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

NURUL FARHANA BINTI OTHMAN

UNIVERSITI TEKNOLOGI MALAYSIA

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

NURUL FARHANA BINTI OTHMAN

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

Faculty of Science
Universiti Teknologi Malaysia

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 ρ = 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.

ABSTRAK

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 Ei = -1600 mV vs Ag / AgCl; kadar imbasan v = 2 mV per saat; pH = 5.0; masa pemendapan pada 10 saat. Berdasarkan voltamogram DPASV yang diperolehidengan 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.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS/ SYMBOLS/ TERMS

ΔE_p	-	Peak Separation
µL	-	Microliter
AES	-	Atomic Emission Spectroscopy
Ag/AgCl	-	Silver/Silver Chloride
ASV	-	Anodic Stripping Voltammetry
BRB	-	Britton Robinson Buffer
Cd	-	Cadmium ion
CNTs	-	Carbon Nanotubes
CV	-	Cyclic Voltammetry
CVD	-	Chemical Vapour Deposition
c-MWCNTs	-	Carboxylic- Multiwall Carbon Nanotubes
DMF	-	Dimethylformamide
DMSO	-	Dimethyl Sulfoxide
DPASV	-	Differential Pulse Anodic Stripping
E_p	-	Peak Potential
E_{acc}	-	Accumulation Potential
E_i	-	Initial Potential
E_f	-	Final Potential
EDX	-	Energy Dispersive X-ray
FAAS	-	Flame Atomic Absorption Spectroscopy
FESEM	-	Field Emission Scanning Electron Microscope
FTIR	-	Fourier Transform Infrared Spectroscopy
GCE	-	Glassy Carbon Electrode
GRC	-	Graphite Reinforcement Carbon
GFAAS	-	Graphite Furnace Atomic Absorption Spectroscopy
H_3BO_3	-	Boric Acid

HCl	-	Hydrochloric Acid
H_2O	-	Water
H_2SO_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
ν	-	Scan rate
V	-	Volt

LIST OF APPENDICES

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 relative 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 c-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 H_2SO_4 and HNO_3 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

Aoki, K., Okamoto, T., Kaneko, H., Nozaki, K. and Negishi, A. (1989) Applicability of Graphite Reinforcement Carbon Used as the Lead of a Mechanical Pencil to Voltammetric Electrodes. *Journal of Electroanalytical Chemistry,* 263, 323-331.

Agui, L., Yanez-Sadeno, P. & Pingarron, J. S. (2008). Role of Carbon Naotubes in Electroanalytical Chemistry: A Review. *Analytical Chemica,* 622,11-47.

Bagotsky, V. S. (2005). *Fundamentals of Electrochemistry* (2nd Edition). New York (USA), Wiley Inc.

Bard, A. J. and Faulkner, L. R. () *Electrochemical Methods: Fundamentals and Application.* (2nd). New York : John Wiley and Sons.

Barisci, J. N., Wallace, G. G., Chattopadhyay, D., Papadimitrakopoulos, F. and Baughman, R. H.(2003). Electrochemical Properties of Single-wall Carbon Nanotube Electrodes. *Journal of the Electrochemical Society,* 150, 409-415.

Brady, N., El Khakani M.A., and Botton G.A. (2002).Singelwalled Carbon Nanotubes Synthesis by Means of UV Laser Vaporization. *Ibi,*. 354, 88-92.

Britto, P.J., Santhanam, K.S.V. and Ajayan P.M. (1996). Carbon nanotube electrode for oxidation of dopamine. *Bioelectrochem. And Bioenergetics,* 46, 121-125.

Bui, M. N., Li, C. A., Han, K. N., Pham, X. And Seong, G.H. (2012) Electrochemical Determination of Cadmium and Lead on Pristine Single-walled Carbon Nanotube Electrodes. *Analytical Science,* 28, 699-704.

Casarett, A. and Doulls, a. (1980).Toxicology: the Basic Science of Poison. New York, Me Millan Publishing Co, 650.

