, 2012; Melucci, Locatelli, & Locatelli, 2013) and differential pulse anodic stripping voltammetry (Somerset, Hernandez, & Iwuoha, 2011).

2.2 Cold Vapor Atomic Absorption Spectrometry

Determination of mercury using atomic absorption spectrometry usually employs the cold vapor technique due to its high volatility at room temperature, and this is intended to improve the analytical sensitivity for mercury (Cantle, 1982; Nordberg, Fowler, Nordberg, & Friberg, 2007; Skoog et al., 2007). Moreover, flow injection system in conjunction with cold vapor atomic absorption spectrometry will provide the shorter reaction time compared to batch system (Río Segade & Tyson, 2003). The procedure to determine mercury by cold vapor atomic absorption spectrometry is that the element must be reduced to the metal from this compound and transferred to the vapor phase (Welz & Sperling, 1999). To convert all forms of mercury to mercuric ions (Hg^{2+}) and to eliminate interfering substances, the solid sample must be digested by heating with concentrated acid so that an aqueous form is gained. The common acids used for digestion are HCl, HNO_3 and H_2SO_4 (Bansal et al., 2014). The sample is then treated with a reducing agent, like stannous chloride ($SnCl_2$) or sodium borohydride ($NaBH_4$), for the conversion of mercuric ions to elemental mercury (Hg) (Ahuja & Jespersen, 2006). Mercury is converted to the gas phase by simply bubbling air through the solution. The carrier gas that can be used for this process is nitrogen or argon (Kopysc, Pyrzynska, Garbos, & Bulska, 2000).

Determination of mercury using cold vapor atomic absorption spectrometry has been studied by researchers. Adlnasab et al. (2014) have synthesized new functionalized magnetic nanoparticles as solid-phase sorbent and were applied for extraction of ultra-trace amounts of Hg(II) from environmental samples. The Fe_3O_4 magnetic nanoparticles functionalized with dithizone were evaluated by cold vapor atomic absorption spectrometry and showed advantages for determination of mercury like higher efficiency, higher selectivity, shorter extraction time, lower toxicity, good recoveries and good precision (Adlnasab et al., 2014). Parodi et al. (2014) used oxidized carbon nanotubes in combination with flow injection cold vapor atomic absorption spectrometry for the preconcentration of Hg(II) and exhibited excellent sensitivity as low as ng L^{-1} of Hg(II) in water samples. Chandio et al. (2014) immobilized dithizone on ammonium lauryl sulfate (ALS) alumina adsorbent to extract and preconcentrate trace amounts of mercury from vegetables and ground water. Mercury made complexation with dithizone immobilized on alumina coated with ALS and evaluated by cold vapor atomic absorption spectrometry.

2.3 Electrochemical Methods

2.3.1 Potentiometry

Potentiometry is an analytical method with zero-current, which is based on measurement of the potential established across a membrane to get information about the analyte. Zero-current condition must be fulfilled to ensure that the reaction at the electrode is in equilibrium (Gründler, 2007). Each type of membrane material shows different ion recognition process. Developments types of membrane materials have been done to gain high selectivity (Wang, 2006). Selectivity, as the excellence of potentiometric sensors, is important to guarantee that the sensor only responds to one type of ion (Gründler, 2007). Potentiometric measurements require an ion-selective electrode, a reference electrode and a potential-measuring device (Wang, 2006).

The ion-selective electrode (ISE) is the main component in the potentiometric sensors, and the important part of ISE is the ion-selective membrane which is positioned between two aqueous phases, namely, the inner solutions containing a target ion at a constant activity and the sample (Zoski, 2007). The ISE is an indicator electrode which selectively measures the activity of a certain ionic species. The focus of the ISE is to sense the activity (i.e. effective concentration) rather than the concentration of ions in the solution. The effective concentration of the ion can be reduced by the ionic interactions with oppositely charged ions (Wang, 2006). The response of the indicator electrode should be reversible, fast and followed the Nernst equation (Khalid, 2013). Numerous advantages from the ISE include wide linear range, not influenced by color or turbidity, not destructive and low cost (Wang, 2006). Because of these advantages, the ISEs are commonly used for analysis in medical, environmental and phycology (Zoski, 2007).

Potentiometry has been used as an electrochemical technique to determine mercury. An ion selective membrane based on poly-o-toluidine Zr(IV) tungstate composite cation exchange material fabricated using solution casting method have been used as potentiometric sensor for Hg(II) (Naushad et al., 2014). This electrode with optimized membarane composition exhibited Nernstian response towards Hg(II) ions in the concentration range 1.0 x 10^{-7} – 1.0 x 10^{-1} M with slope of 28.107 mV per decade change in Hg(II) ion concentration. Ghanei-Motlagh et al. (2014) have prepared Hg(II) sensors based on two bis-thioureas, i.e., 4,4'-bis-(3-phenylthiourea)diphenyl methane (L_1) and 2-2-[10-[(E)-2-(aminocarbothioyl) hydrazono]-1,4-dihydroxy-9(10H)-anthracenyliden]-1hydrazinecarbohioamide (L_2). The best potentiometric response were obtained using membrane sensor based on L_2 with a near Nernstion response of 30.3 mV $decade^{-1}$ towards mercury ions over the activity range 1.0 x 10^{-7} – 1.0 x 10^{-2} M and a limit of detection 7.9 x 10^{-8} M. This proposed method can be applied to determine mercury in waste water sample (Ghanei-Motlagh et al., 2014).

2.3.2 Voltammetry

Voltammetry is electrochemical method which studies the measurement of a current in dependence of an applied potential, which changes with time (Švancara et al., 2012). The current is also linearly dependent upon the concentration of the electroactive species (analyte) involved in a chemical or biological process (Khalid, 2013). The resulting current (ordinate) and the potential (abscissa) can be plotted as voltammogram (Wang, 2006).

Voltammetry is commonly used to study the oxidation and reduction processes, adsorption processes and electron-transfer mechanisms in many fields of chemistry like organic, inorganic, physical and biological (Skoog et al., 2007). In the voltammetric methods, a variable potential difference between a reference electrode and a working electrode is applied. When the potential at the working electrode reaches a value wherein the analyte is oxidized or reduced, the current will increase sharply. Besides working and reference electrode, these methods also require auxiliary electrode (or counter electrode) employed along with a supporting electrolyte which is used to make the solution electrically conductive (Rouessac & Rouessac, 2007; Skoog et al., 2007).

Included in the voltammetric methods are cyclic voltammetry, pulse voltammetry and stripping voltammetry. CV is the technique of measuring current as a function of the applied potential (Gründler, 2007). The applied potential is limited from the initial electrode potential E_i to the final electrode potential E_f (Girault, 2010). Usually two peaks will appear in the cyclic voltammogram, the first peak (forward scan) proves the reaction of the substance initially present in solution, and the second peak proves the product of this reaction when the potential scan is reversed (Gründler, 2007). CV is commonly used to study the product of electrochemical redox reactions in the electrode/solution interface (Colomer-Farrarons & Miribel-Català, 2011). Qualitatively, ΔE_p from the CV can be elucidate whether an electrochemical reaction is reversible (limited by diffusion), irreversible (completely limited) or quasi-reversible (limited by kinetics). Quasi-reversible reaction indicates the surface concentration is controlled by kinetics and diffusion (Girault, 2010). Furthermore, reversible reaction usually has the peak currents wherein their heights are almost identical, so that the ratio of peak current (I_{pa}/I_{pc}) = 1 (Gründler, 2007).

The imposition of a potential pulse to the electrode will increase the ratio of the charging and faradaic currents, so pulse methods could be the solution of the limitation of traditional linear-scan voltammetry (Scholz, 2010; Skoog et al., 2007). Amongst the pulse methods mostly used in electrochemistry are normal pulse voltammetry (NPV), differential pulse voltammetry (DPV) and square wave voltammetry (SWV) (Bard et al., 2007; Gründler, 2007). The concept behind the pulse voltammetric methods is to measure the current when the difference between the desired faradaic curve and the interfering charging current is large. Various electrodes can be used in these methods including solid electrodes, HMDE and rotating electrodes (Skoog et al., 2007).

The NPV is based on the imposition of square wave potential pulses of increasing height at a constant (base) potential wherein no reaction of the analyte occurs (Bard et al., 2007; Wang, 2006). During the pulses, if the electrode potential is more negative than the formal potential of the investigated system, product (reduced form) is generated. A reversible electrode reaction occurs when the product is transformed to the substrate (oxidezed species) again, and the initial distribution of the substrate is renewed. When an irreversible electrode reaction occurs, the product cannot be transformed back to the substrate (Scholz, 2010). The current is measured near the end of each pulse which is usually carried out in an unstirred solution (Bard et al., 2007; Settle, 1997). The sampled current is plotted as a function of the potential of the applied pulses to get the normal pulse voltammogram. The reducible and oxidizable species in solution will give rise to a wave characterized by its half-wave potential and limiting current. The limiting current is proportional to the analyte concentration. The detection limit of the NPV method is about 10^{-6} M (Banica, 2012).

In DPV, fixed potential pulse is applied to the working electrode, superimposed by a series of square wave pulses (Eggins, 2002; Wang, 2006). The current is sampled twice, the first is just before the pulse application ($I_{s,1}$) and the second is near the end of the pulse ($I_{s,2}$). The current difference ($\Delta I_s = I_{s,2} - I_{s,1}$) is determined and plotted against the applied (base) potential (Settle, 1997). The double current sampling can eliminate the capacitive (background) current and enables to detect the analytes present in the solution with the limit of close to 10^{-7} M (Scholz, 2010; Banica, 2012). Differential pulse voltammogram consists of current peak and exhibits a symmetrical peak-shaped pattern. The peak height of the differential pulse voltammogram is proportional to the analyte concentration (Banica, 2012).

The SWV is large-amplitude differential technique applied to the working electrode with a potential waveform consists of a square wave superimposed on a base staircase potential (Bard et al., 2007; Wang, 2006). The current is measured at the end of the forward pulse (I_f) and at the end of the reverse pulse (I_b). The difference between these two currents ($I_f - I_b$) is called net current (I_{net}) which is centered on the redox potential, and plotted against the base staircase potential. The peak current is proportional to the concentration of the analyte (Settle, 1997). SWV has four important parameters involving square wave period (τ), pulse duration ($t_p = \tau/2$), step height (ΔE) and pulse height (ΔE_{sw}) (Bard et al., 2007). Several advantages are offered by SWV including low of background currents, rapid analysis and excellent sensitivity as low as 10^{-8} M (Settle, 1997; Švancara et al., 2012; Wang, 2006).

Stripping voltammetry is electrochemical method wherein the analyte is first deposited on the electrode and then removed (stripped) electrochemically while observing the current as a function of the applied potential (Harvey, 2000). According to that definition, stripping voltammetry has two step procedures. The first step, analyte in the sample solution accumulates on the working electrode surface, usually under stirred condition. This preconcentration step is important for gaining excellent sensitivity. The second step, accumulated analyte is stripped from the electrode by applying a potential scan under unstirred condition. Various potential waveforms can be used for the stripping step, usually differential pulse and square wave. During the stripping step, an analytical signal is gained (Gründler, 2007; Settle, 1997). In a special case in which the analyte cannot be concentrated at the electrode surface by electrolysis, the modified electrode can solve this problem by chemical reaction with immobilization as its basis (Švancara et al., 2012). Stripping methods is excellent for trace metal analysis with extremely low detection limit until 10^{-11} M (Banica, 2012). Moreover, these methods have the excellent selectivity and preparation of the sample is minimal (Settle, 1997). Several working electrodes for stripping methods have been applied involving mercury, gold, silver, platinum and various forms of carbon, but the most popular is the HMDE (Skoog et al., 2007). In the stripping voltammetry, three variations used are anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV) and adsorptive stripping voltammetry (AdSV) (Harvey, 2000). ASV is the most widely used to determine metal ions by cathodic deposition into the mercury electrode (or into nonmercury surface) at a controlled time and potential in which the metal ions is reduced and forms amalgam (Girault, 2010).

Recently, voltammetric methods have been widely used to determine trace amounts of mercury. Ding, Liu, Zhai, Bond, and Zhang (2014) proposed the modification of glassy carbon electrode (GCE) by direct electrodeposition of graphene-gold nanoparticles to its surface. This electrode has been used to determine Hg(II) using ASV. The results showed high selectivity and sensitivity with linear range of 1.0 to 150.0 nM and limit of detection 0.6 nM. GCE modified with dithiocarbamate functional group on polypyrrole modified carbon sphere has been utilized for the selective detection of mercury via linear sweep voltammetry and DPV (Devi, Devasena, Saratha, Tharmaraj, & Pandian, 2014). Under optimized condition, trace levels of mercury can be determined in water samples. Zhou, Chen, Li, and Chen (2013) modified indium tin oxide electrode with graphene oxide, gold nanoparticles and 5-methyl-2-thiouracil. Using DPV, this electrode is very sensitive to detect Hg(II) ion in the linear range of 5.0 – 110.0 nM with limit of detection 0.78 nM.

Guha, Mascarenhas, Thomas, and D'Souza (2014) used CV to study the electrochemical behavior of Hg(II) in CPE modified with poly(Eriochrome Black T). The experimental conditions, such as the concentration of electrolytes, pH, the deposition time, and the deposition potential, were optimized to gain maximum current in the detection of Hg(II) by differential pulse anodic stripping voltammetry (DPASV), therefore a good linear response at low concentration of Hg(II) could be reached in the range 1.0×10^{-8} to 1.0×10^{-7} M and 2.0×10^{-7} to 1.0×10^{-6} M with detection limit of 2.2×10^{-10} M. This electrode has been successfully employed to determine pollutant Hg(II) in the environmental samples. CPE has also been modified with water hyacinth (Eichhornia Crassipes) to determine mercury in aqueous samples (Rajawat, Srivastava, & Satsangee, 2012). The voltammetric responses in the detection of Hg(II) were studied by DPASV and linear range from 400 μgL^{-1} to 800 μgL^{-1} of mercury with limit of detection 195 μgL^{-1} were obtained.

2.4 Chronocoulometry

Chronocoulometry, as a step technique, is a measurement of the time dependence of the flow of charge. In this technique, the experiment starts at a potential where no reaction is occurring and stepped instantaneously to a potential where either the oxidation or reduction occurs. For double-steps chronocoulometry, the reduced form of the redox couple still in the vicinity of the electrode following the forward step can be re-oxidized to the original material during the reverse potential step. The charge measured during this step is then plotted in a charge (Q) vs. square root of time ($t^{1/2}$) graph (Suroviec, 2013).

In the double-steps chronocoulometry, the first step potential is sufficiently negative of the redox potential that all of oxidized species (O) at the electrode surface is instantaneously reduced to reduced form (R) on application of this potential. If the potential is now stepped back to the initial potential, all R at the electrode surface is now converted back to O, and additional R is reoxidized as it diffuses back to the electrode surface.

Charge (Q) is obtained by integrating the current (I) during the potential step. For diffusion only, the charge observed following a potential step to a point significantly more negative (for a reduction) of the formal redox potential is described by the integrated Cottrell equation, known as the Anson equation (Equation 2.1). The Anson equation can be used to calculate A, D, n, and C based on the slope of the Q vs. $t^{1/2}$ plot which called the Anson plot,

$$Q = 2\ n\ F\ A\ C_0\ D_0^{1/2}\ t^{1/2}\ \pi^{-1/2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.1)$$

where n, F, A, C, and D are the number of electrons transferred per ion (eq/mol), Faraday constant (96,485 C/eq), electode surface area (cm^2), concentration of analyte in solution (mol/cm^3) and diffusion coefficient of the analyte (cm^2/s), respectively (Scholz, 2010).

The amount of adsorbed species (mol) on the surface of electrode (cm^{-2}) is defined as surface coverage (Γ) that is important to be determined in the chronocoulometric experiment. The value of the surface coverage can be estimated from Q_{ads} using Equation 2.2 (Scholz, 2010).

$$Q_{ads} = n\ F\ A\ \Gamma \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.2)$$

CHAPTER 3

METHODOLOGY

3.1 Chemical and Reagents

Chemicals and reagents used in this research were analytical grade without any further purification. MWCNT was obtained from Timesnano with purity more than 95%. The zinc/aluminium layered double hydroxide-3(4-hydroxyphenyl)propionate (Zn/Al-LDH-HPP) nanocomposite was synthesized according to the literature (Ahmad et al. 2014). Paraffin oil was purchased from Sigma-Aldrich. Sodium hydroxide (NaOH) was purchased from Sigma-Aldrich and CH_3COOH was purchased from Merck in which both of them were used for pH adjustments. Stock solution of mercury ion was prepared daily by dissolving appropriate amount of $HgCl_2$ obtained from Merck in deionized water. Solutions of supporting electrolytes were prepared by dissolving amount of KCl, LiCl and CH_3COONa supplied by Merck, and NaCl supplied by

Sigma-Aldrich in deionized water. Solutions of metal ions were prepared by dissolving amount of $NiCl_2.6H_2O$, $CaCl_2.2H_2O$, $MgCl_2.6H_2O$ and $ZnCl_2$ purchased from Merck, $BaCl_2.2H_2O$, $CdCl_2.5H_2O$, $SrCl_2.6H_2O$ and $CoCl_2.6H_2O$ purchased from Sigma-Aldrich, and $MnCl_2.4H_2O$ purchased from Fluka in deionized water.

