Determination of Trace Levels of Cadmium(II) in Tap Water Samples by Anodic Stripping Voltammetry with Boron-Doped Diamond Electrode

Chalermpol Innuphat

A Thesis Submitted in Fulfillment of the Requirements for the Degree of
Doctor of Philosophy in Chemistry
Prince of Songkla University
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I hereby certify that this work has not already been accepted in substance for any degree, and is not being concurrently submitted in candidature for any degree.

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(Mr. Chalermpol Innuphat)
Candidate

ชื่อวิทยานิพนธ์ การตรวจวัดแคดเมียมปริมาณน้อยในน้ำประปาด้วยวิธีแอโนดิกสทริปปิงโวลแทมเมตรีโดยใช้ขั้วโบรอนโดปไดมอนด์ (BDD)
ผู้เขียน นายเฉลิมพล อินนุพัฒน์
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บทคัดย่อ

หัววัดที่มีความจำเพาะต่อไอออนประจุบวกสามารถปรับแต่งได้จากปฏิกิริยารีดักชันของกรด 4-อะมิโนเมทิลเบนโซอิก เป็นครั้งแรกสำหรับขั้วโบรอนโดปไดมอนด์ (BDD) ใช้สำหรับวิเคราะห์แคดเมียมในน้ำประปาด้วยการสทริปปิงทางไฟฟ้าเคมี โดยวิธีต้นแบบนี้เกิดจากการใช้ขั้วโบรอนโดปไดมอนด์ปรับแต่งด้วย 0.5 มิลลิโมลาร์ กรด 4-อะมิโนเมทิลเบนโซอิก โดยปฏิกิริยารีดักชันทางไฟฟ้าเคมี โดยนำขั้วปรับแต่งที่ได้มาใช้ในการหาปริมาณแคดเมียม ใช้ไซคลิกโวลแทมเมตรีกวาดศักย์จาก +0.20 ถึง -1.20 โวลต์ เทียบกับขั้วไฟฟ้าอ้างอิงซิลเวอร์/ซิลเวอร์คลอไรด์ ในกระบวนการกราฟติ้งที่นำไปสู่การก่อตัวของพันธะโคเวเลนต์ระหว่างอะตอมคาร์บอนเกิดเป็นผิวฟิล์ม ศึกษาสภาวะที่เหมาะสมของความเข้มข้นตัวตั้งต้นและจำนวนรอบของการกวาดศักย์ซึ่งส่งผลต่อความจำเพาะและความไวในการตรวจวัดแคดเมียม การเคลือบผิวขั้วสามารถตรวจสอบโดยมุมสัมผัสและการใช้เทคนิคไซคลิกโวลแทมเมตรีตรวจวัดแคดเมียม 30.0 มิลลิกรัมต่อลิตร เทียบกับขั้วโบรอนโดปไดมอนด์ที่ไม่ปรับแต่ง พบว่าการปรับแต่งมีประสิทธิผลต่อขั้วโบรอนโดปไดมอนด์ทำให้ได้พีคของแคดเมียมสูงขึ้น เมื่อนำขั้วโบรอนโดปไดมอนด์ที่ปรับแต่งด้วย 0.5 มิลลิโมลาร์ กรด 4-อะมิโนเมทิลเบนโซอิก ใช้วิเคราะห์หาแคดเมียมปริมาณน้อยในน้ำประปาตัวอย่างด้วยวิธีแอโนดิกสทริปปิงโวลแทมเมตรีพบพีคของแคดเมียมที่ศักย์ไฟฟ้า -0.72 V เทียบกับขั้วไฟฟ้าอ้างอิงซิลเวอร์-ซิลเวอร์คลอไรด์ ในสารละลายอะซิเตตบัฟเฟอร์ พีเอช 6.0 ศึกษาสภาวะที่เหมาะสมในการหาปริมาณแคดเมียม ประกอบด้วย เวลาที่ใช้ในการก่อให้เกิดการพอกพูนด้วยไฟฟ้า, ศักย์ไฟฟ้าที่ก่อให้เกิดการพอกพูนด้วยไฟฟ้า, อัตราการสแกนและผลของพีเอช พบว่าขั้วโบรอนโดปไดมอนด์ที่ผ่านการเคลือบด้วยฟิล์มของกรด 4-อะมิโนเมทิลเบนโซอิก ให้ความเป็น

เส้นตรงของกราฟแคดเมียมอยู่ในช่วง 2.0 ถึง 50.0 ไมโครกรัมต่อลิตร ด้วยค่าสหสัมพันธ์ของเส้นตรง (r^2) เท่ากับ 0.9989, n=6 ในแต่ละความเข้มข้น ทำการศึกษาการรบกวนของไอออนอื่น ๆ ต่อการตรวจวัดแคดเมียม พบว่า Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, Al^{3+}, Co^{2+} และ Pb^{2+} มีผลรบกวนน้อยมาก ยกเว้น Ni^{2+} ต่อสัญญาณของแคดเมียมและที่สภาวะเหมาะสมขีดจำกัดต่ำสุดของการตรวจวัดของแคดเมียมเท่ากับ 0.2 ไมโครกรัมต่อลิตร การศึกษาความถูกต้องและแม่นยำของวิธีการทำได้โดยการวิเคราะห์วัสดุอ้างอิงมาตรฐานน้ำธรรมชาติ (Standard Reference Material; SRM1640) พบค่าร้อยละของการได้กลับคืนของแคดเมียมอยู่ระหว่าง 101 ถึง 111 % และให้ค่าความแม่นยำโดยมีค่าเบี่ยงเบนมาตรฐานสัมพัทธ์ (%RSD) อยู่ในช่วงน้อยกว่า 7% นอกจากนี้การเปรียบเทียบผลการวิเคราะห์หาปริมาณแคดเมียมในตัวอย่างน้ำประปาโดยใช้เทคนิคอินดักทีพลีคัพเพิลพลาสมา ออฟติคอลอีมิสชันสเปกโทรเมทรี (ICP-OES) ได้ผลการวิเคราะห์ที่คล้ายคลึงกัน ดังนั้นวิธีการที่ได้ศึกษาขึ้นสามารถนำไปใช้ในการวิเคราะห์หาปริมาณแคดเมียมในตัวอย่างน้ำได้อย่างมีประสิทธิภาพ จากการศึกษาพบระดับการปนเปื้อนของแคดเมียมในน้ำประปาจำนวน 11 ตัวอย่าง ที่เก็บจากก๊อกน้ำของบ้านเรือนประชาชนที่ตั้งอยู่ในเขตเทศบาลนครหาดใหญ่อยู่ในช่วงที่ต่ำกว่าขีดจำกัดต่ำสุดของการตรวจวัดของขั้วไฟฟ้าที่พัฒนาขึ้น จึงสามารถสรุปได้ว่าปริมาณการปนเปื้อนของแคดเมียมในตัวอย่างน้ำไม่เกิน 3.0 ไมโครกรัมต่อลิตร ซึ่งยังคงอยู่ในระดับที่ปลอดภัยสำหรับผู้บริโภคตามมาตรฐานขององค์การอนามัยโลก (WHO)

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ABSTRACT

The specificity to specific cations of a boron-doped diamond (BDD) electrode can be improved by modification via reduction of 4-aminomethyl benzoic acid and was first used as a sensor for the electrochemical stripping analysis of cadmium in tap water. Cyclic voltammetry cycling from +0.20 to -1.20 V versus Ag/AgCl was used for the grafting process leading to the formation of covalent C-C bond on to the film surface. The precursor concentration and number of cycles were optimized correlated to the specificity and sensitivity for cadmium ion detection. The coverage of the electrode was checked by contact angle and cyclic voltammetry measurements of 30.0 mg/l Cd^{2+} in comparison with bare boron-doped diamond electrode to reveal its effectiveness in Cd^{2+} determination. It was then applied for electrochemical determination of cadmium in tap water samples by anodic stripping voltammetry with a single well-defined reduction peak at -0.72 V vs Ag/AgCl in acetate buffer solutions at pH 6.0. Optimal conditions were investigated including deposition time, deposition potential, scan rate and pH. Linear standard addition curve (r^2=0.9989, n=6 for each concentration) in the range of 2.0 to 50.0 µg/l Cd^{2+} was obtained and other dissolved metals including Ca, Mg, Zn, Mn, Fe, Cu, Al, Co and Pb had little interference except for Ni. A detection limit of 0.2 µg/l was achieved. High accuracy (0.44 % error compared with natural water SRM 1640) and reproducibility of the results as well as excellent stability of the electrode material prove the capabilities of this system recovery in the range of 101 to 111% further confirmed the usefulness of the proposed method to analyze cadmium in tap water samples. The results with SRM 1640 were in good agreement with those by ICP-OES. The concentration of cadmium in various water samples from eleven regions at Hatyai city

was found to be lower than detection limit of the modified electrode, therefore it can be concluded that the concentration are lower than the drinking water contamination standard limited level (<3.0 μg/l) issued by the World Health Organization (WHO).

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My parents and my sister for their loves and attention all through my life,

And lastly, my friends in Analytical Chemistry and Heavy metal analysis group who are always of great help.

Chalermpol Innuphat

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LIST OF ABBREVIATIONS AND SYMBOLS

AAS = Atomic absorption spectrometry
AES = Atomic emission spectrometry
AR = A standard grade of analytical reagents
ASV = Anodic stripping voltammetry
BDD = Boron-doped diamond
°C = degrees Celsius
CSV = Cathodic stripping voltammetry
CV = Cyclic voltammetry
DPV = Differential pulse voltammetry
DPASV = Differential pulse anodic stripping voltammetry
DMF = N,N-Dimethylformamide
DMSO = Dimethylsulfoxide
EPA = Environmental protection agency
EDTA = Ethylenediaminetetraacetic acid
FIAAS = Flow injection atomic absorption spectrometry
g = Gram
GFAAS = Graphite furnace atomic absorption spectrometry
h = Hour
HG = Hydride generation
HGAAS = Hydride generation atomic absorption spectrometry
HGAFS = Hydride generation atomic fluorescence spectrometry
HMDE = Hanging mercury drop electrode
HPLC = High performance liquid chromatography
ICP-AES = Inductively coupled plasma atomic emission spectroscopy
ICP-OES = Inductively coupled plasma optical emission spectrometry
ICP-MS = Inductively coupled plasma-mass spectrometry
Ipa = Oxidation peak current

LIST OF ABBREVIATIONS AND SYMBOLS (CONTINUED)

Ipc = Reduction peak current
LOD = Limit of detection
LOQ = Limit of quantification
mA = Milliampere
mg/l = Milligram per liter
min = Minute (time)
ml = Milliliter
mm = Millimeter
mM = Millimole per liter (Millimolar)
mV = Millivolts
mV/s = Millivolts per second
NAA = Neutron-activation analysis
ND = Non detectable
NIST = National institute of standards and technology
nM = Nanomole per liter (Nanomolar)
ppb = Part per billion
ppm = Part per million
PTFE = Polytetrafluoroethylene
r^2 = Correlation coefficient
rpm = Revolutions per minute
RSD = Relative standard deviation
s = Second (time)
SD = Standard deviation
S/N = Signal to noise ratio
SRM = Standard reference Materials
SWASV = Square wave anodic stripping voltammetry
SWV = Square wave voltammetry
$TBAPF_6$ = Tetrabutylammonium hexafluorophosphate

LIST OF ABBREVIATIONS AND SYMBOLS (CONTINUED)

THF = Tetrahydrofuran
USEPA = United states environmental protection agency
v/v = Volume by volume
WHO = World health organization
w/v = Weight by volume
XRF = X-ray fluorescence spectrometry
µg/g = Microgram per gram
µg/l = Microgram per liter
ηg/l = Nanogram per liter
σ = The population standard deviation

LIST OF PAPERS

This thesis is based on the following papers:

Innuphat, C and Chooto, P. 2017. Determination of trace levels of Cd(II) in tap water samples by anodic stripping voltammetry with an electrografted boron-doped diamond electrode. ScienceAsia **43**: 33-41.
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Determination of trace levels of cadmium(II) in tap water samples by anodic stripping voltammetry with boron-doped diamond electrode

CHAPTER 1

1. INTRODUCTION

The main objective of this study was to generate new well chemical modified boron doped diamond electrode for cadmium determination by reduction of diazonium salt. Results were described in four chapters, as follows:

Chapter I is divided into five parts, where the first one reviews physical and chemical properties, sources and potential exposure, toxicity and health effect of cadmium and instrumental analysis of determining cadmium in tap water. The second part contains nature of electrochemical technique including basic knowledge of voltammetry, electrodes, electrolyte and voltammetric techniques. The third part is specific strategy to invent sensitivity contains grafting of diazonium salts, electrogravimetric study of the layer formation process and contact angle. Part four concerns review of literature before the objectives as a last part.

Chapter II is the experimental section describes to five parts include the chemicals and materials, Instruments and apparatus, Methodology, effect of interferences and then finally is the application of this investigation method to tap water samples

Chapter III involves results and discussion consisting of precursors selecting, effect of other ions having possible interference with the detection of Cd^{2+}, The comparison of the calibration and standard addition method for determination of Cd^{2+} in tap water samples, The study of percent recovery of Cd^{2+} in tap water samples and eventually is application of the studied method to tap water samples have been carried out.

Chapter IV offers a general conclusion of this thesis work.

This introduction section starts with general information of cadmium followed by the techniques for cadmium analysis. Next is the specific strategy for electrode modification and finally literature involved.

1.1 Cadmium

Metallic elements in trace amounts are indispensable and essential for cellular growth and for maintenance of metabolic functions. In excessive amounts, they often exert an inhibitory influence on all living forms. Heavy metals are toxic, non-biodegradable and persistent and they gradually accumulate in the living tissues and get distributed throughout the food chain (Locatelli and Torsi, 2002). The determination of heavy metal ions has been of prime importance in environmental monitoring. The presence of elements such as Cd^{2+}, $Pb^{2+}$and As^{3+}, even at low concentrations (<2.0 μg/l) is highly undesirable due to their toxicity (Senthilkumar and

Saraswathi, 2009). It is well known that heavy metal ions are deleterious to human's health. For example, Cd^{2+} ion causes serious cases of acute toxicity and diseases such as lung cancer and kidney failure. In Japan, a bone disease named 'itai-itai' emerged in the mid-fifties especially in children (Hizal and Apak, 2006) as a result of consumption of cadmium-contaminated rice as food because the rice plant was watered with effluents from Cd-Ni battery factories. Prolonged exposure to cadmium ions may lead to bone diseases such as osteomalacia (showing a mixed pattern with osteoporosis) found responsible for itai-itai disease (Hizal and Apak, 2006).

Sensitive methods have received much attention for heavy metal ion detection including inductively coupled plasma atomic electron spectrometry (ICP/AES), mass spectrometry (ICP/MS), flow injection atomic absorption (FIAAS) and high-performance liquid chromatography (HPLC) (Kong *et al.*, 2013) and a variety of electrochemical techniques have been used for the analysis of heavy metals in water resources and food materials. Several reviews provide protocols for the analysis of heavy metal pollutants in the environment (Senthilkumar and Saraswathi, 2009). Electrochemistry has played a prominent role in the determination of heavy metal ions. However, it is a challenge to directly analyze heavy metal ions using the above methods when the concentration of these metal ions is extremely low. The development of highly sensitive metal ion sensor has been comprehensive investigated. Electrochemical sensors have a wide range of applications owing to their small size, low power requirements and sample pretreatment (Fatemi and Sarkar, 2002). Chemical modification of electrode surfaces (Kong *et al.*, 2013) has received numerous studies in recent years and the modified electrodes have been applied in many areas. Metal ion monitoring using an electrochemical technique can save a significant measurement time and operating cost (Senthilkumar and Saraswathi, 2009). Simultaneous determination of a number of metal ions is also possible. Potentiometry, voltammetry and potentiometric stripping analysis were the electrochemical techniques widely applied for trace determination especially Cd^{2+} ions (Stankovic *et al.*, 2007). Anodic stripping voltammetry is a powerful analytical technique for the detection of heavy metal ions because of its high sensitivity, low cost, easy operation and the ability of analyzing element speciation (Li *et al.*, 2009). In the past few years, mercury served as an electrode was widely used for stripping detection of trace heavy metal ions. However, the strong toxicity of mercury made its applications unfriendly to the environment. Extensive research efforts have therefore been devoted to find alternative electrode materials to meet the growing demands for the determination of heavy metals. Bismuth electrodes and composite materials with bismuth are most attractive alternatives to the mercury electrode (Kokkinos and Economou, 2011). Besides, various electrochemical sensors based on some novel materials such as plated metals (Maczuga *et al*., 2013), functionalized conducting polymers (Alizadeh *et al*., 2011), ion selective complexes (Stankovic *et al*., 2011) and biochemical substances (Merli *et al*., 2012) have been constructed for the determination of heavy metals.

The current EPA-recommended methods for metal ion analysis in water samples are inductively couple plasma mass spectrometry (ICP-MS), anodic stripping voltammetry (ASV) and atomic absorption spectroscopy (AAS). These methods are highly sensitive; however ASV is increasingly employed because it has a wide linear dynamic range, low detection limit (µg/l) and multi-element analysis ability. Furthermore, the advantage of ASV over ICP-MS or AAS is simply instrumentation, easy operation, high sensitivity, relatively inexpensive**,** low electrical power requirement and small in size (Swain and McGaw, 2006). This electrochemical method is one of the most favorable techniques for the determination of heavy metal ions, mostly carried out at mercury electrodes (Fischer and Berg, 1999; Korolczuk, 2000; Saito *et al.,* 2001 and Cordon *et al.,* 2002).

With the increasing awareness of conserving the living environment, mercury-free electrodes for the determination of heavy metal ions became more attractive and much more works were performed at mercury-free modified electrodes. Boron-doped diamond (BDD) electrodes have been shown to have a high sensitivity, good selectivity and reproducibility for the determination of Cd^{2+} in tap water samples (March *et al*., 2015). BDD has very similar electrochemical properties to those of Hg, as described in Table 1-1, but yields better detection figures of merit under the condition of several metal ions contaminants. The wider anodic potential limits and lower background currents are the main benefits of BDD over Hg electrode (Swain *et al.,* 2004; Manivannan *et al.,* 2004; Babyak and Smart, 2004 and Wantz *et al.,* 2005). ASV with BDD electrode has been utilized to accurately and sensitively quantify contaminant metal ions in many samples, for example tap waters, river and lake and additionally waste treatment sludge, digestions of river sediment and soil (Davison, 1993; Swain *et al.,* 2004 and Babyak and Smart, 2004). Conductive diamond represents an electrode material that has attracted great interest in electroanalysis, due to its outstanding electrochemical features: wide potential window in aqueous solutions, low background current, long-term stability of the response and low sensitivity to dissolved oxygen (Fujishima *et al.,* 1999). These unique properties of the polycrystalline diamond, together with its extreme robustness, strongly recommend this material to be very well suited for stripping voltammetry analysis of heavy metals, and the results reported thus far are more than promising (Saterlay *et al.,* 2000).

Table 1-1 Comparison of the important BDD and Hg electrode properties for anodic stripping voltammetry

Boron-doped diamond (BDD)	Hg
Wide anodic and cathodic potential limits	Wide cathodic potential limit
Good sensitivity	Good sensitivity
Chemically inert	Interaction with Cl^-
Lower background current	Higher background current
Non-toxic	Toxic
Non-volatile	Volatile
Reusable surface-no pretreatment required	Easily refreshed surface

Source: (Swain and McGaw, 2006).

Among the metal contaminants, a heavy metal ion especially Cd^{2+} is a major pollutant which produces severe ailments including mental retardation in living organisms (Carson and Mumford, 2002). The major sources of cadmium are nickel-cadmium batteries, cadmium pigmented plastics, ceramics, glasses, paints and enamels (Kathirvelu and Goel, 2006).

1.1.1 Analyte and samples

In spite of the fact that the scope of organic and inorganic substances that can be observed by voltammetry in environmental samples is extremely wide, investigation of metal ions is still the major type of utilization. The previously mentioned methods have been applied in the research center to the investigation of all the environmentally relevant trace elements including Cd, Pb, Cu, Zn, Ni, As, Cr, Hg, Co, Se, Bi, Al in waters (Buffle and Tercier-Waeber, 2000); Pb, Cd, Cu, Zn, As, Hg, Se in sediments (Locatelli and Torsi, 2002); and Cd, Pb, Cu, Cr, Zn in soils (Kosakova *et al.,* 1996). For the most part, measurements of metal concentrations, normally after pretreatments or sample acidification, were carried out via these customary methodologies. With respect to analysis of all trace metals, they require entirely clean working practice (Howard and Stratham, 1993).

Cadmium is known as one of the most toxic elements among the heavy metals. The physical and chemical properties of cadmium are explained in the next content.

1.1.2 Physical and chemical properties of cadmium

Cadmium exhibits main physical and chemical properties of heavy metals. Heavy metals are the elements that have the specific gravity excess of 5 g/cm^3 for example cadmium (Cd), lead

(Pb), chromium (Cr), mercury (Hg), copper (Cu) and zinc (Zn). The abnormal amounts of heavy metal accumulated in human are toxic. Normally, only trace amount of heavy metals is found in the environment (Suwannarath, 1995). It is well known that determination of trace heavy metal ions (e.g. Cd^{2+}, Pb^{2+}, Hg^{2+}, $As^{3+/5+}$) is very important in the fields of environment and health. The contamination of utility water with heavy metals such as Cd^{2+} is one of most hazardous environmental and health problems. Those metals are highly toxic to certain organs of both humans and animals, including nervous, immune, reproductive, and gastrointestinal systems (Li *et al.*, 2009). Ingestion of any significant amount of Cd^{2+} causes immediate poisoning as well as damage to the liver and the kidneys due to their inclination to accumulate in the body, low rate of clearance and toxicity. The biological half-life of Cd^{2+} is 10 to 30 years (McGaw and Swain, 2006) and the compounds containing Cd^{2+} are also carcinogenic (Jarup, 1998). Building up of Cd^{2+} levels in the water, air, and soil has been increasing particularly in industrial areas (Liphadzi and Kirkham, 2005).

Cadmium is a soft, malleable, ductile, bluish-white divalent metal (Holleman, *et al.,* 1985). Unlike most other metals, cadmium is resistant to corrosion and is used as a protective plate on other metals. As a bulk metal, cadmium is insoluble in water and is not flammable; however, in its powdered form it may burn and release toxic fumes. A summary of the physical properties of cadmium is given in Table 1-2.

Table 1-2 Physical and chemical properties of cadmium

Properties	Values
Atomic mass	112.4
Atomic number	48
Oxidation state	2, 1, -2
Atomic radius	151 pm
Melting point (s.t.p.)	321.07°C
Boiling point (s.t.p.)	767 °C
Density (20 °C)	8.65 g/cm^3
Heat of fusion	6.21 kJ/mol
Heat of vaporization	99.87 kJ/mol
Heat capacity (25 °C)	26.020 J/(mol·K)
Electron configuration	[Kr] 4d^{10} 5s^2
Young's modulus	50 GPa

Source: https://en.wikipedia.org/wiki/Cadmium (3/10/2017).

1.1.3 Sources and potential exposure of cadmium

Cadmium can be released to the environment through natural activities (volcanoes, wildfires, weathering and erosion of rocks), human activities (tobacco smoking, mining, smelting and refining, fossil fuel combustion, incinerating or recycling used products and waste, and manufacture of phosphate fertilizers). These releases can travel long distances by atmospheric or surface water transport. Atmospheric deposition of cadmium on arable lands along with the application of municipal sewage sludge and phosphate fertilizers has resulted in a gradual increase in cadmium levels in agricultural soils and crops (WHO, 2010).

1.1.4 Toxicity and health effect of cadmium

Cadmium is a highly toxic metal to humans when the element accumulates in the body. People are exposed to them primarily through food, water and air. The International Agency for Research on Cancer has classified Cd and its compounds in group 2B: limited evidence of carcinogenity in animals. The daily intake into human body is 0.28 µg/kg. The World Health Organization have been established the maximum allowable of the contamination levels of heavy metals in drinking water for the consumer safety on the announcement of the Guideline for Drink Water Quality (WHO 2006), which the contaminated levels are listed in Table 1-3. The drinking water standard is 3.0 µg/l of cadmium (WHO, 2006). Cd has been shown to cause severe damage to a variety of organs, including the lung (Manca *et al.*, 1991), liver and kidney (Casalino *et al.*, 2002), testis (Morselt, AFW. 1991), brain (Mendez-Armenta *et al.*, 1991) and even to the placenta (Wier *et al.*, 1990). Oral exposure to Cd may cause renal damage (Satarug and Moore, 2004), osteoporosis (Jarup and Alfven, 2004) and possibly prostate (Waalkes *et al.*, 1991) and renal (Waalkes *et al.*, 1999) cancer. Chronic exposure to even low levels of cadmium could also lead to adverse renal (Jarup *et al.*, 2000) and negative bone effects (Jarup and Alfven, 2004). The main clinical picture of Itai-itai disease was combination of renal and bone effects (Nogawa, K. 1981). The Japanese word ‘itai’ means ‘ouch’ or ‘painful’ in English. The pain results from unusual changes in bone, i.e. osteomalacia with osteoporosis. In May 1968 the Japanese Ministry of Health concluded that Itai-itai disease was developed from osteomalacia with simultaneous renal dysfunction from chronic Cd poisoning, and was under the influence of factors such as pregnancy, lactation, hormonal disorders, ageing, calcium deficiency and others (Ministry of Health and Welfare, 1972).

Table 1-3 The acceptance level of heavy metals contamination in drinking water

Metals	**Maximum value (µg/l)**
Cadmium (Cd)	3
Lead (Pb)	10
Copper (Cu)	2000
Mercury (Hg)	6
Arsenic (As)	10
Manganese (Mn)	400
Chromium (Cr)	50
Nickel (Ni)	70

Source: (WHO, 2006).

Cadmium content of nonpolluted natural waters is generally lower than 1.0 µg/l (Friberg *et al.,* 1986). Median dissolved cadmium concentrations of measured sites at 110 stations around the world were <1.0 µg/l, the highest cadmium levels were recorded is 100.0 µg/l in the Rio Rimao in Peru (WHO/UNEP, 1989). Average levels in the Rhine and Danube in 1988 were 0.1 µg/l (range 0.02 to 0.3 µg/l) (ARW, 1988) and 0.025 µg/l (AWBR, 1988), respectively. Contaminants that may occur in drinking water can also be caused by the presence of cadmium as an impurity in the zinc of various galvanized steel pipes or solders that contain cadmium used in fitting, water coolers, water heaters and taps. Drinking water of shallow groundwater in sensitive areas in Sweden where the soil had been acidified by acid precipitation contained concentrations of cadmium is 5.0 µg/l (Friberg *et al.,* 1986). In Saudi Arabia, with average levels between 1.0 and 26.0 µg/l were found in drinking water source, the water sample were obtained from private wells and rusted plumbing pipes (Mustafa *et al.,* 1988). Levels of cadmium could be higher in areas supplied with soft water of low pH, as this would tend to be more corrosive in plumbing systems containing cadmium. In the Netherlands, for the study of 256 drinking water sources in 1982, cadmium (0.1 to 0.2 µg/l) was detected in only 1% of the drinking-water samples (Ros and Slooff, 1987).

The study of cadmium contamination in tap water is an attractive topic owing to the high toxicity and even low concentration of cadmium can make genuine harmful impacts human, the analytical method becomes significant and then the awareness of the cadmium concentration has been emphasized.

1.1.5 Instrumental analysis of determining cadmium in tap water

The contamination of cadmium in tap water was found to be at the trace levels (Fan *et al.*, 2009), thus the sensitive instrument techniques were required. Electrothermal atomic absorption spectrometry, atomic absorption spectroscopy and inductively coupled plasma mass spectrometry regularly have enough sensitivity to permit the determination of this element in these samples. Anodic stripping voltammetry (ASV) is a stand out amongst the most reasonable methods for the determination of cadmium at low concentrations in water samples attributable to its favorable detection limits, inherent high sensitivity, better specificity and least requirement for sample preparation (Acar, 2001). All about an instrument and apparatus in this research was described in section 2.2

1.2 Nature of electrochemical technique

1.2.1 Basic knowledge of voltammetry

Voltammetry concerns applying potential at the working electrode and the current corresponding with interest process is measured. Normally it is performed in an electrochemical cell with an electrolyte solution and three electrodes. Working electrode and reference electrode are the key segments of voltammetric cells (Buffle, 2005).

1.2.2 Electrodes

In all cases of electrochemical investigation, the response of analyte occurs at the surface working electrode. Subsequently, controlling the potential drops across the working electrode-solution interface is intrigued. In any case, it is difficult to control or measure this interfacial potential with absent placing another electrode in the sample solution. Therefore, two interfacial potentials must be considered, neither of which can be evaluated freely. Consequently, one necessity for this counter electrode is that its interfacial potential stays consistent, with the goal that any changes in the cell potential generate identical changes in interfacial potential for the working electrode only (BAS Epsilon, 2000).

An electrode whosever potential does not change with current is alluded to an ideally non-polarizable electrode, and is described by a vertical district on a current versus a plot of potential. Nevertheless, there is no electrode that acts this way. Subsequently, the interfacial potential of the counter electrode in the 2-electrode system differs as current is gone through the cell. This issue is overwhelmed by utilizing a 3-electrode system, in which the functions of the counter electrode are separated into two electrodes; auxiliary and reference electrodes. In particular, the potential between the working and reference electrodes is controlled and the current goes between the working and auxiliary electrodes. The current going through the reference electrode is additionally reduced by utilizing an inverting operational amplifier for the reference electrode input.

The necessities for the counter electrode of the 2-electrode system incorporate a high exchange current, very large surface area and a high concentration of the species associated in the redox reaction, such that the concentrations are not essentially changed by the entry of a current. Nevertheless, the current going through the reference electrode in the 3-electrode system is lower than the current that goes through the 2-electrode system, the necessity for the reference electrode are less requesting; consequently, smaller, more polarizable electrodes can be utilized. Two broadly utilized aqueous reference electrodes are the saturated calomel electrode and the silver/silver chloride electrode. For Ag/AgCl reference electrode, the redox procedure for this electrode is

$$\mathrm{AgCl} + \mathrm{e}^- \Leftrightarrow \mathrm{Ag} + \mathrm{Cl}^- \qquad \ldots\ldots\ldots\ldots\ldots(1.1)$$

This electrode comprises of a silver wire, covered with silver chloride, which is submerged in a containing chloride ions solution. The electrode utilizes an aqueous solution containing 3 M sodium chloride (or potassium chloride); a permeable porous glass fritz is utilized for the intersection between the reference electrode solution and the sample solution. The potential (E) for any electrode is dictated by the Nernst equation, which relates E to the standard potential (E^0) and the activities of the redox segments. The Nernst equation for the silver/silver chloride electrode is communicated as follows:

$$E = E^0 + \frac{RT}{nF} \ln \frac{1}{a_{\mathrm{Cl}^-}} \qquad \ldots\ldots\ldots\ldots\ldots(1.2)$$

(The activities of the silver chloride and solid silver under standard conditions are unity)
It is generally much more advantageous to consider concentrations instead of activities.
The concentration and the activities are related by the activity coefficient of the solution, γ:

$$a_{\mathrm{Cl}^-} = \gamma_{\mathrm{Cl}^-}[\mathrm{Cl}^-] \qquad \ldots\ldots\ldots\ldots\ldots(1.3)$$

The Nernst equation can consequently be revamped as follows:

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{1}{[Cl^-]} \quad \text{…………… (1.4)}$$

Where $E^{0'}$ is the formal potential and is identified with the standard potential by the equation:

$$E^{0'} = E^0 + \frac{RT}{nF} \ln \frac{1}{[\gamma_{Cl^-}]} \quad \text{…………… (1.5)}$$

It is vital to cite a specific redox potential. For instance, the standard redox potential (E^0) for the silver/silver chloride redox reaction at 25 ^oC is +0.222 V (versus NHE), though the redox potential (E) for the silver/silver chloride reference electrode at this temperature is +0.196 V (versus NHE).

