ELECTROMEMBRANE EXTRACTION AND ELECTROCHEMICAL MEASUREMENT SYSTEM FOR HEAVY METAL IONS DETECTION IN AQUATIC ENVIRONMENTAL SAMPLES

HAMSAWAHINI KUNASHEGARAN

UNIVERSITI TEKNOLOGI MALAYSIA

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HAMSAWAHINI A/P KUNASHEGARAN

A thesis submitted in fulfilment of the requirements for the award of the degree of Doctor of Philosophy (Chemistry)

Faculty of Science
Universiti Teknologi Malaysia

AUGUST 2018

In the name of God, The greatest and The kindest of all,
I dedicate this thesis

Specially to my Husband, Dinesh
For not giving up on me and tolerating my madness

My beloved daughter, Varnikaa
For reminding me of the goodness in this world and inspiring me to be the better version of myself

Prof. Dr. Rahmalan Ahamad, Prof. Dr. Abdull Rahim Bin Mohd Yusuff and Dr. Sathishkumar Palanivel
For guidance, knowledge, patience and trust on me

My beloved Amma and Appa
For always believed in me

My siblings

The whole family

For their endless love, support, encouragement, prayer for my success in completing the journey of my research

ACKNOWLEDGEMENT

First and foremost, I would like to thank God for His blessing and for the strength that lead me this whole journey of this research. I would like to express my deepest gratitude to my current and former supervisors, Prof. Dr. Rahmalan Ahamad and Prof Dr. Abdull Rahim Bin Mohd Yusuf, respectively for their guidance, knowledge, motivation, patience and trust on me throughout this whole work.

My gratitude is also extended to Dr. Sathishkumar Palanivel for his guidance and advice while writing my research papers. My special thanks to Prof. Datuk Dr. Ahmad Fauzi Bin Ismail and his research team members for their technical assistance during my working in Advanced Membrane Technology Research Centre (AMTEC).

Appreciation is also addressed to many other laboratory officers in the Department of Chemistry, Faculty Science their help and assistance. I also appreciated the financial assistance provided by Ministry of Higher Education (MyPhD) during my Ph.D. candidature.

Finally, I am greatly indebted to my parents, siblings and husband for their endless love, concern and encouragement all these years. I was blessed to have their supports and spiritual strength to complete my research and thesis writing. There is no better phrase than “Thank You for Everything and May God Bless all of you.”

ABSTRACT

Water contamination is a worldwide problem which deserves attention due to its negative impact on ecosystem, human health as well as economic growth. Heavy metals are a group of the pollutants that have received particular attention due to their high toxicity even at concentration as low as parts per billion (ppb). Technology advancement in the field of separation and detection of heavy metals has introduced sensitive and selective analytical instruments for real aquatic environmental samples. However, real sample matrices can reduce the quality of results. In modern analytical chemistry, there is a high demand for accurate quantification of trace and ultra-trace of heavy metals from real aqueous samples. In the present study, electromembrane extraction (EME) and electrochemical techniques were combined to develop effective electrodes which can separate, pre-concentrate and determine heavy metals such as Pb(II), Cr(VI) and Cd(II) in real aqueous samples. Electrochemically reduced graphene oxide-graphite reinforced carbon (ErGO-GRC) was utilised in conjunction with square wave anodic stripping voltammetry (SWASV) for the determination of Pb(II). Meanwhile, selective and sensitive determinations of Cr(VI) was carried out using *ex-situ* prepared nafion-coated antimony film on graphite reinforced carbon (NSbFE-GRC) by square wave adsorptive stripping voltammetry (SWAdSV) in the presence of diethyltriamine pentacetic acid (DTPA). *Ex-situ* prepared NSbFE-GRC was also used for simultaneous determination of Pb(II) and Cd(II) by SWASV. Simple polyvinylidene fluoride (PVDF) flat sheet membranes were synthesised and characterised in order to combine these developed electrochemical techniques with EME. Heavy metals were extracted from an aqueous sample solution into an acidic acceptor phase in the lumen of a PVDF membrane bag by the application of voltage across the supported liquid membrane (SLM), consisting of organic solvent and complexing carriers. Parameters affecting the EME were optimised for heavy metals. The PVDF–ErGO–GRC electrode system attained enrichment factors of 40 times and 80% extraction with relative standard deviation (n = 5) of 8.3% for Pb(II). Good linearity in the range of 0.25-2 nM was obtained with correlation coefficient of 0.999. The Pb(II) ions detection limit of PVDF–ErGO–GRC electrode was 0.09 nM. Meanwhile, the PVDF–NSbFE–GRC system attained enrichment factors of 86.6 times, 95.6% extraction, and good linearity in the range of 10-60 pM with correlation coefficient of 0.9933. Furthermore, the limit of Cr(VI) detection was found to be around 0.83 pM for the developed PVDF–NSbFE–GRC electrode. On the other hand, the PVDF–NSbFE–GRC was able to attain enrichment factors of 49.3 and 68.4 times, 82.6% and 114.0% extractions, and good linearity ranging from 2 to 10 pM with correlation coefficients of 0.9953 and 0.9883 for Pb(II) and Cd(II), respectively. Furthermore, the limits of detection for Pb(II) and Cd(II) were found to be around 0.65 pM and 0.60 pM, respectively. A chargeable battery operated portable EME system was developed for quantitative determination of heavy metals. The newly developed single setup electrochemical system was applied to the analysis of real aqueous samples such as tap water, industrial waste water, river water and sea water, and it was able to extract with percentage of extraction in the range of 78.7 -103.0% compared to commercially available direct current power supply.

