VOLTAMMETRIC MEASUREMENT OF COPPER(II) USING MODIFIED CARBON PASTE ELECTRODE WITH ZINC LAYERED HYDROXIDE-2(3-CHLOROPHENOXY)PROPIONATE NANOCOMPOSITE

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ABSTRACT

A multi-walled carbon nanotube (MWCNT) paste electrode modified with zinc layered hydroxide-2(3-chlorophenoxy)propionate (ZLH-CPPA) nanocomposite was evaluated for the voltammetric determination of Cu(II). Experimental conditions were used percentage of modifier, supporting electrolyte, pH and scan rate. The optimum conditions of electrode were obtained with 2.5% (w/w) ZLH-CPPA:MWCNT mass ratio using 4.0×10^{-3} M CH_3COONa as supporting electrolyte with pH adjusted to 2.5 using CH_3COOH and scan rate of 500 mVs^{-1}. Under these conditions, the voltammetric response was linearly dependent on the Cu(II) concentration in the range of $1.0 \times 10^{-9} - 1.0 \times 10^{-6}$ M and $1.0 \times 10^{-5} - 1.0 \times 10^{-3}$ M with a limit of detection 1.0×10^{-10} M. Most metal ions present in excess of 25 times the concentration of Cu(II) did not interfere except from Fe(II), Ba(II), Pb(II) and Ca(II).

PENGUKURAN VOLTAMMETRIK KUPRUM(II) MENGGUNAKAN ELEKTROD PES KARBON TERUBAH SUAI DENGAN NANOKOMPOSIT HIDROKSIDA ZINK BERLAPIS-2(3-KLOROFENOKSI)PROPIONAT

ABSTRAK

Elektrod pes karbon nanotiub berbilang dinding (MWCNT) terubahsuai dengan nanokomposit hidroksida zink berlapis-2(3-klorofenoksi)propionat (ZLH-CPPA) telah dinilai untuk penentuan voltammetrik Cu(II). Keadaan kajian yang digunakan adalah peratusan pengubahsuai, elektrolit penyokong, pH dan kadar imbasan. Keadaan optimum elektrod diperolehi dengan nisbah jisim 2.5% (w / w) ZLH-CPPA: MWCNT menggunakan 4.0×10^{-3} M CH_3COONa sebagai elektrolit sokongan dengan pH diselaraskan kepada 2.5 dengan menggunakan CH_3COOH dan kadar imbasan sebanyak 500 mVs^{-1}. Dalam keadaan ini, rangsangan voltammetrik adalah linear bergantung kepada kepekatan Cu(II) dalam julat $1.0 \times 10^{-9} - 1.0 \times 10^{-6}$ M dan $1.0 \times 10^{-5} - 1.0 \times 10^{-3}$ M dengan had pengesanan 1.0×10^{-10} M. Kebanyakan ion logam yang hadir melebihi 25 kali ganda kepekatan Cu(II) tidak mengganggu kecuali Fe(II), Ba(II), Pb(II) dan Ca(II).

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LIST OF ABBREVIATIONS

Ag/AgCl	Argentum/Argentum chloride
CMCPE	Chemically modified carbon paste electrode
CPE	Carbon paste electrode
CV	Cyclic voltammetry
DPASV	Different pulse anodic stripping voltammetry
DPCSV	Different pulse cathodic stripping voltammetry
DPV	Different pulse voltammetry
E_{pa}	Anodic peak potential
E_{pc}	Cathodic peak potential
i_{pa}	Anodic peak current
i_{pc}	Cathodic peak current
MWCNT	Multiwall carbon nanotube
SCE	Saturated calomel electrode
SWASV	Square wave anodic stripping voltammetry
ZLH-CPPA	Zinc layered hydroxide-2(3-chlorophenoxy)propionate

CHAPTER 1

INTRODUCTION

1.1 Introduction to Copper

Copper is a ductile reddish metal, used in alloys, plumbing (pipes), and electrical cable with excellent electrical conductivity. Copper is one of the first transition element series. All compounds of Cu(I) are diamagnetic and colourless, only for Cu_2O, which is red, and coloured and can be obtained from anion or charge transfer bands. Most Cu(I) compounds are instable in water because Cu(I) compounds are quickly oxidized to Cu(II) compounds (Cotton, Wilkinson, Murillo, & Bochman, 1999).