The above equations demonstrate that varieties in the chloride ion concentration in the electrode change the redox potential. Since there is generally a high chloride concentration over the reference electrode permeable film, there is moderate dispersion of chloride ions from the reference electrode solution into the sample solution; that is, the reference potential will progressively change repetitiveness (BAS Epsilon, 2000).

Every electrochemical cell require no less than two electrodes, due to the potential of a given electrode must be estimated with respect to the other electrode, the potential of which must be consistent (a reference electrode). In potentiometric estimations (for example, estimation of pH), there is no current through the cell and these two electrodes are adequate (it ought to be noticed here that numerous pH and ion-selective electrodes utilized in potentiometric evaluation are combined electrodes, the two electrodes are contained in the same body). However, in a cyclic voltammetry analysis, an outer potential is applied to the cell, and the current response is estimated. Exact control of the outer applied potential is required, yet this is ordinarily unrealistic with a 2-electrode system, because of the potential drop over the cell from the solution resistance (potential drop (E) = current (i) x solution resistance (R)) together with the polarization of the counter electrode that is essential to complete the current measuring circuit. Better potential control is accomplished utilizing a potentiostat and a 3-electrode system, in which case the potential of one electrode (the working electrode) is controlled regarding the reference electrode and also the current goes between the working electrode and the third electrode (the auxiliary electrode).

1.2.3 Electrolyte

A solution of electrolytes is made by adding an ionic salt to a proper dissolvable. The salt must turn out to be completely dissociated in the solvent for produce a conducting solution. The electrolyte solution must have the capacity to dissolve the sample, electrochemically inert over a wide potential territory and pure. Further, it must be chemically inert, i.e. not respond with any reactive species produced in the analysis. On the off chance that the temperature is to be shifted, the electrolyte solution must be having a proper fluid range. Electrolyte solutions can be either aqueous or non-aqueous. An extensive variety of salts can be utilized for aqueous electrolyte solutions. For the redox potentials of specific mixes are pH sensitive, the buffered solutions ought to be utilized for these compounds. Appropriate non-aqueous solvents incorporate acetonitrile, THF, DMF, DMSO, propylene carbonate and methylene chloride. Salts for non-aqueous electrolyte solutions ordinarily comprise a great number of cations (e.g., tetraalkylammonium cations) and vast anions (e.g., tetrafluoroborate, hexafluorophosphate and perchlorate) to guarantee full dissociation and electrochemical silent. Despite the fact that a completely dissociated salt enhances the conductivity of the electrolyte solution, various electrolyte solutions (especially those in view of non-aqueous solvents) have a significant resistance. This prompts a potential drop between the electrodes [termed iR drop or potential drop = current (i) x solution resistance (R)]. A portion of this iR drop can be remunerated by a potentiostat and a 3-electrode system (BAS Epsilon, 2008). Meanwhile, the electrolyte composes and concentration needs thought and optimization for electrochemical examinations.

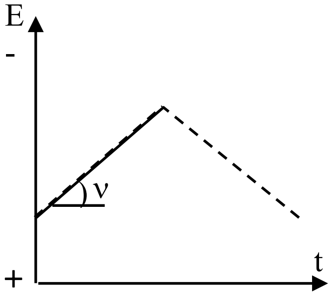
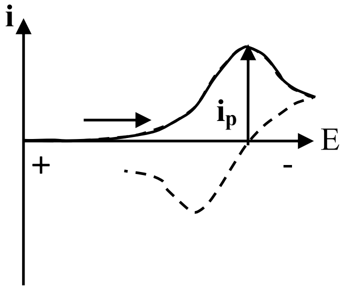
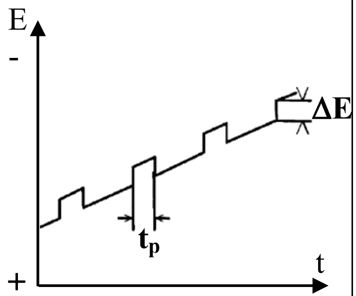
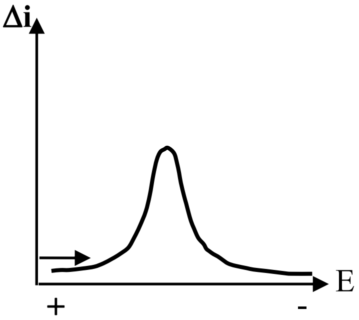
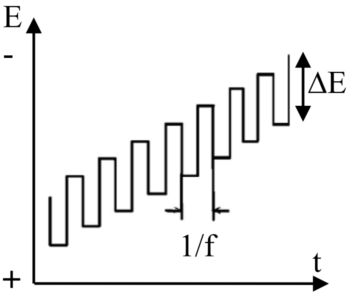
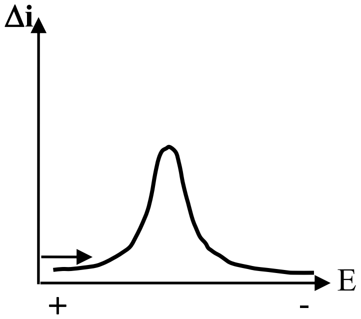
1.2.4 Voltammetric waveform

All types of voltammetry can be viewed active techniques, in the light of there is an applied potential that advances a change in the concentration of electroactive species on the electrode surface by oxidation or reduction of the same, they can be depicted as a function of potential, current and time (Table 1-4). There are diverse voltammetry techniques; linear sweep voltammetry is a simple technique for stripping the electrode. The potential-time waveform is a linear ramp (Table 1-4a). The potential scan is initiated at the deposition potential in ether a positive direction for ASV or a negative direction for CSV. Then the resulting peak current is measured.

The differential pulse voltammetric waveform (Table 1-4b) consists of a slow linear potential ramp (5 to 10 mV/s) upon which small fixed-height potential pulses (5 to 100 mV) are superimposed every 0.5 to 5 s. The advantage of the differential pulse technique is the redeposition of metal ion analyte during the rest period between the pulses. As the potential is pulsed through that at which the metal is stripped, the oxidized metal does not have time to diffuse from the electrode surface. At the end of the potential pulse the stripped metal is redeposited into the electrode to be stripped again during the next pulse cycle (as long as the potential ramp is negative of the reduction potential for the metal ion).

The square wave voltammetry (Table 1-4c) utilizes a square wave potential pulse superimposed upon a staircase ramp. The current is sampled each time the square wave changes polarity. A net current is obtained from the difference between the forward and reverse pulses of a square wave period and it is plotted versus the potential. The high frequency of the square wave requires a high concentration supporting electrode solution to allow the capacitive current to decay rapidly. Detection limits of square wave stripping are normally comparable to differential pulse stripping (Vanysek, 1996).

Table 1-4 Three major voltammetric techniques used for trace-metal analysis and their typical concentration ranges. ν = Potential scan rate; ΔE = Pulse amplitude; f = Frequency; t_d = Preconcentration time; i_p = Peak current

Technique	Imposed function	Recorded function	Typical concentration range (mole/l)
(a) Linear sweep voltammetry (LSV) (cyclic voltammetry dotted line)			10^{-2}-10^{-6}
(b) Differential pulse voltammetry (DPV)			10^{-4}-10^{-7}
(c) Square wave voltammetry (SWV)			10^{-4}-10^{-8}

Source: (Buffle, 2005).

Square wave voltammetry (SWV) and differential pulse voltammetry (DPV) are utilized for both qualitative and quantitative analysis. These strategies exploit computer timing to repeatedly sample current signals at two points with respect to the time of application of a square wave voltage signal to the working electrode. The distinction between the two current values is plotted as a component of the applied DC potential. The resultant is peaks rather than voltammetric waves, relating to the electroactivity of the species in the electrochemical cell. The significant segment of this distinction current is the faradaic current, which flows because of an oxidation or reduction at the electrode surface. The capacitive or charging current component, because of electrical charging of electrode double layer, is largely eliminated. Trace analyses of metallic ions and of organic pharmaceutical compounds are regular applications for these pulses.

1.2.5 Stripping voltammetry

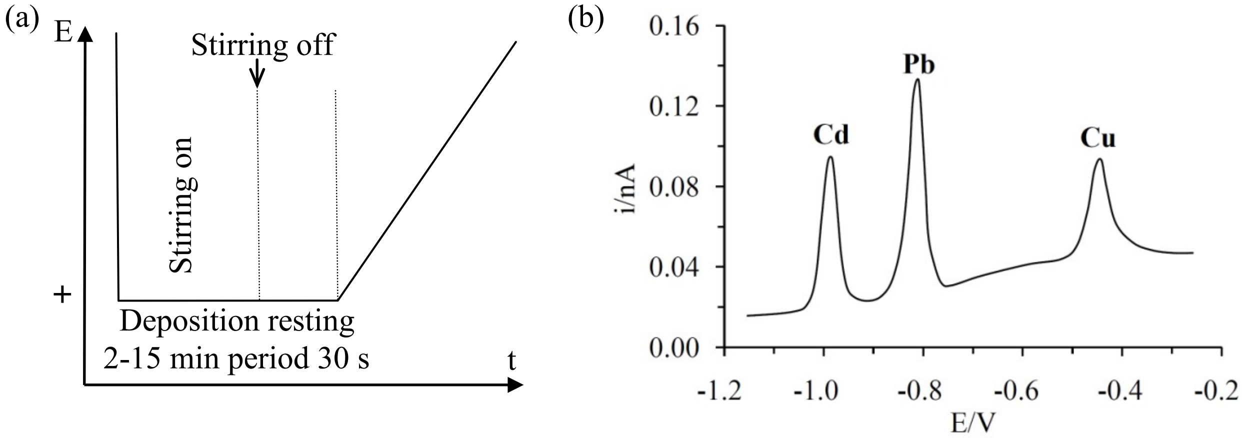


Fig. 1-1 Procedure of stripping voltammetry; (a) excitation signal (b) response curve

Despite the fact that there are different voltammetry techniques, the pulse voltammetry is done with steps and sweep association that enhance the speed and detection limits, it can be considered as a gathering of methods with adjusted potential, the current is observed after that the potential has stayed constant for an adequate time, regularly 40 milliseconds. The segregation of the charging current is therefore done by observing the current just before the end of the pulse, where the load current is insignificant compared with the faradic component (Zoski, 2007), Fig. 1-1 (a). The differential pulse voltammetry (DPV) and also square wave voltammetry (SWV) enhance sensitivity by subtracting the current values observed at two distinct times. SWV consolidates the benefits of the other systems and gives noteworthy changes; the outcome is a response like to a Gaussian signal, described by a phenomenal concealment of the background current and enhances the quality of the quantitative data (Zoski, 2007).

These types of techniques are utilized in the identification and quantitative determination of metals or metal complexes, particularly heavy metals in solution. The techniques typically comprise of a preconcentration of the metals in the electrode surface, trailed by a potential sweep to dissolve preconcentrated species of enthusiasm, making the quantification of them. Contingent upon the nature of the analyte, distinctive modes of concentration analysis are utilized; the most widely recognized is the anodic stripping voltammetry. The stripping voltammetric techniques have lower detection limit than any in case of the regularly utilized electrochemical techniques, and needless of sample preparation, moreover the sensitivity and the selectivity are incredible (Zoski, 2007). The procedure comprises of three main steps, Fig. 1-1 (a) and (b): Procedure of preconcentration: This procedure give diverse modes for preconcentration of the analyte on the working electrode, which can be condensed by two ways, electrochemically (present or absent potential boost) and by adsorptive. This procedure is accomplished the species concentration in volume particularly littler contrasted with volume of the solution. To accomplish reproducible outcomes is essential control the hydrodynamic parameters (pre-concentration time, stirring, temperature, electrode area and initial potential applied. The pre-concentration permits an expansion of sensitivity of other 2 or 3 orders of magnitude, making it practical to operate with analyte concentrations 10^{-10} M or even lower, sensitivities comparable with others techniques not electro-analytical characterized by high sensitivity. Step of resting: After a time perfectly measured, stops electrolysis and stirring, but remains constant initial potential. During this time, is accomplished the homogenizing of the substance on the electrode and recovering the diffusion regime. Step of stripping: The deposited analyte is dictated by stripping itself, through a potential sweep in the contrary direction to the beginning. This sweep can be functioned by different strategies (eg, linear sweep, square wave or differential pulse). The two most normally utilized are the square wave and differential pulse, because of their points of interest. These voltammetry strategies can be characterized by the nature of the accumulation process and dissolution in cathodic and anodic stripping voltammetry, adsorptive stripping voltammetry or potentiometric stripping analysis (Settle, 1997 and Zoski, 2007).

Anodic stripping voltammetry the voltammetry is presently generally perceived as a great apparatus for the investigation of metal ions and some organic compounds in solutions. The accumulation step collect the reducing of metal cations at a constant potential for few minutes, particularly assisted by convection, forming a composite or alloy. The subsequent concentration of the element to be identified in the electrode is considerably greater than in the solution analyzed because of the volume of the electrode is much less in comparison with the volume of solution (Cornelis, R. 2003). Subsequently finish stirring, the potential is changed to a more positive potential through a linear sweep voltammetry, square wave or differential pulse like portrayed above, which brings about oxidation of the metal the alloy or amalgam, returning again to the solution and recording a current peak because of this procedure. The current peak height indicating the detected concentration of the material in the electrode, which is relative to the amount of material dissolved in the solution until they stay fitting experimental parameters, for example, preconcentration time, area of the electrode, time and potential of deposition, temperature, stirring conditions, etc. The accumulation time was depends on the analyte concentration and can up to 20 min to a level of 10^{-9} mol/dm^3. With ASV technique, are detected approximately 15 alloys or metal amalgams or depending of the electrode are composed of Cd, Ti, Bi, Cu, Zn, Ga and In. The examination of traces of other metal ions (Au, Hg, Se and As) might be functioned after that they are deposited as a layer of electroplated metal in solid electrodes build from gold or carbon (Zoski, 2007).

1.2.6 Adsorption at electrodes

The thermodynamic investigation of adsorption is depends on the Gibbs adsorption equation; this portrayal is most common and is autonomous of every format of the interface. At the boundary between two phases in particular 1 and 2, the thermodynamic properties of these two phases change bit by bit over the boundary. Supposing that this transition occurs within a tight district 3 between 1 and 2 (Fig. 1-2), which is bounded by the planes I and II; the thickness of this locale is of molecular dimensions. In this locale the concentrations of the different species vary from those in the area 1 and 2. For each species *i* define the "surface excess" Γ_i as the excess of the surface concentration (amount of moles n_i per unit area A) of component *i* in the locale 3 relative to 1 or 2. The planes I and II are call the Gibbs planes and $\Gamma_i = n_i/A$ is alluded to as "adsorption" (moles per surface). On account of adsorption at a metal electrode from solution just a single Gibbs plane is important since the second one corresponds with the metal surface.

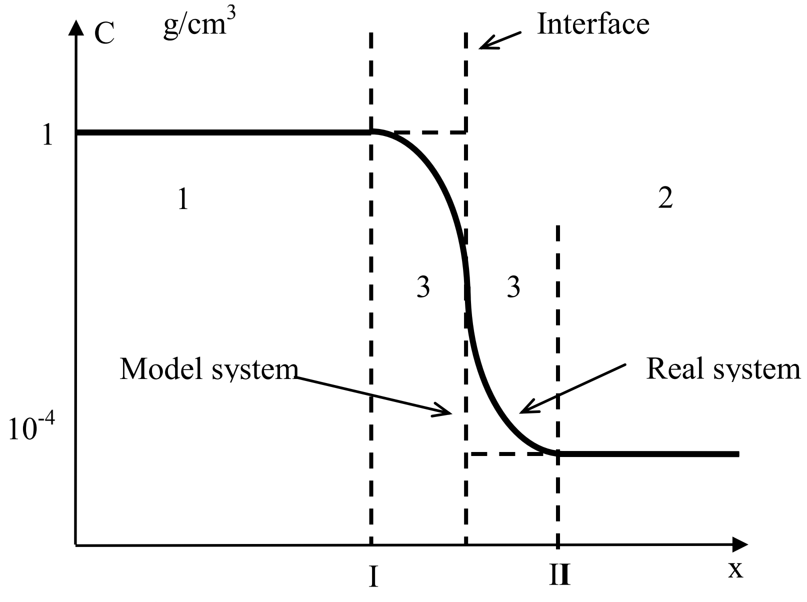


Fig. 1-2 Intermediate region (3) between the phases 1 and 2 (Gamburg and Zangari, 2011)

Under states of constant pressure and temperature the Gibbs adsorption equation has the form

$$d\gamma = -\Sigma_i \Gamma_i d\mu_i \qquad \text{..............(1.6)}$$

Specifically, for a two-component system

$$d\gamma = -\Gamma_i d\mu_i - \Gamma_2 d\mu_2 \qquad \text{..............(1.7)}$$

Another imperative equation is the Gibbs-Duhem equation as for the chemical potential:

$$\chi_1 d\mu_1 + \chi_2 d\mu_2 = 0 \qquad \text{..............(1.8)}$$

For these equations γ is the solid/electrolyte interface energy, x_i is the molar fraction of the component i in the solution. The Gibbs equation (1.6) can be attributed as the surface analogue of equation (1.8).

If consider equation (1.6) for the event of the solvent (water) and a solute (sol) it is conceivable to compose

$$d\gamma = -\Gamma_{sol} d\mu_{sol} - \Gamma_w d\mu_w \qquad \text{..............(1.9)}$$

furthermore, expecting that Γ_w is zero, this rearranges further to

$$d\gamma = -\Gamma_{sol} d\mu_{sol} \qquad \text{..............(1.10)}$$

This equation associated the adsorption of a solute species to the change in interface energy of the electrode; the driving force for adsorption is correspondingly decreased in interface energy.

The range of adsorption of the different species in mainly relies upon the concentration of the species in solution and on the associations between these species. A different set of assumptions will accordingly bring about various forms for the adsorption isotherms, portraying the reliance of adsorption of a specific species on the above variables.

1.2.7 Electron transfer kinetics

Traditionally, voltammograms, in which currents are plotted as a function of applied potential, have been used to describe an electrode reaction at the electrode/electrolyte interface, because the extent of electrode reaction for its activational parameter, i.e., overpotential. The current has two components, faradaic and non-faradaic. The non-faradaic component is normally not related to the electrode reaction and is often regarded as noise for ASV. It can be classified into two types of process to be able to explain and give examples by offered below:

A non-faradaic process involves the accumulation of charges at the metal/solution interface. The structure formed in this process is called the electrical double layer as shown in the Fig. 1-3.

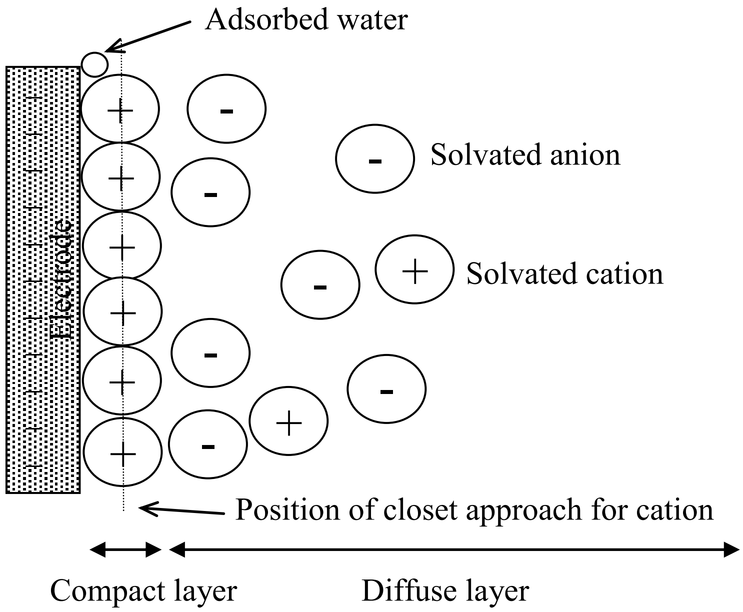


Fig. 1-3 Electrical double layer formed at electrode surface as a result of an applied potential

The double layer resembles a capacitor. The double layer capacitance relies upon the solution composition and somewhat on potential applied to the electrode. The specific capacitance of regular electrodes is ordinarily in the range of 5 to 50 $\mu F/cm^2$. Non-faradaic processes occurring at electrodes cause a flow of non-faradaic currents (additionally called charging currents). The non-faradaic currents value (i_{nf}) can be figured from the equation below:

$$i_{nf} = \frac{dQ}{dt} = \frac{d(C_{dl}A \cdot E)}{dt} = C_{dl}E\frac{dA}{dt} + C_{dl}A\frac{dE}{dt} \qquad \text{...............(1.11)}$$

Where;

Q = the electrical charge

t = time

A = electrode surface area

E = the electrode potential

C_{dl} = specific double layer capacitance (in above equation it is assume that C_{dl} does not change significantly with time). (Bard and Faulkner, 2001)

Since all species present in solution may affect the double layer capacitance, the non-faradaic currents are usually non-specific and they are rarely used to provide analytical signals; however, non-faradaic currents contribute to the background noise (when i_{nf} or noise increase be the cause of analytical sensitivity decrease). Non-faradaic currents are particularly large when surface of the electrode changes with time (e.g. in the case of the dropping mercury electrode). The effects of the non-faradaic processes are still necessary taken into account in using electrochemical data to obtain information about the charge transfer, nature of the electrode-solution interface and associated reactions.

Faradaic processes are associated with electron transfer across the interface as shown in Fig. 1-4.

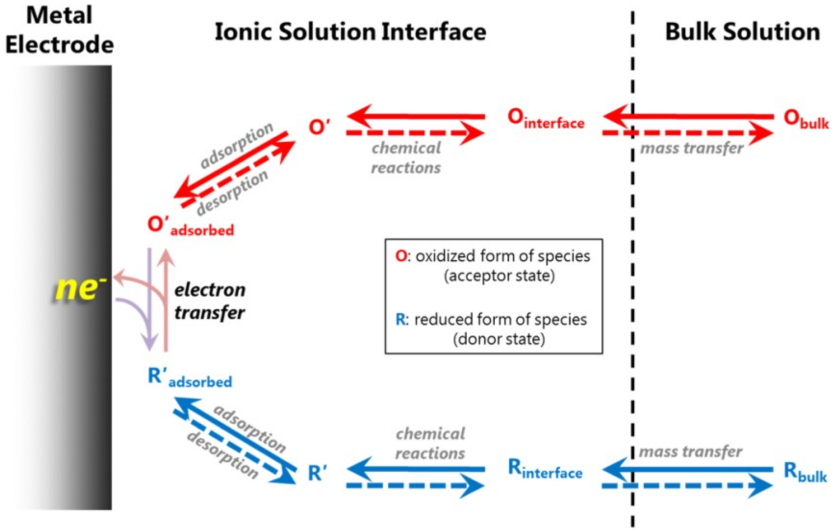


Fig. 1-4 Processes leading to reduction or oxidation of species present at the interface (Kumsa *et al.,* 1986)

The faradaic currents value (i_f) for the example case of Cd^{2+} can be calculated from the equation below:

$$i_f = nFAk\cdot C_{Cd^{2+}} \qquad \ldots\ldots\ldots\ldots\ldots(1.12)$$

Where;

F = faraday constant

A = interfacial area

k = rate constant

$C_{Cd^{2+}}$ = the concentration of Cd^{2+}

n = valance of the complexes which across the interface (n=1 in the present analysis)

Electron transfer may occur via overlapping of orbitals via bridging ligands or via electron tunneling. In any case, a molecule undergoing the electron transfer process must be in near proximity of the electrode surface (usually < 1 nm). Species present in bulk solution may be reduced or oxidized only if they are brought to the electrode surface via a mass transport process. The mass transport was contributions from the diffusion, migration and convection, respectively (http://electrochem.usask.ca).

The word "conventional" in describing approaches to voltammetry is used here to designate well-established techniques or devices, in contrast to more recent developments. With respect to environmental applications, conventional approaches include, in particular, using the following components:

1.1 Macro (typically >100 µm) working electrode is widely used instead of micro-working electrode. They generally incorporate Hg working electrodes (i.e. hanging mercury drop electrodes (HMDE), dropping mercury electrode (DME) and thin mercury film electrodes (TMFE) on glassy carbon or Pt), and, in a couple of cases, solid or chemically modified working electrode.

1.2 Batch cells; although flow-through cells tend to be used more and more. Batch cells are still used routinely.

1.3 Potentiostats, designed for laboratory measurements, which have limitations for field applications. As far as techniques are concerned (Table 1-4), cyclic voltammetry is not sensitive enough for environmental analysis but it is useful to optimize analytical conditions. Direct reduction methods, such as differential pulse polarography, differential pulse voltammetry or square wave voltammetry, been utilized both in the research facility as well as on field to quantify Mn^{2+}, Fe^{2+} and S^{2-} in anaerobic freshwater (Davison, 1993) Nevertheless, for many of trace elements, direct reduction strategies are not sensitive or specific enough and methods with a preconcentration step have needed. ASV or AdSV techniques with various modulations (typically square wave or differential pulse; Table 1-4) have been utilized generally broadly. AdSV has empowered the application scope of voltammetry to be expanded to a numerous of elements. Furthermore, more work is still expected to assess their reliable multi-element analysis. Conversely, ASV techniques have been utilized over 30 years for research facility measurements of trace metals in waters and routine instruments have been produced. In the next section, a description of the way they can be used together as powerful tools in the planning and implementation to invent sensitivity is given.

1.3 Specific strategy to invent sensitivity

1.3.1 Electrografting

Electrografting alludes to the electrochemical reaction that allows organic layers to be appended to solid conducting substrates. This definition can be stretched out to reactions including an electron transfer between the substrate to be modified and the reagent, yet additionally to illustrations where an oxidizing or reducing reagent is added to generate the reactive species. These strategies are fascinating as they provide a real bond between the organic layer and the surface. Electrografting was practical to a variety of substrates along with metals, carbon, their oxides and furthermore dielectrics for example polymers. From the 1980s several strategies have been developed either by oxidation or reduction. Electrografting and electrochemical reaction indicate an electron transfer, as is obviously the case when the substrate is associated with a potential generator. Nonetheless, in numerous cases, when the formation of a coating happens spontaneously whether under activation, it is not clear to recognize electron transfer from different kinds of mechanisms. The different mechanisms will be talked about here and the importance of this segment will be on the reactions that include an electron transfer.

Electrografting thus appears as an efficient technique for surface modification for example silanisation of oxidized surfaces and in addition self-assembly of thiols on gold or another metal. The segment is sorted out into the different reagents that have been utilized for electrografting. These incorporate amines, carboxylates, alcohols, Grignard reagents, vinylics, another onium salts and diazoniums. The diverse trial process utilized for electrografting, the mechanisms of grafting, the structure subsequent layers and the numerous applications that have been improved with these surfaces will be depicted. Surely, electrografting or related strategies have developed from academic studies to industrial utilization and therefore a specific section is given to the latter topic. The electrografting which covers distinctive substrates or strategies will be cited in the diverse sections as following:

1.3.1.1 Oxidative electrografting

1.3.1.1.1 Amines

Adsorption of amines on metals for obviating their erosion has been depicted in numerous studies, yet the covalent electrografting that happens by oxidation can only be noticed on materials that resist oxidative conditions. It can likewise be grafted on Au, Pt (Herlem *et al.,* 1997), p-Si (Herlem *et al.,* 2000), glassy carbon (GC) and carbon fibers (Deinhammer *et al.,* 1996). Electrografting of primary amines is exceptionally effective; however, secondary amines are considerably less reactive and tertiary amines do not respond, probably due to steric obstruction with the surface (Deinhammer *et al.,* 1996).

In regard to the grafting mechanism, it has at first been recommended that the radical cation is acquired after transfer of one electron binds to the surface (Barbier *et al.,* 1990); however, later examinations (Adenier *et al.,* 2004) has been suggested that the neutral aminyl radical binds to the surface as shown in Fig. 1-5.

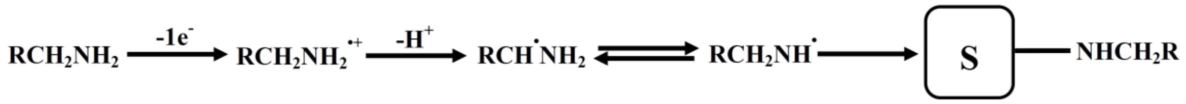


Fig. 1-5 The electrooxidative grafting mechanism of amines

The initial radical cation deprotonates of the amino group to a carbon radical and a hydrogen shift provides the aminyl radical that binding to the surface. This electrografting strategy can be adapted to various types of amines in numerous solvents. It is very easy to implement and a variety of applications have been conducted. The main disadvantage is that the substrates are constrained to carbon, platinum and gold.

1.3.1.1.2 Carboxylates

The oxidative electrografting with carboxylates has just been seen on carbon (carbon felts, carbon fibers and glassy carbon) and was first exibited on aryl acetates (Brooksby *et al.,* 2005), furthermore with acetate (Astudillo *et al.,* 2007) and recently with aminobenzylphosphonic acid (Yang *et al.,* 2005) a mechanism like that of carboxylates. After deprotonation of the relating arylacetic acid to its conjugated base, the cyclic voltammetry of, for instance phenylacetate, demonstrates an irreversible oxidation peak situated at about 1.0 V/SCE that gradually diminishes upon repetitive scanning and almost vanishes after 13 cycles (Andrieux *et al.,* 1997) however after two cycles for naphthylacetate (Brooksby *et al.,* 2005). This diminishing of the voltammetric peak is characteristic of the obstructing of the electrode surface by an organic layer and is not seen with triphenyl acetic acid and diphenyl (bring down electronic reactivity and steric prevention are likely dependable in this case). This organic layer was investigated by cyclic voltammetry (Andrieux *et al.,* 1997) (Brooksby *et al.,* 2005), both in reduction and oxidation for naphthyl-CH_2 groups (Brooksby *et al.,* 2005) connected to the surface, by restraint of the signal of redox probes (Andrieux *et al.,* 1997) (Brooksby *et al.,* 2005), by X-ray photoelectron spectroscopy (XPS) (Andrieux *et al.,* 1997) of 4-nitrobenzyl groups attached to the surface, by atomic force microscopy (AFM) (Brooksby *et al.,* 2005) yet additionally through computational simulation (Astudillo *et al.,* 2007).

The mediator of radicals in the electrografting reaction has been bolstered by the following accompanying investigations. Since acetate (CH_3COO^-) that gives carbocations (seen through the results of their reaction in solution) cannot be electrografted through direct oxidation of the acetate ion (Astudillo *et al.,* 2007), the writers have endeavored to catalyze the oxidation of acetate by the ferrocene (Fc)/ferrocenium (Fc^+) redox couple. In fact, voltammetric curves are typical of redox catalysis, the reversible ferrocene/ferricinium come to be irreversible as the concentration of acetate increments up to 41.0 mM even though the anodic wave dramatically increases. In any case, at the distinction of redox catalysis absent surface complication, the anodic peak of ferrocene diminishes lastly and vanishes upon repetitive scanning. This electrocatalytic experiment reach to the formation of an attached layer that was portrayed with cyclic voltammetry in the event of 4-nitrophenyl groups attached to the electrode and through the restraint of the wave of dioxygen (subsequent to electrografting of methyl groups through oxidation of acetate), but also through modelization of the modified surface. In view of these outcomes, the creators suggest that radicals are in charge of the electrografting reaction by the mechanism as shown in Fig. 1-6.