ABSTRAK

Pencemaran air adalah masalah di seluruh dunia yang patut diberi perhatian disebabkan oleh impak negatif terhadap ekosistem, kesihatan manusia serta pertumbuhan ekonomi. Logam berat merupakan satu kumpulan pencemar yang telah menerima perhatian khusus kerana ketoksikannya yang tinggi walaupun pada kepekatan serendah bahagian per bilion (ppb). Kemajuan teknologi dalam bidang pemisahan dan pengesanan logam berat telah memperkenalkan instrumen analisis yang peka dan selektif bagi sampel persekitaran akuatik. Walau bagaimanapun, matriks sampel sebenar boleh mengurangkan kualiti hasil. Dalam kimia analisis moden, terdapat permintaan yang tinggi bagi kuantifikasi tepat logam berat surih dan ultra surih daripada sampel akueus sebenar. Dalam kajian ini, teknik pengekstrakan elektromembran (EME) dan elektrokimia digabungkan untuk menghasilkan elektrod yang boleh memisahkan, pra-memekatkan dan menentukan logam berat misalnya Pb(II), Cr(VI) dan Cd(II) daripada sampel akueus sebenar. Karbon diperkuatkan grafin oksida-grafit secara penurunan elektrokimia (ErGO-GRC) telah digunakan sempena dengan voltammetri pelucutan anod gelombang segiempat (SWASV) bagi penentuan Pb(II). Sementara itu, penentuan selektif dan sensitif Cr(VI) dijalankan menggunakan filem antimoni yang dilapisi dengan nafion pada karbon diperkuatkan grafit (NSbFE-GRC) yang disediakan dengan voltammetri pelucutan penjerapan gelombang segiempat (SWAdSV) dengan kehadiran asid dietiltriamina pentasetik (DTPA). NSbFE-GRC yang disediakan secara *ex-situ* juga digunakan untuk penentuan Pb(II) dan Cd(II) dengan SWASV. Membran lembaran rata polivinilidena fluorida (PVDF) yang mudah telah disintesis dan dicirikan untuk menggabungkan teknik elektrokimia yang dibangunkan itu dengan EME. Logam berat telah diekstrak daripada larutan sampel akueus ke dalam fasa penerima berasid di dalam lumen beg membran PVDF dengan menggunakan voltan merentasi membran cecair disokong (SLM), yang terdiri daripada pelarut organik dan pembawa pengkompleks. Parameter yang mempengaruhi EME telah dioptimumkan bagi logam berat. Sistem elektrod PVDF-ErGO-GRC mencapai faktor pengayaan 40 kali dan pengekstrakan 80% dengan sisihan piawai relatif (n = 5) 8.3% bagi Pb(II). Lineariti yang baik dalam julat 0.25-2 nM telah diperolehi dengan pekali korelasi 0.999. Had pengesanan ion Pb(II) elektrod PVDF-ErGO-GRC adalah 0.09 nM. Sementara itu, sistem PVDF-NSbFE-GRC mencapai faktor pengayaan 86.6 kali, pengekstrakan 95.6%, dan lineariti yang baik dalam julat 10-60 pM dengan pekali korelasi 0.9933. Tambahan pula, had pengesanan Cr(VI) didapati sekitar 0.83 pM bagi elektrod PVDF-NSbFE-GRC yang dibangunkan. Sebaliknya, PVDF-NSbFE-GRC telah dapat mencapai faktor pengayaan 49.3 dan 68.4 kali, pengekstrakan 82.6% dan 114.0%, dan lineariti yang baik dari 2 hingga 10 pM dengan pekali korelasi masing-masing 0.9953 dan 0.9883 bagi Pb(II) dan Cd(II). Tambahan pula, didapati had pengesanan bagi Pb(II) dan Cd(II) masing-masing adalah sekitar 0.65 pM dan 0.60 pM. Sistem EME mudah alih yang menggunakan bateri boleh dicas semula telah dibangunkan bagi penentuan kuantitatif logam berat. Sistem elektrokimia persediaan tunggal baharu yang dibangunkan itu telah digunakan untuk analisis sampel akueus sebenar misalnya air paip, air sisa industri, air sungai dan air laut, dan ia dapat mengekstrak dengan peratus pengekstrakan dalam julat 78.1-103.0% berbanding pembekal arus terus komersial.

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LIST OF ABBREVIATION

2-MBT	-	2-mercaptobenzothiazole
2-MBT	-	2-mercaptobenzothizole
4-CNPy	-	4-cyanopyridine
4-Cpy	-	4-cyanopyridine
AAS	-	Atomic absorption spectrophotometry
ADDPA	-	ammonium diethyl dithiophosphate
AdSV	-	Adsorptive Stripping voltammetry
Aliquat 336	-	Tricaprylylmethyl ammonium chloride
AlOOH	-	Aluminium oxide hydroxide
AP	-	acceptor phase
ASV	-	Anodic stripping voltammetry
AuNP	-	Gold nano particles
Au-RGO	-	modification of GC electrode with gold - reduced graphene oxide
BDDE	-	boron-doped diamond
BiFe	-	Bismuth film electrode
BRB	-	Britton-Robinson buffer
Cd(II)	-	Cadmium ions
CDC	-	Centre for Disease Control
CE	-	capillary electrophoresis
AE	-	auxilary electrode
CE-C4D	-	capillary electrophoresis with capacitively coupled contactless conductivity detection
CeO_2	-	Cerium(IV) oxide
CF	-	carbon fiber
CH_3COOH	-	acetic acid
CLZ	-	clozapine

CNTs	-	Carbon nanotubes
CPE	-	Carbon paste electrode
Cr	-	Chromium
Cr–DPC	-	Cr-diphenyl carbazide
CSV	-	Cathodic Stripping Voltammetry
CV	-	Cyclic voltammetry
CW	-	carbowax
Cyphos 101	-	phosphonium chloride
D2EHPA	-	di-2-ethylhexylphosphoric acid
DC	-	Direct current
DLLME	-	dispersive liquid–liquid microextraction
DME	-	dropping mercury electrode
DP	-	donor phase
DP	-	donor phase
DPAdSV	-	Differential Pulse Adsorptive Stripping Voltammetry
DPASV	-	Differential pulse anodic stripping voltammetry
DPV)	-	differential pulse voltammetry
DSPE	-	dispersive solid phase extraction
DTPA	-	Diethyltriamine Pentacetic Acid
EDTA	-	Ethylenediaminetetraacetic acid
EF_i	-	enrichment factor of analyte i
EF_{max}	-	maximum attainable EF
EG	-	Exfoliated graphite
EME	-	Electromembrane extraction
EPA	-	US Environmental Protection Agency
ER	-	extraction recovery
ErGO	-	Electrochemically reduced graphene oxide
ErGO-GRC	-	electrochemically reduced graphene oxide
ER_i	-	extraction recovery of analytes i
FAO	-	Joint Food and Agricultural Organization
FESEM	-	Field emission scanning electron microscopy
GC	-	Glassy carbon
GCE	-	Glassy carbon electrode

GF-AAS	-	graphite furnace atomic absorption spectroscopy
GRC	-	graphite reinforcement carbon
H_2SO_4	-	sulphuric acid
HCl	-	hydrochloric acid
HF-LPME	-	hollow fiber-liquid phase microextraction
HMDE	-	hanging mercury drop electrode
HNO_3	-	nitric acid
HPLC	-	High performance liquid chromatography
HP-β-CD	-	Hydroxypropyl-β-cyclodextrin
ICPMS	-	Inductively coupled plasma-mass spectrometry
ICP-OES	-	inductively coupled plasma-optical emission spectrometry
IL	-	Ionic liquids
KOH	-	Potassium Hydroxide
LLE	-	liquid –liquid extraction
LOD	-	Limit of detection
LPME	-	liquid phase microextraction
LSV	-	Linear sweep voltammetry
MFE	-	Mercury film electrode
MWCNT	-	Multi-walled carbon nanotubes
NAA	-	Neutron activation analysis
NaCl	-	sodium chloride
NaMM	-	An antimony film modified sodium montmorillonite
NaOH	-	Sodium hydroxide
NPOE	-	nitrophenyl octyl ether
NPOE	-	2-Nitrophenyl octyl ether
NSbFE-GRC	-	nafion coated-antimony film
OPFP	-	Ionic liquid n-octylpyridinum hexafluorophosphate
PA	-	polyacrylate
Pa-EME	-	parallel electromembrane extraction
PALME	-	parallel artificial liquid membrane microextraction
PANI	-	Polyaniline
Pb(II)	-	Lead
PbNPs-SH-	-	a lead nanoparticles-modified thiol-functionalized

