

TASK SPECIFIC IONIC LIQUIDS MIXED PALM SHELL  
ACTIVATED CARBON AS ION SELECTIVE ELECTRODES FOR  
Cd (II) AND Hg (II) DETECTION

AHMED ABU ISMAIEL

FACULTY OF ENGINEERING

UNIVERSITY OF MALAYA

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**AHMED ABU ISMAIEL**

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Name of Candidate: AHMED ABU ISMAIEL (I.C/Passport No: 2322791 )

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Designation: Lecturer  
Department of Chemical Eng.  
Faculty of Engineering  
University of Malaya  
50603 Kuala Lumpur.

## ABSTRACT

Ion selective electrodes (ISEs) are potentiometric sensors used to measure some of the most critical analytes in environmental laboratory. Despite their easy fabrication, simple usage, and low cost, ISEs suffer from long response times, low response sensitivity, interference by a number of metal ions, long equilibration times and short lifetimes. Therefore, the development of new ISE materials that can address some of these limitations is a worthwhile and challenging topic of research. In this study, the combination of activated carbon with task specific ionic liquids has resulted in a unique new generation paste in which the traditional components have been replaced with alternate materials. The proposed electrodes exhibited improved performance compared to those of conventional type. This improvement is presumably due to the electrode composition. The manipulation of the electrode composition can improve the sensitivity and selectivity in the detection of some heavy metals in aqueous solutions.

The objective of this work is to prepare modified ion selective electrodes and then to use them for determining the heavy metal concentrations in drinking water samples and study of adsorption kinetic of cadmium and mercury ions onto modified palm shell activated carbon.

In this study, palm shell activated carbon modified with trioctylmethylammonium salicylate (TOMAS) was used as a novel electrode component for the potentiometric determination of cadmium ions in water samples. The proposed potentiometric sensor has good operating characteristics when used to determine Cd(II), including a relatively high selectivity; a Nernstian response in a working concentration range of  $1.0 \times 10^{-9}$  to  $1.0 \times 10^{-2}$  M, with a detection limit of  $1 \times 10^{-10}$  M and a slope of  $30.90 \pm 1.0$  mV/decade; and a fast response time ( $\sim 10$  s). The proposed sensor can also be used for at least two months without considerable changes in its response characteristics. No significant

changes in the electrode potential were observed when the pH was varied over the range of 4-9. Another potentiometric sensor composed of palm shell activated carbon modified with trioctylmethylammonium thiosalicylate (TOMATS) was used for the potentiometric determination of mercury ions in water samples. The proposed potentiometric sensor has good operating characteristics towards Hg(II), including a relatively high selectivity; a Nernstian response to Hg(II) ions in a concentration range of  $1.0 \times 10^{-9}$  to  $1.0 \times 10^{-2}$  M, with a detection limit of  $1 \times 10^{-10}$  M and a slope of  $44.08 \pm 1.0$  mV/decade; and a fast response time ( $\sim 5$  s). No significant changes in electrode potential were observed when the pH was varied over the range of 3-9. A potentiometric method was developed for the in situ adsorption kinetic study of cadmium and mercury ions onto modified palm shell activated carbon based on the continuous direct monitoring of cadmium and mercury concentrations by the developed ion selective electrodes. The apparent adsorption rate constant was estimated assuming pseudo-second-order kinetics. Additionally, the proposed electrodes have been successfully used for the determination of the cadmium and mercury contents of real samples without a significant interaction from other cationic or anionic species.

## ABSTRAK

Elektrod ion memilih (ISEs) adalah sensor permeteran upaya yang digunakan untuk mengukur beberapa analit paling kritikal. Walaupun senang dibikin, ringkas diguna dan kos rendah, ISEs mengalami masa sambutan panjang, kepekaan sambutan yang rendah, gangguan dari beberapa ion logam, masa keseimbangan yang panjang dan jangka hayat pendek. Oleh itu, pembangunan bahan ISEs baru yang dapat mengatasi batasan ini adalah berbaloi dan merupakan topik penyelidikan yang mencabar. Dalam kajian ini, pengabungan karbon teraktif dengan cecair berion tugas tentu dapat menghasilkan perekat generasi baru yang unik, yang boleh menggantikan komponen tradisional sebagai bahan gantian. Elektrod yang dicadangkan mempamerkan prestasi yang lebih baik berbanding dengan jenis bahan lazim. Prestasi yang baik ini adalah disebabkan oleh rencaman elektrod. Pengolahan rencaman elektrod boleh memperbaiki kepekaan dan kememilihan dalam mengesan beberapa logam berat dalam larutan berair.

Objektif kajian ini adalah untuk menyediakan elektrod ion memilih terubahsuai dan kemudiannya digunakan bagi menentukan kepekatan logam berat dalam sampel air minuman dan juga membuat kajian kinetik penjerapan bagi ion kadmium dan ion merkuri keatas karbon teraktif dari tempurung kelapa sawit terubah suai.

Dalam kajian ini, tempurung kelapa sawit karbon teraktif yang diubahsuai dengan menggunakan bahan trioktilmetilammonium salisilat (TOMAS) sebagai komponen baru elektrod untuk penentuan permeteran upaya ion kadmium dalam sampel air. Penderia permeteran upaya yang dicadangkan mempunyai ciri operasi yang baik apabila digunakan bagi menentukan Cd(II) termasuklah kememilihan yang tinggi ke arah Cd(II); Sambutan Nernstian Cd(II) dalam julat kepekatan boleh kerja  $1.0 \times 10^{-9}$  sehingga  $1.0 \times 10^{-2}$  M, dengan had pengesanan  $1 \times 10^{-10}$  M dan cerun  $30.90 \pm 1.0$  mV/dekad; dan masa tindak balas yang cepat ( $\sim 10$  s).

Penderia yang dicadangkan boleh juga digunakan sekurang-kurangnya dua bulan tanpa perubahan dalam ciri sambutan. Tiada perubahan ketara didapati dalam elektrod upaya apabila pH diubah dalam julat 4-9.

Satu lagi penderia permeteran upaya yang terdiri daripada tempurung kelapa sawit karbon teraktif yang diubahsuai dengan menggunakan trioktilmetilammonium thiosalisilat (TOMATS) sebagai komponen baru elektrod yang digunakan untuk penentuan permeteran upaya ion merkuri dalam sampel air. Penderia permeteran upaya yang dicadangkan mempunyai ciri operasi yang baik, terhadap Hg(II), termasuklah kememilihan yang tinggi ke arah Hg (II); Sambutan Nernstian Hg (II) dalam julat kepekatan boleh kerja  $1.0 \times 10^{-9}$  sehingga  $1.0 \times 10^{-2}$  M, dengan had pengesanan  $1 \times 10^{-10}$  M dan cerun  $44.08 \pm 1.0$  mV / dekad; dan tindak balas yang cepat masa ( $\sim 5$  s). Tiada perubahan ketara didapati dalam elektrod upaya apabila pH diubah dalam julat 3-9.

Satu kaedah permeteran upaya telah dibangunkan bagi kajian kinetik penjerapan bagi ion kadmium dan ion merkuri keatas tempurung kelapa sawit karbon teraktif, yang diubahsuai berdasarkan pemantauan berterusan kepekatan kadmium dan merkuri secara elektrod ion memilih.

Pemalar kadar penjerapan ketara telah dianggarkan dengan andaian kinetik pseudo tertib kedua. Disamping itu, elektrod yang dicadangkan telah berjaya digunakan bagi penentuan kadmium dan merkuri dalam sampel sebenar tanpa saling tindak bererti dari spesies berkation atau beranion yang lain.

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## LIST OF SYMBOLS AND ABBREVIATIONS

Symbol	Definition
%	Percentage of weight
K	Kelvin
°C	Celcius
nm	nanometer ( $1 \times 10^{-9}$ )
cm <sup>3</sup>	centimeter cubic
m <sup>2</sup> /g	meter square per gram
Å	Angstrom ( $1 \times 10^{-10}$ )
Kg/m <sup>3</sup>	Kilogram per meter cubic
g/mol	Gram per mol
mm	Millimeter
mg	Milligram
cm	Centimeter
g/l	Gram/liter
ppm	part per million
M	Molar
mg/g	milligram/gram
min	Minute
AC	Activated carbon
PSAC	Palm shell activated carbon
BET	Brunauer-Emmett-Teller
FTIR	Fourier transform infrared spectrophotometer
SEM	Scanning electron microscopy
AS	Atomic spectroscopy
ISE	Ion selective electrode

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pH	The negative logarithm of the hydrogen ion concentration
emf	The electromotive force
E	Potential
$E_j$	Junction potential
$k_{ij}^{\text{pot}}$	Potentiometric selectivity coefficient
IUPAC	International union of pure and applied chemistry
TOMAS	Trioctylmethylammonium salicylate
TOMATS	Trioctylmethylammonium thiosalicylate
ASAP	Accelerated surface area and porosimetry analyzer
DOA	Bis(2-ethylhexyl)adipate
DOP	Bis(2-ethylhexyl) phthalate
TOPh	Tris(2-ethylhexyl) phosphate
DOS	Bis(2-ethylhexyl) sebacate
BPh	Butyl phosphate
DBPh	Dibutyl phosphate
TBPh	Tributyl phosphate
NPOE	2-Nitrophenyl octyl ether
RSD	Relative standard deviation
Aliquat® 336	Trioctylmethylammonium chloride
FIM	Fixed interference method
SSM	Separate solution method
MPM	Matched potential method
ILs	Ionic liquids
RTILs	Room temperature ionic liquids
TSILs	Task specific ionic liquids
CWEs	Coated-wire electrodes

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CPEs	Carbon paste electrodes
PVC	Poly(vinyl chloride)
PMMA	Poly(methyl methacrylate)
CNTs	Carbon nanotubes
MWCNTs	Multi-walled carbon nanotubes
CILE	Carbon ionic liquid electrode

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## **CHAPTER 1: INTRODUCTION**

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## CHAPTER 1

### INTRODUCTION

#### 1.1. General perspective

Heavy metals, primarily cadmium, nickel, copper, lead, zinc, mercury, arsenic, and chromium, reach the environment through several anthropogenic sources. Metal bearing effluents are produced by a broad range of sources; for example, copper is produced from the electroplating industry; chromium from the tanning industry, wood preservative and textile industry; mercury from caustic soda and chlorine industries; lead from the burning of fuel in automobiles, lead-acid batteries, and paints; arsenic from fertilizers; and cadmium from batteries and pigmented plastics (Vijayaraghavan et al., 2005, Kathirvelu and Goel, 2006). Low concentrations of heavy metals (<2ppb) are toxic and harmful to humans, plants and animals due to their toxicity and non-biodegradability. Considering the deleterious effects of heavy metals on environment, limits have been placed on their concentration in portable water supplies and effluent discharges by various agencies throughout the world.

The contamination of water resources by heavy metals is a serious environmental problem worldwide. Numerous metals, including mercury, cadmium, chromium, and lead, are known to be significantly toxic (Xiong and Yao, 2009). The determination of the concentration of heavy metal ions has been crucial when dealing with environmental issues. The presence of heavy metals, such as lead, mercury, cadmium, arsenic, and chromium, at low concentrations is highly undesirable due to their toxicity (Sanz-Medel, 1998). Many analytical techniques, including atomic spectroscopy (AS), ion chromatography, and a variety of electrochemical techniques, have been used to analyse heavy metals in medical and environmental samples (Caruso and Montes-Bayon, 2003, Patnaik, 2004, Shaw and Haddad, 2004, Hanrahan et al., 2004, Ibanez et al., 2008).

Determining trace amounts of heavy metals in environmental samples by atomic spectroscopy is difficult due to insufficient instrument sensitivity and/or matrix interferences (Ghaedi et al., 2007).

Among heavy metal contaminants, Cd (II) and Hg (II) are two major water pollutants of strong concern, producing severe ailments in living beings, including mental retardation.

The major sources of cadmium are industrial processes, such as the production of cadmium-pigmented plastics, nickel-cadmium batteries and paints. According to the World Health Organization (WHO) guidelines, the maximum permissible concentration of cadmium in drinking water is 0.005 mg/L. Cadmium can accumulate in the human body, especially in the kidneys, and cause dysfunction; therefore, there is an increasing interest in the determination of cadmium ion content in drinking water due to its toxicity to human health. The most commonly used techniques for the determination of the amount of cadmium ions in aqueous solution include the following: flame atomic absorption spectrometry (FAAS) (Afkhami et al., 2006), electrothermal atomic absorption spectrometry (ETAAS) (Li et al., 2009), inductively coupled plasma mass spectrometry (ICP-MS) (Beiraghi et al., 2012, Guo et al., 2010), atomic fluorescence spectrometry (AFS) (Wen et al., 2009), and high-performance liquid chromatography (HPLC) (Yang et al., 2005). Although these techniques provide accurate results, they have several disadvantages, such as high apparatus cost, complex operation, high operation and maintenance costs, and the requirement of well-controlled experimental conditions. For these reasons, one of the most favourable techniques for cadmium ion determination is the potentiometric method.

Mercury is a toxic bio-accumulative environmental pollutant that affects the nervous system. It is released into the environment through industrial, agricultural, and other anthropogenic processes. Interests in the determination of trace amount of mercury ions have significantly increased during the past few years due to growing environmental concerns. Several analytical techniques, including, cold vapor atomic absorption spectrometry (CV-AAS) (Zavvar Mousavi et al., 2010, Ferrúa et al., 2007), inductively coupled plasma optical emission spectrometry (ICP-OES) (de Wuilloud et al., 2002, dos Santos et al., 2005), X-ray fluorescence spectrometry (Lau and Ho, 1993), inductively coupled plasma mass spectrometry (ICP-MS) (Wuilloud et al., 2004, Matousek et al., 2002) and cold vapor atomic fluorescence spectrometry (CV-AFS) (Jiang et al., 2010, Zi et al., 2009) have been applied for the determination of trace amounts of mercury in analytical samples. Although these methods have good sensitivity, well controlled experimental conditions, and narrow working concentration ranges. However, they have several disadvantages, such as the use of an expensive apparatus, complicated operation, high operation and maintenance costs, and the requirement of well controlled experimental conditions. Because of their advantages in terms of low cost, easy fabrication, simplicity, sensitivity, and fast response time, potentiometric sensors based on ion selective electrodes have attracted much attention in electro-analytical chemistry and have been successfully used to determine trace levels of mercury (Abbas and Mostafa, 2003, Abu-Shawish, 2009, Bakhtiarzadeh and Ab Ghani, 2008, Gupta et al., 2005, Mahajan et al., 2003, Mashhadizadeh and Sheikhshoae, 2003, Mazloum et al., 2000, Singh et al., 2004).



Electrochemistry has played a significant role in the investigation of heavy metal ions in environmental samples since the discovery of polarographic techniques. Heavy metal ion determination by electrochemical methods can save significant measurement time and operating cost using field-deployable units (Senthilkumar and Saraswathi, 2009). There are 3 types of electrochemical techniques: potentiometric, voltametric (amperometric) and coulometric. Potentiometry, the most commonly used of the electrochemical techniques involves the measurement of the potential generated by an electrochemical cell in the absence of appreciable current under essentially equilibrium conditions (Frant and Ross, 1970). The basis of potentiometry is the Nernst equation, which relates the concentrations of electroactive species at the surface of an electrode to the electrode potential. In a potentiometry experiment, the open circuit potential is measured between two electrodes: the *indicator* electrode and the *reference* electrode. The potential of the indicator electrode is sensitive to the concentration of the analyte in solution, and the reference electrode (typically a saturated calomel or silver/silver chloride electrode) provides a stable reference potential for measurement of the potential of the indicator electrode. Therefore, the potential of this electrochemical cell depends upon the analyte concentration. Since the beginning of the twentieth century, potentiometric techniques have been used to locate the end points in titrimetric analytical methods. More recently, methods have been developed in which ion concentrations are obtained directly from the potential of an ion selective membrane electrode. Such electrodes are relatively free from interference and provide a rapid and convenient means to the quantitative estimation of numerous important anions and cations. The equipment required for potentiometric methods is simple and includes an indicator electrode, a reference electrode, and a potential-measuring device. The focus will be directed toward ISEs that measure the activity of heavy metals in water samples.

When compared with other analytical techniques, ion selective electrodes are simple, relatively inexpensive, robust, durable, and ideal for use in field environments. Some other advantages include their very short measurement time, continuous monitoring ability, measurement of the activity rather than the concentration, and indifference to turbidity or sample colour (Imisides et al., 1988). Potentiometric sensors based on ion-selective electrodes are very attractive for the determination of many chemical species because of their many advantages, including low cost, ease of preparation, sensitivity, selectivity, and precision (Zen et al., 2003).

### **1.2 Palm shell activated carbon: Structure, properties, and characterizations.**

Activated carbons form a large and important class of porous solids, and have found a wide range of technological applications. Activated carbon is a micro porous material with a large internal surface area and porosity. The basic structural unit of activated carbon is closely approximated by the structure of pure graphite. The graphite crystal is composed of layers of fused hexagons held by weak van de Waals forces. The layers are held by carbon-carbon bonds. Activated carbon is a disorganised form of graphite, as induced by impurities and the preparation method (activation process). The structure of the activated carbon is formed by imperfect sections of graphene layers, which are bonded together to build a three-dimensional structure, as shown in Fig. 1.1. This structure includes many defects and spaces between the graphitic microcrystallite layers, which are the source of activated carbon porosity (Marsh and Rodríguez-Reinoso, 2006).

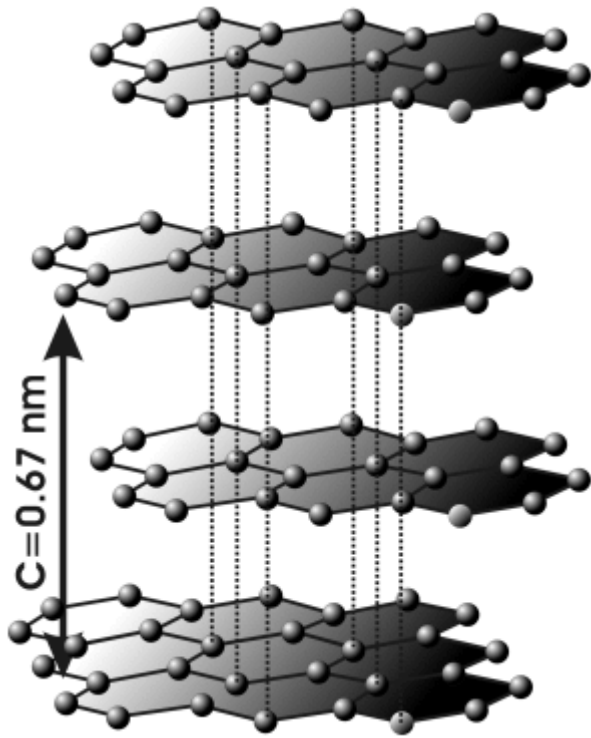


Figure 1.1 : Symbolic view of graphite. (Marsh and Rodríguez-Reinoso, 2006)

According to the IUPAC classification scheme (Sing et al., 1985), the porous structure of activated carbon is formed by three basic classes of pores, as shown in Fig. 1.2. In this figure, pores are classified as follows: (1) macropores, with a pore diameter of greater than 500 Å; (2) mesopores, with a pore diameter between 20-500 Å; and (3) micropores, with a pore diameter of less than 20 Å.

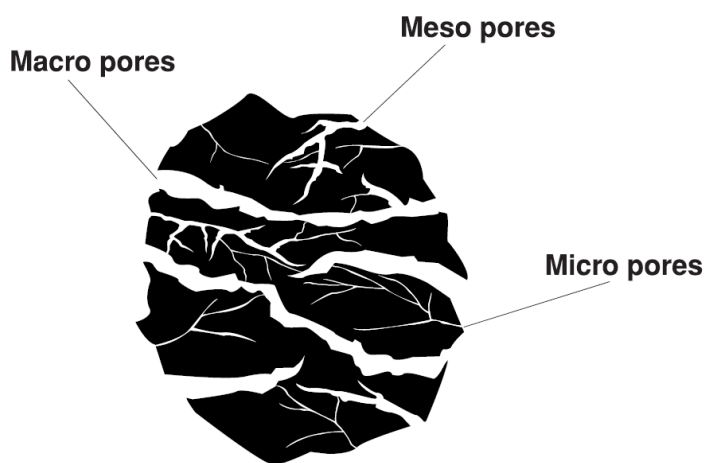


Figure 1.2 : Schematic of the internal pore structure of activated carbon. (Sing et al., 1985)

This structure not only provides different porous structures but also has a significant effect on the bulk density, mechanical strength, and other physical properties of activated carbon. Moreover, activated carbon exhibits a very wide range of interesting physical, chemical, and mechanical properties, thus ensuring a wide range of industrial applications, all of which are structurally dependent.

Many different carbonaceous materials can be used as raw materials for the production of activated carbon. Generally, the raw materials have high carbon and low inorganic contents, such as wood, coal, peat, and agricultural waste. Oil-palm shell is an agricultural by-product from palm-oil processing mills in many tropical countries, including Malaysia. Palm shells have been used to produce activated carbon due to their easy available, low cost, and high carbon and low inorganic contents. Palm shell activated carbon is the most popular and cheapest form of activated carbon, with a wide variety of applications due to its extended surface area, microporous structure, high adsorption capacity, and high surface reactivity. It is an extremely versatile adsorbent of industrial significance and is used in a wide range of applications, principally concerned with the removal of undesired species by adsorption from liquids or gases.

The characterization of activated carbon (AC) is very important for classifying AC for specific uses. Basically, AC is characterized by its physical and chemical properties. As mentioned in (Guo and Lua, 2003) the characteristics of activated carbon depends on the physical and chemical properties of the raw materials as well as the activation method used. A wide range of physical, chemical, and mechanical analytical methods exist for the characterization of carbons (Guo and Rockstraw, 2007). These methods are summarized in Table 1.1.

Table 1.1 : Techniques available for the characterization of activated carbon.

Method	Information provided
Boehm titration	Surface oxygen functionality
Computer simulation	pKa of functional groups
Fourier transform infrared spectroscopy	Surface group functionality
Gas adsorption	Surface areas and energetics, pore size distributions
Magneto-resistance	Electronic properties
Nuclear magnetic resonance	Molecular structure, atom groups
Potentiometric titration	pKa of functional groups
Scanning electron microscopy	Surface characterizations
Small angle X-ray scattering	Total surface area including closed porosity, pore sizes
X-ray photoelectron spectroscopy	Identification of surface functional groups

(Guo and Rockstraw, 2007)

### 1.3 Ionic liquids: Concept, structure, and properties

#### 1.3.1 Chemical structures of room temperature ionic liquids.

Room temperature ionic liquids (RTILs) are air and water stable liquid organic salts, composed of an organic cation and either an organic or an inorganic poly atomic anion. The cations are large, bulky asymmetric organic molecules, such as imidazolium, pyridinium, phosphonium, and sulphonium. The anions are either small inorganic molecules, such as halide, tetrafluoroborate, hexafluorophosphate, and bis(trifluoromethylsulphonyl)imide, or organic molecules, such as alkylsulphate, tosylate, and methanesulphonate. The structures of some ionic liquids are summarized in Fig. 1.3.

The general chemical composition of ionic liquids is surprisingly consistent despite the strong variation in the specific composition and physicochemical properties.

One of the advantages arising from the chemical structures of RTILs is that the alteration of the cation or anion can change properties such as the viscosity, melting point, water miscibility, and density. Therefore, it is not surprising that RTILs have shown tremendous applications in a variety of chemical processes.

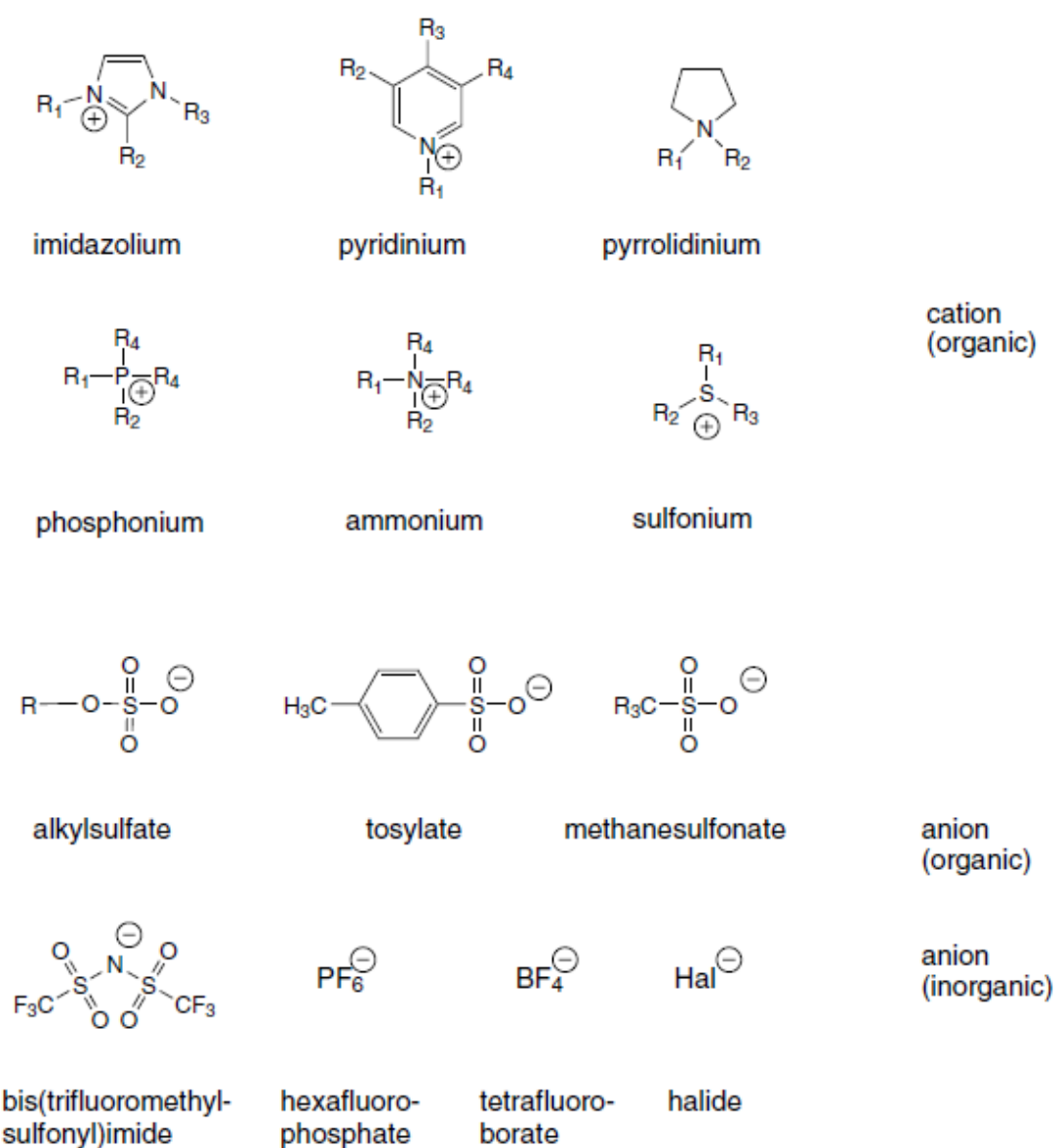


Figure 1.3 : Structures of some ionic liquids (Roland St. Kalb, 2005).

The nature of the cation and the anion determine the physical and chemical properties of the ionic liquid. As a result of the interaction between the properties and the constituent ions of the ionic liquids, it is possible to achieve specific properties by choosing the right combination of anion and cation to create task specific ionic liquids (James H. Davis, 2004). Davis and co-workers first introduced the concept of task specific ionic liquids to describe ILs that incorporate functional groups designed to impart them with particular properties. Task-specific ionic liquids are a unique subclass of ionic liquids that possess a potential spectrum of utility extending far beyond that of more conventional ILs (James H. Davis, 2004). The physical and chemical properties (e.g., high polarity, conductivity, viscosity, Lewis acidity, and hydrophobicity) of task specific ionic liquids can be tuned by varying the structure of the component ions to obtain the desired properties. Ionic liquids (ILs) as well as task specific ionic liquids (TSILs) are finding an increasing number of applications in synthesis, separations, and electrochemistry.

### **1.3.2 Fundamental electrochemical properties of room temperature ionic liquids.**

Typically, room temperature ionic liquids contain a bulky, asymmetric organic cation and a small inorganic/organic anion held together by electrostatic interactions, preventing them from forming a structured lattice (Liu et al., 2005). They exhibit many favourable physico chemical characteristics, which has led to their use in a variety of analytical techniques. All RTILs display a measurable ionic conductivity as well as liquid properties, such as density and viscosity, that can be controlled by the correct choice and/or chemical functionalisation of the ion pair (Jacquemin et al., 2006).

The physicochemical properties of ILs depend on the nature and size of both their cation and anion constituents. Their application in analytical chemistry is due to their unique properties, such as negligible vapour pressure, good thermal stability, tunable viscosity, and miscibility with water and organic solvents, as well as their good extractability for various organic compounds and metal ions (Dupont et al., 2002, Olivier-Bourbigou and Magna, 2002).

#### **1.4 Problem Statement**

The determination of low-level contaminants in ground water has become a major issue during the last several decades. The necessity of monitoring pollutant levels in aqueous solution is becoming increasingly important with time. Unfortunately, the continuous monitoring of water pollutants in the field requires portable fast response sensors with sufficient sensitivity and high selectivity. For these reasons, the determination of pollutants in ground water requires new and improved techniques for rapid and low-cost monitoring.

Ion selective electrodes (ISEs) are potentiometric sensors used to measure some of the most critical analytes in environmental laboratory and point-of-care analysers. Despite their easy fabrication, simple usage, and low cost, ISEs suffer from low response sensitivity, interference by a number of metal ions and short lifetimes. As a result, the development of new ISE materials that can address some of these limitations is a worthwhile and challenging topic of research. The ultimate goals of this study are to increase the sensitivity and selectivity of the proposed electrodes by minimizing the previously mentioned undesirable electrode processes. Additionally, the application of plasticizer-free electrodes can eliminate the leaching of the electrode solvent and sensing components, improving the electrode lifetime.