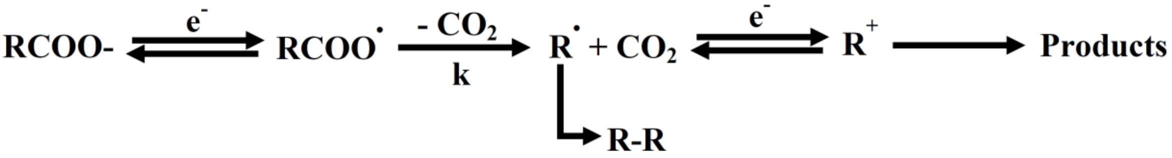


Fig. 1-6 The Kolbe reaction

Electrografting ought to be favoured when the radical builds up near the electrode as it is accessible to react with the surface. Be that as it may, in the situation when it is created by redox catalysis, it is delivered in the solution far from the electrode. In the specific instance of Fig. 1-7, the rate of electron exchange among Fc^+ and AcO^- ought to be closed to the diffusion limit and $CH_3^{\bullet}$ ought to be sufficiently far enough from the electrode not to be entirely reduced, but rather not far enough to be caught by other species as it diffuses back to the electrode.

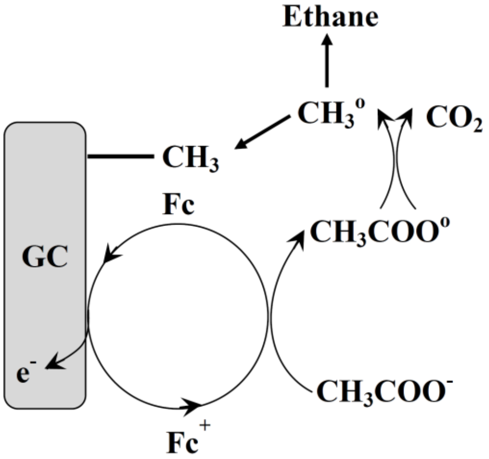


Fig. 1-7 The electrooxidative grafting mechanism of acetate (Astudillo *et al.,* 2007)

Eventually the electrografting of carboxylates can equate with that of alkyl iodides; in both situations alkyl groups are attached to the surface and for alkyliodides and the association of alkyl radicals is obviously settled (see beneath) strengthening that radicals are in charge of the electrografting of carboxylates.

1.3.1.1.3 Alcohols

Alcohols can also be electrografted to carbon through oxidative conditions (Maeda *et al.,* 2001) as shown in Fig. 1-8. In an acidic (0.1 M H_2SO_4) (Maeda *et al.,* 1994) as well as in an aqueous $LiClO_4$ solution (Maeda *et al.,* 1996) of 1-octanol, the anodic peak noticed at +1.85 V/(Ag wire) diminishes upon repetitive scanning. The electrografting of the surface was in a roundabout way shown by reversible waves of catechol and ferricyanide. These waves turned out to be small or vanished completely after electrografting (Maeda *et al.,* 1994), demonstrating an expanded blocking of the electrode with the length of the alkyl chains. Shockingly, the reversible wave of ferricyanide was reestablished by expansion of a surfactant for example, trimethyldodecylammonium as was appeared for long chain alkane thiols (Kawaguci *et al.,* 1993). Electrografting of nitrobenzyl alcohol was additionally exhibited by the observation of the reversible couple of the nitrobenzyl group after transferring the modified electrode to unadulterated solvent. The water contact angle on carbon surfaces electrografted was estimated with different alkanols. For instance, it increased from 64° on a bare carbon electrode to 95° for an electrode electrografted by 1-octanol (within the presence of $LiClO_4$). The relative capacitance ($C_{bare}/C_{modified}$) of the electrografted electrode was found to decline to 0.60 with 1-octanol (Maeda *et al.,* 1996). The conduct of these electrodes, electrografted with -OR groups, within redox probes, was not the same as that of the same electrodes anodized in 0.1M H_2SO_4. For this premise, the creators proposed the reaction appeared in Fig. 1-8 for the modification of the surface (Maeda *et al.,* 1994). The creators additionally recommended that the layer be better packed in the presence of $LiClO_4$ (Maeda *et al.,* 1994) however regardless not as close-packed as the relating self-assembled monolayers (SAMs) (Maeda *et al.,* 1996). The electrografted layer was appeared to oppose ultrasonic cleaning in methanol or water and to be electrochemically stable in the vicinity between 1.5 and -0.5 V/SCE.

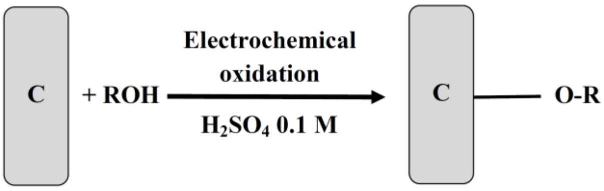


Fig. 1-8 The electrooxidative grafting of alcohols

The examination with the anodization of carbon that reach to oxygen functionalities on the surface, it was exhibited (Maeda *et al.,* 2001) that aromatic moieties at the surface of carbon are oxidised to radical cations that pepper with a nucleophilic assault by alcohols. An assortment of analytical applications has been exhibited for these alkanol-modified surfaces. Such electrodes can be utilized as sensors for alkaline or calcium ions and alkylammonium (Maeda *et al.,* 1996), for dopamine within the sight of an abundance of ascorbic acid (Thiagarajan *et al.,* 2009), for protein containing tests in electrochemical HPLC analysis (Maeda *et al.,* 1996). These adjusted electrodes are additionally helpful to restrain the adsorption of proteins (Liu and Dong, 2000). For instance of these applications, dopamine (reach to 2.0 mM) can be identified in the presence of ascorbic acid (0.2 M) on a glassy carbon electrode electrografted with 1,5-pentanediol. Clearly, much work ought to be done to determine the mechanism of this grafting technique, the structure and compacity of the layers. This technique could be extremely valuable as it ought to effortlessly permit surfaces modified by long chain substituted alkanes to be acquired.

1.3.1.1.4 Grignard reagents

Anodic electrografting of Grignard reagents (RMgX) has been researched on Si, an effortlessly oxidized substrate, however the analyses were performed in additional dry (Grignard reagents are inherently dry as they respond promptly with small amount of water) also without oxygen conditions to stay away the oxidation of Si to SiO_2 (Fellah *et al.,* 2007). Photoanodic grafting has been performed to get designed surface by utilization of a mask (Takakusagi *et al.,* 2007). Thermal grafting is additionally conceivable with Grignard reagents however the layers are of lower quality (Boukherroub *et al.,* 1999). The beginning material is hydrogenated silicon SiH, gotten by treatment of Si by HF as well as NH_4F yet in addition porous silicon (Gros-Jean *et al.,* 2000). The electrooxidative grafting procedure of Si by RMgX. (SH = solvent) (Fellah *et al.,* 2002) can be writen from the equation beneath:

$$\begin{aligned}
\mathbf{RMgX + h^{+}} &\longrightarrow \mathbf{R^{\bullet} + MgX^{+}}\\
\mathbf{SiH + R^{\bullet}} &\longrightarrow \mathbf{Si^{\bullet} + RH}\\
\mathbf{Si^{\bullet} + RMgX + h^{+}} &\longrightarrow \mathbf{SiR + MgX^{+}}\\
\mathbf{Si^{\bullet} + R^{\bullet}} &\longrightarrow \mathbf{-SiR}
\end{aligned}$$

and also

$$\begin{aligned}
\mathbf{R^{\bullet} + SH} &\longrightarrow \mathbf{RH + S^{\bullet}}\\
\mathbf{R^{\bullet} + R^{\bullet}} &\longrightarrow \mathbf{RR}\\
\mathbf{-Si^{\bullet} + SH} &\longrightarrow \mathbf{SiH + S^{\bullet}}
\end{aligned}$$

A protocol has been proposed and is appeared in the diagram above. Oxidation of the organomagnesium compound offers ascend to a radical (R-) that removes a hydrogen atom from the -SiH surface to provide a Si radical. In this manner, this radical can respond electrochemically with RMgX or alkyl radical to produce the altered surface -SiR. The creators have noticed that benzyl magnesium bromide ($C_6H_5CH_2MgBr$) cannot be electrografted and noticed that the comparability of the C_6H_5-CH_2-H bond with that of SiH (≈90 kcal/mol) can clarify this reality. The side responses include the remove of a hydrogen atom from the solvent (SH) by the silicon or the alkyl radical. Strangely, this last reaction could be prove through the perception of a weak re-increment of the SiH band after the anodic current is be off, demonstrating that dangling bonds are repaired by remove of a hydrogen atom from the solvent. An active model has been built up in view of these reactions and a best fit of the model has been gotten by plotting the absorbance of the SiH vibration against the charge devoured (Fellah *et al.,* 2002).

$$\mathbf{-Si\text{-}CH{=}CH_2 + {}^{\bullet}HC{=}CH_2 \longrightarrow -Si\text{-}CH^{\bullet}\text{-}CH_2\text{-}CH{=}CH_2}$$

Fig. 1-9 Growth of the layer with vinylmagnesium derivatives (Fellah *et al.,* 2007)

Twofold and triple bonds are effortlessly broken in the electrografting procedure (one watches more saturated CHs than olefinic CHs). From enthalpy information, the closest undoubtedly procedure for the underlying growth of the layer is exhibited in Fig. 1-9. A while later, the last radical of Fig. 1-9 can react with the solvent, chlorine or other vinylic radicals. For instance, in tetrahydrofuran (THF), removal of a hydrogen atom may contribute to a ring opening with constitution of radicals with carbonyl groups and the consolidation of these radicals would contribute to carbonyl groups interior the layer, which is seen through IR. The stereochemistry of the polyphenyl layer has been precisely examined and it seems to correspond fundamentally to that of poly(p-phenylene). The layers acquired by electrografting of methyl or ethylmagnesium chloride are impervious to oxidation in the clean room condition for up to 55 days (Vegunta *et al.,* 2009). The capacitive performance of alkyl films (for instance Si-$C_{15}H_{31}$ with a thickness of 1.67 nm) have been examined in contact with an aqueous solution. The dielectric coefficient of these films has been estimated and observed to be equivalent to 3.3 (Yu *et al.,* 2000). Eventually, the protocol of this reaction has been precisely settled. It is especially fascinating as it applies to silicon, yet the anhydrous conditions and the low flash point of the solvents that are utilized (ether, tetrahydrofuran) genuinely restrain facilitate uses of this technique.

1.3.1.2 Reductive electrografting

1.3.1.2.1 Vinylics

The electrografting through vinylics has been beforehand audited (Voccia *et al.,* 2006). The accentuation was put on the investigations implemented over the most recent 5 years despite the fact that the significant discoveries of the prior reports are additionally talked about. Toward the start of the 1980s, Lecayon and collaborators found that the electrochemical reduction of acrylonitrile on a metallic cathode prompted the electrografting of a thin polymer layer (Lecayon *et al.,* 1982). From that point forward, a similar research facility at the Commissariat à l'énergie atomique, CEA (France) has distributed various research on this reaction in which they recommended that this polymer is not just deposited however that, all the more critically, a bond is made between the polymer and the surface. Notwithstanding, when a poor solvent of the polymer is utilized, besides the electrografted polymer that remains appended to the electrode even after enthusiastic flushing, a polymer is additionally deposited that can be evacuated after washing. After some initial examinations (Leroy *et al.,* 1985), the procedure has been reached out to an assortment of the structure of the polymer and vinylics has been described. The grafting protocol has been illustrated and the states of the reaction have been stretched out from purely anhydrous to non anhydrous and lastly various applications have been created.

Reaction conditions in a common analysis, a 3-electrode cell set in a glove-box is loaded up with the solvent and reagents that are precisely dried and refined together with the dried supporting electrolyte. The solvents are normally dimethylformamide (DMF), acetonitrile (ACN) and the concentration of the vinylic monomer is usually very high in the 0.1 to 5 M range. The deposition is completed by scanning the potential between the rest potential and -2.1 to -2.6 V versus SCE or kept up at the last potential. Numerously of vinylic compounds can be electrografted including basic monomers for example propenenitrile (methacrylonitrile) (Deniau *et al.,* 2001), acrylonitrile (Deniau *et al.,* 2006), isomers of butenenitrile (Deniau *et al.,* 2006), acrylates (Gabriel *et al.,* 2007), acrylic acid (Ignatova *et al.,* 2006), methacrylates (Combellas *et al.,* 2007), 4-chlorostyrene (Deniau *et al.,* 1990), N-vinyl-2-pyrrolidone (Calberg *et al.,* 1998) and N-methyl pyrrolidone (Bureau *et al.,* 2001).

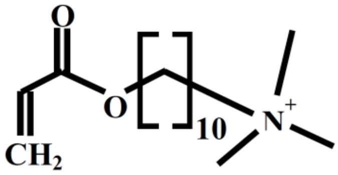


Fig. 1-10 Vinylic monomer with an ammonium group that permits electrografting in aqueous medium (Cecius *et al.,* 2007)

This is absolutely a critical limitation yet it can be eased as it has been demonstrated that a restricted substance of water allows a superior control of the film thickness (Bureau *et al.,* 2005). The reaction can be proceed in aqueous solutions through utilizing uniquely designed monomers by ammonium groups Fig. 1-10 (Cecius *et al.,* 2007). They form micelles in water and the monomer is reduced at lower potential than water subsequently allowing on carbon, the electrografting of a film rise to 120 nm thick. The polymerisation of ammonium monomers should occur inside the micelles and could be a radical procedure at the distinction of the mechanism saw in aprotic solvent.

Eventually, this electrografting technique, which was the first to be found, is currently developed; the mechanism is well entrenched and numerous delightful cases of electrografting of extraordinarily composed polymers have been exhibited. The main disadvantage of the technique is the need to utilize anhydrous conditions and electrografting of vinylics is the needs to work in exceptionally dry and without oxygen solutions, which implies that the procedure must be performed in a glove box.

1.3.1.2.2 Ammonium, phosphonium, sulfonium, iodonium, xenonium and stibonium salts

The electrochemistry of pentafluorophenyl xenonium, iodonium, diazonium, phosphonium and bromonium salts has been examined (Datsenko *et al.,* 1998) and the potentials of the primary irreversible wave have been accounted for. It was found that xenonium is a great oxidant, powerful than diazonium, and that phosphonium is minimal oxidant of all. There is little uncertainty that the protocol of electrografting of bromides and alkyl iodides on mercury and different metals in addition glassy carbon absolutely along with the formation and grafting of alkyl radicals as appeared in Fig. 1-11 (Andrieux *et al.,* 1986). However with Au, Si, Fe, TiN, electrografting is noticed while with Pd and Ag surface complexes are perceived. With Cu, entire electrografting and formation of complexes have been portrayed and it is fascinating to reconsider the electrografting procedure at this metal. Ultimately it ought to be noticed that IC_6H_{13} and $I\text{-}(CH_2)_2\text{-}C_8F_{17}$ can likewise be photografted on metals (Chehimi *et al.,* 2008) (and the layers acquired are fundamentally the same as). The photografting of alkylhalides on diamond surfaces has likewise been accounted for utilizing X-ray beams (Smentkowski and Yates Jr, 1996) and UV irradiation with an Hg arc at $\lambda < 305$ nm (Kim *et al.,* 2008). Alkyl groups have likewise been grafted on non-hydrogenated Si through mechanically scribing within the presence of alkyl halides (bromides, chlorides or iodides) (Yang *et al.,* 2005; Niederhauser *et al.,* 2002). Many stays to be improved for this grafting reaction however it is positively offers fascinating conceivable outcomes for grafting alkyl layers.

$$\mathbf{BuI + 1e^- \longrightarrow Bu^{\bullet} + I^-}$$
$$\mathbf{Bu^{\bullet} + 1e^- \longrightarrow Bu^-}$$

Fig. 1-11 Electrochemical reduction of butyl iodide (Andrieux *et al.,* 1986)

1.3.1.2.3 Diazoniums salts

Aromatic diazonium (Smith and March, 2001; Gribble *et al.,* 2007) salts $ArN_2^+ X^-$ have been referred to quite a while as a reason for the generation of dyes (Zollinger, H. 2004.). One of their essential reactions is dediazonation, the loss of dinitrogen with the constitution of an aryl radical $Ar^{\bullet}$ whichever is the case cation Ar^+. The diazonium salts are stable in aqueous acidic solution, their stability diminishes as the pH increments above pH 2.0 to 3.0 (Pazo-Llorente *et al.,* 2004) and at neutral as well as basic pHs they give diazo-hydroxide and diazoates: Ar-N=N-OH and Ar-N=N-O$^-$. Diazo-hydroxide are quickly changed into diazoates even at neutral pH. They are stable in acetonitrile yet the stability in another aprotic media has not been deliberately researched. Elofson has depicted the electrochemistry of diazonium salts ArN_2^+ at mercury electrodes (Elofson, RM. 1958). In aqueous acidic medium two waves are monitored: the first one is a one electron wave, even though the general procedure includes 4 electrons on the second wave and conduce to phenylhydrazine. Attractively, in concurrence with previous studies (Atkinson *et* *al.,* 1950), they found that a coulometry on a mercury pool gave about solely diphenylmercury and phenylmercuric chloride; their formation was allocated to the response of phenyl radicals with mercury. The associations of radicals (Koval chuk et al., 2004) amid the electrochemical reduction of aryldiazonium salts was additionally seen through the Pschorr synthesis of phenanthrene (Elofson and Gadallah, 1971) and furthermore through electron spin resonance (ESR) in ACN within the presence of a spin-trap (Bard *et al.,* 1974). The primary report specifying the formation of a blocking layer (deactivation of the electrode) is by Parker and collaborators who explored the electrochemical behavior of aryldiazonium salt at metal electrodes for example gold, mercury and platinum (Ahlberg *et al.,* 1980). From their examination, they inferred that the radicals created amid the potential scan contribute to the obstructing of the electrode surface; however, the nature of the resulting blocking layer was not researched. Afterward, it was perceived and recommended that electrochemical reduction of aryldiazonium salts at a glassy carbon electrode permitted the attachment of the aryl radical, created by the reduction of the diazonium salt, to the carbon surface (Allongue *et al.,* 1997).

Before going into the point by point accomplishments of the electrografting of diazonium salts, let us give a concise outline of the reaction and depict a basic electrografting explore different avenues regarding a diazonium salt (Saby *et al.,* 1998; Ortiz *et al.,* 1998) introduce the cyclic voltammogram of 4-nitrobenzenediazonium tetrafluoroborate in H_2SO_4 0.1 M which demonstrates a broad irreversible wave on the first scan that vanishes on the second scan. This behaviour is regular of diazonium salts and the vanishing of the wave relates to the formation of an organic layer on the surface that obstructs the entrance of the diazonium cations to the electrode. After a few cyclic voltammetry scans, through the potential of the voltammetric peak or more negative, an organic layer is established on the electrode surface. Watchful washing by ultrasonication is required to evacuate organic compounds formed in solution and deposited on however not grafted to the surface. On a glossy metallic electrode, this layer can be perceived by the naked eye in the event that it achieves a thickness of no less than 10 nm. This covering can be watched and analysed by different surface investigation procedures for example the simple water contact angle, electrochemical measurements, XPS, IR and numerous different strategies. The layer is firmly attached as it opposes, for instance, sustained ultrasonic washing in an assortment of solvents. This electrografting response can be achieved on an assortment of materials for example metals, carbon, oxides, polymers and semiconductors. The diazonium salts are very simple to prepare. The conventional synthesis relates mixing an aromatic amine with sodium nitrite in a cold aqueous acidic solution, sifting and washing the precipitate (Furniss *et al.,* 1989).

The synthesis can likewise be proceed in aprotic medium (ACN) within the presence of tert-butyl nitrite. In a much easier technique, it is conceivable to prepare the diazonium salt in situ in the electrochemical cell by mixing, for instance, in an aqueous acidic solution the aromatic amine and sodium nitrite and straightforwardly performing the electrolysis or the spontaneous reaction (Baranto and Belanger, 2005). No matter what the method utilized for the production of diazonium salts, one must begin from an aromatic amine and a substantial number of these compounds are accessible commercially. The electrografting of diazonium salts has been beforehand explored in any event to some extent in 2000 (Downard, AJ. 2000), 2001 (Maeda *et al.,* 2001), 2005 (Pinson and Podvorica, 2005) or with emphasis on a specific subject: spontaneous grafting (Barriere and Downard, 2008), carbon (McCreery, RL. 2008) or silicon as substrates (Ciampi *et al.,* 2010), design of sensors and biosensors (Gooding, JJ. 2008; Polsky *et al.,* 2008), electrochemical and atomic force microscopy researched (Downard, AJ. 2009), nanoelectronics with molecules-on-silicon (Aswal *et al.,* 2009) the electrografting of diazonium salts, this technique is presently entrenched. Be that as it may, the requesting of the layers, the possibility of effortlessly controlling the thickness of the layer and the impact of the substrate still needs some more work. In any case, the strategy is currently developed for industrial utilizations.

Electrografting of organic molecules through utilizing different precursors for example amines, carboxylates, alcohols, Grignard reagents, vinylics and diazonium salts has been evaluated. Electrografting by the electrochemical reduction of vinylics at an electrode surface was at first announced 30 years before that. The vast majority of these investigations with vinylics included the utilization of metal as substrate and the formation of a covalent bond between the organic groups and the metal has been obviously illustrated. Curiously, the electrochemical grafting of organic molecules can be assembling to the formation of organometallic complexes. This has been likewise exhibited on account of the electrochemical reduction of diazonium salt on a mercury electrode. The protocols for the electrografting from different precursors have been illustrated and included the formation of a radical that coupling to the electrode surface. Despite the fact that there are not many cases where the nature of the species coupling to the surface is unclear, it appears that the formation of radicals is a general essential for electrografting to happen. In this manner, it can be foreseen that numerous different precursors could be utilized for that reason in future surface modification, radicals could be produced upon electron transfer or cleavage of a proper bond by different means (e.g. ultrasonic treatment, photochemistry, ball milling). The in situ generation of diazonium cations demonstrated exceptionally valuable for the modification of surfaces however the conditions for their formation have not been researched in incredible detail and it will be vital to assure the targeted diazonium cations are extremely formed. Strikingly, the in situ modification approach has been stretched out to nitro derivatives and this can open the route to extra electrografted surfaces in situations where the amine derivative is not commercially accessible. Furthermore, more works are expected to acquire superior information of the structure of the electrografted layers and besides how to regulate it, and additionally its formation and development. For instance, the improvement of experimental conditions to constrain the growth to a monolayer would be to a great degree valuable for some applications. It is intriguing to note that some examinations have revealed a strong influence of the substrate on the nature of the electrografted layers and furthermore on their behaviour. Unmistakably, superior information of the effect of the substrate will be essential. Electrografting from aryl diazonium has attracted a great deal of consideration in the previous 10 years and this is reflected in this content. That is the number of studies involved with diazonium salts speak to around half of the work being performed on electrografting. In any case, extra examinations with amines, including halides and aromatic amines are expected to completely exploit the potential of these precursors in electrografting procedure. On the contrary, a lot of applications have been imagined and exhibited for modified surfaces by means of formation of radicals. These examinations portrayed evidence of idea and additionally genuine applications. It is trusted that the formation of a covalent bond between the electrografted species and the surface will add to an expanding number of applications due to the fact that the presence of such a bond ought to give stability that dependably remains an imperative issue from an application perspective. Likewise, it appears to be conceivable to expect that applications in the areas of sensors, biosensors, composite materials, energy conversion, corrosion protection and numerous others will be produced soon as superior information of the electrografting procedures will wind up accessible.

1.3.2 Grafting of diazonium salts

Attaching aryl groups to surfaces has been described in the literature predominantly through the electrochemical grafting of diazonium salts. A lot of exertion has been advanced recently to create strategies to covalently bind chemical groups to carbon electrodes. A convention at first inspected by Delamar and coworker has risen and includes the grafting of functionalized aryl groups by means of the electrochemical reduction of diazonium salts (Delamar *et al.,* 1992; Pinson and Podvorica, 2005). The acknowledgment and application of this technique by various analysts is essential because of the straightforwardness with which diazonium salts bearing an extensive variety of functional groups can be incorporated, and also the structure and stability of the subsequent layer (Allongue *et al.,* 1997). Functionalized phenyl films have been used in various basic examinations of the electrochemical reactivity of carbon electrode treated (Saby *et al.,* 1997). The reduction of diazonium salts has additionally been utilized to modify silicon and metal surfaces (Henry de Villeneuve *et al.,* 1997). Considering the quantity of studies exploiting this attachment scheme so far, obviously the utilization of this strategy to control the textural and surface chemical properties will turn out to be more widespread. Therefore, an entire comprehension of the film deposition process and structure is required for an effective application. The functionalization of carbon electrodes with aryl groups can be achieved via a two-step process. The initial step the aryl radical was also be produced by electrochemical reduction of diazonium salt. This is followed by the covalent attachment process in which radicals diffuse to the surface and form covalent bond monolayer (Delamar *et al.,* 1992). Kariuki and McDermott have already researched the nucleation and growth of functionalized aryl films on graphite electrodes (Kariuki and McDermott 1999). The experiment showed that free aryl radicals can be electrochemically produced that bond with surface, resulting in the formation of a surface-bound phenyl group as illustrated in Fig. 1-12. The research reported here as elaborated in previous work by identifying a necessary condition to generate phenyl multilayer films on glassy carbon (GC) and probing the resulting film structure. The influence of aryl film thickness and structure on the glassy carbon electrodes are characterized as a function of deposition time. This study employs scanning force microscopy (SFM) and infrared reflection absorption spectroscopy (IRRAS) to exhibit that the electrochemical reduction of diazonium salts will induce to the formation of multilayer films on glassy carbon (GC) electrodes under certain circumstances; specifically, the deposition period (10 to 30 min).

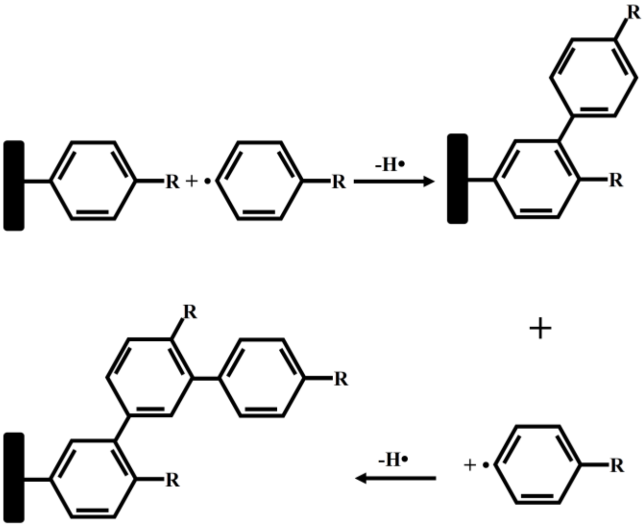


Fig. 1-12 Schematic delineation of the anticipated mode of multilayer formation by means of the attachment of aryl radicals in solution to the aryl moieties bound to the carbon surface. The hydride radicals produced in this mechanism can react with solvent or other aryl radicals (Kariuki and McDermott, 2001)

As for all the grafting processes, the first and most common argument for a covalent grafting relies on the chemical stability of the polyphenylene layers. First, the films remain stable after six months at air exposure (Bahr *et al.,* 2001). The layers were also observed to be resistant to severe rinsing procedures (Henry de Villeneuve *et al.,* 1997) (such as HF rinsing in the case of the grafting on Si) and to sonication procedures (Chausse *et al.,* 2002 and Laforgue *et al.,* 2005), long or in various solvents (Lyskawa *et al.,*2006). The stability of the films was also investigated electrochemically by applying very negative or positive potentials at the grafted electrode. D'Amours and coworker demonstrated that the electrochemical polarization of the modified electrode could remove some aggregates generated during the process but could not completely free the electrode from the polyphenylene film (D'Amour and Belanger 2003).

The diazonium salts or diazonium compounds are the class of normally unstable organic compounds which can be prepared by a standard diazotisation procedure including the treatment of aromatic amines with sodium nitrite within the presence of a mineral acid (HCl) (Hurley and McCreery, 2004). In this study electrodeposited organic layers are on the the electrode surface utilizing the diazonium cations produced in situ from the relating amines. One electron exchange from the electrode surface to the diazonium salt outcomes aryl radical formation subsequent to discharging of N_2 (Fig. 1-13). From Chira and her gathering study (Chira *et al.*, 2017) the erosion protection activity of organic layers electrodeposited on a copper surface utilizing electrochemical reduction of the diazonium salts was shown for some aromatic compounds, with different functional groups (for example alcohol, acids, halogens) or diverse of alkane chains lengths (Fig 1-14), to form organic multi layers onto copper surface by means of diazonium chemistry utilizing their amino moieties. She has selected that structures due to fascinate in the impact of the substitution, and in addition in the influence of the electron donating or electron withdrawing subgroups in the phenyl ring. It was discovered that erosion restraining efficiency rise to 90%. The greatest erosion restraining was acquired for 4-(4-aminophenyl)butyric acid and the least for 4-fluoroaniline. An association between the chemical nature and the inhibition efficiency of the substituent in the defensive layer was established. Also, an association of the the chemical nature with inhibition efficiency of the substituents display in the aromatic compounds was discovered. Strangely, the electrodeposited layers have a decent adhesion because of chemical bonds and could be additionally utilized as a preliminary in a multiple layer defensive methodology (Chira *et al.*, 2017).

