ELECTRODEPOSITION OF CARBOXYLATED MULTIWALL CARBON NANOTUBE ON GRAPHITE REINFORCEMENT CARBON FOR VOLTAMMETRY DETECTION OF CADMIUM

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A dissertation in partial fulfilment of the requirement for the award of the degree of Master of Science (Chemistry)

Faculty of Science
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2013
Dedicated to my beloved family…
ACKNOWLEDGEMENT

In the name of Allah, the most Gracious and the Most Merciful
Alhamdulillah, all praised to Allah S.W.T for His Blessing and permission, I have finally completed my master degree dissertation, and for the strength and guidance which accompanied my life.

I would like to express my gratitude to Prof. Dr. Rahmalan Ahamad and Assoc. Prof. Dr. Nor Aziah Buang for their continuous guidance, advice and constant support throughout this project. Their invaluable help of constructive comments and suggestions throughout the experimental and thesis work have contributed to the success of this research.

I also wish to extend my gratitude to all technical staff members En. Yassin, Pn. Mariyam and Pn. Ramlah for their collaboration and assistance while carrying out my laboratory work. Million words of thank to my fellow friends and colleagues who show their concern and support all the way. Thanks for the friendship and memories.

Last but not least, my deepest gratitude goes to my beloved parents; Othman Abu Hassan and Hapsah Idris, also to my siblings for their endless love, prayers and encouragement. Also not to forget, to those who indirectly contributed in this research, your kindness means a lot to me. Thank you very much.
ABSTRACT

