

CHAPTER 1

INTRODUCTION

1.1 Introduction

Electrochemical techniques traditionally have found significant applications in environment analysis (Locatelli and Torsi, 2001), organic (He *et al.*, 2005) and inorganic synthesis (Zhang *et al.*, 2005). Inorganic, physical, analytical and biological chemists widely use electrochemical method, such as cyclic voltammetry, stripping voltammetry, for a variety of purposes, including fundamental studies of oxidation and reduction processes in many media, electron transfer, adsorption processes on electrode surface (Ravichandran and Baldwin, 1981), and reaction mechanisms and speciation (Labuda *et al.*, 1995). The common characteristic of electrochemical methods is that they involve the application of a potential (E) to the electrode and the measuring of the current (i) flowing through the electrochemical cell (Bard, 2000). In various case, the applied potential is varied or the current measured over a period of time (t). Thus electrochemical techniques can be described as some function of E, i, and t.

Today a great variety of analytical method describes various traditional and newly developed methods for the selective and sensitive determination of metal ions at trace level. Particularly in the light of the new challenges posed by environmental samples. One field the offers great potential in this respect is that included by electrochemical techniques. Trace element of metals, particularly with heavy metals are continuous dispersed into the general environment from mining, pouring, casting, processing and using metals (Apostoli, 2002). Metals are elements with physical and chemical properties depending on their low number of electron in the external orbital therefore with the learning to form positive ions (Apostoli, 2002). In the biological systems the elements tend to lose electrons and to form positive ions originating coordination compounds. The complexes are composing at least one atom of a metal which coordinates other specific atom or molecules called ligand, such as aminic (NH_2), oxydrilic (-OH), disulfuric (-SS), carboxylic (-COOH) and Oxalate (-OOC-COO-). These groups also pertain to important molecules with catalytic, structure or transport functions (Apostoli, 2002).

The determination of metals in water, food and soil has gained a lot of interest because of the importance of many elements to human health. This interest is justified by the wide exposure in the workplace and in the general environment and impaired health of the general population by the ingestion of food and beverages contaminated by metals such as fish contaminated by mercury, drinking water by arsenic, rice by cadmium (Apostoli, 2002). The interest arises from three cases of concern, nutritional, toxicological (Yebra-Biurrun and Garcia-Garrido, 2001) and precious metals, such as Ca, Fe, Mg, Zn, Co and Al are necessary for maintenance of optimum health and toxicological since certain metals such as Pb, Cd, As and Hg are detrimental to optimum health (Yebra-Biurrun and Garcia-Garrido, 2001). Many elements are physiologically present in the human body and for some of them an essential role in the biological systems has long been recognized (Apostoli, 2002). The essential elements are involved in different multiple functions and structures (coenzymes, transport proteins, hormones, specific receptor sites). It could be stated that their main role in the coenzymes activity (Apostoli, 2002), in particular, Zn is a good activating several hundreds of enzymes.

The bioavailability and toxicity of an element are determined by the chemical form of the element. Oxidation state and solubility are particularly important factors for bioavailability (Christensen, 1995). Chromium, lead, cadmium, arsenic and mercury are harmful to human health. The toxic effects of these metals are partly due to direct inhibition of the enzymes systems, partly due to the indirect alteration of the essential metal ions equilibrium and to the consequent inhibition of their biological availability (Abernathy *et al.*, cited in Apostoli, 2002). Effects caused by metals are various from irritant and acute or chronic systematic toxic results to teratogenic, mutagenic and carcinogenic (Apostoli, 2002). Over the last 40-50 years the use of lead in gasoline has presented the main source of lead emitted into the atmosphere and adsorbed by soil, plants and animals. The chemical form of lead such as lead sulfide, lead carbonate and lead sulfate are widely distributed in the environment (Christensen, 1995). Humans are continuously exposed to lead from natural such as drinking water, soil, industrial emission, car exhaust, contaminated food and beverages (Christensen, 1995). Acute lead poisoning is associated with anorexia, dyspepsia and constipation followed by diffuse paroxysmal abdominal pain (Christensen, 1995). At higher concentrations (4 μM), encephalopathy may occur, long term lead exposure may generate irreversible functional and morphological renal changes. At low

exposure level, the adverse effects on the enzyme activities of the heme-part way have been used for biological monitoring of lead exposure. (Zielhuis, 1975, 1977; Moor and Goldberg, 1985 cited in Christensen, 1995).