PF/GCE	-	polysiloxane film GC electrode
PDMS	-	polydimethylsiloxane
PhACs	-	pharmaceutical active compounds
PMMA	-	polypropylene membrane bonded in-between two poly-methyl methacrylate
PP	-	Polypropylene
ppb	-	parts per billion
PPHF	-	Polypropylene hollow fiber
PPSD	-	Portable power supply device
Pt	-	platinum
PTFE	-	Polytetra fluoroethylene
PVDF	-	Polyvinlidine fluoride
RE	-	reference electrode
rGO	-	reduced graphene oxide
$Ru(bpy)_3]^{2+}$	-	Tris(bipyridine)ruthenium(II)
SAMs	-	self-assembled monolayers
SbNP	-	Antimony nano particles
SbNP	-	antimony nanoparticles
SCP	-	Stripping chrono potentiometry
SDME	-	single-drop microextraction
SFFTCCV	-	stripping fast Fourier transform continuous cyclic voltammetry
SFOD-ME	-	Solidified floating organic drop - microextraction
SLM	-	supported liquid membrane
SMDE	-	static mercury drop electrode
SnNP	-	Tin nanoparticles
SPCE	-	screen printed carbon electrode
SPE	-	Screen printed electrode
SPME	-	solid-phase microextraction
SWAdSV	-	Square Wave Adsorptive Stripping Voltammetry
SWASV	-	Square Wave Anodic Stripping Voltammetry
SWCNT	-	single-wall carbon nanotubes
TBP	-	tributhylphosphate

UV	-	ultraviolet
WE	-	working electrode
WHO	-	World Health Organization
XRF	-	X-ray Fluorescence Spectrometry

LIST OF SYMBOL

g	-	Gram
c	-	Concentration
E_{acc}	-	Deposition potential
E_f	-	Final potential
E_i	-	Initial potential
E_p	-	Peak potential
Hz	-	Hertz
I_p	-	Peak current
M	-	Molar
mM	-	Milimolar
mg	-	Milligram
min	-	Minutes
mL	-	Milliliter
mm	-	Millimeter
ppb	-	Part per billion
r^2	-	Correlation coefficient
mgL^{-1}	-	Milligram per liter
s	-	Seconds
t_{acc}	-	Deposition time
V	-	Voltage
v/v	-	Volume per volume
^{o} C	-	Degree Celsius
mA	-	Micro ampere
µL	-	Micro Liter
μgL^{-1}	-	Microgram per liter
µM	-	Micro molar

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CHAPTER 1

INTRODUCTION

1.1 Background of Research

Water contamination is a worldwide problem which deserves attention due to its negative impact on eco-system, human health as well as economic growth (Ben Salem *et al.* 2014; Kim & Kang 2016). Heavy metals, as one of the pollutant categories receive concern due to their high toxicity even at concentration as low as parts per billion (ppb). Furthermore, the toxicity of heavy metals can be increased by transformation to more toxic compounds due to their average long-life. Depending on the type and speciation of heavy metal, it accumulates mainly in bones, brain, kidney and muscles, which may cause serious illnesses such as anaemia, kidney diseases, nervous disorders and sickness or even death among (Chen *et al. 2012;* Ben Salem *et al.* 2014; D. Wang *et al.* 2016). In infant and children, exposure to heavy metals above the standard level can result in delays in physical and mental development (Y. Wang *et al*. 2016a; Liu *et al*. 2014; Xia *et al.* 2016). Therefore, the determination of heavy metals has contributed to the awareness among human to provide beneficial guidance on the physiological effect on body and environment.

There are numerous analytical techniques such as graphite furnace atomic absorption spectroscopy (GF-AAS) (Dokpikul *et al*. 2018; Behbahani *et al*. 2015; Cervantes *et al*. 2017; Schneider *et al*. 2017; Zhong *et al*. 2016), inductively coupled plasma mass spectroscopy (ICP-MS) (Cervantes *et al*. 2017), neutron activation analysis (NAA) (Namieśnik & Rabajczyk 2012) have been proposed for the determination of heavy metal ions. These analytical techniques are advantages in terms of sensitivity and multiple elemental analysis. However, these instruments incur high cost. Nowadays, voltammetry techniques are much interested for the determination of heavy metal ions, due to their highly sensitive, low cost, simple operation and minimum use of reagents as well as suitable for speciation measurements (Y. Wang *et al*. 2016b; Liu e*t al.* 2014). However, heavy metal in aquatic environmental samples are usually obtained in extreamely low level of concentration such as sub-ppb or ppt. Moreover, aquatic environmental samples are too complex for a direct measurement due to matrix interferences. These diffuculties can be overcome by separating and preconcentrating the heavy metal ions prior to the determination by any analytical techniques. Thus, there is a need to develop an effective analytical method which allows separating, detecting and quantifying low levels of heavy metal ions in aqueous environmental samples.

1.2 Problem Statement

Sampling, sample preparation, separation, detection and data analysis are the most important steps in analytical process. When dealing with real sample matrix samples each step equally important for collecting reproducible and reliable data. Technology advancement in the field of separation and detection have introduced sensitive and selective analytical instrument. However, real sample matrices can reduce the quality of results. In modern analytical chemistry, there is a high demand for accurate quantification of trace and ultra-trace of heavy metals from real aqueous sample matrices. Hence, the determination of trace heavy metals depends on instruments that capable of reaching detection limits as low as good selectivity. However, to achieve this practice the number of interfering compounds must be kept to a minimum to avoid severe matrix interference. In addition, there is also a demand for pre-concentration of trace heavy metals to reach lower concentration limits for sufficient detection. Recently, integrated and automated systems have been increasing popular to reduce analysis time and labour. However, the demand for highly time-efficient systems becomes challenging for separation of heavy metals from real sample matrices.

The problems associated with heavy metals in the environment clearly demand for an effective sustainable green analytical method which can simultaneously pre-concentrate, separate, and detect with lower detection limits. Several approaches such as ion-exchange separation (Aydin *et al*. 2011; Cechinel e*t al*. 2017), single-drop micro-extraction (SDME) (Manzoori *et al*. 2009), dispersive liquid–liquid microextraction (DLLME) (Zhou *et al*. 2011; Dokpikul *et al.* 2018; López-García *et al. 2013),* solid phase extraction (SPE) (Cervantes *et al.* 2017; Pourreza & Naghdi 2014) and dispersive solid phase extraction (DSPE) (Fasih Ramandi & Shemirani 2015; Behbahani *et al.* 2015) are available for the separation and pre-concentration of heavy metal ions from aqueous environmental samples. However, such procedures are time-consuming and prone to contamination.

Electromembrane extraction (EME) is a new concept of hollow fiber-liquid phase microextraction (HF-LPME) in which an electrical field serves as a driving force for the analytes to transfer between the donor phase (DP) and the supported liquid membrane (SLM) and also between the SLM and the acceptor phase (AP) (Fotouhi *et al*. 2011; Gjelstad *et al.* 2006). Interestingly, the combination of EME and electrochemical studies has been popular in detecting pharmaceutical active compounds (PhACs) such as sufentanil (Ahmar e*t al*. 2013), morphine (Ahmar *et al.* 2014), dextromethorphan (Fakhari *et al.* 2014), diclofenic (Mofidi *et al.* 2017) and clozapine (Rouhollahi *et al*. 2016) due to the unique opportunities of addressing the challenges of green analytical chemistry by providing effective process of separating, pre-concentrating and detecting while minimizing its environmental impact.

Studies published utilize modified solid electrodes such screen printed (Fakhari *et al.* 2014; Ahmar *et al.* 2013) , carbon paste (Mofidi *et al.* 2017), and glassy carbon (Kamyabi & Aghaei 2016a; Kamyabi & Aghaei 2016b) electrodes where the solution from AP is collected using microsyringe and the pH of the solution adjusted before the analyte can be detected using electrochemical techniques. This is due to the low volume and inappropriate condition of aqueous AP in EME such as pH and type of buffer solution, which is not suitable for conventional electrochemical measurements. Therefore, the purpose of this research is to develop an electrochemical electrode system with EME as a part of the electrode that can directly separate, pre- concentrate and detect heavy metal ions in real aqueous environmental samples.