The compounds of Cu(II) are paramagnetic and coloured (Chang, 1998). In aqueous solution, almost all Cu(II) salts are blue, the colour being due to the presence of the hexaaquacopper(II) ion, $[Cu(OH_2)_6]^{2+}$, except copper(II) chloride which is green. A concentrated aqueous solution of copper(II) chloride is green, due to the presence of complex ions such as the nearly planar tetrachlorocuprate(II) ion, $[CuCl_4]^{2-}$. When diluted, the colour of the solution changes to blue. The colour transformation is due to the successive replacement of chloride ions in the complexes by water molecules, the final colour being that of the hexaaquacopper(II) ion (Rayner-Canham, 1996).

Copper occurs naturally in a wide range of mineral deposits as azurite, malachite, bornite, in sulphides as in chalcopyrite ($CuFeS_2$), coveline (CuS), chalsosine (Cu_2S), and in oxide like cuprite (Cu_2O). Copper is also found in many kinds of food, drinking water and human body. In food, copper can be found in whole grains cereals, legumes, oysters, organ meats, dark chocolate, vegetables, nuts, and shellfish. Copper has wide variety of uses in domestic and industry applications. Copper is used in electroplating, microelectronic applications, electrical wire, piping, roof construction, and catalyst in the chemical industry (Northey, Haque, & Mudd, 2013; Stern et al., 2007).

The living organism carries out biological functions used copper as catalytic cofactor in redox process of protein for growth and development (Tapiero, Townsend, & Tew, 2003). Copper is an essential component of metalloenzymes, where participates in the oxidized Cu(II) and reduced Cu(I) states. As component of metalloenzymes, copper plays a number of roles in metabolism reactions in human body, including metabolism of nitrogen compounds, regulation of RNA and DNA transcription process, angiogenesis, the synthesis of essential compounds, and oxygen transport (McArdle & Ralph, 2001; Tobiasz, Walas, Landowska, & Konefał-Góral, 2012).

Copper concentration in human tissues over the range of 0.7 and 7.8 mg kg^{-1} and in the blood varies in the range of 0.8-21.6 mg L^{-1} (Kabata-Pendias, & Mukherjee, 2007). Copper is needed in the formation of blood and several enzyme systems, including superoxide dismutase, which detoxifies free radicals (Stern, 2010). Besides human, plants and animals also required copper as an essential micro-nutrient. In plants, copper is an important element that plays a significant role in photosynthesis, disease resistance, regulation of water, and in seed production. Thus, the metal plays many roles in plants, animals and humans. Copper deficiency causes some symptoms include iron deficiency anemia, osteoporosis, brain disturbances, ruptured blood vessels, increased susceptibility to infections due to poor immune function, loss of pigment in the hair and skin, weakness, fatigue, poor thyroid function, breathing difficulties, skin sores, and irregular heartbeat (Bonham, Connor, Hannigan, & Strain, 2002).

Copper is an essential element for human being, but it causes Wilson's disease, Menke's syndrome, hypoglycemia, gastrointestinal cattarch, and dyslexia at above a save level intake. In excess copper on the cell of human body can damage the cell membrane and leakage of internal enzymes. It can be cytotoxic and causes high reactive oxygen species, peroxidation of lipid in membranes, cleavage of DNA and RNA molecules, and direct oxidation of proteins. Excessive copper accumulate in liver, brain, and some other organs can cause liver cirrhosis, degenerative changes in brain and some endocrine organs (Ndlovu, Arotiba, Sampath, Krause, & Mamba, 2012).

Food, drinking water, and copper-containing diet supplements are the main source of copper for human (Cockell, Bertinato, & L'Abbé, 2008; Kabata-Pendias, & Mukherjee, 2007). In human adult, save level intake of copper in a range 0.6 to 1.6 mg per day is absorbed then recycled actively in the digestive track, tissues and fluids (Tapier et al., 2003). According to WHO and Ordinance of the Ministry of Health and Human Welfare of Poland, the maximum limits of copper for several foods are given in Table 1.1 (Kabata-Pendias, & Mukherjee, 2007). In Malaysia, the maximum permitted copper in the drinking water and bottled water is 1.0 mg L^{-1} and in the mineral water is 1 mg L^{-1} (Lembaga Penyelidikan Undang-Undang, 2007).

1.2 Introduction to Zinc Layered Hydroxide

The layered double hydroxide (LDH) and layered hydroxide salts (LHS) compounds are layered compounds which have brucite-type (magnesium hydroxide) structure. Their structures are built by placing of two-dimensional units connected to each other through the weak forces. The layers in the compound associated each other by covalent bond and the weak interactions hold the stacking of the layer with Van der Waals forces for neutral layers compound, and electrostatic forces for charged layers compound (Arizaga, Satyanarayana, & Wypych, 2007).