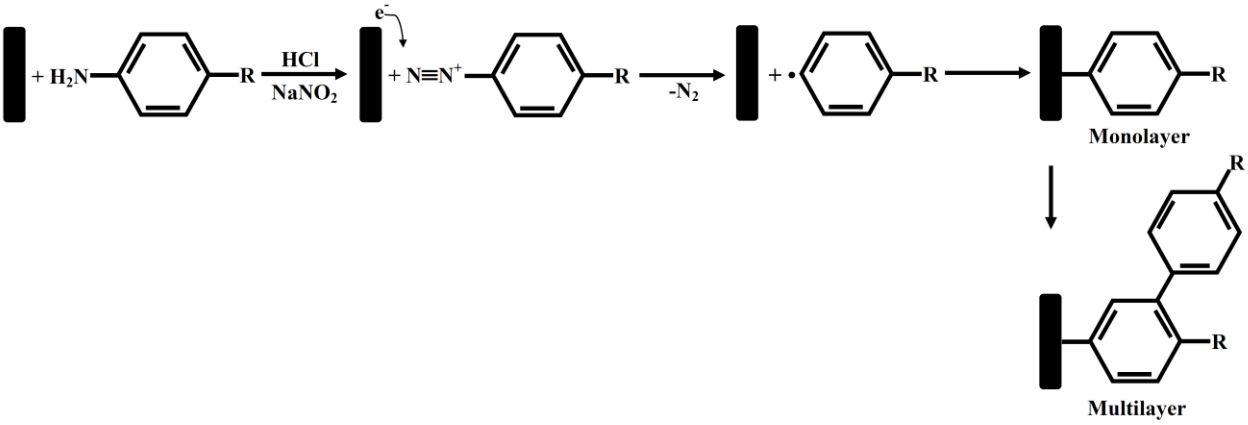
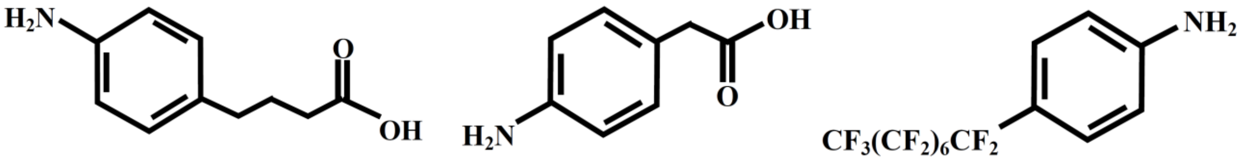
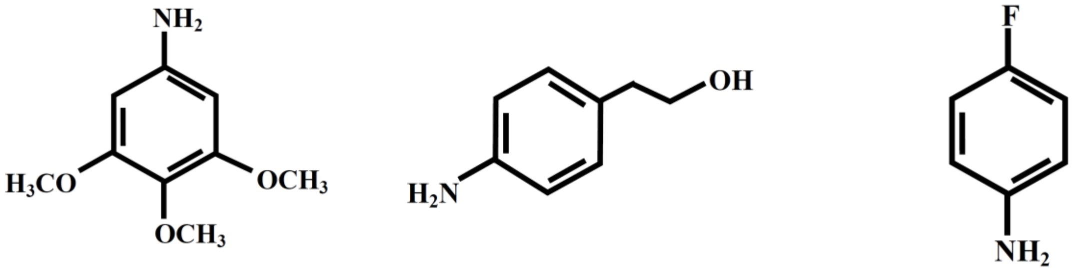


Fig. 1-13 Scheme of the electrodeposition reaction utilized for defensive layer formation on electrode surface. Amino moieties are removed during the electrodeposition procedure (Seck, *et al.*, 2015 and Chira *et al.*, 2017)



4-(4-Aminophenyl)butyric acid   4-aminophenylacetic acid   4-(heptadecafluorooctyl)aniline



3,4,5-trimethoxyaniline   4-aminophenethyl alcohol   4-fluoroaniline

Fig. 1-14 Certain aromatic organic compounds with different functional groups and lengths of alkane chains (Chira *et al.*, 2017)

1.3.3 Electrogravimetric investigation of the layer formation process

Quartz crystal microbalance (QCM) is a method helpful to observing the mass of immobilized particles by means of progress in the resonant frequency which could make specifically identified with the covered mass of organic film on the electrode (Öztürk *et al.*, 2016). The frequency (f) of an oscillation is diminished by the film covering on the surface of quartz crystals. The relationship between resonant frequency shift (Δf) and surface mass density (Δm/A) of a thin layer film on QCM, can be determined using Sauerbrey equation below:

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q \mu_q}}\Delta m = -C_f \Delta m \qquad \ldots\ldots\ldots\ldots\ldots(1.13)$$

Where:

Δf = frequency shift

Δm = mass change

μ_q = The shear modulus (2.947×10^{11} g/cm s^2)

ρ_q = the piezoelectric quartz crystal density (2.65 g/cm^3)

A = active surface area of the QCM electrodes

f_0 = measured frequency of the QCM

C_f = constant characterization of quartz crystal microbalance sensors

(the calculated value of Cf is 0.902 Hz/ng as for a 9 MHz quartz crystal)

The adjustment in the quartz crystal frequency previously, amid, and afterwards electrodeposition was monitored. The Sauerbrey relationship is utilized to change over the measured change of frequency to a quantified electrodeposited mass (Dixon, M.C. 2008). In this study QCM is not used to quantify electrodeposited mass, due to the equipment limitation. Instead the contact angle to specify film formation on the surface electrode which will be mentioned in the next topic.

1.3.4 Contact angle

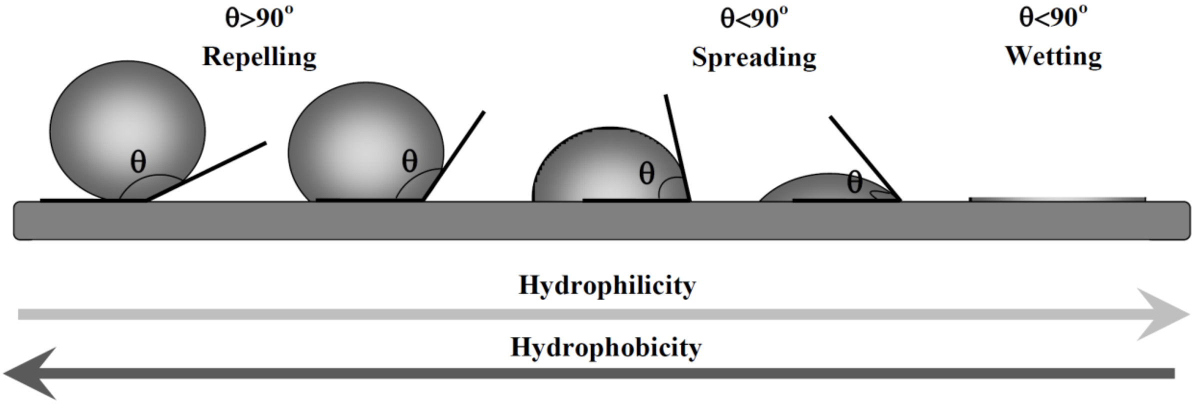


Fig. 1-15 Contact angle values and water drop behavior at the solids of different levels of hydrophobicity

The hydrophobic/hydrophilic attributes of solids assumes a key part in various procedures for example, flotation, wetting, cleaning technologies, enhanced oil recovery, superhydrophobicity, plants protection, liquid spreading, etc. Practically, hydrophobicity and hydrophilicity are relative terms acquainted with defining relative affinity of interaction of a liquid spreading with a solid surface. The degree of wetting (wettability) is determined by a force balance between cohesive and adhesive forces. The angle between the surface of the liquid and the outline of the contact surface is described as the contact angle (θ), that value is identified with values of surface energy for materials. The different contact angle of water spreading and forming drops with a solid surface is appeared in Fig. 1-15. It is for the most part, but instead discretionarily, expected a contact angle $\theta < 90°$ shows that the liquid droplet undergoing incompletely wetted on solid. A surface portrayed by the water contact angle is smaller than 90° the solid surface is considered hydrophilic. The hydrophilic effect is referred to the water-preferring and furthermore, at very low contact angles, complete wetting occurs when the contact angle is $\theta \approx 0°$, as the droplet turns into a flat puddle. A non-wetting liquid creates a contact angle $\theta > 90°$ with the solid then the surface is called as hydrophobic. Water drops that fall on a surface tend to form rounded drops or beads on hydrophobic surfaces. Some materials which highly rough surfaces may have the water contact angle is above 140°, owing to the presence of air pockets under the liquid drop. These are called superhydrophobic surfaces and can be improved hydrophobicity through the proper modifications for example micro-patterning, roughening, etching or machining. Then again, when the water contact angle is greater than 0°, at that point crafted by spreading, W_S, is negative.

$$W_S = W_A - W_C \qquad \text{..............(1.14)}$$

The dependence between the adhesion and cohesion are identified with surface tension of the solution were calculations in the following form:

$$W_A = \sigma_{LV}(1+\cos\theta) \qquad \text{..............(1.15)}$$

$$W_C = 2\sigma_{LV} \qquad \text{..............(1.16)}$$

Where;

W_A = the work of adhesion

W_C = the work of cohesion

σ_{LV} = liquid/vapor interfacial tensions

Hence:

$$W_S = \sigma_{LV}(1+\cos\theta) - 2\sigma_{LV} = \sigma_{LV}(\cos\theta - 1) \qquad \text{..............(1.17)}$$

The principal way to characterize the thermodynamic equilibrium of the system interfaces in a solid-liquid-gas contour line was followed by Young's equation is made under the assumptions of spreading of non-reactive liquid on an ideal (physically and chemically inert, smooth, homogeneous and rigid) solid surface as:

$$\sigma_{SV} = \sigma_{SL} = \sigma_{LV}\cos\theta \qquad \text{..............(1.18)}$$

Where;

σ_{SL} = solid/liquid interfacial tensions

σ_{SV} = solid/vapor interfacial tensions

σ_{LV} = liquid/vapor interfacial tensions

The basic problem related with the equilibrium contact angle is identified with the structure and prospect of the solid surface, as the genuine solids are rough. This is however not true in the case of most real surfaces. Surface roughness can influence emphatically wettability and estimations of the apparent contact angles. In order to get the actual contact angle, surface roughness parameter r was presented and characterized as:

$$r = \frac{A_{\mathrm{real}}}{A_{\mathrm{geometrical}}} \quad \text{..............(1.19)}$$

Where;

A_{real} = real areas of the surface

$A_{geometrical}$ = geometrical areas of the surface

σ_{LV} = is the liquid/vapor surface energy.

For r > 1 Young equation was adjusted by Wenzel. The Wenzel equation:

$$\cos\theta_{w} = r - \cos\theta \quad \text{..............(1.20)}$$

Where;

θ_{w} = Wenzel contact angle

The Wenzel's equation alludes to purported homogeneous wetting on rough surfaces (Whyman *et al.,* 2008) i.e. at the point when the liquid totally infiltrates scratches, grooves and cavities as seen in (Fig. 1-16). Another circumstance, heterogeneous wetting regime refers to the state in which air bubbles are entrapped inside the pores and grooves between roughness elements underneath the liquid phase (Fig. 1-16) and is portrayed by the Cassie-Baxter equation:

$$\cos\theta_{CB} = r_{f'} f' \cos\theta + f' - 1 \quad \text{..............(1.21)}$$

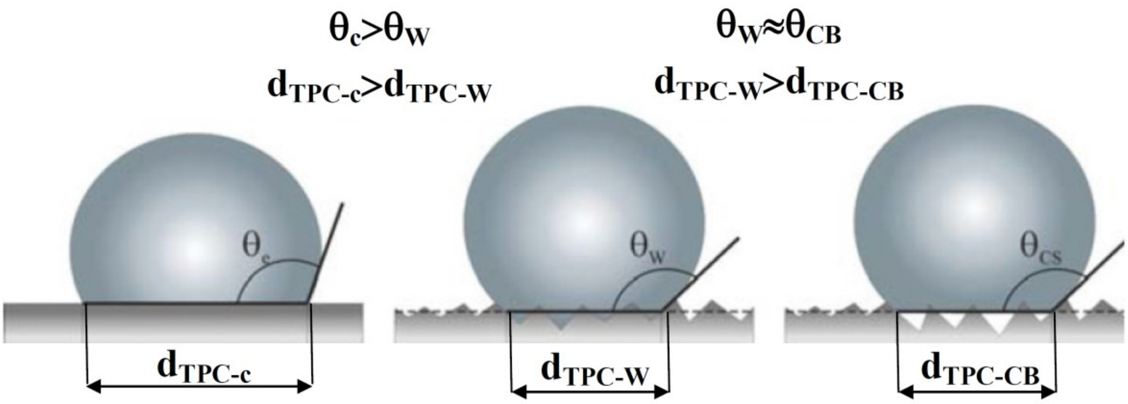
Where;

θ_{CS} = Cassie-Baxter contact angle

f' = fraction of the projected area that is wet by a liquid

$r_{f'}$ = roughness ratio of the wet area

Whenever f' = 1 then $r_{f'}$ is equivalent r and Cassie-Baxter equation (1.21) simplifies to Wenzel equation (1.20). As of late examined (Letellier *et al.,* 2007), the marvel of higher estimations of modified contact angle hydrophobic surfaces can also be produced by hindrance spreading of a liquid over a rough surface. Additionally, the spreading of water drops impinging on structured rough surfaces can be naturally captured by edge grooves. Contact angle is a broadly utilized investigation for characterization of hydrophilic and hydrophobic membranes behavior (Tylkowski *et al.,* 2010), the impact of crosslinking and modification on the latter (Valtcheva *et al.,* 2014)



Young equation

Homogeneous wetting
Wenzel equation

Heterogeneous wetting
Cassie-Baxter equation

Fig. 1-16 Water drop behavior and contact angle on smooth and rough hydrophobic surface

1.4 Review of literature

Several methods have been investigated to determine cadmium at trace level including inductively coupled plasma-mass spectrometry (ICP-MS) (Thompson and Christopher, 2013), graphite furnace atomic absorption spectrometry (GFAAS) (Santos *et al.,* 2002), atomic emission spectrometry (AES) especially when coupled with inductively coupled plasma (ICP-AES) (Zougagh *et al.,* 2002), X-ray fluorescence spectrometry (Golob *et al.,* 2005) and neutron activation analysis (NAA) (Fajgelj and Byrne, 1995). Nevertheless, these methods have the weaknesses of complicated equipment, high maintenance and operation costs, expensive apparatus and well-controlled experimental conditions requirement.

Electroanalytical techniques especially stripping analysis are outstanding as fantastic procedures for the determination of trace chemical species with the benefit of low cost, easy operation, high sensitivity and also the ability to perform element speciation (Hu *et al.,* 2003). Stripping analysis is all around perceived as a stand out amongst the most reasonable methods for determination of trace metal levels. Its noteworthy sensitivity is ascribed to the combination of an efficient preconcentration step with advanced measurement procedures that create an extremely favorable signal to background-noise ratio since a preconcentration of the target metals on the surface electrode. The concentration of the reduced metal following the deposition step is normally 100 to 1000 times greater than the concentration of the original (Wang J. 2000). The technique comprises of three steps. To start with, metal ions are deposited onto a surface electrode which is conducted at an appropriate potential. The sample solution is stirred amid this step in order to boost increase amount of metal deposited. Second, stirring is ceased with the goal that the solution will turn out to be calm. Third, the deposit metals are stripped off the electrode by the potential scanning. The observed current amid the stripping step can be identified with the amount of the metal in the sample solution. The stripping step may comprise of a negative or a positive potential scan, inventing either cathodic or an anodic current respectively. Therefore, Anodic stripping voltammetry (ASV) includes the accumulation of electroactive material at the electrode by the utilization of a potential well negative of its E^o following which a potential scan is started from the deposition potential in the anodic direction then Cathodic stripping voltammetry (CSV) includes an anodic deposition step followed by applied potential is scanned in a cathodic direction.

The modernized equipment for ASV measurement is extremely cost effective because it is small size and does not request a powerful supply. This makes field deployment possible and is a major favorable attitude over ICP or AAS. Normally, the lower detection limit of ASV is not as low as the lower detection limit of the spectrometric analytical techniques, however still sufficient for a large portion of the undertakings said above (Langeloth *et al.,* 2010). Anodic stripping voltammetry is an acknowledged strategy for trace metal ion investigated the contamination of water. ASV includes a two step method sequences: (i) electroreducing the ions as in a negative potential to form metal deposits on the surface electrode, whereby preconcentrating the analytes and (ii) specifically electrooxidizing each metal during a moderate potential scan in the direction of positive potentials (Swain *et al.,* 2004). The method, when combined with a proper electrode material, normally gives low detection limits for various metal ions with a good precision and wide linear dynamic range. Also, the method possesses capable to identifying trace multielement, inexpensive instrument and minimum maintenance. The instrumentation or methods of analysis is field comfortably and low power consumption without cooling requirement or ventilation (Swain *et al.,* 2004).

Notwithstanding varying of the scaning direction, the way in which the potential is scanned may likewise contrast. Linear sweep voltammetry (LSV) is the simply technique where the potential is continuously changed as a linear function of time. Other generally utilized techniques are differential pulse voltammetry (DPV) and square wave voltammetry (SWV), which provides a lower detection limit than LSV. This is a result of its pulsed waveform which estimates the current in pulses by taking two measurements and recording the distinction as the potential is expanded. This helps to lessen the background current. The waveforms from each pulse be associated upon each other to form a staircase waveform since the pulse amplitude is constant while the potential increases in little augmentations.

Even though the determination of metals by ASV can be performed with a variety of electrodes as well as strategies, the following development review indicates that the electrode of our choice, BDD, increases the sensitivity well. One of the extensively used electrode materials for ASV is mercury. Nowadays however, mercury electrodes are considered undesirable due to the toxicity of both metallic mercury and mercury salts employed for the preparation of mercury electrode and alternative environmentally friendly electrode materials are required (Yi *et al.,* 2012). Several new types of mercury-free electrodes have recently been developed for sensitive metal determinations, including bismuth film electrodes (Yi *et al.,* 2012 and Wang *et al.,* 2000), gold-coated electrodes (Wang and Tian, 1993 and Zhang and Wang, 2005), silver electrodes (Brand *et al.,* 1997 and Krasnodebska-Ostrega and Piekarska, 2005), glassy carbon electrodes (Di and Zhang, 2003), carbon paste electrodes(Roa-Morales *et al*., 2005), carbon nanotube electrodes (He *et al*., 2004) or screen-printed carbon electrodes (Honeychurch *et al*., 2002). Various types of carbon electrodes have likewise been researched for this examine. The first case is the screen printed carbon powder electrode as specified previously. Another illustration is the analyzation of Cd^{2+} and Pb^{2+} at multi-walled carbon nanotubes modified glassy carbon electrode (Hu *et al*., 2003). With the comparative relation of bare glassy carbon, the modified electrode displayed increased sensitivity for Cd^{2+}. The linear dynamic range for the identification of Cd^{2+} was from 2.5×10^{-8} to 1×10^{-5} mol/l (2.8 μg/l to 0.1 mg/l) for deposition (preconcentration) time of 5 min. These figures of merit were equivalent to those acquired with with boron-doped diamond thin films utilizing a 3 min deposition time (no stirring) (Swain *et al*., 2004). Diamond displays a background current density that is exhibits around one order of magnitude less than for glassy carbon, prompting enhanced signal-to-noise (S/N) ratio. The utilization of nitrogen doped diamond-like carbon films (DLF) electrodes for the investigation of Pb^{2+}, Cu^{2+} and Cd^{2+} was also reported (Zeng *et al*., 2002).

BDD electrodes have really drawn a great deal of interest to be applied in a variety of area because of their better properties, polar molecules less adsorption, incorporating extraordinary robustness with a low level of background interference and attractively wider electrochemical potential window in aqueous solution (McGaw and Swain, 2006 and Fierro *et al*., 2012). It has been utilized to measure manganese in tea (Saterlay *et al*., 1999) as well as lead in tap water (Chooto *et al*., 2010) and river sediment. Anodic stripping voltammetry of heavy metals at BDD electrodes has been proved to extend several outstanding features (Compton *et al*., 2001) to determine silver (Saterlay *et al*., 2000) and simultaneous detection of lead and copper (Prado *et al*., 2002). Diamond is an optional alternate electrode that has a large number of the same attributes as Hg and, consequently, appears to be a feasible material for this electroanalytical determination. The diamond electrodes have been utilized for both cathodic and anodic stripping voltammetry. For instance, high quality diamond displays: (i) extensive overpotentials for oxygen reduction and hydrogen evolution, (ii) an extensively overpotential for the oxygen evolution (wide positive window), (iii) less background current, (iv) prevention of electrode fouling, (v) quick electrode reaction which have rapid electron transfer kinetics kinetics for metal deposition and stripping reactions, and (vi) do not interaction with metal deposits. The characteristic properties of diamond make it preferably suited for the ASV investigation of Pb^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+} and Ag^{+}. Boron-doped diamond has been utilized for the determination of Pb^{2+} in river sediments by means of cathodic stripping voltammetry (Farre *et al.*, 2003). The electrode has additionally been effectively utilized for the determination of Mn^{2+} in tea samples through anodic stripping voltammetry (Compton *et al.*, 1999). Babyak and Smart (Babyak and Smart, 2004) investigated the electroanalytical determination of trace levels of cadmium and lead with boron-doped diamond electrode. Boron-doped nanocrystalline diamond (BDND) thin film electrodes were utilized for the quantification of Ag^{+}, Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+} in numerous contaminated water samples utilizing anodic stripping voltammetric. Differential pulse voltammetry was utilized to recognize these metal ions in tap water, well water, lake water, sludge from wastewater treatment and soil. The electrochemical outcomes were contrasted with the data from atomic absorption spectroscopy (AAS) and additionally inductively coupled plasma mass spectrometry (ICP-MS) determinations of the identical samples. Diamond appears to function well in this electroanalytical application, providing a low limit of quantitation, a wide linear dynamic range, good response accuracy and excellent response precision. For the investigation of Pb^{2+}, bare diamond electrode provided a response nearly indistinguishable to that obtained with mercury-coated glassy carbon electrodes (Swain *et al.*, 2004). Manivannan (Manivannan *et al.*, 2004) studied on the interaction of Pb and Cd during anodic stripping voltammetric analysis at boron-doped diamond electrodes. Highly boron doped diamond (BDD) films were used for simultaneous determination in micro molar concentrations level of Cd and Pb for the investigation of their associations. In this study, differential pulse anodic stripping voltammetry (DPASV) was utilized for this identification. This approach can comprehend the conceivable identification of trace metals at BDD electrodes without the assistance of mercury. These metals exhibit stripping at their typical characteristic potentials, in solutions containing these metals together Pb with Cd, and Pb or Cd alone. The mixed solutions (range of concentrations from 1.0 to 5.0 μM) resulting in good separate stripping peaks for both Cd and Pb were obtained and the differential stripping peak currents for the individual metals increased linearly ith the increase of metal concentration. There were mutual interferences because of Cd-Pb associations, however these can be considered with the assistance of three dimensional calibration curves. Compton studied on the detection of cadmium by using boron doped diamond electrodes: surfactant inhibited stripping voltammetry. Square wave anodic stripping voltammetry of cadmium at boron doped diamond electrodes was investigated within an acoustic field, silent conditions and afterward in the presence of the non-ionic surfactant Triton X-100. The effect of optimised insonation was to increase the sensitivity from 0.63 (in the quiescent conditions) to 3.78 μA/μM and to diminish the detection limit by an order of magnitude from 10^{-8} to 10^{-9} mol/l. More recently, Compton and co-worker (Compton *et al.*, 2001) studied the detection of lead in a river sediment at boron-doped diamond electrode employing microwave-enhanced anodic stripping voltammetry (Compton *et al.*, 2001).

Electrochemical modification of carbon electrode through chemical reduction of aromatic diazonium derivatives has been widely utilized for modification of several carbon materials, for example glassy carbon (Fan *et al.*, 2009), graphite (Picot *et al.*, 2011), graphene (Mooste *et al.*, 2015) and carbon nanotube (Bravoa *et al.*, 2015). It is all around perceived as a very exceptionally adaptable and simple way to graft with various organic functional groups onto carbon surfaces for variety of applications. Moreover, the diazonium modified surface electrode has been observed to stable after long period of time storage in air as well as organic solvents. The greatest stability of the diazonium modified electrode and the adaptability of the diazonium modification method are especially appealing for electrochemical stripping analysis. Therefore, its characteristic can be applied well to Cd^{2+} analysis.

A chemically modified electrode is an essential research area in materials science and electrochemistry. Recently, special attention many efforts have been paid to develop sensors using covalently modified electrodes used for biotechnological applications and analytical purposes. A variety of chemical pretreatment strategies have been proposed to modifying at the electrode carbon surface (Murray, RW. 1984). To improve the surface carbon functionality, oxidized surface functional groups (quinone, hydroxylic, carboxylic also with others ketonic groups) have been studied. These methods are incorporated with the advanced oxidation process, that is, a treated with highly oxidising acids, oxygen plasma radiation also heating in high temperature air. Thus, the subsequent resulting functional layer is less regular and now and then the surface electrode appears to be possible with roughened surfaces or harmed under these modifying processes. Electrochemically strategies of covalent immobilization of carbon electrode surfaces (Downard, AJ. 2000) has also been developed, which an ordinary modification procedure is done under these relatively mild condition so that functional layer increased are gotten contrasted with those framed by the oxidizing methods. Generally, these methods depend on electrochemical reduction or oxidation of a variety of organic functional groups; for instance reduction of aryl diazonium salts and oxidation of carboxylates, amines or alcohols. The previous report of aryl diazonium covalent modification was first developed by Bourdillon and his gathering (Bourdillon *et al.,* 1992). Electrochemical reduction of aryl diazonium salts is a versatile technique for the covalent modifying graphitic carbon surfaces. Consequently, the grafting on carbon electrodes of a wide range of functional groups with various physical and chemical properties can be promptly available (Barrire and Downard, 2008 and Pinson and Podvorica, 2005). Likewise, the surfaces modification of carbon with an electrochemical method (for example the potential sweeps and potentiostatic methods) permits the fine adjustment of modifier level (i.e. thickness) grafted on the surface electrode just by controlling by coulombic charging consumed in the modification procedure (Brooksby and Downard, 2004). As the one electron reduction of aryl diazonium salt at a carbon electrode lead to produce the covalent bond formation between aryl groups and carbon atoms on the electrode surface. As checked on by Downard (Downard, AJ. 2000), the proposed method has been used to modification of numerous carbon electrodes for example glassy carbon (Allongue *et al*., 1997), highly oriented pyrolytic graphite (HOPG) (Kariuki and McDermott, 1999), carbon fiber (Bath *et al*., 2001) and porous graphite carbon sphere (Harnisch *et al*., 2001). In the recent years, application of bulk single walled carbon nanotubes (SWCNTs) (Bahr *et al*., 2001) and individual SWCNTs (Kooi *et al*., 2002) was exploited. The modification is very simple, low cost and a modified electrode is described for long-term stable, then different kinds of electrochemical sensors have been progressed through the electrochemical reduction of an aryl diazonium salt; for instance, development of an amperometric glucose biosensor (Bourdillon *et al.,* 1992), flow detectors (Downard and Roddick, 1997), voltammetric differentiation of dopamine (DA) and ascorbic acid (AA) (Downard *et al.,* 1995), and detection of alkaline phosphatase (Dequaire *et al.,* 1999).

The modification of carbon surface via diazonium salts reduction became even more attractive in the past decade (Allongue *et al*., 1997). Delamar and his gathering were the first to exhibit that the reduction of an aryl diazonium cation managed the relating aryl radical, which can additionally reactions of carbon atoms with these substrates to produce result the covalent bonding of this aryl group be in accordance with Fig. 1-3 (Delamar *et al*., 1992). Recently, Andrieux and Pinson have exhibited that the two mechanistic scenarios for the aryl radical generation can be considered, which incorporates the electron exchange and the cleavage of dinitrogen previously the covalent bond formation (Andrieux and Pinson, 2003). This modification procedure is extremely appealing on the grounds that it was kept away from the use of oxidative conditions which can contribute to the adverse oxidation of the carbon substrate (Hoffman *et al*., 1991) The extensive assortment of substituted aryl groups that were grafted onto the surface of a glassy carbon electrode was recently reviewed (Downard, AJ. 2000). The particular substituent on the aryl group can be utilized to impart valuable properties to the chemically modified electrode and to intricate most complicated chemical structures that can advances in the versatile application (Delamar *et al.,* 1992 and Pinson and Podvorica, 2005). For instance, ionizable substituents for example -SO_3H, -COOH and -$N(C_2H_5)_2$ can also be utilized to bind metal complexes that can be furthermore chemically reduced to produce metal-metal oxide species (Marwan *et al.,* 2005). Ionizable groups can likewise provide charge selectivity property that is valuable for sensing utilization (Downard *et al.,* 1995). In addition, the substituent could be chosen to allow further chemistry for example immobilized enzymes (Bourdillon *et al.,* 1992) and electroactive groups (Ghodbane *et al.,* 2004) and to perform combinatorial chemistry (Coulon *et al.,* 2002). On the contrary, a noteworthy the defect of the modification approach in view of aryl diazonium salt is that the synthesis of the salt is required. Certainly, synthesis and isolation of the diazonium salt are not always constant. The synthesis is regularly completed in acidic media from the corresponding amine by utilizing $NaNO_2$ as a reactant (Bernard *et al.,* 2003). Conversely, it may interest to have a modification method that will evade this synthesis by utilizing the amine as a precursor. Attractively, the chemical modification of powder activated carbon, which makes utilization of an amine and leans on the in situ generation of the diazonium salt (generated in situ from sodium nitrite), has been researched in incredible detail by the groups of Strano and Pandurangappa (Strano *et al.,* 2003 and Pandurangappa *et al.,* 2002). Furthermore, Morita *et al*., (Morita *et al.,* 2004) and Blankespoor *et al*., (Blankespoor *et al.,* 2005) announced that an certain aromatic amine can be changed into a diazonium through the procedure of standard diazotization (Furniss *et al.,* 1989) and that the following solution can be employed for modifying carbon (Morita *et al.,* 2004 and Blankespoor *et al.,* 2005) or gold (Laforgue *et al.,* 2005) electrode by electrochemical reduction.

From the aforementioned literature review, it is clear that there are great varieties of techniques for cadmium analysis. However, electrochemistry is the method of choice because a number of advantages such as speed and cost effectiveness. Moreover, the most important key of electrochemical method is the electrode. Among a large number of electrodes available, BDD is the best alternative due to its sensitivity and inertness. Finally, to make the electrode more responsive to cadmium, electrografting is applied. Preliminary investigation reveals that diazonium salts has the greatest potential in cadmium determination.

1.5 Objectives

The objective of the study was to establish the optimum condition for modification of boron-doped diamond electrodes with functional aryl diazonium salt, carboxylic acid groups, 4-aminomethyl benzoic acid tailor to the electrode surface. The prepared electrodes were then used for the analysis of trace levels of Cd^{2+} in tap water by stripping voltammetry.

CHAPTER 2

2. EXPERIMENTAL

2.1 Chemicals and materials

2.1.1 Standard chemicals

- Cadmium nitrate stock standard solution (1,000 mg/l) (Carlo Erba, Italy)
- Cobalt nitrate stock standard solution (1,000 mg/l) (J.T. Baker, USA)
- Copper nitrate stock standard solution (1,000 mg/l) (Carlo Erba, Italy)
- Iron nitrate stock standard solution (1,000 mg/l) (J.T. Baker, USA)
- Lead nitrate stock standard solution (1,000 mg/l) (Fluka, Switzerland)
- Mercury nitrate stock standard solution (1,000 mg/l) (Merck, Germany)
- Nickel nitrate stock standard solution (1,000 mg/l) (J.T. Baker, USA)
- Zinc nitrate stock standard solution (1,000 mg/l) (J.T. Baker, USA)

2.1.2 NIST reference solution

A reference material® (1640, henceforth referred to as SRM 1640) was procured for testing from the National Institute of Standards and Technology (NIST). The standard contained certified amounts of metals (Table 2-1, 2-2, 2-3).

Table 2-1 Certified Mass Fractions

Element	µg/kg	Element	µg/kg
Al	52.0 ± 1.5	Mn	121.5 ± 1.1
As	26.67 ± 0.41	Mo	46.75 ± 0.26
B	301.1 ± 6.1	Pb	27.89 ± 0.14
Ba	148.0 ± 2.2	Sb	13.79 ± 0.42
Be	34.94 ± 0.41	Se	21.96 ± 0.51
Cd	22.79 ± 0.96	Si	7.62 ± 0.25
Co	20.28 ± 0.31	Sr	124.2 ± 0.7
Cr	38.6 ± 1.6	V	12.99 ± 0.37
Fe	34.3 ± 1.6		

Source: (Taylor, 1995).

Table 2-2 Reference Mass Fractions

Element	µg/kg	Element	µg/kg
Ca	7.045 ± 0.089	Ni	27.4 ± 0.8
Cu	85.2 ± 1.2	Rb	2.00 ± 0.02
K	994 ± 27	Si	4.73 ± 0.12
Li	50.7 ± 1.4	Zn	53.2 ± 1.1
Mg	5.819 ± 0.056		
Na	29.35 ± 0.31		

Source: (Taylor, 1995).

Table 2-3 Information Mass Fraction

Element	µg/kg
Tl	<0.1

Source: (Taylor, 1995).

According to the supplier, the sample was prepared in the following manner (Taylor, 1995). A sample of about 3500 litre of natural (fresh) water was obtained from the United States Geological Survey (USGS) at Clear Creek County Offices in Colorado, USA. It was passed through a 0.1 µm ultrafilter and acidified with nitric acid. Analysis of the water by ICP-MS, before and after the stabilization process, revealed that cobalt, beryllium, selenium, arsenic and zinc decreased in concentration during the stabilization process. These elements were adjusted to their original concentrations by the addition of the appropriate salts. The stabilized solution was then pumped through an ultrafilter, past a UV light source (purpose of sterilization), and then to a bottling station. At the bottling station, the containers were first rinsed with the sample and then filled with it for storage. A unit of this SRM consists of approximately 250 ml of natural fresh water, which has been filtered and stabilized with nitric acid at a concentration of 0.5 mol/l. The solution is preserved in a polyethylene bottle sealed in an aluminized plastic bag to maintain stability (Cellarosi, 2004).