Cadmium exists in the earth's crust, in ambient and workplace air, food and water (Christensen, 1995). Cadmium is introduced into water bodies from smelting, metal plating, cadmium–nickel batteries, phosphate fertilisers, mining, pigments, stabilizers, alloy industries and sewage sludge (Rao *et al.*, 2006). The primary sources of cadmium exposure for humans are food and tobacco smoke (Arnold *et al.*, 2006). In humans, the largest amounts of cadmium are deposited in the kidneys and liver (Jarup *et al.*, 1998). Because the body has no mechanism to excrete cadmium, cadmium accumulates in tissues. The half-life of cadmium in the human kidney cortex is exceptionally long: 10–30 years (Jarup *et al.*, 1998). **Itai–itai** disease, which developed in numerous inhabitants of the Jinzu River basin in Toyama Prefecture, is the most severe form of chronic cadmium (Cd) poisoning caused by prolonged oral Cd ingestion (Inaba *et al.*, 2005). Its toxicity arises from the strong affinity of Cd²⁺ in for thiol groups, displacing biological important element Zn (Honeychurch *et al.*, 2002).

Minamata disease is the first well studied and the most serious Hg poisoning occurred through consumption of Hg-contaminated fish and other seafood due to the Hg contaminated wastewater, which was discharged from an industrial plant into the coastal area in **Minamata**, Japan (Harada, 1995). There are the multiple pathways of mercury contamination through air, water, food pharmaceuticals, cosmetic products, etc (Zahir *et al.*, 2005). Inorganic Hg released into the environment from natural or anthropogenic sources is transformed to organic Hg (mainly methylated form), which is then accumulated in higher trophic animals through food chain (Boudou and Ribeyre, 1997; Morel *et al.*, 1998). The organic form of mercury is most toxic, particularly methylmercury, it passes the blood brain barrier owing to its lipid solubility (Tschounwou *et al.*, 2003). Toxicological effects of elemental Hg (Hg⁰) exposure include erethism, tremor, paresthesia, respiratory and renal failures, cardiac arrest and cerebral oedema, while subclinical exposure may induce kidney, behavioral, and cognitive dysfunctions (Yoshida, 1998, Kales and Goldman, 2002). Toxic effects on the respiratory, cardiovascular and gastrointestinal system have been shown following acute exposure to elementary mercury (Zahir *et al.*, 2005).

Copper is an essential nutrient for living organisms (Voutsina *et al.*, 2001) as a constituent of several enzymes and as a redox catalyst in a variety of metabolism pathways. Copper is serving as catalytic co-factor of various enzymes required for respiration, oxidative damage response and iron uptake. Excess copper accumulated in the cell catalyzes the generation of reactive hydroxyl radicals causing damage to DNA, proteins and lipids (Voutsina *et al.*, 2001). Excessive amounts of copper in the body can also pose a risk. Acute copper toxicity can result in liver disease and severe neurological defect (Adams and Keen, 2005). Among complexed species of copper hydroxyl species $[\text{Cu}(\text{OH})^+]$ and $[\text{Cu}(\text{OH})_2]$ display some toxicity (He *et al.*, 2004). While copper inorganic carbon species such as $(\text{CuHCO}_3)^+$, CuCO_3 and $[\text{Cu}(\text{CO}_3)_2]^{2-}$ are much less toxic or not toxic at all (Wang *et al.*, 2002; Huang and Wang, 2002).

Various techniques are employed to recover of precious metal from industrial wastes. The main separation techniques are: solvent extraction, leaching precipitation, electro-oxidation and ion-exchange (Chmielewski *et al.*, 1997). There are two important aspects for recovery, one is economy and to save raw materials and the second is the protection of the environment from dispersed toxic of heavy metal (Chmielewski *et al.*, 1997). Electrochemical approaches for metal recovery have been studied. The electrochemical recovery of gold and silver (Spitzer and Bertazzoli, 2004) from cyanide solution using titanium and vitreous carbon cathodes was studied. It was found that the recovery were obtained 76% and 84% of gold on titanium and vitreous carbon respectively. Furthermore, the recover of silver from synthetic photographic using activated carbon was studied (Adani *et al.*, 2005). It was found that the carbons were pretreated with 0.5 M sulfuric and nitric acids at 25 °C, it had resulted in significant silver recoveries of 98.5% and 95% from sodium and ammonium thiosulfate solutions, respectively.