Cohen, M.L. (2001).Nanotube, Nanoscience and Nanotechnology. *Material Science and Engineering,*15, 1-11.

Constant, M. G. V. D. B. (1986).Determination of Copper, Cadmium and Lead in Seawater by Cathodic Stripping Voltammetry of Complexes with 8-Hydroxyquinoline. *J. Electroanalytical Chemica,* 2125, 111-121.

Datsyuk, V., Kalyva, M., Papagelis, K., Parthenios, J., Tasis, D., Siokou, A., Kallitsis, I. and Galiotis, C. (2008).Chemical Oxidation of Multiwalled Carbon Nanotubes. *Carbon,* 46, 833-840.

Demetriates, D., Economou, A. and Voulgaropoulos. (2003). A Study of Pencil-Lead Bismuth-Film Electrodes for the Determination of Trace Metals by Anodic Stripping. *Analytica Chimica Acta,* 519, 167-172.

Ditkulchaimongkol, J. and Munchareon, S. (2012) Design and Fabrication of a Simple Electrode for Undegraduates to Study the Quantitative Electrochemical Analysis. *Pure and Applied Chemistry International Conference,* 325-329.

Devi, R., Yadav, S. and Pundir, C.S. (2011). Electrochemical Detection of Xanthine in Fish Meat by Xanthine Oxidase Immobilized on Carboxylated Multiwalled Carbon Nanotubes/Polyanaline Composite Film. *Biochemical Engineering Journal,* 58-59, 143-158.

Es'shagi, Z., Goldsefidi, M. A. Siafy, A., Tanha, A. A., Zohre, R. and Alian-Nezhadi, Z. (2010).Carbon Nanotube Reinforced Hollow Fiber Solid/liquid Phase Microextraction: A Novel Extraction Technique For the Measurement of Caffeic Acid in *Echinacea purpurea* Herbal Extracts Combined With High-performance Liquid Chromatography. *Journal of Chromatography,* 1217**(17)**, 2678-2775.

Ensafi, A. A., Khayamian, T. and Benvivi, A. (2006). Simultaneous Determination of Copper, Lead and Cadmium by Cathodic Adsorptive Stripping Voltammetry Using Artificial Neural Network *Analytical Chemistry Acta,*561, 225-232.

Fifield, F. W. and Kealey, D. (2000). *Principles and Practice of Analytical Chemistry.* Canada, Wiley VCH.

Fischer, E. and Constant, M. G. (1999). Anodic Stripping Voltammetry of Lead and Cadmium Using a Mercury Film Electrode and Thiocyanate. *Analytica Chemica Acta,* 385, 273-280.

Geckeler, K.E. and Premkumar, T. (2011). Carbon Nanotubes: Are They Dispersed or Dissolved in Liquids? *Nanoscale Research Letters,* 6, 136.

Gooser, D. K. Jr. (1993).*Cyclic Voltammetry: Simulation and Analysis of Reaction Mechanism.* Canada, Wiley VCH.

Gulaboski, R. & Pereira, C. M. (2008). Electroanalytical techniques and instrumentation in food analysis. In: *Handbook of food analysis instruments*, Semih Ottles (Ed.), Taylor & Francis, 379-402.

Gong, Z.Q., Ahmad Suraji, A.N. and Ab Ghani, S. (2011). Electrochemical Fabrication, Characterization and Application of Carboxylic Multiwalled Carbon Nanotube Modified Composite Pencil Graphite Electrode. *Electrochemical Acta*, 65, 257-265.

Gong, K., Dong, Y., Xiong, S., Chen, Y.and Mao, L. (2004) Novel Electrochemical Method for Sensitive Determination of Homocysteine with Carbon nanotube-based Electrodes. *Biosensor and Bioelectroni,*. 20, **(2)**, 253-259.