1.3 Objectives of the Study

The objectives of this study are as follows:

a) To determine the potential complexing carriers using liquid-liquid extraction technique for selected heavy metal ions;
b) To examine electrochemical response of the selected heavy metal ions under conditions suitable for the acceptor phase;
c) To investigate the transport of the selected heavy metal ions across the EME using PVDF flat sheet membrane; and
d) To develop and apply portable power supply device for EME system of heavy metals in real samples such as tap, river, sea and industrial waste water.

1.4 Scope of the Study

This study was conducted to investigate a simultaneous separation, pre-concentration, and detection system for heavy metal ions such as Cr(VI), Pb(II), and Cd(II) based on combination of voltammetry technique with EME. In achieving the objectives of the research there are few important tasks need to be carried out and five research scopes have been identified for accomplishing the objectives. The scopes are:

1) Preliminary study was conducted by optimizing parameters for liquid –liquid extraction (LLE) such as six (6) type of complexing carriers (4-cyanopyridine (4-Cpy), 2-mercaptobenzothiazole (2-MBT), Tricaprylylmethyl ammonium chloride (Aliquat 336), tributhylphosphate (TBP), di-2-ethylhexylphosphoric

acid (D2EHPA), trihexyl(tetradecyl)phosphonium chloride (Cyphos 101) four (4) types of organic solvents (toluene, n-octanol, n-heptane and NPOE), pH and type of stripping phase. This was investigated to understand the complexing and stripping ability between carrier and heavy metal ions. The selection of appropriate acceptor phase of heavy metal ion from carrier is very crucial, as this aqueous phase condition was used to develop the electrochemical detection for earlier mentioned heavy metal ions.

2) Heavy metal ions were detected using voltammetry technique based on the AP of LLE by using solid electrode. The solid electrodes used in this study were nafion coated-antimony film (NSbFE-GRC) and electrochemically reduced graphene oxide (ErGO-GRC) modified on graphite reinforcement carbon as substrate material. The ex-situ prepared NSbFE-GRC was used to selectively detect Cr(VI) with the presence of DTPA using square wave adsorptive stripping voltammetry (SWAdSV). NSbFE-GRC was also utilized for simultaneous detection of Cd(II) and Pb(II) by using square wave anodic stripping voltammetry (SWASV). Whereas, ErGO-GRC was used to selectively detect Pb(II) using SWASV.

3) EME study was carried out by applying voltage using DC supply system with the appropriate carrier in organic solvent supported by a fabricated PVDF membrane which interposed between the aqueous sample matrix containing the targeted heavy metal ions and acceptor phase. Polyvinylidene (PVDF) membrane with different polymer percentage concentration (12%, 17% and 22%) fabricated and characterized to determine the functional groups, water contact angles, thickness and porosity of membrane. In order to optimize the EME, parameters such as the influence of membrane composition on extraction voltage, extraction time, pH of the donor phase, stirring rate, carrier concentration, organic solvent and agarose gel were assessed.

4) Portable power supply device (PPSD) was developed and used as portable sampling system for selective and simultaneous EME to separate and pre-

concentrate Pb(II), Cd(II) and Cr(VI) in real samples such as tap, river, sea and industrial waste water prior to detect using voltammetry techniques.

1.5 Significance of Study

The quick separation, pre-concentration and determination of trace and ultratrace quantities of heavy metal in sample matrices with complex or variable composition by simple method has become the major interest in analytical chemistry. The construction of sensitive EME with GRC modified electrode have fast response, linear dynamic range, low cost, environmentally friendly and ease for preparation had been adding an advantage. Furthermore, this developed analytical technique was able to comply with the principle of sustainable development and green chemistry.

Rapid growths of electromembrane studies demand the development of portable power supply device (PPSD) with battery. A portable power supply device (PPSD) with chargeable Li-ion battery have made on-site sampling or extraction. This developed portable device might be a powerful tool with combination of EME and voltammetry for simultaneous separation, pre-concentration and detection of trace level Pb(II), Cd(II) and Cr(VI) present in real aqueous samples. This may be open up possibilities of development of other technical configurations in the future such as a portable EME or chronoamperometry system with software.

1.6 Novelty of Study

Till 2015, no research was carried out on the application of EME as a part of the electrochemical electrode system that can directly separate, pre-concentrate and detect heavy metal ions in real environmental samples. However, the combination of these methods started to get attention for heavy metal ions such as Hg(II) (Kamyabi & Aghaei 2016a) and As (III) (Kamyabi & Aghaei 2016b) after the publication by Hamsawahini *et al.* (2015). Moreover, this is the first sudy that reported on the development of a portable power supply device (PPSD) using chargable lithium ion battery for on-site EME sampling.

1.7 Thesis Outline

This thesis consists of six chapters. Chapter 1 describes in detail the research background, problem statement, objectives, scope as well as significance of the study. Chapter 2 compiles the literature review of separation and pre-concentration methods and voltammetry techniques for heavy metals. Chapter 3 describes methodologies and applications that involve LLE, voltammetry, electromembrane and portable power supply device development.

Chapter 4 describes the preliminary studies conducted to investigate potential complexing carriers using liquid-liquid extraction technique for heavy metal ions including Cr(VI), Pb(II), and Cd(II). ICPMS and AAS used to determine the efficiency of metal extraction using complexing carriers. The results obtained used in developing EME technique for respective metals. This chapter also discusses on modified graphite reinforcement carbon electrodes in determination of Cr(VI), Pb(II), and Cd(II) using voltammetry techniques. NSbFE-GRC and ErGO-GRC used to determine the presence of Cr(VI), Pb(II), and Cd(II) in water samples such as industrial waste water, river water, sea water and tap water.

Chapter 5 reports the development of EME using fabricated flat sheet PVDF membrane for Cr(VI), Pb(II), and Cd(II). EME techniques combined voltammetry techniques discussed in Chapter 4 which simultaneouly separate, pre-concentrate and determine Cr(VI), Pb(II), and Cd(II) in water samples such as industrial waste water, river water, sea water and tap water. Furthermore, this chapter describes the developed portable power supply device for EME and its efficiency for Cr(VI), Pb(II) and Cd(II) selective and simultaneous extraction in real samples such as tap, river, sea and industrial waste water. Finally, Chapter 6 summarizes the overall results obtained with suggestions for future work.

REFERENCES

Ahmar, H., Fakhari, A. R., Tabani, H., and Shahsavani, A. (2013). Optimization of Electromembrane Extraction Combined with Differential Pulse Voltammetry Using Modified Screen-Printed Electrode for the Determination of Sufentanil. *Electrochim. Acta.* 96, 117–123.

Ahmar, H., Tabani, H., Hossein Koruni, M., Davarani, S. S. H., and Fakhari, A. R. (2014). A New Platform for Sensing Urinary Morphine Based on Carrier Assisted Electromembrane Extraction Followed by Adsorptive Stripping Voltammetric Detection on Screen-Printed Electrode. *Biosens. Bioelectron.* 54, 189–94.