2.1.3 Additional Chemicals and Solvents

- 3-Aminophenol (Assay 98.0% min), AR grade (Fluka, Switzerland)
- 4-aminomethyl benzoic acid (Assay 99.0% min), AR grade (Fluka, Switzerland)
- Glacial Acetic Acid (Assay 99.0% min), AR grade (RCI Labscan, Ireland)
- Acetophenone (Assay 99.0% min), AR grade (Scharlau Chemie S.A, Spain)
- Aluminium nitrate (Assay 98.0% min), AR grade (ASP, Australia)
- Ammonium acetate (Assay 97.0% min), AR grade (Ajax Finechem, Australia)
- Calcium nitrate (Assay 99.0% min), AR grade (Ajax Finechem, Australia)
- Manganese chloride (Assay 99.0% min), AR grade (Carlo Erba, Italy)
- Manganese sulfate (Assay 99.0% min), AR grade (Ajax Finechem, Australia)
- Magnesium chloride (Assay 99.0% min), AR grade (Carlo Erba, Italy)
- Magnesium nitrate hexahydrate (Assay 99.0% min), AR grade (Merck, Germany)
- Nitric acid 69-70% (w/v), AR grade (J.T. Baker, USA.)
- Potassium chloride (Assay 99.8% min), AR grade (Ajax Finechem, Australia)
- Potassium nitrate (Assay 99.5% min), AR grade (Ajax Finechem, Australia)
- Sodium acetate (Assay 99.8% min), AR grade (Ajax Finechem, Australia)
- Sodium chloride (Assay 99.5% min), AR grade (Merck, Germany)
- Sodium nitrate (Assay 99.0% min), AR grade (Ajax Finechem, Australia)
- Tetrabutylammonium hexafluorophosphate, $TBAPF_6$ (Assay 98.0% min), AR grade (Fluka, Switzerland)
- Ultra pure water resistivity 18 MΩ obtained by passing deionized water through a ELGA water purification system (ELGA, England)

2.1.4 Samples

Tap water samples (Hatyai city, in the South of Thailand, approximately 30 km. from Songkhla province; in August 2015). The samples were collected from eleven regions at Hatyai city (Appendix A). Sample must be collected in clean polyethylene bottles and analyzed inmediately, this is mandatory for pH. For the other parameters, if immediate analysis is not possible, refrigerate the sample at $4^{o}C$ and analyze within 48 hours.

2.2 Instruments and apparatus

2.2.1 Autolab potentiostat

- Powerlab 2/20, coupled with Potentiostat (ADInstrument, Australia) and controlled by EChem software as shown in Fig. 2-1
- Nitrogen gas, High purity 99.99%, (TIG, Thailand)

2.2.2 Inductively couple plasma optical emission spectrometer

- Inductively couple plasma optical emission spectrometer, Optima 4300 DV (Perkin-Elmer, USA)

2.2.3 Electrochemical cell and electrodes (Fig. 2-2).

- Ag/AgCl (3.0 M KCl) served as the reference electrodes (Metrohm, Switzerland
- Boron-doped diamond electrode (3.0 mm diameter) as a working electrode (Windsor Scientific Ltd., UK)
- Platinum wire as an auxiliary electrodes (Number 6.1204.120, Metrohm, Switzerland)
- 50 ml of Electrochemical cell (Metrohm, Switzerland)

2.2.4 Apparatus

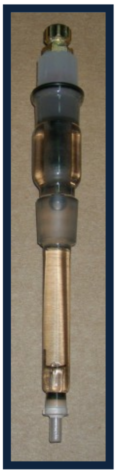
- General glassware such as volumetric flasks 10, 25, 50, 100, 250, 500, 1000 ml; Beakers 50, 100, 500, 1000 ml
- Microbalance Model TC-254 (Denver Instrument, USA)
- Microlitre pipette model: SL200 (20-200 µl) (Rainin, USA)
- Microlitre pipette model: SL1000 (100-1000 µl) (Rainin, USA)
- pH meter Model 225 (Denver Instrument, USA)
- pH meter Model pHscan3 (Eutech Instrument, Netherlands)
- Polyethylene bottles
- Polypropylene bottles

2.2.5 Materials

- Alumina powder 0.05 micron diameter (Buehler, USA)

Fig. 2-1 Powerlab 2/20, coupled with Potentiostat (ADInstrument, Australia)

Electrochemical cell and electrodes



Ag/AgCl (3 M KCl)
(Reference electrode)

BDD
(Working electrode)

Platinum wire
(Auxiliary electrode)

Fig. 2-2 Electrochemical cell and electrodes

2.3 Methodology

2.3.1 Preparation of stock standard solutions

Stock standard solution of 1,000 µg/l Cd was prepared by using 1,000 mg/l Cd standard solution and diluted for the corresponding concentrations.

2.3.2 Preparation of glassware and plasticware

The glassware and plasticware were soaked in 10% (v/v) nitric acid for overnight, and then rinsed at least three times with ultra pure water (Farghaly, 2003).

2.3.3 Working electrode preparation

The BDD electrode was polished at the beginning of the experiments with 0.05 micron diameter alumina powder (Buehler, USA) and was rinsed thoroughly with ultra pure water to obtain a clean, renewed electrode surface. The electrode was connected to the potentiostat and placed in ultra pure water; a constant potential of 600 mV for 2 min after completion of the anodic sweep to fully oxidize all metal deposits prior to the next measurement. The electrochemical pre-treatment was repeated daily. The polishing was reformed only when the contamination of the electrode surface was suspected (Swain *et al.,* 2004). However, an electrode used in untreated tap waters may need frequent polishing. Whenever the proper functioning of the electrode deteriorated, the treatment with the alumina was repeated. In previous work (Kirowa-Eisner, 1997), a stable background and a stable response were obtained after a series of about 20 anodic stripping runs in the supporting electrolyte that was carry out under conditions typical for the determination of cadmium with 30 s deposition time.

2.3.4 Selection of precursors

(a) The various precursors to generate the films

Compounds containing the carbon skeleton of the precursor (monomers), a molecule of any of a class of compounds, mostly organic, that can react with other molecules to form very large molecules or polymers. The essential feature of a monomer is polyfunctionality, the capacity to form chemical bonds to at least two other monomer molecules. Bifunctional monomers can form only linear, chain like polymers, but monomers of higher functionality yield cross-linked, network polymeric products.

The electrochemical grafting was carried out under stirring (400 rpm) in a cyclic voltammetry mode (5 cycles) between +0.20 and -1.20 V vs. Ag/AgCl at 100 mV/s in acidic medium (HCl, pH=2.0). The effect of various types of thin film modified on the surface electrode with 30.0 mg/l Cd^{2+} was performed. The operating parameters at the optimum conditions obtained from section 2.3.6 were applied with various types of films as shown in Table 2-4. The thin film modified yielding high current and good peak shape was selected.

Table 2-4 Grafting precursors for under investigation

No.	**The precursors to generate films**
1	2-Butanone
2	Acetophenone
3	Dimedone
4	Benzophenone
5	Benzoquinone
6	Xanthene
7	Anthrone
8	Tetrabutylammonium hexafluorophosphate, $TBAPF_6$
9	Anthraquinone
10	4-aminomethyl benzoic acid

(b) Influence of precursor concentrations

The concentration of a selected precursor was investigated in the range of 0.0 to 5.0 mM for acetate buffer solutions with the same procedure and parameters above. The experiment was run three times for each concentration.

2.3.5 Reference electrode

The porous position should be immersed in a 3.0 M aqueous sodium chloride solution (or potassium chloride). The reference electrode should also be removed from the electrochemical cell and stored in this solution between experiments (this is especially imperative when utilizing non aqueous solvent systems). Periodically, air bubbles can form in the solution next to the porous point; these ought to be evacuated by delicately flicking the end of the electrode (BAS Epsilon, 2000).

2.3.6 Optimization of operating conditions

The optimization was completed by varying the required parameters and keeping other parameters consistent. The optimum value was then utilized for all investigations. The optimization tests were carried out by utilizing 30.0 mg/l cadmium stock solution. The parameters for Powerlab 2/20, coupled with Potentiostat and controlled by EChem software were summarized in Table 2-5.

Table 2-5 Optimized operating conditions for Powerlab 2/20 coupled with Potentiostat

Parameters	Optimum conditions
Pulsing	SWASV
Purging times (min)	≥5
Electrolyte	Acetate buffer, pH 6.0
Deposition potential (V)	-1.10
Deposition time (min)	6
Equilibration time (s)	30
Frequency (Hz)	10
Scan rate (mV/s)	100
Amplitude (mV)	40

2.3.6.1 Pulsing for stripping signal

The sensitivity of optimized SWASV proved to be more than that result of differential pulse anodic stripping voltammetry (DPASV). Square wave anodic stripping voltammetry (SWASV) was optimized for the determination of Cd in tap water samples. Optimum voltammograms were obtained by applying 6 min of a deposition potential at -1.10 V (vs. Ag/AgCl, 3.0 M KCl). Voltammetric parameters were optimized to obtain maximum sensitivity, retaining good peak resolution and well discrimination from background. Optimal parameters were: frequency 10 Hz, pulse amplitude 4 mV and scan rate 100 mV/s.

2.3.6.2 Purging time

The purges of inert gas is to minimize of oxygen from the working station. Oxygen is electroactive, and can be decreased effortlessly; consequently it must be expelled from the solution if the system under investigation undergoes reduction reaction. Oxygen is ordinarily evacuated by bubbling an inert gas (for example argon or nitrogen) through the solution for about 5 min. If a stationary solution experiment is to be performed, it is imperative that the stirring is ceased and the solution is permitted to become calm before the investigation is begun despite the fact that a covering layer of inert gas over the solution can be maintained during the experiment. The purge time in this study was varied from 1 to 6 min.

2.3.6.3 Stirring rate

Stirring the solution on the accumulation stage has a significantly affects on the current response since it influences the rate at which electroactive molecules are conveyed from the bulk solution to the electrode surface (this procedure is alluded to as mass transfer). In numerous voltammetric experiments, there is no stirring, and the main development of mass transfer is diffusion (this offers ascend to the tailed peak shape saw in cyclic voltammetry). The techniques without stirring are alluded to as stationary solution techniques. The studies of stirring speed on the electrochemical grafting stage 200, 400, 600 and 800 rpm was employed in this study it was found that the amount of co-deposited film particle increased with an increase in stirring speed and the highest cocentration of film was recorded at 400 rpm.

2.3.6.4 Nitric acid concentration

Throughout the process, the pH of solution plays an important role because of its effectiveness on electrode surface and film formation interaction. This important variable value was studied with 0.2 M KNO_3 solution with the pH range of 1.0 to 8.0 (adjusted with nitric acid concentrations from 0.0 to 0.1 M; 0.00, 1×10^{-6}, 1×10^{-5}, 1×10^{-4}, 1×10^{-3}, 1×10^{-2} and 1×10^{-1} M) then tested the grafted film ability by concentration of 30.0 mg/l Cd^{2+}. Three replicates were performed for each. In the final result after optimize electrolyte was found acetate buffer solutions pH 6.0 shows the best respound for cadmium determination, then use acetate buffer solutions pH 6.0 for instant.

2.3.6.5 Electrolyte

(a) Types of electrolyte

The effect of various types of electrolyte on the current of Cd.30.0 mg/l Cd^{2+} was investigated. The operating parameters at the optimum conditions obtained from section 2.3.6 were applied with various types of ionic salts as shown in Table 2-6. The electrolyte yielding high current and good peak shape was selected.

Table 2-6 Electrolytes under investigation

No.	Electrolyte
1	KNO_3
2	$NaNO_3$
3	KCl
4	NaCl
5	CH_3COONH_4
6	CH_3COONa
7	Acetate buffer solutions 0.1M acetic acid + 0.1M sodium acetate

(b) pH of electrolyte

After confirmation of the best electrolytes for cadmium detection is acetate buffer solutions, the pH was varied. The pH of electrolyte was investigated in the range of 2.0 to 7.0 for acetate buffer solutions with the same procedure and parameters above. The experiment was run three times for each concentration.

2.3.6.6 Deposition potential

To accomplish greatest sensitivity in the voltammetric response, most importantly the deposition potentials were inspected with standard solution containing 30.0 mg/l Cd^{2+} and suitable electrolyte solutions, which was varied from -0.80 to -1.30 V with 0.10 increscent (-0.80, -0.90, -1.00, -1.10, -1.20, -1.30 V) versus silver/silver chloride reference electrode. The stripping voltammogram was recorded in the square wave mode with the same conditions and same parameters in section 2.3.6. Three replicates of square wave mode were performed for each potential.

2.3.6.7 Deposition time

To increase peak current and to enhance the sensitivity of the method, the impact of deposition time was researched. For Cd^{2+} concentration of 30.0 mg/l and selected electrolyte acetate buffer solutions pH 6.0 (0.1 M acetic acid 52.2 ml + 0.1 M sodium acetate 947.8 ml), deposition time periods between 1 to 8 min (1, 2, 3, 4, 5, 6, 7, 8 min) were experimented with the deposition potential of -1.10 V in stirred solution versus silver/silver chloride reference electrode.

2.3.6.8 Scan rate and step potential

The scan rate is related to step potential of square wave mode. Therefore, when increasing step potential, the scan rate is increased automatically. Then the effect of scan rate on peak current was studied by varying scan rates the range of 10 to 200 mV/s. The concentration of Cd^{2+} used was 30.0 mg/l in acetate buffer solutions pH 6.0 (0.1M acetic acid 52.2 ml + 0.1M sodium acetate 947.8 ml).

2.3.6.9 Amplitude

The effect of amplitude on peak current was studied by varying amplitudes in the range of 10 to 60 mV with 10 mV increment (10, 20, 30, 40, 50, 60 mV). The concentration of Cd^{2+} used was 30.0 mg/l in acetate buffer solutions pH 6.0. (data not shown)

2.3.6.10 Equilibration time

The dependence of the anodic peak current on the equilibration time for Cd^{2+} concentrations was studied. The peak current was found to increase with increasing equilibration time, indicating an enhancement of Cd^{2+} uptake at the electrode surface. Normally, the increase in the response current continues to a maximum signal level (presumably corresponding to either saturation or an equilibrium surface coverage).

The influence of equilibration time on peak current was carried out by varying equilibration time in a range of 0 to 40 s; flux increment of 0, 10, 20, 30 and 40 s. The dependence of deposition efficiency upon equilibration time was studied with 30.0 mg/l Cd^{2+} in acetate buffer solutions pH 6.0.

2.3.7 Analytical performances of ASV methods

2.3.7.1 Linear range

The stock standard solution of Cd^{2+} was diluted with ultra pure water to obtain various concentrations with the range from 2.0 to 50.0 μg/l. The 50.0 ml of each concentration was analyzed by Powerlab 2/20, coupled with Potentiostat at the optimum conditions taken from section 2.3.6. The linear dynamic range was obtained by plotting the peak current versus the concentration. The linearity of response was evaluated from the correlative coefficient of the linear curve.

2.3.7.2 Limit of detection (LOD)

The limit of detection is characterized by IUPAC as the smallest concentration that can be detected with a certainty of over 95% confidence level. Limit of detection for ASV techniques was determined based on $3\sigma/m$ (Coelho *et al.,* 2002) where;

σ = the standard deviation of 10 measurements of blank signal*

m = the slope of the calibration graphs

*Blank signal obtained was the signal of 2.0 μg/l Cd^{2+} adding in blank solution, due to the fact that no peak appeared at blank solution.

2.3.7.3 Limit of quantification (LOQ)

The limit of quantification is expressed as the smallest concentration that can be quantified with appropriate precision and accuracy. Typically the limit of quantification is assessed as the signal to noise ratio (S/N) that is comparable to 10 times of the standard deviation of the noise ($S/N=10\sigma$). The determination of the limit of quantification for ASV techniques was examined based on $10\sigma/m$ (Coelho *et al.,* 2002) where;

m = the slope of a linear calibration line

σ = the standard deviation of 10 repeated measurements of blank signal*

* Blank signal obtained was the signal of 2.0 μg/l Cd^{2+} adding in blank solution, due to the fact that no peak appeared at blank solution.

2.3.7.4 Accuracy

The accuracy of analytical method was evaluated from certified reference material. The accuracy of the considered method was performed by analysizing the Standard Reference Material (SRM), Trace Elements in Natural Water (SRM 1640) from the USA. 20.0 ml of standard was diluted to 100.0 ml by acetate buffer solutions pH 6.0 electrolyte solutions. The stripping peak was performed with the optimum conditions in section 2.3.6 and three replicates were performed for each. The concentration of Cd^{2+} was evaluated by standard addition method using Powerlab 2/20, coupled with Potentiostat. The outcomes from experimental and certified values were compared and then the percent of the error was examined.

The accuracy term is the measurement of exact value of the analyte concentration or agreement between measured value and certified value or an accepted reference value. Regularly, the accuracy value is expressed in terms of relative percent error as follows:

$$\% \text{ Error} = \frac{|\text{Measured value} - \text{Real value}|}{\text{Real value}} \times 100 \qquad \ldots\ldots\ldots\ldots\ldots(2.1)$$

2.3.7.5 Precision

Precision is a measurement of the degree of repeatability of an analytical technique under the similar condition. Regularly it is expressed as a percentage of the relative standard deviation (%RSD) for a statistically significant number of samples. The calculation of %RSD is given below:

$$\%\text{RSD} = \frac{\text{SD}}{\overline{\text{X}}} \times 100 \quad ; \quad \text{SD} = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \overline{x})^2}{(n-1)}} \qquad \ldots\ldots\ldots\ldots\ldots(2.2)$$

Where;

SD = standard deviation values

n = the count of mean values

x_i = each individual value to calculate the mean

$\overline{x}$ = the mean of the data

In this study, the precisions were investigated by measuring the degree of repeatability for analyses of cadmium standard solutions in the concentration of 2.0, 10.0 and 50.0 µg/l. The experiments for each standard solution were repeated 10 times.

2.3.7.6 Recovery

The terms recovery (R) is utilized to indicate the yield of an analyte at a preconcentration or a dilution stage in an analytical method. Normally, the recovery value is displayed as a percent recovery (% R) and can be calculated from the equation underneath:

$$\% \text{ Recovery} = \frac{\text{Measured value}}{\text{Real value}} \times 100 \qquad \ldots\ldots\ldots\ldots\ldots(2.3)$$

In this study, the % recovery was obtained from tap water sample spiked with 5.0, 10.0 and 20.0 µg/l of Cd^{2+}. The stripping peak was performed with the optimum conditions in section 2.3.6 and three replicates were performed for each.

2.3.7 Preparation of modified electrode

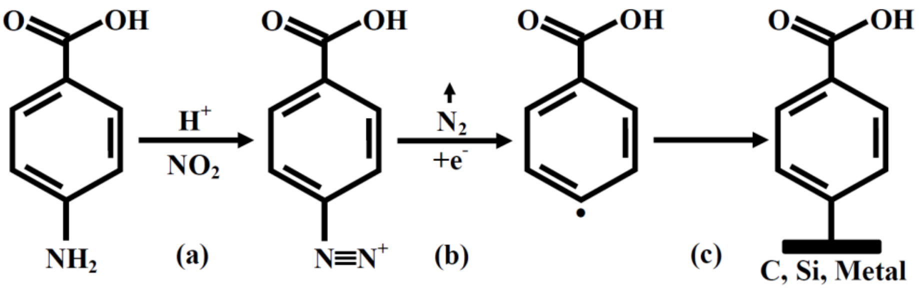


Fig. 2-3 Electrochemical reduction of diazonium salts grafting procedure (a) Spontaneous reaction of diazonium salts (b) Electrochemical reduction and (c) Surface grafting on the electrode (Seck, *et al.*, 2015)

As it is well known, an interesting alternative method that is currently broadly used to attach of organic layers to electrodes surfaces is the electrochemical reduction of an aryl diazonium salts. As first illustrated (Delamar *et al.*, 1992), it prompts the covalent attachment of the organic groups to the surface. Two primary methods can be easily synthesize a aromatic diazonium salts in an acidic aqueous medium of $NOBF_4$ starting from an amine in the presence of $NaNO_2$ in an organic medium (Le Floch *et al.*, 2009 and Allongue *et al.*, 1997) or in situ generation (Pandurangappa *et al.*, 2009 and Chamoulaud and Belanger, 2007) via the reaction of an aqueous nitrite solution (tetrabutylammonium hexafluorophosphate, $TBAPF_6$) with an amino group (Fig. 2-3). The electrochemical surface modification thin films were performed by electrochemical reduction of diazonium salts on the surface of electrode. Diazonium salts were directly created by the spontaneous reaction of diazonium salts utilizing an aromatic amine exhibiting satisfactory relative displacements in the in the para position to the amino group ($-NH_2$). In situ conversion of a diazonium salt ($-N_2^+$) from amine was completed with solutions of aqueous nitrite and acidic medium (HCl, pH=2.0). Fig. 2-3 shows the electrochemical reduction of diazonium salts to immobilize organic layers on electrodes on electrodes surface. Electrochemical grafting of aryl diazonium salts was carried out by stirring at 400 rpm in a cyclic voltammetry mode (5 cycles) between +0.20 and -1.20 V vs. Ag/AgCl at 100 mV/s. The aqueous electrolyte was composed of 10.0 mM $TBAPF_6$, 0.5 M HCl and 0.5 mM 4-aminomethyl benzoic acid.

2.3.8 General procedure for determination of cadmium

Stripping voltammetric measurements were performed with a BDD electrode and the target metal is Cd^{2+} in the presence of dissolved oxygen. Before its utilization, the BDD electrode was polished with 0.05 µm alumina slurry. The three electrodes were immersed into a 50.0 ml electrochemical cell containing pH 6.0 acetate buffer solutions. The deposition potential of -1.10 V for measurements of Cd^{2+} was applied to the BDD electrode working electrode in the stirred solution. Following the preconcentration step for 6 min, the stirring was stopped; and after 30 s, the voltammogram was recorded by sweeping the potential from -1.00 to -0.30 V (with scaning rate 100 mV/s, a frequency of 10 Hz, amplitude of 40 mV, and potential step of 25 mV). Aliquots of the Cd^{2+} standard solution were introduced after recording the background voltammograms. The peak currents were measured at -0.72 V vs. Ag/AgCl. A 30 s conditioning step at +0.30 V (with stirred solution) was performed to fully oxidize all metal deposits prior to the next measurement. All experiments were carried out at room temperature. The whole mechanism comprises of accumulation, reduction, and stripping stages which can be represented, respectively, as follows:

$(Cd^{2+})_{(solution)}$ + diazonium $salts_{(electrode\ surface)} \leftrightarrow Cd^{2+}$-diazonium $salts_{(electrode\ surface)} + 2H^+$
(accumulation stage, pH=6.0)
Cd^{2+}-diazonium $salts_{(electrode\ surface)} + 2e^- \rightarrow Cd^0$-diazonium $salts_{(electrode\ surface)}$
(deposition stage, $E_{applied}$ = -1.10 V, 6 min)
Cd^0-diazonium $salts_{(electrode\ surface)} \leftrightarrow (Cd^{2+})_{(solution)} + 2e^-$
(stripping stage, $E_{applied}$ = -1.00 to -0.30 V, Epa = -0.72 V)

2.4 Effect of interferences

The effect of various common ions was evaluated with respect to their interferences with the stripping peak of Cd^{2+} by adding foreign ions to 50.0 ml solution containing 20.0 µg/l of Cd^{2+}. The chemicals used as interference include $Ca(NO_3)_2{\cdot}4H_2O$, $MgCl_2{\cdot}6H_2O$, $Zn(NO_3)_2$, $MnCl_2{\cdot}4H_2O$, $Fe(NO_3)_2$, $Cu(NO_3)_2$, $Al(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2$, $Pb(NO_3)_2$ and $Ni(NO_3)_2$. The stripping was performed with the optimum conditions in section 2.3.6 and three replicates were performed for each.

2.5 Application of this investigation method to tap water samples

2.5.1 Sampling

Tap water samples (Hatyai city, in the South of Thailand, approximately 30 km. from Songkhla; in August 2015) were collected in clean polyethylene bottles (the polyethylene bottles was cleaned by soaking with a 10% HNO_3 solution overnight, and then rinsing at least three times with ultra pure water). The water samples were taken from the sampling sites around Hatyai city

(Appendix A) by means of polyethylene bottles with the volume between 1.0 and 1.5 l. Prior to the actual sampling, the bottle was filled with the tap water and emptied several times. Then, it was left full for about half an hour before being emptied and refilled with a fresh sample (Farghaly, 2003). The tap water samples were collected from eleven regions at Hatyai city after 15 min by opening the taps.

2.5.2 Sample pretreatment

The suspended matter was separated from water samples by filtration through Whatman No. 42 filter paper. The filtrate is then acidified to pH 1.3 by the addition of nitric acid. This prevents the adsorption of analyte ions onto the walls of the container, and causes dissociation of metal, thereby making these ions available for the analysis. The acidified samples were stored at -4 °C before being experimented. The digestion step is not essential due to the fact that the tap water samples ordinarily do not have any particulate matter or noteworthy organic content (Farghaly, 2003).

CHAPTER 3

3. RESULTS AND DISCUSSION

3.1. Precursors selecting

3.1.1 The various precursors to generate the films

The electrochemical grafting was conducted by stirring condition at 400 rpm in a cyclic voltammetry mode (5 cycles) between +0.20 and -1.20 V vs. Ag/AgCl at 100 mV/s. The effect of various types of thin film modified on the current of 30.0 mg/l Cd^{2+} was performed. The operating parameters at the optimum conditions obtained from section 2.3.6 were applied with various types of films precursors including 2-Butanone, Acetophenone, Dimedone, Benzophenone, Benzoquinone, Xanthene, Anthrone, $TBAPF_6$, Anthraquinone and 4-aminomethyl benzoic acid (Table 2-4). The thin film modified that yielding high current and good peak shape is 4-aminomethyl benzoic acid in methanol with 10.0 mM $TBABF_6$ due to the electrochemical surface modification thin films were performed by electrochemical reduction of diazonium salts on the surface of electrode. Diazonium salts were directly created by the spontaneous reaction of diazonium salts utilizing an aromatic amine exhibiting satisfactory relative displacements in the in the para position to the amino group ($-NH_2$) (Bélanger and Pinson, 2011). The electrochemical reduction of diazonium salts grafting on the electrode surface as illustrated in Fig. 2-3

3.1.2 Effect of precursors concentrations (4-aminomethyl benzoic acid)

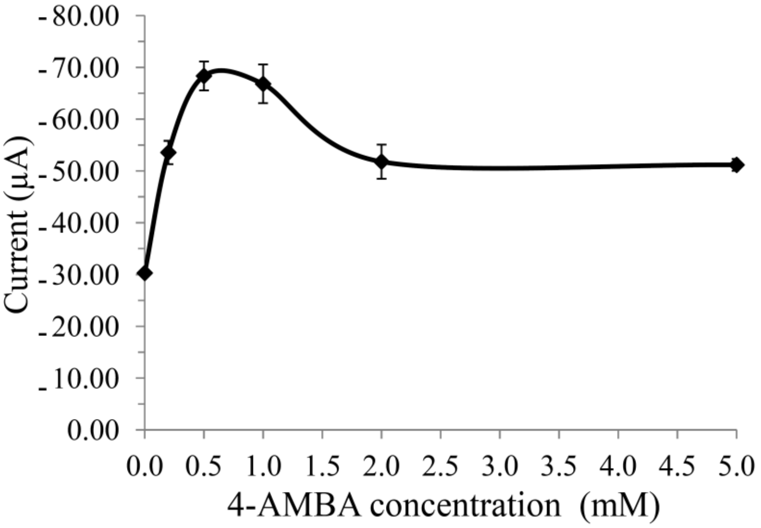


Fig. 3-1 Peak currents from BDD electrode at concentration of 30.0 mg/l Cd^{2+} with various concentrations of 4-aminomethyl benzoic acid (4-AMBA) 0.0, 0.2, 0.5, 1.0, 2.0 and 5.0 mM in acetate buffer solutions pH 6.0 with scan rate of 100 mV/s

The dependence of the peak currents of Cd^{2+} on the concentration of 4-aminomethyl benzoic acid is depicted in Fig. 3-1. It is apparent that 4-aminomethyl benzoic acid film can increase peaks height of Cd^{2+} oxidation, a sharp increase in the response signal can be observed with increasing concentration of 4-aminomethyl benzoic acid from 0.0 to 0.5 mM followed by a decrease from 1.0 to 5.0 mM. When the concentration of 4-aminomethyl benzoic acid was very high, the formation of a thick layer probably partially blocked the conductive surface of the electrode, resulting in the decrease of electrodeposition sites (Seck, *et al.,* 2015). The optimum concentration with the highest current is 0.5 mM, which was selected for further experiments.

3.1.3 Effect of electrolytes concentration for film formation

The effects of electrolytes concentration at 0.5, 1.0, 5.0, 10.0 and 15.0 mM $TBAPF_6$ on the peak currents of Cd^{2+} were also carefully investigated. It was found that Cd^{2+} had the best electrochemical responses in 10.0 mM $TBAPF_6$ as shown in Table 3-1 and Fig 3-2, which was chosen as a supporting electrolyte for voltammetric determination of the Cd^{2+} for further experiments.

Table 3-1 Electrochemical response of cadmium in various electrolyte concentration for film formation

Electrolytes concentration, $TBAPF_6$ (mM)	Current (µA)			Average	SD	%RSD
	I	II	III			
0.5	32.631	30.362	31.789	31.594	1.147	3.630
1.0	37.256	39.245	38.956	38.486	1.075	2.792
5.0	47.268	48.348	49.314	48.310	1.024	2.119
10.0	58.654	59.265	60.445	59.455	0.910	1.531
15.0	60.123	57.265	60.987	59.458	1.948	3.276

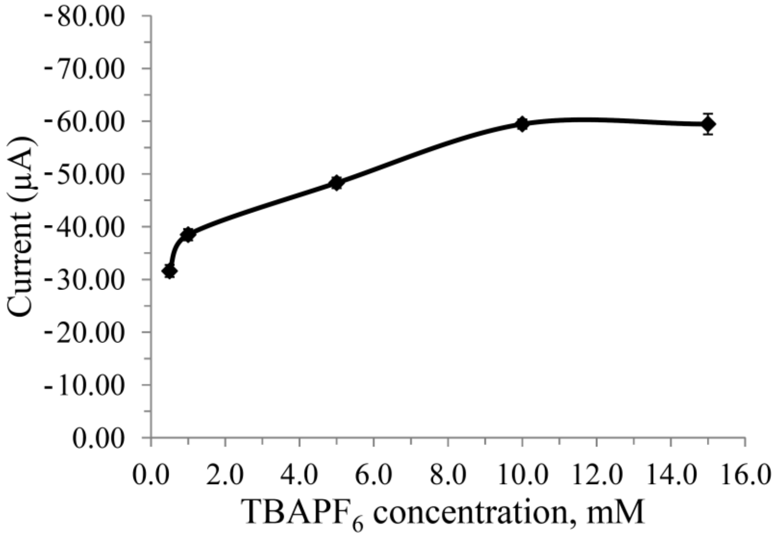


Fig. 3-2 Peak currents from BDD electrode at concentration of 30.0 mg/l Cd^{2+} in various concentrations of TBAPF$_6$ 0.5, 1.0, 5.0, 10.0 and 15.0 mM (pH 2.0, as an electrolyte for film formation) in acetate buffer solutions pH 6.0 with scan rate of 100 mV/s

3.1.4 Effect of pH for film formation

Since the electrografting on electrode surfaces depends mainly on acidity, pH is one of the effective parameters strongly influencing the peak current due to the fact that most active radical species might be formed at low pH. The pH range of 1.0 to 8.0 was investigated using cyclic voltammetry in 10.0 mM TBAPF$_6$ as an electrolyte. As shown in Figure 3-3 the cyclic voltammograms at pH 1.0 and 2.0 present almost identical behavior, namely a sharp reduction wave almost at the same position with a peak at about -1.08 V. The current drops sharply after the peak in the case of pH 1.0 and 2.0 because the film is substantially less conductive when it is in fully reduced form. At pH more than 2.0 the reduction peak is broad and moves to considerably more negative potential, which is believed to be due to the resistive nature of the film at these pH's. It should also be noted here that the peak potential and the shape of this wave also vary significantly with the thickness and preparation methods of different diazonium films (Nicholas *et al.,* 2015). The best explanation here is that lower value of R_{CT} of the diazonium film is observed at lower pH. The charge-transfer resistances measured for each pH reported by Baranton and Belanger for the electrochemical reduction of several types of diazonium cations on carbon surface revealed that the decrease in pH is accompanied by a significant decrease in R_{CT} (Baranton and Belanger, 2005). The pH effect may be caused by higher concentrations of smaller, more mobile counter ions (H$^+$), facilitating charge transfer via hopping through the polymer. With the increase of pH more than 2.0, the broad reduction peak continuously increases due to greater extent of charge-transfer resistance at the electrode surface. Due to the fact that high acidity has a greater tendency to cause possible interferent reactions, pH 2.0 was selected as an optimum condition in order to obtain maximum sensitivity in quantitative analytical measurements.