Determination of cadmium ion at trace and sub-trace levels is still challenging due to high cost and limited capability of analytical instrumentation. A simple, low cost, non-toxic graphite reinforcement carbon (GRC) electrode modified with carboxylated multiwall carbon nanotubes (c-MWCNT) was prepared by electrodeposition process and used for the determination of cadmium ions at sub-part per billion (sub-ppb) levels. The study involved investigation of electrochemical performance of GRC with different hardness and size. The carboxylated-functionalized MWCNT was characterized by Fourier Transform Infrared Spectrophotometer (FTIR) and Field Emission Scanning Electron Microscope-Energy Dispersive X-ray analysis (FESEM-EDX). FESEM was also used to investigate the surface morphology of the c-MWCNT/GRC electrode. The newly developed electrode was successfully used for the detection of cadmium ion in 0.04 M Briton Robinson Buffer (BRB) by differential pulse anodic stripping voltammetry (DPASV). Some important operational parameters including pH of the buffer, initial potential, scan rate and accumulation time were optimised. Optimum conditions for the DPASV technique was obtained as follows: initial potential $E_i = -1600$ mV vs. Ag/AgCl (satd.); scan rate $\rho = 2$ mV per sec.; pH = 5.0; deposition time of 10 sec. Based on the DPASV of cadmium ion peak height at -0.78 V vs. Ag/AgCl (Sat’d), the c-MWCNT was found to enhance the anodic peak current of cadmium ion by a factor of 7 fold compared to that peak produced using a bare GRC electrode. Linear calibration curves were obtained from 1 ppb to 5 ppb with detection limit of 0.004 ppb and limit quantification of 0.012 ppb ($R^2=0.966$) respectively. The results suggest that the newly developed c-MWCNT/GRC has a potential to be a simple, efficient, low cost and disposable electrode system for the determination of cadmium ions at a very low concentration level.
Penentuan ion kadmium pada kadar surih dan sub-surih masih mencabar kerana kos analisis yang tinggi dan keupayaan instrumentasi yang terhad. Satu kaedah yang mudah, berkos rendah, menggunakan grafit tetulang karbon (GRC) elektrod diubahsuai dengan karbosilik tiubnano karbon multi berdinding (c-MWCNT) telah disediakan melalui kaedah elektroenapan dan digunakan untuk penentuan ion kadmium pada kadar sub-per bilion (sub-ppb). Kajian ini melibatkan penentuan prestasi elektrokimia GRC pada kekerasan dan saiz yang berbeza. Pencirian karbosilat MWCNT yang difungsikan adalah menggunakan kaedah Spektroskopi Inframerah Fourier Transformasi (FTIR) dan Bidang Pelepasan Imbasan Mikroskop Elektron-Tenaga Sebaran sinar-X (FESEM-EDX). FESEM juga digunakan untuk menyiasat morfologi permukaan elektrod c-MWCNT/GRC. Elektrod yang baru dibangunkan ini telah berjaya digunakan untuk pengesanan ion kadmium dalam penimbal 0.04 M Britain Robinson (BRB) melalui kaedah voltammetri perlucutan anodik denyut pembeza (DPASV). Beberapa parameter penting bagi operasi ini termasuk pH larutan penimbal, potensi awal, kadar imbasan dan masa pengumpulan telah dioptimumkan. Keadaan optimum yang dicapai untuk teknik DPASV telah diperolehi seperti berikut: potensi awal $E_i = -1600 \text{ mV vs Ag/AgCl}$; kadar imbasan $v = 2 \text{ mV per saat}$; $pH = 5.0$; masa pemendapan pada 10 saat. Berdasarkan voltamogram DPASV yang diperolehdengan ketinggian puncak ion kadmium pada -0.78 V vs Ag / AgCl, kehadiran c-MWCNT telah didapati dapat meningkatkan puncak anodik ion kadmium pada faktor 7 kali ganda berbanding puncak yang dihasilkan menggunakan elektrod GRC tidak terubah suai. Julat keluk penentu ukuran untuk teknik DPASV diperolehi daripada 1 ppb hingga 5 ppb dengan had pengesanan 0.004 ppb dan had kuantifikasi pada 0.012 ppb (R2 = 0.966). Keputusan menunjukkan bahawa elektrod c-MWCNT/GRC ini mempunyai potensi untuk menjadi satu sistem yang mudah, cekap, berkos rendah dan boleh dipakai buang bagi tujuan penentuan ion kadmium pada tahap kepekatan yang sangat rendah.
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<td>( \Delta E_p )</td>
<td>Peak Separation</td>
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<td>( \mu L )</td>
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<td>AES</td>
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<td>Dimethylformamide</td>
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<td>Dimethyl Sulfoxide</td>
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<td>Energy Dispersive X-ray</td>
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<td>FAAS</td>
<td>Flame Atomic Absorption Spectroscopy</td>
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<td>FESEM</td>
<td>Field Emission Scanning Electron Microscope</td>
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<td>FTIR</td>
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<td>GCE</td>
<td>Glassy Carbon Electrode</td>
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<td>GRC</td>
<td>Graphite Reinforcement Carbon</td>
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<td>GFAAS</td>
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<td>H(_3)BO(_3)</td>
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HCl - Hydrochloric Acid
H$_2$O - Water
H$_2$SO$_4$ - Sulfuric Acid
HNO$_3$ - Nitric Acid
ICP - Inductive Couple Plasma
Ip - Peak Current
KBr - Potassium Bromide
KCl - Potassium Chloride
K$_4$[Fe(CN)$_6$] - Potassium hexacyanoferrate
KMnO$_4$ - Potassium Permanganate
LOD - Limit of Detection
LOQ - Limit of Quantification
LSV - Linear Sweep Voltammetry
MeCN - Acetonitrile
Mn - Manganese
Mm - Millimetre
mV/s - Millivolt per seconds
M - Molar
MWCNTs - Multiwall Carbon Nanotubes
MS - Mass Spectrometry
NaOH - Sodium Hydroxide
Nd - Neodymium
Ni - Nickel
Ppm - Part per million
Ppb - Part per billion
Rpm - Rotation per minute
SWCNTs - Single Wall Carbon Nanotubes
Sec - Seconds
t$_{acc}$ - Accumulation time
THF - Tetrahydrofuran
$\nu$ - Scan rate
V - Volt
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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Carbon nanotubes (CNTs) represent an important material in nanotechnology. Since the re-discovery of this material by Iijima in 1991, it has attracted enormous interest and remarkable attention due to their unique properties (Iijima, 1991). It has a simple atomic configuration that leads to the unique geometric, mechanical, electronic, thermal and chemical properties (Wang, 2006). These peculiar properties of CNTs have made them as an attractive material for the surface modifier and electrochemical sensor.