Akanda, M. R., Sohail, M., Aziz, M. A., and Kawde, A. N. (2016). Recent Advances in Nanomaterial-Modified Pencil Graphite Electrodes for Electroanalysis. *Electroanal*. 28(3), 408–424.

Albendín, G. (2016). Miniaturized and Direct Spectrophotometric Multi-Sample Analysis of Trace Metals in Natural Waters. *Anal. Biochem.* 497, 18–23.

Ambrosi, A., Bonanni, A., Sofer, Z., Cross, J. S., and Pumera, M. (2011). Electrochemistry at Chemically Modified Graphenes. *Chem-Eur*. *J.* 17(38), 10763–10770.

Andruch, V., Kocúrová, L., Balogh, I. S., and Škrlíková, J. (2012). Recent Advances in Coupling Single-Drop And Dispersive Liquid-Liquid Microextraction with UV-vis Spectrophotometry and Related Detection Techniques. *Microchem. J. 102*, 1–10.

Annibaldi, A., Illuminati, S., Truzzi, C., and Scarponi, G. (2011). SWASV Speciation of Cd, Pb and Cu for the Determination of Seawater Contamination in the Area Of the Nicole Shipwreck (Ancona Coast, Central Adriatic Sea). *Marine. Poll. Bull.* 62(12), 2813–2821.

Aoki, K., Okamoto, T., Kaneko, H., Nozaki, K., and Negishi, A. (1989). Applicability of Graphite Reinforcement Carbon Used as the Lead Of A Mechanical Pencil to Voltammetric Electrodes. *J. Electroanal. Chem.* 263(2), 323–331.

Araujo-Barbosa, U., Peña-Vazquez, E., Barciela-Alonso, M. C., Costa Ferreira, S. L., Pinto dos Santos, A. M., and Bermejo-Barrera, P. (2017). Simultaneous Determination and Speciation Analysis of Arsenic and Chromium in Iron Supplements Used for Iron-Deficiency Anemia Treatment by HPLC-ICP-MS. *Talanta*. 170, 523–529.

Arancibia, V., Nagles, E., Rojas, C., and Gomez, M. (2013). Ex situ Prepared Nafion-Coated Antimony Film Electrode for Adsorptive Stripping Voltammetry of Model Metal Ions in the Presence of Pyrogallol Red. *Sens Actuators B Chem*. 182, 368–373.

Asensio-Ramos, M., Ravelo-Pérez, L. M., González-Curbelo, M. Á., and Hernández-Borges, J. (2011). Liquid Phase Microextraction Applications in Food Analysis. *J. Chromatogr. A.* 1218(42), 7415–7437.

Ashraf, A., Saion, E., Gharibshahi, E., Kong, C., Mohamed, H., Elias, S., and Abdul, S. (2017). Distribution of Heavy Metals in Core Marine Sediments of Coastal East Malaysia by Instrumental Neutron Activation Analysis and Inductively Coupled Plasma Spectroscopy. *Appl. Radiat. Isot.* 132, 222–231.

Ashrafi, A. M., Cerovac, S., Mudrić, S., Guzsvány, V., Husáková, L., Urbanová, I., and Vytřas, K. (2014). Antimony Nanoparticle-Multiwalled Carbon Nanotubes Composite Immobilized at Carbon Paste Electrode for Determination of Trace Heavy Metals. *Sens Actuators B Chem*. 191, 320–325.

Ashrafi, A. M., and Vytřas, K. (2012). New Procedures for Voltammetric Determination of Copper (II) using Antimony Film-Coated Carbon Paste Electrodes. *Electrochim. Acta*. 73, 112–117.

Aydin, F., Yasar, F., Aydin, I., and Guzel, F. (2011). Determination of Lead Separated Selectively with Ion Exchange Method from Solution onto BCW in Sirnak, East Anatolia of Turkey. *Microchem. J.* 98(2), 246–253.

Bahadir, Z., Bulut, V. N., Hidalgo, M., Soylak, M., and Marguí, E. (2016). Cr Speciation in Water Samples by Dispersive Liquid–Liquid Microextraction Combined With Total Reflection X-ray fluorescence spectrometry. *Spectrochim. Acta. Part B. At. Spectrosc.* 115, 46–51.

Balchen, M., Gjelstad, A., Rasmussen, K. E., and Pedersen-Bjergaard, S. (2007). Electrokinetic Migration of Acidic Drugs Across a Supported Liquid Membrane. *J. Chromatogr. A*. 1152(1–2), 220–225.

Barceló, C., Serrano, N., Ariño, C., Díaz-Cruz, J. M., and Esteban, M. (2016). Ex-situ Antimony Screen-printed Carbon Electrode for Voltammetric Determination of Ni(II)-ions in Wastewater. *Electroanal.* 28(3), 640–644.

Barczak, M., Tyszczuk-rotko, K., Metelka, R., and Vytr, K. (2014). Lead Film Electrode Prepared with the Use of a Reversibly Deposited Mediator Metal in Adsorptive Stripping Voltammetry of Nickel, *Electroanal.* 26(9), 2049–2056.

Bårdstu, K. F., Ho, T. S., Rasmussen, K. E., Pedersen-Bjergaard, S., and Jönsson, J. A. (2007). Supported Liquid Membranes in Hollow Fiber Liquid-Phase Microextraction (LPME) - Practical Considerations in the Three-Phase Mode. *J. Sep. Sci.* 30(9), 1364–1370.

Bas, B., Jakubowska, M., Jez, M., and Ciepiela, F. (2010). Novel Renovated Silver Ring Electrode for Anodic Stripping Analysis of Pb(II) and Cd(II) Traces in Water Samples Without Removal of Oxygen and Surfactants. *J. Electroanal. Chem.* 638(1), 3–8.

Basheer, C., Tan, S. H., and Lee, H. K. (2008). Extraction of Lead Ions by Electromembrane Isolation. *J. Chromatogr. A.* 1213(1), 14–18.

Basheer, C., Vetrichelvan, M., Valiyaveettil, S., and Lee, H. K. (2007). On-site Polymer-Coated Hollow Fiber Membrane Microextraction and Gas Chromatography-Mass Spectrometry of Polychlorinated Biphenyls and Polybrominated Diphenyl Ethers. *J. Chromatogr. A.* 1139(2), 157–164.

Behbahani, M., Ghareh Hassanlou, P., Amini, M. M., Omidi, F., Esrafili, A., Farzadkia, M., and Bagheri, A. (2015). Application of Solvent-Assisted Dispersive Solid Phase Extraction as a New, Fast, Simple and Reliable Preconcentration and Trace Detection of Lead and Cadmium Ions in Fruit and Water Samples. *Food. Chem.* 187, 82–88.

Ben Salem, Z., Capelli, N., Laffray, X., Elise, G., Ayadi, H., and Aleya, L. (2014). Seasonal Variation of Heavy Metals in Water, Sediment and Roach Tissues in a Landfill Draining System Pond (Etueffont, France). *Ecol. Eng.* 69, 25–37.

Berduque, A., O'Brien, J., Alderman, J., and Arrigan, D. W. M. (2008). Microfluidic Chip for Electrochemically-Modulated Liquid-Liquid Extraction of Ions. *Electrochem. Commun.* 10(1), 20–24.

Bhowal, A., and Datta, S. (2001). Studies on Transport Mechanism of Cr(VI) Extraction from an Acidic Solution Using Liquid Surfactant Membranes. *J. Membr. Sci.* 188(1), 1–8.