Table 1.1

The maximum limit of the presence of copper in foods

Food	Limit of reporting (mg kg^{-1})
Fruit juices	5.0
Fats and oils	0.1-0.4
Wheat, grain, flour	6.0
Powdered milk	6.0

The layered double hydroxide (LDH) and layered hydroxide salts (LHS) compounds can retain chemical species with positive and negative charges which compatible to those of the layers charge. Layered double hydroxide (LDH) is derived from the brucite-like (magnesium hydroxide) structure having divalent and trivalent cations at hydroxide layers as shown in Figure 1.1. The general formula of layered double hydroxide is represented by $[M^{2+}{}_{1-x} M^{3+}{}_x(OH)_2 (A^{n-})_{x/n}.yH_2O$, where M^{2+} and M^{3+} is the metallic cation and A is the counterion with charge n^- (Arizaga et al., 2007). Structure of layered hydroxide salt (LHS) is similar with layered double hydroxide (LDH), but the positive charges of the layers are generated when some hydroxide ions are replaced with water molecules, other types of oxoanions, or generating materials with anionic exchange capacity (Marangoni, Mikowski, & Wypych, 2010).

Layer hydroxide salts (LHS) can be represented by the general formula of $M^{+2}(OH)_{2-x}(A^{-n})_{x/n}.yH_2O$, where M^{2+} is the metallic cation (e.g., Mg^{2+}, Ni^{2+}, Zn^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, and Cu^{2+}) and A is the counterion with charge n^-. The electrostatic charge in the layered hydroxide salts is stabilized by counterion with negative charge in the second coordination sphere of metal (Arizaga, Mangrich, da Costa Gardolinski, & Wypych, 2008; Marangoni, Ramos, & Wypych, 2009). The layered hydroxide salts have the ability to intercalate the interlayer inorganic or organic anions because the formation of layered hydroxide salt by lamellar units which is stacked along the basal direction with weak bonds (Arizaga et al., 2008; Hussein, Ghotbi, Yahaya, & Abd Rahman, 2009).

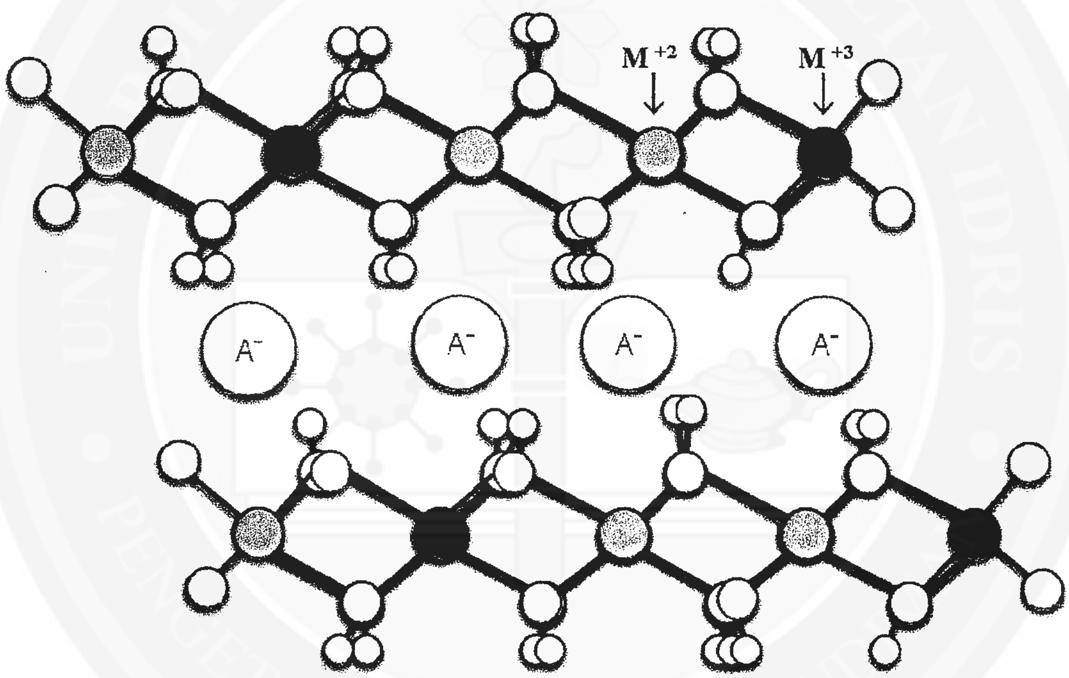

Figure 1.1. Schematic of the structure of a generic layered double hydroxide (LDH) (Arizaga et al., 2007).