3.2 Instrumentations

Dionized water used for preparation of solutions was from EASY pure LF, Barnstead (USA). Electrochemical data were obtained with a three-electrode system using a Gamry Potentiostat Series-G750 (USA). A saturated Ag/AgCl electrode supplied from BASi (USA), a platinum wire and CNTPEs (unmodified and modified) were used as the reference, counter and working electrodes, respectively. All pH measurements were accomplished with a digital pH-meter, Orion model 915600, Mass (USA), equipped with a glass electrode. The metal ion concentrations of sample solutions were determined using Mercury Analyzer model Perkin-Elmer, Mercury Analysis System FIMS 100. A Fourier transform infrared (FTIR) spectrum of Zn/Al-LDH-HPP, Zn/Al-LDH-HPP modified CNTPE and CNTPE were recorded by Nicolet model 6700 in the range of 500 – 4000 cm^{-1} using KBr disc method. Surface morphology of the Zn/Al-LDH-HPP modified CNTPE was observed by field emission scanning electron microscope (FESEM) model Hitachi SU 8020 UHR.

3.3 Preparation of Unmodified and Modified CNTPE

In order to prepare unmodified CNTPE, MWCNT and paraffin oil were mixed until obtaining a uniform paste (ratio of CNT: paraffin, 75:25, % w/w). Nanocomposites Zn/Al-LDH-HPP (modifier) in composition ratios (% w/w) of 2.5, 5.0, 7.5, and 10.0; were added to the pastes and mixed to produce the final modified CNTPEs. Both unmodified and modified CNTPEs were finally obtained by packing the pastes into the Teflon cylindrical tubes (i.d. 2.8 mm) and arranged with copper wires serving as the external electric contacts. The electrode surfaces were polished on the filter papers to get smooth, uniform and fresh surfaces before each measurement.

3.4 Cyclic Voltammetric Measurements

For all measurements, the three electrodes namely reference electrode, counter electrode and working electrode (unmodified or modified CNTPE) were immersed in a 50 mL beaker containing 2.0 x 10^{-4} M Hg(II) at room temperature (± 25^{o}C), and the solution was stirred using a magnetic stirrer during the measurement. A Hg(II) solution was prepared by dissolving 27.15 mg mercury dichloride ($HgCl_2$) (molecular weight of 271.52 g/mol) in deionized water in a 500 mL volumetric flask. The solutions were degassed for 15 minutes before every measurement by bubbling with nitrogen gas to eliminate the dissolved oxygen. The pH of the solutions containing Hg(II) was adjusted at 5.0 by acetic acid and sodium hydroxide. The signal of the accumulated unmodified and modified CNTPEs were measured using cyclic voltammetric by scanning the potential from -0.6 to +0.6 V versus Ag/AgCl with a scan rate of 100 mV s^{-1} performed in each solution.

3.5 The Effect of Percentage of Modifier

The effect of the amount of Zn/Al-LDH-HPP nanocomposite on the voltammetric response of modified CNTPE was investigated by preparing several electrodes with the constant mass of MWCNT which were mixed with different mass of the Zn/Al-LDH-HPP. Various composition of the Zn/Al-LDH-HPP nanocomposites in the MWCNT were prepared with four ratios, i.e., 2.5, 5.0, 7.5 and 10.0 (% w/w).

For all electrodes, MWCNTs (0.15 g) were weighed and mixed with the amount of Zn/Al-LDH-HPP that is given in the Table 3.1. Paraffin oils were also added in the mixtures until obtaining the uniform pastes. The mixtures were then packed into the Teflon cylindrical tube and arranged with copper wire.

Each of Zn/Al-LDH-HPP modified CNTPEs was immersed in the beaker containing mercury solution with concentration of 2.0 x 10^{-4} M and 0.5 M KCl as supporting electrolyte at pH 5.0. Voltammetric measurement was carried out by scanning the potential from -0.6 to +0.6 V versus Ag/AgCl with a scan rate of 100 mV s^{-1}. The resulted I_{pa} was observed and then plotted against the percentage of Zn/Al-LDH-HPP. The optimum percentage of Zn/Al-LDH-HPP was then determined to be employed in subsequent experiments.

Table 3.1

Weight of Zn/Al-LDH-HPP nanocomposites for the preparation of modified CNTPEs

Percentage (%)	Weight of Zn/Al-LDH-HPP (g)
2.5	0.0038
5.0	0.0075
7.5	0.0112
10.0	0.0150

3.6 The Effect of Supporting Electrolyte

The effect of supporting electrolyte in the Hg(II) determination was studied in different types of supporting electrolyte (KCl, LiCl, NaCl and CH_3COONa). Mercury dichloride (27.15 mg) and KCl were dissolved in deionized water in a 500 mL volumetric flask to get the concentration of 2.0 x 10^{-4} M for Hg(II) and 0.5 M for KCl. This method was also applied for other supporting electrolytes. The supporting electrolytes which were weighed are given in the Table 3.2. The voltammetric measurement of 2.0 x 10^{-4} M Hg(II) at the Zn/Al-LDH-HPP modified CNTPE with optimum percentage of modifier was done for each type of supporting electrolytes by scanning the potential from -0.6 to +0.6 V versus Ag/AgCl with a scan rate of 100 mV s^{-1}. Supporting electrolyte showing the best response was chosen to be applied in subsequent experiments.

3.7 The Effect of pH

The effect of the solution pH to the voltammetric response of Zn/Al-LDH-HPP modified CNTPE was studied in the pH range between 2.0 and 8.0. The pH value of the solution containing 2.0 x 10^{-4} M Hg(II) and supporting electrolyte which was chosen at the previous experiment was adjusted by adding a small amount of CH_3COOH for acid values and 0.1 M NaOH solution for base values. The NaOH solution was prepared by dissolving 0.20 mg NaOH (molecular weight of 40.00 g/mol) in deionized water in a 50 mL volumetric flask.

Table 3.2

Weight of salts required for the preparation of supporting electrolyte solutions

Salts	Molecular weight (g/mol)	Weight of salt (g)
KCl	74.55	18.64
LiCl	42.39	10.60
NaCl	58.44	14.61
CH_3COONa	82.03	20.51

Voltammetric measurements were then investigated for each pH values using Zn/Al-LDH-HPP modified CNTPE with optimum percentage of modifier by scanning the potential from -0.6 to +0.6 V versus Ag/AgCl with a scan rate of 100 mV s^{-1}, and the resulted anodic peak current (I_{pa}) was then plotted against the pH value. The optimum pH was then selected for subsequent experiments.

3.8 The Effect of Scan Rate

The effect of scan rate to the voltammetric response of Zn/Al-LDH-HPP modified CNTPE was studied in various scan rates. Cyclic voltammetric measurements were carried out in the solution containing 2.0 x 10^{-4} M Hg(II) with optimum conditions of modifier percentage, supporting electrolyte and pH by varying scan rate from 20 to 100 mV s^{-1} and 100 to 500 mV s^{-1}. The resulted I_{pa} was observed in the variation of scan rate. The scan rate with optimum I_{pa} was applied for subsequent experiments.

3.9 The Effect of Electrode Regeneration

Several cleaning solutions involving 0.1 M of NH_4Cl, 0.1 M of HCl, 0.1 M of HNO_3, 0.1 M of $NaNO_3$ and H_2O were used to observe the effect of electrode surface regeneration in the voltammetric measurements. The Zn/Al-LDH-HPP modified CNTPE was immersed in the solution containing 2.0 x 10^{-4} M Hg(II) and 0.5 M KCl, and then voltammetric measurement was done under optimum experimental conditions. After the measurement, the Zn/Al-LDH-HPP modified CNTPE which had adsorbed Hg(II) at its surface was immersed in the cleaning solution and then the voltammetric measurement was done again with the same conditions as previous. Besides the cleaning solutions, the mechanical polishing was also used to observe the effect of the electrode surface regeneration in the voltammetric measurements. Firstly, the voltammetric measurement was done with the same way as applied in the cleaning solutions. After the measurement, the Zn/Al-LDH-HPP modified CNTPE which had adsorbed Hg(II) at its surface was polished and then the voltammetric measurement was done again with the same conditions as previous.

3.10 Chronocoulometry Studies

The three electrode, namely Ag/AgCl electrode, platinum electrode and Zn/Al-LDH-HPP modified CNTPE with optimum percentage of modifier were immersed in the solution containing 2.0 x 10^{-4} M Hg(II) and 0.5 M of supporting electrolyte with the optimum pH. The process involved in chronocoulometry is diffusion which only used mode of mass transport requiring a quiescent solution, therefore this experiment was carried out in unstirred condition. The double potential-steps chronocoulometric measurements were then carried out with the initial potential steps from -1.10 V to 1.10 V versus Ag/AgCl.

3.11 Interference Studies

Several metal ions, such as Ni(II), Ba(II), Ca(II), Cd(II), Mn(II), Sr(II), Co(II), Mg(II) and Zn(II) were selected to investigate the influence of interference to the voltammetric response of Zn/Al-LDH-HPP modified CNTPE with 10 and 25-folds (2.0 x 10^{-3} M and 5.0 x 10^{-3} M). Stock solution of Hg(II) with concentration of 2.0 x 10^{-3} M was prepared by dissolving 0.27 g $HgCl_2$ (molecular weight of 271.52 g/mol) in deionized water in a 500 mL volumetric flask, then 10 mL of this solution was transferred in a 100 mL volumetric flask. The amount of salt was weighed and dissolved in deionized water, then also transferred in a 100 mL volumetric flask. The volumetric flask containing 10 mL of Hg(II) and salt was then added with dionized water until 100 mL. The amount of salt weighed for the preparation of 100 mL of 2.0 x 10^{-3} M and 5.0 x 10^{-3} M interfering ions solution is given in Table 3.3 and Table 3.4, respectively. Voltammetric measurements of 2.0 x 10^{-4} M Hg(II) were done with the presence of the interfering ions at the optimum experimental conditions. The resulted I_{pa} from the Hg(II) solution with the presence of the interfering ions was compared to the resulted I_{pa} from Hg(II) solution without interfering ions.

Table 3.3

Weight of salts required for the preparation of 2.0 x 10^{-3} M interfering ion solutions

Salts	Molecular weight (g/mol)	Weight of salt (mg)
$NiCl_2.6H_2O$	237.70	47.54
$BaCl_2.2H_2O$	244.26	48.85
$CaCl_2.2H_2O$	147.02	29.40
$CdCl_2.5H_2O$	228.36	45.67
$MnCl_2.4H_2O$	197.91	39.58
$SrCl_2.6H_2O$	266.62	53.32
$CoCl_2.6H_2O$	237.93	47.59
$MgCl_2.6H_2O$	203.30	40.66
$ZnCl_2$	136.28	27.26

Table 3.4

Weight of salts required for the preparation of 5.0 x 10^{-3} *M interfering ion solutions*

Salts	Molecular weight (g/mol)	Weight of salt (mg)
$NiCl_2.6H_2O$	237.70	118.85
$BaCl_2.2H_2O$	244.26	122.13
$CaCl_2.2H_2O$	147.02	73.51
$CdCl_2.5H_2O$	228.36	114.18
$MnCl_2.4H_2O$	197.91	98.96
$SrCl_2.6H_2O$	266.62	133.31
$CoCl_2.6H_2O$	237.93	118.96
$MgCl_2.6H_2O$	203.30	101.65
$ZnCl_2$	136.28	68.14

3.12 Calibration Curve, Limit of Detection, Repeatability and Reproducibility

Different concentration of Hg(II) solutions from 1.0 x 10^{-3} M to 1.0 x 10^{-10} M were used for construction of calibration curve and determination of detection limit. Firstly, the Hg(II) solution with concentration of 1.0 x 10^{-2} M was prepared by dissolving 0.27 g $HgCl_2$ (molecular weight of 271.52 g/mol) in deionized water in a 100 mL volumetric flask.

Then, the Hg(II) solution with concentration of 1.0 x 10^{-3} M was prepared by transferring 10 mL of 1.0 x 10^{-2} M Hg(II) in a 100 mL volumetric flask and the deionized water was added until 100 mL. This dilution method was also employed for the preparation of the Hg(II) solution with concentration of 1.0 x 10^{-4} M - 1.0 x 10^{-10} M. The voltammetric measurements of the 1.0 x 10^{-3} M - 1.0 x 10^{-10} M Hg(II) were done under optimum experimental conditions, and the resulted I_{pa} was plotted against the Hg(II) concentration to construct the calibration curves.

The repeatability of the Zn/Al-LDH-HPP modified CNTPE was evaluated by performing five measurements of 2.0 x 10^{-4} M Hg(II) under optimum experimental conditions. For the reproducibility study of the Zn/Al-LDH-HPP modified CNTPE, four electrodes were prepared in a completely same manner and they were used for determination of 2.0 x 10^{-4} M Hg(II) under optimum experimental conditions.

3.13 Determination of Hg(II) in Real Samples

To evaluate the applicability of the proposed method for the analysis of real samples, the Zn/Al-LDH-HPP modified CNTPE was employed to determine Hg(II) in marine animal samples including fish and shellfish purchased from local market in Tanjung Malim. The measurement of Hg(II) in real samples was done by cyclic voltammetry and its results were validated with recovery study and measuring the mercury content of the samples by mercury analyzer (CVAAS). The samples were digested first before the measurements. For the preparation of digestion, the samples were dried by oven at 80 °C until reached the constant weight. The dried samples (0.50 g) were then weighed and prepared with triplicates for each sample. The weighed samples were placed in a 50 mL beakers and added with 15 mL of concentrated HNO_3 (65%) obtained by Merck. The digestions were done at 110 °C about 3 hours on the hotplate. After the beakers were sufficiently cool, the liquid samples were filtered by Whatman No. 1 filter paper and diluted with deionized water in the 100 mL volumetric flasks.

For the recovery study, the water samples were spiked with 1.0×10^{-8} M Hg(II). The mean of the recovery was calculated as a percentage of the total mercury concentration founded and the mercury concentration added to the samples. The recovery study was performed by cyclic voltammetric measurement under optimum experimental conditions.

For the preparation of the voltammetric measurement, 1.0 mL of the liquid sample was transferred in a 100 mL volumetric flask and added to the amount of supporting electrolyte. The pH value of the sample was adjusted by adding 0.1 M

NaOH solutions until it reached the optimum pH. This voltammetric measurement was done under optimum experimental conditions. The concentration of Hg(II) in the samples was determined by using calibration curve prepared previously.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterizations of Zn/Al-LDH-HPP, CNTPE and Zn/Al-LDH-HPP Modified CNTPE

4.1.1 Fourier Transform Infrared (FTIR)

The FTIR spectra of Zn/Al-LDH-HPP, CNTPE and Zn/Al-LDH-HPP modified CNTPE are shown in Figure 4.1, Figure 4.2 and Figure 4.3, respectively. The FTIR spectrum of Zn/Al-LDH-HPP shows a broad band peak at 3409 cm^{-1} which can be attributed to OH stretching. The peak at 1459 cm^{-1} is attributed to the stretching vibration of the aromatic ring of C=C. The band around 1582 cm^{-1} is attributed to the C=O carboxylate ion that indicates the presence of HPP in the interlayer of the LDH.

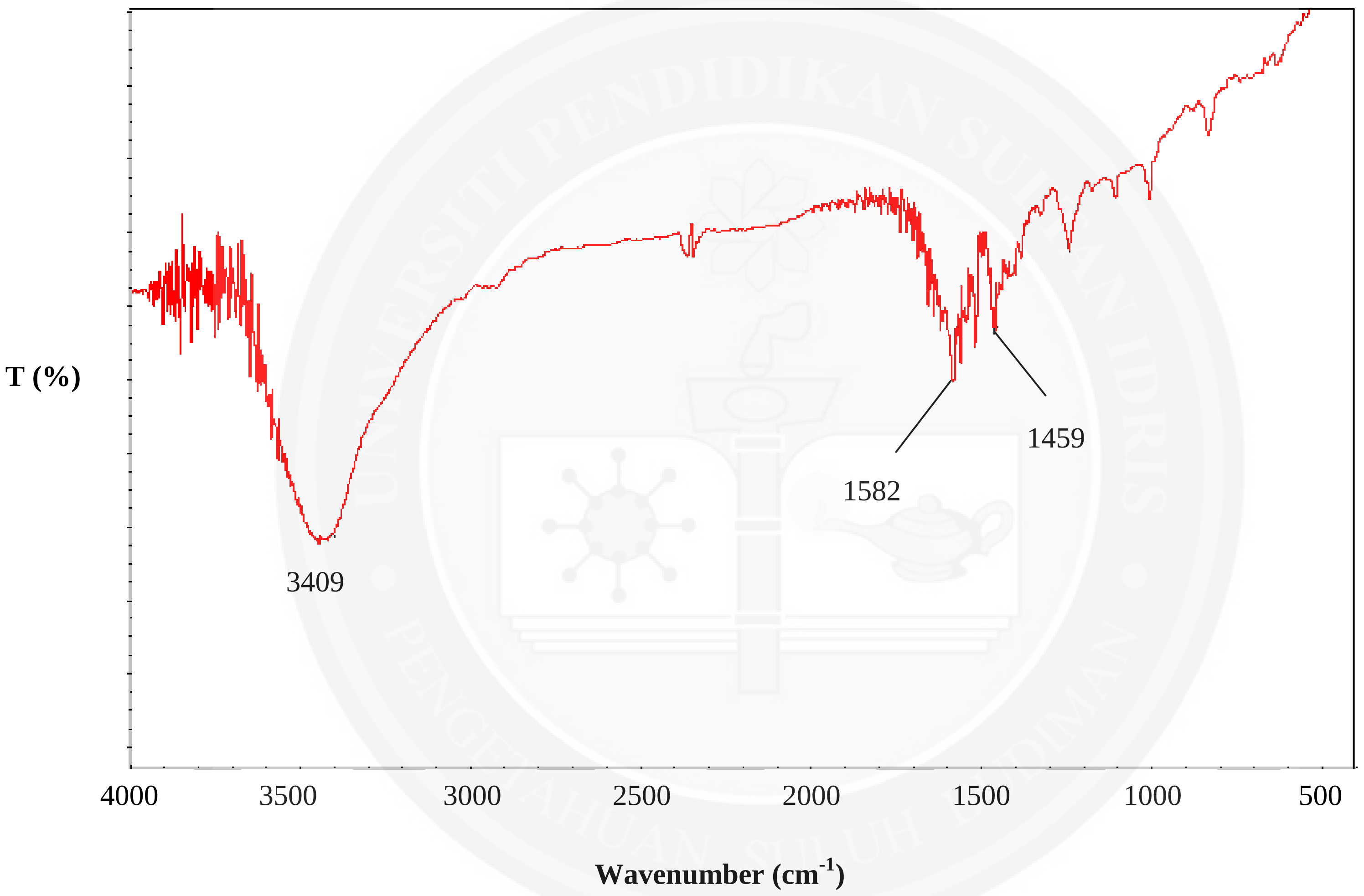

Figure 4.1. FTIR spectrum of Zn/Al-LDH-HPP.