Bian, Y., Bian, Z.-Y., Zhang, J.-X., Ding, A.-Z., Liu, S.-L., and Wang, H. (2015). Effect of the Oxygen-Containing Functional Group of Graphene Oxide on the Aqueous Cadmium Ions Removal. *Appl. Surf. Sci.* 329, 269–275.

Bobrowski, A., Królicka, A., Maczuga, M., and Zarębski, J. (2014). A Novel Screen-Printed Electrode Modified with Lead Film For Adsorptive Stripping Voltammetric Determination of Cobalt and Nickel. *Sens Actuators B Chem*. 191, 291–297.

Bobrowski, A., Putek, M., and Zarebski, J. (2012). Antimony Film Electrode Prepared In Situ in Hydrogen Potassium Tartrate in Anodic Stripping Voltammetric Trace Detection of Cd(II), Pb(II), Zn(II), Tl(I), In(III) and Cu(II). *Electroanal.* 24(5), 1071–1078.

Bobrowski, A., Kalcher, K., and Kurowska, K. (2009). Microscopic and Electrochemical Characterization of Lead Film Electrode Applied in Adsorptive Stripping Analysis. *Electrochim. Acta*. 54(28), 7214–7221.

Bobrowski, A., Krolicka, A., and Zarebski, J. (2009). Characteristics of Voltammetric Determination and Speciation of Chromium - A review. *Electroanal.* 21(13), 1449 -1458.

Buffle, J. (2005). Voltammetric Environmental Trace-Metal Analysis and Speciation : from Laboratory to In Situ Measurements, *Trends Anal. Chem.* 24(3), 172-190.

Carasek, E., and Merib, J. (2014). Membrane-based microextraction techniques in analytical chemistry: A review. *Anal. Chim. Acta*. 880, 8–25.

Carrington, N.A., Yong, L. and Xue, Z.L. (2006). Electrochemical Deposition of Sol-Gel Films for Enhanced Chromium(VI) Determination in Aqueous Solutions. *Anal. Chim. Acta*. 572(1), 17–24.

Cechinel, M. A. P., Mayer, D. A., Mazur, L. P., Silva, L. G. M., Girardi, A., Vilar, V. J. P., Augusto de Souza, A., and Guelli U. de Souza, S. M. A. (2017). Application of Ecofriendly Cation Exchangers (Gracilaria Caudata and Gracilaria Cervicornis) for Metal Ions Separation and Recovery from a Synthetic Petrochemical Wastewater: Batch and Fixed Bed Studies. *J. Clean. Prod.* 172, 1928–1945.

Cervantes, A., Rodríguez, R., Ferrer, L., Cerdà, V., and Leal, L. O. (2017). Automatic Solid Phase Extraction of Cadmium Exploiting a Multicommutated Flow System Previous ICP-MS Detection: Application to Tobacco Samples. *Microchem. J.* 132, 107–111.

Chanthasakda, N., Nitiyanontakit, S., and Varanusupakul, P. (2015). Electro-Enhanced Hollow Fiber Membrane Liquid Phase Microextraction of Cr(VI) Oxoanions in Drinking Water Samples. *Talanta*. 148, 680-685.

Chatzitheodorou, E., Economou, A., and Voulgaropoulos, A. (2004). Trace Determination of Chromium by Square-Wave Adsorptive Stripping Voltammetry on Bismuth Film Electrodes. *Electroanal.* 16(21), 1745–1754.

Chen, C., Niu, X., Chai, Y., Zhao, H., and Lan, M. (2013). Bismuth-Based Porous Screen-Printed Carbon Electrode with Enhanced Sensitivity for Trace Heavy Metal Detection by Stripping Voltammetry. *Sens. Actuators B Chem*. 178, 339–342.

Chen, H. M., Chang, R. C., and Wu, J. L. (2007). A Low-Voltage Integrated Current-Mode Boost Converter for Portable Power Supply. *Proceedings of the IEEE International Conference on Electronics, Circuits, and Systems*. 1316–1319.

Chen, G., Hao, X., Li, B. L., Luo, H. Q., and Li, N. B. (2016). Anodic Stripping Voltammetric Measurement of Trace Cadmium at Antimony Film Modified Sodium Montmorillonite Doped Carbon Paste Electrode. *Sens. Actuators B. Chem*. 237, 570–574.

Chen, L., Tang, Y., Wang, K., Liu, C., and Luo, S. (2011). Direct Electrodeposition of Reduced Graphene Oxide on Glassy Carbon Electrode and its Electrochemical Application. *Electrochem. Commun.* 13(2), 133–137.

Chen, L., Xu, Z., Liu, M., Huang, Y., Fan, R., Su, Y., Hu, G., Peng, X., and Peng, X. (2012). Lead Exposure Assessment from Study Near a Lead-Acid Battery Factory in China. *Sci. Total. Environ.* 429, 191–198.

Chua, C. K., and Pumera, M. (2013). Reduction of Graphene Oxide with Substituted Borohydrides. *J. Mater. Chem. A.* 1(5), 1892-1898.

Chua, C. K., Sofer, Z., and Pumera, M. (2012). Graphite Oxides: Effects of Permanganate and Chlorate Oxidants on the Oxygen Composition. *J. Eur. Chem.* 18(42), 13453–13459.

Collins, C. J., Berduque, A., and Arrigan, D. W. M. (2008). Electrochemically Modulated Liquid-Liquid Extraction of Ionized Drugs Under Physiological Conditions. *Anal. Chem.* 80(21), 8102–8108.

Cote, L. J., Kim, J., Tung, V. C., Luo, J., Kim, F., and Huang, J. (2011). Graphene Oxide as Surfactant Sheets. *Pure Appl. Chem.* 83(1), 95-110.

Cote, L. J., Kim, J., Zhang, Z., Sun, C., and Huang, J. (2010). Tunable Assembly of Graphene Oxide Surfactant Sheets: Wrinkles, Overlaps and Impacts on Thin Film Properties. *Soft. Matt*. 6(24), 6096-6101.

Cui, S., Tan, S., Ouyang, G., and Pawliszyn, J. (2009). Automated Polyvinylidene Difluoride Hollow Fiber Liquid-Phase Microextraction of Flunitrazepam in Plasma and Urine Samples for Gas Chromatography/Tandem Mass Spectrometry. *J. Chromatogr. A.* 1216(12), 2241–2247.

Czop, E., Economou, A., and Bobrowski, A. (2011). A Study of In Situ Plated Tin-Film Electrodes for the Determination of Trace Metals by Means of Square-Wave Anodic Stripping Voltammetry. *Electrochim. Acta.* 56(5), 2206–2212.

Dadfarnia, S., Shakerian, F., and Shabani, A. M. H. (2013). Suspended Nanoparticles in Surfactant Media as a Microextraction Technique for Simultaneous Separation and Preconcentration of Cobalt, Nickel and Copper Ions for Electrothermal Atomic Absorption Spectrometry Determination. *Talanta*, 106, 150–154.

Dadfarnia, S., and Haji Shabani, A. M. (2010). Recent Development in Liquid Phase Microextraction for Determination of Trace Level Concentration of Metals - A Review. *Anal. Chim. Acta.* 658(2), 107–119.