Numerous investigations and publications have been produced since the first application of carbon nanotubes as sensor was reported by Britto in 1996. It is now well recognized that carbon nanotubes in sensors and modified electrodes can promotes electron transfer, increasing sensitivity and impart resistance against surface fouling (Rivas et al., 2009). The presence of pentagonal defect on the tube surface, the electronic structure and their dimension contributed to the electrocatalytic effect. These suggest that a wide variety of analytes can be determined by electrodes modified with functionalised CNT.

This study utilized a low cost graphite reinforcement carbon (GRC) as the based material to support CNT layer electrode for the detection of cadmium ion. GRC is made from a common graphite pencil which is normally used as lead in mechanical pencil (Tavares and Barbeira, 2008). Although this graphite pencil
electrode is relatively new, the literature described the successful use of GRC in determination of various applications as voltammetric sensors (Tavares and Barbeira, 2008). The usage of this type of electrode leads to lower cost, renewable electrode, non-toxic and convenient as compared to other conventional carbon electrodes.

Cadmium (Cd) is a well-known heavy metal recognized as the most toxic contaminants towards the environmental and industry. This toxicity is reported due to their ability to induce severe alteration in various organ and tissue that may cause the deterioration of cell-adhesion, DNA-related process, cell proliferation and worsening the cell signalling and energy metabolism even at lower concentration dosage (Invanoveine et al., 2004). Once it is absorbed, it may accumulate in soft tissues, mainly in kidney and liver, subsequently harm the liver system, cause kidney failure and pulmonary disease. Cadmium has long half-life in living organism, including microorganism and microalgae, which is essentially an emergent poison towards the living system (Ensafi et al., 2006). The unusual extended half-life of cadmium in human body has created much attention to their great toxicological and carcinogenic activity.

Cadmium can be found widely in nature, including mainly in foods and cigarettes. The inhale of tobacco from cigarettes may introduce cadmium towards the body system. The extended half-life of cadmium in living organism has the implication of bioaccumulation process along the food chain (Ensafi et al., 2006). Besides, there are extensive use of cadmium in industry for the production of pigment, anti-corrosion coatings, alloys and batteries. This consequence introduces this heavy metal to the soil, water and air which causes the environmental pollution. Cadmium is also relatively related to the zinc-refining process, mining, fossil fuel, steel mills, metallurgical and industrial discharge (Li-yuan et al., 2007). This heavy metal affect from the industrial waste water can be easily widespread through water, which acts as main nature carrier (Ensafi et al., 2006).

Therefore, the determination of cadmium has contributes to the awareness among human to provide beneficial guidance on the physiological effect on body and environment (Li-yuan et al., 2007). Various types of analytical techniques had been
used in determination of cadmium such as FAAS, GFAAS, XRF, ICP-AES and ICP-MS. However, most of the techniques require high cost instrumentation and time consuming. On the other hand, the detection of cadmium via electrochemical method is potentially rapid, high sensitivity, low of cost and environmentally friendly.

1.2 Problem of Statement

One of the most serious problems faced by mankind and the environment is the presence of cadmium in nature. As reported, this heavy metal is extremely a toxic contaminant that may affect the environment and living organism. The cadmium tends to accumulate and has a long half life when absorbed in the living system which results in the emergence of toxicity. Cadmium is commonly found in nature as it is the natural component of the earth crust. Besides, cadmium is always used in the industry such as electroplating, and batteries, paint and alloys production. It can be easily widespread through water, soil and air. Its ability to enter the living organism may result in the interference and alteration of metabolic process in various organ and tissue. They will cause the health effects and pollute the environment even at a lower dosage. The accumulation and extended half-life of the cadmium lead to bio-accumulation process along the food chain, contributing to the sources of cadmium being introduced into human life.