## 1.5 Objectives and scope of work

The main objective of this study is to develop and evaluate the performance of novel ion selective electrodes for the determination of Cd(II) and Hg(II) in aqueous solutions. The research will include preparation of the ISEs, determination of their analytical characteristics, and their applications in the monitoring of ion concentration in drinking water samples and in the study of adsorption kinetics.

The specific objectives of the study are as follows:

1. To prepare palm shell activated carbon paste electrode based on trioctylmethylammonium salicylate (TOMAS) as both an ionophore and plasticizer for the determination of cadmium ions in aqueous solution.
2. The use of the proposed electrode to determine the cadmium ion content in real water samples.
3. The application of the developed ion selective electrodes for the study of the reaction kinetics and kinetic analytical methods by continuous monitoring of the adsorption rate of cadmium ions from aqueous solution onto the modified palm shell activated carbon.
4. To prepare palm shell activated carbon paste electrode based on trioctylmethylammonium thiosalicylate (TOMATS) as both an ionophore and plasticizer for the determination of mercury ions in aqueous solution.
5. The application of the proposed electrode in the determination of mercury ion contents in real water samples.
6. The use of the developed ion selective electrodes for the study of the reaction kinetics and kinetic analytical methods by continuous monitoring of the rate of adsorption of mercury ions from aqueous solution onto the modified palm shell activated carbon.

## **1.6 Significance of the study**

This work reports significant, novel results pertaining to the detection and measurement of two hazardous heavy metals in aqueous media cadmium and mercury. These novelties can be summarized as follows:

1. To the best of my knowledge, am the first to propose this electrochemical sensor, based on a task specific ionic liquids carbon paste electrode, to detect cadmium and mercury in aqueous solution.
2. More importantly, this work is the first to demonstrate that TSILs can have dual functions, acting as an ionophore and plasticizer. This finding will likely have a strong impact on potentiometric sensor technology because ionophores and plasticizers are usually different materials.
3. The proposed electrodes showed better sensitivity (detection limit below 1 ppm) than the electrodes reported in the literature allowing the detection of some heavy metal ions via complexation with the ionic liquids at the activated carbon surface.
4. The proposed ion selective electrodes have been successfully used for reaction kinetic studies and kinetic analytical methods by the continuous monitoring of the adsorption rate of cadmium and mercury ions onto modified palm shell activated carbon.

## 1.7 Thesis Structure

This thesis consists of five chapters. Chapter 1 provides a general overview of ion selective electrodes and outlines the main objectives of the research. Chapter 2 is a literature review, covering the historical background, general principles, and properties of ion selective electrodes as well as previous studies in the field of ion selective electrodes, i.e. classical ion selective electrodes and some advances in the investigation of heavy metals. Works related to PVC ion selective electrodes, coated wire ion selective electrodes, and carbon paste ion selective electrodes are described. Finally, new trends in the preparation of chemically modified ion selective electrodes and recent studies related to high performance carbon composite electrodes using ionic liquids are discussed. Chapter 3 presents the methodology used in this work, which includes the preparation and characterization of modified palm shell activated carbon paste electrodes based on trioctylmethylammonium salicylate (TOMAS) or trioctylmethylammonium thiosalicylate (TOMATS) as both the ionophore and plasticizer for Cd(II) or Hg(II) determination, respectively, as well as the methods for the determination of the kinetic adsorption parameters using ion-selective electrode (ISE) potentiometry with the proposed electrodes and conventional adsorption kinetic methods. Chapter 4 discuss the results drawn from this research, specifically the electrode response and the factors that affect the response, such as the pH, potentiometric selectivity coefficients, dynamic response time, and electrode life time. The scanning electron microscopy results, potentiometric adsorption kinetics, and analytical applications of the new proposed electrodes are presented. Chapter 5 presents a summary of the conclusions, future challenges, and prospects.

## **CHAPTER 2: LITERATURE REVIEW**

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## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Century of progress

The history of ion-selective electrodes (ISEs) (Buck and Lindner, 2001) begins with the discovery of the pH response of thin film glass membranes by Cremer in 1906, thus making ISEs the oldest class of chemical sensors. They are superior to other sensor types in a variety of applications, including in the biomedical, industrial, and environmental fields. The glass pH electrode is the most widespread sensor, being present in virtually every laboratory. Although the performance of the best glass and crystalline membrane sensors remains unsurpassed, the chemical versatility of these materials is limited, which imposes restrictions on the range of available analytes. During the last several decades, the research and development of potentiometric sensors has shifted primarily towards the more versatile and tunable solvent polymeric membrane ISEs (Bakker et al., 1997). These sensors originated in the early 1960s, completely replaced older analytical methods in various biomedical applications, and gained a foothold in clinical chemistry.

Since the end of the 1960s, the use of ion selective electrodes has been a foundation of analytical chemistry, as documented by the extensive and ever expanding literature on this topic.

Research on ion-selective electrodes is perhaps one of the most eminent examples for interdisciplinary research in chemistry. Indeed, a great body of data on the preparation and practical use of ion selective electrodes has been accumulated.

Studies developing various membrane electrodes and their applications began in the late 1960s. With the invention of these electrodes, potentiometry has begun to be used in many fields, such as for the determination of environmental pollution, clinical analyses,

and biochemical and biomedical studies. These electrodes possess unique characteristics for determining a number of ionic, molecular, and gaseous species.

Pungor and Hallos-Rokosinyi eventually succeeded in preparing the first workable ion selective electrode with a precipitate-based heterogeneous membrane (Pungor and Hallos-Rokosinyi, 1961). However, the most dramatic success in this area stems from Frant Ross's development of the first ion exchange membrane composed of a single crystal. This  $\text{LaF}_3$  ion selective electrode for fluoride determination is, with the glass electrode, still the most successful product in this field (Frant and Ross, 1966).

Liquid membranes containing dissolved ion exchangers were first used by Sollner and Shean, but these membranes only show selectivity toward the sign of the ion charge rather than the type of ion. Ion Selective electrode techniques based on membranes have recently garnered the attention of researchers in many areas. The interest in ion-selective electrodes has grown over recent years, as they are easy-to-use devices that allow the rapid and accurate analytical determination of chemical species at relatively low concentrations, with a reasonable selectivity and at low cost (Antonisse and Reinhoudt, 1999, Bakker et al., 1997, Bühlmann et al., 1998).

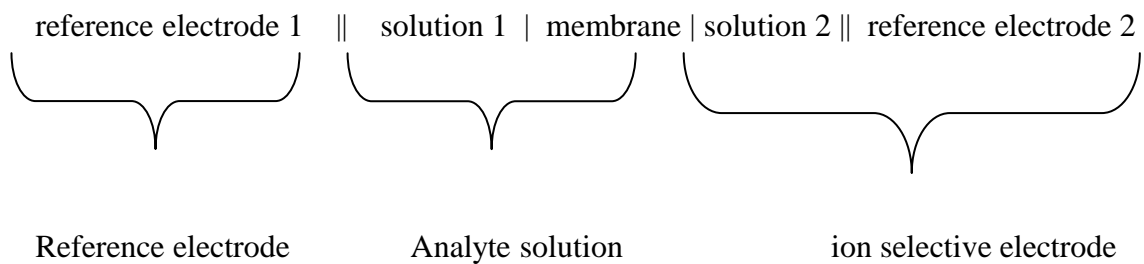
The development of such analytical devices and their application have progressed far, having been heavily stimulated by a variety of individual theories, membrane models, and more intuitive attempts aimed at providing a deeper understanding and access to new techniques.

## **2.2 General principles, construction, and properties of ion selective electrodes.**

A common setup for measurements with ion-selective electrodes is depicted in Fig. 2.1. An ion sensitive membrane is placed between two aqueous phases, i.e., a sample and an internal filling solution. A reference  $\text{Ag}/\text{AgCl}$  electrode is placed into the inner filling solution, which contains the ions that the electrode is responsive to. The external reference electrode is placed in the sample and usually has a salt bridge to prevent

sample contamination. The membrane is an essential part of the sensor and is made of glass (oxide or chalcogenide), crystalline material (monocrystalline or polycrystalline) or water-immiscible liquids (highly plasticized polymers, solvent-impregnated porous films, etc.).

The electrochemical cell for an ISE can be generally represented as (Koryta and Stulik, 1983, Buck, 1968):



where the double lines denote a junction potential. The electromotive force (emf) of the cell is:

$$E = E_2 - E_1 + E_{j2} + E_{j1} + \Delta^{\beta}_{\alpha}\Phi_i \quad (2.1)$$

where  $E_2$  and  $E_1$  are the potentials for the half cell reactions of reference electrodes 2 and 1, respectively. The symbols  $E_{j2}$  and  $E_{j1}$  refer to the junction potentials at the salt bridge of reference electrodes 2 and 1, respectively. The junction potential can not be measured directly but calculated from the difference between the electromotive force of a concentration cell with transference and without transference. The symbol  $\Delta^{\beta}_{\alpha}\Phi_i$  refers to the galvanic potential produced across the membrane and it is depends on the ion concentration in the solution.

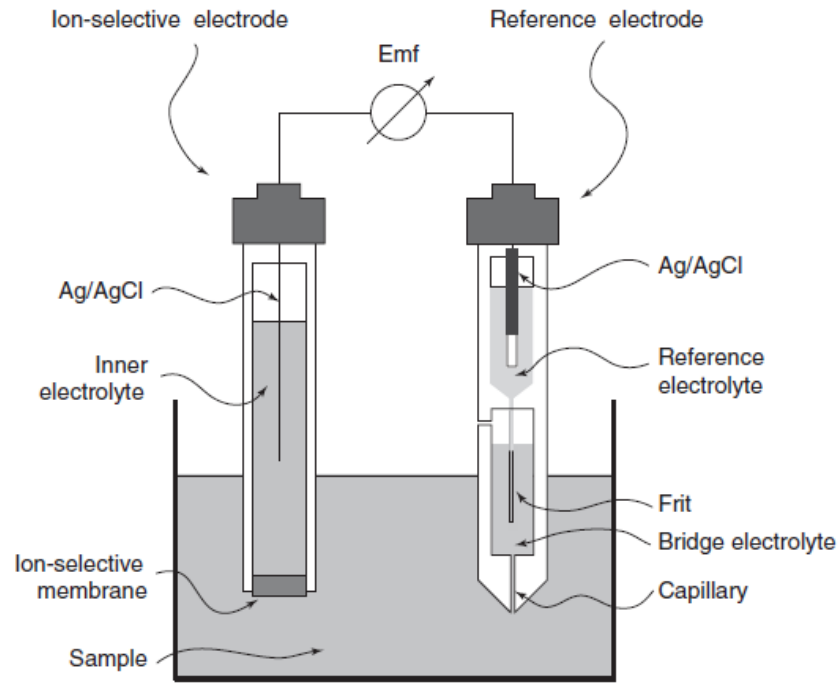


Figure 2.1: Experimental setup for ion-selective electrodes.

If all potentials except the membrane potential are kept constant, the Nikolskii-Eisenman equation (Eisenman et al., 1957) holds true:

$$E = E_0 + \frac{RT}{z_i F} \ln (a_i + k_{ij}^{\text{pot}} a_j^{z_i/z_j}) \quad (2.2)$$

where  $RT/F$  is the Nernstian factor,  $z_i$  and  $z_j$  are the charges and  $a_i$  and  $a_j$  are the activities of the ion of interest and interfering ion, respectively,  $k_{ij}^{\text{pot}}$  is the potentiometric selectivity coefficient, and  $E_0$  is a constant that includes the standard potential of the electrode, the reference electrode potential, and the junction potential. The nomenclature used in describing ion selective electrodes is in accordance with the appropriate international convention (Irving et al., 1978, IUPAC, 1976). In practice, one chooses an electrode with a very small  $k_{ij}^{\text{pot}}$  value or chemically removes interfering ions when they constitute a significant problem.

According to the IUPAC recommendation, the essential properties of an ion-selective electrode are characterized by such parameters as the detection limit, linear response



range, and sensitivity, which are obtained by calibrating the electrode over a large concentration range.

Detection limit: According to the IUPAC recommendation (IUPAC, 1976), the detection limit of an ion selective electrode is the lowest concentration that can be detected by the method. It can be calculated using the cross point method of the two extrapolated linear sections of the ion selective calibration curve. The observed detection limit is often governed by the presence of other interfering ions or impurities in the solution. A typical calibration plot is shown in Fig. 2.2.

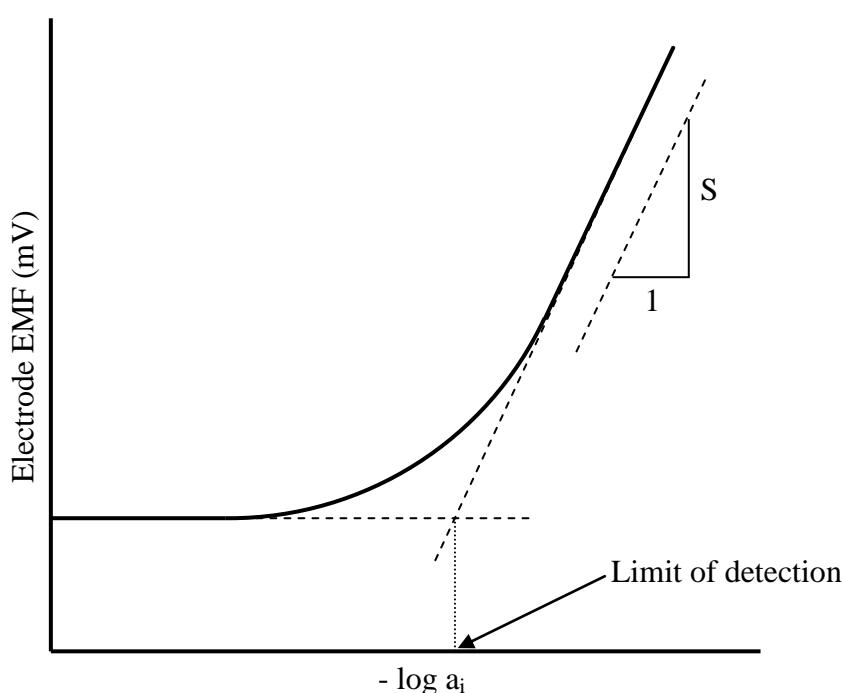


Figure 2.2 : Typical response plot of an ion selective sensor. (IUPAC, 1976)

Response time: The IUPAC definition of the response time has changed over time (IUPAC, 1976, Couto and Montenegro, 2000, Buck and Cosofret, 1993, Buck and Lindner, 1994). According to the original IUPAC recommendations, the response time was defined as the time between the addition of the analyte to the sample solution and the time at which the limiting potential was reached (Buck and Lindner, 1994). Fig. 2.3 illustrates the typical response time  $t_R$  ( $\Delta E/\Delta t$ ).

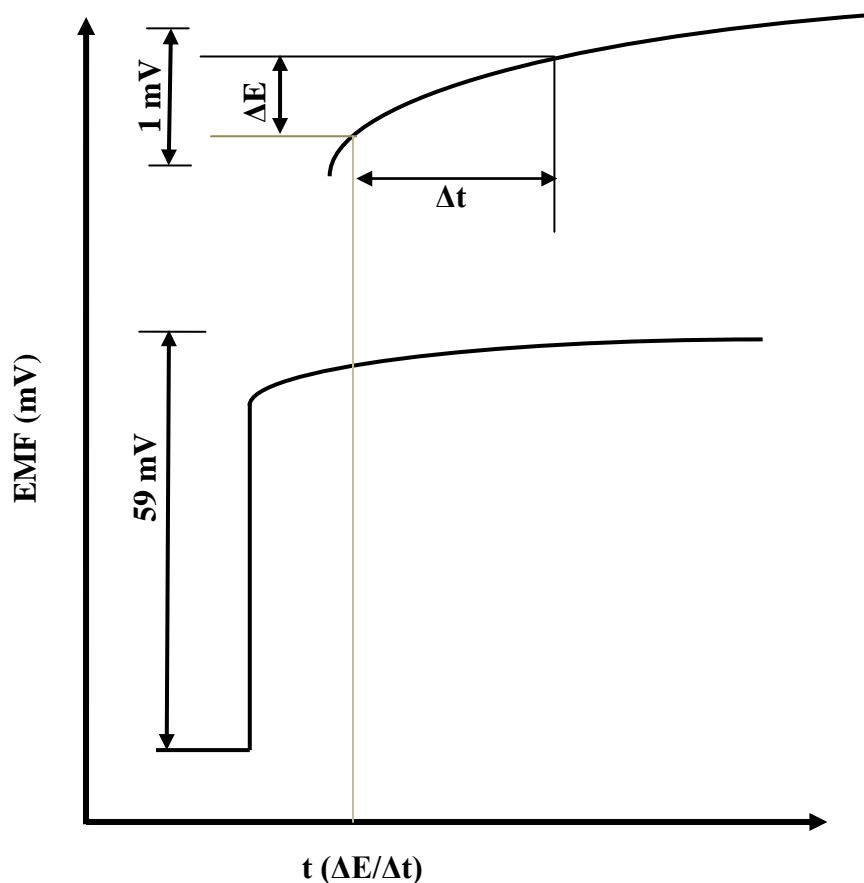


Figure 2.3 : Typical response time. (Buck and Lindner, 1994)

Selectivity: Selectivity is one of the most important characteristics of an ion selective electrode. Selectivity is defined as the ability of the ISE to distinguish the ion of interest from interfering ions and is measured in terms of the selectivity coefficient. The selectivity coefficients were established and first published in 1976 (IUPAC, 1976) and updated in 2000 (Burnett et al., 2000). Various methods have been used to determine selectivities. The IUPAC suggests two methods, the fixed interference method (FIM) and the separate solution method (SSM). There are also alternative methods, such as the matched potential method (MPM).

The matched potential method does not depend on the Nicolsky–Eisenman equation at all. In this method, the potentiometric selectivity coefficient is defined as the activity ratio of primary and interfering ions that give the same potential change under identical conditions. Fig. 2.4 illustrates the typical ion selective sensor response plot.

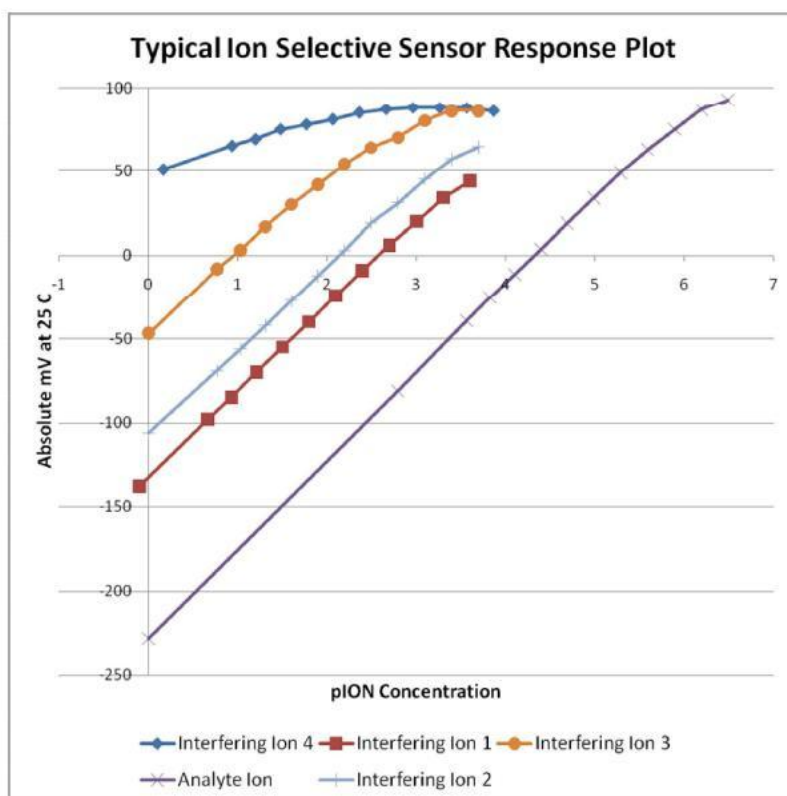


Figure 2.4 : Typical ion selective sensor response plot. (Patko, 2009)

Sensor selectivity improvement is often desired for specific applications. While the progress in the design of new highly selective ionophores for ISEs is discussed below, the focus of this section will be selectivity as a sensor characteristic, methods of its determination, and general approaches to its improvement. Unfortunately, there are large discrepancies in the selectivity data, published over decades, mainly because of the use of inappropriate methods for selectivity determination.

Slope: According to the Nernst equation, the theoretical value of the slope of the linear part of the measured calibration curve of the electrode:  $59.16 \text{ [mV/log}(a_x)]$  at 298 K for a singly charged ion or  $59.16/2 = 29.58 \text{ [mV per decade]}$  for a doubly charged ion. A useful slope can be regarded as 50-60 [mV per decade] or 25-30 [mV per decade] for singly or doubly charged ions, respectively. However, in certain applications, the value of the electrode slope is not crucial and a poor value does not exclude its usefulness.

### **2.3 Classical ion selective electrodes and some advances in their investigation of heavy metals**

Ion selective electrodes are electroanalytical sensors with a membrane whose potentials reflect the activity of the ion to be determined in solution. Ion-selective electrodes can be classified according to electrode type and composition: glass, solid state, liquid membrane, enzyme substrate, gas-sensing, bacterial, etc. (Morf, 1981). Among these categories, this work will focus on liquid membrane electrodes, which are widely used in many applications.

Liquid membrane electrodes are based on water-immiscible liquid substances impregnated in a polymeric membrane. Membrane-active recognition can be achieved by a liquid ion exchanger or a ligand that forms a complex with the target metal ion.

A number of liquid membrane electrodes based on conventional polymeric membranes, coated wires, and carbon paste electrodes utilizing various neutral ionophores have been created for the determination of metal ions. Conventional polymeric membrane ISEs have high detection limits due to the leaching of primary ions from the inner filling solution due to the inner side's rather concentrated solution of the primary ion.

Considering these limitations, most of ISEs mentioned in Tables 2.1 and 2.2 lack the sensitivity and selectivity required for the determination of trace concentrations of heavy metals. Among the different types of modified electrodes, the chemically modified carbon paste electrode is the most scrutinized one. Carbon paste electrodes offer very attractive properties for the electrochemical investigation of heavy metals over polymeric membranes and coated-wire electrodes.

### **2.3.1 PVC ion Selective electrodes**

An example of a liquid membrane electrode is the conventional PVC membrane electrode. PVC has attracted much attention as the principal for making conventional liquid membranes and has been used in ISEs based on valinomycin (Ammann et al., 1983) and other neutral carrier sensors (Bakker and Chumbimuni-Torres, 2008, Kharitonov, 2006, Attas, 2009, Abu-Shawish et al., 2009). Indeed, the PVC matrix concept was the essential breakthrough that led to the almost universal clinical use of ISEs for determining electrolytes among other applications.

Ion-selective electrodes based on macrocyclic ligands are extensively used for the determination of many heavy metal ions (Umezawa, 1990, Janata et al., 1998, Janata et al., 1994). Macrocyclic ligands have some desirable characteristics, such as being lipophilic, uncharged, and promoting cation transfer between the solution and the membrane by carrier translocation. The selection of macrocyclic ligands for ion sensing can be determined by structural studies on the interaction between ligands and ions. Thus, macrocyclic compounds have attracted widespread attention because of the unique properties of these types of compounds (Janata et al., 1998, Janata et al., 1994, Shih, 1992, Izatt et al., 1985, Izatt et al., 1991).

A large number of macrocyclic ligands have been synthesized in various shapes and sizes and used in the fabrication of poly(vinyl chloride) (PVC) membrane electrodes for the determination of heavy metal ions (Brzozka, 1988, Amini et al., 1999, Shamsipur et al., 1999).

Table 2.1 illustrates the linear range, detection limit, slope, response time, and applications of several reported PVC ion-selective electrodes for the detection of some heavy metals.

**Table 2.1** : Several PVC ion selective electrodes for determination of some heavy metals and their applications.

<i>Metal ions</i>	<i>Ionophore</i>	<i>Slope (mV/decade)</i>	<i>Detection limit (M)</i>	<i>Response time (s)</i>	<i>Applications</i>	<i>Reference</i>
Cu <sup>2+</sup>	2,2-[1,2-ethandiyl bis(nitrilomethylidene)-bis]cresole	29.2±0.3	3.6×10 <sup>-6</sup> M	<10	determination of copper in brass and urine	( <i>Fakhari et al., 2005</i> )
Cu <sup>2+</sup>	Bis(2-hydroxyacetophenone)butane-2,3-dihydrazone	29.6	3.0 × 10 <sup>-8</sup>	<15	determination of Cu <sup>2+</sup> in drinking and river water samples	( <i>Gholivand et al., 2007</i> )
Co <sup>2+</sup>	5-amino-3-methylisothiazole	29.5±0.2	3.9×10 <sup>-7</sup>	12	Determination of Co <sup>2+</sup> in real samples	( <i>Singh et al., 2007</i> )
Ni <sup>2+</sup>	N,N-bis-(4-dimethylamino-benzylidene)-benzene-1,2-diamine	30.0±1.0	(8.0±1.0) × 10 <sup>-8</sup>	<10	determination of Ni <sup>2+</sup> in water samples	( <i>Mashhadizadeh et al., 2003</i> )
Ni <sup>2+</sup>	Tetraazamacrocyclic	29.5	2.98 × 10 <sup>-6</sup>	8	Determination of Ni <sup>2+</sup> in chocolates samples	( <i>Singh and Saxena, 2007</i> )

**Table 2.1, continued**

<i>Metal ions</i>	<i>Ionophore</i>	<i>Slope (mV/decade)</i>	<i>Detection limit (M)</i>	<i>Response time (s)</i>	<i>Applications</i>	<i>Reference</i>
Cr <sup>3+</sup>	4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one	19.7 ± 0.3	5.8 × 10 <sup>-7</sup>	<10	determination of Cr(III) in wastewaters of chromium electroplating industries	(Zamani et al., 2006)
Cr <sup>3+</sup>	Tri- <i>o</i> -thymotide	20.0 ± 0.1	2.0 × 10 <sup>-7</sup>	15	determine Cr(III) quantitatively in electroplating industry waste samples	(Gupta et al., 2006b)
Co <sup>2+</sup>	18-membered macrocyclic diamide	29.5	6.0 × 10 <sup>-7</sup> M	10	Determination of Co <sup>2+</sup> in wastewater samples	(Shamsipur et al., 2001)
Pb <sup>2+</sup>	1,3-bis(N-furoylthioureido)benzene	30.0 ± 1.3	1.9 × 10 <sup>-6</sup> M	14	determination of lead in soils	(Wilsona et al., 2010)
Pb <sup>2+</sup>	Pyridine carboximide derivatives	26.0 – 33.1	4 × 10 <sup>-7</sup>	~ 20 – 30	assay of lead in rocks	(Hassan et al., 2003)



**Table 2.1, continued**

<i>Metal ions</i>	<i>Ionophore</i>	<i>Slope (mV/decade)</i>	<i>Detection limit (M)</i>	<i>Response time (s)</i>	<i>Applications</i>	<i>Reference</i>
Hg <sup>2+</sup>	Nylon-6,6 Sn(IV) phosphate	28.09	$1 \times 10^{-7}$	40	measurements of Hg <sup>2+</sup> in the drain water	<i>(Khan and Akhtar, 2009)</i>
Hg <sup>2+</sup>	1,3-bis(2-methoxybenzene)triazene	$30.2 \pm 0.3$	$5.0 \times 10^{-8}$	15	determination of Hg <sup>2+</sup> in water samples	<i>(Rofouei et al., 2009)</i>
Hg <sup>2+</sup>	4-(4-Methoxybenzilidenimin) Thiophenole	$29.24 \pm 0.82$	$8 \times 10^{-7}$	$\leq 10$	Determination of Hg <sup>2+</sup> in soil sample	<i>(Ghaedi et al., 2006)</i>
Cd <sup>2+</sup>	Tetrathia-12-crown-4	$29 \pm 1$	$1.0 \times 10^{-7}$ M	<10 s	determination of Cd <sup>2+</sup> in different water samples	<i>(Shamsipur and Mashhadizadeh, 2001)</i>
Cd <sup>2+</sup>	N,N,N',N'-Tetradodecyl-3,6-dioxaoctanedithioamide	32	$1.0 \times 10^{-8}$	4 hours	determination of Cd <sup>2+</sup> in Yeast and Arabidopsis cell	<i>(Plaza et al., 2005)</i>

### 2.3.2 Coated-wire ion selective electrodes

Coated-wire ion selective electrodes were first developed in 1971; these first electrodes were based on the  $\text{Ca}^{2+}$  - didecylphosphate/dioctylphenyl phosphonate system (Cattrall and Freiser, 1971) and comprised of PVC film or another suitable polymeric matrix substrate containing dissolved electroactive species coated on a conducting substrate (generally a metal, although any material whose conductivity is substantially higher than that of the film can be used). Electrodes of this sort are simple, inexpensive, durable, and reliable in the concentration range of  $10^{-1}$  M to  $10^{-6}$  M for a wide variety of both organic and inorganic cations and anions.

Coated-wire electrodes (CWEs) refer to a type of ISEs in which an electroactive species is incorporated into a thin polymeric support film coated directly on a metallic wire conductor (Al-Saraj et al., 2003, Ibrahim et al., 2007). Different materials can serve as central conductors. An extensive study (Cattrall and Freiser, 1971) revealed that the wire support did not react with the membrane component but had no substantial influence on the potentiometric response of the electrode. The substrate in the wire-type electrode is usually platinum wire, but silver, copper, and graphite wires have also been used. CWEs are prepared simply by dipping the central conductor into a solution containing the dissolved polymer, plasticizer, and electroactive substance and then allowing the solvent to evaporate. CWEs sometimes exhibit better selectivity than conventional electrodes with an internal solution. Their simple designs, low cost, mechanical flexibility of miniaturization, and microfabrication have widened the ranges of applications for wire-type electrodes, especially in the field of medicine and environmental studies (Cunningham and Freiser, 1986, Freiser, 1986, James et al., 1972).