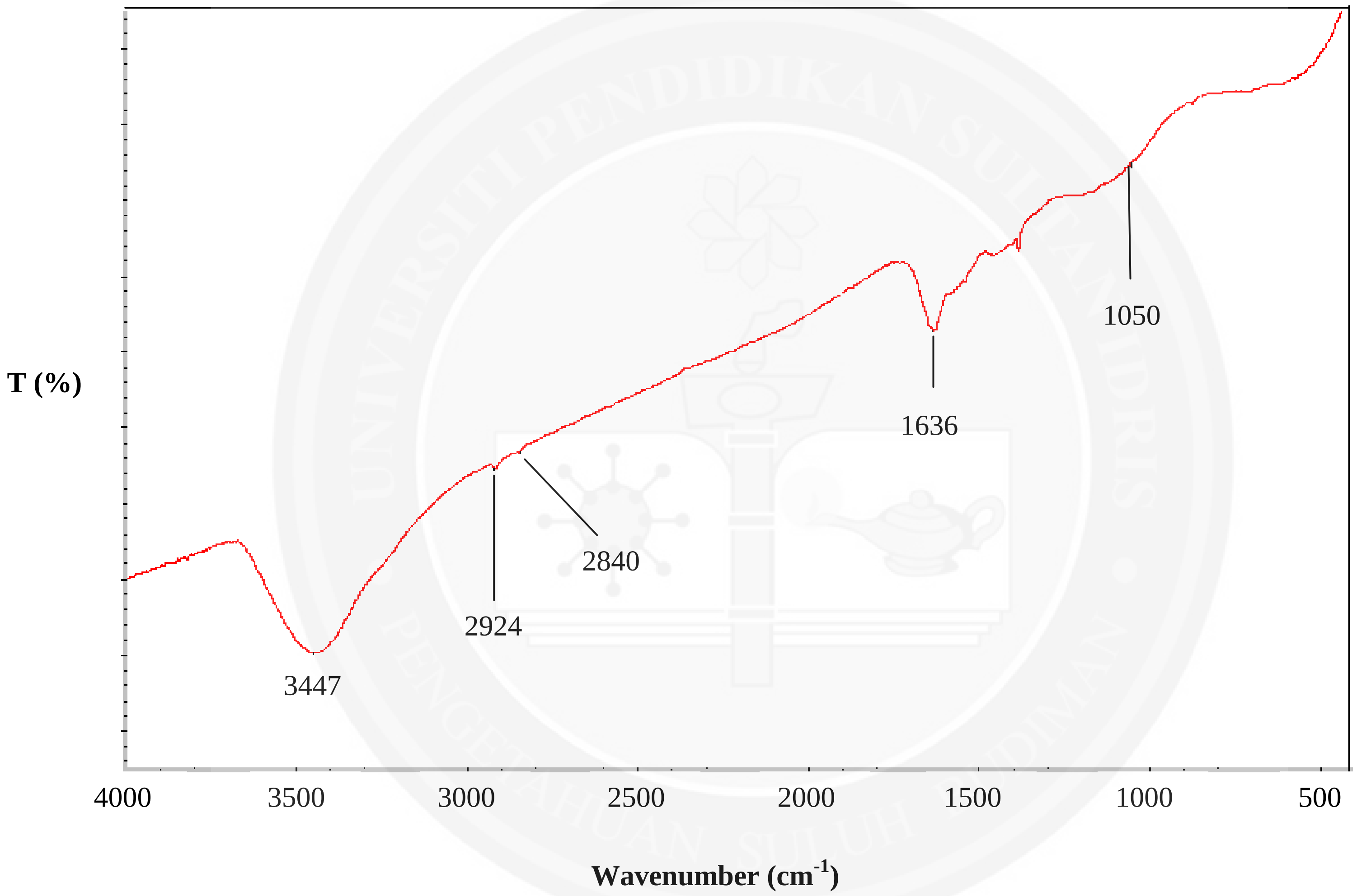

Figure 4.2. FTIR spectrum of CNTPE.

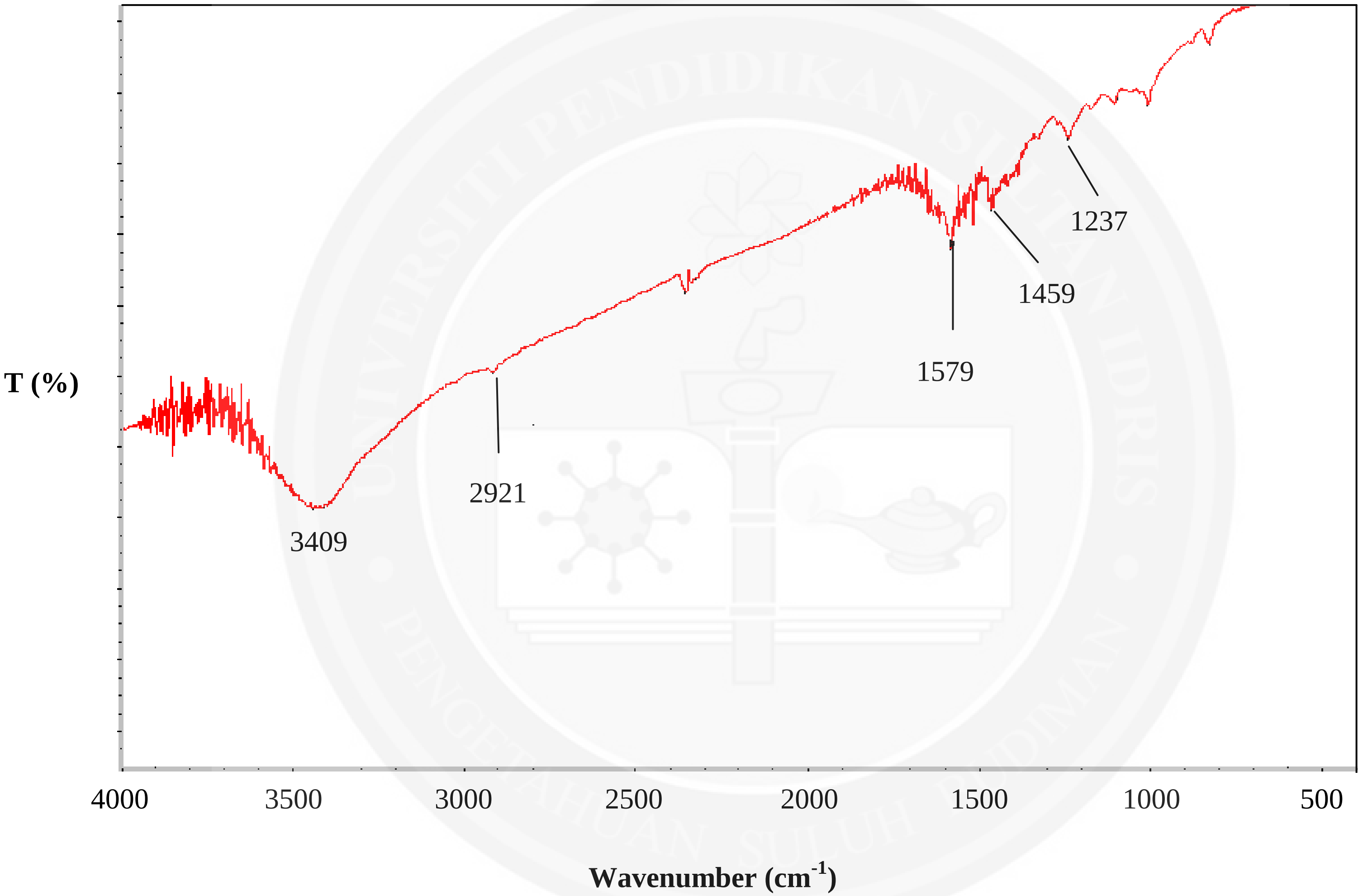

Figure 4.3. FTIR spectrum of Zn/Al-LDH-HPP modified CNTPE.

The FTIR spectrum of CNTPE shows two width bands at 3447 cm^{-1} and 1050 cm^{-1} which can be attributed to the presence of hydroxyl groups (-OH) on the surface of the MWCNT. Two peaks at 2924 cm^{-1} and 2840 cm^{-1} are attributed to the stretching vibration of C-H bond. The peak at 1636 cm^{-1} is attributed to the stretching vibration of C=C bond.

The Zn/Al-LDH-HPP modified CNTPE shows all the characteristic peaks of MWCNT and Zn/Al-LDH-HPP. The broad band centered at 3409 cm^{-1} attributed to OH stretching, the peak at 2921 cm^{-1} are attributed to the stretching vibration of C-H bond, the peak at 1579 cm^{-1} is attributed to the C=O carboxylate ion and the peak at 1459 cm^{-1} is attributed to the stretching vibration of the aromatic ring of C=C. The new peak at 1237 cm^{-1} is attributed to the stretching vibration of C-O bond which indicates the Zn/Al-LDH-HPP nanocomposites incorporated in the CNTPE.

4.1.2 Field Emission Scanning Electron Microscope (FESEM)

The FESEM was used to observe the morphology of CNTPE and Zn/Al-LDH-HPP modified CNTPE surface. The FESEM images of CNTPE and the Zn/Al-LDH-HPP modified CNTPE are shown in Figure 4.4. From this figure, it can be seen that the surface of CNTPE (without Zn/Al-LDH-HPP) only shows the existence of MWCNT. But, the surface of the Zn/Al-LDH-HPP modified CNTPE shows the existence of MWCNT and Zn/Al-LDH-HPP nanocomposites. It can be concluded that the Zn/Al-LDH-HPP nanocomposites incorporated in the CNTPE.

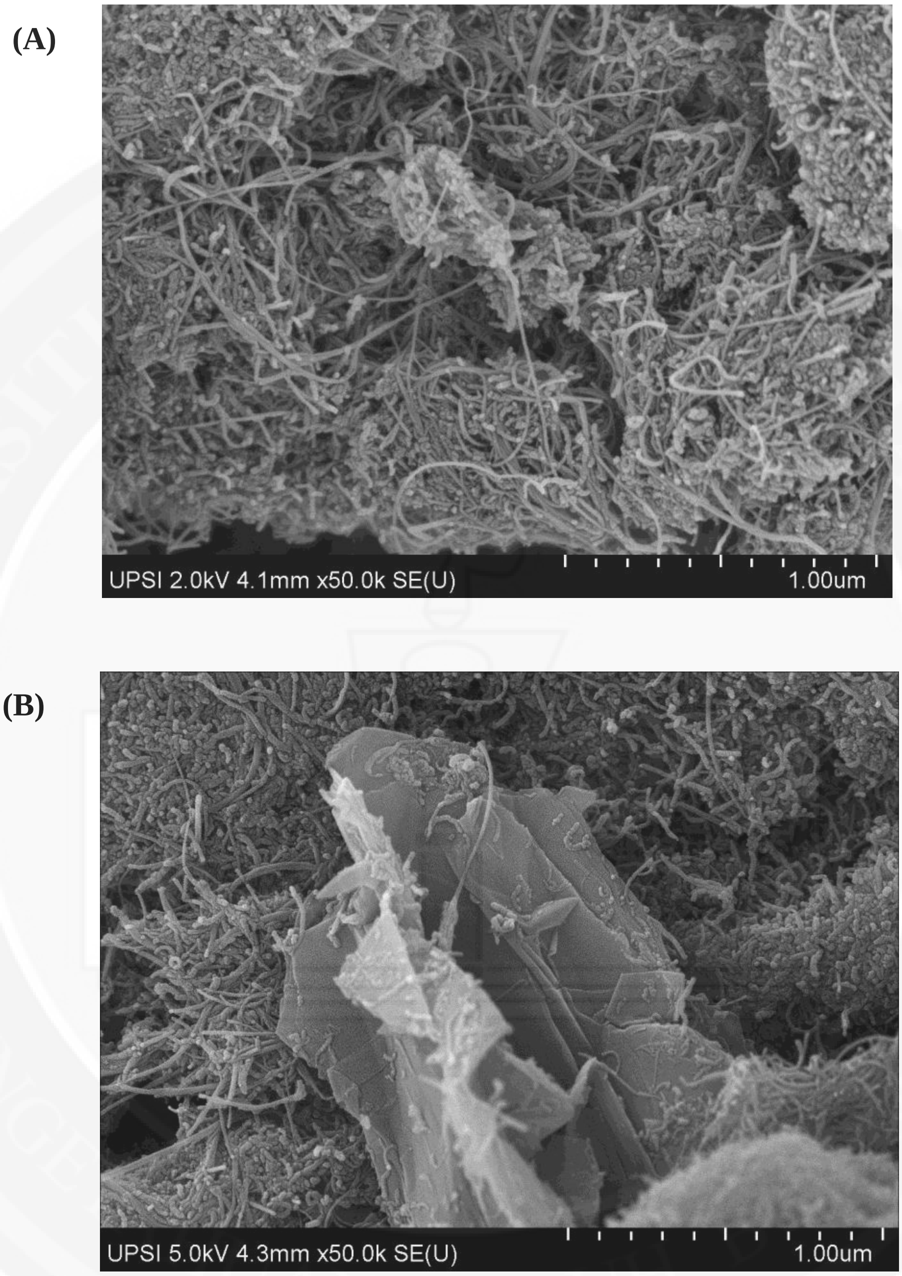

Figure 4.4. FESEM images of (A) CNTPE and (B) Zn/Al-LDH-HPP modified CNTPE.

4.2 Voltammetric Behavior of Hg(II) on the Zn/Al-LDH-HPP Modified CNTPE

Different parameters including percentage of modifier, type of supporting electrolyte, pH and scan rate were optimized using one variable at the time procedure, and were used to study the voltammetric behavior of Zn/Al modified CNTPE. During the investigation process, each variable was changed while the others were kept constant. Cyclic voltammogram of unmodified and modified CNTPE obtained in 2.0×10^{-4} M Hg(II), 0.5 M KCl as supporting electrolyte, adjusted at pH 5.0 and scan rate 100 mV s^{-1} is shown in Figure 4.5.

Cyclic voltammetry studies on electrochemical behavior of 2.0 x 10^{-4} M Hg(II) carried out on both unmodified and modified CNTPE showed that the voltammograms on these two electrode surfaces differ significantly. Figure 4.5 curve (a) shows the cyclic voltammograms of Hg(II) on the unmodified and curve (b) shows the cyclic voltammograms of Hg(II) Zn/Al modified CNTPE. In the Zn/Al modified CNTPE, a substantial enhancement of the anodic and cathodic peak currents are observed in comparison with the unmodified CNTPE which only shows background currents. This indicates the presence of the Zn/Al-LDH-HPP nanocomposite in the CNTPE is vital for the response obtained.

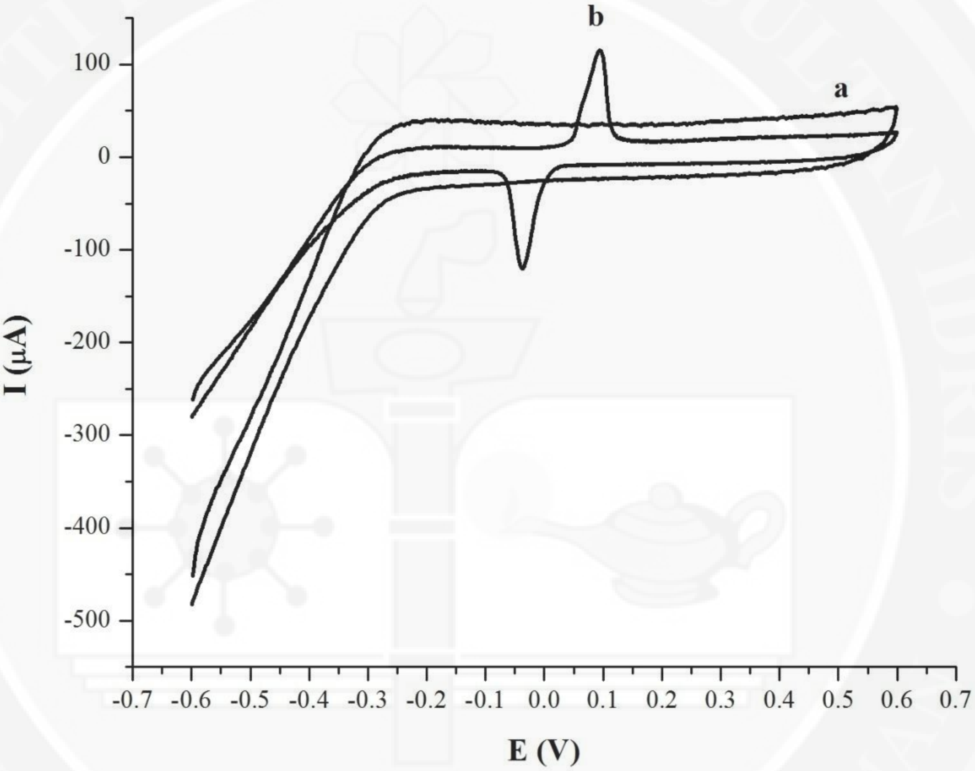

Figure 4.5. Cyclic voltammograms of (a) unmodified CNTPE and (b) Zn/Al-LDH-HPP modified CNTPE towards 2.0 × 10^{-4} M Hg(II) in 0.5 M KCl buffered at pH 5.0 and scan rate 100 mV s^{-1}.