1.2 Basic knowledge

Stripping analysis are the most widely used for environmental monitoring, food analysis and medicine (Brainina *et al.*, 2000). Stripping voltammetric techniques are based on the recording of the current, which flows between the working electrode and auxiliary electrode, due to the reduction or oxidation of species present in the solution and the current resulting from the

redox processes is plotted as a function of potential, E (O'Neill, 1994). The resulting voltammogram is related to the chemical identity of the redox species with magnitude of the potential axis and on its concentration with magnitude of the current at a given potential (O'Neill, 1994). Therefore, voltammetric techniques provides both a qualitative and quantitative analysis for electroactive species. Potential and current are two functions to complete the circuit for current flow. Therefore, three electrodes are generally used, the working electrode as which the redox reaction of interest is taking place at applied potentials measured relative to the reference electrode through which no current flows, with the circuit being completed by an auxiliary or counter electrode (O'Neill, 1994). The three electrodes are connected through a potentiostat that ensures the desired potential is applied between the working electrode and reference electrode is kept at sufficient potential to drive the appropriate oxidation or reduction to balance the current produced at the working electrode (Widrig *et al.*, 1990).

Many techniques of voltammetry with variable imposed modulations of potential have been developed in particular to increase sensitivity (Buffle and Tercier-Waeber, 2005). Table 1 gives the most important of voltammetric techniques. Cyclic voltammetry is not sensitive enough for trace analysis but it is useful to study the mechanism of electron transfer. Stripping voltammetry is most widely used for trace metal and speciation analysis. The remarkable sensitivity of stripping analysis is attributed to its preconcentration step. The three type of commonly used are anodic, cathodic and adsorptive stripping voltammetry. All types of stripping voltammetry involves two step. The first step, the analyze species is accumulate onto a suitable working electrode, during a given time period by application of a sufficient negative potential, under convection conditions that favor the mass transport of analyze towards the electrode. This preconcentration step results in the exceptional sensitivity that can be achieved. During the second step, the accumulated analyte is measured or stripped from the electrode by the application of potential scan. When the potential reaches a value at the vicinity for the redox potential of the reduced species or adsorbed species, reduction or oxidation take place, giving rise to a current that flows between working and reference electrodes. The current during the scan is monitored and is plotted with respect potential. One can think of the potential as the intensive variable applied to the working electrode, and one can think of the current as the extensive variable corresponding to the rate of an electrode reaction in response to the potential

perturbation (Bard and Zoski, 2000). The peak potential (E_p) provides qualitative information while the magnitude of the peak current (i_p) is proportional to the species concentration in the sample (Economou *et al.*, 1994). Any number of potential waveforms can be used for the stripping analysis (this is, differential pulse, square wave, linear sweep). The most common wave forms are differential pulse and square wave due to the bias against charging current. However, square wave has additional advantages of faster scan rate and increased sensitivity compared to differential pulse.

Adsorptive stripping voltammetry, the analyte is adsorbed on the electrode by means of a non-electrolytic process prior to voltammetric scan. Voltammetric stripping with a negative going potential scan or constant cathodic current can be used for detecting the adsorbed complex. Most procedures involve the reduction of the metal in the adsorbed complex although it is possible also to exploit the reduction of the ligand (Wang, 2000). The response of the surface confined species is directly related to its surface concentration (Wang, 2000). The measured peak height depended the accumulation time and the accumulation potential. Additional factors include the surface properties of the compound, the electrode area and some instrumental parameters (Esteban and Casassas, 1994).

Techniques for environmental monitoring of heavy metal is important for trace metal determination are spectroscopic (in particular, graphite furnace atomic absorption spectroscopy, inductively coupled plasma mass spectroscopy), neutron activation analysis and voltammetric. The advantage of spectroscopic techniques compared to voltammetric techniques is that they are applicable to a large number of elements and a small sample volume. However, the disadvantage of spectroscopic techniques is the expensiveness of instruments and high cost of maintenance and measuring of total concentration only. Therefore, speciation measurements and preconcentration step of the analyses are feasible only by coupling them with separation and extraction procedures. However, such steps significantly increase the risk of contaminations or chemical species modifications during sample storage or sample handling. In contrast, the characteristics of voltammetric techniques are suited for automatic speciation measurement and preconcentration step with no sample change and avoid the contaminations are avoided. The specific features and versatility of stripping voltammetric techniques include: high sensitivity and low detection limit (depending on analyte), wide range of concentration of analytes, both of

organic and inorganic, relative simplicity and low cost of equipment, multi-element determination in a single run, a large array of solvent (aqueous, mixed, aprotic) can be used and continuous automatic flow analysis on-site environmental monitoring.