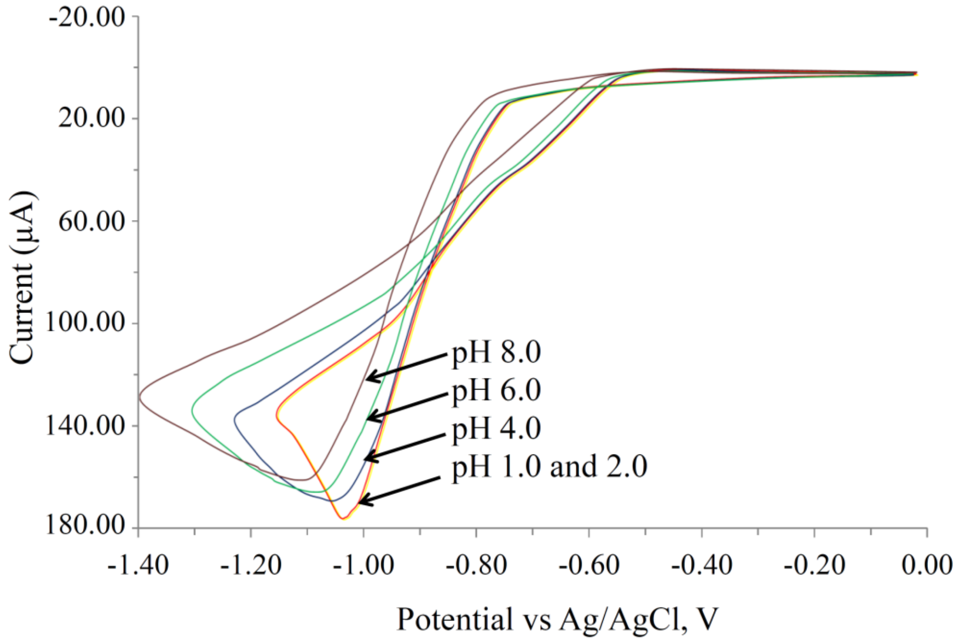


Fig. 3-3 Cyclic voltammograms of electrografting of BDD electrodes at different solution pH values pH 1.0, 2.0, 4.0, 6.0 and 8.0 with 0.5 mM 4-aminomethyl benzoic acid as precursors, 10.0 mM TBABF$_6$ as an electrolyte with scan rate 100 mV/s

3.1.5 Electrografting BDD electrode with 4-aminomethyl benzoic acid

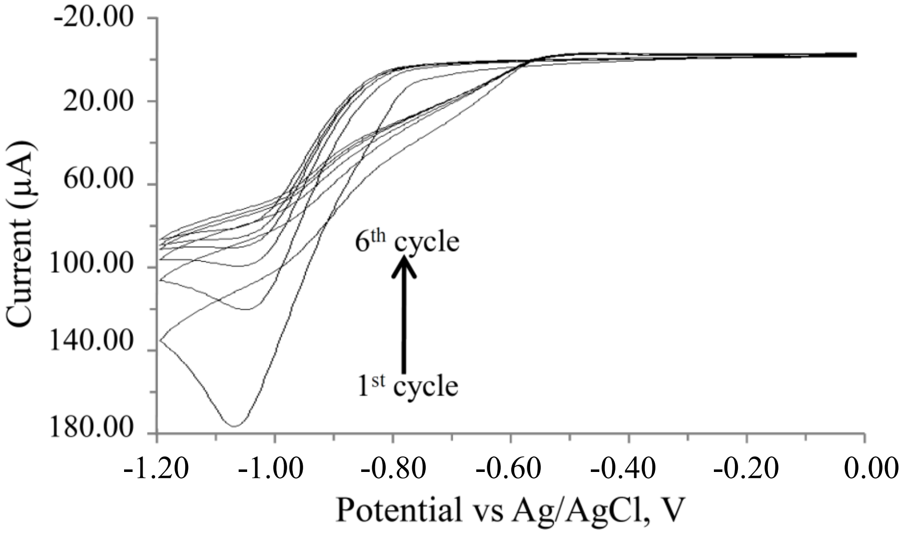


Fig. 3-4 Electrografting of BDD electrodes with 0.5 mM 4-aminomethyl benzoic acid with 10.0 mM $TBABF_6$ as an electrolyte. The 1st, 2nd, 3rd, 4th, 5th and 6th potential CV cycles for scan rate 100 mV/s

The reduction of diazonium salts is carried out in the narrow potential range between +0.20 and -1.20 V as shown in Fig. 3-3. The broad reduction peak present in the first cycle is presumably attributed to the reduction ca. -1.08 V of the corresponding diazonium species to form an aryl radical which reacts with the electrode surface and results in dimensioning of the peak. It can therefore be assumed that the same phenomenon occurred in the current study, namely; the covering of BDD electrodes by corresponding aryl layers.

3.1.6 Evolution of the wettability

For the characterization of the wettability of the electrolyte on the BDD modified electrode, the droplets of distilled water after grafting with 4-aminomethyl benzoic acid were found to induce the increase of the contact angle from 22° to 68° (Fig. 3-4), indicating that the hydrophobicity is much more greater with the presence of the aromatic ring.

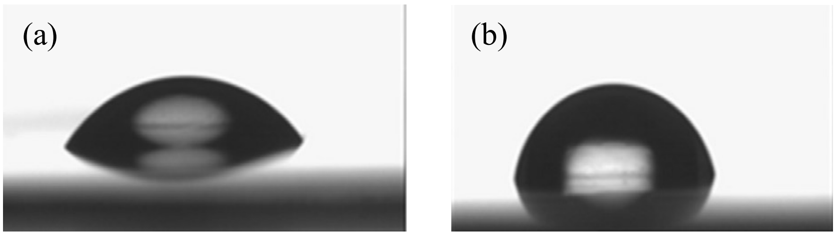


Fig. 3-5 Images of distilled water droplets on carbon thin film electrode surface (a) before and (b) after functionalization with thiophenol groups in 5.0 mM $NaNO_2$ (5 cycles at a scan rate of 100 mV/s) (Seck, *et al.*, 2015)

3.1.7 Cyclic voltammogram of Cd^{2+}

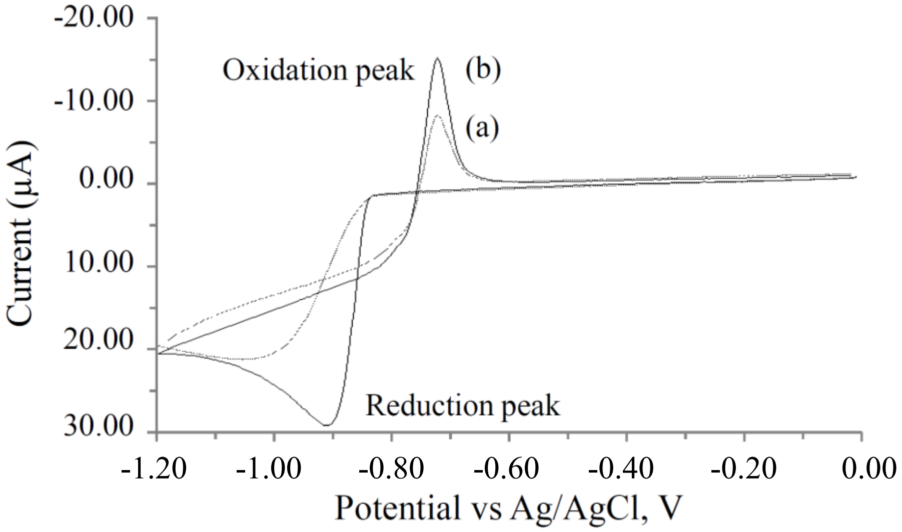


Fig. 3-6 Cyclic voltammogram of 30.0 mg/l Cd^{2+} at (a, dash line) bare BDD electrode and (b, solid line) the modified electrode in pH 6.0 acetate buffer solutions with scan rate of 100 mV/s

The overlay of CV voltammograms for 30.0 mg/l Cd^{2+} in the absence (curve a) and presence (curve b) of electrografting BDD electrode is shown in Fig. 3-5. The deposition peak was observed at -0.92 V vs Ag/AgCl corresponding to preconcentration of Cd^{2+} onto a BDD electrode surface at negative potentials. On the reverse scan, the single well defined stripping peak appeared at potential around -0.72 V vs. Ag/AgCl with electrografting BDD electrode surface. The results presented above confirm that the distribution and configuration adopted by diazonium salts after immobilization on the electrode surface play an important role in the voltammetric behavior of redox species in solution. As can be seen for modified electrode (b, solid line), the well defined redox couple ascribed to 30.0 mg/l Cd^{2+} with grater current was observed, confirming that the modified electrode was better electrochemical performance.

3.1.8 Comparison of Cd^{2+} stripping voltammogram between differential pulse and square wave modes

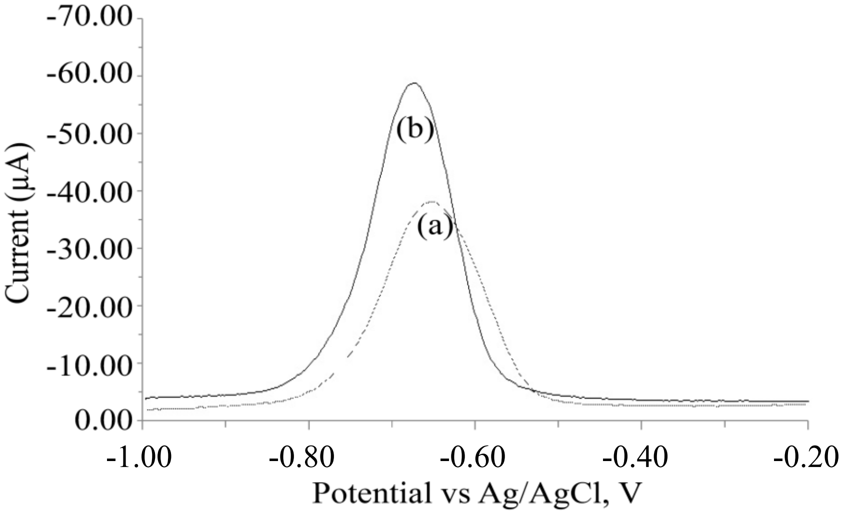


Fig. 3-7 Stripping voltammogram of Cd^{2+} in differential pulse mode (a, dash line) and square wave mode (b, solid line) of 30.0 mg/l Cd^{2+}; deposition time and potential: 2 min, 1.00 V, frequency 10 Hz, amplitude of 4 mV and potential step of 25 mV

At first, a comparison of Cd^{2+} stripping voltammogram between differential pulse (DPASV) and square wave (SWASV) modes was conducted. The stripping peak for 30.0 mg/l Cd^{2+} in differential pulse mode at BDD electrode modified with 0.5 mM 4-aminomethyl benzoic acid occurs at -0.69 V. It displays 3.92 μA of current peak. For the square wave mode, the current of the stripping peak for 30.0 mg/l Cd^{2+} at -0.72 V is 6.10 μA. As shown in Fig. 3-6, the current from SWASV is higher than that of DPASV. The stripping methods (SWASV and DPASV) are more precise than non-stripping. They allow having a lower detection limit, as the samples are concentrated and therefore smaller concentrations can be analyzed. The most precise method is DPASV and a good compromise between precision and speed was found in the SWASV method. Unfortunately, in this study DPASV did not appear to be precise and therefore several calibration points had to be omitted in order to have acceptable results, as these ignored values seemed to be spurious and low sensitivity. Besides, we had to repeat several times the measures for the tap water sample because the curves were not superimposable. As the manipulations were done exactly in the same way in a row, problems should come from the nature of the system or equipment itself. Consequently, the square wave mode was chosen for all experiments.

3.1.9 The electrochemical response of Cd^{2+} stripping on bare and benzoic acid-modified BDD electrode

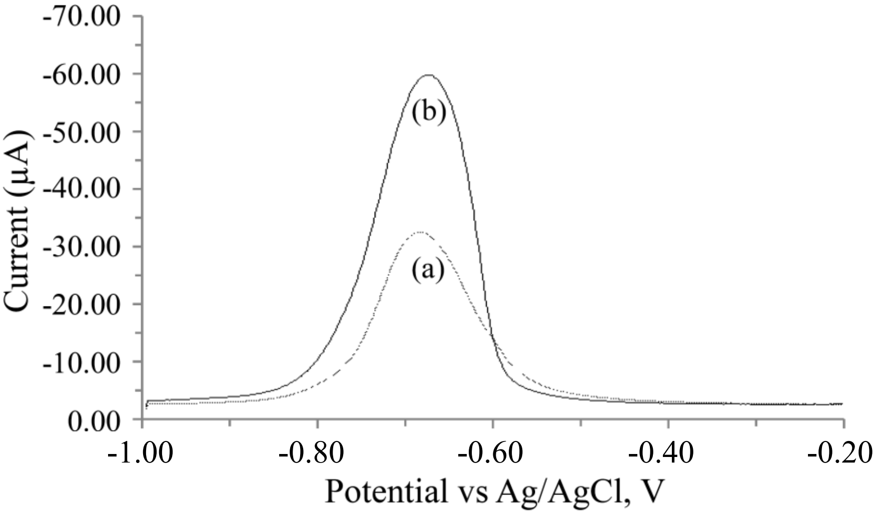


Fig. 3-8 SWASV of Cd^{2+} at (a, dash line) bare BDD electrode and (b, solid line) the modified electrode. Experimental conditions; deposition/measurement solution: pH 6.0 acetate buffer solutions containing 30.0 mg/l Cd^{2+}; deposition time and potential: 2 min, 1.00 V, frequency 10 Hz, amplitude of 4 mV and potential step of 25 mV

Fig. 3-7 shows square wave anodic stripping voltammograms (SWASV) of Cd^{2+} at bare and benzoic acid-modified BDD electrode, both reflecting well-defined peak at -0.72 V. The anodic peak current of Cd^{2+} at the benzoic acid-modified BDD electrode 58.5 µA was about two times that at the bare BDD electrode (32.0 µA). The increases in anodic peak current are attributed to the electrostatic interaction between the negatively charged electrografting BDD electrode and the positively charged metal ions that facilitates the preconcentration of Cd^{2+} which are beneficial for Cd^{2+} determination.

3.1.10 Type of electrolyte solution

Electrolyte solutions are required in controlled potential experiments to decrease the resistance of solution, to eliminate electromigration effects and to maintain a constant ionic strength. An electrolyte solution is made by adding an ionic salt to an appropriate solvent. Cd^{2+} has different electrochemical behaviors in different electrolytes. In the studies, various electrolytes with the concentration of 0.1 M were evaluated for their suitabilities for the Cd^{2+} determination at the electrode surface with various types of ionic salt including KNO_3, $NaNO_3$, KCl, NaCl, CH_3COONH_4, CH_3COONa and acetate buffer solutions. Among them, acetate buffer solutions was found to provide the best current and peak shape and therefore was chosen for further studies. The effect of electrolyte on the peak currents of Cd^{2+} in SWASV is shown in Table 3-2 and as a bar graph in Fig. 3-9

Table 3-2 Electrochemical response of cadmium in different types of supporting electrolytes

Type of electrolyte	Current (µA)			Average	SD	%RSD
	I	II	III			
KNO_3	53.212	51.245	55.225	53.227	1.990	3.739
$NaNO_3$	48.153	46.225	43.123	45.834	2.538	5.537
KCl	33.312	32.145	36.125	33.861	2.046	6.042
NaCl	35.214	33.156	34.232	34.201	1.029	3.010
CH_3COONH_4	60.242	65.561	63.193	62.999	2.665	4.230
CH_3COONa	46.538	42.561	43.156	44.085	2.145	4.866
Acetate buffer	69.242	70.561	66.193	68.665	2.240	3.263

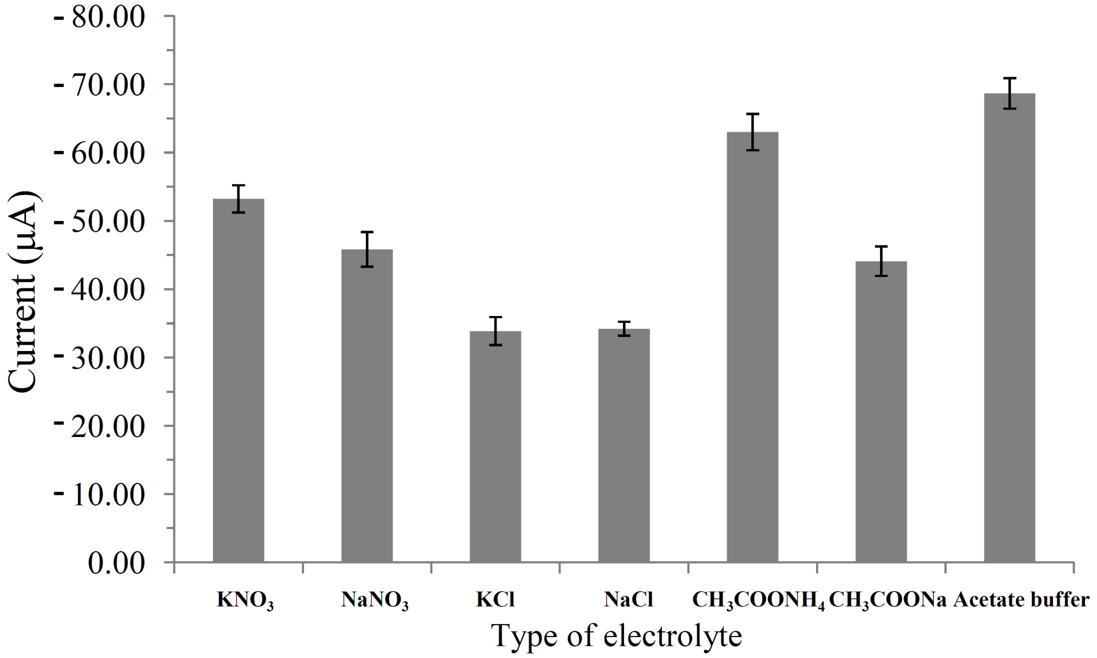


Fig. 3-9 Effect of supporting electrolyte on the SWASV peak currents. Experimental conditions; deposition/measurement solution: pH 6.0 solutions containing 30.0 mg/l Cd^{2+}; deposition time and potential: 2 min, 1.00 V, frequency 10 Hz, amplitude of 4 mV and potential step of 25 mV

3.1.11 Effect of pH on Cd^{2+} determination

The effect of pH 2.0 to 7.0 on the peak current of Cd^{2+} in SWASV is shown in Table 3-3 and Fig. 3-10. The obtained results indicated the rapid enhancement of the peak current of Cd^{2+} with ascending of pH to the maximum approximately at pH 6.0 and then started to decrease substantially. This might be due to the fact that when the measurement solution has a higher pH value, the metal ion easily hydrolyzes (March *et al.*, 2015). With lower pH value, hydrogen ion was reduced more easily (Lima *et al.*, 2011). At lower pH, proton competes with cadmium ion at the electrode surface which in turn interferes Cd^{2+} deposition. pH 6.0 was therefore chosen for further study.

Table 3-3 Electrochemical response of cadmium in various pH values

pH of acetate buffer solutions	Current (µA)			Average	SD	%RSD
	I	II	III			
2.0	30.739	30.201	29.932	30.291	0.411	1.357
3.0	47.253	45.265	42.023	44.847	2.640	5.887
4.0	53.412	52.145	57.325	54.294	2.700	4.973
5.0	65.204	69.256	64.132	66.197	2.703	4.083
6.0	69.242	70.561	65.193	68.332	2.797	4.094
7.0	67.568	62.568	63.256	64.464	2.710	4.204

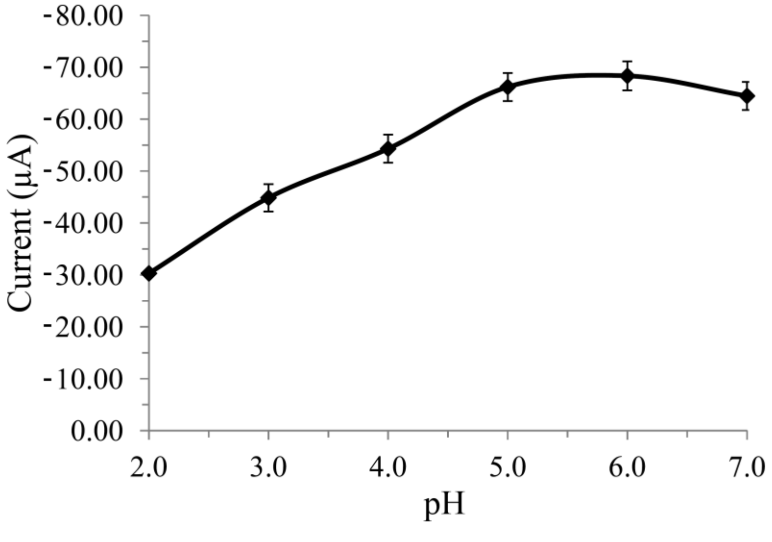


Fig. 3-10 Peak currents of 30.0 mg/l Cd^{2+} in acetate buffer solutions at different pH

3.1.12 Deposition potential

The effect of deposition potentials on the stripping peak currents of 30.0 mg/l Cd^{2+} was studied in the potential range from -0.80 to -1.30 V with the results shown in Table 3-4 and Fig. 3-11. The negative shifts of deposition potential can obviously improve the extent of Cd^{2+} reduction on the surface electrode and increase the peak current. However, the peak current does not change significantly with the deposition potentials more negative than -1.10 V. Moreover, the background current became higher when the potentials were more positive than -1.10 V. The results reflect the optimum deposition potential of -1.10 V at which further experiment was then performed under this condition to achieve high sensitivity and better response.

Table 3-4 Electrochemical response of cadmium in various deposition potentials

Deposition potential (V)	**Current (μA)**			**Average**	**SD**	**%RSD**
	I	**II**	**III**			
-0.80	30.739	30.201	28.356	29.765	1.250	4.199
-0.90	47.253	45.265	42.023	44.847	2.640	5.887
-1.00	65.258	65.265	59.568	63.364	3.287	5.188
-1.10	69.242	70.561	67.193	68.999	1.697	2.460
-1.20	71.235	68.265	66.358	68.619	2.458	3.582
-1.30	67.568	62.568	63.256	64.464	2.710	4.204

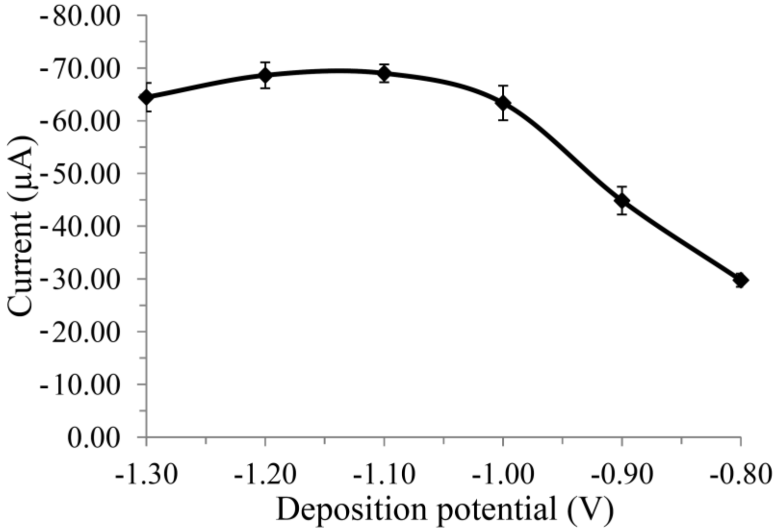


Fig. 3-11 Effect of deposition potentials on the SWASV peak currents. Conditions: 30.0 mg/l Cd^{2+} in 50.0 ml acetate buffer solutions pH 6.0

3.1.13 Deposition time

For the effect of the deposition time screened within a range of 1 to 8 min on the stripping currents of 30.0 mg/l Cd^{2+}, longer deposition times should increase the peak current because more Cd^{2+} could be deposited Table 3-5 and Fig. 3-12. When the deposition time increases, the stripping peak currents increase greatly and become almost constant unit beyond 6 min which reflects surface saturation. Even though at 7 min deposition time seems to be reasonable to obtain additional sensitivity, to make the proposed technique much more competitive, the shortest time as possible is selected (Table 3-14). Those who can sacrifice their analysis time can select 7 min if they wish to obtain a little more sensitivity.

Table 3-5 Electrochemical response of cadmium in different deposition time

Deposition time (min)	**Current (μA)**			**Average**	**SD**	**%RSD**
	I	**II**	**III**			
1	46.947	45.625	42.235	44.936	2.430	5.409
2	47.002	50.132	51.465	49.533	2.291	4.625
3	54.433	51.931	56.478	54.281	2.277	4.195
4	57.253	61.245	58.657	59.052	2.025	3.429
5	64.889	65.485	62.568	64.314	1.541	2.396
6	65.789	67.568	69.654	67.670	1.935	2.859
7	70.145	66.568	68.241	68.318	1.790	2.620
8	70.235	66.254	68.321	68.270	1.991	2.916

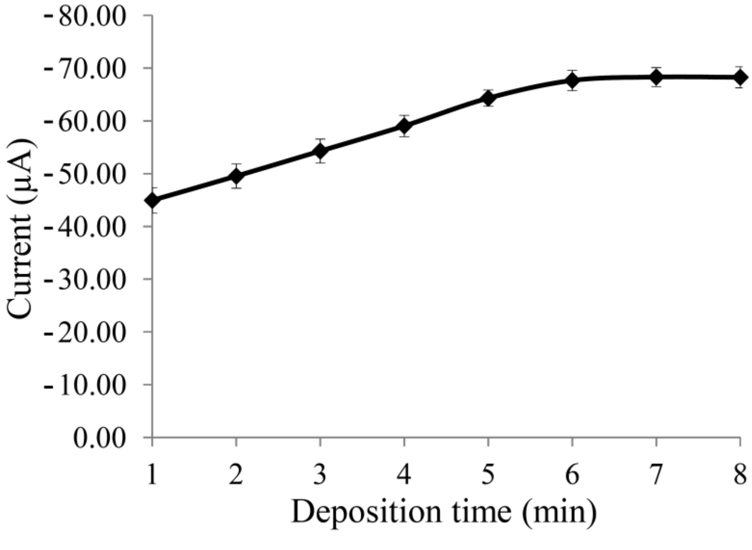


Fig. 3-12 Effect of deposition time on the SWASV peak currents. Conditions: 30.0 mg/l Cd^{2+} in 50.0 ml acetate buffer solutions pH 6.0

3.1.14 Scan rate

The scan rate was screened from 10 to 200 mV/s. As shown in Fig. 3-13, the peak height was small at lower scan rate and increased rapidly at higher scan rate with the best result of better current and greater stability of peak potential at a scan rate of 100 mV/s. At more than 200 mV/s, the signal peak becomes broader and shifts to much more positive stripping potentials. A scan rate of 100 mV/s was therefore selected for further experiments.

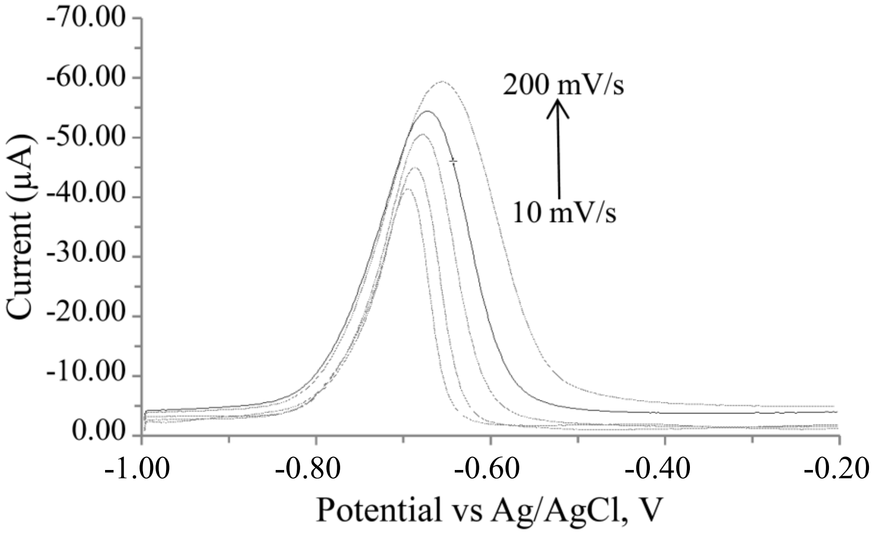


Fig. 3-13 Effect of scan rates 10, 20, 50, 100 and 200 mV/s on the stripping voltammograms. Conditions: 30.0 mg/l Cd^{2+} in 50.0 ml acetate buffer solutions pH 6.0, 0.5 mM 4-aminomethyl benzoic acid; Deposition potential, -1.10 V vs Ag/AgCl; Deposition time, 6 min; pulse amplitude, 4 mV

3.1.15 Linear range

The linear range was determined the ultra pure water containing 50.0 ml at different concentrations of cadmium in acetate buffer pH 6.0, 0.5 mM 4-aminomethyl benzoic acid with the deposition potential of -1.10 V and 6 min deposition time (optimum conditions). The linear range is determined by plotting the current versus the concentration of standard solution.

The calibration curves of cadmium at various concentrations are shown in Table 3-6 and Fig. 3-14 (a and b). It was found that the linear dynamic range was obtained in the concentration range 2.0 to 50.0 μg/l Cd^{2+} with the correlation coefficient of 0.9989. At low cadmium concentration relative standard deviation (%RSD) was found to be increased, due to the fact that at low concentration of cadmium ions, the effect of other ions became important for efficiency of cadmium deposition on the electrode (Seck, *et al.*, 2015).