Over the course of the study of coated wire electrodes the list of analyte species has been expanded to include not only most inorganic ions commonly of interest but also organic species that are anionic or cationic under appropriate solution conditions. Table 2.2 describes some coated wire ion selective electrodes used for the determination of heavy metals and their applications.

**Table 2.2 :** Several coated-wire ion selective electrodes used for the determination of some heavy metals and their applications.

<i>Metal ions</i>	<i>Ionophore</i>	<i>Slope (mV/decade)</i>	<i>Detection limit (M)</i>	<i>Response time (s)</i>	<i>Applications</i>	<i>References</i>
Cu <sup>2+</sup>	1,8-bis(2-Hydroxynaphthaldiminato)3,6-Dioxaoctane	29.0± 0.5	1.0 × 10 <sup>-6</sup>	10-15	Determination of copper in rock and wastewater samples	(Ardakani et al., 2006)
Cu <sup>2+</sup>	Thiosemicarbazone	29.2	3.0×10 <sup>-6</sup>	10–50	Determination of copper in real samples	(Ardakani et al., 2004)
Pb <sup>2+</sup>	N,N'-bis(3-methyl salicylidine)-p-phenyl methane diamine	30.3 ± 0.6	2.0 x 10 <sup>-5</sup>	<15	Lead determination in mineral rocks and wastewater	(Mazlum et al., 2003)
Pb <sup>2+</sup>	2-(2-ethanoloxymethyl)-1-hydroxy-9,10-anthraquinone	29± 0.2	8.0 x 10 <sup>-8</sup>	~10	Determination of lead in spring water samples	(Riahi et al., 2003)
Co <sup>2+</sup>	2,3,4:9,10,11-dipyridine-1,5,8,12-tetramethylacrylate-1,3,5,8,10,12-hexaazacyclotetradeca-2,9-diene	29.5	6.8×10 <sup>-9</sup>	8	determination of Co <sup>2+</sup> in real and pharmaceutical samples	(Singh et al., 2009)

**Table 2.2, continued**

<i>Metal ions</i>	<i>Ionophore</i>	<i>Slope (mV/decade)</i>	<i>Detection limit (M)</i>	<i>Response time (s)</i>	<i>Applications</i>	<i>Reference</i>
Cd <sup>2+</sup>	cetylpyridinium–tetraiodocadmate	29.8	$6 \times 10^{-7}$	3	Determination of cadmium in some alloys and polluted water	( <i>Abbas and Zahran, 2005</i> )
Cd <sup>2+</sup>	Orion cadmium ion-selective electrode model 94-48A	29.3	$1.5 \times 10^{-6}$	1	Determination of cadmium in natural water.	( <i>Trojanowicz et al., 1998</i> )
Cr <sup>3+</sup>	tricaprylmethylammonium (Aliquat 336)	18.7±0.5	$2.1 \times 10^{-6}$	<5	chromium(III) determination in some food materials and various types of plants	( <i>Khalil et al., 2004</i> )
Ni <sup>2+</sup>	benzylbis(thiosemicarbazone)	29.0±0.5	$4.0 \times 10^{-8}$	~15	determination of Ni <sup>2+</sup> in edible oil and wastewater of electroplating samples	( <i>Ganjali et al., 2002</i> )

### 2.3.3 Carbon-paste ion selective electrodes

Carbon paste electrodes are well known, useful materials for potentiometric sensors. Adams was the first to use a carbon paste electrode, demonstrating the concept of a paste comprised of carbon particles and organic liquid (Adams, 1958). His discovery was overlooked by other investigators until Kuwana et al. in 1964 performed research making the first contribution to the advancement of chemically modified carbon-paste electrodes, which are described in the reviews of Kalcher (Kalcher, 1990, Kalcher et al., 1995). Carbon-paste electrodes are ion-selective electrodes composed of a carbon powder and ionophore mixed with a pasting liquid (an organic binder). In comparison with ion selective electrodes, which are based on polymeric membranes, carbon paste electrodes are inexpensive, easier to prepare and use, renewable, chemically inert and do not require internal solution, provide high response stability and low ohmic resistance ( $<10\Omega$ ), and are suitable for a variety of sensing and detection applications. In recent years, these advantages have been exploited for various measurements including potentiometric measurements (Kalcher et al., 1995, Arrigan, 1994).

Carbon paste electrodes (CPEs) are especially useful for the detection of heavy metals and organic compounds in controlling the level of pollutants in medical and environmental samples.

Carbon is a very important electrode material and is widely used due to its low cost, easy functionalisation, great versatility, broad potential window, and chemical inertness. Various forms of carbon, such as glassy carbon, impregnated graphite, carbon fibres, carbon films, carbon nanotubes, and activated carbon, could be used as electrode materials. Palm shell, a waste product of palm kernel oil production, represents an important group of carbonaceous materials with unique mechanical, physical, and electrochemical properties.

The ionophore for the determination of metal cations is usually an organic polymer (Abu-Shawish, 2008, Abu-Shawish et al., 2008), complexing agent (Abu-Shawish, 2009, Svancara et al., 2001, Molina-Holgado et al., 1995), ion exchanger (Lu et al., 2000, Mousavi et al., 2001), crown ether (Agraz et al., 1991, Walcarius, 1999) or mineral (Navratilova and Kula, 2000, Kula and Navratilova, 1996, Kula et al., 1999, Walcarius, 1996). Typically, the ionophore is directly embedded in the paste of the electrode, which consists of a mixture of graphite and liquid binder.

Table 2.3 shows some applications of carbon paste ion selective electrodes for potentiometric measurements of heavy metals.

**Table 2.3** : Several carbon paste ion selective electrodes for determination of some heavy metals and their applications.

<i>Metal ions</i>	<i>Ionophore</i>	<i>Slope (mV/decade)</i>	<i>Detection limit (M)</i>	<i>Response time (s)</i>	<i>Applications</i>	<i>References</i>
Cu <sup>2+</sup>	2-mercapto-5-(1-methyl-5-nitroimidazole-2-yl)-1,3,4-thiadiazole	31.0±0.5	3.5 (±0.2)×10 <sup>-9</sup>	~5	Determination of Cu(II) ion in hair and water samples	(Mashhadizadeh et al., 2008a)
Cu <sup>2+</sup>	2-mercapto-5-(5-nitrofuran-2-yl)-1,3,4-thiadiazole	31.0±0.5	4.1×10 <sup>-9</sup>	~5	Determination of Cu(II) ion in hair and water samples	(Mashhadizadeh et al., 2008a)
Cu <sup>2+</sup>	2-mercapto-5-(5-nitrothiophen-2-yl)-1,3,4-thiadiazole	31.0±0.5	4.1×10 <sup>-8</sup>	~5	Determination of Cu(II) ion in hair and water samples	(Mashhadizadeh et al., 2008a)
Cu <sup>2+</sup>	5-(pyridin-2-ylmethyleneamino)-1,3,4-thiadiazole-2-thiol	28.7±0.3	1.0×10 <sup>-9</sup>	<5	Determination of Cu <sup>2+</sup> ions in spiked and natural water	(Mashhadizadeh et al., 2010)



**Table 2.3, continued**

<i>Metal ions</i>	<i>Ionophore</i>	<i>Slope (mV/decade)</i>	<i>Detection limit (M)</i>	<i>Response time (s)</i>	<i>Applications</i>	<i>Reference</i>
Cu <sup>2+</sup>	3,4-dihydro-4,4,6-trimethyl-2(1H)-pyrimidine thione	30±2	7.0×10 <sup>-7</sup>	~45	Determination of Cu <sup>2+</sup> in electronics waste sample	( <i>Abbaspour and Moosavi, 2002</i> )
Cu <sup>2+</sup>	Tetraethyl thiuram disulfide	43.1	4.0×10 <sup>-8</sup>	3.4	Determination of Cu <sup>2+</sup> in lubricant oil wastes	( <i>Gismera et al., 2004</i> )
Cu <sup>2+</sup>	silica gel with dipyridyl group	28.4 (±1.0)	8.0 × 10 <sup>-8</sup>	~50	Determination of copper in waste water	( <i>Javanbakht et al., 2007</i> )
Cr <sup>3+</sup>	1-[(2-hydroxy ethyl) amino]-4-methyl-9H-thioxanthen-9-one	20.51	1.6 × 10 <sup>-7</sup>	~8	Determination of Cr <sup>3+</sup> ion in various real samples	( <i>Ghaedi et al., 2010</i> )
Cr <sup>3+</sup>	2-acetylpyridine and nanoporous silica gel	19.8 ± 0.2	8.0 × 10 <sup>-9</sup>	~55	Determination of Cr(III) in food samples	( <i>Zhou et al., 2009</i> )

**Table 2.3, continued**

<i>Metal ions</i>	<i>Ionophore</i>	<i>Slope (mV/decade)</i>	<i>Detection limit (M)</i>	<i>Response time (s)</i>	<i>Applications</i>	<i>Reference</i>
Co <sup>2+</sup>	Cyclam	28.4	2.5×10 <sup>-6</sup>	~8 s	Determination of cobalt (II) ions in wastewater of acidic cobalt electroplating bath	<i>(Pouretedal and Keshavarz, 2005)</i>
Hg <sup>2+</sup>	tetrazolium–triiodomercurate	55.5±0.4	4×10 <sup>-6</sup>	30-50s	Determination of Hg <sup>2+</sup> in spiked wastewater, metal amalgams and dental alloy	<i>(Abbas and Mostafa, 2003)</i>
Hg <sup>2+</sup>	Ethyl-2-(benzoylamino)-3-(2-hydroxy-4-methoxyphenyl)-2-propenoate	48.5±1.0	1.0×10 <sup>-7</sup>	~5s	Determination of mercury in spiked wastewater and an amalgam sample gave	<i>(Mashhadizadeh et al., 2006)</i>

**Table 2.3, continued**

<i>Metal ions</i>	<i>Ionophore</i>	<i>Slope (mV/decade)</i>	<i>Detection limit (M)</i>	<i>Response time (s)</i>	<i>Applications</i>	<i>Reference</i>
Hg <sup>2+</sup>	Substituted thiourea	28.4 ± 1.0	7.0 × 10 <sup>-8</sup>	~35s	Monitor the mercury(II) ion concentration in waste water and fish samples	( <i>Javanbakht et al., 2009</i> )
Cd <sup>2+</sup>	3,5-dinitro-N-(tri-2-pyridyl methyl) benzamide	30 ± 1	1.82 × 10 <sup>-7</sup>	~50s	Determination of Cd(II) in well water	( <i>Abbastabar-Ahangar et al., 2009</i> )
Pb <sup>2+</sup>	Dithiodibenzoic (DTB) acid	21.8	5.01 × 10 <sup>-8</sup>	40s	Determination of lead in solder alloys	( <i>Gismera et al., 2006</i> )
Cd <sup>2+</sup>	2-mercapto-5-(3-nitrophenyl)-1,3,4-thiadiazole	29.4±1.0	2.0×10 <sup>-8</sup>	~6s	Detect Cd(II) ion in hair and water samples	( <i>Mashhadizadeh et al., 2008b</i> )
Cu <sup>2+</sup>	5,8-dihydroxy-1,4-naphthoquinone	-	1.5 x 10 <sup>-6</sup>	50 s	Determination of Cu(II) in metal alloys	( <i>Chaisuksant et al., 2008</i> )

**Table 2.3, continued**

<i>Metal ions</i>	<i>Ionophore</i>	<i>Slope (mV/decade)</i>	<i>Detection limit (M)</i>	<i>Response time (s)</i>	<i>Applications</i>	<i>Reference</i>
Cr <sup>3+</sup>	2-hydroxy-3-methoxy-benzaldehyde-hydrazine-carbothioamide	27.82	$1.26 \times 10^{-6}$	< 30 s	Determine the chromium contents in the wastewater	<i>(Cui et al., 2009)</i>
Hg <sup>2+</sup>	Cyclodextrins	20	$0.9 \times 10^{-7}$	20 s	Determination of mercury in HClO <sub>4</sub> media	<i>(Roa-Morales et al., 2005)</i>
Pb <sup>2+</sup>	Thiram	29.8 (±0.2)	$7.3 \times 10^{-8}$	10s	Determination of lead in waste water and black tea samples	<i>(Ganjali et al., 2010)</i>

## **2.4 New trends in the preparation of chemically modified ion selective electrodes.**

Potentiometric sensor technology is still limited in scope and thus cannot address all environmental monitoring needs. Nevertheless, vast arrays of potentiometric sensors have been applied in recent years to monitor a wide range of inorganic and organic pollutants.

Most of the potentiometric sensors originated in the early 1960s, completely replacing older analytical methods in various analytical applications and gaining a foothold in environmental chemistry. Most of the advantages of solid state ISEs, such as robustness and cost effectiveness, are also found in their polymeric counterparts, but the unique versatile matrix allows a significant increase in the number of available analytes. Indeed, the list of detectible analytes is extremely long, today approaching 100 species, a number far beyond that of numerous other analytical techniques (Bühlmann et al., 1998, Bakker et al., 1999). The extraordinary measuring range of ISEs (in some cases, exceeding eight orders of magnitude in concentration) is also an important intrinsic property of this analytical method. Note that these properties are complemented by their simplicity, a distinct advantage of ISEs. Here, the focus will be on the modern directions of sensor research. The great success of ISEs achieved during the past decades has not reverted the field into a stagnating mature discipline rather; there are several dynamically developing research directions that continue to tempt the analytical chemistry community, opening new horizons.

### **2.4.1 Electrode materials and performance optimization**

Generally, ion-selective electrodes are made of a plasticized matrix, a highly lipophilic ionophore or ion-carrier, and lipophilic ionic sites. Each component is critical to the performance of the electrode. Adjusting the membrane composition is key to obtaining enhanced analytical responses and superior electrode selectivities. Additionally, the membrane components must have adequate lipophilicity such that each component is

retained in the membrane phase for sufficiently long times. The immobilization of ionophores and ionic sites in the electrodes can completely eliminate leaching effects (Rosatzin et al., 1992). In this respect, considerable efforts have been undertaken to produce electrode systems with longer lifetimes (Puntener et al., 2002, Reinhoudt et al., 1994). For many years, the plasticizers applied in potentiometric sensors have been organic solvents, such as bis(2-ethylhexyl) phthalate, bis(2-ethylhexyl) sebacate, and 2-nitrophenyl octyl ether, originating from the plastic industry (Murphy, 2001). In recent years, novel materials have been developed for making electrodes without any plasticizer.(Heng, 2000, Heng and Hall, 2001, Qin et al., 2002).

The application of plasticizer-free electrodes can eliminate the leaching of the electrode solvent and sensing components, improving the lifetime of the sensor. However, the diffusion coefficient of a plasticizer-free electrode is approximately two orders of magnitude smaller than that of a plasticized electrode (Michalska et al., 2004, Long and Bakker, 2004), which may lead to longer response times for the former, especially for bulk optodes.

Ionic liquids (ILs) are molten salts with melting points close to or below room temperature. They are composed of two asymmetrical ions of opposite charges that loosely fit together (usually bulky organic cations and smaller anions). The good solvating properties, high conductivity, non-volatility, low toxicity, large electrochemical window (i.e., the electrochemical potential range over which the electrolyte is neither reduced nor oxidized on the electrodes), and good electrochemical stability make ILs suitable for many electrochemical applications. Recently, novel ion selective sensors based on ILs have been developed (Hapiot and Lagrost, 2008).

The recent rise in the number of publications clearly indicates the scientific and engineering community's increasing interest in these exciting and unique solvents.

ILs are excellent materials for preparing membranes for ISEs due to their polymer plasticizing ability and ionic nature. Coll et al. (2005) reported a remarkable selective response to the highly hydrophilic sulphate anion using a hydrophobic IL ([BMIM][PF<sub>6</sub>]) to prepare the poly(vinyl chloride) (PVC) membranes used in anion selective electrodes (Coll et al., 2005). This property allows ILs to be used as ionic additives in conventional ISE membranes. The response to the target sulphate ions was, however, still generated by the ionophore, polyazacycloalkane. Recently, (Shvedene et al., 2006) has reported a method to use ILs in various polymer membranes, both as the plasticizer and the ion-responsive medium. 1-Butyl-2,3-dimethylimidazolium bis(trifluoro-methylsulphonyl)imide ([BDMIM][Tf<sub>2</sub>N]) and dodecylethyldiphenylphosphonium bis(trifluoro-methylsulphonyl)imide ([DEDPP][Tf<sub>2</sub>N]) were used to plasticize the PVC and poly(methyl methacrylate) (PMMA) membranes and to instill them with ion-selecting ability. Good and stable responses to (relatively hydrophobic) cations and anions were obtained with these electrodes, and they were also found to be suitable for analyzing surfactants compositions (Shvedene et al., 2006).

Room temperature ionic liquids (RTILs), based on imidazolium, pyridinium, and phosphonium cations, have been studied as an anion-exchangers and plasticizers for poly (vinyl chloride) (PVC)-based potentiometric ion-selective membranes (Peng et al., 2008).

#### **2.4.2 High performance carbon composite electrode using ionic liquids**

Carbon electrodes are widely used in electroanalytical investigations because of their chemical inertness, wide potential window, low background current, and suitability for different types of analysis. Carbon materials that have been widely used in the preparation of solid electrodes include glassy carbon, carbon fibres, carbon black, various forms of graphite (from graphite powder to the highly oriented pyrolytic graphite), activated carbon, and carbon nanotubes (Merkoci et al., 2005, Gooding, 2005, Gong et al., 2005, Rubianes and Rivas, 2003, Antiochia et al., 2004, Chicharro et al., 2005, Aroua et al., 2008, Issabayeva et al., 2006). Based on these varieties of carbon, several types of carbon electrodes that are suitable for electrochemical applications are available. Among these electrodes, carbon paste electrodes (CPE) are the most popular. Carbon paste electrodes (CPE) usually employ paraffin oils as non-electrolytic binders. These non-polar pasting liquids fulfill some of the important criteria for a suitable electrode, such as chemical inertness, insulating properties, non-volatility, and water immiscibility (Adams, 1958, Svancara et al., 2001, Rice et al., 1983). Another successful class of binders, liquid organophosphates, has the attractive property of high ion-pairing ability (Kalcher, 1990, Kalcher et al., 1995, Svancara et al., 1996, Svancara et al., 1998). However, they suffer from lower stability and rather atypical signal-to-noise characteristics requiring special pretreatment. A robust (solid phase) carbon paste electrode has been introduced by preparing the electrode using molten phenanthrene mixed with graphite. The mixture was then left to harden, and the paste was modified in situ after packing in a holder (Diewald et al., 1994).

Generally, organic liquids used as a paste binder component are non-conductive mineral oils, such as Nujol or paraffin. Due to its chemical inertness as well as good adhesive properties, this non-conductive viscous liquid is always preferred for the fabrication of traditional carbon paste electrodes. Nevertheless, mineral oil binders have two obvious



disadvantages. The first is that mineral oil is not component-fixed because it is the result of various petroleum refining and crude oil processing practices, and the unaccounted ingredients may have unpredictable effects on detection and analysis. The second disadvantage is that this binder is not conductive, which somewhat weakens the electrochemical response of CPE and is especially disadvantageous to trace detection. Therefore, the use of a considerably viscous simplex liquid with chemical inertness and electrochemical conductivity as a pasting binder may be an ideal alternative for improving paste electrodes (Liua et al., 2005, Ganjali et al., 2009).

A new strategy for the fabrication of a novel carbon ionic liquid electrode (CILE) based on the use of the pyridinium-based ionic liquid, n-octylpyridinium hexafluorophosphate, as a binder is presented by Maleki et al., 2006. This electrode not only provides a very low background, comparable to common carbon paste electrodes, but also has a surprisingly high electrochemical performance. This electrode combines many of the desirable features of previous variations of CPE, carbon nanotubes, and edge plane pyrolytic graphite electrodes. One of the important and potent characteristic of this electrode is its ability to lower the overpotential of electroactive compounds, particularly biomolecules and to increase the rate of electron transfer processes, which is attributed to the modification of the microstructure of the electrode surface by the ionic liquid binder (Maleki et al., 2006).

(Safavi et al., 2007) constructed a potentiometric ion sensor based on a mixture of graphite powder and the ionic liquids N-octylpyridinium hexafluorophosphate [OPy][PF<sub>6</sub>] and [BMIM][PF<sub>6</sub>]. Because the electrode membranes do not include an ionophore, the electrode response is based solely on the partition of the ions between the aqueous phase and the electrode membrane. The selectivity of these sensors was not studied but is assumed to be low.

Recently, carbon nanotubes (CNTs) have also been used in carbon paste electrodes (Rezaei and Damiri, 2008, Siswana et al., 2008, Li et al., 2008). CNTs have very interesting physicochemical properties, such as an ordered structure with a high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior, and high surface area (Ajayan, 1999). The combination of these characteristics makes CNTs unique materials with the potential for diverse applications (Kostarelos et al., 2007, Lacerda et al., 2006, Lacerda et al., 2005, Singh et al., 2006).

A new type of carbon paste electrode composed of multi-walled carbon nanotubes (MWCNTs) and ionic liquid was prepared for investigation of Hg(II) (Khani et al., 2010). Using MWCNTs and displacement of paraffin oil with [BMIM][BF<sub>4</sub>] greatly enhanced the potentiometric sensitivity and provided good reproducibility, low response time, and long-term stability. Thus, the combination of MWCNTs with ionic liquid in the presence of 1-(2-ethoxyphenyl)-3-(3-nitrophenyl)triazene provides a promising carbon paste matrix in the potentiometric sensing of Hg(II).

## **2.5 Conclusion**

Based on the information presented above, two brief conclusions can be made herein. First, the boom in electrochemistry with carbon pastes has led to the rise of a new family of carbon paste electrodes based on ionic liquids. Pioneering attempts with carbon paste electrodes based on ionic liquid were initiated ten years ago. Second, despite their easy fabrication, simple usage, wide applicable concentration range, and low cost, ISEs still suffer from long response times, low response sensitivities, interference by a number of ions, long equilibration times, and short lifetimes. As a result, investigating new materials to develop ISEs that can address some of these limitations is a worthwhile and challenging topic of research. In this study, a combination of activated carbon with task specific ionic liquids has resulted in a unique new generation paste, in which traditional components are replaced with alternative materials. The proposed electrodes showed improved performance characteristics relative to conventional electrodes. This improvement presumably originates from the electrode composition. The manipulation of the electrode composition can improve the sensitivity and selectivity of the detection of some heavy metals in aqueous solution. The ultimate goals of this area of research are to enhance the sensitivity and selectivity of the proposed electrodes by minimizing the previously mentioned undesirable electrode processes. Additionally, the application of plasticizer-free electrodes can eliminate the leaching of the electrode solvent and sensing components, improving the electrode lifetime.

## **CHAPTER 3: METHODOLOGY**

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## CHAPTER 3

### METHODOLOGY

In this study, different types of ion-selective electrodes will be constructed and used for the determination of cadmium and mercury ions. Chemically modified palm shell activated carbon paste electrodes will be used to achieve this goal.

#### 3.1 Chemicals and reagents

Analytical reagent grade chemicals and distilled, de-ionized water were used to prepare all aqueous solutions. Commercially available granular palm shell activated carbon (PSAC) was provided by Bravo Green Sdn Bhd, Malaysia. Activated carbon powder with particle sizes  $<40\mu\text{m}$  were used throughout the potentiometric experiments. For kinetic studies, granular activated carbon was sieved to three series with particle size ranging from 0.50 to 0.60, 0.60 to 0.85, and 1.4 to 1.7 mm; washed with distilled water to remove fines and dirt; and dried in an oven at  $110\text{ }^{\circ}\text{C}$  for 24 h. The pH of the solutions was adjusted by adding appropriate amounts of concentrated hydrochloric acid (1M HCl) and/or sodium hydroxide (2M NaOH).

Metal salts were purchased from Merck, and aqueous metal solutions were prepared by dissolving appropriate quantities of metal salts in de-ionized water. Sodium salicylate was purchased from R&M chemicals. Trioctylmethylammonium chloride (Aliquat® 336), trioctylmethylammonium thiosalicylate (TOMATS) and 2-nitrophenyl octyl ether (NPOE) were purchased from Sigma-Aldrich. The plasticizers bis(2-ethylhexyl)adipate (DOA), bis(2-ethylhexyl) phthalate (DOP), tris(2-ethylhexyl) phosphate (TOPh), bis(2-ethylhexyl) sebacate (DOS), butyl phosphate (BPh), dibutyl phosphate (DBPh), and tributyl phosphate (TBPh) were purchased from Merck.

### 3.2 Apparatus

All potentiometric measurements were made using a pH/ion meter (Metrohm-781, Germany) and pH Module (Metrohm-867), permitting real-time potential data collection using the proposed electrode in conjunction with a double junction Ag/AgCl reference electrode (Fig. 3.1). The temperature of the cell holder was maintained at 25 °C and measured under constant stirring with a magnetic stirring bar at a rate such that no bubbles or vortexes were formed.

The electrochemical cell used in this study was constructed are follows:

$\text{Ag(s),AgCl(s)} \mid \text{KCl(3M sat.)} \parallel \text{Sample solution} \mid \text{modified palm shell activated carbon paste electrode.}$

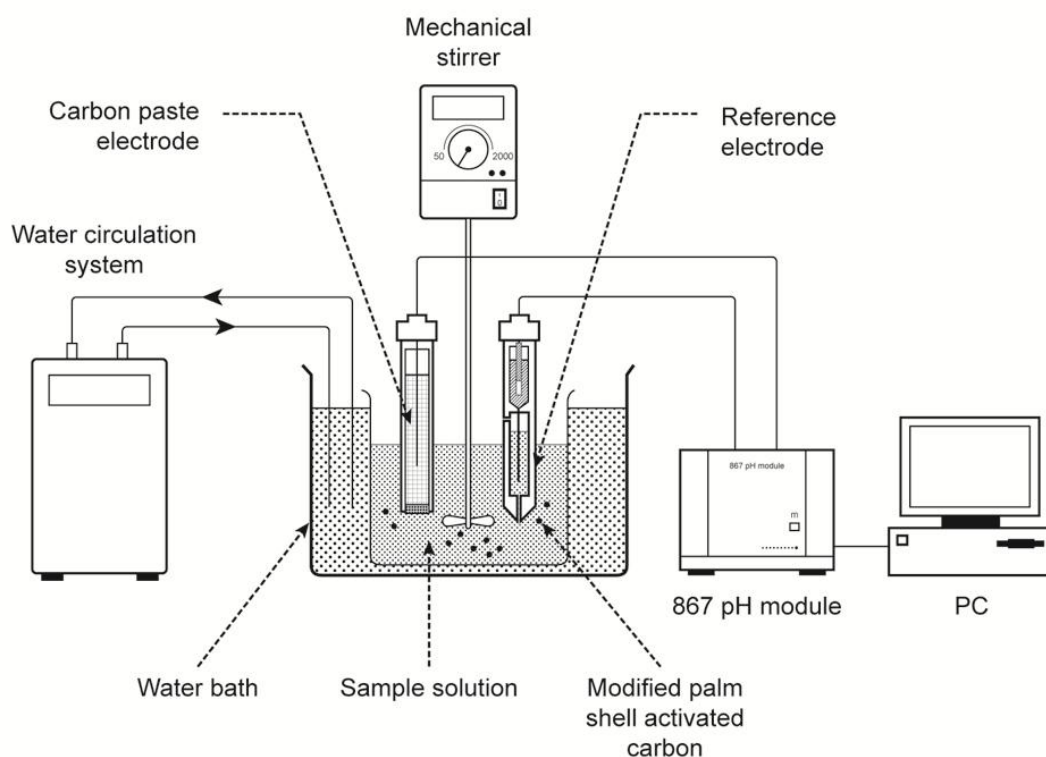


Figure 3.1 : Potentiometric experimental setup

The electrode surfaces morphology and elemental analysis of the palm shell activated carbon were obtained using field emission scanning electron microscope AURIGA cross beam workstation (Carl Zeiss) equipped with EDAX (AMETEK, advanced microanalysis solutions) at an accelerating voltage of 25 kV (Fig. 3.2).



Figure 3.2 : Photo of Scanning electron microscope AURIGA cross Beam Workstation (FESEM laboratory, Faculty of Engineering, University of Malaya) .

The BET surface area, pore size and total pore volume of palm shell activated carbon samples were determined using  $N_2$  adsorption at 77 K using a Micromeritics ASAP 2020 surface area and porosity analyzer as shown in Fig. 3.3. The weight of the samples was around 0.2 g. All the samples were degassed under vacuum at 120 °C for 12 h before nitrogen adsorption in a vacuum system at about 1 atm. The Micromeritics ASAP 2020 performs automated analysis. It is capable of performing simultaneously BET multi-point and single point surface area, Langmuir surface area, t-method micropore and BJH adsorption/desorption distribution.



Figure 3.3 : Micromeritics ASAP 2020 surface area and porosity analyzer

Metal ion sample concentration was analyzed by inductivity coupled plasma optical emission spectrometer ICP-OES. (PerkinElmer, model ICP optima 7000DV) (Fig. 3.4). Metal ions standards with concentration 1 ppm, 5 ppm, 10 ppm, 20 ppm, 40 ppm, 60 ppm, 100 ppm and, 200 ppm were used to calibrate the instrument each time before starting the analysis of the samples.

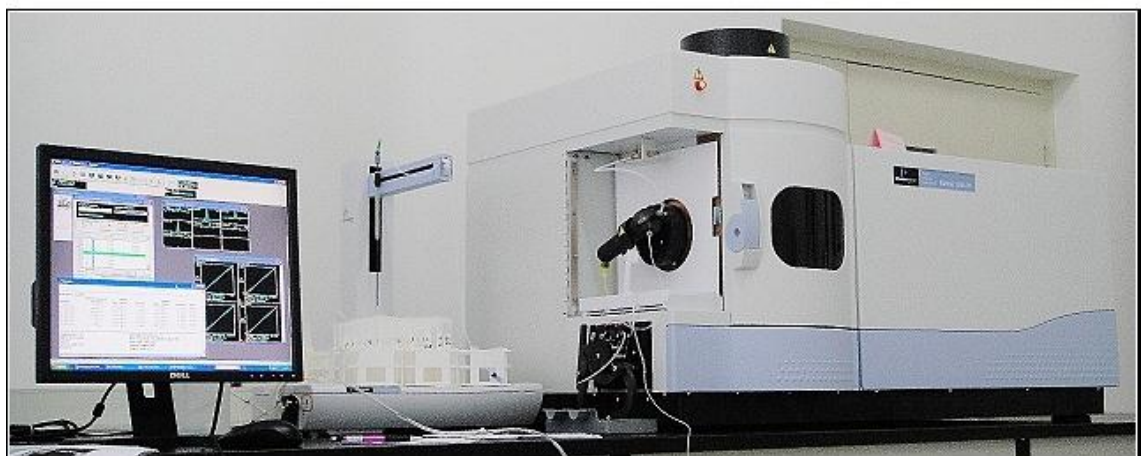


Figure 3.4 : Inductivity coupled plasma optical emission spectrometer ICP-OES.