Table 1 The major voltammetric techniques used for trace-metal analysis and their typical concentration ranges. V = Potential scan rate; ΔE = Pulse amplitude; f = Frequency; t_d = Preconcentration time; i_p = Peak current; E_p = Peak potential (Buffle and Tercier-Waeber, 2005).

Technique	Imposed function	Recorded function	Conc. range (mole L)
Linear sweep voltammetry (LSV) (cyclic voltammetry dotted line)			$10^{-2} - 10^{-6}$
Differential pulse voltammetry (DPV)			$10^{-4} - 10^{-7}$
Square wave voltammetry (SWV)			$10^{-4} - 10^{-8}$
Anodic Stripping Voltammetry (ASV) with linear scan (full line) or modulations (e.g. DP → DPASV or SW → SWASV; dotted line)			$10^{-6} - 10^{-11}$
Adsorptive stripping voltammetry (AdSV) (with or without modulation)			$10^{-6} - 10^{-12}$
Stripping Chronopotentiometry (SCP)			$10^{-5} - 10^{-9}$

1.3 Literature review

1.3.1 Chemically modified electrodes

Chemically modified electrode is an attractive topic for research over the past two decades in many aspects of science and technology. CMEs have potential applications in diverse fields such as electrolysis (Chen *et al.*, 1997), chemical sensors (Eftekhari, 2001), and corrosion protection (Shi *et al.*, 2006). The main benefits for analytical application include acceleration electron transfer reactions, selective preferential accumulation and interferential exclusion. Such features can provide higher selectivity, detectability and stability to amperometric, potentiometric and voltammetric device. Chemically modified electrode which is an electrode which has been considerably treated with some reagents, has attractive property. There are great variety of possibility to design electrodes for various purposes and application. Chemically modified electrode provide one approach to the development of analytical techniques from a deliberate immobilization of a modifier agent onto the electrode surface. The importance immobilized reagent-based systems lies in minimizing the amount of expensive reagent for a specific analysis and hence over-all cost. Compared to conventional electrodes, greater control of electrode characteristics and reactivity is achieved by surface modification, since the immobilization transfers the physical chemistry properties of the modifier to the electrode surface. Chemically modified electrode is necessary interface between the solution and the measurement electronics: it provides selectivity, increases sensitivity and influence over-all stability. In trace analysis, during the accumulation step, CMEs preconcentrate analytes onto electrode surface, allowing lower concentration to measured than it possible in absence of preconcentration step. The preconcentration step acts as a separation step, removing the analyze species of interest from the sample solution.

Before CMEs, there are various working electrodes applied to electroanalysis. The development of stripping voltammetry is connected with the use of mercury and carbon electrodes. Toxicity of mercury and trouble in working with hanging mercury is well known. Thus, the advent of CMEs is developed. However, mercury electrode is used most frequently in analysis of environmental samples (Locatelli and Torsi, 2001). The modified of mercury film electrodes are also widely used. It is based on the deposition on a conventional metal electrodes

(e.g. silver, platinum), including those prepared by glassy carbon electrode (Adeloju *et al.*, 1999), impregnated graphite electrode (Lukaszewski *et al.*, 1996) and carbon paste electrode (Farghaly, 2004). The mercury film is deposited prior to analysis by adding Hg(II) ions in sample solution. It exhibits the properties of mercury electrode. Gold film electrode (Fonticelli *et al.*, 2004) are traditionally used for determination of electro-positive elements (e.g. Hg, As, Cu). Glassy carbon, platinum and carbon paste electrode serve as substrates of gold film electrodes. The gold film is deposited on electrode surface by an electrolytic method (Fonticelli *et al.*, 2004). The main problem with gold electrodes in analytical procedure is the regeneration of their surface (Watson *et al.*, 1999). It was found that reaction products could not be removed completely from electrode surface during electrochemical regeneration. Carbon paste electrode is a mixture of carbon powder and pasting medium (Baldwin *et al.*, 1986). The carbon paste electrode is considered to be chemically modified electrode only when an additional reagent was added.