Furthermore, the redox potential of Hg(II) at the Zn/Al-LDH-HPP modified CNTPE as one of the important parameters in cyclic voltammetry was also studied in terms of voltammetric behavior. As shown in Figure 4.5 curve (b), in the forward scan, the anodic peak current is observed at a potential (E_{pa}) of 93.86 mV corresponding to the oxidation of Hg(0) to Hg(II), and in the reverse scan, the cathodic peak current is observed at a potential (E_{pc}) of -37.94 mV corresponding to the reduction of Hg(II) to Hg(0). Before this redox reaction takes place, the accumulation of Hg(II) at the Zn/Al-LDH-HPP modified CNTPE surface occurs by complexation that involves the properties (chemical and physical) of Hg(II) and the complexing ability of the Zn/Al-LDH-HPP nanocomposite (Lu, He, Zeng, Wan, & Zhang, 2003). The overall mechanism that gives rise to the voltammetric response is then suggested;

(1) $(Hg^{2+})_{aq}$ + (Zn/Al-LDH-HPP)*surf.* $\longrightarrow$ $(Hg^{2+}$ — Zn/Al-LDH-HPP)*adsorb*

(2) $(Hg^{2+}$ — Zn/Al-LDH-HPP)*adsorb* + $2e^-$ $\longrightarrow$ (Hg^0)*surf.* + Zn/Al-LDH-HPP

(3) (Hg^0)*surf.* $\longrightarrow$ (Hg^{2+})*aq* + $2e^-$

In the previous study, Marcolino-Junior et al. (2007) suggested the similar mechanism of the voltammetric response for the CMCPE in the determination of Hg(II) (Marcolino-Junior, Janegitz, Lourenção, & Fatibello-Filho, 2007). In the first step (1), Hg(II) is accumulated at the Zn/Al-LDH-HPP modified CNTPE surface by forming a complex with Zn/Al-LDH-HPP nanocomposites. In the next step (2), Hg(II) in the complexed form is reduced to Hg(0). In the final step (3), Hg(0) is oxidized to Hg(II) producing a sensitive anodic peak.

4.3 The Effect of Percentage of Modifier

In the previous discussion, significant enhancement of anodic and cathodic peak was performed while the Zn/Al-LDH-HPP nanocomposite present in the CNTPE. So, further study about the Zn/Al-LDH-HPP nanocomposite in different amounts is needed to find out its effect on the voltammetric response. Amongst the important features of the CNTPE, the nature and amount of the nanomaterial used have been reported to significantly influence the sensitivity and selectivity of mercury determination (Janegitz et al., 2011). Therefore, different compositions of Zn/Al-LDH-HPP nanocomposites for the preparation of Zn/Al-LDH-HPP modified CNTPEs were investigated with the ratio of 2.5, 5.0, 7.5 and 10.0 (% w/w). Figure 4.6 shows the resulted I_{pa} from Hg(II) measurements plotted with the different of the Zn/Al-LDH-HPP nanocomposites in CNTPEs.

Figure 4.6 shows decreasing of the I_{pa} with the increasing amount of the Zn/Al-LDH-HPP. As seen, the electrode with 2.5% (w/w) of Zn/Al-LDH-HPP in the CNTPE has the maximum I_{pa}. The continuous increase of the amount of the Zn/Al-LDH-HPP leads to a decrease in the I_{pa}, most probably owing to decrease in the MWCNT content of the paste, and as a result the conductivity of the electrode surface is decreasing (Afkhami, Bagheri, et al., 2012). But, the I_{pa} increases from 5.0% to 7.5% (w/w) of Zn/Al-LDH-HPP, it is probably because 7.5% of modifier enables more Hg(II) ions adsorbed in the interlayer of Zn/Al-LDH-HPP than 5.0%. The best ratio of the Zn/Al-LDH-HPP in MWCNT paste composition was 2.5% (w/w) that performs the best voltammetric response of the Hg(II) measurement. Therefore, this ratio was applied in all experiments.

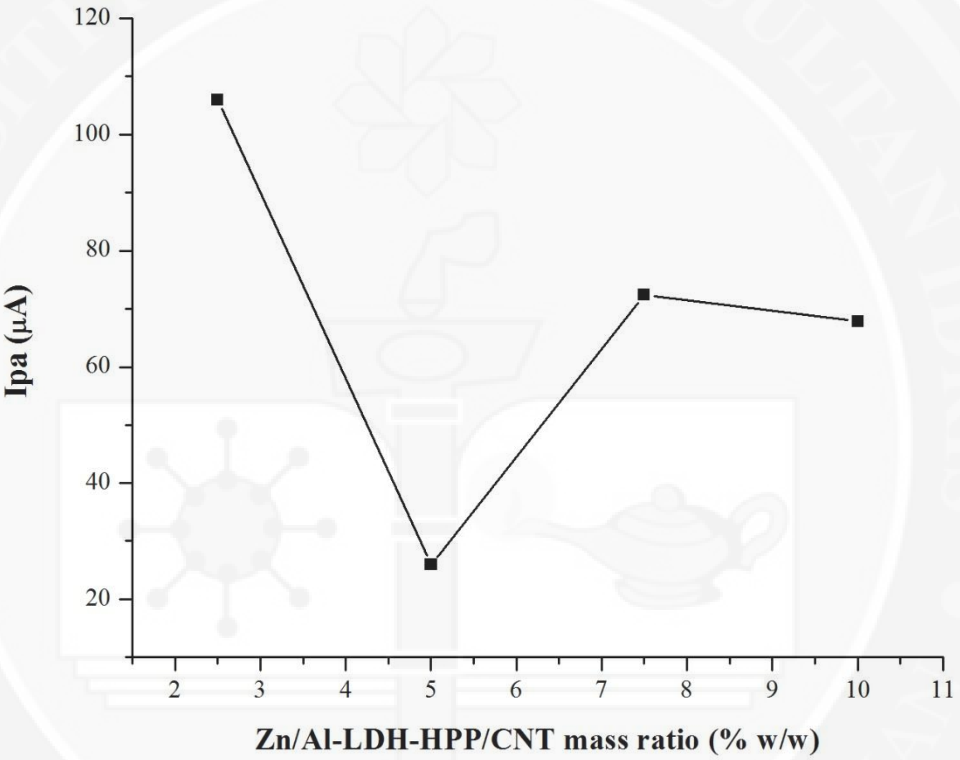

Figure 4.6. Graph of the relationship between I_{pa} value and different amount of Zn/Al-LDH-HPP nanocomposite in the CNTPE obtained by CV for 2.0×10^{-4} M Hg(II) in 0.5 M KCl buffered at pH 5.0 and scan rate 100 mV s^{-1}.

The enhancement of voltammetric response on the Zn/Al-LDH-HPP modified CNTPE indicates that both of the components in the paste involving the Zn/Al-LDH-HPP nanocomposite and the CNT (particularly MWCNT in this study) have the important role for accumulation of Hg(II) on the surface electrode. The Zn/Al-LDH-HPP nanocomposite can improve the catalytic electrochemical reactions of the carbon paste electrode due to the high surface area (Švancara et al., 2012). While, the MWCNT has a high electrical conductivity and high surface area which allow to detect a small amounts of Hg(II), so a high sensitivity can be achieved (Gao & Huang, 2013).

4.4 The Effect of Supporting Electrolyte

Supporting electrolyte is important in the electrochemical reaction due to its dissolved ion in the solution which is mobile and able to support current flow. The mobile ion from the supporting electrolyte allows for measuring the electrode potential in the electrochemical cell (Zoski, 2007). Different supporting electrolytes will have different properties that will affect the voltammetric measurement. Therefore, the types of the supporting electrolytes were investigated to get the best voltammetric response of the Zn/Al-LDH-HPP modified CNTPE. The metals have different electrochemical behaviors in different electrolytes. The effect of different salt solutions (as supporting electrolyte), such as KCl, NaCl, LiCl and CH_3COONa, on the voltammetric behavior of the Zn/Al-LDH-HPP modified CNTPE was investigated.

Figure 4.7 shows the cyclic voltammograms of 2.0 x 10^{-4} M Hg(II) at the Zn/Al-LDH-HPP modified CNTPE with KCl, LiCl, NaCl and CH_3COONa as supporting electrolytes, and the results from the cyclic voltammetric measurement of Hg(II) in different supporting electrolytes are given in Table 4.1. It can be seen from Figure 4.7, the I_{pa} for KCl, NaCl and LiCl occur at more negative potential compare to CH_3COONa. Moreover, the I_{pc} did not appear when used CH_3COONa as supporting electrolyte. The CH_3COONa is not suitable as supporting electrolyte in the cyclic voltammetric measurement of Hg(II) due to the absence of the I_{pc} which can be attributed to the irreversibility of the redox reaction of mercury.

When the measurements were performed in KCl, NaCl and LiCl solutions, all of them perform well defined peak currents due to the presence of I_{pa} and I_{pc}, but the highest I_{pa} was obtained in KCl solution as shown in Table 4.1. The presence of a number of Cl^- ions enhance sensitivity for detection of Hg(II) (Hezard et al., 2012), therefore KCl was chosen as supporting electrolyte to determine Hg(II) in all experiments.

4.5 The Effect of pH

The effect of the solution pH in the 2.0 x 10^{-4} M Hg(II) and 0.5 M KCl as supporting electrolyte was studied in the pH range of 2.0 – 8.0. The pH was adjusted by adding few amounts of CH_3COOH and NaOH solution using dropper. The graph of the relationship between resulted I_{pa} and pH value is shown in Figure 4.8. The voltammetric response was strongly pH dependent.

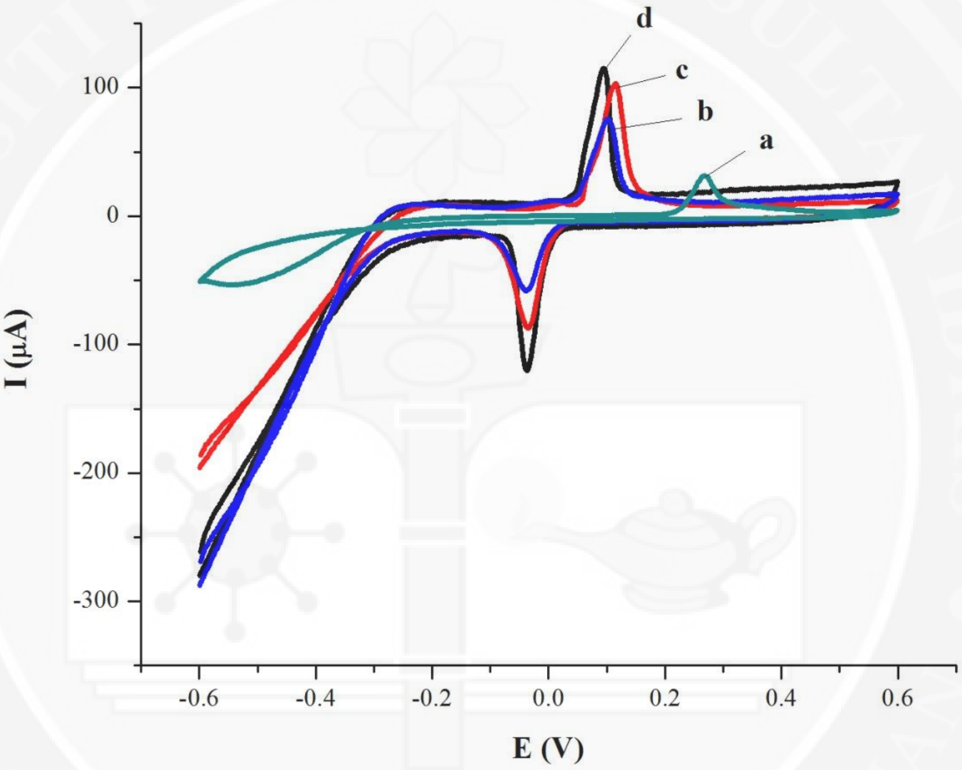

Figure 4.7. Cyclic voltammograms of (a) 0.5 M CH_3COONa, (b) 0.5 M NaCl, (c) 0.5 M LiCl and (d) 0.5 M KCl towards 2.0×10^{-4} M Hg(II), pH 5.0 and scan rate 100 mV s^{-1} at Zn/Al-LDH-HPP modified CNTPE.

Table 4.1

The effect of different type of supporting electrolyte to the I_{pa} value of Zn/Al-LDH-HPP modified CNTPE in 2.0 x 10^{-4} M Hg(II)

Type of Supporting Electrolyte	I_{pa} (μA)	I_{pc} (μA)
KCl	106.0	110.4
LiCl	95.33	92.53
NaCl	69.72	64.47
CH_3COONa	30.96	-

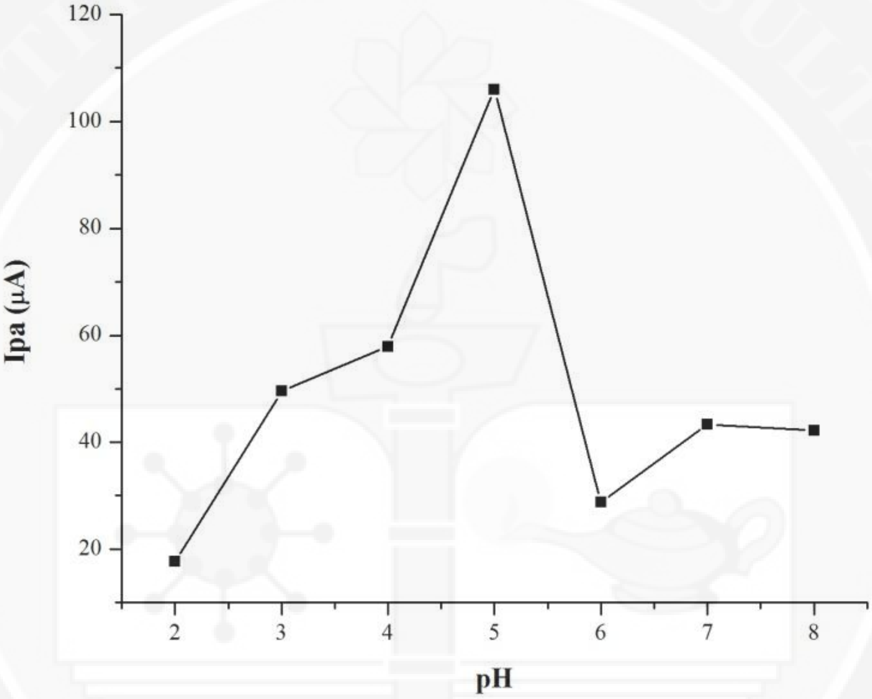

Figure 4.8. The relationship between I_{pa} value and pH obtained by CV for 2.0 × 10^{-4} M Hg(II) in 0.5 M KCl and scan rate 100 mV s^{-1} at Zn/Al-LDH-HPP modified CNTPE.

As shown in Figure 4.8, the I_{pa} values increase from pH 2.0 to 5.0, and reach the maximum value at pH 5.0. After pH 5.0, the I_{pa} values decrease and shown a trend to level up at pH 6.0 – 8.0. From the results, it can be concluded that the optimum I_{pa} is obtained at pH 5.0. A proton ion (H^+) can compete with Hg(II) in complexation with Zn/Al-LDH-HPP nanocomposite at the surface of the Zn/Al-LDH-HPP modified CNTPE (Afkhami, Madrakian, et al., 2012). Therefore, the I_{pa} values decrease at pH lower than 5.0. Meanwhile, the I_{pa} values decrease from pH 5.0 to 6.0 due to the cation hydrolysis, so diminishing the concentration of Hg(II) in the solution (Rajabi, Roushani, & Shamsipur, 2013). Therefore, pH 5.0 was used as optimum pH for all experiments.

4.6 The Effect of Scan Rate

Variations of scan rates were applied to study its effect to the voltammetric response. The variations of scan rates were made in two kinds including from 20 to 100 mV s^{-1} and 100 to 500 mV s^{-1}. This study was done by cyclic voltammetry in 2.0 x 10^{-4} M Hg(II) with 0.5 M KCl as supporting electrolyte at pH 5.0 using Zn/Al modified CNTPE. For the variations of the scan rates from 20 to 100 mV s^{-1}, the resulted I_{pa} values are plotted versus scan rates as shown in Figure 4.9. The results from the cyclic voltammetric measurement of Hg(II) in different scan rates are given in Table 4.2 for scan rates from 20 to 100 mV s^{-1} and Table 4.3 for scan rates from 100 to 500 mV s^{-1}.