The zinc layered hydroxide compound is zinc compound with general formula of $Zn_5(OH)_8X_2$ (X= Cl, Br, I, NO_3, CH_3COO, etc), which derive a structure from layered zinc hydroxide nitrate $[Zn_5(OH)_8(NO_3)_2].2H_2O$ having brucite like layers with one quarter of octahedrally coordinated zinc atom replaced by tetrahedrally coordinated zinc atom located below and above plane as shown in Figure 1.2. The empty space at tetrahedral zinc atoms causes charge in the layer hydroxides. The anions are located in the interlayer space in order to balance the layer charge (Demel, Pleštil, Bezdička, Janda, Klementová, & Lang, 2011).

The reaction of aqueous zinc salt solution with solution containing OH^{-} have resulted immediate precipitation of layer hydroxide salts due to homogeneous nucleation in the solution. The precipitation become crystal of the layered hydroxide salts in the solution. The crystal is two-dimensional and the resultant particles have plate-like or sheet-like shape (Hosono, Fujihara, Kimura, & Imai, 2004). The zinc hydroxide and anion stacked each other in lamellar unit form the layered compound. The zinc layered hydroxide compound as layered material has great potential to be used in optical and electrical applications, sensor, and photoelectrical nanodevices (Hussein, Hashim, Yahaya, & Zainal, 2010).

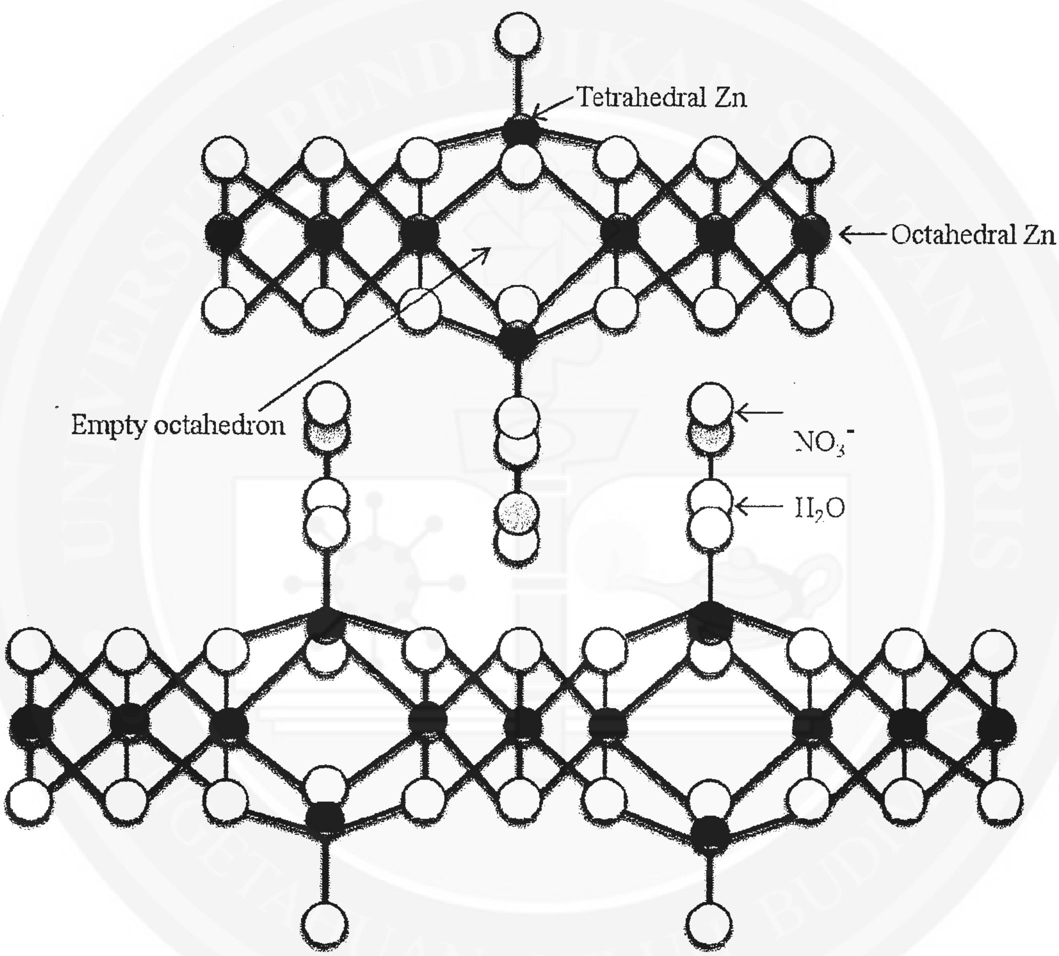

Figure 1.2. Structure of zinc hydroxide nitrate (Arizaga et al., 2007).