1.3.2 Chemically modified carbon paste electrodes

Chemically modified carbon paste electrode was first described by Adams in 1958 (Adams, 1958 cited in Olson and Adams, 1960). Carbon paste electrodes are prepared by mixing electrical conducting graphite powder and modifier with a suitable pasting medium such as mineral oil (Wang *et al.*, 2001). The paste mixture is then packed into a suitable electrode body. The most popular body of carbon paste electrodes are various, syringe tubes, glass tubes and Teflon tubes whose end hole can be easily refilled with a new portion of the paste (Stadlober *et al.*, 1996). The easy constructions equipped with a piston for extrusion of the paste (Walcarius, 1999) are frequently used including commercially available products from Metrohm. For most CPEs, the actual diameter of the end hole forming the suitable carbon paste surface is being chosen from 2 to 10 mm, which is handy for a majority of electrochemical measurement (Svancara and Schachl, 1999). A copper wire is usually employed to make electrical contact, it was placed in the back of the paste mixture. Prior to the measurements the modified electrode was smoothed out on a piece of transparent paper to get a fresh surface (Hu *et al.*, 2003).

The graphite powder is usually a multicrystalline powder with an average particles of 0.01- 0.02 mm; smaller particles is 0.001 mm show lower background currents and using the larger particles slightly broader peak (Wang *et al.*, 2001). The properties of conventional paste

mixtures from spectroscopic graphite and paraffin oil were found satisfactory for a majority of applications, including popular modifications. The spectroscopic graphite is now commonly available in the market and may be ordered from Aldrich, Sigma, Fluka or Merck. These products absolutely prevail in the composition of carbon paste used in recent years.

Common liquid medium are paraffin oil, silicone oil and mineral oil. The nonelectrolytic mediums, two logotype products (Nujol®Aldrich and Uvasol®Merck) of spectroscopic paraffin oil are dominantly used. It is appeared in almost paper. Generally, the rate of electron transfer is decreased with the additional of pasting mediums (Wang *et al.*, 2001). The non polar pasting mediums fulfill all the important standard; both are considerably chemically inert, non volatile, water insoluble and having fine consistency of paste mixtures.

The most common procedure for preparing CMCPes is directly mixing particulate matter into the paste. A good modifier in carbon paste electrode has four requirements:

(1) The modifier should be insoluble in the analyze solution or they should at least strongly adsorb to the paste components in order to avoid dissolution of the molecules from the electrode surface during the measurement.

(2) The modifier should not have the same redox potential as the analyze.

(3) The anion part of the modifier should have insoluble salt when it interacts with the analyze in the solution (Abdollahi, 1995).

(4) The modifier should be sensitive enough with low percentage in the electrode and be able to preserve physical stability as well as electrical conductivity of the electrode (Abdollahi, 1995).

The optimum ratio between pasting liquid and graphite powder is determined by the desired consistency and properties of the paste and its capability of forming enough active site in modified paste. The amount of modifier in the paste usually varies between 10 to 30% w/w (Svancara *et al.*, 1996). The optimum ratio between graphite, modifier and medium is usually about 0.55:0.35:0.10 % w/w (Huang *et al.*, 1994).

Carbon paste electrode has been widely applied in electroanalysis because they serving on the various of supporting electrolyte, low background current, using both positive and negative potential, using in electrocatalytic, various alternative procedures for pretreating, conditioning and regenerating the electrode surface. In addition, providing measurements

simultaneously with several CPEs (Hu *et al.*, 2003) and specific kinetic reaction (affected by carbon paste composition). The interaction of analyze-electrode surface is the basic of chemical accumulation (adsorption, ion-pairing, complexation, bioaccumulation, hydrophobic interaction). The best method of increasing the sensitivity at a CPE is the use of an electrode surface which is able to selectively accumulated analyte from the solution under carefully controlled conditions.

Type of modifier in voltammetric analysis. The accumulation of analyte in solution can be performed at the electrode modified with a suitable receptor (Murray *et al.*, 1987). The analyte accumulation in a small volume at a CPE modifying surface usually precedes detection and its main purpose is to improve detectability. In addition, the selective interactions between analyte and the immobilized reagent serve as a separation step, thus improving the electrode selectivity. Typical modifier can be divided in to several groups:

(1) Analytical reagents and compounds. This modifier can be accumulated metal ions on electrodes surface, like dimethylglyoxime (Baldwin *et al.*, 1986), 8-hydroxyquinoline (Cai *et al.*, 1995), derivative of 2-naphthol (Khan, 1998), 1, 4-bis(prop-2'-enyloxy)-9, 10-anthraquinone (Mousavi *et al.*, 2001), Crown ethers (Ijeri and Srivastava, 2000) and N-p-chlorophenylcinnamo-hydroxamic acid (Degefa *et al.*, 1999). Baldwin firstly used dimethylglyoxime (Baldwin *et al.*, 1986) and its derivative (Prabhu *et al.*, 1987) as modifier for carbon paste electrode for determination of nickel(II) and copper(II) respectively. Nickel can be also determined with CPE modified with dimethylglyoxime at low levels (Baldwin *et al.*, 1986). Its voltammetric response is not effected by many other metal ions due to the specific complexation and the medium exchange involves in the preconcentration step. Furthermore, Dimethylglyoxime as modifier for simultaneously determination of mercury, cobalt, nickel and palladium at carbon paste electrode have been reported (Zhang *et al.*, 1996) which can be used to determine the metal ions down to 10^{-8} M for 120 s of accumulation time. Recently, the simultaneous determination of lead(II) and cadmium(II) was developed with diacetyldioxime modified carbon paste electrode (Hu *et al.*, 2003) and it was applied to determination of Pb^{2+} and Cd^{2+} in water samples. Some reagents of this type contained in the paste may be slightly soluble in water and hence have to be stabilized against dissolution by fixing with an additional adhesion agent (Zhang *et al.*, 1996). Therefore, dimethylglyoxime is a chelating agent which can form complexes with metal ions and can be used as good modifier in electroanalysis method.

(2) Ion exchangers. A group of substances with ion-pairing properties have been widely used as modifiers for carbon paste electrode mainly to preconcentrate certain analytes in the bulk solution. If one of the ions involved is electroactive, immobilization of an ion-exchanger reaction can be measured with voltammetry techniques. The first modification of carbon paste electrode with cation exchanger resin is developed in order to study its analytical determination of Cu^{2+} (Wang *et al.*, 1984). In the following years, some publications appeared using this method (Kalcher, 1986; Hernandez *et al.*, 1989). The research has developed CPEs containing anion-exchangers for determination of inorganic anions (Kalcher, 1986). Hexacyanoferrate (II) and (III) were accumulated from pH 2 solution onto a CPE modified with the weakly basic anion exchanger Amberlite LA2. This electrode could be applied to the determination of hexacyanoferrate in wine down to 6 ppb iron. Lately, cetyltrimethylammonium bromide (CTAB) served again as a reliable modifier to preconcentrate and direct some less common metal species (Stadlober, 1996; Stanlober, 1997) whereas chromatographic packing agent Amberlite IRC 718 can be recommended for speciation analysis (Viana, 1999). The selectivity of the ion exchange accumulation reaction can be controlled and reproducibility achieved by controlling the sample solution pH and ionic strength.

(3) Clay minerals and zeolites. Clay and zeolites modified CPEs have accomplished broader utilization in the field of electroanalysis. These substances of both natural and synthetic origin represent a group of hydrated crystalline aluminosilicates that are capable of acting as both ion exchanger and adsorbents. The clay mineral especially montmorillonite can be mixed directly with carbon paste (Kula and Navratilova, 1996). Carbon paste electrode modified with zeolite *A* have optimized the voltammetric analysis of Ag^+ (Wang and Martinez., 1988). Interesting, the determination of $1 \text{ mg L}^{-1} \text{ Ag}^+$ was not affected by the present of 10 mg L^{-1} of co-existing metal ions such as Co(II), Mn(II), Ca(II), Pb(II), Cu(II) and Ti(IV) because they did not compete with silver for exchange sites. Cu(II) species were measured by square wave voltammetry in ammonia buffer (pH 9) after accumulation in phosphate buffer (pH 6) using a zeolite X modified carbon paste electrode (Bing and Kryger, 1996; Chen *et al.*, 1997). These procedure was applied to the determination of cadmium(II) and zinc(II) by performing the preconcentration in ammonia buffer and detect in phosphate buffer (Chen *et al.*, 1997). Surprisingly HNO_3 0.1 M was used as electrolyte for the regeneration of electrode surface.