Heimann, R.B., Evsyukov, S.E. and Koga, Y. (1997). Carbon Allotropes: A suggested Classification Scheme Based on Valence Orbital Hybridization. *Carbon,* 35, 10-11.

Hezard, T., Fajerweg, K., Evrard, D., Colliere, V., Behra, P. and Gros, P. (2012). Gold Nanoparticles Electrodeposited on Glassy Carbon Using Cyclic Voltammtery: Application to Hg (II) Trace Analysis. *Journal of Electroanalytical Chemistry,* 664, 46-52.

Hilding, J., Grulke, E. A, Zhang, G. A. and Lockwood, F. (2003).Dispersion of Carbon Nanotubes in Liquids. *Journal of Dispersion Science and Technology*, 24**(1)**, 1-41.

Hou, Pen-Xiang., Liu, C. And Cheng, Hui-Ming. (2008). Purification of Carbon Nanotubes. *Carbon,* 46, 2003-2025.

Hu, G. and Hu, S. (2009). Carbon Nanotubes –Based Sensors: Principles and Application in Biomedical Systems. *Journal of Sensors,* 2009, 40.

Iijima, S. (1991).Helical Microtubules of Graphitic Carbon. *Nature*1001, 354, 56-57

Ivanoviene, L. Staneviciene, I. Lesaukaite, V. Sadauskiene, I. Ivanov, L. (2004) Activities of tRNA and Leucyl-tRNA synthetase and Programme Cell Dea in The Liver of Mice Under Experimental Cadmium Poisoning. *Trace. Elem. Elec,*. 21, 180-184.

Kaneko, H., Yamada, M. and Aoki, K. (1990) Determination of Dopamine in Solution of Ascorbic acid at Graphite-Reinforcement Carbon Electrodes by Differential Pulse Voltammtery. *Analytical Science*, 6, 439-442.

Kathi, J., Rhee, K. Y. and Lee, H. J. (2009).Effect of Chemical Functionalization of Multiwalled Carbon Nanotubes with 3-Aminopropyltriethoxysilane on Mechanical and Morphological Properties of Epoxy Nanocomposites, Composites: Part A, 40, 800-809.

Kempemgowda, R. G. and Malingappa, P. (2012). A Binderless, Covalently Bulk Modified Electrochemical Sensor: Application to Simultaneous Determination of Lead and Cadmium at Trace Level.

Kuznetsova, A., Mawhinney, B., Naumenko, V., Yates Jr., J.T., Liu, J and Smalley, R.E. (2000). Enhancement of Adsorption Inside of Single-walled Carbon Nanotubes: opening the Entry Ports. *Chemical Physics Letter*, 321, 292-296.

Lee, S.J., Bailk, H.K., Yoo, J-E.and Han, J.H. (2002). Large Scale Synthesis of Carbon Nanotubes by Plasma Rotating Arc Discharge Technique. *Diam. Rel. Materia*, 11, 914-917.

Levent, A. K., Yardim, Y. and Sentruk, Y. (2009).Volta metric Behaviour of Nicotine at Pencil Graphite Electrode and its Enhancement Determination in the Presence of Anionic Surfactant. *Electrochemica Act.*, 55, 190-195.

Li-yuan, C., Yun-nen, C., Yu-de S, Hao, C. and Qing-zhu, L. (2007) Adsorption and Removal of Cadmium (II) from Aqueous Solutions by Bio-formulation. *Trans Nonferrous Metal Society of China*, 17, 1057-1062.

Lin, Y., Lu, F., Tu, Y. and Ren, Z. (2004). Glucose Biosensor Based on Carbon Nanotubes Nanoelectrodes Ensembles. *Nano Letter*,. 4, 191-195.

Loos, J., Grossiord, N., Koning, C. E. and Regev, O. (2007). On the Fate of Carbon Nanotubes: Morphological Characterization. *Comp. Sci. Technol*, 67,783-788.