1.3 Significance of Study

The existence of copper in our life is very important because it is used for domestic purpose, agricultural and industry (Mazloum-Ardakani, Akrami, Kazemian, & Zare, 2009). Copper is also an essential element for human beings as it is needed in the formation of blood and several enzyme systems, including superoxide dismutase, which detoxifies free radicals (Singh, Mehtab, & Jain, 2006; Stern, 2010; Tobiasz, Walas, Landowska, & Konefał-Góral, 2012). It is incorporated into a variety of organics which perform specific metabolic functions. Copper is an essential element not only for human beings but also for plants and animal. In plant, it plays an important role in carbohydrate and lipid metabolism (Kendüzler & Türker, 2003). In animals, it is found widely in tissues, with concentration in liver, muscle, and bone.

Copper can potentially to be harmful toward human's health associated with both very low and very high intakes (Georgopoulos, Wang, Georgopoulos, Yonone-Lioy, & Lioy, 2006). Copper has two oxidation states, Cu(I) and Cu(II), this chemical species can be very useful to play role as a reducing or oxidizing cofactor in various biochemical reactions. But this chemical species can catalyze the production of free radicals, in particular through Fenton chemistry, thus leading to the damage of proteins, DNA, and other biomolecules (Diopan et al., 2008; Shestivska et al., 2011; Sochor et al., 2010;). Human long-term exposure to copper can cause acute gastrointestinal effects include stomachaches, dizziness, vomiting and diarrhoea (Lagos, Maggi, Peters, & Reveco, 1999). High level of copper in the environment could lead to accumulation within food chain and harm to human health. Our body can tolerate copper ions level up to maximum 3.0 mg L^{-1} per day (Oztekin, Ramanaviciene, & Ramanavicius, 201; Tapiero et al., 2003). Excessive copper in our body may cause diseases such as Menke's syndrome and Wilson's disease (Tapiero et al., 2003).

The application of copper in the industry and domestic makes global problem because the presence of copper in industrial waste water, mostly from electroplating, disposal of mining washings, refineries, and the use of copper as a base compound for antifouling paints. Moreover, the corrosion in copper pipes increasing the concentration of copper in drinking watern (Chatterjee & Sengupta, 2011; Stern, 2010). Thus, in view of its utility as well as toxicity it is very important for us to determine the level of copper ion in environmental samples.

There are several analytical methods which have been used to determine copper at low concentrations such as inductively coupled plasma optical emission spectrometry (ICP-OES) (Carrilho, Nóbrega & Gilbert, 2003), electrothermal atomic absorption spectrometry (EAAS) (Queiroz, Rocha, Knapp, & Krug, 2002; Ivanova, Benkhedda, & Adams, 1998), X-ray fluorescence (XRF) (Capote, Marcó, Alvarado, & Greaves, 1999), flame atomic absorption spectrometry (FAAS) (Lopes, Almeida, Santos, & Lima, 2006), and inductively couple plasma mass spectrometry (ICP-MS) (Szpunar, Bettmer, Robert, Chassaigne, Cammann, Lobinski, & Donard, *et al.,*1997). Even though ICP-OES and AAS are techniques used the most in the determination of trace copper, the low concentration level parental solution is not compatible with the detection limits of this technique (Chaiyo, Chailapakul, Sakai, Teshima, & Siangproh, 2013) and these methods are not only inconvenient and expensive but also time-consuming (Chapman, Long, Datskos, Archibald, & Sepaniak, 2007).

The determination of trace metal ions needs method not only high sensitivity but also low cost. Electroanalytical method can be the suitable method because this technique is low cost, high sensitivity, easy operation, and the ability for portability (Ashkenani & Taher, 2012). The electroanalytical method used solid materials such as mercury, gold, platinum, and carbon for working electrode. Currently, the various carbon forms are preferred used as working electrode because carbon has broad potential window, low background current, low cost, inert, good conductivity and resistance to environmental and chemical hazards (Oztekin et al., 2010). Graphite, glassy carbon (Oztekin & Yazicigil, 2009; Wang, Lu, Hocevar, Farias, & Ogorevc, 2000), and carbon nanotubes (Ashkenani & Taher, 2012; Faria & Fatibello-Filho, 2009; Janegitz et al, 2011) are carbon forms mostly used as materials of working electrode.