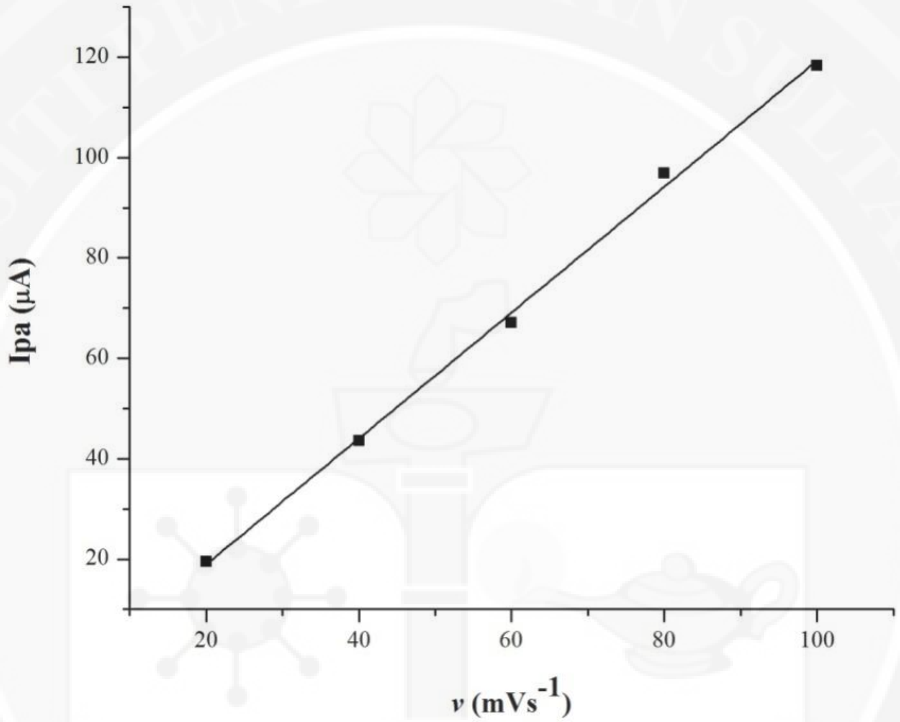

Figure 4.9. The relationship between I_{pa} value and scan rate obtained by CV for 2.0 × 10^{-4} M Hg(II) at Zn/Al-LDH-HPP modified CNTPE in 0.5 M KCl buffered at pH 5.0.

Table 4.2

The effect of different scan rate (20 to 100 mV s^{-1}*) to the cyclic voltammetric measurement of Zn/Al-LDH-HPP modified CNTPE in 2.0 x* 10^{-4} *M Hg(II) and 5.0 KCl at pH 5.0*

Scan rate (mV s^{-1})	I_{pa} (μA)	I_{pc} (μA)	E_{pa} (mV)	E_{pc} (mV)	ΔE_p
20	19.57	27.18	63.98	-20.02	84.00
40	43.54	31.33	77.89	-29.81	107.70
60	67.12	62.50	85.96	-31.84	117.80
80	96.97	84.47	97.99	-43.81	141.80
100	118.3	85.43	95.99	-43.91	139.90

Table 4.3

The effect of different scan rate (100 to 500 mV s^{-1}*) to the cyclic voltammetric measurement of Zn/Al-LDH-HPP modified CNTPE in 2.0 x* 10^{-4} *M Hg(II) and 5.0 KCl at pH 5.0*

Scan rate (mV s^{-1})	I_{pa} (μA)	I_{pc} (μA)	E_{pa} (mV)	E_{pc} (mV)	ΔE_p
100	118.3	85.43	95.99	-43.91	139.90
200	234.1	183.20	126.00	-71.91	197.91
300	288.90	225.50	141.19	-87.81	229.0
400	341.90	288.90	153.90	103.90	257.80
500	392.30	337.40	165.90	-113.90	279.80

Figure 4.9 shows that the maximum I_{pa} value is obtained at scan rate 100 mV s^{-1}. So, the scan rate of 100 mV s^{-1} was applied in all experiments. The scan rates higher than 100 mV s^{-1} are not recommended to be chosen to determine Hg(II) although they have higher values of I_{pa} as shown in Table 4.3. This is due to the larger separation of E_{pa} and E_{pc}, so they have ΔE_p which are larger than ΔE_p of 100 mV s^{-1} leading to the irreversible reaction (Eggins, 2002).

The I_{pa} values increase linearly with the scan rates as shown in Figure 4.9. The regression equation for the line is $I_{pa} = 1.2544v – 6.167$, where I_{pa} is the anodic peak current and v is the scan rate, and the correlation coefficient is 0.9972. The I_{pa} is proportional to v, thus indicates the process in the determination of Hg(II) involved adsorption-controlled process (Daud et al., 2013).

It can be seen in Table 4.2, when the anodic and cathodic peaks increase with the increasing of scan rates, the anodic peak potentials shifted to more positive values, while the cathodic peak potentials shifted to more negative values. The difference in peak potential values ($\Delta E_p = E_{pa} - E_{pc}$) at the scan rates from 20 to 100 mV s^{-1} is between 84.00 – 139.90 mV. This ΔE_p is larger than ΔE_p of reversible reaction (59 mV). Therefore, the redox reaction in the cyclic voltammetric measurement of Hg(II) is quasi-reversible.

4.7 The Effect of Electrode Regeneration

In this study, regenerations of the electrode surface were carried out using washing solution (0.1 M NH_4Cl, 0.1 M HCl, 0.1 M HNO_3, 0.1 M $NaNO_3$ and H_2O) and mechanical polishing. The result of the regeneration condition of Zn/Al-LDH-HPP modified CNTPE under optimum experimental conditions is given in Table 4.4.

The percentage of I_{pa} loss was used to determine the effect of the washing solutions and mechanical polishing. The percentage of I_{pa} loss from the highest to the lowest is HNO_3, HCl, NH_4Cl, $NaNO_3$, H_2O and mechanical polishing. It was found that mechanical polishing was a proper regeneration for this aim due to the lowest of I_{pa} loss. The renewed active surface of the electrode after regeneration enables it to remove the weakly adsorbed species and the irreversible contamination from the electrode surface, therefore can enhance the sensor selectivity and ignore the effects of interference, if proper regeneration is applied (Alizadeh, Ganjali, & Zare, 2011; Rajabi et al., 2013).

4.8 Chronocoulometry Studies

Chronocoulometric technique is particularly useful to study the adsorbed electroactive species on an electrode surface. A double step chronocoulometry experiment was employed in 2.0×10^{-4} M Hg(II) with 0.5 M KCl as supporting electrolyte at pH 5.0 using Zn/Al-LDH-HPP modified CNTPE.

Table 4.4

The regeneration condition of Zn/Al-LDH-HPP modified CNTPE

Regeneration condition	Ipa/µA		I_{pa} loss (%)[a]
	Before regeneration	After regeneration	
NH_4Cl (0.1 M)	139.7	115.3	17.47
HCl (0.1 M)	138.3	103.0	25.52
HNO_3 (0.1 M)	133.2	84.1	36.86
$NaNO_3$ (0.1 M)	138.7	130.3	6.06
H_2O	138.0	134.7	2.39
Mechanical polishing	137.7	136.6	0.80

[a] $$I_{pa} \text{ loss } (\%) = \frac{I_{pa}(\text{before}) - I_{pa}(\text{after})}{I_{pa}(\text{before})} \times 100$$

The potential which was applied in the first step (forward step) was -1.1 V in which the Hg(II) ion that was adsorbed at the electrode surface would be reduced to Hg(0). In the second step (reverse step), the applied potential was 1.1 V in which Hg(0) at the electrode surface was oxidized and converted back to Hg(II). In the chronocoulometry experiment, the total charge (Q) that passed during the time following a potential step was measured as a function of time, so that the Q was plotted versus the square root of time ($t^{1/2}$) as shown in Figure 4.10.

Plot of Q and ($t^{1/2}$) has a linear relationship. From the plot of total Q versus $t^{1/2}$ given by Anson equation, the diffusion coefficient (D) and the charge of adsorbed species (Q_{ads}) of Zn/Al-LDH-HPP can be estimated from the slope and intercept, respectively, using integrated Cottrell equation (Anson, 1966; Sanghavi, Hirsch, Karna, & Srivastava, 2012). As can be seen in Figure 4.10, there are two plots with opposite slope. The first slope shows the increase of total Q due to the increase of total amount of Hg(II) ion that reduced to Hg(0). The second slope shows the decrease of total Q due to the oxidation of Hg(0) to Hg(II) ion. The difference in the intercepts of these two plots results Q_{ads}.

With an electrode area value (A) of 0.0616 cm^2, the D and Q_{ads} were found to be 8.185 cm^2 s^{-1} and 5.1758 x 10^{-3} C, respectively. According to the equation: $Q_{ads} = nFA\Gamma$, the surface coverage (**Γ**) of Zn/Al-LDH-HPP modified CNTPE can be obtained as 4.3535 x 10^{-7} mol cm^{-2}, which has larger than the previous reported value of 4.93 x 10^{-11} mol cm^{-2} (Daud et al., 2013). This indicates that CMCNTPE has a rather high sensitivity towards Hg(II).

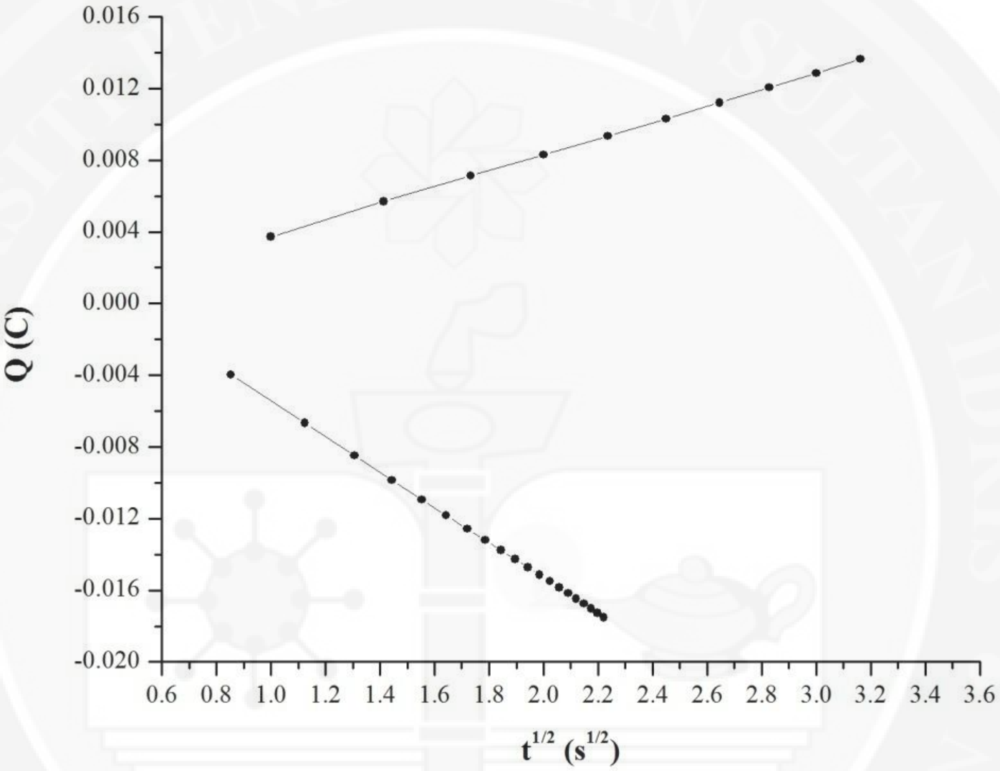

Figure 4.10. The relationship between Q and t$^{1/2}$ of the double step chronocoulograms of 2.0 × 10^{-4} M Hg(II) at Zn/Al-LDH-HPP modified CNTPE in 0.5 M KCl (pH 5.0) at scanning potential of -1.1 to 1.1 V.

4.9 Interference Studies

In order to evaluate the selectivity of the Zn/Al-LDH-HPP modified CNTPE to determine Hg(II), the common existing interferences of inorganic species were checked as interfering species in this research. The interfering ions used in this experiment were Ni(II), Ba(II), Ca(II), Cd(II), Mn(II), Sr(II), Co(II), Mg(II) and Zn(II). The interference studies were carried out using standard addition method by placing the Zn/Al-LDH-HPP modified CNTPE into the solutions containing 2.0 x 10^{-4} M Hg(II) with addition 10-folds and 25-folds of metal ions under optimum experimental conditions. The I_{pa} values from the solution containing Hg(II) and interfering ions were compared with the I_{pa} values from the solution only containing Hg(II).

The decrease of I_{pa} values for each metal ion presented in the solution to determine Hg(II) is shown in Figure 4.11. It is found from the voltammetric responses (Figure 4.9) that 10-folds of metal ions (2.0 x 10^{-3} M) and 25-folds of metal ions (5.0 x 10^{-3} M) for Ba(II), Ca(II), Cd(II), Co(II), Mg(II), Mn(II), Ni(II) and Sr(II), did not interfere in the determination of Hg(II). This indicates that the Zn/Al-LDH-HPP modified CNTPE is more selective to detect Hg(II) compare to the other metal ions. Meanwhile, Zn(II) ion has influence on the signal of 2.0 x 10^{-4} M Hg(II) even at 10-folds, this probably owing to the Zn(II) ion forms complexes with the Zn/Al-LDH-HPP nanocomposites and prevent the accumulation of Hg(II) on the surface of the Zn/Al-LDH-HPP modified CNTPE (Afkhami, Madrakian, et al., 2012).

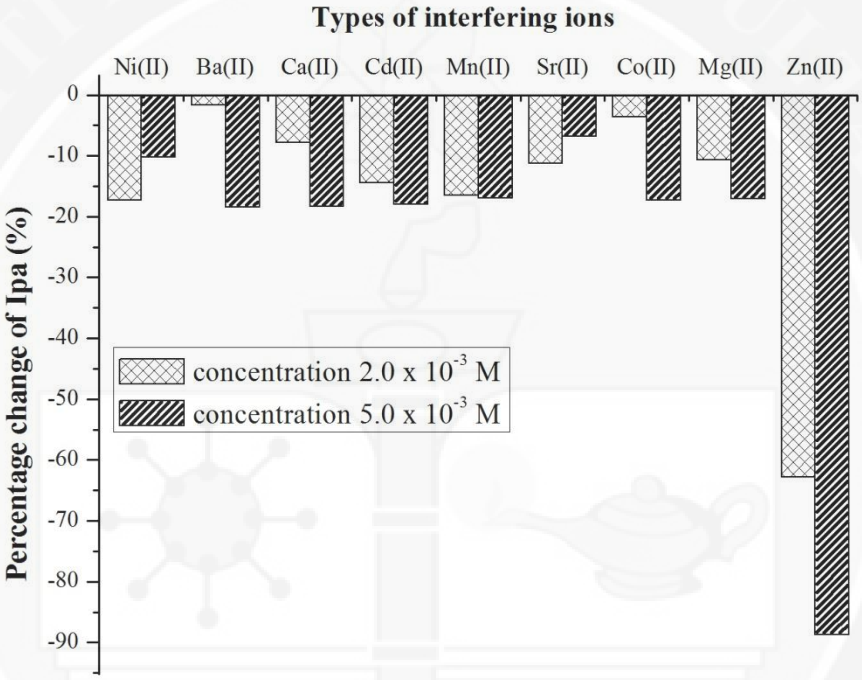

Figure 4.11. Effect of 2.0 x 10^{-3} M and 5.0 x 10^{-3} M interfering ions to 2.0 × 10^{-4} M Hg(II) at Zn/Al-LDH-HPP modified CNTPE in 0.5 M KCl, pH 5.0 and scan rate 100 mV s^{-1}.

4.10 Calibration Curve, Limit of Detection, Repeatability and Reproducibility

The analytical features of the proposed method were observed through the linear range, limit of detection, repeatability and reproducibility. The voltammetric responses of different concentrations of Hg(II) solution from 1.0 x 10^{-3} M to 1.0 x 10^{-10} M were carried out under optimum experimental conditions. The resulted I_{pa} values were plotted against the concentration of Hg(II) as shown in Figure 4.12 and Figure 4.13.

Figure 4.12 and Figure 4.13 show that the I_{pa} linearly increase with the increase of Hg(II) concentration in the range of 1.0 x 10^{-9} – 1.0 x 10^{-7} M with a linear regression equation of I_{pa} (μA) = -3.59 log [Hg^{2+}] + 46.133, R^2 = 0.9926 and 1.0 x 10^{-7} – 1.0 x 10^{-3} M with a linear regression equation of I_{pa} (μA) = -33.818 log [Hg^{2+}] + 255.412, R^2 = 0.9963. The value of the detection limit obtained was 5.0 x 10^{-10} M. Linear range and detection limit from this proposed Zn/Al-LDH-HPP modified CNTPE were compared with some reported modified carbon paste electrodes as given in Table 4.5. This table shows that sensitivity of Zn/Al-LDH-HPP modified CNTPE is better than or equal to other carbon paste electrodes.

The repeatability of the electrode was evaluated by performing five determinations with the solution containing 2.0 x 10^{-4} M of Hg(II) under optimum experimental conditions. Table 4.6 shows the repeatability of Zn/Al-LDH-HPP modified CNTPE in the voltammetric response of 2.0 x 10^{-4} M Hg(II). It was found that the Zn/Al-LDH-HPP modified CNTPE has a good repeatability with the relative standard deviation of I_{pa} was 1.71%.