Davarani, S. S. H., Moazami, H. R., Keshtkar, A. R., Banitaba, M. H., and Nojavan, S. (2013). A Selective Electromembrane Extraction of Uranium (VI) Prior to Its Fluorometric Determination in Water. *Anal. Chim. Acta.* 783, 74–79.

Demetriades, D., Economou, A., and Voulgaropoulos, A. (2004). A Study of Pencil-Lead Bismuth-Film Electrodes for the Determination of Trace Metals by Anodic Stripping Voltammetry. *Anal. Chim. Acta*. 519(2), 167–172.

Dokpikul, N., Chaiyasith, W. C., Sananmuang, R., and Ampiah-Bonney, R. J. (2018). Surfactant-Assisted Emulsification Dispersive Liquid-Liquid Microextraction Using 2-Thenoyltrifluoroacetone as a Chelating Agent Coupled with Electrothermal Atomic Absorption Spectrometry for the Speciation of Chromium in Water and Rice Samples. *Food Chem.* 246, 379–385.

Dzygiel, P., and Wieczorek, P. P. (2010). *Supported Liquid Membranes and their Modifications: Definition, Classification, Theory, Stability, Application and Perspectives*. Vladimir S. Kislik. *Liquid Membranes*. (pp. 73 – 140). Netherlands: Elsevier.

Eibak, L. E. E., Rasmussen, K. E., Øiestad, E. L., Pedersen-Bjergaard, S., and Gjelstad, A. (2014). Parallel Electromembrane Extraction in the 96-well Format. *Anal. Chim. Acta.* 828, 48–52.

Encke, L. F. (1970). The Chemistry and Manufacturing of the Lead Pencil. *J. Chem. Edu.* 47(8), 575–576.

Es'Haghi, Z., Khalili, M., Khazaeifar, A., and Rounaghi, G. H. (2011). Simultaneous Extraction and Determination of Lead, Cadmium and Copper in Rice Samples by a New Pre-Concentration Technique: Hollow Fiber Solid Phase Microextraction Combined with Differential Pulse Anodic Stripping Voltammetry. *Electrochim. Acta.* 56(9), 3139–3146.

Esrafili, A., Yamini, Y., Ghambarian, M., and Ebrahimpour, B. (2012). Automated Preconcentration and Analysis of Organic Compounds by On-Line Hollow Fiber Liquid-Phase Microextraction-High Performance Liquid Chromatography. *J. Chromatogr. A.* 1262, 27–33.

Esrafili, A., Yamini, Y., Ghambarian, M., and Moradi, M. (2011). Dynamic Three-Phase Hollow Fiber Microextraction Based on Two Immiscible Organic Solvents with Automated Movement of the Acceptor Phase. *J. Sep. Sci.* 34(1), 98–106.

Fakhari, A. R., Koruni, M. H., Ahmar, H., Shahsavani, A., and Movahed, S. K. (2014). Electrochemical Determination of Dextromethorphan on Reduced Graphene Oxide Modified Screen-Printed Electrode after Electromembrane Extraction. *Electroanal.* 26(3), 521–529.

Fasih Ramandi, N., and Shemirani, F. (2015). Selective Ionic Liquid Ferrofluid Based Dispersive-Solid Phase Extraction For Simultaneous Preconcentration /Separation of Lead and Cadmium in Milk and Biological Samples. *Talanta*, 131, 404–411.

Feng, Q. M., Zhang, Q., Shi, C. G., Xu, J. J., Bao, N., and Gu, H. Y. (2013). Using Nanostructured Conductive Carbon Tape Modified with Bismuth as the Disposable Working Electrode for Stripping Analysis in Paper-Based Analytical Devices. *Talanta*, 115, 235–240.

Fernandes, A., Oliveira, D., Santos, C., Rossana, S., Rita, A., and Nogueira, A. (2017). The Use of Diluted Formic Acid in Sample Preparation for Macro- and Microelements Determination in foodstuff Samples Using ICP OES. *J. Food. Compost. Anal.* 66, 7–12.

Fotouhi, L., Yamini, Y., Molaei, S., and Seidi, S. (2011). Comparison of Conventional Hollow Fiber Based Liquid Phase Microextraction and Electromembrane Extraction Efficiencies for the Extraction of Ephedrine from Biological Fluids. *J. Chromatogr. A.* 1218(48), 8581–8586.

Gao, C., Yu, X.-Y., Xu, R.-X., Liu, J.-H., and Huang, X.-J. (2012). AlOOH-Reduced Graphene Oxide Nanocomposites: One-Pot Hydrothermal Synthesis and Their Enhanced Electrochemical Activity for Heavy Metal Ions. *ACS Appl. Mater. Interfaces.* 4(9), 4672–4682.

Gao, X., Jang, J., and Nagase, S. (2010). Hydrazine and Thermal Reduction of Graphene Oxide: Reaction Mechanisms, Product Structures, and Reaction Design. *J. Phys. Chem. C.* 114(2), 832–842.

Ghambarian, M., Yamini, Y., and Esrafili, A. (2012). Developments in Hollow Fiber Based Liquid-Phase Microextraction: Principles and Applications. *Microchim. Acta*. 177(3–4), 271–294.

Gjelstad, A., Jensen, H., Rasmussen, K. E., and Pedersen-Bjergaard, S. (2012). Kinetic aspects of Hollow Fiber Liquid-Phase Microextraction and Electromembrane Extraction. *Anal. Chim. Acta.* 742, 10–16.

Gjelstad, A., Rasmussen, K. E., and Pedersen-Bjergaard, S. (2007). Simulation of Flux During Electro-Membrane Extraction Based on the Nernst-Planck Equation. *J. Chromatogr. A.* 1174(1–2), 104–111.

Gjelstad, A., Rasmussen, K. E., and Pedersen-Bjergaard, S. (2006). Electrokinetic Migration Across Artificial Liquid Membranes Tuning the Membrane Chemistry to Different Types of Drug Substances. *J. Chromatogr. A.* 1124(1–2), 29–34.

Gong, T., Liu, J., Liu, X., Liu, J., Xiang, J., and Wu, Y. (2016). A Sensitive and Selective Sensing Platform Based on CdTe QDs in the Presence of L -Cysteine for Detection of Silver, Mercury and Copper Ions in Water and Various Drinks. *Food. Chem.* 213, 306–312.

Gumpu, M. B., Veerapandian, M., Krishnan, U. M., and Rayappan, J. B. B. (2017). Simultaneous Electrochemical Detection of Cd(II), Pb(II), As(III) and Hg(II) Ions using Ruthenium(II)-Textured Graphene Oxide Nanocomposite. *Talanta*. 162, 574–582.

Guo, H.L., Wang, X.F., Qian, Q.Y., Wang, F.B., and Xia, X.H. (2009). A Green Approach to the Synthesis of Graphene Nanosheets. *ACS Nano*. 3(9), 2653–2659.

Guo, Z., Li, D. D., Luo, K. X., Li, Y. H., Li, H. Y., Zhao, Q. N., Li, M. M., Zhao, Y. T., Sun, T. S., and Ma, C. (2017). Simultaneous determination of trace Cd(II), Pb(II) and Cu(II) by differential pulse anodic stripping voltammetry using a reduced graphene oxide-chitosan/poly-L-lysine nanocomposite modified glassy carbon electrode. *J. Colloid Interface Sci.* 490, 11–22.