(4) Humic substances. A new approach of electroanalytical of trace metal analysis was carried out on carbon paste electrode modified with humic acids. The determination of the accumulated analyte at the electrode surface can be measured by the voltammetric techniques. Due to the fact that humic acids possess functional groups of complexing abilities such as carboxyl and phenolic hydroxyl groups (Wang *et al.*, 1998). The modified carbon paste electrode with humic acids exhibits good affinity to some metal ions and provides a sensitivity route to the quantification of these metals. These include determination of mercury (Navratilova and Kula, 1992), silver (Navratilova and Kula, 1993), copper and lead (Jeong *et al.*, 1994). Based on a similar principle, there was a procedure for analysis of bismuth using a sodium humate modified carbon paste electrode (Wang *et al.*, 1997). The humic acids have shown some advantages such as low cost and high enrichment efficiency. However, to directly use humic substances as the modifier of carbon paste electrode several analytical disadvantages exist, such as that it is difficult to use humic acids when prepared carbon paste electrode in the pH acid solution, it causes background current and base line drift in voltammetric measurements.

(5) Silica. Carbon paste modified with silica immobilized inorganic films or organic functional groups permit one to carry out selective preconcentration of various species. Silica is covered with surface hydroxyl groups and exhibits ion exchange or adsorption capabilities for metals (Walcarius *et al.*, 1999). Silica gel displays high specific surface area and porosity. Therefore, silica can be the materials for modified carbon paste electrode. Carbon paste electrode modified with silica has recently attracted much attention in the field of electroanalytical chemistry (Walcarius, 1998) because the attractive properties of these materials to a selected redox process. Organically modified silicates keep considerable promise in the development of new devices for electrochemical application due to their good mechanical and chemical stability (Collinson, 1998). The wide range of organic functionalities grafted on silica, the covalent attachment of amine groups on silica gel surfaces by reaction with aminopropyl-triethoxysilane has been investigated (Van der Voort and Vansant, 1997). The resulting material is liable to preconcentrate copper(II) from dilute solution (Leyden *et al.*, 1975). In addition, The functional group attached to the silica gel surface was 3-(2-thiobenzimidazolyl) propyl, which is able to complex Hg(II) ions (Aleixo *et al.*, 1993).

(6) Biological modifier. Certain microorganisms can accumulate metal ions (Shengjun and Holcombe, 1991). It is possible to determine metal ions by voltammetry following a bioaccumulation step at the electrode. The research was investigated the ability of algae modified carbon paste electrode to preconcentrate Cu^{2+} (Gardia-Torresdey *et al.*, 1988). The *Eisenia bicyclies* alga modified carbon paste electrode was used to preconcentrate Cu^{2+} at a pH 5 solution and voltammetrically measured with detection limit of 1.0×10^{-6} M which emphasizes the ion exchange nature of accumulation process. Other biological applications in this procedure include *Sphagnum* moss (Ramos *et al.*, 1993), *Datura Innoxia* (Wang *et al.*, 1992) and *Pennisetum* (Ouanguipat *et al.*, 2003) modified CPEs, which also allow metal ions accumulation by ion exchange. The high binding capacities of the moss and the reversible metals ions understanding have made these materials attractive for trace metal quantitative analysis and have been employ to the accumulation of Pb^{2+} (Ramos *et al.*, 1993). The biological materials bring a new modifier of selectivity to metal ions determination.

1.3.3 Quinone compounds and their roles

Quinone compounds are common to numerous natural products and they are associated with anticancer, antibacterial, antimalarial and fungicide activities (Molfetta *et al.*, 2005). Coenzyme Q (CoQ) or ubiquinone (2,3-dimethoxy-5-methyl-6-polyprenyl-1,4-benzoquinone) is the only lipid redox molecule that is endogenously synthesized in mammals. This compound functions as an electron carrier in the respiratory chain. In its reduced form (ubiquinol), CoQ is also a powerful anti-oxidant that can react with oxygen radicals and lipoperoxides to prevent damage to biomolecules in different tissues and cell compartments (Turunen *et al.*, 2004). In addition, quinone compounds are used in wide variety of applications in industries, such as oxygen absorber, recovery of precious metals, and catalyst of hydrogen peroxide manufacturing (Salimi *et al.*, 1999). Quinone consists of mainly benzoquinones, anthraquinones, and naphthoquinones. In Figure 1, the greatest highlight of quinones is the ability to compose a reversible oxidation-reduction cycle. It is possible that quinone compounds can have various value of the standard redox potential concerned by their functional groups. Anthraquinone derivatives have been widely used in analytical chemistry, mainly as strong chelating agents and chromophores (Zhu and Li, 1998).