### **3.3 Preparation of Palm Shell Activated Carbon**

The Activated Carbon used in the study was palm shell-based and produced by physical activation process with steam as the activating agent. It was supplied by one of Malaysian companies. Activated carbon was sieved into three series, with particle sizes that ranged from 0.50 to 0.60, 0.60 to 0.85 and 1.4 to 1.7 mm. Then washed with de-ionized water to remove fines and dirt, oven dried at 110 °C for a day, cooled in desiccators, stored in plastic containers and analyzed by using ASAP 2020 and SEM.

### **3.4 Modified palm shell activated carbon paste based on trioctylmethylammonium salicylate (TOMAS) selective electrode for Cd(II) determination.**

#### **3.4.1 Preparation of trioctylmethylammonium salicylate (TOMAS)**

Trioctylmethylammonium salicylate was synthesized according to (Egorov et al., 2008) as a slightly yellowish viscous liquid (yield: 85%), analyzed by nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR), then used without further purification. The reaction is illustrated in Fig. 3.5. Aliquat® 336 (0.1 mol) was mixed with an equal molar amount of sodium salicylate in 200mL of acetone. The mixture was shaken for 5 h and left overnight. The precipitate was then filtered off, and acetone was evaporated from the filtrate using a rotary evaporator. The obtained RTIL was rinsed 10 times with a large amount of distilled water, and the remaining liquid was heated to 100 °C under reduced pressure for 5 h. A clear, slightly yellowish, viscous liquid (TOMAS) was obtained. TOMAS is clear liquid with a density of slightly less than 1 g cm<sup>-3</sup> (0.945). TOMAS is immiscible with water. FTIR, <sup>1</sup>H and <sup>13</sup>C NMR spectra confirmed the identity of the obtained TOMAS.

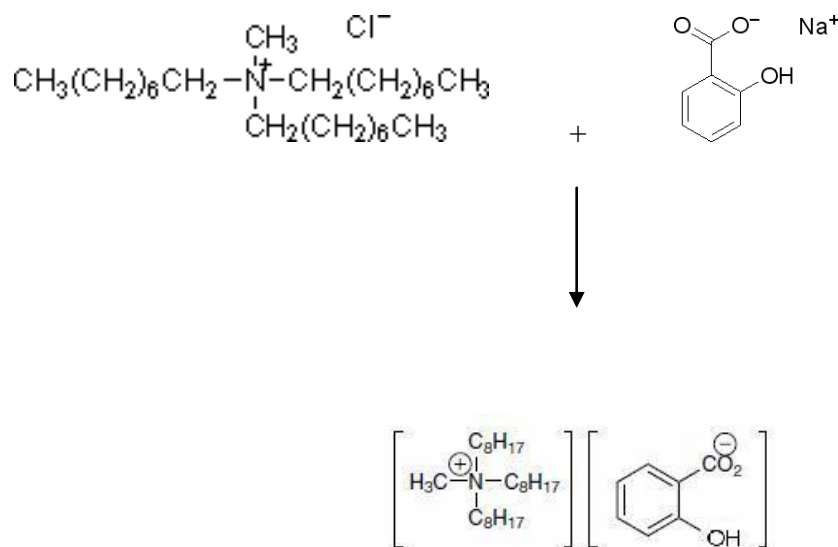


Figure 3.5 : Synthetic pathway for trioctylmethylammonium salicylate (TOMAS)

### 3.4.2 Preparation of carbon paste electrode based on TOMAS and potential measurements

Modified palm shell activated carbon paste was prepared by hand mixing the determined quantities of palm shell activated carbon powder and TOMAS. The optimal paste quality was obtained by mixing 0.18 g PSAC and 0.12 g TOMAS corresponding to a ratio of 60:40 (%). The constituents were thoroughly hand mixed in a 50 mm petridish to produce the optimal paste quality and then the paste was poured and packed into empty glassy carbon electrode (5mm diameter) connected to the pH/ion meter by a thin copper wire to produce an electrical contact. The composite surface was polished on weighing paper until the surface displayed a shiny appearance. The surface was rinsed carefully with double-distilled water prior to each experiment. The electrode is stored in a desiccator when it is not in use to avoid adsorption of contaminants.

The potentiometric measurements were conducted as follows: The modified carbon paste electrode and reference electrode were placed in 50 mL of a stirred, 0.1 M Cd(II) solution until the potential reading was constant. The standard addition method was

used to investigate the electrode response characteristics. Cadmium salt standard solutions were added so that the cadmium concentration ranged between  $10^{-10}$  and  $10^{-1}$  M. Pipette the suitable volume (0.2-100 $\mu$ L) of cadmium standards into a 50 mL water in measuring beaker and measure the potential in the appropriate way for the ion to be measured (i.e. with stirring and sufficient time for stable reading). The potential readings were recorded after each addition when stable values had been obtained. The concentration of solutions was checked by inductivity couple plasma.

The electrode potential of the electrochemical cell  $E_{\text{cell}}$  is described by the following Nernst equation:

$$E_{\text{cell}} = E_{\text{cons}} + 2.303 \frac{RT}{zF} * \log a \quad (3.1)$$

where  $E_{\text{cons}}$  is a constant term (the sum of the standard potential and liquid junction potential),  $R$  is the ideal gas constant,  $T$  is the absolute temperature,  $F$  is the Faraday constant,  $z$  is the charge of the ion, and  $a$  is the activity of the ion. At low concentrations, the activity value  $a$  can be replaced with the concentration value  $C$ . The prelogarithmic factor  $2.303 \frac{RT}{zF}$  is obtained from the slop ( $S$ ) of the plot of  $E_{\text{cell}}$  versus  $\log C$ , and the equation becomes:

$$E_{\text{cell}} = E_{\text{cons}} + S \log C \quad (3.2)$$

Potentiometric selectivity of this electrode towards different cations was calculated with the matched potential method (MPM) (Gadzekpo and Christian, 1984).

In this method, the activity of Cd(II) was increased from  $a_i = 1.0 \times 10^{-5}$  M (primary ion) to  $\acute{a}_i = 5.0 \times 10^{-5}$  M, and the corresponding potential change ( $\Delta E$ ) was measured. Then a solution of an interfering ion ( $a_j$ ) in the concentration range of  $1.0 \times 10^{-1} - 1.0 \times 10^{-2}$  M was added to a new primary ion ( $\acute{a}_i$ ) until the same potential change ( $\Delta E$ ) was recorded. The selectivity factor,  $k_{ij}^{\text{pot}}$ , was calculated for each interferent using the following equation:

$$k_{ij}^{\text{pot}} = (\acute{a}_i - a_i) / a_j \quad (3.3)$$

### 3.4.3 Preparation of impregnated palm shell activated carbon with TOMAS

For the preparation of impregnated palm shell activated carbon with task-specific ionic liquids, 1 g of the activated carbon samples and 0.00-0.3 g TOMAS were placed in 250 mL Erlenmeyer flasks with 50 ml methanol. The solutions were then agitated in an orbital shaker at 180 rpm and 25 °C for 2 days. Subsequently, the solutions were evaporated, and the remaining impregnated palm shell activated carbon was weighted. The overall loading of TOMAS on palm shell activated carbon was calculated using the weight loss data for virgin and impregnated palm shell activated carbon.

### 3.5 Modified palm shell activated carbon paste based on trioctylmethylammonium thiosalicylate (TOMATS) selective electrode for Hg(II) determination.

In this work palm shell activated carbon grafted with trioctylmethylammonium thiosalicylate (TOMATS) (structure as shown in Fig. 3.6) was used in developing a new potentiometric sensor for determination of Mercury in water samples. The investigation of TOMATS in ion selective electrode was used in order to fully understand its functions as both ionophore and plasticizer in potentiometric sensor.

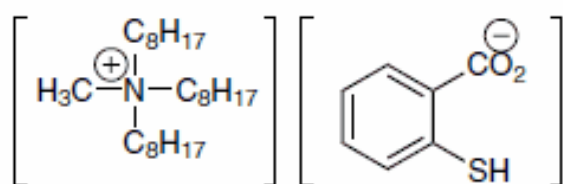


Figure 3.6 : Chemical structure of TOMATS.

### **3.5.1 Preparation of carbon paste electrode based on TOMATS and potential measurements**

Modified palm shell activated carbon paste was prepared by making the following changes to the procedure in section 3.4.2. The paste was obtained by mixing 0.15 g PSAC and 0.15 g TOMATS in the ratio 1:1 (w/w).

The potentiometric measurements were conducted as mention in section 3.4.2. Hg(II) solutions were used for the experiments described in section 3.4.2.

### **3.5.2 Preparation of impregnated palm shell activated carbon with TOMATS**

To prepare impregnated palm shell activated carbon with task-specific ionic liquids, 1 g activated carbon series and 0.05-0.3 g TOMATS were used for the experiments described in section 3.4.3.

### **3.6 Kinetic studies**

The kinetic parameters of the adsorption process were determined using a potentiometric method. The results of the proposed procedure were compared with those obtained using inductively coupled plasma (ICP).

In the potentiometric kinetic method, the adsorption rate constant and the adsorption characteristics of cadmium or mercury ions onto modified palm shell activated carbon were investigated in situ. Ion-selective electrode (ISE) potentiometry, based on the selective, direct and continuous monitoring of cadmium or mercury ions with the proposed electrodes, were used (see Fig. 3.1). The reference and working electrodes were immersed in a stirred aqueous solution containing 50 mL of a 60 mg/L metal solution, and the electrode potential was measured. After stabilization, 0.1 g of modified palm shell activated carbon was rapidly added to 50 mL of a 60 mg/L metal solution with stirring. The electrode potential was then continuously recorded until equilibrium was established. The process was repeated for 40, 20, and 10 mg/L metal solutions.

The potential difference  $\Delta E$  between the readings at the beginning of the experiment and at any time  $t$  can be used to calculate the decrease in the metal free concentration based on the following equation:

$$C_{ad,i} = C_o (1 - 10^{-\Delta E_i/S}) \quad (3.4)$$

Where  $C_{ad,i}$  is the concentration of adsorbed metal at time  $t$ ,  $C_o$  is the total metal concentration in the solution, and  $S$  is the slope of the calibration curve.

The apparent adsorption rate constants were estimated from the adsorption data using the pseudo second order adsorption kinetics equation (Ho and McKay, 1999):

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3.5)$$

Where  $q_e$  (mg/g) and  $q_t$  (mg/g) are the amounts adsorbed at equilibrium and at any time  $t$  (min),  $k_2$  is the rate constant of the pseudo second order reaction.

The initial adsorption rate  $h$  (mg/g min) is calculated using the following equation (Ho and McKay, 1999):

$$h = k_2 q_e^2 \quad (3.6)$$

In the conventional kinetic study using the batch adsorption technique, the adsorption experiments were carried out in 250 mL Erlenmeyer flasks at different temperatures between 10 and 35 °C. In each experiment, 50 mL of a M (II) solution of a concentration varying between 10 and 60 mg/L was treated with a known amount of modified activated carbon (0.1 g). Then, the solutions were shaken in an orbital shaker at 180 rpm for a specified period of time. Subsequently, the adsorbent was separated from the solution using Whatmann filter paper No 42.

The equilibrium concentrations of M (II) remaining in solution were measured by ICP instrument. The metal uptake by the modified activated carbon was calculated as follows:

$$q_e = \frac{V (C_o - C_e)}{m} \quad (3.7)$$

Where  $q_e$  is the amount of metal ion adsorbed per gram of modified activated carbon (mg/g),  $V$  is the sample solution volume (L),  $C_o$  is the initial M (II) concentration (mg/L),  $C_e$  is the equilibrium M (II) concentration (mg/L), and  $m$  is the weight of the adsorbent.

The percentage of metal ions removal (%) from aqueous solutions was calculated as follows:

$$Removal (\%) = 100 \frac{(C_o - C_e)}{C_o} \quad (3.8)$$

### 3.7 Analytical experiments

In coordination with the staff of the Palestinian Water Authority, water samples were collected from four domestic wells nearest to the waste water collection area in the Gaza Strip (Palestine). To assure that the collected sample was from groundwater and not water standing in the well, it was originally proposed that the well should be pumped for at least 1-2 h prior to the collection of the sample. Approximately 500 mL of water for each sample was taken in laboratory certified clean bottles and labelled with the sample location, date, and time of sample collection. The sample was stored at 4 °C and shipped to Malaysia, where the heavy metal contents were analyzed by ICP-OES and the proposed ISEs.

## **CHAPTER 4: RESULTS AND DISCUSSION**

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## CHAPTER 4

### RESULTS AND DISCUSSION

#### **4.1 Cadmium (II) and mercury (II) selective electrodes based on palm shell activated carbon modified with task specific ionic liquids**

In this study, improved versions of Cd(II) and Hg(II) selective electrodes using palm shell activated carbon based on task specific ionic liquids were prepared. Trioctylmethylammonium salicylate (TOMAS) and trioctylmethylammonium thiosalicylate (TOMATS) in ion selective electrodes were investigated to fully understand their functions as both an ionophore and plasticizer in potentiometric sensors.

##### **4.1.1 Cadmium and mercury electrode responses**

The behaviour of potentiometric sensors with carbon paste electrodes depends on the composition of the electrode material used and the condition of the contact solution. It is known that the response of an ion selective electrode depends not only on the nature and amount of an ionophore but also on the nature and the amount of the plasticizer. The influence of the plasticizer type and concentration on the characteristics of the studied cadmium electrode was investigated using eight plasticizers with different polarities, including DOA, DOP, TOPh, DOS, BPh, DBPh, TBPh and NPOE. Different plasticizer/PSAC/TOMAS (w/w) ratios were studied to determine the influence of the amount of plasticizer in the electrode. The obtained results are presented in Table 4.1. These results show that the potentiometric responses of the electrodes modified with conventional plasticizers were unsatisfactory, whereas those of the proposed electrode towards Cd(II) ions were greatly improved in the presence of TOMAS as both an ionophore and a plasticizer. The conventional plasticizer weakens the electrochemical response of the CPE and is especially disadvantageous for trace detection. Therefore,

the use of the considerably viscous simplex TOMAS ionic liquid, which is chemically inert and electrochemically conductive, as a pasting binder may be an ideal alternative for an improved paste electrode. One of the key characteristics of the proposed electrode is its ability to lower the overpotential of electroactive compounds and to increase the rate of electron-transfer processes, which is believed to be due to the modification of the microstructure of the electrode surface with TOMAS as the binder.

Table 4.1 : Composition and optimization of cadmium selective electrode

No.	TOMAS (%)	PSAC (%)	Plasticizer (%)	working concentration range (M)	Slope (mV dec <sup>-1</sup> )	R <sup>2</sup>
1	40	60	0	1.0×10 <sup>-9</sup> to 1.0×10 <sup>-2</sup>	30.90	0.99
2	10	50	40 (NPOE)	1.0×10 <sup>-7</sup> to 1.0×10 <sup>-2</sup>	27.46	0.85
3	10	50	40 (DOP)	1.0×10 <sup>-7</sup> to 1.0×10 <sup>-2</sup>	27.31	0.82
4	10	50	40 (DOS)	2.5×10 <sup>-7</sup> to 1.0×10 <sup>-2</sup>	26.10	0.74
5	10	50	40 (DOA)	2.5×10 <sup>-7</sup> to 1.0×10 <sup>-2</sup>	26.29	0.81
6	10	50	40 (BPh)	1.0×10 <sup>-6</sup> to 1.0×10 <sup>-2</sup>	44.85	0.79
7	10	50	40 (DBPh)	1.0×10 <sup>-6</sup> to 1.0×10 <sup>-2</sup>	20.70	0.72
8	10	50	40 (TBPh)	1.0×10 <sup>-6</sup> to 1.0×10 <sup>-2</sup>	38.92	0.75
9	10	50	40 (TOPh)	1.0×10 <sup>-6</sup> to 1.0×10 <sup>-2</sup>	23.38	0.75

Several electrode compositions were investigated by varying the ratio of palm shell activated carbon and TOMAS for the systematic investigation of each paste composition. The particular 40 wt % of task specific ionic liquid composition typically used for the paste preparations demonstrates unique properties in terms of mobility versus plasticization level. In this regard, the use of a 40 wt % TOMAS/PSAC matrix is significant. The paste matrix composition should, therefore, be optimized with respect to other criteria such as structural integrity. The highest quality paste was obtained by mixing PSAC and TOMAS in a ratio of 60:40 (%).

The calibration for the developed electrode over a wide range of Cd(II) solution activities is shown in Fig. 4.1. The slope of the calibration curve (30.9 mV/dec) is close to the curve that is predicted (29.5 mV/dec for bivalent cation) by the Nernst equation, indicating that the electrode was sensitive to Cd(II) over a wide range of activities ( $1 \times 10^{-9}$  -  $1 \times 10^{-2}$  M).

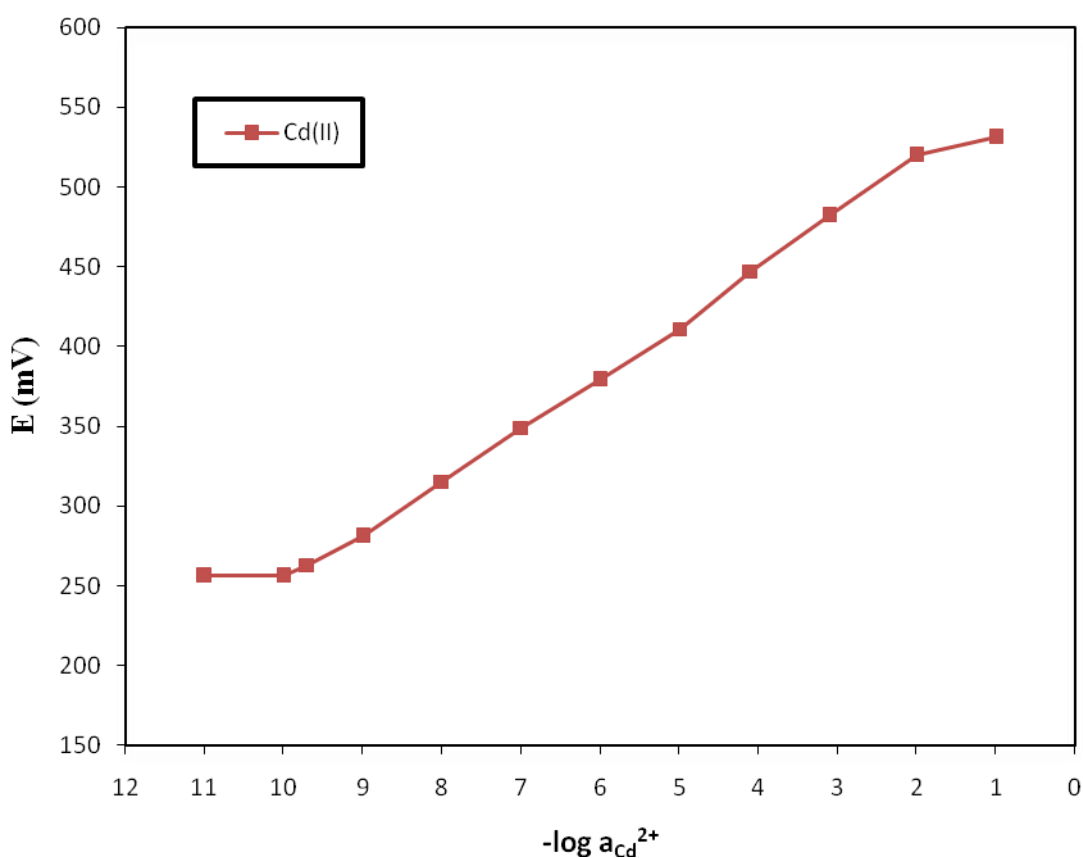


Figure 4.1 : Calibration curve for palm shell activated carbon paste electrode based on TOMAS over a wide range of solution Cd(II) .

In addition, the electrode showed a linear response over this range of activities, with a departure from linearity (i.e., a loss of sensitivity) at activities lower than  $10^{-9}$  M Cd(II).

The unique sensitivity and selectivity towards Cd(II) obtained for a given electrode depends on the coordinate interaction between TOMAS and the Cd(II) ion, which may be explained by the chelating effect of the ortho-positioned carboxylate group on the TOMAS molecule on the palm shell activated carbon, in addition to the known formation of metal-hydroxides (Alizadeh et al., 2011).

For the mercury electrode, the calibration for the developed electrode over a wide range of solution Hg(II) activities is shown in Fig. 4.2. The slope of the calibration curve (44.08 mV/dec) is close to that predicted theoretically by the Nernst equation (58.16 mV/dec for monovalent cations), which may be attributed to the formation of monovalent mercury complexes on the electrode surface.

This finding indicates that the electrode was sensitive to Hg(II) over a wide range of Hg(II) activities ( $1 \times 10^{-9}$  -  $1 \times 10^{-2}$  M).

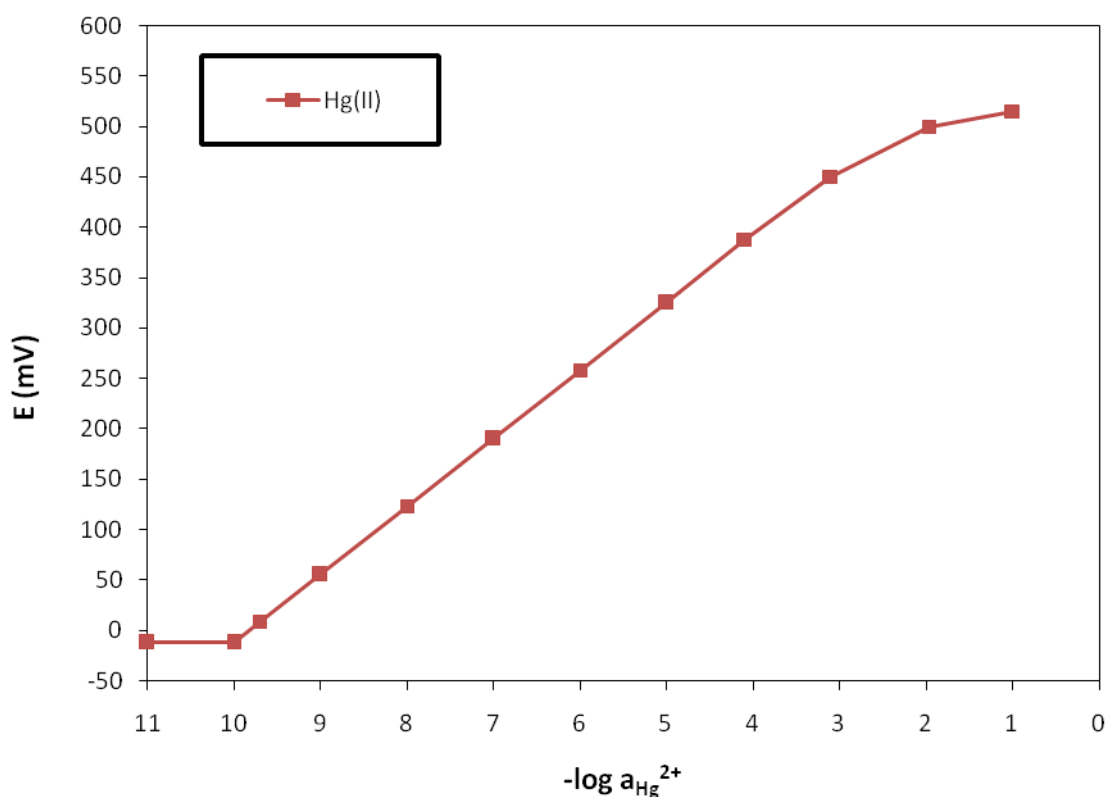


Figure 4.2 : Calibration curve for a modified palm shell activated carbon paste electrode over a wide range of Hg(II) activities.

In addition, the electrode showed a linear response over this range of activities, with a departure from linearity (i.e., loss of sensitivity) at activities lower than  $10^{-9}$  M Hg(II). The unique sensitivity and selectivity towards Hg(II) obtained for this electrode is due to the coordinate interaction between TOMATS and Hg(II) ions, as shown later in SEM and EDAX results, which may be explained by the chelating effect of the ortho-positioned carboxylate group on the TOMATS molecule impregnated on palm shell activated carbon in addition to the known formation of metal-thiolates (Roland St. Kalb, 2005).

TSILs (TOMAS and TOMATS), which were used as the solvent mediator and plasticizer, have certain desirable properties and characteristics, such as high lipophilicity, high molecular weight, and low vapour pressure. Additionally, their viscosities and dielectric constants were adequate for the construction of an ion selective electrode with desirable analytical properties, such as selectivity, sensitivity, fast response, and long lifetime. The critical response characteristics of the proposed electrode were evaluated according to IUPAC recommendations (Buck and Lindner, 1994).

#### **4.1.2 Effect of pH on Electrodes Response**

The pH of each solution was verified, and its effect on the electrode potential at various metal concentrations was studied. For this purpose, several Cd(II) and Hg(II) concentrations ( $1.0 \times 10^{-6}$  M,  $1.0 \times 10^{-4}$  M and  $1.0 \times 10^{-3}$  M) were prepared, and the potential variations of the electrode over a pH range of 1-12 were followed. The pH was adjusted by adding small volumes of hydrochloric acid (1 M) and/or sodium hydroxide (2 M) to the sample solution.

For cadmium electrode, the obtained results are shown in Fig. 4.3. It can be seen that the electrode potential remain almost constant in the pH range of 4-9. The change in potential at higher pH values may be due to the formation of hydroxy complexes of

Cd(II) (Ensafi et al., 2009). At lower pH values, a sharp decrease in the electrode response is observed; this result is due to the protonation of carboxylic groups situated in the selective cavities of TOMAS.

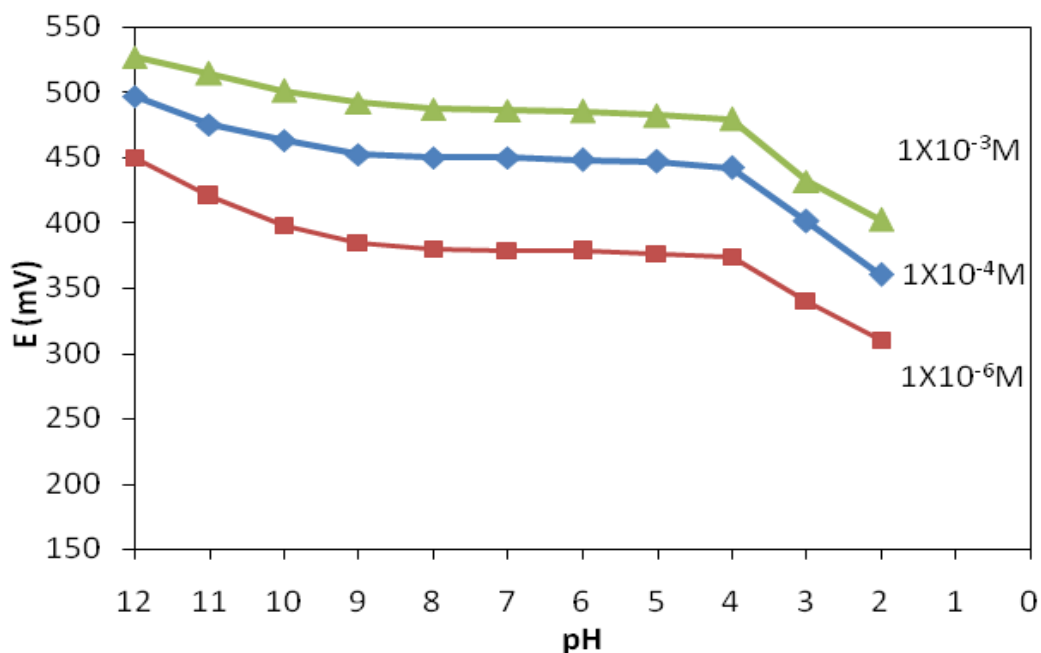


Figure 4.3: Effect of pH on the potential response of Cd(II) palm shell activated carbon paste electrode.

For the mercury electrode, the results, shown in Fig. 4.4, indicate that the potential remained constant in the pH range of 3-9, which can be used as the working pH range of the proposed electrode. However, outside this range, the electrode responses changed slightly. The diminished potential at pH >9 was due to the interference of OH<sup>-</sup> on the plain. The response at pH <3 seemed ascribable to the competitive blinding of protons to the ligands on the electrode surface.

Under more acidic conditions, the ligand may be protonated and thereby losing its capacity to form a complex with the metal ions. When the pH is nearly neutral, the

fundamental cation is  $[\text{HgOH}]^+$ , which reacts with TOMATS. The drift of potential values at pH is attributed to the formation of mercury(II) hydroxide.