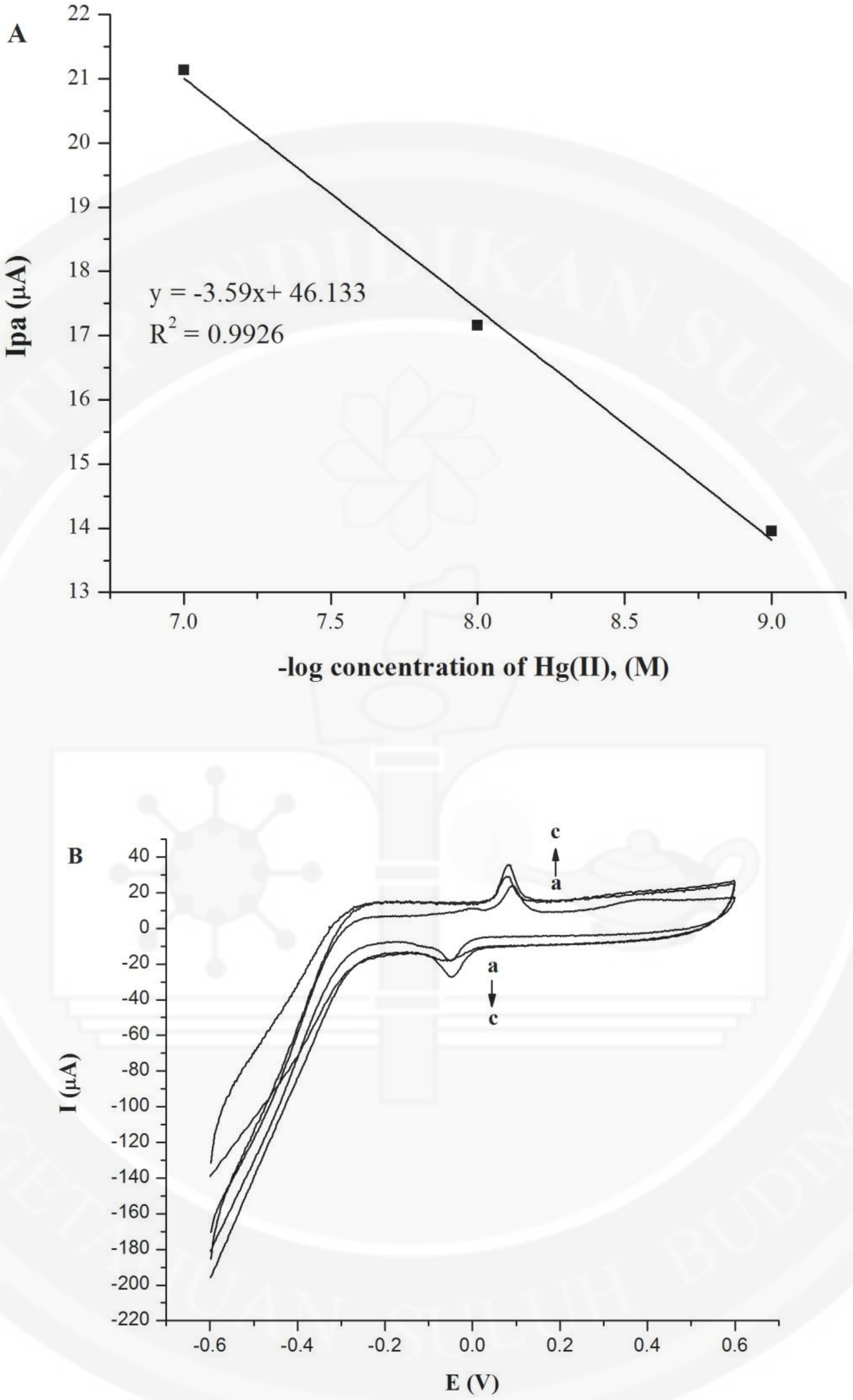

Figure 4.12. (**A**) Plot of I_{pa} versus – log of (1.0 × 10^{-9} M – 1.0 × 10^{-7} M) Hg(II); **(B)** Cyclic Voltammograms of (a) 1.0 × 10^{-9} M, (b) 1.0 × 10^{-8} M, (c) 1.0 × 10^{-7} M Hg(II) in 0.5 M KCl (pH 5.0), scan rate 100 mV s^{-1} at Zn/Al-LDH-HPP modified CNTPE.

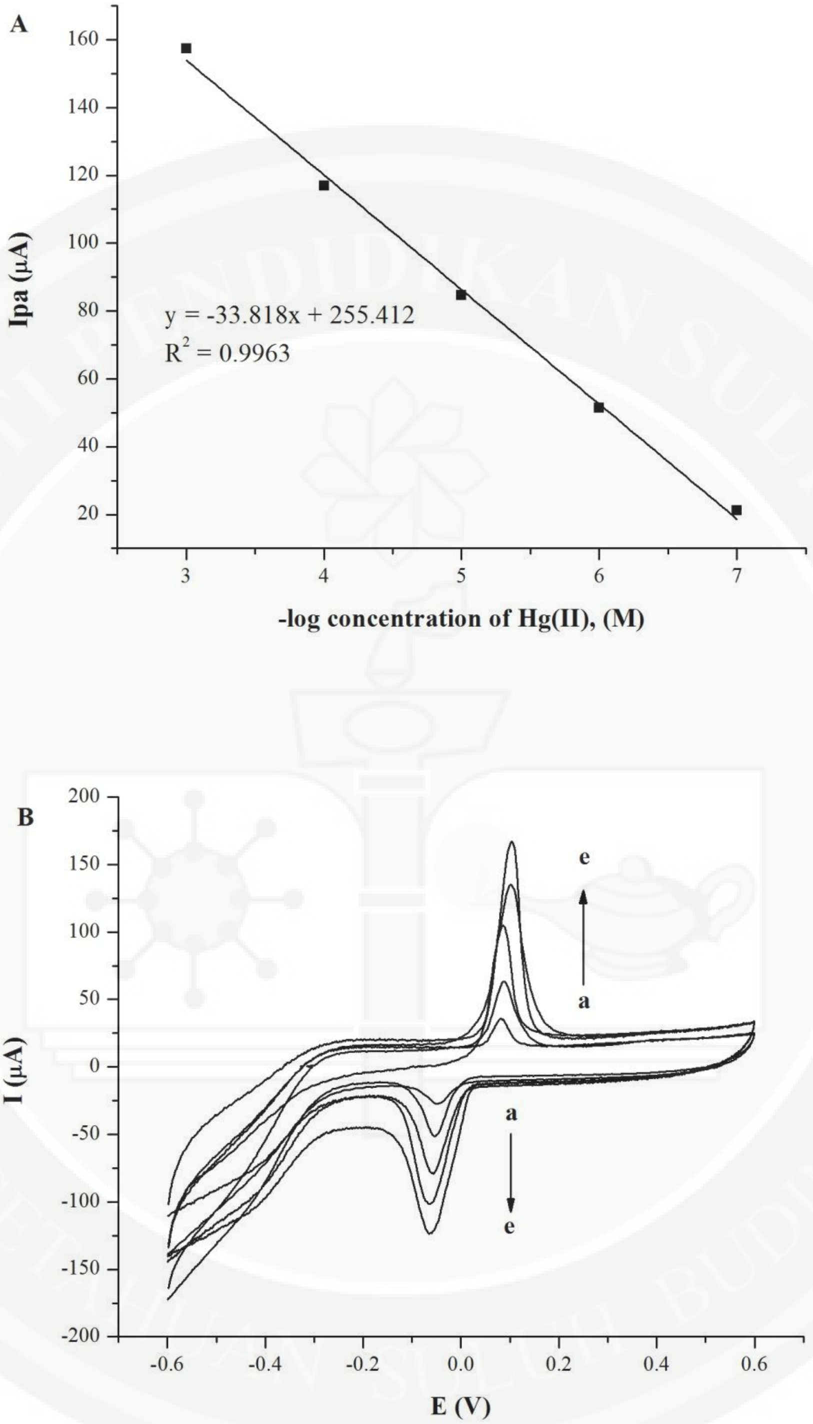

Figure 4.13. **(A)** Plot of I_{pa} versus – log of (1.0×10^{-7} M – 1.0×10^{-3} M) Hg(II); **(B)** Cyclic Voltammograms of (a) 1.0×10^{-7} M, (b) 1.0×10^{-6} M, (c) 1.0×10^{-5}, (d) 1.0 x 10^{-4} M, (e) 1.0 x 10^{-3} M Hg(II) in 0.5 M KCl (pH 5.0), scan rate 100 mV s^{-1} at Zn/Al-LDH-HPP modified CNTPE.

Table 4.5

Comparison of some characteristics of the different modified carbon paste electrodes for the determination of Hg(II)

Modifier	Electrode	Method	Concentration range (M)	Detection limit (M)	References
Nitro benzoyl diphenylmethylen-phosphorane (N-BDMP)	MCPE[a]	SWASV[b]	4.98×10^{-8} – 9.97×10^{-6}	4.09×10^{-8}	(Afkami, Madrakian, et al. 2012)
Crosslinked chitosan	MCNTPE[c]	LSASV[d]	6.7×10^{-9} – 8.3×10^{-8}	2.4×10^{-9}	(Janegitz, et al., 2011)
Hybrid mesostructured silica nanoparticles	MCPE	SWASV	2.5×10^{-8} – 1.0×10^{-6}	2.3×10^{-8}	(Sánchez, Morante-Zarcero, Pérez-Quintanilla, Sierra, & del Hierro, 2012)
MWCNT and Schiff base	MCPE	SWASV	2.0×10^{-9} – 7.0×10^{-7}	9.0×10^{-10}	(Afkhami, Soltani-Felehgari, Madrakian, Ghaedi, & Rezaeivala, 2013)
Nano-silica and Schiff base	MCPE	SWASV	2.49×10^{-9} – 4.98×10^{-6}	2.49×10^{-10}	(Afkhami, Bagheri, et al., 2012)
Zn/Al-LDH-HPP	MCNTPE	CV[e]	1.0×10^{-9} – 1.0×10^{7} 1.0×10^{-7} – 1.0×10^{-3}	5.0×10^{-10}	This work

[a] Modified carbon paste electrode.

[b] Square wave anodic stripping voltammetry

[c] Modified CNTPE

[d] Linear sweep anodic stripping voltammetry

[e] Cyclic voltammetry

Table 4.6

Repeatability of Zn/Al-LDH-HPP modified CNTPE in the cyclic voltammetric response of 2.0 x 10^{-4} *M Hg(II) in 0.5 M KCl at pH 5.0*

Replicates	I_{pa} (μA)
1	100.40
2	99.06
3	101.50
4	100.20
5	103.60

RSD = 1.71%

The reproducibility of the response of the Zn/Al-LDH-HPP modified CNTPE was also studied whereby four electrodes were prepared in a same manner and they were investigated by performing the determination of 2.0 x 10^{-4} M of Hg(II) under optimum experimental conditions. Table 4.7 shows the reproducibility of Zn/Al-LDH-HPP modified CNTPE in the voltammetric response of 2.0 x 10^{-4} M Hg(II) under optimum experimental conditions. The relative standard deviation from the response between the electrodes was found to be 1.36%. The high repeatability and reproducibility indicated that the Zn/Al-LDH-HPP modified CNTPE was considered for analysis of real samples.

4.11 Determination of Hg(II) in Real Samples

Determination of Hg(II) in real samples is used to assess the performance of the fabricated sensor in practical applications. In this research, the real samples were from marine animal samples including fish and shellfish. The liquid samples which were acid owing to the digestion process were adjusted to pH 5.0 by adding 0.1 M NaOH solution. The cyclic voltammetry measurements of the real samples were carried out under optimum experimental conditions. The results were validated by recovery experiment and also compared to the results from standard mercury analyzer.

Table 4.7

Reproducibility of Zn/Al-LDH-HPP modified CNTPE in the cyclic voltammetric response of 2.0 x 10^{-4} *M Hg(II) in 0.5 M KCl at pH 5.0*

Electrodes	I_{pa} (μA)
1	132.40
2	134.80
3	135.20
4	133.00

RSD = 1.36%

For recovery experiment, the cyclic voltammetric measurements of Hg(II) contents in waste water samples were done by spiking with 1.0 x 10^{-8} M Hg(II) solution under optimum experimental conditions with triplicate measurement. The results are shown in Table 4.8, and the recoveries are in the range of 98.30 – 99.57%, indicating that the sensor might be sufficient for reliable determination of trace amount of Hg(II) in real samples.

The fabricated sensor was also assessed to determine Hg(II) in fish and shellfish by comparing the cyclic voltammetric results, which were determined by calibration curve, with those obtained by mercury analyzer. As shown in Table 4.9, no significant difference between these results obtained by the two methods, indicating the fabricated sensor might be sufficient to determine trace amounts Hg(II) in marine animal samples.

Table 4.8

Determination of Hg(II) in waste water samples (n = 3)

Sample	Measured (nM)	Added (nM)	Found (nM)	Recovery (%)
Waste water 1	8.80	10.0	18.63	98.07
Waste water 2	11.41	10.0	21.32	99.21
Waste water 3	8.12	10.0	17.81	96.18

Table 4.9

Validation of results by the proposed method to the standard (Mercury Analyzer model Perkin-Elmer, Mercury Analysis System FIMS 100) method on the determination of Hg(II) in marine animal samples (n = 3)

Sample	Proposed Method	Mercury Analyzer
Fish 1	4.235 ± 0.077 μg/g	4.274 ± 0.078 μg/g
Fish 2	5.491 ± 0.025 μg/g	5.599 ± 0.041 μg/g
Shellfish	3.908 ± 0.053 μg/g	3.982 ± 0.083 μg/g

CHAPTER 5

CONCLUSION

5.1 Conclusion

The best composition of modifier (Zn/Al-LDH-HPP) in the CNTPE was obtained by ratio of 2.5% (w/w). The other parameters were 0.5 M KCl as supporting electrolyte at pH 5 and scan rate of 100 mV s^{-1}. These optimum experimental conditions were applied in all measurements, and before each measurement the electrode was polished to remove the adsorbed Hg(II).

The Zn/Al-LDH-HPP modified CNTPE developed in this work was suitable to determine Hg(II) because it was selective to Hg(II) ion. Moreover, many metal ions did not give significant interference effect to the Zn/Al-LDH-HPP modified CNTPE in the determination of Hg(II) except Zn(II). The Zn/Al-LDH-HPP modified CNTPE has a high sensitivity to detect Hg(II) ion under optimum experimental conditions performed with the detection limit of 5.0 x 10^{-10} M and linear range of 1.0 x 10^{-9} – 1.0 x 10^{-7} M and 1.0 x 10^{-7} – 1.0 x 10^{-3} M. Due to its selectivity and high sensitivity, the Zn/Al-LDH-HPP modified CNTPE has been successfully applied to detect Hg(II) content in the marine animal samples including fish and shellfish. The measurement resulted from the cyclic voltammetry using Zn/Al-LDH-HPP modified CNTPE had no significant difference compared to the mercury analyzer.

Stripping voltammetry is one of the electrochemical methods that is widely used in the Hg(II) determination using carbon paste electrode. Therefore, in the further research, Zn/Al-LDH-HPP modified CNTPE can also be used for stripping voltammetry to determine mercury in other real samples. Anodic stripping voltammetry is a technique mostly used among the other stripping voltammetry techniques for detection of metal ions. This technique is usually combined with square wave or differential pulse to obtain low detection limit, good selectivity and high sensitivity.

REFERENCES

Abbaci, A., Azzouz, N., & Bouznit, Y. (2014). A new copper doped montmorillonite modified carbon paste electrode for propineb detection. *Applied Clay Science*, *90*, 130-134.

Abdolmohammad-Zadeh, H., Rezvani, Z., Sadeghi, G. H., & Zorufi, E. (2011). Layered double hydroxides: A novel nano-sorbent for solid-phase extraction. *Analytica Chimica Acta*, *685*, 212-219.

Adlnasab, L., Ebrahimzadeh, H., Asgharinezhad, A. A., Aghdam, M. N., Dehghani, A., & Esmaeilpour, S. (2014). A Preconcentration procedure for determination of ultra-trace mercury(II) in environmental samples employing continuous-flow cold vapor atomic absorption spectrometry. *Food Analytical Methods*, *7*, 616-628.

Afkhami, A., Bagheri, H., Khoshsafar, H., Saber-Tehrani, M., Tabatabaee, M., & Shirzadmehr, A. (2012). Simultaneous trace-levels determination of Hg(II) and Pb(II) ions in various samples using a modified carbon paste electrode based on multi-walled carbon nanotubes and a new synthesized Schiff base. *Analytica Chimica Acta*, *746*, 98-106.

Afkhami, A., Madrakian, T., Sabounchei, S. J., Rezaei, M., Samiee, S., & Pourshahbaz, M. (2012). Construction of a modified carbon paste electrode for the highly selective simultaneous electrochemical determination of trace amounts of mercury(II) and cadmium(II). *Sensors and Actuators B*, *161*, 542-548.

Afkhami, A., Soltani-Felehgari, F., Madrakian, T., Ghaedi, H., & Rezaeivala, M. (2013). Fabrication and application of a new modified electrochemical sensor using nano-silica and a newly synthesized Schiff base for simultaneous determination of Cd^{2+}, Cu^{2+} and Hg^{2+} ions in water and some foodstuff samples. *Analytica Chimica Acta*, *771*, 21-30.

Ahmad, S. N., Hashim, N., Yusri, N. H., Isa, I. M., Kamari, A., Mohamed, A., Damanhuri, M. I. M. (2014). Synthesis and characterization of layered-double hydroxide 3-(-4-hydroxyphenyl) propionate nanocomposite. *Nano Hybrids*, *7*, 53-67.

Ahuja, S., & Jespersen, N. (2006). *Modern Instrumental Analysis* (Vol. 47). Oxford: Elsevier.

Alizadeh, T., Ganjali, M. R., & Zare, M. (2011). Application of an Hg^{2+} selective imprinted polymer as a new modifying agent for the preparation of a novel highly selective and sensitive electrochemical sensor for the determination of ultratrace mercury ions. *Analytica Chimica Acta*, *689*, 52-59.

Anson, F. C. (1966). Innovations in the study of adsorbed reactants by chronocoulometry. *Analytical Chemistry*, *38*, 54-57.

Attard, G. A., Ye, J. Y., Jenkins, P., Vidal-Iglesias, F. J., Herrero, E., & Sun, S. G. (2013). Citrate adsorption on Pt {*h k l*} electrodes and its role in the formation of shaped Pt nanoparticles. *Journal of Electroanalytical Chemistry*, *688*, 249-256.