Ly, S. W., Jung, Y.S., Kim, M.H, Han, I. K. and Jung,W.W. (2004) Determination of Caffeine Using a Simple graphite Pencil Electrode with Square-Wave Anodic Stripping Voltammetry. *Microchimica Acta*, 146:207-213.

Matters, J.P. and Banks, C.E. (2012). Electrochemical Utilisation of Chemical Vapour Deposition Grown Carbon Nanotube as A Sensor. *Vacuum*, 86, 507-519.

McCreery, R.L. (1991). Carbon Electrode: Structural Effect on Electron Transfer Kinetics. *Electroanalytical Chemistry,* Marcel Dekker, New York, NY. USA, 17, 221-374.

Morrow, H. (2001) Cadmium and Cadmium Alloys. New York, JohnWiley and Sons, Inc., 471-507.

Musameh, M., Lwarence, N. S. and Wang, J. (2005).Electrochemical Activation of Carbon Nanotube. *Electrochemistry Communication,* 7, 14-8.

Oheme, F. W. (1978). Toxicity of Heavy Metals in the Environment. New York: Marcel Dekker.

Park,Tae-Jin., Banarjee, S., Hemraj-Benny, T. and Wong, S.S.(2006). Purification Strategies and Purity Visualization Techniques for Singe-Walled Carbon Nanotubes. *Journal of Material Chemistry,*16, 141-154.

Pastorin, G. (2011). *Carbon Nanotube: From Bench Chemistry to Promising Biomedical Application.* Singapore: Pan Stanford Publishing Pte. Ltd.

Pavia, D. L., Lampman, G. M., Kriz, G. S. and Vyvyan, J. (2009). *Introduction to Spectroscopy.* (4^{th}). USA: Books/Cole Cengage Learning.

Peter, T. K. and William, R. H. (1983).Cyclic Voltammtery. *Journal of Chemical Education*, 60 (9), 702-706.

Pirad, S.L., Douven, S., Bossout, C., Heyen, G., and Pirard, J.P. (2007). A Kinetic Study of Multi-walled Carbon Nanotubes Synthesis by Catalytic Chemical Vapor Deposition Using a Fe-Co/Al2O3. *Catalyst. Carbon*, 45, 1167-1175.

Prato, M., Tasis, D., Tagmatarchis, N. and Georgakilas, V. (2003). Soluble Carbon Nanotubes. *Chem. Eur. J,* 9, 4000-4008.

Raghu, K., Chandrasekar, A.and Sankaran K.R. (2010). Electrochemical Behavior and Differential Pulse Voltametric Determination of an Antineoplastic Drug Bicalutamide and Pharmaceuticals Formulations using Glassy Carbon Electrode. *International Journal of Chemical Research,*2**(2)** 05-16.

Ripp, J. (1996). *Analytical Detection Limit Guidance & Laboratory Guide for Determining Method Detection Limits*. Winconsin.

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

Salimi, A., Banks C.E. and Compton R.G. (2004). Abrasive Immobilization of Carbon Nanotubes on a Basal Plane Pyrolytic Graphite Electrode: Application to the Detection of Epinephrine**.** Analyst. 129, 225-228.

Santhosh, P., Manesh, K. M., Gopalan, A., Lee, Kwang-Pill. (2007). Novel Amperometric Carbon Monoxide Sensor Based on Multiwall Carbon Nanotubes Grafted with Polydiphenylamine – Fabrication and Performance. *Sensors and Actuators B: Chemical,* 125**(1),** 92-99.

Skoog, D. A., Holler, F. J. and Nieman, T. A. (2004). *Fundamentals of Analytical Chemistry*. (8^{th}). USA : Thomson Brooks/Cole.

Shimoda, R., Nagamine, T., Takagi, H., Mori, M., and Waalkes, M. P. (2001). Induction of apoptosis in cells by cadmium: Quantitative negative correlation between basal or induced metallothionein concentration and apoptoticrate. *Toxicol.Sci*., 64, 208 –215.