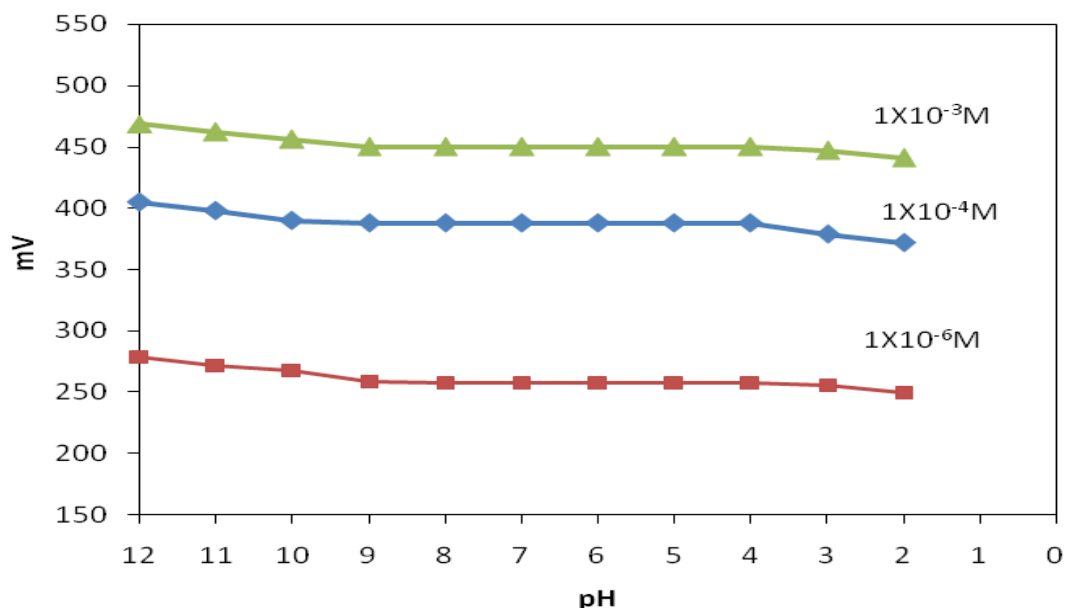


Figure 4.4 : Effect of pH on the potential response of Hg(II) palm shell activated carbon paste electrode.

#### 4.1.3 Potentiometric Selectivity Coefficients

It is well known that the selectivity behaviour of an electrode is one of the most important factors in its evaluation, which is measured in terms of the selectivity coefficient. The selectivity coefficient not only depends on ion charge and concentration, but it can also be affected by the type of interaction between the ion and the ionophore. The selectivity factor,  $\log k^{\text{pot}}$  is a measure of the preference of ion selective electrode for interfering ion relative to the primary ion to be measured. A selectivity factor  $\log k^{\text{pot}}$  below 1 indicates that the preference is for the primary ion.

Table 4.2 show that the electrode exhibited better selectivity for the cadmium (II) ion over a wide variety of other metal ions. The values of the selectivity coefficients, listed in Table 4.2, reflect a very high selectivity of this electrode for cadmium (II) ion over most of the tested species.  $\text{Hg}^{2+}$  and  $\text{Fe}^{2+}$  caused only slight interference. However, they

do not cause any interference at low concentration. This phenomenon suggests a high stability of the complex between cadmium and TOMAS.

Table 4.2. Selectivity coefficient values of various interfering ions with Cd(II) selective electrodes based on TOMAS using matched potential method (MPM).

Interferent ion, j	$-\log k_{\text{potCd}^{2+}, j}$	Interferent ion, j	$-\log k_{\text{potCd}^{2+}, j}$
$\text{Cu}^{2+}$	3.26	$\text{Na}^+$	4.71
$\text{Hg}^{2+}$	2.47	$\text{K}^+$	4.54
$\text{Ca}^{2+}$	3.95	$\text{Ni}^{2+}$	3.29
$\text{Mg}^{2+}$	4.15	$\text{Cr}^{3+}$	4.21
$\text{Zn}^{2+}$	3.83	$\text{Co}^{2+}$	3.37
$\text{Al}^{3+}$	3.74	$\text{Ag}^+$	3.10
$\text{Fe}^{3+}$	2.98	$\text{Pb}^{2+}$	4.02

The selectivity sequence of the employed modified CPE for different inorganic cations approximately obeys the order:  $\text{Hg}^{2+} > \text{Fe}^{3+} > \text{Ag}^+ > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Al}^{3+} > \text{Zn}^{2+} > \text{Ca}^{2+} > \text{Pb}^{2+} > \text{Mg}^{2+} > \text{Cr}^{3+} > \text{K}^+ > \text{Na}^+$ .

It is worth mentioning that TOMAS has excellent selectivity for the Cd(II) ions over other metal ions; this selectivity may be due to the design of TOMAS to contain negatively charged O-donor groups that enhance its complexing ability for the Cd(II) ion over other metals. Here, it is critical to note the existence of a rule of ligand design that permits fairly predictable control of selectivity on the basis of metal ion size. Ionic radius is an important parameter in the formation and stability of metal complexes. (Hancock and Martell, 1989). Moreover, Cd(II) (ionic radii 0.97Å) ions show a strong tendency towards ligands with donating atoms of hard character, such as N and O. However, it is clear that more work needs to be performed in this area to establish the



relative coordinating abilities of TOMAS to a variety of metal ions of different types and sizes.

To investigate the effect of counter ions on the potential response of the electrode, cell potentials were measured using constant concentrations of  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{CdCl}_2$  and  $\text{CdSO}_4$  under the same experimental conditions. It was found that in  $1.0 \times 10^{-4}\text{M}$  solutions of different counter ions, the values of electrode potential were the same (449 mV), indicating a negligible influence of counter ions on the response behaviour of the electrode.

The values of the selectivity coefficients, listed in Table 4.3, reflect a very high selectivity of this electrode for mercury (II) ion over most of the tested species *j*.  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  caused only slight interference. However, they do not cause any interference at low concentration. As shown in Table 4.3, it can be observed, that the proposed electrode based on TOMATS exhibited better selectivity for mercury (II) ion over a wide variety of other metal ions. This is due to the stability of the complex between mercury and TOMATS.

Table 4.3 : Selectivity coefficient values of various interfering ions with Hg(II) selective electrode using matched potential method (MPM).

Interferent ion, j	$-\log k_{\text{Hg}^{2+}, j}^{\text{pot}}$	Interferent ion, j	$-\log k_{\text{Hg}^{2+}, j}^{\text{pot}}$
$\text{Cu}^{2+}$	3.05	$\text{Na}^+$	4.89
$\text{Cd}^{2+}$	3.64	$\text{K}^+$	4.64
$\text{Ca}^{2+}$	4.89	$\text{Ni}^{2+}$	3.72
$\text{Mg}^{2+}$	4.48	$\text{Cr}^{3+}$	4.10
$\text{Zn}^{2+}$	3.96	$\text{Co}^{2+}$	3.33
$\text{Al}^{3+}$	3.92	$\text{Ag}^+$	3.05
$\text{Fe}^{3+}$	4.24	$\text{Pb}^{2+}$	3.02

#### 4.1.4 Dynamic Response Time

The response time of the electrode is one of the most important characteristics of the ion selective electrode. According to IUPAC recommendations, the response time of an ion selective electrode is defined as the time between the addition of the analyte to the sample solution and the time when limiting potential has reached its steady state value within  $1 \pm \text{mV}$ . In this study, the response time of the electrode was tested by measuring the time required to achieve a steady state potential (within  $1 \pm \text{mV}$  of the final equilibrium value) after successive immersion in a series of  $\text{M(II)}$  ions. The results, shown in Figs. 4.5 and 4.6 indicate that the response time of the electrodes was approximately 10s for the solution of cadmium ion and 5s for the solution of mercury ion in the concentration range of  $1 \times 10^{-8} - 1 \times 10^{-4} \text{M}$ . This result is probably due to the fast complexation of  $\text{M(II)}^+$  ions by the TSILs (TOMAS and TOMATS) molecule dispersed in the palm shell activated carbon paste matrix.

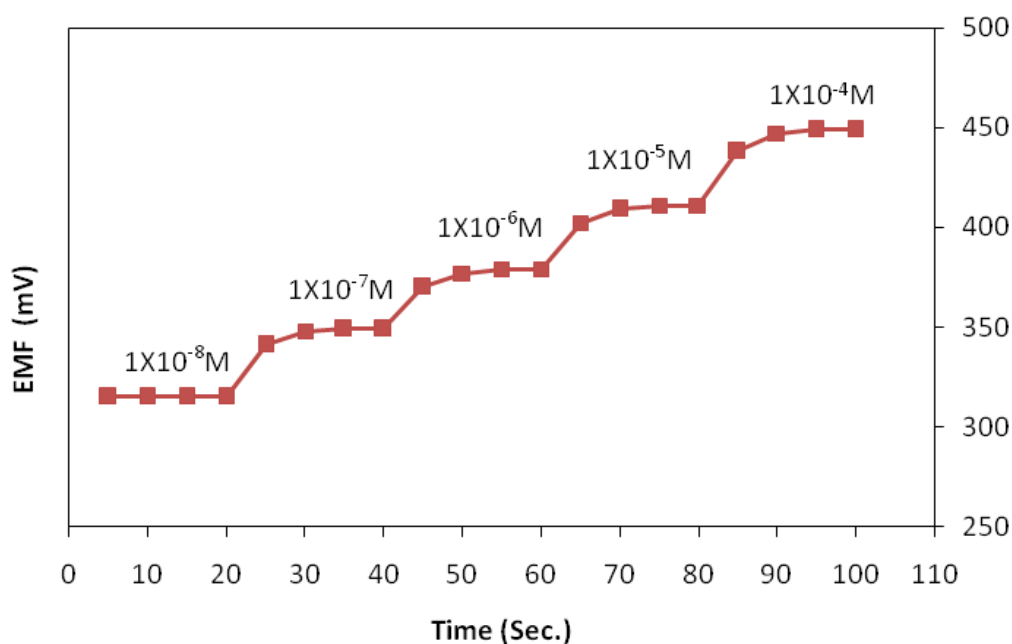


Figure 4.5 : Response time of the electrode obtained by successive increase of Cd(II) ion concentrations.

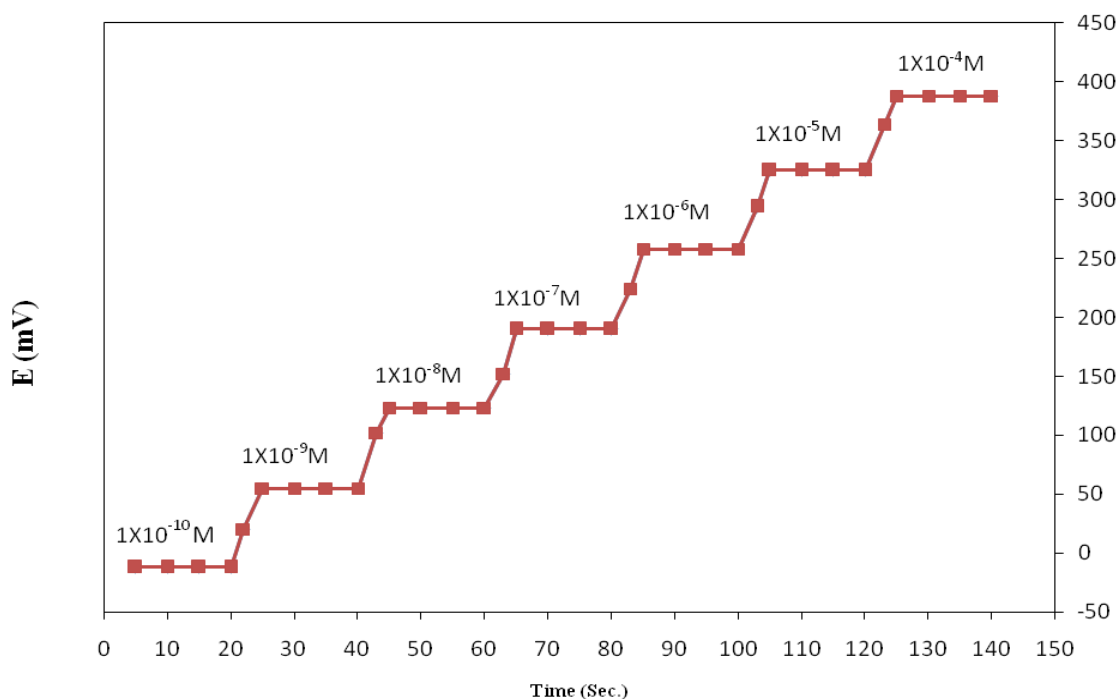


Figure 4.6 : Response time of the electrode obtained by successive increase of Hg(II) ion.

#### 4.1.5 Electrodes Life Time

The life time of the electrode depends on the distribution coefficient of the electrode compositions between the aqueous phase and the electrode phase. Accordingly, the life time of the electrode must depend on the electrode components.

In this work, the life time of the electrodes was determined by performing periodic calibrations with standard solutions and calculating the slopes over M (II) ion concentration ranges of  $1 \times 10^{-9}$  to  $1 \times 10^{-2}$  M. For the cadmium electrode, the obtained results showed that the present electrode had a lifetime of over 70 days (Table 4.4). During this time, the detection limit of the electrode remained almost constant, and the slope of the electrode response decreases from 30.9 to 28.03 mV per decade. Therefore, the electrode can be used for at least two months without a considerable change in its response characteristic towards Cd(II) ions, which may be due to the stability of TOMAS on palm shell activated carbon.

Additionally, the solubility of TOMAS in water is approximately  $2.0 \pm 0.2 \times 10^{-4}$  M, which significantly decreases the possibility of the electrode components leaching into the solution.

Table 4.4 : Cadmium electrode response during 70 days

Time period (day)	Slope (mV/decade)	Limit of Detection (M)
1	30.90	$1 \times 10^{-10}$
7	30.90	$1 \times 10^{-10}$
20	30.85	$1 \times 10^{-10}$
30	29.38	$1 \times 10^{-10}$
50	28.21	$1 \times 10^{-9}$
70	28.03	$1 \times 10^{-9}$

For the mercury electrode, the obtained results showed that the lifetime of the present electrode was over 90 days (Table 4.5). During this time, the detection limit of the electrode remained almost constant and the slope of the electrode response decreases from 44.08 to 42.17 mV per decade. Therefore, the electrode can be used for at least 3 months, without a considerable change in their response characteristic towards Hg(II) ions, which may be due to the stability of TOMATS on palm shell activated carbon.

Table 4.5 : Mercury electrode response during 90 days

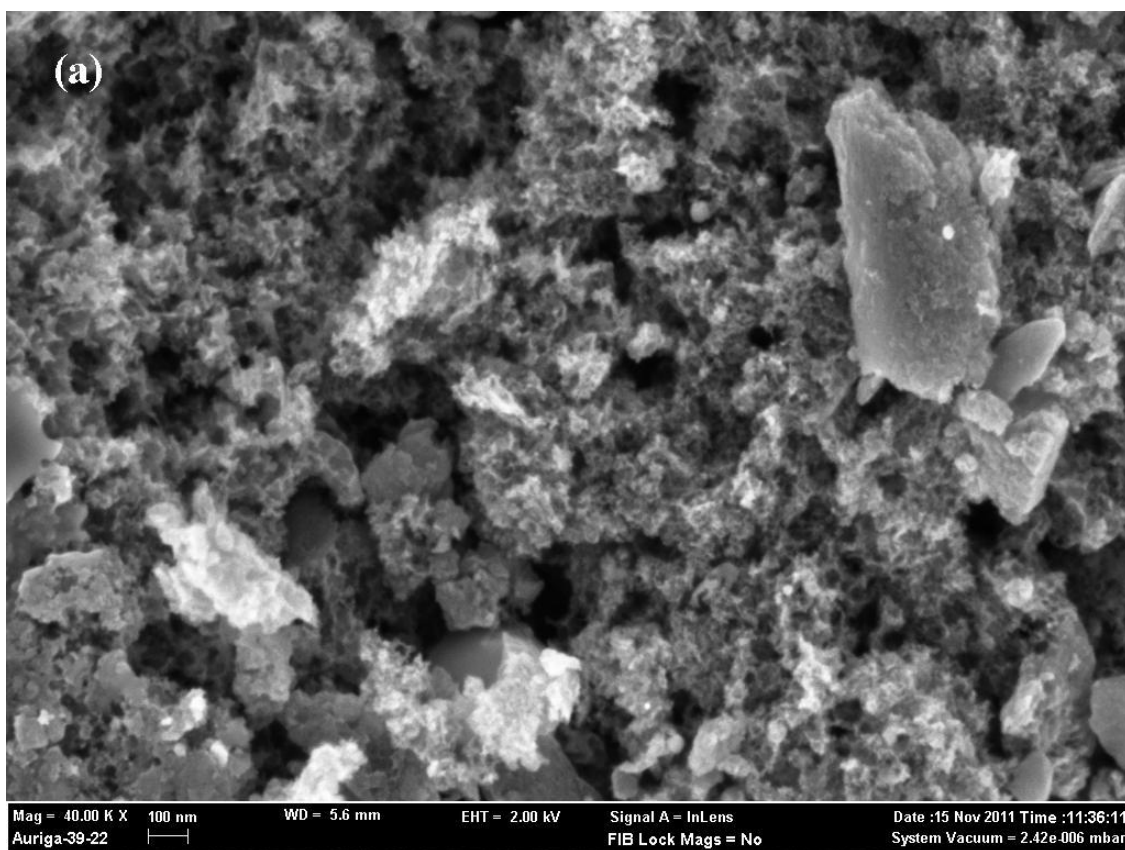
Time period (day)	Slope (mV/decade)	Limit of Detection (M)
1	44.08	$1 \times 10^{-10}$
7	44.08	$1 \times 10^{-10}$
20	44.08	$1 \times 10^{-10}$
30	43.86	$1 \times 10^{-10}$
50	43.29	$1 \times 10^{-10}$
70	42.86	$1 \times 10^{-9}$
90	42.17	$1 \times 10^{-9}$

## 4.2 The characterizations of the palm shell activated carbon

### 4.2.1 Scanning Electron Microscopy Studies

Surface morphology plays a significant role in determining the surface availability of activated carbon. Scanning electron microscopy was used to observe the surface morphology at high resolution and to study the variation in surface texture. Figures 4.7 and 4.8 show the typical morphological features of palm shell activated carbon paste electrode based on TOMAS and TOMATS, respectively using scanning electron microscopy (SEM). The pure PSAC surface (Figures 4.7a and 4.8a) has good porosity and smooth surfaces with long linear ridges and rough surfaces with oval ridges and micropores. Figures 4.7b and 4.8b show the SEM images of the paste films based on TOMAS and TOMATS respectively. As shown, the active TSILs on the paste films are more uniformly distributed across the electrode surface with good homogeneity and unique structure. The reproducibility of the electrode surface is usually improved by the homogeneous placement of the active TSILs. The best results are obtained when the components are well mixed into the carbon paste preparation. Significant differences in

the initial surface structure of the paste and the paste surface after it was dipped in a  $1 \times 10^{-4}$  M metal solution for 30 min are seen. SEM micrographs obtained at the same magnifications indicate significant improvement in the microstructure of the proposed electrodes. It can be seen that after binding the TOMAS with Cd (II), and TOMATS with Hg (II), the morphology changes. Aggregates of white needles were observed on the surface (Figures. 4.7c and 4.8c), which were presumably complexes formed between the TSILs and the metal ions.



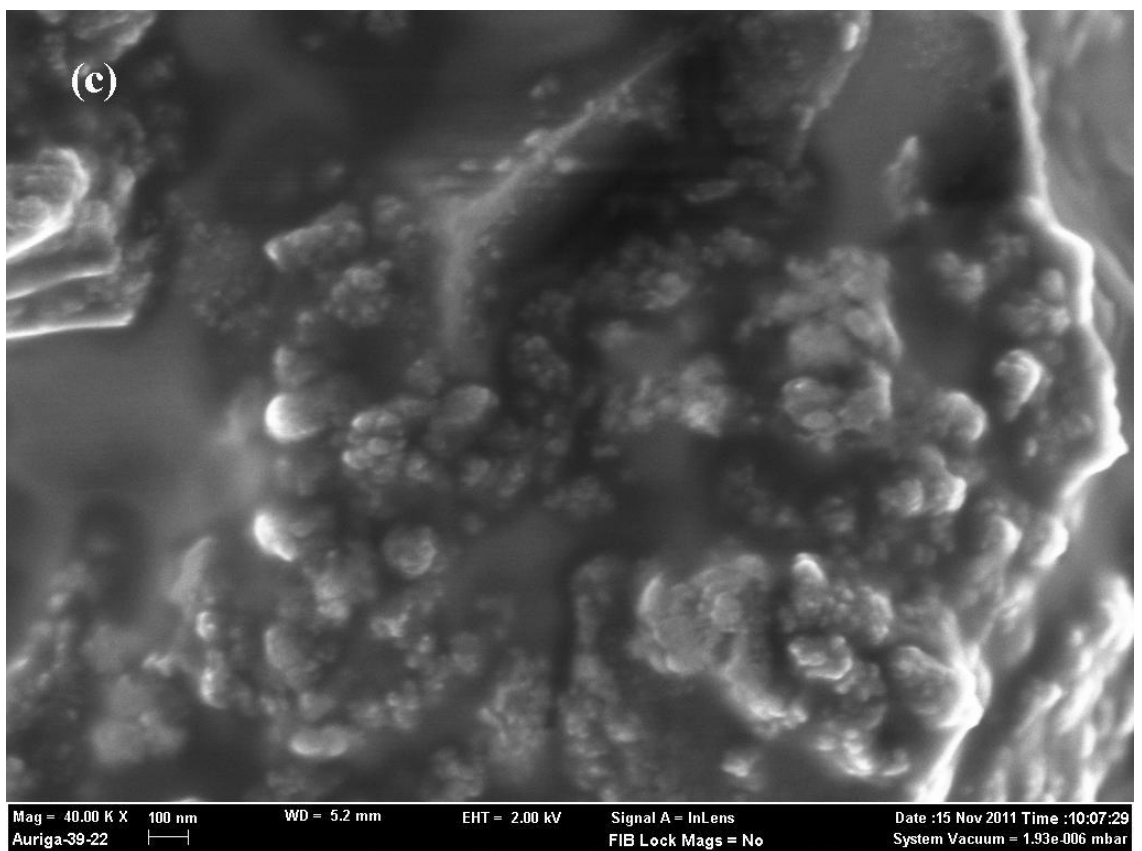
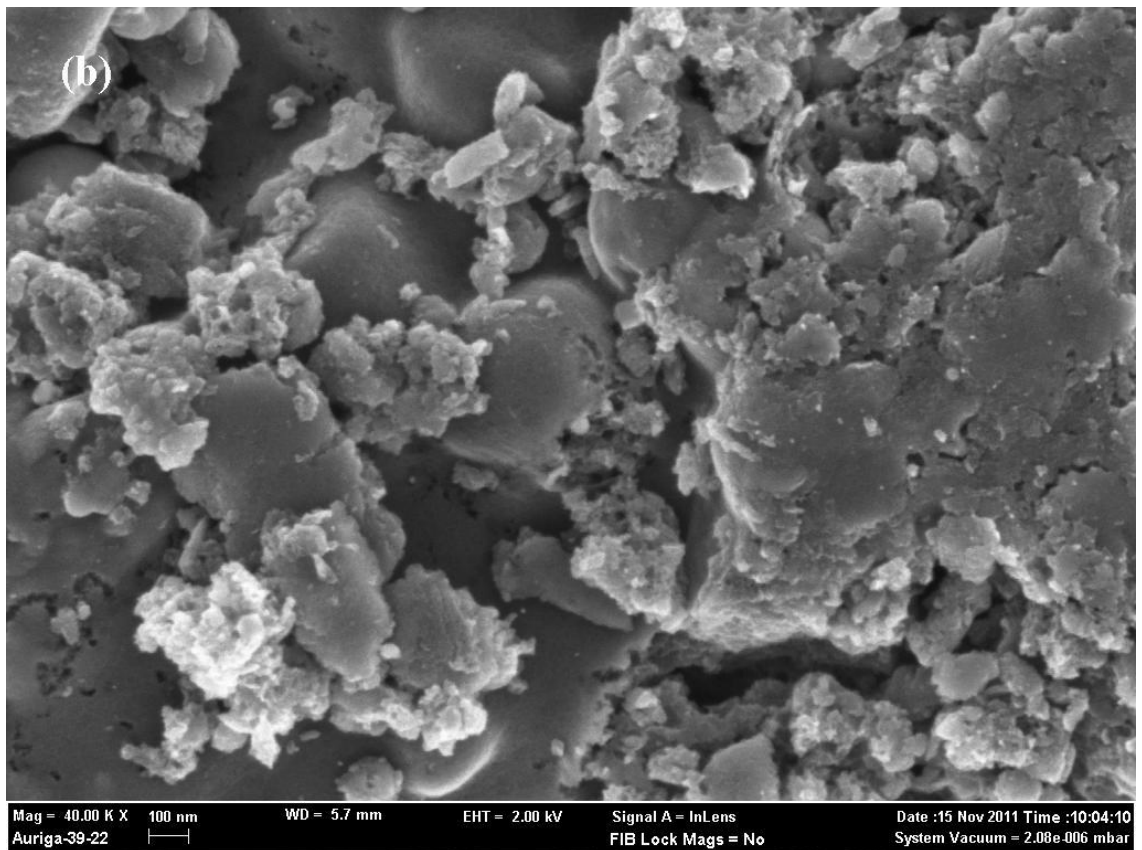
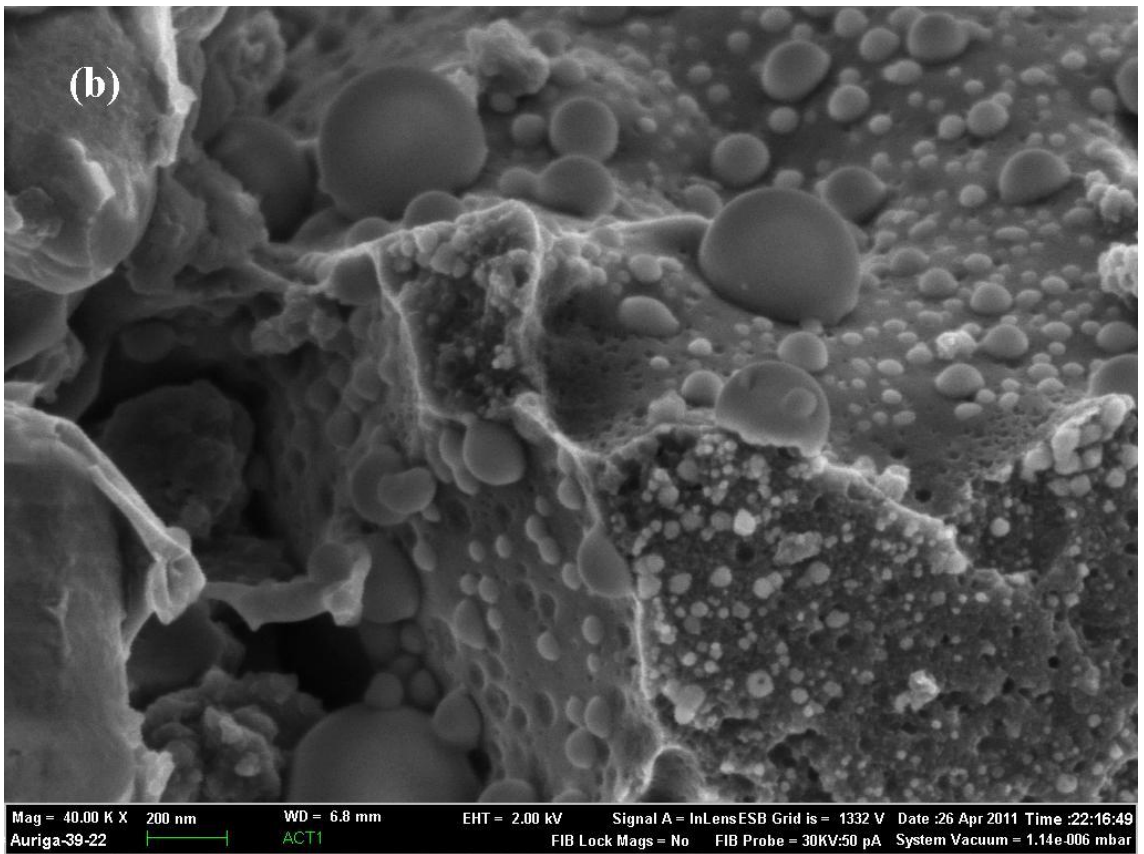
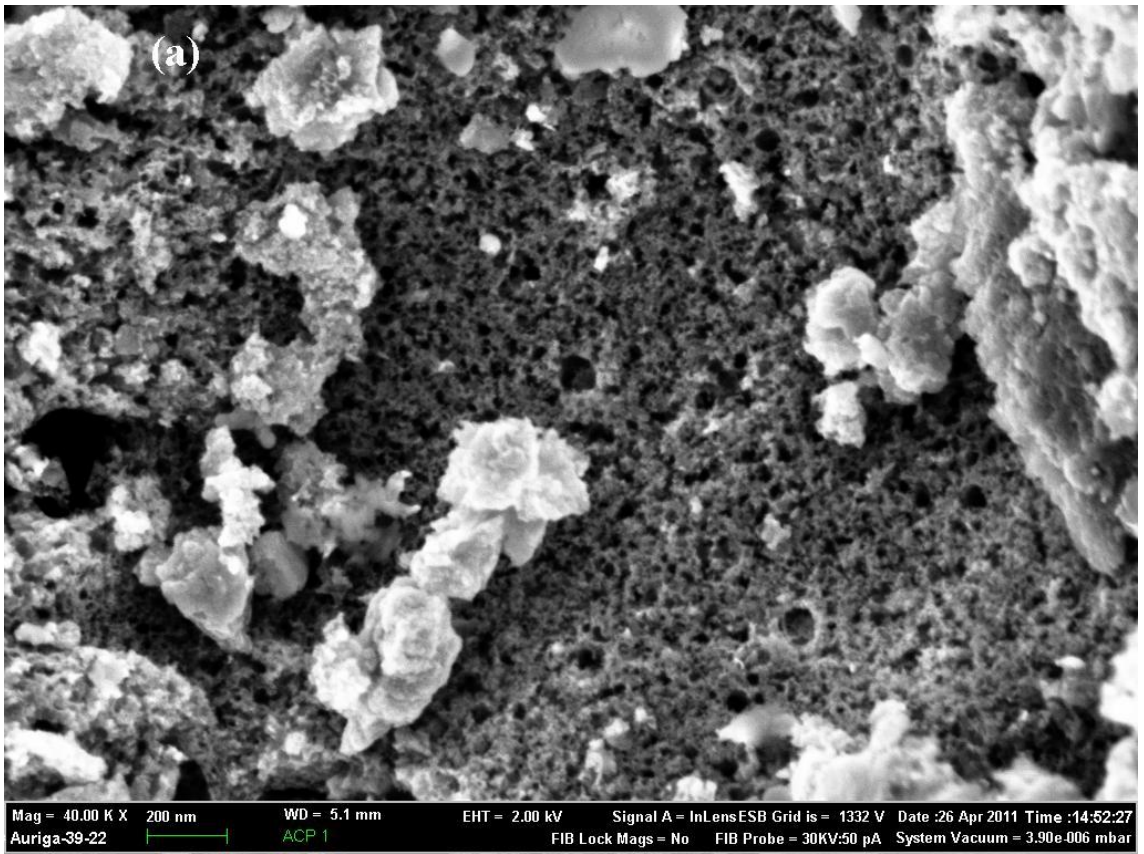