Table 3-6 The current of cadmium stripping response at different concentrations

Cd^{2+} conc. (µg/l)	**Current (µA)**			**Average**	**SD**	**%RSD**
	I	**II**	**III**			
0.0	0.000	0.000	0.000	0.000	0.000	0.000
2.0	0.454	0.373	0.512	0.446	0.070	15.642
5.0	0.653	0.654	0.636	0.648	0.010	1.562
10.0	1.125	1.097	1.175	1.132	0.040	3.490
20.0	1.756	1.715	1.852	1.774	0.070	3.963
50.0	3.875	3.876	3.807	3.853	0.040	1.027

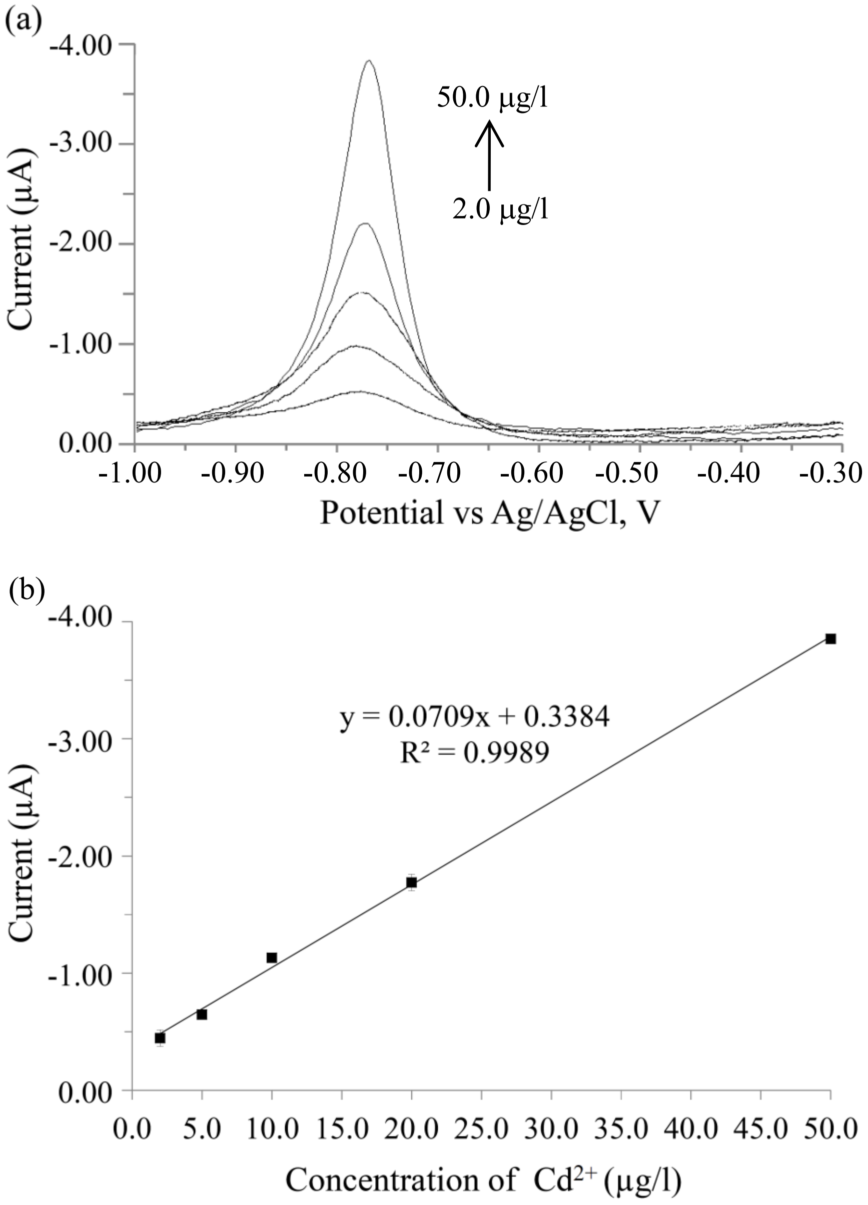


Fig. 3-14 (a) Square wave anodic stripping voltammograms of water samples after spiking with 2.0, 5.0, 10.0, 20.0 and 50.0 µg/l of Cd^{2+} standard solution and (b) corresponding calibration curve. Conditions; accumulation potential, -1.10 V; accumulation time, 6 min; acetate buffer solutions pH 6.0, 0.5 mM 4-aminomethyl benzoic acid; scan rate, 100 mV/s

Fig. 3-14(a) shows square wave voltammetry measurements of water with different concentrations of Cd^{2+} with the optimum conditions to obtain the calibration curve and detection limit. The calibration curve shows the linearity within the range of 2.0 to 50.0 µg/l with a correlation coefficient of 0.9989 with the linear regression equation of Cd^{2+} of $i_p = 4.458x - 11.73$ (i_p: µA, x: µg/l) as shown in Fig. 3-14(b).

3.1.16 Limits of detection and quantitation

The limit of detection of Cd^{2+} was calculated by LOD=3N/m (Lima *et al*., 2011) where N is the standard deviation of replicate blank responses (n=10) and m is the slope of the calibration curve to obtain its value of 0.2 µg/l. The limits of quantification, LOQ, defined as 10N/m, were found to be 0.6 µg/l. The relative standard deviation was 0.989% (n=10) for repetitive determinations of 2.0 µg/l of Cd^{2+}. The results demonstrated that the proposed technique was reproducible and reliable for the detection of Cd^{2+} at trace level and can be used for real samples analysis. In this scenario LOD is the limit to express the capability of the technique in detection the analyte in comparison with other available techniques. In contrast, LOQ shows the concentration of an analyte that can be reliably measured by the proposed method. The current of blank was carried out for evaluating detection limit of Cd^{2+} is shown in Table 3-7.

Table 3-7 Current from 10 replicates of 2.0 µg/l cadmium (n=10)

Replicate	**Current (µA)**
1	0.454
2	0.447
3	0.457
4	0.448
5	0.458
6	0.446
7	0.447
8	0.454
9	0.448
10	0.450
Average current; µA	0.451
SD (σ)	0.004
%RSD	0.989
Calibration Slope (m)	0.071
LOD (3σ/m); µg/l	0.2
LOQ (10σ/m); µg/l	0.6

3.1.17 Accuracy and precision (Certified reference materials and real sample analysis)

The accuracy of proposed method was tested by determining the Cd^{2+} content of certified reference materials, natural water SRM 1640 from the National Institute of Standards and Technology (NIST), USA. Stripping peaks for Cd^{2+} in the NIST sample occur at potentials of at -0.72 V vs. AgCl. The certified values and the analytical results are presented in Table 3-8.

Table 3-8 The comparison of the experimental and certified values for cadmium determination in certified reference materials (n=5) by the method under investigation

Certified reference materials	**Certified value (µg/l)**	**Found[a] (µg/l)**	**Error (%)**	**Recovery (%)**
Natural Water SRM 1640	22.82 ± 0.96	22.72 ± 0.90 (% RSD = 0.326)	0.44	99.56

[a] Mean ± Standard deviation (n=5)

From the results in Table 3-9, the determined concentrations of cadmium in SRM 1640 from the proposed method were in good agreement with the certified values. Satisfactory recovery of 99.56% (n=5) was obtained, proving that the proposed method is suitable for analyzing tap water samples.

In addition, the precision of the proposed method was also evaluated as %RSD of ten replication measurements. The %RSD values obtained from this method were 0.989, 3.489 and 1.027% for cadmium concentration of 2.0, 10.0 and 50.0 µg/l, respectively. The results are shown in Table 3-9.

Table 3-9 The currents for evaluating the precision

Replicate	Current (µA)		
	2.0 µg/l	10.0 µg/l	50.0 µg/l
1	0.454	1.125	3.875
2	0.447	1.190	3.845
3	0.457	1.145	3.916
4	0.448	1.085	3.815
5	0.458	1.145	3.880
6	0.446	1.127	3.925
7	0.447	1.186	3.855
8	0.454	1.169	3.912
9	0.448	1.080	3.925
10	0.450	1.097	3.930
Average	0.451	1.135	3.888
SD	0.004	0.040	0.040
%RSD	0.989	3.489	1.027

3.2 Effect of other ions

Table 3-10 Influence of some potential interfering ions on the voltammetric response of 20.0 µg/l Cd^{2+} under the optimum conditions

Foreign ions	Concentration (µg/l)	Signal change (%)
Ca^{2+}	2600	-5.56
Mg^{2+}	1000	-5.35
Zn^{2+}	1000	-5.89
Mn^{2+}	400	-5.36
Fe^{2+}	200	-5.56
Cu^{2+}	200	-5.98
Al^{3+}	80	-5.89
Co^{2+}	40	-5.78
Pb^{2+}	40	-5.96
Ni^{2+}	20	-5.75

In order to study the selectivity of proposed method, some metal ions were tested to evaluate possible interference with the detection of Cd^{2+}. The ions were considered to interfere seriously when they gave a current signal change to the extent of more than 5%. The experimental results for typical ions present in tap water samples are given in Table 3-10. The peak current of Cd^{2+} was not significantly affected by substantial excess of Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+} and Al^{3+}. However, Co^{2+}, Pb^{2+} and Ni^{2+} have significant influence on the stripping response of Cd^{2+} because they do not only compete with Cd^{2+} for the substitution on the surface electrode but also can form intermetallic compounds with Cd^{2+} to prevent its accumulation on the electrode (Yi *et al.*, 2012). However, the influence of weakly interfering ions can be manipulated by standard addition method. Thus, the results demonstrated sufficient selectivity of the proposed method.

3.3 The comparison of the calibration and standard addition method for determination of Cd^{2+} in tap water samples

The experiment was performed to compare the standard methods of calibration and standard addition for determination of Cd^{2+} in tap water samples after 6 min deposition. The results are shown in Table 3-11 and Fig. 3-15.

Table 3-11 The comparison of stripping peak current between calibration and standard addition method for Cd^{2+} determination in tap water samples

Cd^{2+} conc. (µg/l)	**Current (µA)**							
	Calibration				**Standard addition**			
	Rep.1	**Rep.2**	**Rep.3**	**Average**	**Rep.1**	**Rep.2**	**Rep.3**	**Average**
0.0	BDL	BDL	BDL	-	BDL	BDL	BDL	-
2.0	0.360	0.315	0.326	0.334	0.454	0.373	0.512	0.446
5.0	0.581	0.579	0.565	0.575	0.653	0.654	0.636	0.648
10.0	1.050	1.030	1.095	1.058	1.125	1.097	1.175	1.132
20.0	1.681	1.635	1.839	1.718	1.756	1.715	1.852	1.774
50.0	3.785	3.805	3.750	3.780	3.875	3.876	3.807	3.853

BDL: below the detection limit. [compared with the limit of detection (LOD)]

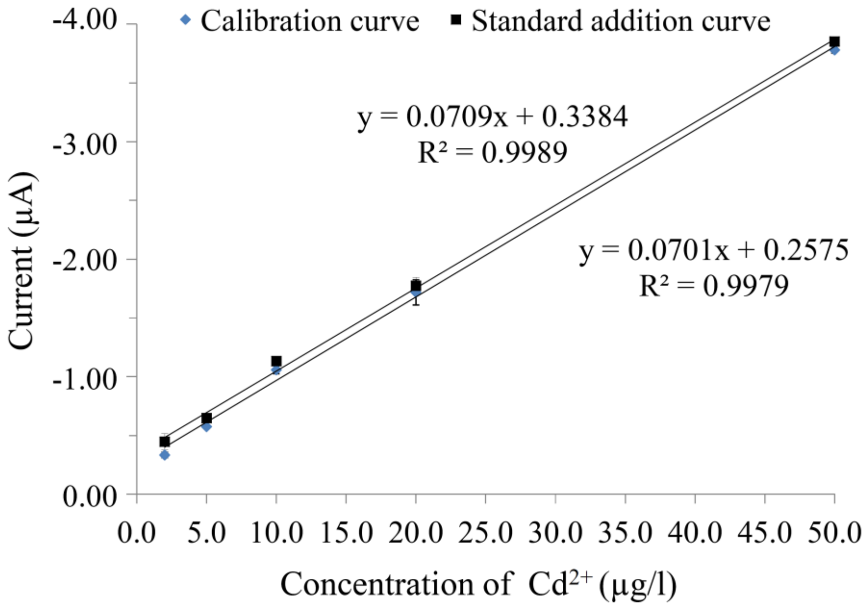


Fig. 3-15 The comparison of calibration curve and standard addition curve for Cd^{2+} determination in tap water samples

The slopes of calibration curve and standard addition for Cd^{2+} in Fig. 3-15 were compared using two-way ANOVA as shown in Appendix B and it was found that the slopes of both methods were not significant different at the 95% confidence level ($P>0.05$), suggesting that the matrix does not affect the analysis. Despite the fact that the slopes of calibration curve and standard addition method are not significantly different, certain ions (Table 3-10) obviously affect the peak current of the analyte which might result in lower sensitivity. Therefore, the standard addition was considered to be more suitable method for Cd^{2+} determination in tap water samples.

3.4 The study of percent recovery of Cd^{2+} in tap water samples

The proposed technique was applied to the analysis of Cd^{2+} in tap water sample collected from 11 sites in Hatyai city as shown in Appendix A, 500 ml for each. The two samples used were the water from different places in Hatyai city including tap water from 1st and 2nd regions. The standard addition method was performed by spiking a tap water sample with different concentrations of Cd^{2+} with the results in Table 3-12. The recoveries values were ranged between 101.00 and 111.20%. The results obtained by the proposed method were compared with those obtained by the inductively coupled plasma optical emission spectrometry (ICP-OES). The concentrations of Cd^{2+} in sample were deduced from the linear range of the regression equation. All of the samples were measured without any further treatment. The results are listed in Table 3-

12. The excellent average recoveries of two water samples suggest that the studied method developed in this work has practical significance and is able to satisfactorily determine of Cd^{2+} in tap water samples. Statistical analysis of the results by two-way ANOVA (F-test) (Appendix C and D) revealed that factors calculated did not exceed the theoretical value (95% confidence limits for three degrees of freedom) or there is no significant difference between the proposed methods and the standard method. Compared with other ASV techniques using modified electrodes, the proposed method exhibits better figures of merit as shown in Table 3-13, revealing that this technique is among those with the highest sensitivity.

Table 3-12 Determination of Cd^{2+} in tap water samples (n=4) spiked with 5.0, 10.0 and 20.0 µg/l of Cd^{2+}

Sample	Spiked (µg/l)	Present method[b] (µg/l)	Recovery (%)	ICP-OES method (µg/l)	Difference (%)
Tap water 1[a]	0.0	ND[c]	-	ND	-
	5.0	5.56±0.30	111.20	5.25±0.34	5.6
	10.0	10.65±0.27	106.50	10.35±0.29	2.8
	20.0	20.55±0.26	102.75	20.78±0.29	1.1
Tap water 2[a]	0.0	ND	-	ND	-
	5.0	5.28±0.21	105.60	5.58±0.38	5.7
	10.0	10.35±0.40	103.50	10.14±0.37	2.0
	20.0	20.20±0.39	101.00	20.25±0.42	0.2

[a] Water sample 1st and 2nd region was selected for standard addition test
[b] Mean ± Standard deviation (n=4)
[c] Not detected

Table 3-13 Comparison of the proposed method for determination of Cd^{2+} in water samples with other anodic stripping voltammetric methods

Modified electrode	Method	Deposition time (s)	Linear range (µg/l)	Detection limit (µg/l)	Reference
(Bi/MCNTs-CPE)	SWASV	200	1 to 60	0.3	(Luo *et al.*, 2013)
Sb nano/BDD	LSASV	120	50 to 500	38.10	(Toghill *et al.*, 2009)
Bi/CNT/GCE	SWASV	300	2 to 100	0.70	(Wang *et al.*, 2008)
0.2 M 4-aminomethyl benzoic acid/BDD	SWASV	360	2 to 50	0.2	This work

3.5 Application of the studied method to tap water samples

3.5.1 Determination of Cd^{2+} in tap water samples using the studied method

The studied method was applied to the determination of Cd^{2+} in tap water sample from eleven regions at Hatyai city, in the South of Thailand; in August 2015.

The real samples examined here had the pH values summarized in Table 3-14. The displayed natural pH values of tap water samples are higher than 6.0 thus these samples were analyzed after acidification to pH 1.3 with HNO_3.

Table 3-14 pH values of the tap water sample under investigation

Sample	pH
1st regions	6.2
2nd regions	6.1
3rd regions	6.2
4th regions	6.3
5th regions	6.3
6th regions	6.2
7th regions	5.9
8th regions	6.2
9th regions	6.2
10th regions	6.4
11th regions	6.4

A typical stripping voltammogram obtained in tap water sample is shown in Fig. 3-14. The voltammogram shows the oxidation process of Cd^{2+}, the stripping peaks of cadmium are well shaped and are characterized by stripping peak potential values of -0.72 V.

Table 3-15 The results of standard addition calibration curve of Cd^{2+} in tap water sample from the 1st region by the studied method under investigation

Cd^{2+} conc. (µg/l)	**Current (µA)**				**SD**	**%RSD**
	Rep.1	**Rep.2**	**Rep.3**	**Average**		
Sample 1st	(BDL)	(BDL)	(BDL)	(BDL)	-	-
Sample 1st+2.0 µg/l	0.454	0.373	0.512	0.446	0.070	15.642 [a]
Sample 1st+5.0 µg/l	0.653	0.654	0.636	0.648	0.010	1.562
Sample 1st+10.0 µg/l	1.125	1.097	1.175	1.132	0.040	3.490
Sample 1st+20.0 µg/l	1.756	1.715	1.852	1.774	0.070	3.963
Sample 1st+50.0 µg/l	3.875	3.876	3.807	3.853	0.040	1.027

BDL: below the detection limit. [compared with the limit of detection (LOD)]

[a] At very low cadmium concentration e.g. 2.0 µg/l influence of some potential interfering ions begin affect with peak current

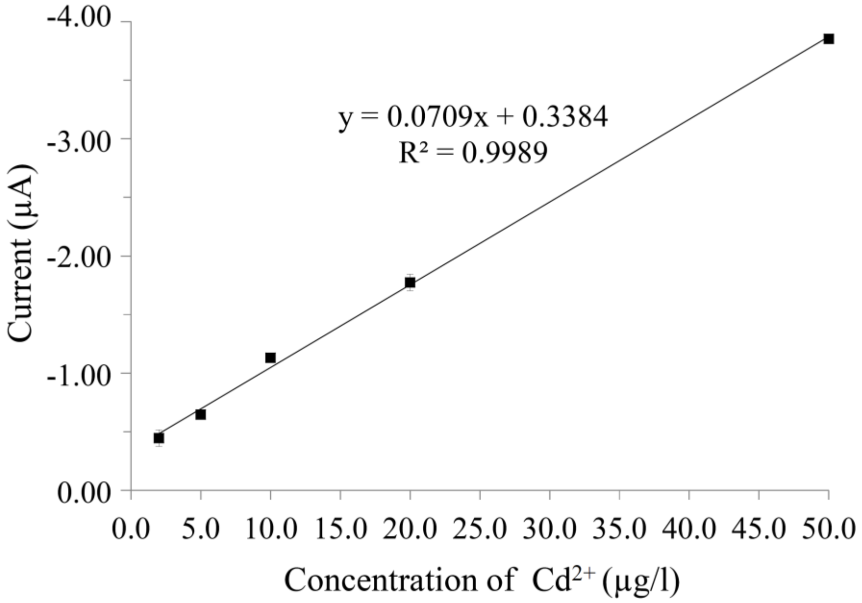


Fig. 3-16 Standard addition calibration curve of Cd^{2+} in tap water sample from the 1st region, Cd^{2+} ranging concentrations from 2.0 to 50.0 µg/l

The results of Cd^{2+} determination in tap water samples from eleven regions at Hatyai city are shown in Table 3-16. The results suggested that the concentrations of Cd^{2+} in tap water samples were at the trace levels.

Table 3-16 The concentration of Cd^{2+} in tap water sample from eleven regions at Hatyai city in the South of Thailand by the studied method under investigation

Regions	**Cd^{2+} concentration (μg/l)**
1	BDL
2	BDL
3	BDL
4	BDL
5	BDL
6	BDL
7	BDL
8	BDL
9	BDL
10	BDL
11	BDL

BDL: below the detection limit. [compared with the limit of detection (LOD)]
Limits of detection obtained by ICP-OES for cadmium determination is 0.1 μg/l
(data from Central Equipment Division, Faculty of Science, Prince of Songkla University)

The concentrations of Cd^{2+} in various tap water samples were found to be below the detection limits which are within the range of the standard in water by World Health Organization, which reflected the maximum allowable contaminant cadmium levels in the drink water recommendation (WHO 2006) to be less than 3.0 μg/l. Therefore, tap water samples under the investigation are safe for public health in terms of cadmium concentration.

3.5.2 Comparison between the studied method and ICP-OES for Cd^{2+} determination in tap water samples

To further evaluate of a method, the results of the SWASV analysis of tap water sample were compared with those provided by ICP-OES. Due to low concentration of metal ions to be detected, an instrument equipped with an electrothermal atomizer was used. In order to achieve a satisfactory signal to noise ratio (S/N), tap water samples used in the SWASV analysis were prepared, using the sampling method as described in section 2.5.1. After the SWASV analysis, the same solutions were analysed by ICP-OES.

The results from determination of Cd^{2+} using the studied method (ASV) and ICP-OES are presented in Table 3-17. The means of Cd^{2+} concentration in tap water sample determined by using the studied method (ASV) and ICP-OES were compared.

From the statistical evaluation, it was found that the amount of Cd^{2+} by using the two methods was not detected in almost every sample. The results provided by the studied method (ASV) and ICP-OES were in a good agreement [The limit of detection (LOD) of ICP-OES is 0.1 µg/l, data from Central Equipment Division, Faculty of Science, Prince of Songkla University].

Table 3-17 The concentration of Cd^{2+} in tap water sample determined by the studied method under investigation and ICP-OES

Regions	**Pb Concentration (µg/l)**	
	ASV	**ICP-OES**
1	BDL	BDL
2	BDL	BDL
3	BDL	BDL
4	BDL	BDL
5	BDL	BDL
6	BDL	BDL
7	BDL	BDL
8	BDL	BDL
9	BDL	BDL
10	BDL	BDL
11	BDL	BDL
Mean	-	-
P-Value	-	

BDL: below the detection limit. [compared with the limit of detection (LOD)]
Limits of detection obtained by ICP-OES for cadmium determination is 0.1 µg/l
(data from Central Equipment Division, Faculty of Science, Prince of Songkla University)

CHAPTER 4

4. CONCLUSION

Cadmium is known as one of the most toxic elements among the heavy metals. Cadmium can be released to the environment through natural and human activities (WHO, 2010). Cadmium is a highly toxic metal to humans when the element accumulates in the body. People are exposed to them primarily through food, water and air. The World Health Organization has been established the maximum allowable of drinking water standard is 3.0 µg/l of cadmium metal contaminated levels in drinking water for the consumer safety on the announcement of the Guideline for Drink Water Quality (WHO 2006). The study of cadmium contamination in tap water is an intensive point and the analytical method becomes significant then the awareness amount of the cadmium concentration has been emphasized.

Direct determination of Cd^{2+} in tap water samples with electrochemical technique were obtained through the present study. It has been demonstrated that the BDD electrodes modified with 0.2 M 4-aminomethyl benzoic acid can be used for analysis of trace Cd^{2+} in tap water by SWASV with exhibited high sensitivity and accuracy. The optimized working conditions were described. The detection limits of 0.2 µg/l for Cd^{2+} were obtained. Therefore, the proposed electrode will offer potential applications for monitoring of tap water samples to reveal better sensitivity, simpler sample preparation, shorter analysis time and easier operational processing. The accuracy of the proposed method was verified by analyzing of the SRM 1640 natural water standard with the certified value of 22.82±0.96 µg/l yielded Cd^{2+} concentration of 22.72±0.90 µg/l (n=5). The results of Cd^{2+} in natural water samples analyzed by the developed method were in good agreement with those obtained by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). The concentration of Cd^{2+} in tap water samples were found to be lower than the drinking water contamination standard limited level 3.0 µg/l issued by the World Health Organization (WHO) and Provincial Waterworks Authority of Thailand. The new electrode has advantages of simplicity and speed, as well as good reproducibility and stability, the sensitivity and relatively high stability of the electrode will open a new way for the determination of the heavy metal ions.

For further study, onsite and multi-element determination in drinking water can be introduced to improve the valuable of obtaining conditions of the diazonium salts modified BDD electrode on the analytical performance characteristics for heavy metal detection by ASV.

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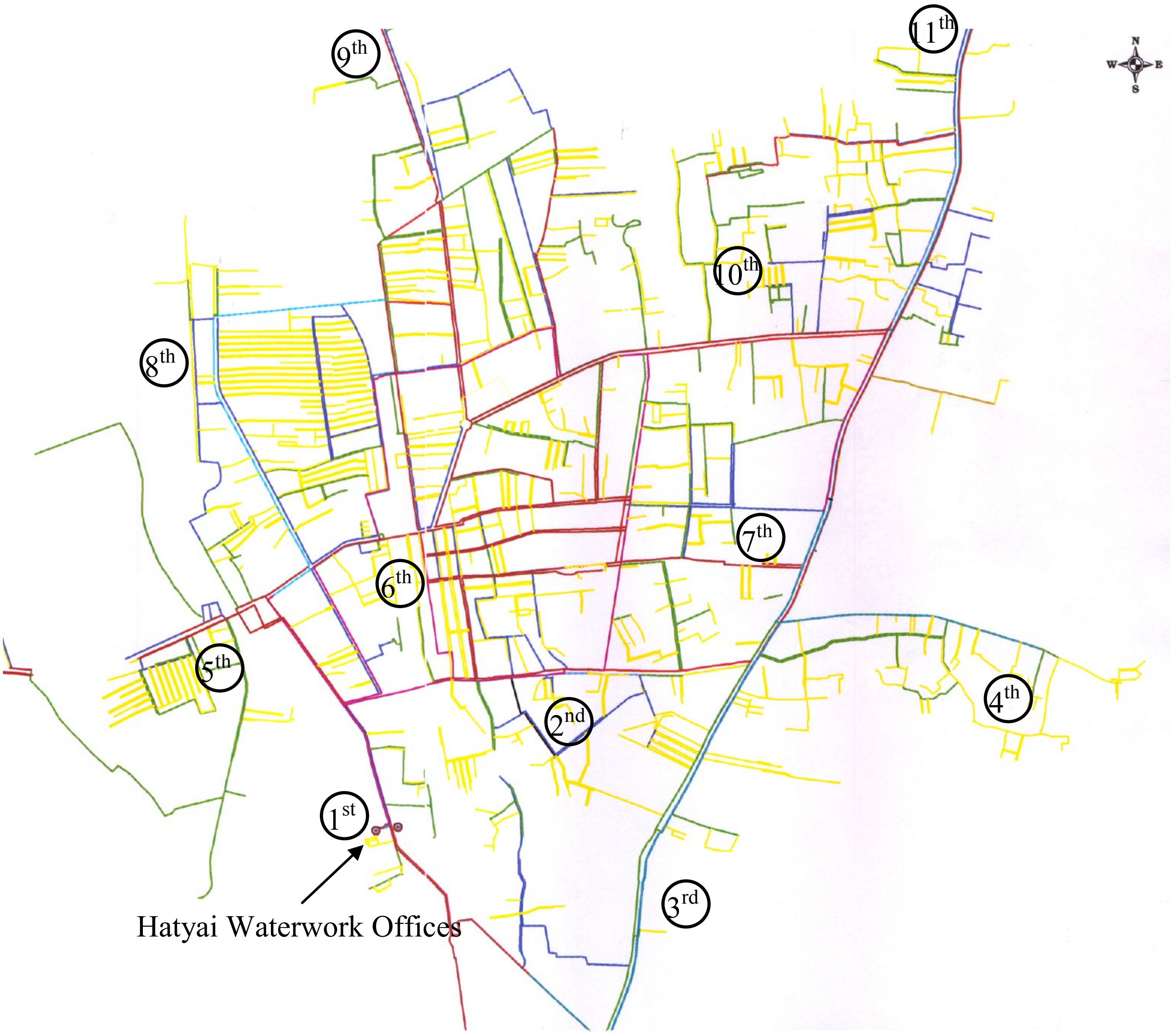
APPENDICES

Appendix A

Map shows the location to collect tap water samples around Hatyai city, in the South of Thailand, approximately 30 km. from Songkhla; in August 2015



Source; Hatyai Waterwork Offices, 2007

Appendix B

Statistical Analysis: The compared of slopes of standard addition and calibration curve for cadmium by using two-way ANOVA (F-test)

Anova: Two-Factor With Replication

SUMMARY	2.0 µg/l	5.0 µg/l	10.0 µg/l	20.0 µg/l	50.0 µg/l	Total
Calibration curve						
Count	3	3	3	3	3	15
Sum	1.0010	1.7250	3.1750	5.1550	11.3400	22.3960
Average	0.3337	0.5750	1.0583	1.7183	3.7800	1.4931
Variance	0.0006	0.0001	0.0011	0.0114	0.0008	1.6427
Standard addition						
Count	3	3	3	3	3	15
Sum	1.3390	1.9430	3.3970	5.3230	11.5580	23.5600
Average	0.4463	0.6477	1.1323	1.7743	3.8527	1.5707
Variance	0.0049	0.0001	0.0016	0.0049	0.0016	1.6213
Total						
Count	6	6	6	6	6	
Sum	2.3400	3.6680	6.5720	10.4780	22.8980	
Average	0.3900	0.6113	1.0953	1.7463	3.8163	
Variance	0.0060	0.0017	0.0027	0.0075	0.0025	

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Sample	0.0452	1	0.0452	16.7236	0.0006	4.3512
Columns	45.6395	4	11.4099	4224.9946	0.0000	2.8661
Interaction	0.0026	4	0.0007	0.2441	0.9099	2.8661
Within	0.0540	20	0.0027			
Total	45.7413	29				

Appendix C

Statistical Analysis: Statistical evaluations for cadmium analysis in tap water 1st sample by present method and ICP-OES by using two-way ANOVA (F-test)

Anova: Two-Factor With Replication

SUMMARY	0.0 µg/l	5.0 µg/l	10.0 µg/l	20.0 µg/l	Total
Present method					
Count	4	4	4	4	16
Sum	0.0000	22.2300	42.6000	82.2160	147.0460
Average	0.0000	5.5575	10.6500	20.5540	9.1904
Variance	0.0000	0.0905	0.0777	0.0673	61.0933
ICP-OES method					
Count	4	4	4	4	16
Sum	0.0000	21.0000	41.4120	83.1120	145.5240
Average	0.0000	5.2500	10.3530	20.7780	9.0953
Variance	0.0000	0.1131	0.0844	0.0845	62.8772
Total					
Count	8	8	8	8	
Sum	0.0000	43.2300	84.0120	165.3280	
Average	0.0000	5.4038	10.5015	20.6660	
Variance	0.0000	0.1143	0.0946	0.0794	

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Sample	0.0724	1	0.0724	1.1191	0.3006	4.2597
Columns	1857.6119	3	619.2040	9572.7471	0.0000	3.0088
Interaction	0.3935	3	0.1312	2.0278	0.1368	3.0088
Within	1.5524	24	0.0647			
Total	1859.6302	31				

Appendix D

Statistical Analysis: Statistical evaluations for cadmium analysis in tap water 2nd sample by present method and ICP-OES by using two-way ANOVA (F-test)

Anova: Two-Factor With Replication

SUMMARY	2.0 µg/l	5.0 µg/l	10.0 µg/l	20.0 µg/l	Total
Present method					
Count	4	4	4	4	16
Sum	0.0000	21.1300	41.4050	80.7910	143.3260
Average	0.0000	5.2825	10.3513	20.1978	8.9579
Variance	0.0000	0.0428	0.1569	0.1496	59.2774
ICP-OES method					
Count	4	4	4	4	16
Sum	0.0000	22.3110	40.5560	81.0170	143.8840
Average	0.0000	5.5778	10.1390	20.2543	8.9928
Variance	0.0000	0.1438	0.1368	0.1798	58.9366
Total					
Count	8	8	8	8	
Sum	0.0000	43.4410	81.9610	161.8080	
Average	0.0000	5.4301	10.2451	20.2260	
Variance	0.0000	0.1049	0.1387	0.1421	

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Sample	0.0097	1	0.0097	0.0961	0.7592	4.2597
Columns	1770.5199	3	590.1733	5831.3965	0.0000	3.0088
Interaction	0.2611	3	0.0870	0.8600	0.4753	3.0088
Within	2.4289	24	0.1012			
Total	1773.2196	31				

Paper I

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Determination of trace levels of Cd(II) in tap water samples by anodic stripping voltammetry with an electrografted boron-doped diamond electrode

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ABSTRACT: A boron-doped diamond electrode modified by 0.5 mM 4-aminomethyl benzoic acid was used for electrochemical determination of Cd^{2+} in tap water samples by anodic stripping voltammetry. This method is based on the electrochemical reduction of 4-aminomethyl benzoic acid on the electrode followed by the determination of Cd^{2+} with a single well-defined reduction peak at −0.72 V versus Ag/AgCl in acetate buffer solutions at pH 6.0. Optimal conditions were established with respect to electrode pretreatment, time accumulation, potential accumulation, scan rate, and pH. Accurate ($r^2 = 0.9989$, $n = 6$) calibration curves were obtained for Cd^{2+} concentrations ranging between 2 ppb and 50 ppb. Other dissolved metals (Ca, Mg, Zn, Mn, Fe, Cu, Al, Co, Pb, and Ni) have no interference on the Cd^{2+} calibration curves. The achieved detection limit was 0.2 ppb. High accuracy and reproducibility of the results as well as excellent stability of the electrode material proves superb capabilities of this Cd^{2+} detection system. Recovery in the range of 97–102% further confirmed the usefulness of the proposed method to analyse Cd^{2+} in tap water samples. The results with SRM1640 were in good agreement with those by inductively coupled plasma optical emission spectrometry.