Shevchenko, V., Kitsitzin, A., Vinogradova, A. and Stein, R. (2003) Heavy Metals in Aerosols over the Seas of the Russian Artic. *Sci Total Environment,* 306, 11-25.

Sun, N., Mo, W. M., Shen, Z. L. and Hu, B. X. (2005).Adsorptive Stripping Voltammetric Technique for the Rapid Determination of Tobramcyin on the Hanging Mercury Electrode. *J. Pharm. Biomed. Anal.*, 38**(2)**, 256-262.

Sotiropoulou, S. and Chaniotakis, N.A. (2003). *Carbon Nanotube Array-based Biosensor*. Anal. Bioanal. Che., 375: 103-105.

Stetter, J.R., Maclay, G. J., Baltes, H., brand, O., Fedder, K., Hierold, C., Korvink, J. G. And Tabata, O. (2008). Chapter 10. Carbon Nanotubes and Sensors: a Review. *Advanced Micro and Nanosystem,* 1,357-379.

Tassel, J. J. V. and Randall, C. A. (2006). Mechanism of Electrophoretic Deposition. *Key Engineering Materials,* 314, 167-174.

Tavares, P. H. C. P. and Barbeira, P. J.S. (2008). Influence of Pencil Lead Hardness on Voltammetric Response of Graphite Reinforcement Carbon Electrode. *J. Apply Electroche,*.38,827-832.

Trykowski, G., Biniak, S., Stobinski, L. And Lesiak, B. (2010) Preliminary Investigations into the Purification and Functinalization of Multiwall Carbon Nanotubes. *Acta Physica Polonica.* 118, 2-5.

Valentini, .F, Amine, A., Orlanducci, S., Terranova, M.L.and Palleschi G. (2003) Carbon nanotube purification: preparation and characterization of carbon nanotube paste electrodes. *Analytical Cemistry.*, 75, 5413.

Vural, T., Kuralay, F., Bayram, C., Abaci, S. and Denbkas, E.B. (2010). Preparation of Physical/Electrochemical Characterization of Carbon Nanotube-chitosan Modified Pencil Graphite Electrode. *Applied Surface Science,* 257,622-627.

Wahab, R., Ansari, S. G., Kim, Y. S., Mohanty, T. R., Hwang, I. H. and Shin, H. C. (2008). Immobilization of DNA on Nano-Hydroxyapatite and Their Interaction with Carbon Nanotubes. *Synthetic Metals.* Article In Press.

Waisberg, M., Joseph, P., Hale, B. and Beyersmann, D. (2003).Molecular and Cellular Mechanisms of Cadmium Carcinogenesis. *Toxicology Letter*, 192-195.

Wang, J. (1985). *Stripping Analysis: Principles, Instrumentations and Applications.* Deerfield Beach, FL, VCH Publisher.

Wang, J. (2006). *Analytical Chemistry.* 3rd Edition. Canada, USA. Wiley-VCH Inc.

Wu, K., Hu, S., Fei, J. and Bai, W. (2003). Mercury-free Simultaneous Determination of Cadmium and Lead at a Glassy Carbon Electrode Modified with Multi-wall Carbon Nanotubes. *Analytical Chimica Acta,* 489, 215-221.

Jeon, In-Yup., Chang, D, W., Kumar, N. A. and Baek, Jong-Beom. (2011). Functionalization of Carbon Nanotubes-Polymer Nanocomposites. *In-Tech,* 92-110.

Yudianti, R., Onggo, H., Sudirman, Saito,Y., Iwata, T. and Azuma, J. (2011). Analysis of Functional Group Sited on Multiwall Carbon Nanotube Surface. *The open material Science Journal,* 5, 242-247.

Zhang. Q. L., Lian. H. Z. & Chen. H.Y. 2005.Separation of Caffeine and Theophylline in Poly (dimethysiloxane) Micro Channel Electrophoresis with Electrochemical Detection.*Journal of Chromatography,*1098, 172-17.