Figure 4.7: SEM images of (a) Pure PSAC, (b) PSAC paste electrode based on TOMAS and (c) PSAC paste electrode surface after it was dipped in  $1 \times 10^{-4}$  M Cd(II)





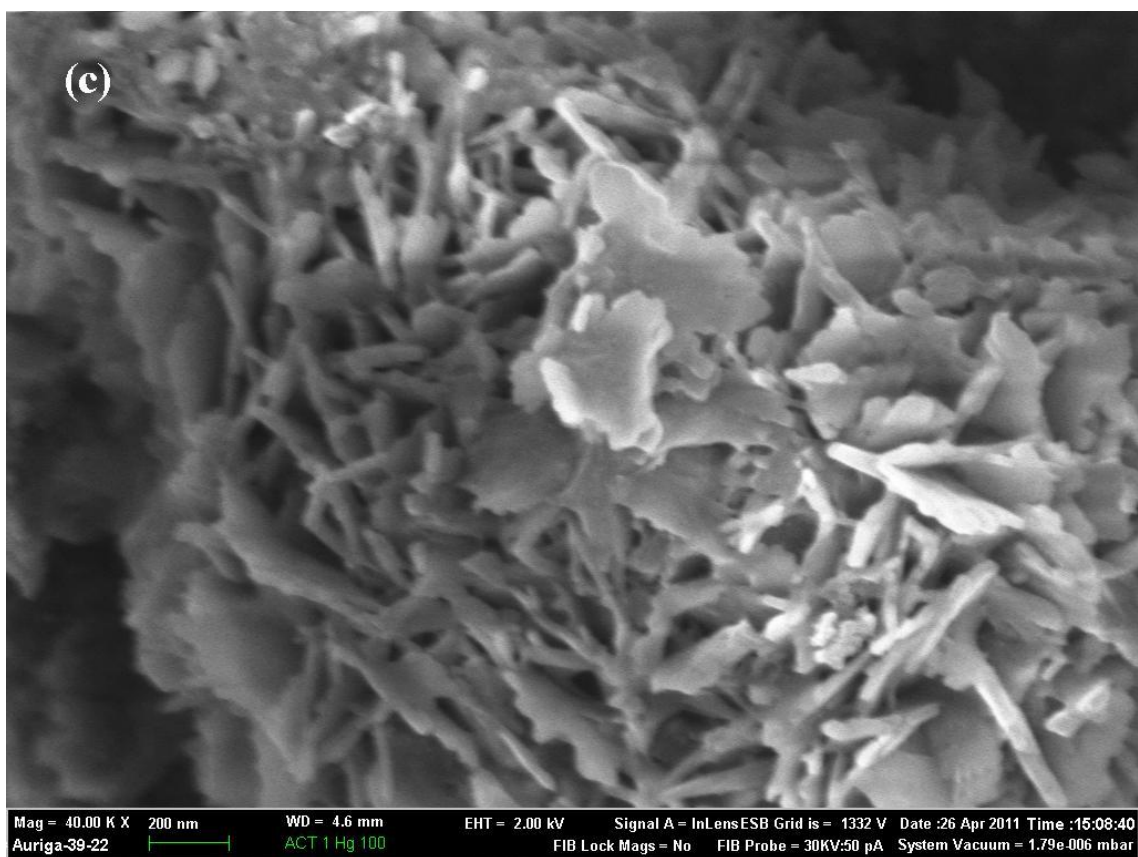
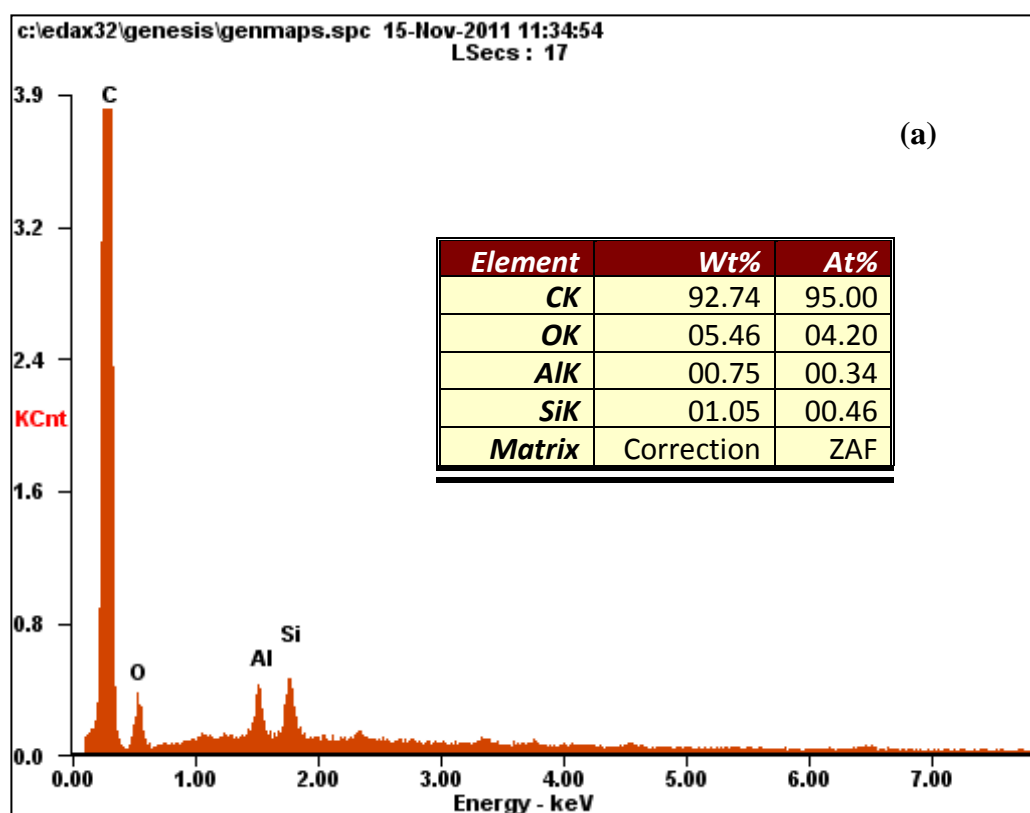
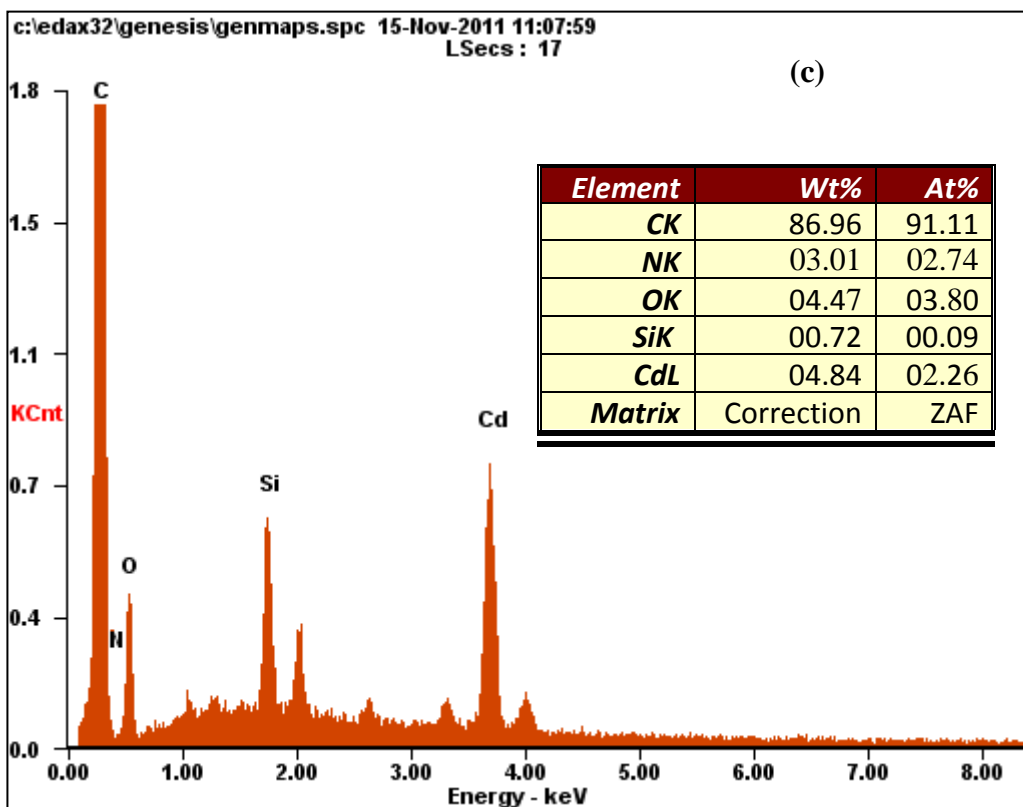
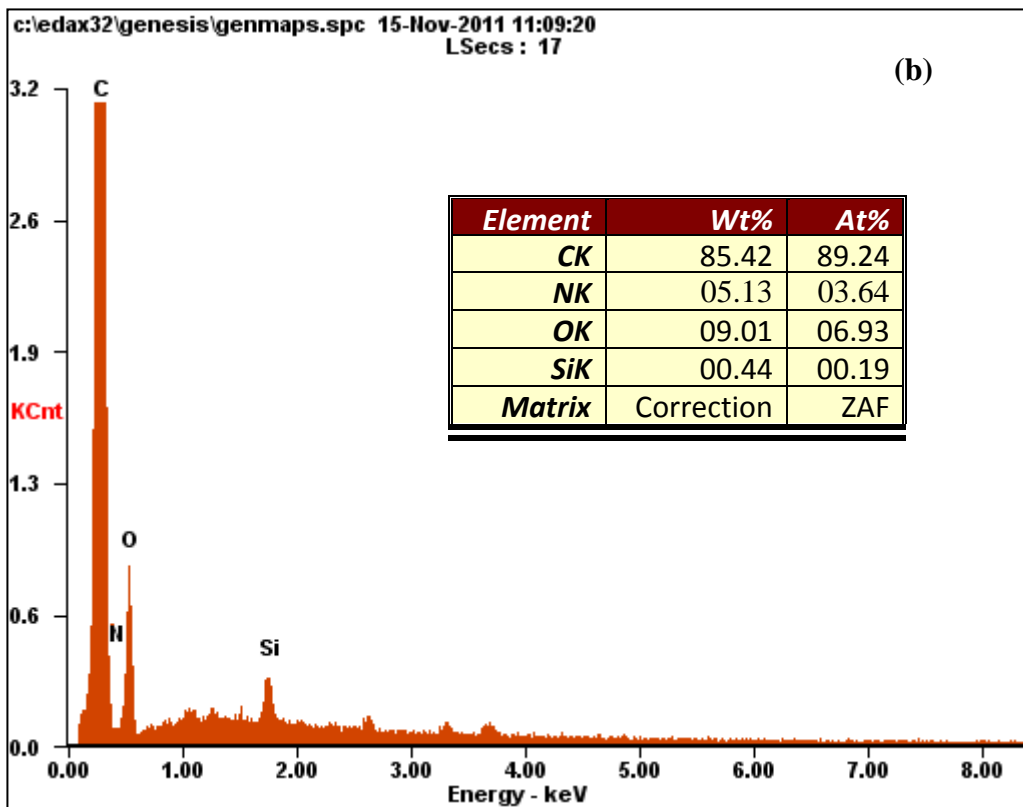


Figure 4.8 : SEM images of (a) Pure PSAC, (b) PSAC paste electrode based on TOMATS and (c) PSAC paste electrode surface after it was dipped in  $1 \times 10^{-4}$  M Hg(II)

#### 4.2.2 Energy dispersive X-ray analysis (EDAX)

EDAX analysis was employed to confirm the presence of TSILs and metal ions on the surface of PSAC. The corresponding EDAX spectrum and the composition table are shown in Figures 4.9 and 4.10. From Figure (4.9a), in the case of virgin palm shell activated carbon, the characteristic peaks of oxygen is smaller to its peak in Figure (4.9b), this result indicates that TOMAS was impregnated at the PSAC. Based on figure (4.9c), a significant amount of cadmium is present in the sample and is uniformly distributed, whereas in figure (4.9d), the amount of cadmium is less than that in figure (4.9c). The results show that cadmium becomes the principal element of the modified palm shell activated carbon surface. This was due to the fact that cadmium ions were chemisorbed on the surface of modified palm shell activated carbon, whereas the cadmium ions were physisorbed on the surface of virgin palm shell activated carbon. Therefore, EDAX analysis provides direct evidence for the specific adsorption of cadmium ions onto the surface of modified palm shell activated carbon.





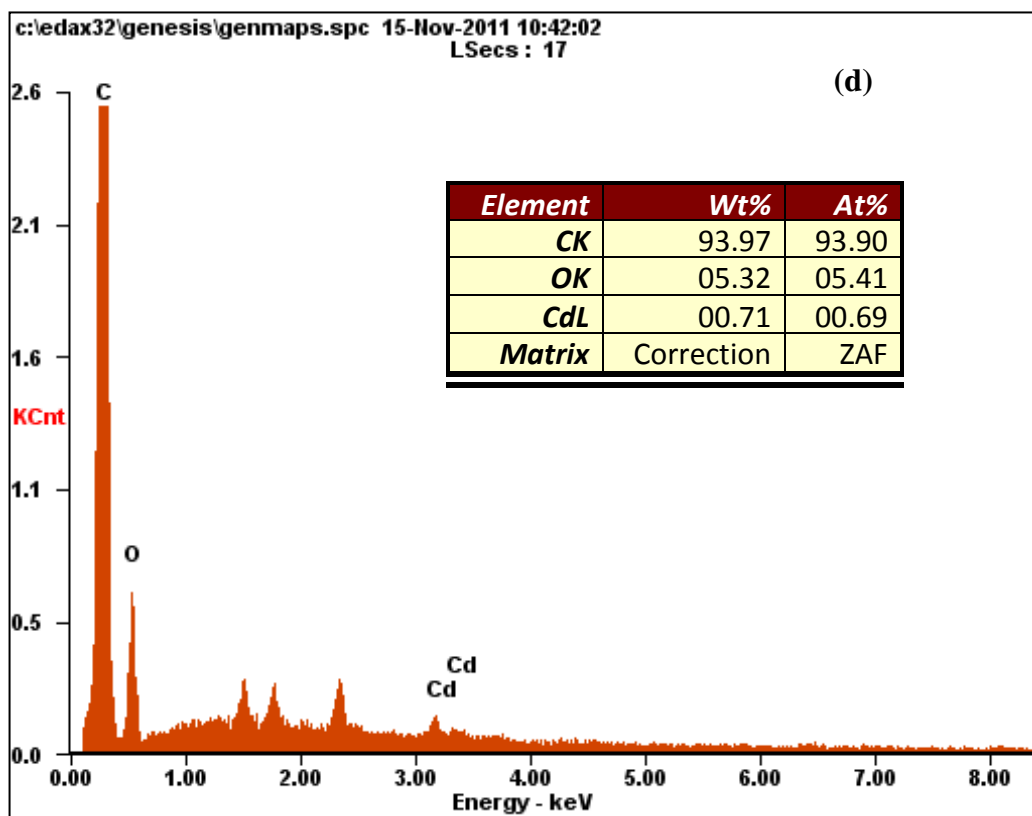
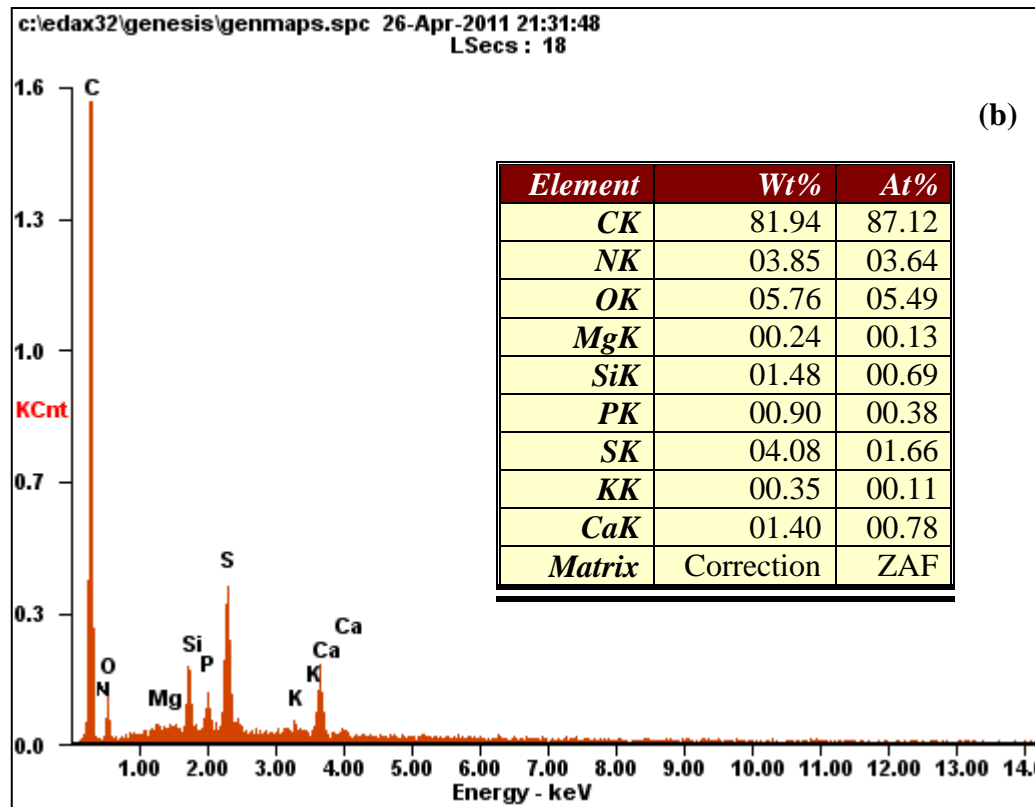
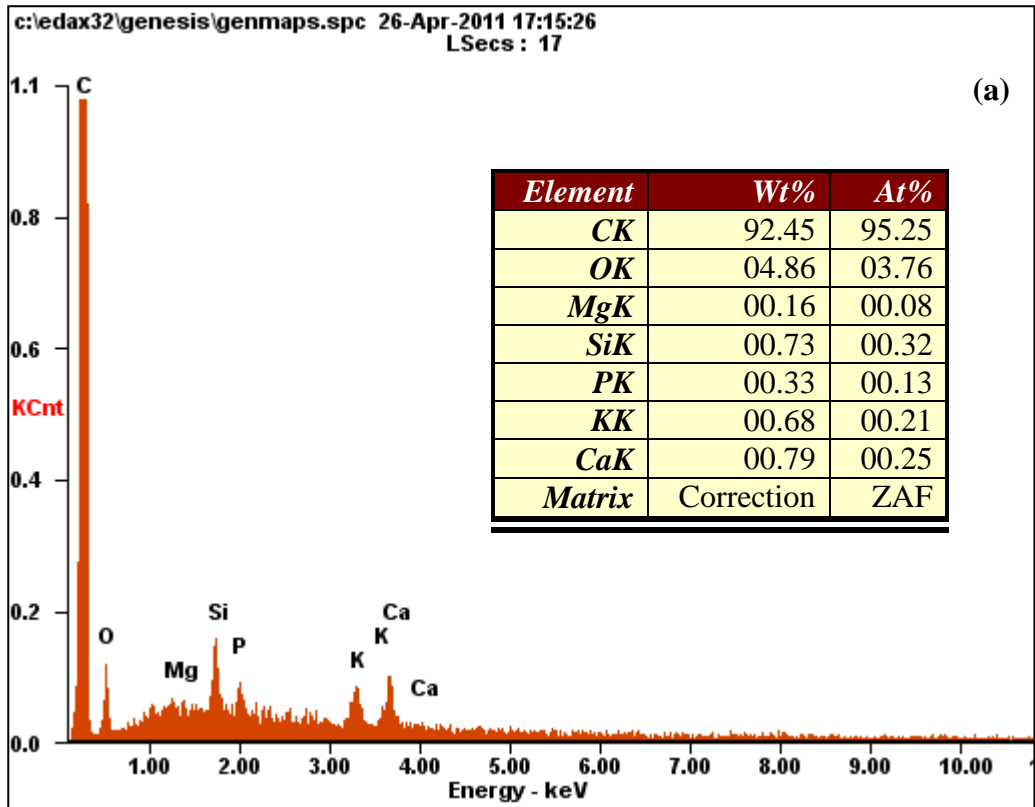


Figure 4.9: EDAX spectrum of palm shell activated carbon: (a) Virgin palm shell activated carbon, (b) Palm shell activated carbon modified with TOMAS, (c) palm shell activated carbon modified with TOMAS adsorbed with cadmium and (d) Virgin palm shell activated carbon adsorbed with cadmium.

From Figure (4.10a), in the case of virgin palm shell activated carbon, the characteristic peaks of nitrogen and sulfur do not appear, while they appear in Figure (4.10b), this indicate that TOMATS was impregnated at the PSAC. From Figure (4.10c), it is clear that a significant amount of mercury is present in the sample and is uniformly distributed, while in Figure (4.10d), the amount of mercury is less than that in Figure (4.10c). The results show that mercury becomes the principal element of the modified palm shell activated carbon surface. This was due to the fact that mercury ions were chemisorbed on the surface of modified palm shell activated carbon, while the mercury ions were physisorbed on the surface of virgin palm shell activated carbon.



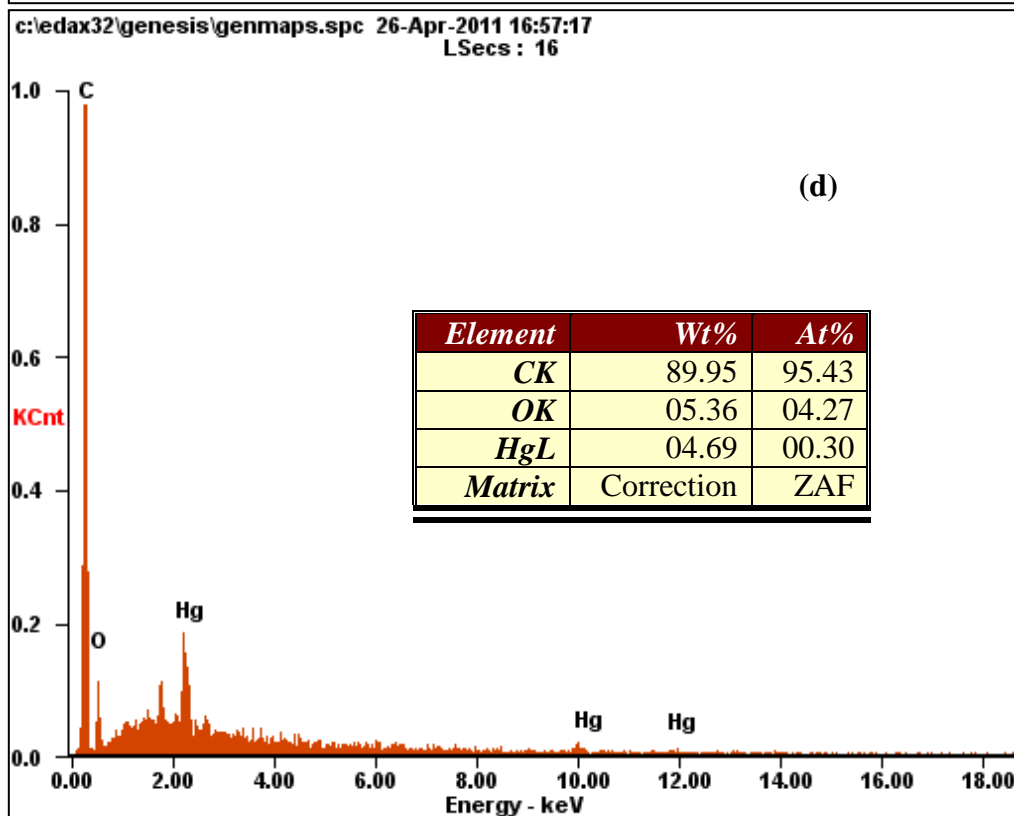
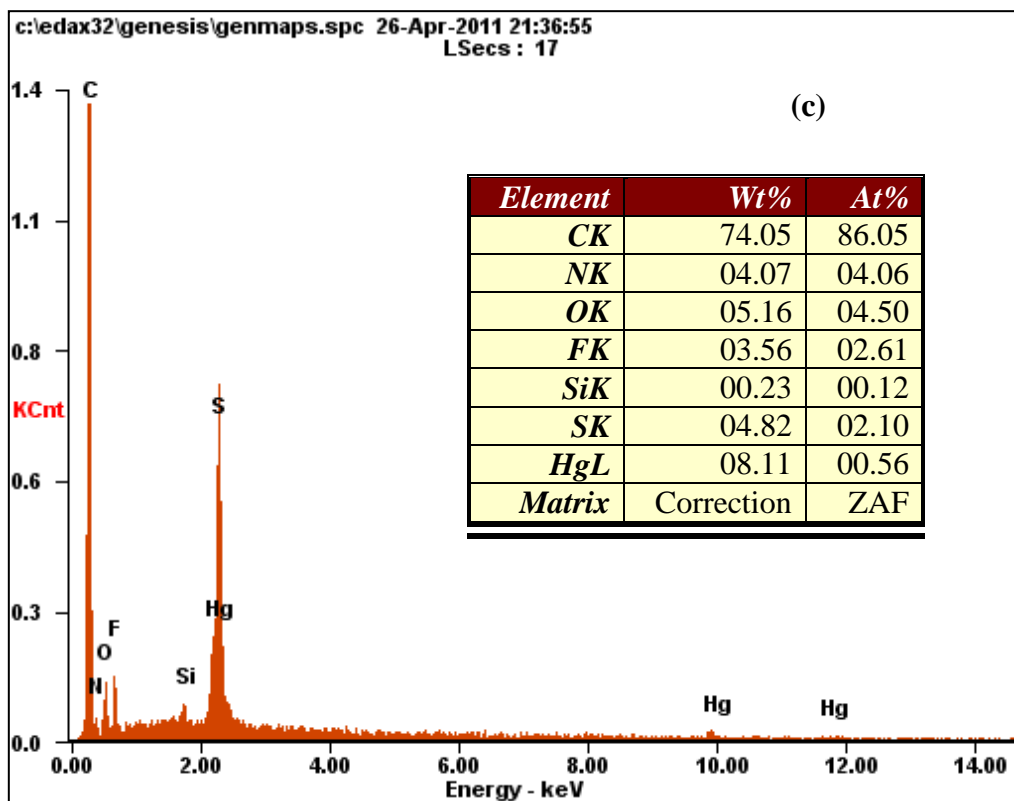


Figure 4.10: EDAX spectrum of palm shell activated carbon: (a) Virgin palm shell activated carbon, (b) Palm shell activated carbon modified with TOMATS, (c) palm shell activated carbon modified with TOMATS adsorbed with mercury and (d) Virgin palm shell activated carbon adsorbed with mercury.

### 4.2.3 Surface area and pore size analysis

Nitrogen adsorption-desorption isotherms were recorded for the virgin and grafted palm shell activated carbon. The specific surface area obtained according to the Brunauer-Emmett-Teller (BET) model of virgin palm shell activated carbon was  $636.163 \text{ m}^2\text{g}^{-1}$  at 77 K, using  $\text{N}_2$  as adsorbate.

The specific surface area decreased to  $4.88850 \text{ m}^2\text{g}^{-1}$  upon impregnated with the task specific ionic liquids (TOMAS). As shown in Figure 4.11, increasing the impregnation ratio will decrease the specific surface area due to filling of the pores of palm shell activated carbon with active TOMAS functional groups.

Table 4.6 summarizes the pore properties of the virgin and modified palm shell activated carbon samples. The specific surface area of the activated carbon decreased with increasing weight of TOMAS, as stated above, and this result may account for a smaller specific surface area. Accordingly, the average pore diameter increased from 1.845 nm for the virgin samples to 5.271 nm for the samples impregnated with TOMAS, and the total pore volume decreased from  $0.2934 \text{ cm}^3/\text{g}$  for the virgin activated carbon to  $0.006442 \text{ cm}^3/\text{g}$  for the samples impregnated with TOMAS. This result was attributed to the development of microporous and mesoporous structure.

The specific surface area decreased to  $107.692 \text{ m}^2\text{g}^{-1}$  by impregnated with task specific ionic liquids TOMATS. As shown in Figure 4.12, with increasing of impregnation ratio will decrease specific surface area due to filling the pores of palm shell activated carbon surfaces by active TOMATS functional groups.

Table 4.7 summarizes the pore properties of the virgin and modified palm shell activated carbon samples. The specific surface area of the activated carbon decrease with increasing weight of TOMATS, as stated above, and this may account for the smaller specific surface area. Accordingly, the average pore diameter increased from 1.845 nm for the virgin activated carbon to 2.409 nm for the samples impregnated with

TOMATS, and the total pore volume decreased from the virgin 0.2934 to 0.06485 cm<sup>3</sup>/g by impregnated with TOMATS. This was attributed to the development of microporous and mesoporous structure.

Table 4.6 : Surface parameters estimated by BET method using N<sub>2</sub> as adsorbent at 77 K for the activated carbon samples impregnated with TOMAS.