Bagotsky, V. S. (2006). *Fundamentals of Electrochemistry*. New Jersey: John Wiley & Sons.

Banica, F. G. (2012). *Chemical Sensors and Biosensors: Fundamentals and Applications*. West Sussex: John Wiley & Sons.

Bansal, N., Vaughan, J., Boullemant, A., & Leong, T. (2014). Determination of total mercury in bauxite and bauxite residue by flow injection cold vapour atomic absorption spectrometry. *Microchemical Journal*, *113*, 36-41.

Bard, A. J., & Faulkner, L. R. (2001). *Electrochemical Methods: Fundamentals and Applications*. New York: Wiley.

Bard, A. J., Stratmann, M., & Schäfer, H. J. (2007). *Encyclopedia of Electrochemistry*. Berlin: Wiley-VCH.

Basile, F., Benito, P., Fornasari, G., Rosetti, V., Scavetta, E., Tonelli, D., & Vaccari, A. (2009). Electrochemical synthesis of novel structured catalysts for H_2 production. *Applied Catalysis B*, *91*, 563-572.

Bergaya, F., Theng, B. K. G., & Lagaly, G. (2006). *Handbook of Clay Science*. Oxford: Elsivier.

Bernalte, E., Marín Sánchez, C., & Pinilla Gil, E. (2012). Gold nanoparticles-modified screen-printed carbon electrodes for anodic stripping voltammetric determination of mercury in ambient water samples. *Sensors and Actuators B*, *161*, 669-674.

Bernalte, E., Sánchez, C. M., & Gil, E. P. (2011). Determination of mercury in ambient water samples by anodic stripping voltammetry on screen-printed gold electrodes. *Analytica Chimica Acta*, *689*, 60-64.

Bianchini, C., Curulli, A., Pasquali, M., & Zane, D. (2014). Determination of caffeic acid in wine using PEDOT film modified electrode. *Food Chemistry*, *156*, 81-86.

Böckris, J. O. M., Reddy, A. K. N., & Gamboa-Aldeco, M. E. (2002). *Modern Electrochemistry, 2A: Fundamentals of Electrodics*. New York: Kluwer Academic Publishers.

Boening, D. W. (2000). Ecological effects, transport, and fate of mercury: A general review. *Chemosphere*, *40*, 1335-1351.

Campbell, F. W., & Compton, R. G. (2010). The use of nanoparticles in electroanalysis: An updated review. *Analytical and Bioanalytical Chemistry*, *396*, 241-259.

Cantle, J. E. (1982). *Atomic Absorption Spectrometry*. Amsterdam: Elsevier.

Chandio, Z. A., Talpur, F. N., Khan, H., Afridi, H. I., Khaskheli, G. Q., & Mughal, M. A. (2014). On-line preconcentration and determination of ultra trace amounts of mercury using surfactant coated alumina modified by dithizone with cold vapor atomic absorption spectrometry. *RSC Advances*, *4*, 3326-3331.

Clarkson, T. W., Magos, L., & Myers, G. J. (2003). The toxicology of mercury-current exposures and clinical manifestations. *New England Journal of Medicine*, *349*, 1731-1737.

Colomer-Farrarons, J., & Miribel-Català, P. L. (2011). *A CMOS Self-Powered Front-End Architecture for Subcutaneous Event-Detector Devices*. New York: Springer.

Dal Borgo, S., Jovanovski, V., & Hocevar, S. B. (2013). Antimony film electrode for stripping voltammetric measurement of Hg(II) in the presence of Cu(II). *Electrochimica Acta*, *88*, 713-717.

Dar, R. A., Brahman, P. K., Tiwari, S., & Pitre, K. S. (2012). Electrochemical studies of quinine in surfactant media using hanging mercury drop electrode: A cyclic voltammetric study. *Colloids and Surfaces B*, *98*, 72-79.

Daud, N., Yusof, N. A., & Nor, S. M. M. (2013). Electrochemical characteristic of biotinyl somatostatin-14/nafion modified gold electrode in development of sensor for determination of Hg(II). *International Journal of Electrochemical Science*, *8*, 10086-10099.

Daud, N., Yusof, N. A., & Tee, T. W. (2011). Development of electrochemical sensor for detection of mercury by exploiting His-Phe-His-Ala-His-Phe-Ala-Phe modified electrode. *International Journal of Electrochemical Science*, *6*, 2798-2807.

Devi, S., Devasena, T., Saratha, S., Tharmaraj, P., & Pandian, K. (2014). Dithiocarbamate post functionalized polypyrrole modified carbon sphere for the selective and sensitive detection of mercury by voltammetry method. *International Journal of Electrochemical Science*, *9*, 670-683.

Devnani, H., & Satsangee, S. P. (2013). Voltammetric trace determination of mercury using plant refuse modified carbon paste electrodes. *Environmental Monitoring and Assessment*, *185*, 9333-9342.

Ding, L., Liu, Y., Zhai, J., Bond, A. M., & Zhang, J. (2014). Direct electrodeposition of graphene-gold nanocomposite films for ultrasensitive voltammetric determination of mercury(II). *Electroanalysis*, *26*, 121-128.

Duan, X., & Evans, D. G. (2006). *Layered Double Hydroxides*. New York: Springer.

Eggins, B. R. (2002). *Chemical Sensors and Biosensors*. West Sussex: John Wiley & Sons.

Ensafi, A. A., Allafchian, A. R., Saraji, M., & Farajmand, B. (2012). In-situ differential pulse anodic stripping voltammetry combined with hollow fiber-based liquid-three phase micro extraction for determination of mercury using Au-nanoparticles sol–gel modified Pt-wire. *Talanta*, *99*, 335-341.

Fink, L., & Mandler, D. (2010). Thin functionalized films on cylindrical microelectrodes for electrochemical determination of Hg(II). *Journal of Electroanalytical Chemistry*, *649*, 153-158.

Fu, X. C., Chen, X., Guo, Z., Xie, C. G., Kong, L. T., Liu, J. H., & Huang, X. J. (2011). Stripping voltammetric detection of mercury(II) based on a surface ion imprinting strategy in electropolymerized microporous poly(2-mercaptobenzothiazole) films modified glassy carbon electrode. *Analytica Chimica Acta*, *685*, 21-28.

Fu, X. C., Wu, J., Nie, L., Xie, C. G., Liu, J. H., & Huang, X. J. (2012). Electropolymerized surface ion imprinting films on a gold nanoparticles/single-wall carbon nanotube nanohybrids modified glassy carbon electrode for electrochemical detection of trace mercury(II) in water. *Analytica Chimica Acta*, *720*, 29-37.

Gao, C., Guo, Z., Liu, J. H., & Huang, X. J. (2012). The new age of carbon nanotubes: An updated review of functionalized carbon nanotubes in electrochemical sensors. *Nanoscale*, *4*, 1948-1963.

Gao, C., & Huang, X. J. (2013). Voltammetric determination of mercury(II). *TrAC Trends in Analytical Chemistry*, *51*, 1-12.

Ghanei-Motlagh, M., Fayazi, M., & Taher, M. A. (2014). On the potentiometric response of mercury(II) membrane sensors based on symmetrical thiourea derivatives—Experimental and theoretical approaches. *Sensors and Actuators B*, *199*, 133-141.

Gholivand, M. B., & Mohammadi-Behzad, L. (2014). Fabrication of a highly sensitive sumatriptan sensor based on ultrasonic-electrodeposition of Pt nanoparticles on the ZrO_2 nanoparticles modified carbon paste electrode. *Journal of Electroanalytical Chemistry*, *712*, 33-39.

Gholivand, M. B., Malekzadeh, G., & Derakhshan, A. A. (2014). Boehmite nanoparticle modified carbon paste electrode for determination of piroxicam. *Sensors and Actuators B*, *201*, 378-386.

Giacomino, A., Abollino, O., Malandrino, M., & Mentasti, E. (2008). Parameters affecting the determination of mercury by anodic stripping voltammetry using a gold electrode. *Talanta*, *75*, 266-273.

Giannakopoulos, E., Deligiannakis, Y., & Salahas, G. (2012). Electrochemical interfacial adsorption mechanism of polyphenolic molecules onto Hanging Mercury Drop Electrode surface (HMDE). *Journal of Electroanalytical Chemistry*, *664*, 117-125.

Giannetti, B. F., Moreira, W. A., Bonilla, S. H., Almeida, C. M. V. B., & Rabóczkay, T. (2006). Towards the abatement of environmental mercury pollution: An electrochemical characterization. *Colloids and Surfaces A*, *276*, 213-220.

Gilman, S. (2013). Coulometric study of rates of oxalic acid adsorption at a polycrystalline Platinum Electrode. *Journal of Electroanalytical Chemistry*, *692*, 53-59.

Gilman, S. (2014). Rate of adsorption of methanol at a polycrystalline platinum electrode in acid solution. *Journal of Electroanalytical Chemistry*, *712*, 47-54.

Girault, H. H. (2010). *Analytical and Physical Electrochemistry*. New York: CRC Press.

Goha, K. H., Lim, T. T., Banas, A., & Dong, Z. (2010). Sorption characteristics and mechanisms of oxyanions and oxyhalides having different molecular properties on Mg/Al layered double hydroxide nanoparticles. *Journal of Hazardous Materials*, *179*, 818-827.

Gong, J., Zhou, T., Song, D., & Zhang, L. (2010). Monodispersed Au nanoparticles decorated graphene as an enhanced sensing platform for ultrasensitive stripping voltammetric detection of mercury(II). *Sensors and Actuators B*, *150*, 491-497.

Gründler, P. (2007). *Chemical Sensors: An Introduction for Scientists and Engineers*. Berlin: Springer.

Guha, K. S., Mascarenhas, R. J., Thomas, T., & D’Souza, O. J. (2014). Differential pulse anodic stripping voltammetric determination of Hg^{2+} at poly (Eriochrome Black T)-modified carbon paste electrode. *Ionics*, *20*, 849-856.

Guo, X., Zhang, F., Evans, D. G., & Duan, X. (2010). Layered double hydroxide films: Synthesis, properties and applications. *Chemical Communications*, *46*, 5197-5210.

Harvey, D. (2000). *Modern Analytical Chemistry*. New York: McGraw-Hill.

Hernández-Santos, D., González-García, M. B., & García, A. C. (2002). Metal-nanoparticles based electroanalysis. *Electroanalysis*, *14*, 1225-1235.

Hezard, T., Fajerwerg, K., Evrard, D., Collière, V., Behra, P., & Gros, P. (2012). Gold nanoparticles electrodeposited on glassy carbon using cyclic voltammetry: Application to Hg(II) trace analysis. *Journal of Electroanalytical Chemistry*, *664*, 46-52.

Holmes, P., James, K. A. F., & Levy, L. S. (2009). Is low-level environmental mercury exposure of concern to human health? *Science of the Total Environment*, *408*, 171-182.

Hoyo, C. D. (2007). Layered double hydroxides and human health: An overview. *Applied Clay Science*, *36*, 103-121.

Iwashita, A., Nakajima, T., Takanashi, H., Ohki, A., Fujita, Y., & Yamashita, T. (2007). Determination of trace elements in coal and coal fly ash by joint-use of ICP-AES and atomic absorption spectrometry. *Talanta*, *71*, 251-257.

Jacobs, C. B., Peairs, M. J., & Venton, B. J. (2010). Review: Carbon nanotube based electrochemical sensors for biomolecules. *Analytica Chimica Acta*, *662*, 105-127.

Janata, J. (2009). *Principles of Chemical Sensors*. New York: Springer.

Janegitz, B. C., Figueiredo-Filho, L. C. S., Marcolino-Junior, L. H., Souza, S. P., Pereira-Filho, E. R., & Fatibello-Filho, O. (2011). Development of a carbon nanotubes paste electrode modified with crosslinked chitosan for cadmium(II) and mercury(II) determination. *Journal of Electroanalytical Chemistry*, *660*, 209-216.

Janegitz, B. C., Figueiredo-Filho, L. C., Vicentini, F. C., Ribeiro, M. F. M., Suarez, W. T., Fatibello-Filho, O., Metters, J. P., & Banks, C. E. (2014). Development of a carbon nanotube paste electrode modified with zinc phosphate for captopril determination in pharmaceutical and biological samples. *Analytical Methods*, *6*, 1324-1329.

Kempegowda, R. G., & Malingappa, P. (2012). Covalently modified multiwalled carbon nanotubes as a new voltammetric interface for the determination of mercury at picomolar level. *Electrochemistry Communications*, *25*, 83-86.

Kenduzler, E., Ates, M., Arslan, Z., McHenry, M., & Tchounwou, P. B. (2012). Determination of mercury in fish otoliths by cold vapor generation inductively coupled plasma mass spectrometry (CVG-ICP-MS). *Talanta*, *93*, 404-410.

Khalid, M. A. A. (2013). *Electrochemistry*. Rijeka: InTech.

Khanna, V. K. (2012). *Nanosensors: Physical, Chemical, and Biological*. Boca Raton: CRC Press.

Koniari, A., & Avranas, A. (2011). Adsorption of cetyltrimethylammonium bromide and/or cetyldimethylbenzylammonium chloride on partly covered hanging mercury drop electrode. *Journal of colloid and interface science*, *362*, 164-171.

Kopysc, E., Pyrzynska, K., Garbos, S., & Bulska, E. (2000). Determination of mercury by cold-vapor atomic absorption spectrometry with preconcentration on a gold-trap. *Analytical Sciences*, *16*, 1309-1312.

Korolczuk, M., & Rutyna, I. (2008). New methodology for anodic stripping voltammetric determination of methylmercury. *Electrochemistry Communications*, *10*, 1024-1026.

Kozin, L. F., & Hansen, S.C. (2013). *Mercury Handbook: Chemistry, Applications and Environmental Impact*. Cambridge: The Royal Society of Chemistry.

Lemos, V. A., & dos Santos, L. O. (2014). A new method for preconcentration and determination of mercury in fish, shellfish and saliva by cold vapour atomic absorption spectrometry. *Food Chemistry*, *149*, 203-207.

Leopold, K., Foulkes, M., & Worsfold, P. J. (2009). Gold-coated silica as a preconcentration phase for the determination of total dissolved mercury in natural waters using atomic fluorescence spectrometry. *Analytical Chemistry*, *81*, 3421-3428.

Li, F., & Duan, X. (2006). *Layered Double Hydroxides*. New York: Springer.

Li, M., Ni, F., Wang, Y., Xu, S., Zhang, D., & Wang, L. (2009). LDH modified electrode for sensitive and facile determination of iodate. *Applied Clay Science*, *46*, 396-400.

Locatelli, C., & Melucci, D. (2012). Voltammetric determination of ultra-trace total mercury and toxic metals in meals. *Food Chemistry*, *130*, 460-466.

Londonio, A., Fujiwara, F., Rebagliati, R. J., Gómez, D., & Smichowski, P. (2012). Determination of mercury in size fractionated road dust samples by flow injection-cold vapor-atomic absorption spectrometry. *Microchemical Journal*, *105*, 77-82.

Lu, J., He, X., Zeng, X., Wan, Q., & Zhang, Z. (2003). Voltammetric determination of mercury(II) in aqueous media using glassy carbon electrodes modified with novel calix[4]arene. *Talanta*, *59*, 553-560.

Manzi-Nshuti, C., Songtipya, P., Manias, E., Jimenez-Gasco, M. M., Hossenlopp, J. M., & Wilkie, C. A. (2009). Polymer nanocomposites using zinc aluminum and magnesium aluminum oleate layered double hydroxides: Effects of LDH divalent metals on dispersion, thermal, mechanical and fire performance in various polymers. *Polymer*, *50*, 3564-3574.

Marcolino-Junior, L. H., Janegitz, B. C., Lourenção, B. C., & Fatibello-Filho, O. (2007). Anodic stripping voltammetric determination of mercury in water using a chitosan-modified carbon paste electrode. *Analytical Letters*, *40*, 3119-3128.

Martinis, E. M., Bertón, P., Olsina, R. A., Altamirano, J. C., & Wuilloud, R. G. (2009). Trace mercury determination in drinking and natural water samples by room temperature ionic liquid based-preconcentration and flow injection-cold vapor atomic absorption spectrometry. *Journal of Hazardous Materials*, *167*, 475-481.

Martín-Yerga, D., González-García, M. B., & Costa-García, A. (2013). Electrochemical determination of mercury: A review. *Talanta*, *116*, 1091-1104.

Martín-Yerga, D., González-García, M. B., & Costa-García, A. (2012). Use of nanohybrid materials as electrochemical transducers for mercury sensors. *Sensors and Actuators B*, *165*, 143-150.

Masuda, T., Sonsudin, F., Singh, P. R., Naohara, H., & Uosaki, K. (2013). Potential-dependent adsorption and desorption of perfluorosulfonated ionomer on a platinum electrode surface probed by electrochemical quartz crystal microbalance and atomic force microscopy. *The Journal of Physical Chemistry C*, *117*, 15704-15709.

McCreery, R. L. (2008). Advanced carbon electrode materials for molecular electrochemistry. *Chemical Reviews*, *108*, 2646-2687.

Melucci, D., Locatelli, M., & Locatelli, C. (2013). Trace level voltammetric determination of heavy metals and total mercury in tea matrices (*Camellia sinensis*). *Food and Chemical Toxicology*, *62*, 901-907.

Merkoçi, A., Pumera, M., Llopis, X., Pérez, B., del Valle, M., & Alegret, S. (2005). New materials for electrochemical sensing VI: Carbon nanotubes. *TrAC Trends in Analytical Chemistry*, *24*, 826-838.

Mousty, C. (2010). Biosensing applications of clay-modified electrodes: A review. *Analytical and Bioanalytical Chemistry*, *396*, 315-325.