KEYWORDS: voltammetric analysis, ASV, Cd^{2+}

INTRODUCTION

The contamination of utility water with heavy metals such as Cd^{2+} is one of the most hazardous environmental and health problems. Those metals are highly toxic to certain organs of both humans and animals, including nervous, immune, reproductive, and gastrointestinal systems[1]. Ingestion of any significant amount of Cd^{2+} causes immediate poisoning as well as damage to the liver and the kidneys because of their tendency to accumulate in the body, toxicity, and low clearance rate. The biological half-life of Cd^{2+} is 10–30 years[2] and compounds containing Cd^{2+} are also carcinogenic[3]. Building up of Cd^{2+} levels in the water, air, and soil has been increasing, particularly in industrial areas. Workers can be exposed to Cd^{2+} in air from the smelting and refining of metals, or from the air in industrial plants that make Cd^{2+} products such as batteries, coatings, or plastics. Even cigarettes are a significant source of Cd^{2+} exposure. Although there is generally less Cd^{2+} in tobacco than in food, the lungs absorb Cd^{2+} more efficiently than the stomach[4]. Some sources of phosphate in fertilizers contain Cd^{2+} up to the amounts of 100 mg/kg[5,6], which can lead to an increase in the concentration of Cd^{2+} in soil as found in New Zealand[7]. In addition, Nickel-cadmium batteries are one of the most popular and most common cadmium-based products. Environmental exposure to Cd^{2+} has been particularly problematic in Japan where many people have consumed rice that was grown in Cd^{2+} contaminated irrigation water. This phenomenon is known under the name itai-itai disease[8]. The determination of trace level Cd^{2+} in water samples therefore plays an important role in the environmental pollution monitoring due to the cumulative toxicity of Cd^{2+}.

Sensitive methods to determine trace amount of Cd^{2+} have received much attention and many techniques have been developed. Typical methods of metal ion analysis include inductively coupled plasma-mass spectrometry[9], X-ray fluorescence spectrometry (XRF)[10], and atomic absorption spectrometry (AAS)[11]. However, these techniques use expensive and sophisticated instruments and are time consuming, which severely restricts their practical applications[1]. Anodic stripping voltammetry is a well established method for trace analysis of heavy metals. The equipment for ASV measurement is inexpensive because of its small size and does not demand a high power supply. This makes field deployment possible and constitutes a big advantage over AAS or ICP. Generally, the detection limit of ASV is not as low as the detection limit of the spectrometric measurements, but still adequate for most of the tasks mentioned above[12]. One of the extensively used electrode materials for ASV is mercury. Nowadays, however, mercury electrodes are considered undesirable due to the toxicity of both metallic mercury and mercury salts employed for its preparation. Alternative environmentally friendly electrode materials are therefore required[13]. Several new types of mercury-free electrodes have recently been developed for sensitive metal determinations, including bismuth film electrodes[13,14], gold-coated electrodes[15,16], silver electrodes[17,18], glassy carbon electrodes[19], carbon paste electrodes[20–22], carbon nanotube electrodes[23], or screen-printed carbon electrodes[24].

Boron-doped diamond (BDD) electrodes can be applied in a variety of areas due to their superior properties, including extreme robustness with a low level of background interference, less adsorption of polar molecules, and wide potential window in aqueous media[2,25]. It has been used to quantify manganese in tea[26] as well as lead in tap water[27] and river sediment. Anodic stripping voltammetry BDD has been proved to possess outstanding features[28] to determine silver[29] and simultaneous detection of lead and copper[30].

This paper reports the detection of Cd^{2+} by ASV on BDD electrode based on simple and selective electrochemical reduction of Cd^{2+} on diazonium-modified electrode with interference study. The method was verified by analysing standard material and was then applied to the analysis of Cd in Hatyai tap water. The modification of carbon through the electrochemical or chemical reduction of aromatic diazonium derivatives has been extensively used for modification of various carbon materials, such as glassy carbon[31], graphite[32], graphene[33], and carbon nanotube[34]. It is well-recognized as a very versatile and simple way to graft a wide variety of functional groups onto carbon surfaces for various applications. Furthermore, the diazonium-modified electrode has been found to be stable to long-term storage in air and organic solvents. The high stability of the diazonium-modified electrode and the versatility of the diazonium modification method are particularly attractive for stripping analysis. Due to these characteristics, the method can therefore be applied well to Cd^{2+} analysis.

MATERIALS AND METHODS

Reagents and solutions

All reagents were used as received without any further treatment. Cd^{2+} standards were prepared in-house from Cd^{2+} nitrate Atomic Spectroscopy Standard Solution. KNO_3 as a supporting electrolyte was supplied by Ajax Finechem. All other reagents and the metal salts used for the interference experiments (all nitrates except $MnCl_2 \cdot 4\,H_2O$ and $MgCl_2 \cdot 6\,H_2O$) were of analytical-reagent grade with the highest purity commercially available. All subsequent solutions were prepared by using deionized water of resistivity not less than 18 MΩ cm (ELGA water purification system, England). Nitrogen gas (99.99%) was used to deaerate the testing solutions for 2 min. Laboratory glassware was kept overnight in 10% (v/v) HNO_3 solution and rinsed with deionized water before use. Standard solutions of Cd^{2+} were prepared by diluting the respective stock solutions with high purity deionized water and stored in polyethylene bottles before use.

The reference sample analysed was NIST (National Institute of Standards and Technology) SRM 1640 trace elements in natural water. NIST SRM 1640 is composed of natural fresh water from Clear Creek, Colorado, USA. The sample was filtered and stabilized with HNO_3 to a concentration of 0.5 M. The certified value of Cd^{2+} was 22.82 ± 0.96 ppb.

Sampling and digestion

Tap water samples were collected between August and September 2015 in different regions within the city of Hatyai, Songkhla, Thailand. An aliquot of 500 ml of tap water sample was digested by mixing with 2 ml of concentrated HNO_3 and 2 ml of KNO_3 and then placed in cleaned polyethylene bottles.

Instrumentation

Cyclic voltammetry (CV) and square wave anodic stripping voltammetry (SWASV) were performed with a Powerlab 2/20 with Potentiostat (ADInstrument, Australia) controlled by ECHEM. The three-electrode system consisted of an Ag/AgCl/3 M KCl reference electrode, a platinum counter electrode, and a BDD electrode with inner diameter of 3 mm (Windsor Scientific Ltd., UK) was used as a working electrode. All electrochemical measurements were carried out in a 50 ml cell and the pH of solutions were measured by pH meter Model 510 (Eutech instruments, USA).

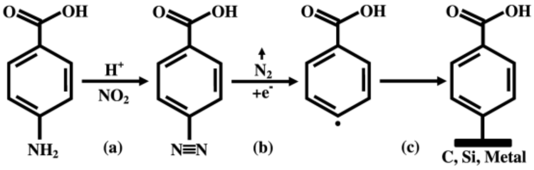

Fig. 1 Grafting process through the electrochemical reduction of diazonium salts. (a) Spontaneous diazotization, (b) electrochemical reduction, and (c) grafting on the electrode surface.

Preparation of modified electrode

The modification of thin films by electrofunctionalization was electrochemically performed by the reductive electrolysis of diazonium salts on the electrode surface. Diazonium salts were directly generated in the electrochemical cell by the spontaneous diazotization method using an aromatic amine presenting an adequate substituent in the para-position relative to the amino group ($-NH_2$). The in situ transformation of the amine into a diazonium salt ($-N_2^+$) was carried out with an aqueous nitrite solution (10 mM tetrabutylammonium hexafluorophosphate, $TBAPF_6$) in acidic medium (HCl, pH = 2). Fig. 1 shows the electrochemical reduction of diazonium salts to immobilize organic layers on the electrodes surface. The electrochemical grafting was carried out under stirring (400 rpm) in a cyclic voltammetry mode (5 cycles) between 0.2 and −1.2 V versus Ag/AgCl at 100 mV/s. The aqueous electrolyte was composed of 10 mM $TBAPF_6$, 0.5 M HCl and 0.5 mM 4-aminomethyl benzoic acid.

Cd^{2+} determination procedure

Stripping voltammetric measurements were performed with a BDD electrode and the target metal Cd^{2+} in the presence of dissolved oxygen. Prior to its use, the BDD electrode was polished with a 0.05 µm alumina slurry. The three electrodes were immersed into a 50 ml electrochemical cell containing pH 6.0 acetate buffer solutions. A deposition potential of −1.10 V for measurements of Cd^{2+} was applied to the BDD electrode in the stirred solution. Following a preconcentration step of 120 s, the stirring was stopped; and after 30 s, the voltammogram was recorded by sweeping the potential from −1.0 to −0.3 V (with scan rate 10 mV/s, a frequency of 10 Hz, amplitude of 4 mV, and potential step of 25 mV). Aliquots of the Cd^{2+} standard solution were introduced after recording the background voltammograms. The peak currents were measured at −0.72 V. A 30 s conditioning step at +0.3 V (with stirred solution) was applied to fully oxidize all metal deposits prior to the next measurement. All experiments were carried out at room temperature.

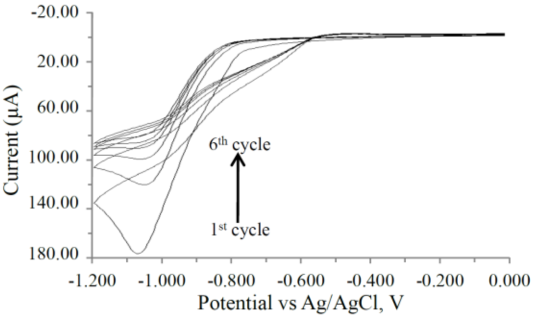

Fig. 2 Electrografting of BDD electrodes with 0.5 mM 4-aminomethyl benzoic acid in methanol with 10 mM $TBAPF_6$ as an electrolyte with the 1st, 2nd, 3rd, 4th, 5th, and 6th potential CV cycles for scan rate 100 mV/s.

RESULTS AND DISCUSSION

Electrografting BDD electrode with 4-aminomethyl benzoic acid

The reduction of diazonium salts was carried out in a narrow potential range between 0.2 and −1.2 V (Fig. 2). The broad reduction peak present in the first cycle (at −1.08 V) is presumably attributed to the reduction of the corresponding diazonium species to form an aryl radical which reacts with the electrode surface. It can therefore be assumed that the same phenomenon occurred in the current study, namely, is the covering of BDD electrodes by the corresponding aryl layers.

Evolution of the wettability

To characterize the wettability of the electrolyte on the BDD modified electrode, the droplets of distilled water after grafting with 4-aminomethyl benzoic acid were found to induce an increase in the contact angle from 22° to 68° (figure not shown), indicating that the hydrophobicity is greater with the presence of the aromatic ring.

Cyclic voltammogram of Cd^{2+}

The overlay of CV voltammograms for 30.0 mg/l Cd^{2+} in the absence (curve a) and presence (curve b) of electrografted BDD electrode is shown in Fig. 3. The deposition peak was observed at −0.92 V versus Ag/AgCl corresponding to preconcentration of Cd^{2+} onto a BDD electrode surface at negative

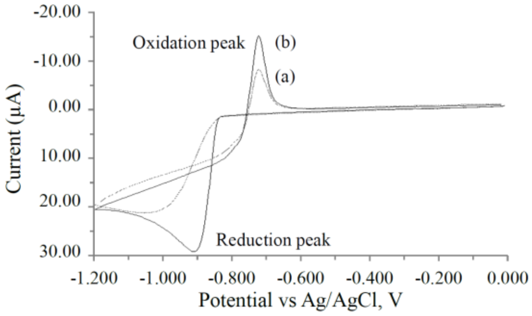

Fig. 3 Cyclic voltammogram of 30.0 mg/l Cd^{2+} at (a, dashed line) bare BDD electrode and (b, solid line) the modified electrode in pH 6.0 acetate buffer solutions with scan rate of 100 mV/s.

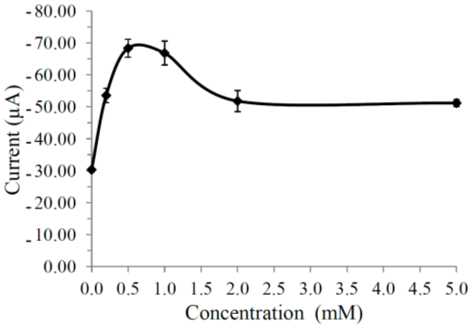

Fig. 5 Peak currents from BDD electrode at concentration of 30.0 mg/l Cd^{2+} with various concentrations of 4-aminomethyl benzoic acid 0.0, 0.2, 0.5, 1.0, 2.0, and 5.0 mM in acetate buffer solutions pH 6.0 with scan rate of 100 mV/s.

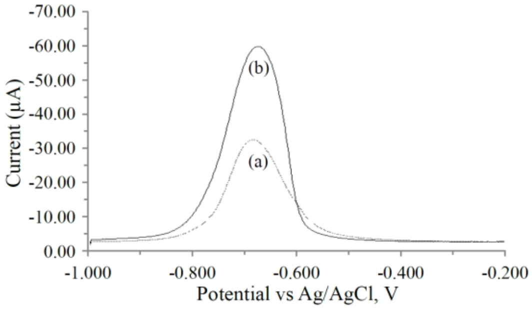

Fig. 4 SWASV of Cd^{2+} at (a, dashed line) bare BDD electrode and (b, solid line) the modified electrode. Experimental conditions: deposition/measurement solution, pH 6.0 acetate buffer solutions containing 30.0 mg/l Cd^{2+}; deposition time, 120 s, potential 1.0 V, frequency 10 Hz, amplitude of 4 mV, and potential step of 25 mV.

potentials. On the reverse scan, the single well defined stripping peak appeared at potential around −0.72 V versus Ag/AgCl with electrografted BDD electrode surface.

The electrochemical response of Cd^{2+} stripping on bare and benzoic acid-modified BDD electrode

Fig. 4 shows square wave anodic stripping voltammograms (SWASV) of Cd^{2+} at bare and benzoic acid-modified BDD electrode, both reflecting well-defined peak at 0.72 V. The anodic peak current of Cd^{2+} at the benzoic acid-modified BDD electrode (58.5 µA) was about twice of that at the bare BDD electrode (32.0 µA). The increases in anodic peak current are attributed to the electrostatic interaction between the negatively charged electrografted BDD electrode and the positively charged metal ions that facilitates the preconcentration of Cd^{2+} which are beneficial for Cd^{2+} determination.

Effect of concentration of 4-aminomethyl benzoic acid

The dependence of the peak Cd^{2+} currents on the concentration of 4-aminomethyl benzoic acid is depicted in Fig. 5. It is apparent that 4-aminomethyl benzoic acid film can increase peaks height of Cd^{2+} oxidation, a sharp increase in the response signal can be observed with increasing concentration of 4-aminomethyl benzoic acid from 0.0–0.5 mM followed by a decrease from 1.0–5.0 mM. When the concentration of 4-aminomethyl benzoic acid was very high, the formation of a thick layer probably partially blocked the conductive surface of the electrode, resulting in a decrease of electrodeposition sites. The optimum concentration with the highest current was 0.5 mM, which was selected for further experiments.

Electrolyte and pH dependence for film formation

Since the electrografting on electrode surfaces depends mainly on acidity, pH can be one of the effective parameters strongly influencing the peak current. The pH range of 1.0–8.0 (data not shown) was investigated using cyclic voltammetry in 10 mM $TBAPF_6$ as an electrolyte. With the increase of pH from 1.0–2.0, the peak current continuously increases due to greater extent of complex formation of Cd^{2+} with 4-aminomethyl benzoic acid at the electrode surface. However, with pH values higher

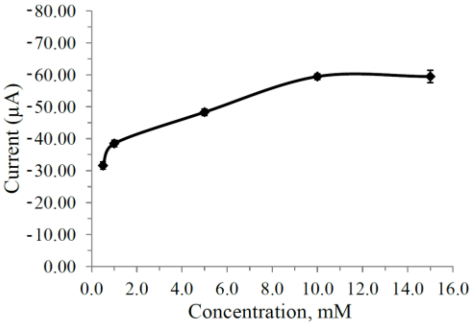

Fig. 6 Peak currents from BDD electrode at concentration of 30.0 mg/l Cd^{2+} in various concentrations of $TBAPF_6$ 0.5, 0.1, 5.0, 10.0, and 15.0 mM (pH 2, as an electrolyte for film formation) in acetate buffer solutions pH 6.0 with scan rate of 100 mV/s.

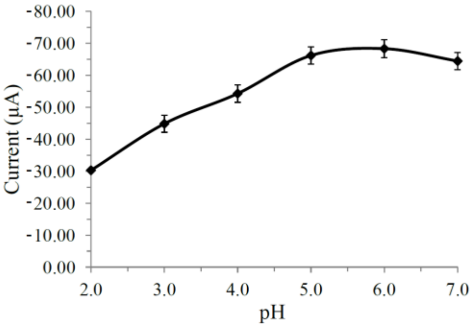

Fig. 7 Peak currents of 30 mg/l Cd^{2+} in acetate buffer at different pH values.

than 2.0 the peak current decreased drastically possibly due to the formation of insoluble metal hydroxide complex, $Cd(OH)_2$. Thus pH 2.0 was selected as an optimum condition in order to obtain maximum sensitivity in quantitative analytical measurements. The effects of electrolytes concentration at 0.5, 1.0, 5.0, 10.0, and 15.0 nM $TBAPF_6$ on the peak currents of Cd^{2+} were also carefully investigated. It was found that Cd^{2+} had the best electrochemical responses in 10 mM $TBAPF_6$ (Fig. 6), which was chosen as a supporting electrolyte for voltammetric determination of the Cd^{2+} for further experiments.

Effect of pH on Cd^{2+} determination

The effect of pH 1.0–7.0 on the peak current of Cd^{2+} in SWASV is shown in Fig. 7. The results indicate a rapid enhancement of the peak current of Cd^{2+} with ascending of pH to a maximum approximately at pH 6.0 and then a progressive decrease. This might result from the higher pH value, at which the metal ion easily hydrolyses[35]. At lower pH value, hydrogen ion are reduced more easily[36], which in turn interfere with Cd^{2+} deposition. pH 6.0 was therefore chosen for further studies.

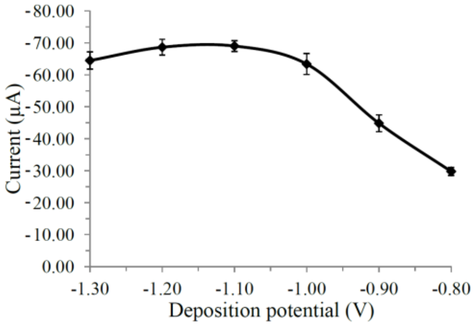

Fig. 8 Effect of deposition potentials on the SWASV peak currents. Conditions: 30.0 mg/l Cd^{2+} in 50 ml acetate buffer pH 6.0.

Deposition potential

The effect of deposition potentials on the stripping peak currents of 30.0 mg/l Cd^{2+} was studied in the potential range from −0.80 to −1.30 V (Fig. 8). The negative shifts of deposition potential can clearly improve the extent of Cd^{2+} reduction on the surface electrode and increase the peak current. The peak current however does not change significantly with the deposition potentials to values more negative than −1.10 V. Moreover, the background current increased when the potentials were more positive than −1.10 V. The results reflect an optimum deposition potential of −1.10 V at which further experiments were then performed to achieve high sensitivity and better response.

Deposition time

For the effect of the deposition time screened within a range of 1–8 min on the stripping currents of 20.0 µg/l Cd^{2+}, longer deposition times should increase the peak current because more Cd^{2+} could be deposited (Fig. 9). When the deposition time increases, the stripping peak currents increase greatly and are almost constant beyond 6 min which reflects surface saturation. Thus 6 min was chosen for all subsequent analysis.

Scan rate

The scan rate was screened from 10–200 mV/s. As shown in Fig. 10, the peak height was small at lower

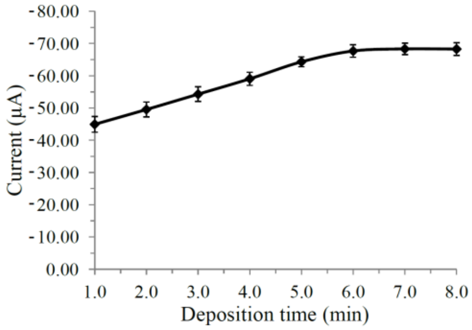

Fig. 9 Effect of deposition time on the SWASV peak currents. Conditions: 30.0 mg/l Cd^{2+} in 50 ml acetate buffer pH 6.0.

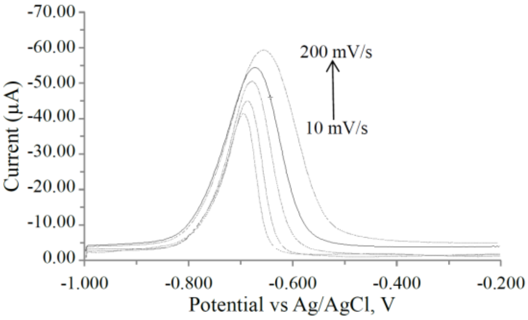

Fig. 10 Effect of scan rates 10, 20, 50, 100, and 200 mV/s on the stripping voltammograms. Conditions: 30.0 mg/l Cd^{2+} in 50 ml acetate buffer pH 6.0, 0.5 mM 4-aminomethyl benzoic acid; deposition potential, −1.1 V versus Ag/AgCl; deposition time, 6 min; pulse amplitude, 4 mV.

scan rate and increased rapidly at higher scan rate with the best result of better current and greater stability of peak potential at a scan rate of 100 mV/s. At more than 200 mV/s, the signal peak becomes broader and shifts to much more positive stripping potentials. A scan rate of 100 mV/s was therefore selected for further experiments.

Limits of detection and quantitation

Fig. 11a shows square wave voltammetry measurements of water with different concentrations of Cd^{2+} with the optimum conditions to obtain the calibration curve and detection limit. The calibration curve shows linearity within the range of 2–50 ppb with a correlation coefficient of 0.9989 with the linear regression equation of Cd^{2+} of $i_p = 4.458x - 11.73$ (i_p: μA, x: μg/l).

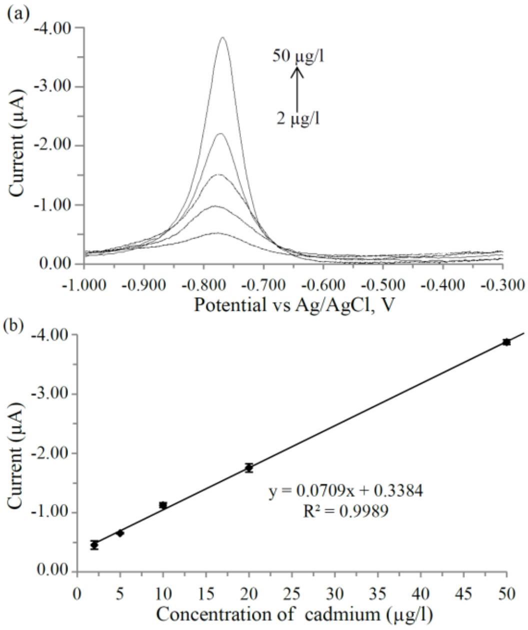

Fig. 11 SWAS voltammograms of water sample. After spiking with 2.0, 5.0, 10.0, 20.0, and 50.0 μg/l of Cd^{2+} standard solution. Conditions; accumulation potential, −1.10 V; accumulation time, 6 min; acetate buffer pH 6.0, 0.5 mM 4-aminomethyl benzoic acid; scan rate, 100 mV/s.

The limit of detection of Cd^{2+} was calculated by LOD $= 3N/m$[36], where N is the standard deviation of replicate blank responses ($n = 9$) and m is the slope of the calibration curve to obtain its value of 0.2 μg/l. The limits of quantification defined as $10N/m$, were found to be 0.6 μg/l. The relative standard deviation was 3% ($n = 10$) for repetitive determinations of 20.0 μg/l of Cd^{2+}. The results demonstrate that the proposed technique was reproducible and reliable for the detection of Cd^{2+} at trace level and can be used for real samples analysis.

Certified reference materials and real sample analysis

The accuracy of the proposed method was tested by determining the Cd^{2+} content of certified reference materials, natural water SRM 1640 from NIST. Stripping peaks for Cd^{2+} in the NIST sample occur at potentials of −0.72 V versus AgCl. The certified value (22.82 ± 0.96 μg/l) and the analytical results (22.72 ± 0.90 μg/l, $n = 5$) gave a satisfactory recovery of 99.02% ($n = 5$), proving that the proposed method is suitable for analysing tap water sample.

Table 1 Determination of Cd^{2+} in tap water samples ($n = 4$) spiked with 5, 10, and 20 μg/l of Cd^{2+}.

Sample	Spiked (μg/l)	Present method (μg/l)[b]	Recovery (%)	ICP-OES method (μg/l)	Difference (%)
Tap water 1[a]	0	ND[c]	–	ND	–
	5	5.56 ± 0.35	–	5.25 ± 0.65	6.2
	10	10.65 ± 0.52	101.8	10.35 ± 0.45	3.0
	20	20.35 ± 0.24	97.0	20.78 ± 0.32	2.2
Tap water 2[a]	0	ND	–	ND	–
	5	5.28 ± 0.25	–	5.58 ± 0.48	6.0
	10	10.35 ± 0.58	101.4	10.14 ± 0.65	2.1
	20	20.20 ± 0.68	98.5	20.25 ± 0.56	0.2

[a] Water sample 1st and 2nd region was selected for standard addition test

[b] Mean ± Standard deviation ($n = 4$)

[c] Not detected

Table 2 Comparison of the proposed method to determine Cd^{2+} in water sample with other anodic stripping voltammetric methods.

Modified electrode	Method	Deposition time (s)	Linear range (μg/l)	Detection limit (μg/l)	Reference
(Bi/MCNTs-CPE)	SWASV	7200	1–60	0.3	Ref. 37
Sb nano/BDD	LSASV	120	50–500	38.10	Ref. 38
Bi/CNT/GCE	SWASV	300	2–100	0.70	Ref. 39
0.2 M 4-aminomethyl benzoic acid/BDD	SWASV	360	2–50	0.2	This work

The proposed technique was applied to the analysis of Cd^{2+} in tap water sample collected from 11 sites in Hatyai city, 500 ml for each. The standard addition method was performed by spiking a tap water sample with different concentrations of Cd^{2+} with the results in Table 1. The recoveries values were between 97 and 102%. The results obtained by the proposed method were compared with those obtained by the inductively coupled plasma optical emission spectrometry (ICP-OES). Statistical analysis of the results by the Student's t-test and variance ratio F-test (Table 1) revealed that factors calculated did not exceed the theoretical value (95% confidence limits for three degrees of freedom) or there was no significant difference between the proposed methods and the standard method. Thus the technique provides a good alternative for the determination of Cd^{2+} in tap water sample. Compared with other ASV techniques using modified electrodes, the proposed method exhibits better figures of merit (Table 2), revealing that this technique is among those with the highest sensitivity.

Effect of other ions

To study the selectivity of the proposed method, some metal ions were tested to evaluate the possible interference with the detection of Cd^{2+}. The ions were considered to interfere seriously when they gave a current signal change of more than 5%. The experimental results for typical ions present in tap water samples are given in Table 3. The peak current of Cd^{2+} was not significantly affected by substantial excess of Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, and Al^{3+}. However, Co^{2+}, Pb^{2+}, and Ni^{2+} significantly influenced the stripping response. These ions not only compete with Cd^{2+} for the substitution on the surface electrode but can also form intermetallic compounds with Cd^{2+} to prevent its accumulation on the electrode[13]. However, the influence of weakly interfering ions can be corrected by standard addition method. Thus the results demonstrate sufficient selectivity of the proposed method.

Table 3 Potential ion interference on the voltammetric response of 20.0 μg/l Cd^{2+} under optimum conditions.

Foreign ions	Concentration (μg/l)	Signal change (%)
Ca^{2+}	2600	−5.56
Mg^{2+}	1000	−5.35
Zn^{2+}	1000	−5.89
Mn^{2+}	400	−5.36
Fe^{2+}	200	−5.56
Cu^{2+}	200	−5.98
Al^{3+}	80	−5.89
Co^{2+}	40	−5.78
Pb^{2+}	40	−5.96
Ni^{2+}	20	−5.75

CONCLUSIONS

A simple and accurate method was developed for the analysis of trace Cd^{2+} in drinking water using the BDD electrode in combination with SWASV. The electrode exhibited a single stripping anodic signal at −0.72 V, of which the intensity increased linearly with Cd^{2+} concentration range of 2–50 µg/l. The detection limit achieved with 0.2 M 4-aminomethyl benzoic acid-modified BDD electrode for Cd^{2+} was 0.2 ppb. Good repeatability (recoveries between 96 and 102%, $n = 4$) and reproducibility (recovery of 99.02%, $n = 5$) in the measurements were also obtained. The method was applied with tap water samples to reveal better sensitivity, simpler sample preparation, shorter analysis time and easier operational processing. The accuracy of the proposed method was verified by analysing the SRM 1640 natural water standard with the certified value of 22.82 ± 0.96 µg/l yielded Cd^{2+} concentration of 22.72 ± 0.90 µg/l ($n = 3$). The recoveries of the method by spiking were in the range of 85–105%. The results of Cd^{2+} in natural water samples analysed by the developed method (FI-DPASV) were in good agreement with those obtained by Inductively Coupled Plasma-Optical Emission Spectrometry. The concentration of Cd^{2+} in tap water samples were found to be lower than the drinking water contamination standard limited level 3.0 µg/l issued by the World Health Organization and Provincial Waterworks Authority of Thailand.

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List of Publication and Poster presentation

Publication:

Innuphat, C and Chooto, P. 2016. Determination of trace levels of cadmium(II) in tap water samples by anodic stripping voltammetry with 4-aminomethyl benzoic acid modified boron-doped diamond electrode. ScienceAsia **43**: 33-41. DOI 10.2306/scienceasia1513-1874.2017.43.033

Poster presentation:

Chalermpol Innuphat, Pipat Chooto and Puchong Wararatananurak. Detection of trace levels of Pb^{2+} in tap water by stripping voltammetry with boron-doped diamond (BDD) electrode. 3W Research Fair 2013 @3W Expo 2013 (Water, Wastewater & Waste Treatment) 22-24 January 2013, BITEC, Bangkok, Thailand.