Weight of impregnated TOMAS (g /1 g PSAC)	Specific surface area (m <sup>2</sup> /g)	Pore diameter (nm)	Total pore volume (cm <sup>3</sup> /g)
0.00 <sup>a</sup>	636.163	1.845	0.2934
0.05	512.959	2.154	0.2762
0.1	250.452	2.234	0.1399
0.2	200.934	2.366	0.1189
0.3	4.88850	5.271	0.006442

<sup>a</sup> Virgin palm shell activated carbon

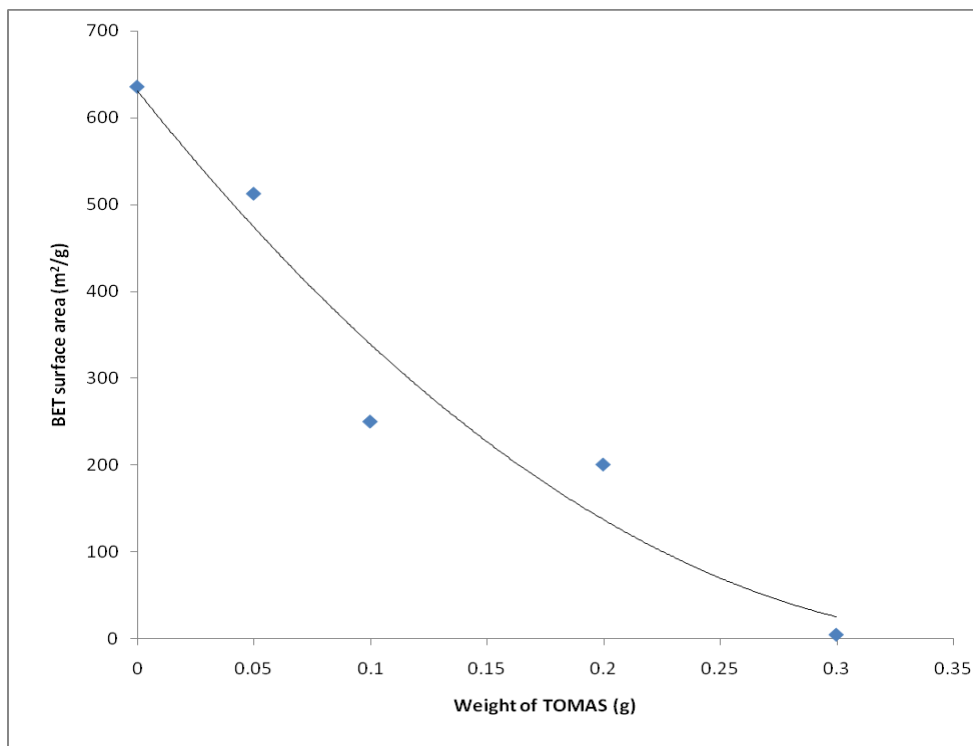


Figure 4.11 : BET specific surface area (m<sup>2</sup>g<sup>-1</sup>) as a function of TOMAS weight grafted on 1 g palm shell activated carbon.



Table 4.7 : Surface parameters estimated by BET method using N<sub>2</sub> as adsorbent at 77 K for the activated carbon samples impregnated with TOMATS.

Weight of impregnated TOMATS (g /1g PSAC)	Specific surface area (m <sup>2</sup> /g)	Pore diameter (nm)	Total pore volume (cm <sup>3</sup> /g)
0.00 <sup>a</sup>	636.163	1.845	0.2934
0.05	513.089	2.159	0.2769
0.1	364.550	1.829	0.1667
0.2	275.943	2.243	0.1548
0.3	107.692	2.409	0.06485

<sup>a</sup> Virgin palm shell activated carbon

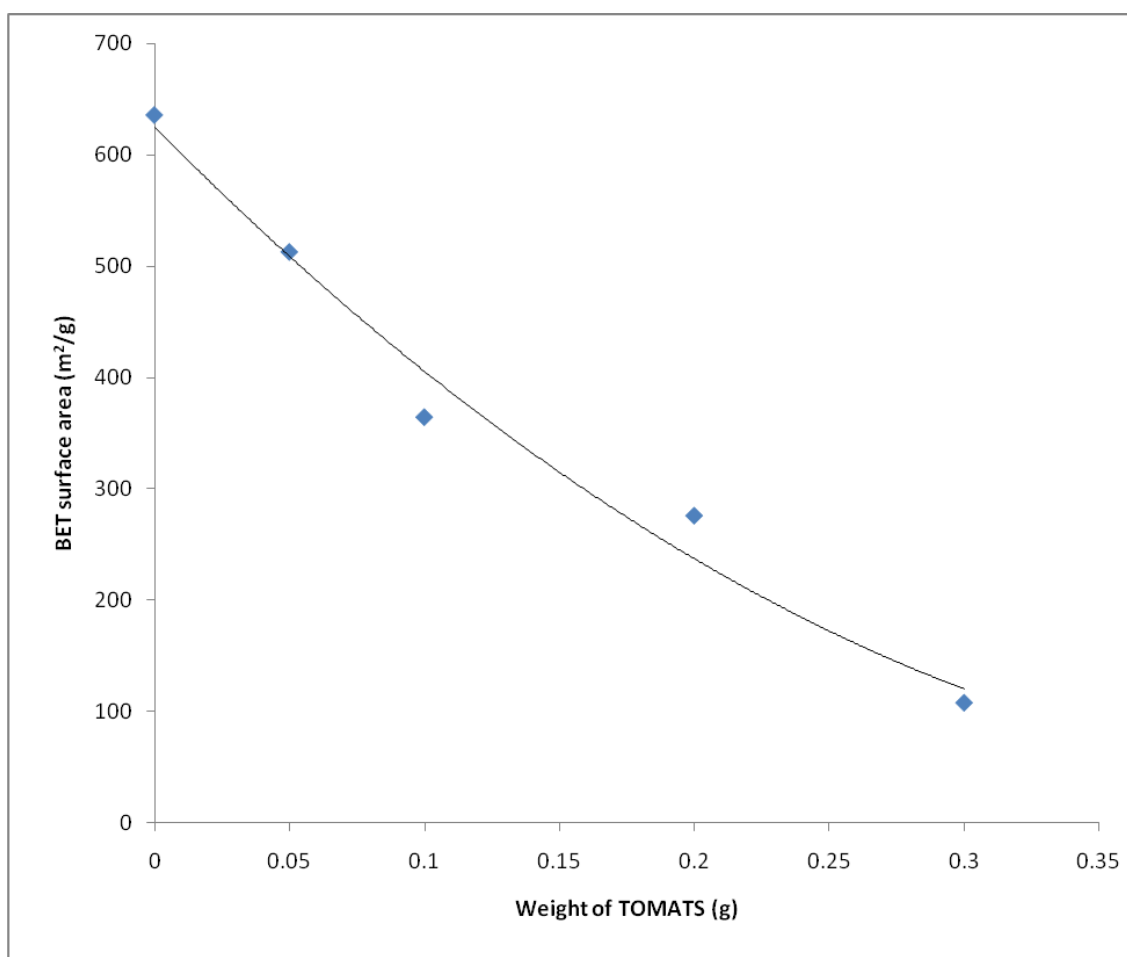


Figure 4.12 : BET specific surface area (m<sup>2</sup>g<sup>-1</sup>) as a function of TOMATS weight grafted on 1 g palm shell activated carbon.

### 4.3 Kinetics applications

The proposed electrodes have been used for kinetic adsorption studies of cadmium (II) and mercury (II) on palm shell activated carbon impregnated with TOMAS and TOMATS, respectively. The purposes of these in situ kinetic investigations were to develop a potentiometric kinetic method to study the kinetic parameters of cadmium and mercury adsorption.

Kinetic models were used to study the mechanism of adsorption process steps, such as mass transport and chemical reaction processes. The experiment was based on the ISE technique because the proposed ion selective electrodes are able to directly monitor the free M (II) concentration without requiring separation processes or disturbing the binding equilibrium. The results were compared with those obtained by the conventional adsorption kinetic method. The kinetics of Cd (II) and Hg (II) adsorption on the modified palm shell activated carbon were analyzed using pseudo-second-order models (Ho and McKay, 1999).

The values of the rate constant of pseudo-second-order  $k_2$  ( $\text{g mg}^{-1}\text{min}^{-1}$ ), the adsorption capacity at equilibrium  $q_e$  (mg/g), and the initial adsorption rate  $h$  (mg/g min) are determined from the slope and intercept of the plot of  $t/q_t$  against  $t$  according to the equation 3.5 (Figs. 4.13 and 4.14). The values are given in Tables (4.8 and 4.9).

The linearity of the plot of these kinetic models was determined by the correlation coefficient of the plot, which can also be regarded as an indicator of the efficiency of the kinetic model.

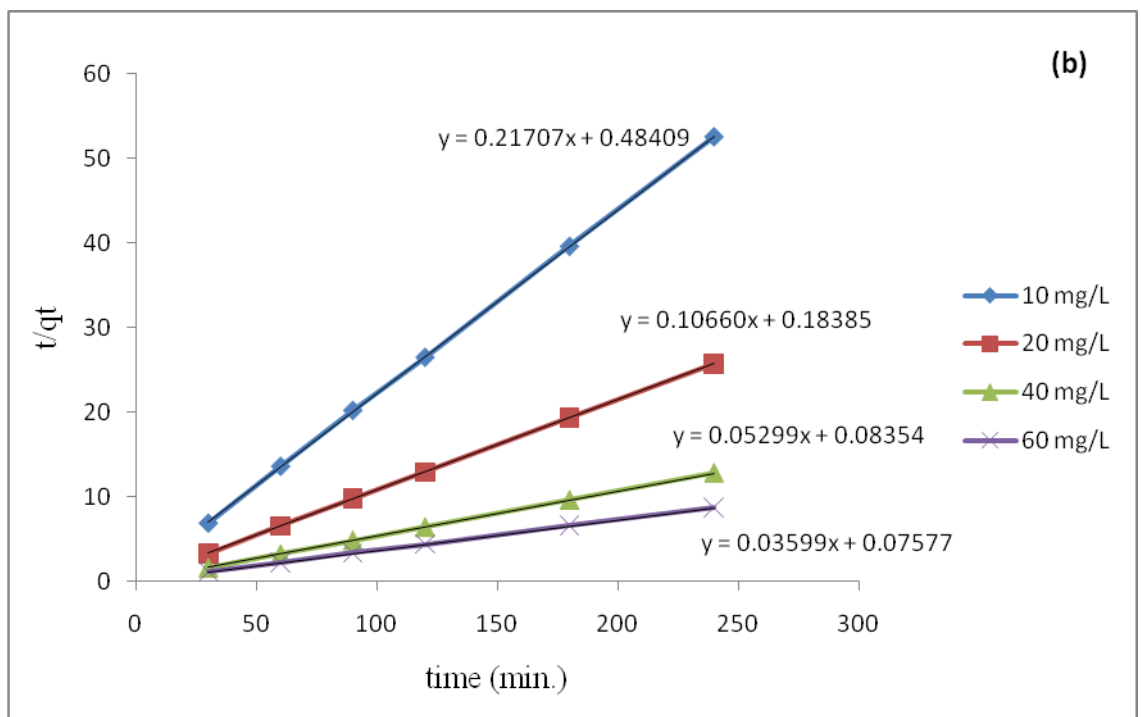
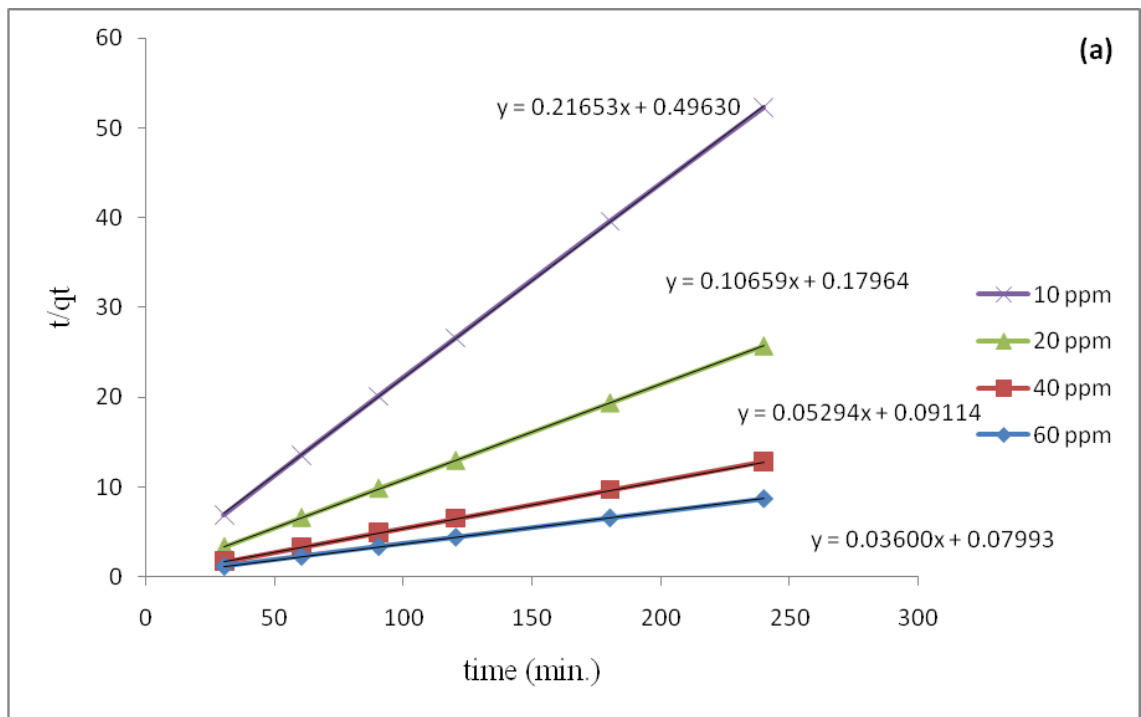


Figure 4.13 : Pseudo second order kinetic plots of Cd (II) ion adsorption onto modified palm shell activated carbon (experimental conditions: adsorbent 0.1g/50mL, Cd(II) initial concentration range from 10 – 60 mg/L, pH 8 and orbital shaking of 3 hours at 180 rpm incubated at  $30 \pm 2$  °C. (a) Results using ISE method and (b) using kinetic conventional method.

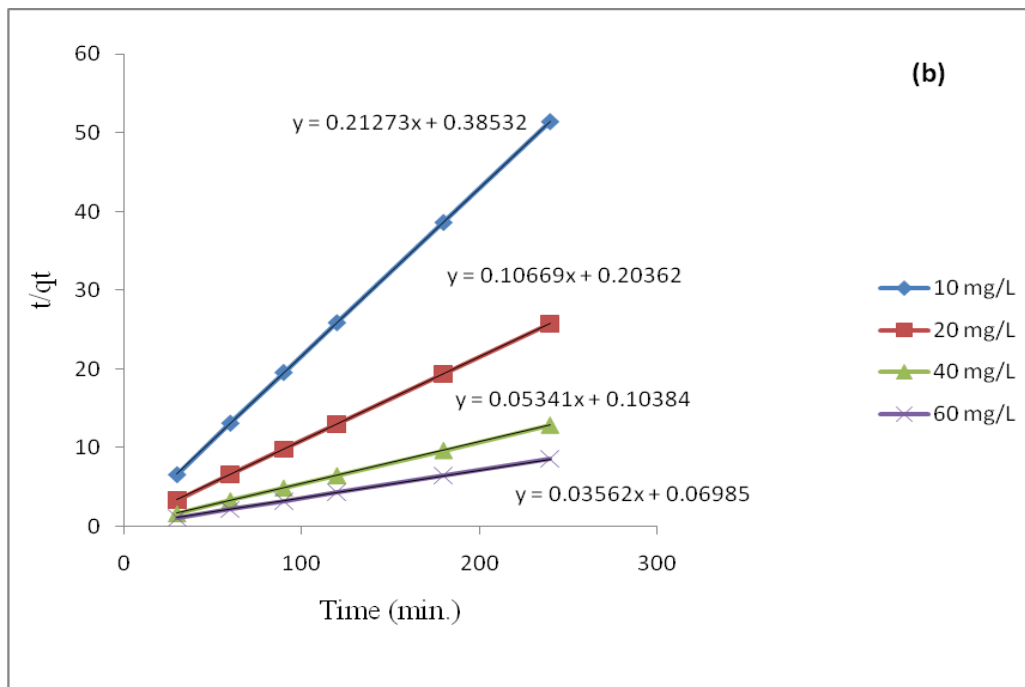
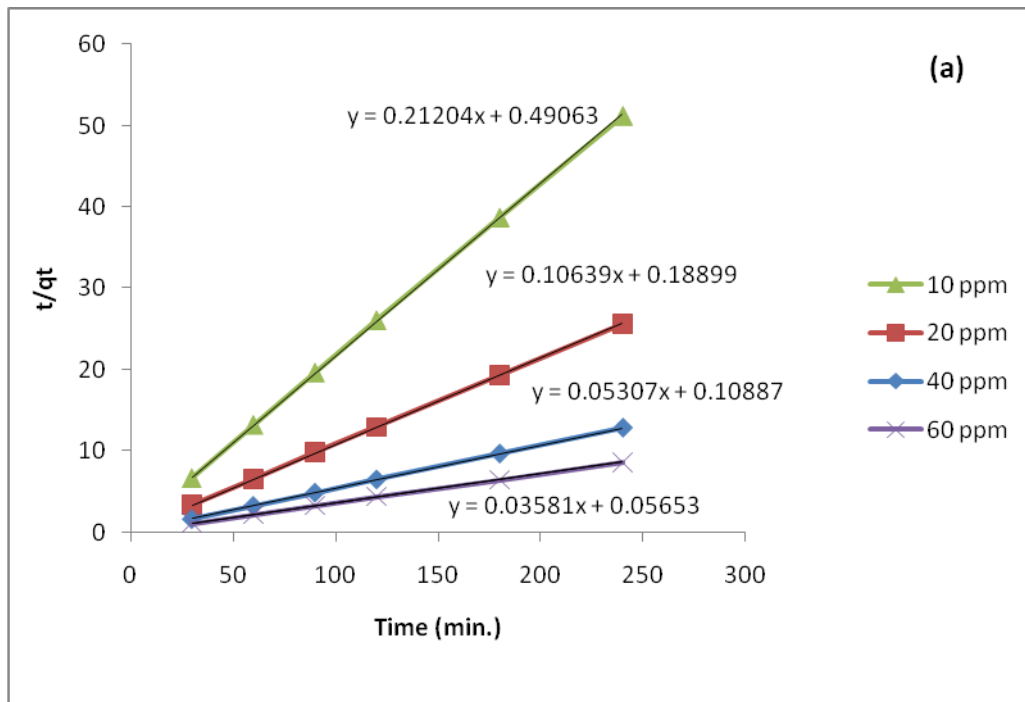


Figure 4.14 : Pseudo second order kinetic plots of Hg (II) ion adsorption onto modified palm shell activated carbon (experimental conditions: adsorbent 0.1g/50ml, Hg(II) initial concentration range from 10 – 60 mg/L, pH 8 and orbital shaking of 3 hours at 180 rpm incubated at  $30 \pm 2^\circ\text{C}$ . (a) Results using ISE method and (b) using kinetic conventional method.

Tables (4.8 and 4.9) summarize the values of the pseudo-second-order parameters using ion-selective electrode (ISE) potentiometry with the proposed electrode and compare these values with those obtained by the conventional adsorption kinetic method. The results show good agreement with those obtained using ICP-OES. The high values of the correlation coefficients for the pseudo-second-order kinetic model indicate that the adsorption system is most likely best described by this model. Moreover, the agreement between the calculated adsorption capacities determined using pseudo second order plots and the experimental values are convincing. This result indicates that cadmium and mercury adsorption followed pseudo second-order kinetics, and that Cd(II) and Hg(II) ions were adsorbed onto modified palm shell activated carbon surfaces via chemical interaction. This result confirmed the chemisorption aspect of the adsorption process. The decrease in  $k_2$  values with an increase in the initial metal ion concentration is a common phenomenon observed with a variety of adsorbents used for the adsorption of metal ions. Many factors can contribute to this initial concentration effect on the adsorption rate. Increasing the metal concentration in solution seems to reduce the diffusion of metal ions in the boundary layer and enhance the diffusion in the solid. Another possible cause is the progressive decrease in covalent interactions relative to the electrostatic interactions of the sites, with a lower affinity for M(II) with an increase in initial metal concentration.

The effect of contact time on the adsorption of Cd (II) and Hg (II) was studied by keeping particle size, initial concentration, adsorbent dose, and pH constant. The results showed that, adsorption increased rapidly during the first 3 h, after which the adsorption reached an equilibrium state. Figs. 4.15 and 4.16 show that a 3 h contact time was required to attain adsorption equilibrium for the metal solution. During this time, over 90% of the metal was adsorbed due to the initial availability of free TSILs on the modified activated carbon surface. Over time, the coordinate interaction between TSILs

and M (II) ions occurred, and adsorption became nearly constant until the end of the experiment. It can be concluded that the binding of metals with TSILs was high in the initial stages, beyond which the reactive functional groups of TSILs were increasingly depleted. Subsequently, it became difficult for the metal ions to occupy the modified activated carbon surface.

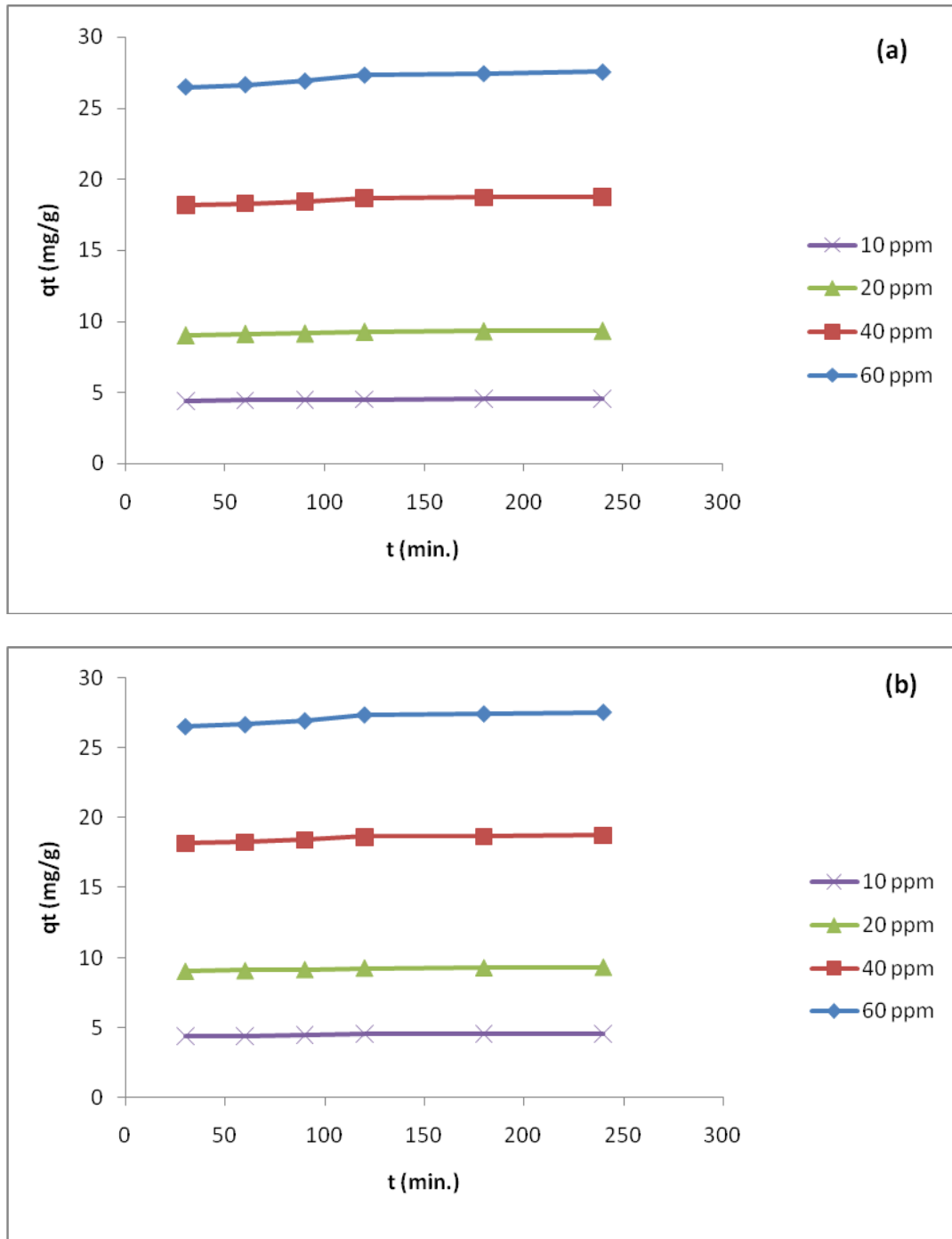


Figure 4.15 : Plot of adsorption capacity versus time for the adsorption of cadmium ions on modified palm shell activated carbon using (a) the ISE method and (b) the conventional kinetic methods

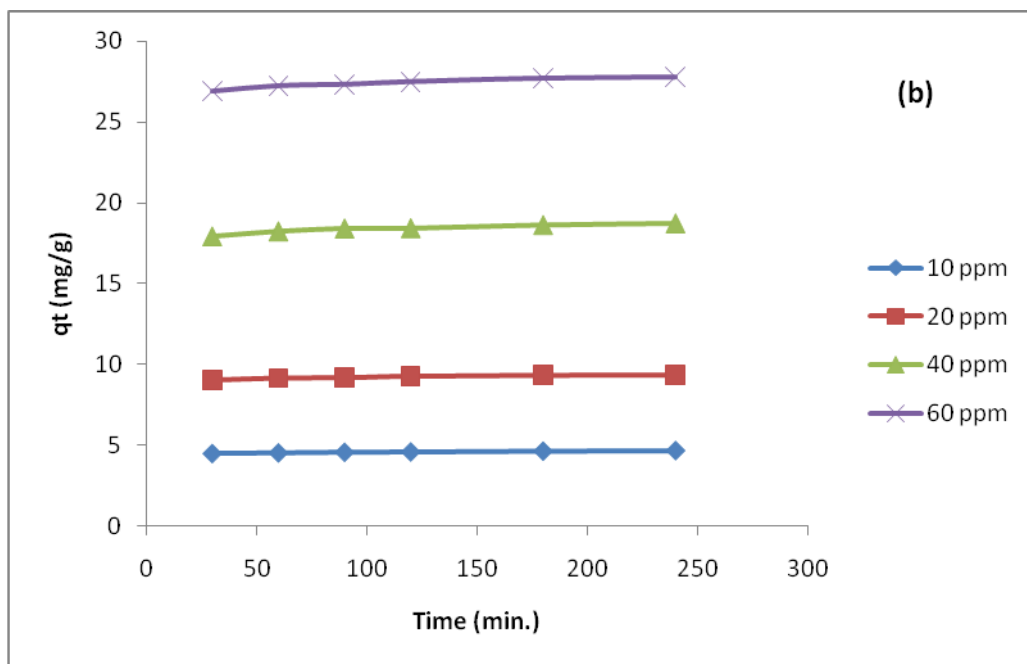
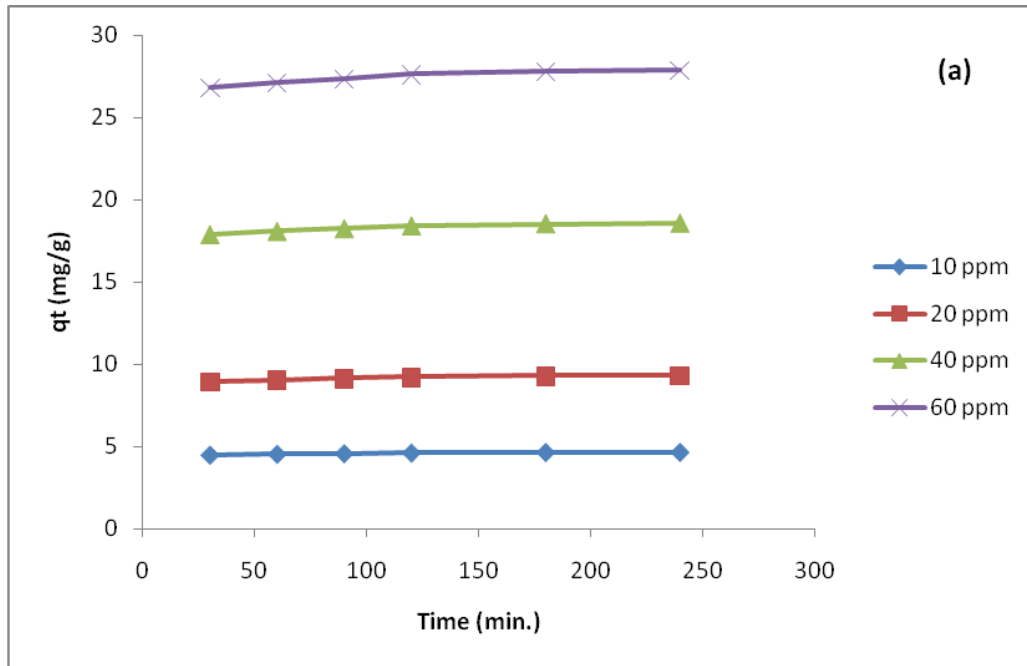


Figure 4.16 : Plot of adsorption capacity versus time for the adsorption of mercury ions on modified palm shell activated carbon using (a) the ISE method and (b) the conventional kinetic method.



For the cadmium electrode, both the ISE results and conventional kinetic studies of the rate constant value  $k_2$  generally depend on the initial cadmium concentration. As shown in Fig. 4.17, the values of the rate constant increased from 0.017 to 0.097 g/mg min upon a decrease in the initial cadmium concentration. Thus, for higher initial adsorbate concentrations, longer times are required to reach equilibrium; in turn, the  $k_2$  values decreases.