Mousty, C., Vieille, L., & Cosnier, S. (2006). Laccase immobilization in redox active layered double hydroxides: A reagentless amperometric biosensor. *Biosensors and Bioelectronics*, *22*, 1733-1738.

Moyo, M., Okonkwo, J. O., & Agyei, N. M. (2014). Maize tassel-modified carbon paste electrode for voltammetric determination of Cu(II). *Environmental monitoring and assessment*, 1-11.

Musumeci, A. W., Mortimer, G. M., Butler, M. K., Xu, Z. P., Minchin, R. F., & Martin, D. J. (2010). Fluorescent layered double hydroxide nanoparticles for biological studies. *Applied Clay Science*, *48*, 271-279.

Nagles, E., Arancibia, V., & Ríos, R. (2012). Determination of lead and cadmium in the presence of quercetin-5'-sulfonic acid by adsorptive stripping voltammetry with a hanging mercury drop electrode and a nafion-coated mercury film electrode. *International Journal of Electrochemical Science*, *7*, 4545-4558.

Naushad, M., Rangreez, T. A., & Alothman, Z. A. (2014). A mercury ion selective electrode based on poly-o-toluidine Zr(IV) tungstate composite membrane. *Journal of Electroanalytical Chemistry*, *713*, 125-130.

Nevado, J. J. B., Martín-Doimeadios, R. C. R., Bernardo, F. J. G., & Moreno, M. J. (2005). Determination of mercury species in fish reference materials by gas chromatography-atomic fluorescence detection after closed-vessel microwave-assisted extraction. *Journal of Chromatography A*, *1093*, 21-28.

Niu, X., Ding, Y., Chen, C., Zhao, H., & Lan, M. (2011). A novel electrochemical biosensor for Hg^{2+} determination based on Hg^{2+}-induced DNA hybridization. *Sensors and Actuators B*, *158*, 383-387.

Nordberg, G. F., Fowler, B. A., Nordberg, M., & Friberg, L. (2007). *Handbook on the toxicology of metal*. Burlington: Elsevier.

Nordberg, G. F., Fowler, B. A., Nordberg, M., & Friberg, L. (2007). *Handbook on the Toxicology of Metals*. Oxford: Academic Press.

Okçu, F., Ertaş, H., & Ertaş, F. (2008). Determination of mercury in table salt samples by on-line medium exchange anodic stripping voltammetry. *Talanta*, *75*, 442-446.

Parodi, B., Londonio, A., Polla, G., Savio, M., & Smichowski, P. (2014). On-line flow injection solid phase extraction using oxidised carbon nanotubes as the substrate for cold vapour-atomic absorption determination of Hg(II) in different kinds of water. *Journal of Analytical Atomic Spectrometry*, *29*, 880-885.

Perioli, L., Posati, T., Nocchetti, M., Bellezza, F., Costantino, U., & Cipiciani, A. (2011). Intercalation and release of antiinflammatory drug diclofenac into nanosized ZnAl hydrotalcite-like compound. *Applied Clay Science*, *53*, 374-378.

Pourbeyram, S. (2014). Electrocatalytic determination of H_2O_2 on the electrode modified by LBL assembly of polyoxometalates via zirconium ion glue. *Sensors and Actuators B*, *192*, 105-110.

Pourreza, N., & Ghanemi, K. (2009). Determination of mercury in water and fish samples by cold vapor atomic absorption spectrometry after solid phase extraction on agar modified with 2-mercaptobenzimidazole. *Journal of Hazardous Materials*, *161*, 982-987.

Pyhtilä, H., Perämäki, P., Piispanen, J., Niemelä, M., Suoranta, T., Starr, M., Nieminen, T., Kantola, M., & Ukonmaanaho, L. (2012). Development and optimization of a method for detecting low mercury concentrations in humic-rich natural water samples using a CV-ICP-MS technique. *Microchemical Journal*, *103*, 165-169.

Radhi, M. M., Tan, W. T., Ab Rahman, M. Z. B., & Kassim, A. B. (2010). Electrochemical redox of Hg^{2+} mediated by activated carbon modified glassy carbon electrode. *International Journal of Electrochemical Science*, *5*, 615-629.

Rajabi, H. R., Roushani, M., & Shamsipur, M. (2013). Development of a highly selective voltammetric sensor for nanomolar detection of mercury ions using glassy carbon electrode modified with a novel ion imprinted polymeric nanobeads and multi-wall carbon nanotubes. *Journal of Electroanalytical Chemistry*, *693*, 16-22.

Rajawat, D. S., Kumar, N., & Satsangee, S. P. (2014). Trace determination of cadmium in water using anodic stripping voltammetry at a carbon paste electrode modified with coconut shell powder. *Journal of Analytical Science and Technology*, *5*, 1-8.

Rajawat, D. S., Srivastava, S., & Satsangee, S. P. (2012). Electrochemical determination of mercury at trace levels using *Eichhornia Crassipes* modified carbon paste electrode. *International Journal of Electrochemical Science*, *7*, 11456-11469.

Ramezani, S., Ghobadi, M., & Bideh, B. N. (2014). Voltammetric monitoring of Cd(II) by nano-TiO_2 modified carbon paste electrode sensitized using 1,2-bis-[o-aminophenyl thio] ethane as a new ion receptor. *Sensors and Actuators B*, *192*, 648-657.

Río Segade, S., & Tyson, J. F. (2003). Determination of inorganic mercury and total mercury in biological and environmental samples by flow injection-cold vapor-atomic absorption spectrometry using sodium borohydride as the sole reducing agent. *Spectrochimica Acta Part B*, *58*, 797-807.

Rivas, G. A., Rubianes, M. D., Pedano, M. L., Ferreyra, N. F., Luque, G., & Miscoria, S. A. (2009). *Carbon Nanotubes: A New Alternative for Electrochemical Sensors*. New York: Nova Science Publishers.

Rives, V. (2001). *Layered Double Hydroxides: Present and Future*. New York: Nova Science Publishers.

Rodrigues, J. A., Rodrigues, C. M., Almeida, P. J., Valente, I. M., Gonçalves, L. M., Compton, R. G., & Barros, A. A. (2011). Increased sensitivity of anodic stripping voltammetry at the hanging mercury drop electrode by ultracathodic deposition. *Analytica Chimica Acta*, *701*, 152-156.

Rouessac, F., & Rouessac, A. (2007). *Chemical Analysis: Modern Instrumentation Methods and Techniques*. West Sussex: John Wiley & Sons.

Rubianes, M. D., & Rivas, G. A. (2003). Carbon nanotubes paste electrode. *Electrochemistry Communications*, *5*, 689-694.

Safavi, A., & Farjami, E. (2011). Construction of a carbon nanocomposite electrode based on amino acids functionalized gold nanoparticles for trace electrochemical detection of mercury. *Analytica Chimica Acta*, *688*, 43-48.

Sánchez, A., Morante-Zarcero, S., Pérez-Quintanilla, D., Sierra, I., & del Hierro, I. (2012). Determination of Hg(II) in natural waters using a carbon paste electrode modified with hybrid mesostructured silica nanoparticles. *Sensors and Actuators B*, *163*, 38-43.

Sanghavi, B. J., Hirsch, G., Karna, S. P., & Srivastava, A. K. (2012). Potentiometric stripping analysis of methyl and ethyl parathion employing carbon nanoparticles and halloysite nanoclay modified carbon paste electrode. *Analytica Chimica Acta*, *735*, 37-45.

Scholz, F. (2010). *Electroanalytical Methods: Guide to Experiments and Applications*. New York: Springer.

Seifie-Makrani, R., Sajjadi, N., Younesi, O., & Bagheri, H. (2014). A new strategy for determination of captopril as a hypertension drug using ZnO nanoparticle modified carbon paste electrode. *International Journal of Electrochemical Science*, *9*, 1799-1811.

Settle, F. A. (1997). *Handbook of Instrumental Techniques for Analytical Chemistry*. New Jersey: Prentice-Hall, Inc.

Sharifi, E., Salimi, A., Shams, E., Noorbakhsh, A., & Amini, M. K. (2014). Shape-dependent electron transfer kinetics and catalytic activity of NiO nanoparticles immobilized onto DNA modified electrode: Fabrication of highly sensitive enzymeless glucose sensor. *Biosensors and Bioelectronics*, *56*, 313-319.

Shi, W., Wei, M., Evans, D. G., & Duan, X. (2010). Tunable photoluminescence properties of fluorescein in a layered double hydroxide matrix and its application in sensors. *Journal of Materials Chemistry*, *20*, 3901-3909.

Sistani, P., Noori, A., Motlagh, M. F., Tamijani, A. H., Imani, E., Shadram, Y., Rahimzadeh, R., Ebrahimi, B., Sarebanhassanabadi, M., Negahdary, M., & Majdi, S. (2014). Manufacturing a modified carbon paste electrode with catalase enzyme-Au nanoparticles for electrochemical sensing of hydrogen peroxide and their electrocatalytic properties. *International Journal of Electrochemical Science*, *9*, 3680-3690.

Skoog, D. A., Holler, F. J., & Crouch, S. R. (2007). *Principles of Instrumental Analysis*. Belmont: Thomson.

Somerset, V. S., Hernandez, L. H., & Iwuoha, E. I. (2011). Stripping voltammetric measurement of trace metal ions using screen-printed carbon and modified carbon paste electrodes on river water from the Eerste-Kuils River System. *Journal of Environmental Science and Health Part A*, *46*, 17-32.

Suroviec, A. H. (2013). Introduction to electrochemistry. *Journal of Laboratory Chemical Education*, *1*, 45-48.

Švancara, I., Kalcher, K., Walcarius, A., & Vytřas, K. (2012). *Electroanalysis with Carbon Paste Electrodes*. Boca Raton: CRC Press.

Švancara, I., Vytřas, K., Barek, J., & Zima, J. (2001). Carbon paste electrodes in modern electroanalysis. *Critical Reviews in Analytical Chemistry*, *31*, 311-345.

Tchinda, A. J., Ngameni, E., & Walcarius, A. (2007). Thiol-functionalized porous clay heterostructures (PCHs) deposited as thin films on carbon electrode: Towards mercury(II) sensing. *Sensors and Actuators B*, *121*, 113-123.

Thomas, T., Mascarenhas, R. J., D'Souza, O. J., Detriche, S., Mekhalif, Z., & Martis, P. (2014). Pristine multi-walled carbon nanotubes/SDS modified carbon paste electrode as an amperometric sensor for epinephrine. *Talanta*, *125*, 352-360.

Tonelli, D., Scavetta, E., & Giorgetti, M. (2013). Layered-double-hydroxide-modified electrodes: Electroanalytical applications. *Analytical and Bioanalytical Chemistry*, *405*, 603-614.

Trikeriotis, M., & Ghanotakis, D. F. (2007). Intercalation of hydrophilic and hydrophobic antibiotics in layered double hydroxides. *International Journal of Pharmaceutics*, *332*, 176-184.

Tuantranont, A. (2013). *Applications of Nanomaterials in Sensors and Diagnostics*. Berlin: Springer.

Vashist, S. K., Zheng, D., Al-Rubeaan, K., Luong, J. H., & Sheu, F. S. (2011). Advances in carbon nanotube based electrochemical sensors for bioanalytical applications. *Biotechnology Advances*, *29*, 169-188.

Vicentini, F. C., Silva, T. A., Pellatieri, A., Janegitz, B. C., Fatibello-Filho, O., & Faria, R. C. (2014). Pb(II) determination in natural water using a carbon nanotubes paste electrode modified with crosslinked chitosan. *Microchemical Journal*, *116*, 191-196.

Violante, A., Pucci, M., Cozzolino, V., Zhu, J., & Pigna, M. (2009). Sorption/desorption of arsenate on/from Mg-Al layered double hydroxides: Influence of phosphate. *Journal of Colloid and Interface Science*, *333*, 63-70.

Virtanen, J. K., Rissanen, T. H., Voutilainen, S., & Tuomainen, T. P. (2007). Mercury as a risk factor for cardiovascular diseases. *Journal of Nutritional Biochemistry*, *18*, 75-85.

Wanekaya, A. K. (2011). Applications of nanoscale carbon-based materials in heavy metal sensing and detection. *Analyst*, *136*, 4383-4391.

Wang, J. (2006). *Analytical Electrochemistry*. New Jersey: John Wiley & Sons.

Wei, J., Yang, D., Chen, H., Gao, Y., & Li, H. (2014). Stripping voltammetric determination of mercury(II) based on SWCNT-PhSH modified gold electrode. *Sensors and Actuators B*, *190*, 968-974.

Welz, B., & Sperling, M. (1999). *Atomic Absorption Spectrometry*. Berlin: Wiley-VCH.

Wiener, J. G., Krabbenhoft, D. P., Heinz, G. H., & Scheuhammer, A. M. (2003). Ecotoxicology of mercury. *Handbook of Ecotoxicology*, *2*, 409-463.

Wu, D., Zhang, Q., Chu, X., Wang, H., Shen, G., & Yu, R. (2010). Ultrasensitive electrochemical sensor for mercury(II) based on target-induced structure-switching DNA. *Biosensors and Bioelectronics*, *25*, 1025-1031.

Xu, H., Zeng, L., Xing, S., Shi, G., Xian, Y., & Jin, L. (2008). Microwave-radiated synthesis of gold nanoparticles/carbon nanotubes composites and its application to voltammetric detection of trace mercury(II). *Electrochemistry Communications*, *10*, 1839-1843.

Xu, Y., Liu, X., Ding, Y., Luo, L., Wang, Y., Zhang, Y., & Xu, Y. (2011). Preparation and electrochemical investigation of a nano-structured material Ni^{2+}/MgFe layered double hydroxide as a glucose biosensor. *Applied Clay Science*, *52*, 322-327.

Yáñez-Sedeño, P., Pingarrón, J. M., Riu, J., & Rius, F. X. (2010). Electrochemical sensing based on carbon nanotubes. *TrAC Trends in Analytical Chemistry*, *29*, 939-953.

Yang, J., Yu, C., Fan, X., Ling, Z., Qiu, J., & Gogotsi, Y. (2013). Facile fabrication of MWCNT-doped NiCoAl-layered double hydroxide nanosheets with enhanced electrochemical performances. *Journal of Materials Chemistry A*, *1*, 1963-1968.

Yang, P., Gao, X., Wang, L., Wu, Q., Chen, Z., & Lin, X. (2014). Amperometric sensor for ascorbic acid based on a glassy carbon electrode modified with gold-silver bimetallic nanotubes in a chitosan matrix. *Microchimica Acta*, *181*, 231-238.

Yi, H. (2003). Anodic stripping voltammetric determination of mercury using multi-walled carbon nanotubes film coated glassy carbon electrode. *Analytical and Bioanalytical Chemistry*, *377*, 770-774.

Yildiz, G., Oztekin, N., Orbay, A., & Senkal, F. (2014). Voltammetric determination of nitrite in meat products using polyvinylimidazole modified carbon paste electrode. *Food Chemistry*, *152*, 245-250.

Yin, H., Cui, L., Ai, S., Fan, H., & Zhu, L. (2010). Electrochemical determination of bisphenol A at Mg-Al-CO_3 layered double hydroxide modified glassy carbon electrode. *Electrochimica Acta*, *55*, 603-610.

Yin, H., Zhou, Y., Cui, L., Liu, X., Ai, S., & Zhu, L. (2011). Electrochemical oxidation behavior of bisphenol A at surfactant/layered double hydroxide modified glassy carbon electrode and its determination. *Journal of Solid State Electrochemistry*, *15*, 167-173.

Yuan, S., Peng, D., Song, D., & Gong, J. (2013). Layered titanate nanosheets as an enhanced sensing platform for ultrasensitive stripping voltammetric detection of mercury(II). *Sensors and Actuators B*, *181*, 432-438.

Zahir, F., Rizwi, S. J., Haq, S. K., & Khan, R. H. (2005). Low dose mercury toxicity and human health. *Environmental Toxicology and Pharmacology*, *20*, 351–360.

Zhang, T., Lang, Q., Zeng, L., Li, T., Wei, M., & Liu, A. (2014). Substituent effect on the oxidation peak potentials of phenol derivatives at ordered mesoporous carbons modified electrode and its application in determination of acidity coefficients (p*K*a). *Electrochimica Acta*, *115*, 283-289.

Zhang, W. B., Su, Z. F., Chu, X. F., & Yang, X. A. (2010). Evaluation of a new electrolytic cold vapor generation system for mercury determination by AFS. *Talanta*, *80*, 2106-2112.

Zhang, X. Y., Wang, Q. C., Zhang, S. Q., Sun, X. J., & Zhang, Z. S. (2009). Stabilization/solidification (S/S) of mercury-contaminated hazardous wastes using thiol-functionalized zeolite and Portland cement. *Journal of Hazardous Materials*, *168*, 1575-1580.

Zhang, X., Ju, H., & Wang, J. (2008). *Electrochemical Sensors, Biosensors and Their Biomedical Applications*. Massachusetts: Academic Press.

Zhang, Y., & Adeloju, S. B. (2008). A novel sequential injection-cold vapour atomic absorption spectrometric system for rapid and reliable determination of mercury. *Talanta*, *74*, 951-957.

Zhou, N., Chen, H., Li, J., & Chen, L. (2013). Highly sensitive and selective voltammetric detection of mercury(II) using an ITO electrode modified with 5-

methyl-2-thiouracil, graphene oxide and gold nanoparticles. *Microchimica Acta*, *180*, 493-499.

Zhou, Y., Tang, W., Dang, F., Chai, S., & Zhang, L. (2014). Electrochemical characterization of poly-beryllon II modified carbon paste electrode and its application to selective determination of pyrocatechol and hydroquinone. *Colloids and Surfaces B*, *118*, 148-153.

Zoski, C. G. (2007). *Handbook of Electrochemistry*. Oxford: Elsevier.

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