Carbon paste electrode can be prepared by mixing graphite and binder paste, and added modifier for chemically modified carbon paste electrode (CMCPE) (Ashkenani & Taher, 2012). The chemically modified carbon paste electrode (CMCPE) is able to increase the sensitivity of measurement with further lower detection limit. The modifiers should be suitable for increasing the performance of the carbon paste electrode. The nanomaterials (Beitollahi, Raoof, & Hosseinzadeh, 2011; Yang, Zhou, Zhang, Zhang, Jiao, & Li, 2009), organic polymers (Bontempelli, Comisso, Toniolo, & Schiavon, 1997), and inorganic ion exchangers (Walcarius, 1999) are modifier which mostly used to determine trace metal. One of the most important effects of modifier is decreasing the redox potential required for the electrochemical reaction (Shahrokhian, Hamzehloei, Thaghani, & Mousavi, 2004). The accumulation of target analyte on the electrode through adsorption by modifier is enhancing the sensitivity and selectivity of the electrochemical measurements (Fathirad, Afzali, Mostafavi, Shamspur, & Fozooni, 2013).

Nowadays, carbon nanotube (CNT) has attracted attention in electrochemistry due to their structure with high aspect ratio, high mechanical strength, high thermal conductivity, and high electrical conductivity (Ajayan, 1999; Beitollahi, Karimi-Maleh, & Khabazzadeh, 2008; Ganjali, Motakef-Kazami, Faridbod, Khoee, & Norouzi, 2010; Merkoci, 2007). They widely used as materials for electrode because they have capability to promote electron transfer reaction and improve the sensitivity of electroanalitycal measurement. The application of multi-walled carbon nanotube (MWCNT) as material for electrode have been reported to result in low detection limits and high sensitivities (Fang, Wei, Li, Wang, & Zhang, 2007; Zheng & Song, 2009). Moreover, the multi-walled carbon nanotube modified electrodes have been improved the voltammetric determinations of organic (Beitollahi, Karimi-Maleh, & Khabazzadeh, 2008; Shahrokhian, Kamalzadeh, Bezaatpour, & Boghaei, 2008) and inorganic compounds (Ganjali, Motakef-Kazami, Faridbod, Khoee, & Norouzi, 2010).

Zinc layered hydroxide-2(3-chlorophenoxy)propionate nanocomposite is an anionic clay material. Zinc layered hydroxide-2(3-chlorophenoxy)propionate nanocomposite including layered hydroxide salts (LHS) compound that have potential applications for ion exchange, catalyst, absorption, separation, and composite materials (Xingfu, 2008). Interestingly, zinc layered hydroxide-2(3-chlorophenoxy) propionate nanocomposite could have the synergistic effect of mechanical stability of the inorganic network with the intrinsic chemical reactivity of the attached organic functional group. These materials can serve as matrices for electroactive ions because they are usually able to incorporate ions by an ion-exchange process, like polymeric ionomers (Mousty, 2004). Due to the properties of zinc layered hydroxide-2(3-chlorophenoxy) propionate nanocomposite, it can be excellent modifier to modified multi-walled carbon nanotubes. In the voltammetric measurement, the modified carbon nanotubes paste electrodes have shown enhancement in the detection of trace metal with low detection limit. The modified multi-walled carbon nanotube with zinc layered hydroxide-2(3-chlorophenoxy)propionate nanocomposite using voltammetric measurement can be suitable method for analysis of a large number of environmental samples, which does not require sample pretreatment.

1.4 Electrochemistry

Electrochemistry is study about the chemical changes caused by the passage of electrical properties and the production of electrical energy by chemical reactions. In its application to analytical chemistry, this generally involves the measurement of some electrical property related to concentration of some particular chemical species. The electrical properties that are most commonly measured are potential or current, voltage, resistance and conductance, or combinations of these (Allen & Larry, 2001).

Electrochemical methods of analysis have grown greatly in application and importance over the last 40 years, and these have been largely due to the development and improvement of electronic systems permitting refinements in the measurement of the critical characteristics mentioned in the foregoing. There are many purposes in electrochemical measurement, such as determination of trace metal ions or organic