Anthraquinone is used in paper industry as a catalyst to increase the pulp production yield (Yoon *et al.*, 2001). The electrochemical behavior of different quinone derivatives has studied considerable attention during the past decade (Pournaghi-Azar and Golabi, 1988; Pournaghi *et al.*; 1995; Tissot and Huissoud, 1996). It is well known these compounds are characterized by a two electron reductions (Pournaghi-Azar and Golabi, 1988; Pournaghi *et al.*, 1995). The first reduction step to semiquinone anion radical is usually reversible, while the second step to a dianion is a nearly reversible or an irreversible process, depending on the experimental conditions applied. Nevertheless, a single two electron reduction step is observed in the presence of proton donors (Tissot and Huissoud, 1996). The anthraquinone derivatives have shown strong adsorption tendencies on various electrode materials including Hg (Almeida *et al.*, 1999), graphite (Zhang and Anson, 1992), and glassy carbon (Salimi *et al.*, 1999).

Previous studies have shown Cu^{2+} and Ni^{2+} form complexes with 1,2-dihydroxyanthraquinone (Das and Mandal, 1996). These complexes has been studied by the spectroscopic method and the effective stability constant of the Cu^{2+} complex is 5.135×10^{29} while that of the Ni^{2+} complex is 3.445×10^{25} . In addition, 1,2-dihydroxyanthraquinone is used for the spectroscopic determination of Cu^{2+} (Shiu and Chan, 1995). In addition, The enrichment of Fe(III), Co(II), Ni(II) and Cu(II) by solid phase extraction with 1,8-dihydroxyanthraquinone anchored to silica gel before their determination by flame atomic absorption spectrometry (Goswami and Singh, 2002). The resulting lowest concentration for quantitative recovery was 4.0 (Cu), 3.3 (Fe), 6.6 (Co) and 4.0 (Ni) ng mL^{-1} .

In the case of chemically modified electrode, the well known analytic reagent, alizarin red S (dihydroxyanthraquinone sulfonate) has been used to modify the electrode in the determination of Cu^{2+} (Filho *et al.*, 1999) and the detection limit was 1.7×10^{-8} M. Carbon paste electrode modified with alizarin red S has been used in the determination of scandium. The detection limit was found to be 6.0×10^{-10} M (Zhang *et al.*, 2001). In addition, the trace measurement of zirconium based on the cathodic adsorptive stripping voltammetry of the zirconium-alizarin red S complex at a carbon paste electrode, the results showed that the complex can be adsorbed on the surface of CPE (Li *et al.*, 2001). Furthermore, the utility of carbon paste electrode modified with 2,3-dicyano-1,4-naphthoquinone for voltammetric determination of silver(I), the procedure is based on the formation of silver(I) complex with

2, 3-dicyano-1,4-naphthoquinone by the accumulation from the aqueous solution (Khodari *et al.*, 1994). The detection limit of these method is 5.0×10^{-8} M. In addition, the determination of lead (II) has been successfully performed by carbon paste electrode modified with 1,4-bis (prop-2'-enyloxy)-9, 10-anthraquinone (Mousavi *et al.*, 2001). These method is based on complex formation with the modifier. The developed method was applied to lead detection in waste waters. However, the electroanalysis of metal ions at so far. The aim of the present investigation was to develop a new chemistry modified electrode for the selective preconcentration and quantification of metal ions at trace level.

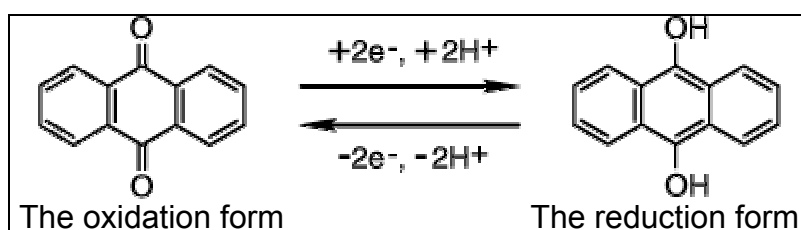


Figure 1 The oxidation and reduction form of anthraquinone

1.4 The objectives

1. To develop chemically modified carbon paste electrodes with quinone compounds for determination of metals by stripping voltammetry.
2. To apply chemically modified carbon paste electrode for quantitative analysis of metals in water sample.
3. To get the fundamental information for thesis which can be useful for more applications.