The problems associated with cadmium in the environment clearly demand for a simple analytical method with lower detection limits. Electrochemical methods traditionally have found important application and most sensitive method in sample analysis of cadmium at lower cost. Furthermore, they offer unique opportunities of addressing the challenges of green analytical chemistry, which provide effective process monitoring while minimizing its environmental impact. The electrode itself can be a powerful tool to meet the needs of many electroanalytical problems. Nowadays, the development of miniaturize analysis instrument with low cost and less demand on service operation, sufficient sensitivity and selectivity had been a major interest among the researcher. The modifications of GRC electrode surface as opposed to a new approach in developing new electrode system with improved
qualities is of crucial need. Moreover, much electrode development has concentrated on developing simple, low cost and environmental friendly electrode with higher sensitivity. Graphite reinforcement carbon (GRC) is an alternative electrode that is environmental friendly, inexpensive and disposable. This non-toxic electrode was reported to have such a good reproducibility wave compared to the conventional carbon electrode.

The modification of GRC electrodes with CNTs offers the capability of promoting electron transfer reaction and improves sensitivity in voltammetric techniques. CNTs have been widely used to modify electrodes in the field of sensor technology. The unique structure and properties such as good electrical conductivity, larger surface area, chemical stability and high strength present an opportunity for CNTs to be used as a good modifier in developing novel electrodes at low cost, simplicity and sensitivity for metal ion detection (Stetter et al., 2008). Therefore, the purpose of this research is to develop simple, low cost disposable graphite reinforcement carbon (GRC) electrode system modified with MWCNTs for detection of cadmium. This works aim to describe the voltammetric behaviour of cadmium using modified and bare electrode.

1.3 Objectives of Study

The objectives of this research are:

1. To study on the voltammetry characterizations of various types and size of GRC electrodes.

2. To modify the GRC electrode with carboxylated MWCNT by electrodeposition process, i.e. carboxylic-MWCNTs or e-MWCNT/GRC.
3. To determine the effect of carboxylated MWCNT modified GRC electrode towards detection of cadmium ion.

4. To optimise the voltammetry detection of cadmium on c-MWCNT modified GRC via differential pulse anodic stripping voltammetry (DPASV).

1.4 Scope of Study

The research involved preparation of the c-MWCNT/GRC electrode and investigation of electrochemical behaviour of cadmium ion on the modified electrode in comparison with the bare electrode. In achieving the objectives of the research there are few important task need to be carried out and six research scopes have been identified for accomplishing the objectives, the scopes are:

1. Pretreatment of CNTs with H₂SO₄ and HNO₃ acid mixture to improve the electron transfer properties and allow further functionalisation. The characterization of functionalized CNTs was carried out by Fourier Transform Infrared Spectrophotometer (FTIR) and Field Emission Scanning Electron Microscope-Energy Dispersive X-Ray Analysis (FESEM-EDX).

2. Cyclic voltammetric studies on voltammetry behaviour of bare GRC at different hardness and size.

3. The electrodeposition of MWCNTs on to GRC electrode by using a cyclic voltammetry electrochemical processing to modify the substrate electrode surface with MWCNTs.
4. Development of new electroanalytical method through the investigation of the optimum conditions of electroanalytical studies of the modified electrode to detect cadmium by differential pulse anodic stripping voltammetry (DPASV).

5. The study only focusing in detection cadmium ion from standard solution.

6. Applications of optimized parameters for both techniques are include the effect of increasing concentration of cadmium to peak current ($I_p$). From the graph, regression equation, $R^2$ value, linearity range, limit of detection (LOD) and limit quantification (LOQ) were obtained.

1.5 Significance of Study

The quick determination of trace quantities of heavy metal by simple methods has become the major interest in analytical chemistry. The construction of sensitive electrode with fast response and have linear dynamic range, low cost, environmentally friendly and ease for preparation had been adding an advantage. Since, there are not much attention had been done on none conventional graphite reinforcement electrode (GRC), modified with carbon nanotubes, this will provide a significance virgin opportunities studies area to be explored for detection of cadmium ion.
REFERENCES