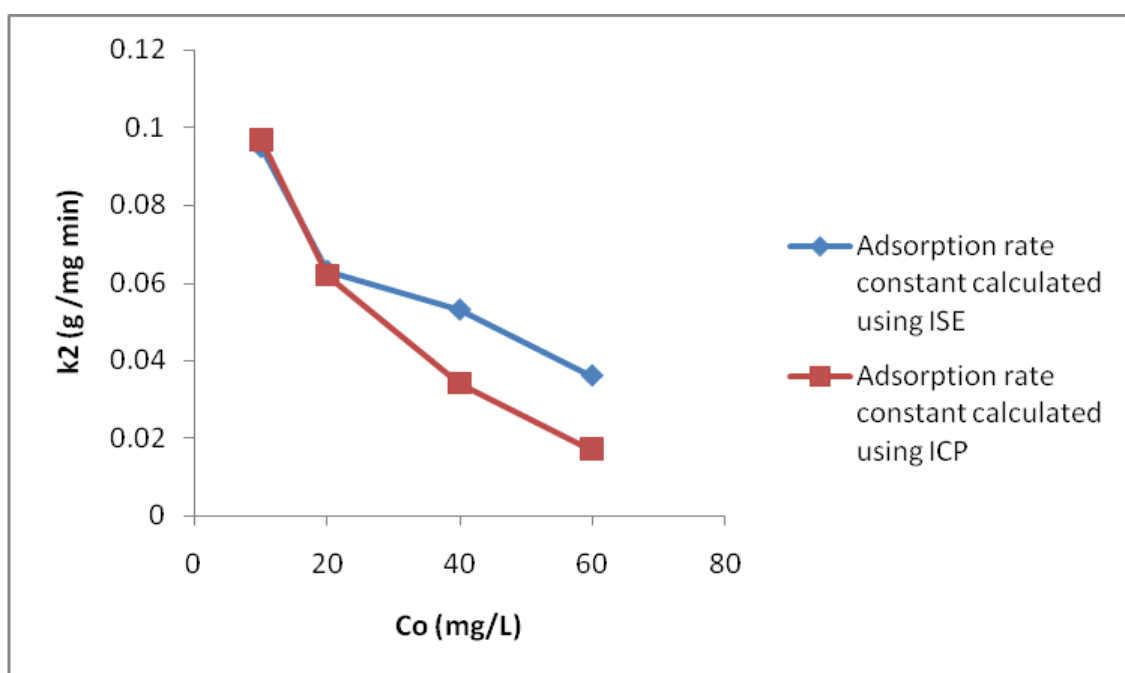


Figure 4.17 : Adsorption rate constant versus initial concentration for cadmium ion adsorption onto modified palm shell activated carbon.

For the mercury electrode, both the ISE results and conventional kinetic studies of the rate constant,  $k_2$ , usually depend on the initial mercury concentration. As shown in Fig. 4.18, the values of the rate constant increased from 0.018 to 0.117 g/mg min for a decrease in the initial mercury concentration. Thus, the higher the initial concentration of the adsorbate, the longer the time required to reach equilibrium. Thus, the  $k_2$  values decrease.

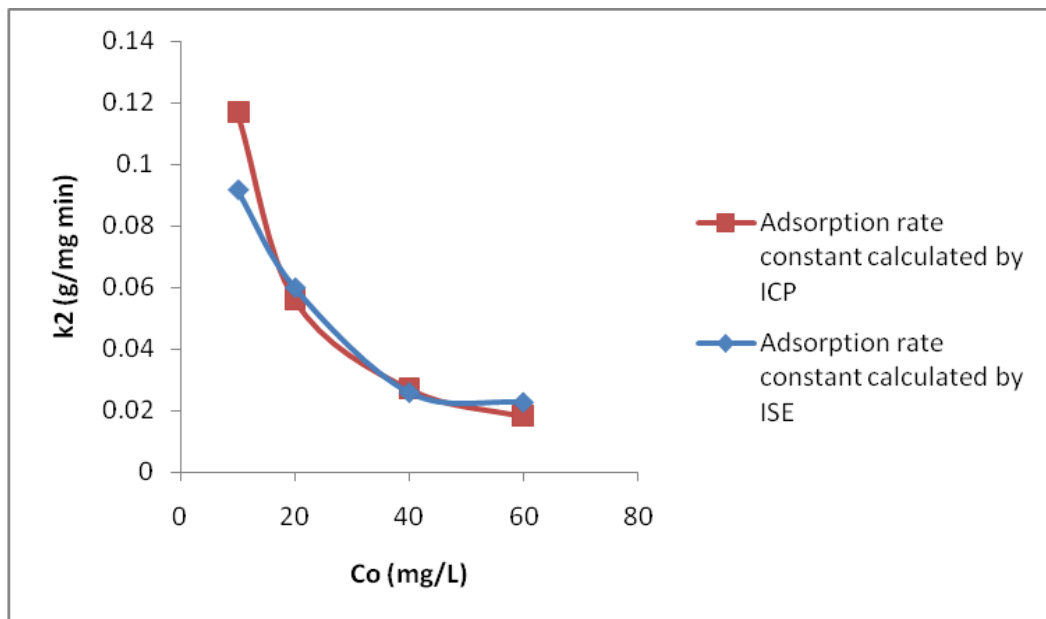


Figure 4.18 : Adsorption rate constant versus initial concentration for the adsorption of mercury ions onto modified palm shell activated carbon.

The second order rate constants were used to calculate the initial adsorption rate  $h$  given by equation 3.6.

The calculated  $h$  values are plotted against the initial concentration, as shown in Figs. 4.19 and 4.20. Both the ISE results and conventional kinetic studies indicate that the value of the initial adsorption rate  $h$  usually depends on the initial adsorbate concentration.

For the cadmium electrode, the initial adsorption rate  $h$  was found to increase with increasing initial cadmium concentration; however, the adsorption rate value began to decrease at higher initial concentrations. This decrease may be due to high solute concentrations slowing the adsorption process. For all initial concentrations, the same amount of adsorbent was used, which might not have been sufficient for the cadmium ions to adsorb quickly when the initial concentration was overly high.

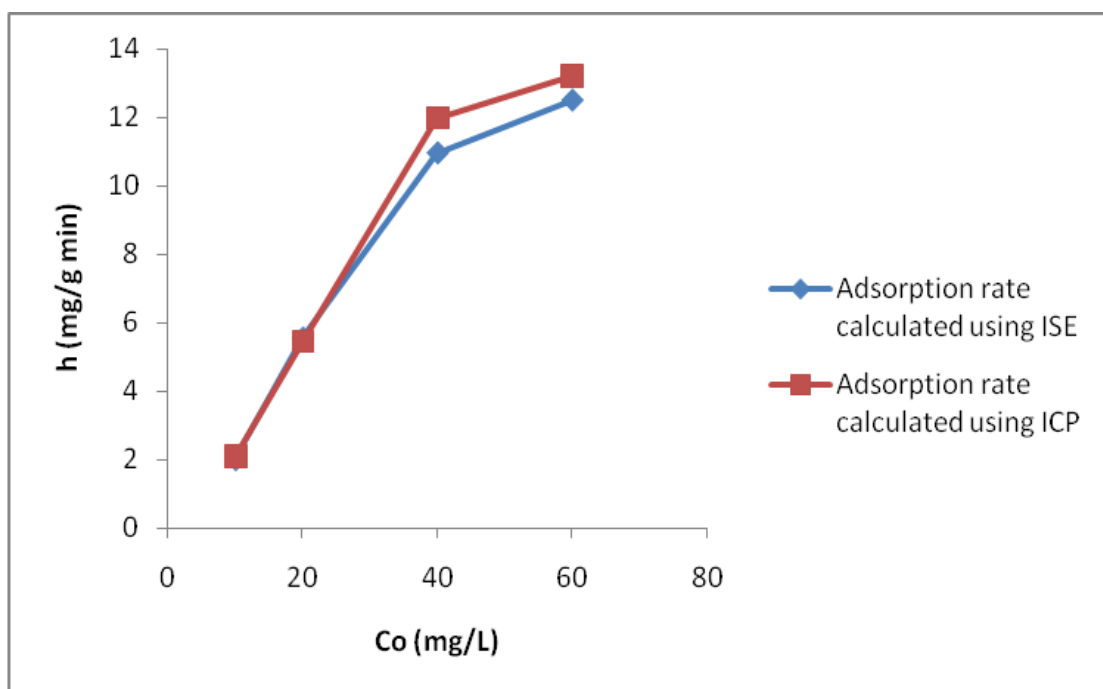


Figure 4.19 : Initial adsorption rate versus initial concentration for the adsorption of cadmium ions onto modified palm shell activated carbon.

For the mercury electrode, the initial adsorption rate,  $h$ , was also found to increase with increasing initial mercury concentration; however, the value began to decrease for higher initial concentrations. This decrease may be due to high solute concentrations slowing the adsorption process, given that the same amount of adsorbent was used for all initial concentrations, which might be insufficient for the mercury ions to quickly adsorb when the initial concentration was too high.

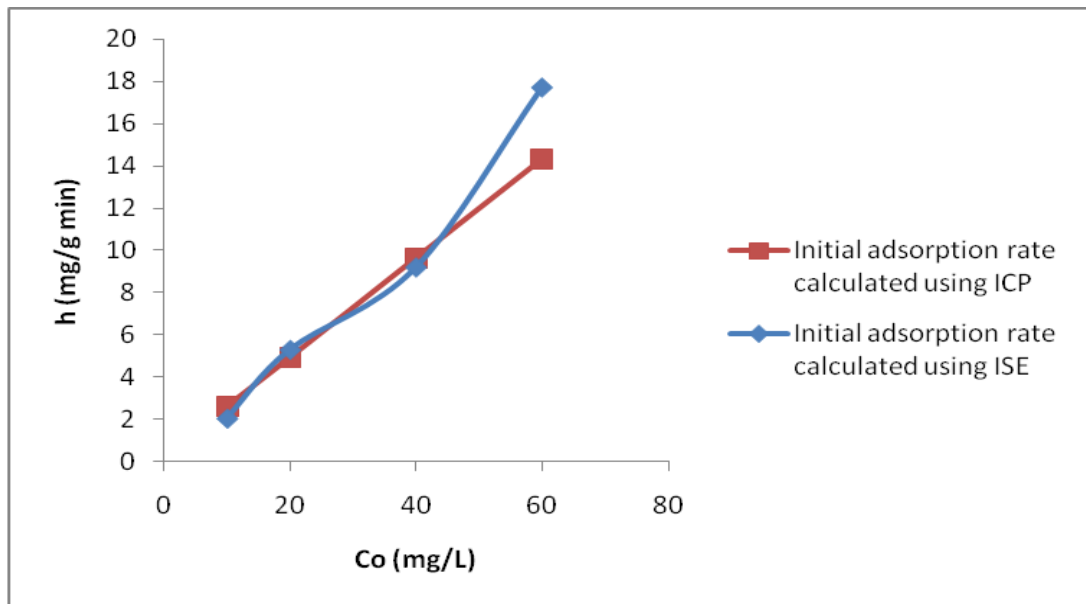


Figure 4.20 : Initial adsorption rate versus initial concentration for the adsorption of mercury ions onto modified palm shell activated carbon

Table 4.8 : Kinetic parameters for adsorption of cadmium ions on modified palm shell activated carbon (experimental conditions: adsorbent 0.1g/50mL, Cd(II) initial concentration range from 10 – 60 mg/L, pH 8 and orbital shaking at 180 rpm Incubated at  $30 \pm 2$  °C).

C <sub>o</sub> (mg/L)	kinetic parameters using ISE					kinetic parameters using ICP					RSD <sup>a</sup> (%)	Recovery (%)
	q <sub>e</sub> (exp)	q <sub>e</sub> (cal)	k <sub>2</sub>	h	R <sup>2</sup>	q <sub>e</sub> (exp.)	q <sub>e</sub> (calc.)	k <sub>2</sub>	h	R <sup>2</sup>		
10	4.587	4.618	0.095	2.015	1	4.581	4.607	0.097	2.066	1	0.09	100.13
20	9.339	9.382	0.063	5.567	1	9.34	9.381	0.062	5.439	1	0.01	99.99
40	18.798	18.889	0.053	10.972	1	18.79	18.87	0.034	11.97	1	0.03	100.04
60	27.574	27.778	0.036	12.511	1	27.64	27.79	0.017	13.2	1	0.17	99.76

<sup>a</sup> Relative standard deviation for q<sub>e</sub> from experimental results using ISE and ICP

Table 4.9 : Kinetic parameters for adsorption of mercury ions on modified palm shell activated carbon (experimental conditions: adsorbent 0.1 g /50 mL, Hg(II) initial concentration range from 10 – 60 mg/L, pH 8 and orbital shaking at 180 rpm Incubated at  $30 \pm 2$  °C).

C <sub>o</sub> (mg/L)	kinetic parameters using ISE					kinetic parameters using ICP					RSD <sup>a</sup> (%)	Recovery (%)
	q <sub>e</sub> (exp)	q <sub>e</sub> (cal)	k <sub>2</sub>	h	R <sup>2</sup>	q <sub>e</sub> (exp.)	q <sub>e</sub> (calc.)	k <sub>2</sub>	h	R <sup>2</sup>		
10	4.667	4.716	0.092	2.038	1	4.689	4.701	0.117	2.595	1	0.23	100.3
20	9.947	9.399	0.060	5.291	1	9.348	9.373	0.056	4.911	1	0.20	100.3
40	19.999	18.843	0.026	9.185	1	18.67	18.72	0.027	9.63	1	0.46	100.7
60	28.029	27.925	0.023	17.690	1	28	28.07	0.018	14.32	1	0.37	99.5

<sup>a</sup> Relative standard deviation for q<sub>e</sub> from experimental results using ISE and ICP

#### **4.4 Analytical applications**

The groundwater aquifer is the most important fresh water source in the Gaza Strip; however, it is severely polluted, mainly by salt water, nitrates, heavy metals, and other pollutants. Several domestic wells have shown high cadmium and mercury concentrations (Shomar, 2007). These wells are located in regions with intense agriculture, wastewater treatment plants, and solid waste dumping sites. The main contamination sources are the unregulated discharge of domestic and industrial solid waste, water waste, and agricultural waste from fertilizers and pesticides.

Classical methods have been used to determine the contents of these pollutants, such as gravimetry, spectrophotometry, and chromatography.

These methods are time-consuming and tedious and require experts. Moreover, they produce additional waste and are expensive. In addition, these methods cannot be used for all samples and are largely unavailable in Gaza.

The proposed electrodes have been mainly used in the determination of the amount of cadmium (II) and mercury (II) ions in water samples.

Water samples were collected from four domestic wells nearest to the waste water collection area in the Gaza Strip (Palestine).

Statistical treatment of analytical applications results: One of the most important properties of a new analytical method is that it should be free from systematic error, where, the value obtained, after its application, should be very close to the true value. This property may be tested by applying the method to a standard sample. However, random errors make it most unlikely that the measured amount even if there were no systematic error. This comparison between the obtained and the expected values is expressed mathematically in what is called the recovery values. In this work Cd(II) and Hg(II) contents measured by the proposed electrode were compared with those obtained

by ICP-OES (Table 4.10 and 4.11). Almost 100% recovery was calculated for each of the applications in this work, high precision was observed as indicated by the very low standard deviation values. These results show that Cd(II) concentrations obtained with the proposed electrode were similar to those obtained by ICP with deviations below 4% for all samples, whereas the deviations for Hg(II) were below 2% for all samples. These values reflect high accuracy and precision of the proposed electrodes.

Table 4.10 : Potentiometric determination of Cd(II) in water samples using the proposed electrode and ICP.

<b>Sample<sup>a</sup></b>	<b>Cd (II) (mgL<sup>-1</sup>)<sup>b</sup></b>			
	<b><i>Proposed electrode</i></b>	<b><i>ICP</i></b>	<b><i>RSD%</i></b>	<b><i>Recovery%</i></b>
(1)	0.575	0.55	3.19	104.6
(2)	0.464	0.446	2.90	104.2
(3)	0.480	0.491	1.55	97.8
(4)	0.423	0.412	1.92	102.8

*a From some ground water wells in Gaza Strip.*

*b Mean data for three replicate measurements.*



Table 4.11 : Potentiometric determination of Hg(II) in water samples using the proposed electrode and ICP.

Sample <sup>a</sup>	Hg (II) (mgL <sup>-1</sup> ) <sup>b</sup>			
	Proposed electrode	ICP	RSD%	Recovery%
(1)	1.353	1.363	0.54	99.2
(2)	1.472	1.443	1.39	102.0
(3)	1.483	1.499	0.74	99.0
(4)	1.408	1.404	0.18	100.3

*a From some ground water wells in Gaza Strip.*

*b Mean data for three replicate measurements*

#### **4.5 Comparison of the response for the proposed Cd(II) and Hg(II) electrodes with other reported electrodes**

The comparative study of the proposed electrode with some recently developed cadmium and mercury electrodes is summarised in Tables 4.12. and 4.13. The results show the superiority of the proposed electrode in terms of its wider linear range, Nernstian slope, and lower detection limit.

Table 4.12 : Comparison of the proposed Cd-PSACPE electrode with previously reported electrodes.

<i>Ionophore</i>	<i>Slope</i>	<i>Linear range</i>	<i>Detection limit</i>	<i>Response time (s)</i>	<i>Ref.</i>
	<i>(mV/decade)</i>	<i>(mol L<sup>-1</sup>)</i>	<i>(mol L<sup>-1</sup>)</i>		
4-hydroxy salophen	30.1 ± 1	1.0×10 <sup>-6</sup> to 1.0×10 <sup>-1</sup>	8.4×10 <sup>-7</sup>	20	(Ensaifi et al., 2009)
N,N_-[bis(pyridin-2-yl)formylidene]butane-1,4-diamine	30	7.9×10 <sup>-8</sup> to 1.0×10 <sup>-1</sup>	5.0×10 <sup>-8</sup>	10	(Gupta et al., 2007)
dicyclohexano-24-crown-8	30.0±1.0	3.0×10 <sup>-5</sup> to 1.0×10 <sup>-1</sup>	-	23	(Gupta et al., 2006a)
Tripodal amine	29.4 ± 0.6	1.6 × 10 <sup>-6</sup> – 1.0× 10 <sup>-2</sup>	1.6 × 10 <sup>-6</sup>	10	(Khamjumhol et al., 2011)
2,2_-(1Z,1_Z)-(1E,1_E)-(1,2-phenylenebis(methan-1-yl-1-ylidene)bis(azaan-1-yl-1-ylidene)bis(methylene)bis(azan-1-yl-1-ylidene)bis (methan-1-yl-ylidene) diphenol	30.0 ± 0.2	5.0×10 <sup>-9</sup> to 1.0×10 <sup>-1</sup>	3.1×10 <sup>-9</sup>	11	(Gupta et al., 2009)

**Table 4.12, continued**

<i>Ionophore</i>	<i>Slope</i>	<i>Linear range</i>	<i>Detection limit</i>	<i>Response time (s)</i>	<i>Ref.</i>
	<i>(mV/decade)</i>	<i>(mol L<sup>-1</sup>)</i>	<i>(mol L<sup>-1</sup>)</i>		
3,5-Dinitro-N-(tri-2-pyridyl methyl) benzamide	30 ± 1	2.16 × 10 <sup>-7</sup> –1.00 × 10 <sup>-1</sup>	1.82 × 10 <sup>-7</sup>	50	(Abbastabar-Ahangar et al., 2009)
N1, N2-dicyanoethyl-N1, N2-bis(pyridin-2-ylmethyl) benzene-1, 2-diamine	29.5	2.5 × 10 <sup>-7</sup> – 1.0 × 10 <sup>-1</sup>	7.8 × 10 <sup>-8</sup>	12	(Singh et al., 2011)
tetrathia-12-crown-4	29 ± 1	4.0 × 10 <sup>-7</sup> – 1.0 × 10 <sup>-1</sup>	1.0 × 10 <sup>-7</sup>	<10	(Shamsipur and Mashhadizadeh, 2001)
N,N-(4methyl-1,2-phenylene) diquinoline-2-carboxamide	29.9 ± 0.5	1.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-1</sup>	8 × 10 <sup>-7</sup>	3–8	(Rezaei et al., 2008)
TOMAS	30.90 ± 1	1.0 × 10 <sup>-9</sup> to 1.0 × 10 <sup>-2</sup>	1.0 × 10 <sup>-10</sup>	10	<i>This work</i>

Table 4.13 : Comparison of the proposed Hg-PSACPE electrode with previously reported electrodes

<i>Ionophore</i>	<i>Slope</i>	<i>Linear range</i>	<i>Detection limit</i>	<i>Response time (s)</i>	<i>Ref.</i>
	<i>(mV/decade)</i>	<i>(mol L<sup>-1</sup>)</i>	<i>(mol L<sup>-1</sup>)</i>		
Tetrazolium–triiodomercurate	55.5±0.4	1×10 <sup>-3</sup> - 6×10 <sup>-6</sup>	4×10 <sup>-6</sup>	30-50	<i>(Abbas and Mostafa, 2003)</i>
N,N'-bis(salicylaldehyde)-phenylenediamine	58.8 ± 0.3	3.2 × 10 <sup>-7</sup> - 3.2 × 10 <sup>-4</sup>	1.5 × 10 <sup>-7</sup>	≥10	<i>(Abu-Shawish, 2009)</i>
Diamine donor ligand	25 ± 0.1	1.25 × 10 <sup>-5</sup> - 1.0 × 10 <sup>-1</sup>	8.9 × 10 <sup>-6</sup>	10	<i>(Gupta et al., 2005)</i>
1-(2-ethoxyphenyl)-3-(3-nitrophenyl)triazene	29.3 ± 0.2	1.0 × 10 <sup>-4</sup> - 5.0 × 10 <sup>-9</sup>	2.5 × 10 <sup>-9</sup>	~5	<i>(Khani et al., 2010)</i>
Bis[5-((4-nitrophenyl)azosalicylaldehyde)]	30±1	5 × 10 <sup>-2</sup> - 7 × 10 <sup>-7</sup>	2.0(±0.1)×10 <sup>-7</sup>	<10	<i>(Mashhadizadeh and Sheikhshoae, 2003)</i>
4-(4-N,N-dimethylphenyl)-2,6-diphenylpyrilium tetrafluoroborate	34	1.0 × 10 <sup>-8</sup> - 1.0 × 10 <sup>-3</sup>	1.0 × 10 <sup>-8</sup> M	about 3 min	<i>(Yu et al., 2007)</i>
Ethyl-2-(benzoylamino)-3-(2-hydroxy-4-methoxyphenyl)-2-propenoate	48.5±1.0	3.0×10 <sup>-7</sup> - 3.1×10 <sup>-2</sup>	1.0×10 <sup>-7</sup>	~5	<i>(Mashhadizadeh et al., 2006)</i>
Substituted thiourea	28.4 ± 1.0	1.0 × 10 <sup>-7</sup> - 1.0 × 10 <sup>-1</sup>	7.0 × 10 <sup>-8</sup>	~35	<i>(Mehran et al., 2009)</i>

**Table 4.13, continued**

<i>Ionophore</i>	<i>Slope</i>  <i>(mV/decade)</i>	<i>Linear range</i>  <i>(mol L<sup>-1</sup>)</i>	<i>Detection limit</i>  <i>(mol L<sup>-1</sup>)</i>	<i>Response time (s)</i>	<i>Ref.</i>
Cyclodextrins	20	$0.9 \times 10^{-7} - 1.0 \times 10^{-1}$	$0.9 \times 10^{-7}$	20	<i>(Roa-Morales et al., 2005)</i>
<i>N,N</i> -dimethylformamide-salicylacylhydrazone	29.6	$6.2 \times 10^{-7} - 8.0 \times 10^{-2}$	$5.0 \times 10^{-7}$	<30	<i>(YE et al., 2006)</i>
TOMATS	$44.08 \pm 1.0$	$1.0 \times 10^{-9}$ to $1.0 \times 10^{-2}$	$1.0 \times 10^{-10}$	~5	<i>This work</i>

## **CHAPTER 5: CONCLUSIONS, FUTURE CHALLENGES, AND PROSPECTS**

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## CHAPTER 5

### CONCLUSIONS, FUTURE CHALLENGES, AND PROSPECTS

#### 5.1 Conclusions

As indicated by this work, the use of TSILs in electrochemical sensing is a promising and exciting area of research that definitely merits further exploration. The combination of TSILs with electrochemical sensors has the potential to broaden or even revolutionize the range of analytical methods.

The results presented herein demonstrate the utility of TSILs as both plasticizers and ionophores in the preparation of new ion selective electrodes for the determination of heavy metal ions. In this work, two types of ion selective electrodes were constructed.

First, a palm shell activated carbon modified with trioctylmethylammonium salicylate (TOMAS) was used for the potentiometric determination of cadmium ions in water samples, yielding the following important findings:

- In this work, TOMAS, which is considerably viscous, water immiscible, and electrochemically conductive, was used as both the ionophore and plasticizer.
- Palm shell activated carbon grafted with TOMAS enhances the potentiometric characters and enlarges the active surface area at the proposed electrode.
- The modified electrode shows excellent potentiometric response, sensitivity, selectivity, and stability.
- The electrode was successfully applied for the determination of cadmium content in drinking water samples. The electrode shows better sensitivity towards Cd(II) ion determination by potentiometry than ion coupled plasma-mass spectrometry, atomic adsorption spectrometry, and voltammetry.

- The modified palm shell activated carbon paste electrode is very simple and inexpensive.
- The proposed electrode shows good sensitivity and satisfactory reproducibility. Moreover, investigations of real samples show that the proposed Cd(II) ion detection methodology offers a wide linear range, a lower limit of detection, and low interference by other heavy metal ions often present in real samples.
- The experimental results for both analytical and kinetic applications using the proposed electrode agree very well with those obtained using ICP.
- The experiment indicates that the proposed electrode is able to directly monitor the cadmium ion concentration without requiring a separation process or disturbing the binding equilibrium.
- The sensitivity and relatively high stability of the electrode opened a new avenue for the detection of heavy metal ions via complexation with ionic liquids at the activated carbon surface.
- A potentiometric method for the in vitro adsorption kinetic study of Cd (II) onto modified palm shell activated carbon has been developed based on the continuous monitoring of the rate of adsorption using of an ion-selective electrode (ISE).
- ISE potentiometry proved to be a reliable technique for studying the whole adsorption rate of cadmium ions onto modified palm shell activated carbon. The constructed ISEs were able to continuously monitor cadmium concentrations in aqueous solution, without the need for the separation of cadmium species, in a rapid adsorption process.



- The apparent adsorption rate constant was estimated assuming pseudo-second-order kinetics.

A second potentiometric sensor was constructed from palm shell activated carbon modified with trioctylmethylammonium thiosalicylate (TOMATS) and used for the potentiometric determination of mercury ions in water samples. TOMATS is a novel, high performance, ionic liquid for the determination of mercury ions in water samples. TOMATS contains no fluorine and is absolutely stable to any hydrolysis. It therefore does not release HF or fluorides, is non-corrosive, and is much easier to dispose of. The low toxicity of the cation is known from studies on related compounds, such as trioctylammonium chloride and thiosalicylic acid and its salts are typically classified as irritants.

Several important results of this work are as follows:

- This new sensor for trace measurements of mercury ions is suitable for in situ monitoring.
- The portability and excellent sensitivity of this electrochemical technique make it very attractive for the field monitoring of trace mercury in water samples.
- The modified electrode shows excellent potentiometric response, sensitivity, selectivity, and stability. The electrode was successfully applied for the determination of mercury content in drinking water samples.
- These characteristics and the typical applications presented in this work make the electrode suitable for measuring the mercury content in real samples without a significant interaction from other cationic or anionic species.

- A potentiometric method for the in vitro adsorption kinetic study of Hg(II) onto modified palm shell activated carbon has been developed based on the continuous monitoring of the ion adsorption rate using of an ion-selective electrode (ISE).
- The study of the adsorption rate of mercury ions onto modified palm shell activated carbon was accomplished using the ISE technique. The continuous monitoring of mercury ion concentrations in aqueous solution without the need for the separation of mercury species enabled us to observe all of the kinetic adsorption parameters. The proposed application of ISE to the adsorption studies presents new features in this field of research.
- The apparent adsorption rate constant was estimated assuming pseudo second order kinetics.

## **5.2 Future challenges and prospects**

The following topics are of interest for future research:

- As a general strategy, the method used in this research may be expanded to the construction of ion selective electrodes for other heavy metals.
- This work has provided several novel alternatives to conventional plasticizers for use in ion selective electrodes. Each alternative has its own strengths and weaknesses, but all show some promise. The concepts and materials presented here can certainly be improved upon, and additional work is needed to further understand their benefits and limitations.
- The sensing layer can be tuned to be more selective or sensitive to certain heavy metals by changing its work function. This modification can be accomplished in part by employing TSILs with different cations and anions that accept or donate electrons to varying degrees. Therefore, by simply changing the IL structure in

the electrode sensing layer, it is possible to change the work function of the material and hence its affinity for certain heavy metals.

- The functional group loading seems to be approximately the same for TOMAS and TOMATS grafted onto palm shell activated carbon. Several other commercially available task specific ionic liquids can be used as the ionophore and plasticizer in the synthesis of new ion selective electrodes for the determination of heavy metals in aqueous solutions.
- Additional studies are also required to determine whether the metal ions can be effectively removed from aqueous solutions using modified palm shell activated carbon with other commercially available task specific ionic liquids.

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## **Appendix A**

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## List of publications

- 1- Chemical Engineering Journal 225 (2013) 306-314 "Palm shell activated carbon impregnated with task-specific ionic liquids as a novel adsorbent for the removal of mercury from contaminated water".
- 2- International Journal of Environmental Science and Technology (in press) "Cadmium (II) selective electrode based on palm shell activated carbon modified with task specific ionic liquid: kinetics and analytical applications".
- 3- The World Congress on Engineering and Technology (CET), International Conference on Chemical Engineering – China indexed by Ei Compendex and ISTP. "Potentiometric determination of trace amounts of mercury (II) in water sample using a new modified palm shell activated carbon paste electrode based on Kryptofix 5".
- 4- Sensors & Actuators, B: Chemical (Review article submitted) "Uses of Ion selective electrodes in determination of heavy metals in water and other environmental samples".