Guzsvány, V., Nakajima, H., Soh, N., Nakano, K., and Imato, T. (2010). Antimony-Film Electrode for the Determination of Trace Metals by Sequential-Injection Analysis/Anodic Stripping Voltammetry. *Anal. Chim. Acta.* 658(1), 12–17.

Hamsawahini, K., Sathishkumar, P., Ahamad, R., and Yusoff, A. R. M. (2015) A Sensitive, Selective and Rapid Determination of Lead(II) Ions in Real-Life Samples Using an Electrochemically Reduced Graphene Oxide-Graphite Reinforced Carbon Electrode. *Talanta*. 144, 969 – 976.

Hamsawahini, K., Sathishkumar, P., Ahamad, R., and Yusoff, A. R. M. (2016). PVDF-ErGO-GRC Electrode: A Single Setup Electrochemical System for Separation, Pre-concentration and Detection of Lead Ions in Complex Aqueous Samples. *Talanta.* 148, 101 – 107.

Harrison, J. A., and Shoesmith, D. W. (1971). The Electrochemical Reduction of Organic Acids. *J. Electroanal. Chem. Interfacial. Electrochem.* 32(1), 125–135.

Herrero, E., Arancibia, V., and Rojas-Romo, C. (2014). Simultaneous Determination of Pb^{2+}, Cd^{2+} and Zn^{2+} by Adsorptive Stripping Voltammetry Using Clioquinol as a Chelating-Adsorbent Agent. *J. Electroanal. Chem.* 729, 9–14.

Hidalgo, C. R., Ramos-Payán, M., Ocaña-González, J. A., Martín-Valero, M. J., and Bello-López, M. Á. (2015). Agar Films Containing Silver Nanoparticles as New Supports for Electromembrane Extraction. *Anal. Bioanal. Chem.* 407(5), 1519–1525.

Ho, T. S., Vasskog, T., Anderssen, T., Jensen, E., Rasmussen, K. E., and Pedersen-Bjergaard, S. (2007). 25,000-Fold Pre-Concentration in a Single Step With Liquid-Phase Microextraction. *Anal. Chim. Acta.* 592(1), 1–8.

Ho, T. S., Pedersen-Bjergaard, S., and Rasmussen, K. E. (2002). Recovery, enrichment and selectivity in liquid-phase microextraction: Comparison with Conventional Liquid-Liquid Extraction. *J. Chromatogr. A.* 963(1–2), 3–17.

Hocevar, S. B., Ivan, S., Ogorevc, B., and Vytr, K. (2007). Antimony Film Electrode for Electrochemical Stripping Analysis. *Anal. Chem*. 79(22), 8639–8643.

Hosseiny Davarani, S. S., Sheikhi, N., Nojavan, S., Ansari, R., and Mansori, S. (2015). Electromembrane Extraction of Heavy Metal Cations from Aqueous Media Based on Flat Membrane: Method Transfer from Hollow Fiber to Flat Membrane. *Anal. Methods.* 7(6), 2680–2686.

Huang, C., Gjelstad, A., and Pedersen-Bjergaard, S. (2015). Exhaustive Extraction of Peptides by Electromembrane Extraction. *Anal. Chim. Acta.* 853(1), 328–334.

Huang, C., Eibak, L. E. E., Gjelstad, A., Shen, X., Trones, R., Jensen, H., and Pedersen-Bjergaard, S. (2014). Development of a Flat Membrane Based Device for Electromembrane Extraction: A New Approach for Exhaustive Extraction of Basic Drugs from Human Plasma. *J. Chromatogr. A.* 1326, 7–12.

Huang, H., Chen, T., Liu, X., and Ma, H. (2014). Ultrasensitive and Simultaneous Detection of Heavy Metal Ions based on Three-Dimensional Graphene-Carbon Nanotubes Hybrid Electrode Materials. *Anal. Chim. Acta.* 852, 45–54.

Hummer, S. W., and Offeman, E. R. (1957). Preparation of Graphitic Oxide. *J. Am. Chem. Soc*. 208(1937), 1939.

Islam, M. A., Al-mamun, A., Hossain, F., Quraishi, S. B., Naher, K., Khan, R., Das, S., and Tamim, U. (2017). Contamination and Ecological Risk Assessment of Trace Elements in Sediments of the Rivers of Sundarban Mangrove Forest, Bangladesh. *Marine. Poll. Bull.* 124(1), 356–366.

Ito, R., Kawaguchi, M., Sakui, N., Honda, H., Okanouchi, N., Saito, K., and Nakazawa, H. (2008). Mercury Speciation and Analysis in Drinking Water by stir Bar Sorptive Extraction with In Situ Propyl Derivatization and Thermal Desorption-Gas Chromatography-Mass Spectrometry. *J. Chromatogr. A.* 1209(1–2), 267–270.

Jagasia, P., Mohapatra, P. K., Raut, D. R., Dhami, P. S., Adya, V. C., Sengupta, A., Gandhi, P.M., and Wattal, P. K. (2015). Pertraction of Radio-Cesium from Acidic Feeds Across Supported Liquid Membranes Containing Calix-Crown-6 Ligands in a Fluorinated Diluent. *J. Membr. Sci.* 487, 127–134.

Jain, R., and Singh, R. (2016). Microextraction Techniques for Analysis of Cannabinoids. *Trends Anal. Chem.* 80, 156–166.

Jalbani, N., and Soylak, M. (2015). Separation-Preconcentration of Nickel and Lead in Food Samples by a Combination of Solid-Liquid-Solid Dispersive Extraction using SiO2 Nanoparticles, Ionic Liquid-Based Dispersive Liquid-Liquid Micro-Extraction. *Talanta.* 131, 361–365.

Jeannot, M. A, and Cantwell, F. F. (1996). Solvent Microextraction into a Single Drop. *Anal. Chem.* 68(13), 2236–2240.

Jönsson, J. Å., and Mathiasson, L. (2000). Membrane-based Techniques for Sample Enrichment. *J. Chromatogr. A.* 902(1), 205–225.

Jorge, M., Gulaboski, R., Pereira, C. M., and Cordeiro, M. N. D. S. (2006). Molecular Dynamics Study of 2-Nitrophenyl Octyl Ether and Nitrobenzene. *J. Phys. Chem. B.* 110(25), 12530–12538.

Jorge, E. O., Rocha, M. M., Fonseca, I. T. E., and Neto, M. M. M. (2010). Studies on the Stripping Voltammetric Determination and Speciation of Chromium at a Rotating-Disc Bismuth Film Electrode. *Talanta.* 81(1–2), 556–564.

Jovanovski, V., Hrastnik, N. I., and Ho, S. B. (2015). Copper Film Electrode for Anodic Stripping Voltammetric Determination of Trace Mercury and Lead, *Electrochem. Commun.* 57, 1–4.

Jovanovski, V., Hočevar, S. B., and Ogorevc, B. (2009). Ex situ Prepared Antimony Film Electrode for Electrochemical Stripping Measurement of Heavy Metal Ions. *Electroanal.* 21(21), 2321–2324.

Juang, R. S., Kao, H. C., and Wu, W. H. (2004). Analysis of Liquid Membrane Extraction of Binary Zn(II) and Cd(II) from Chloride Media with Aliquat 336 based on Thermodynamic Equilibrium Models. *J. Membr. Sci.* 228(2), 169–177.

Jung, J. R., and Ahn, S. Il. (2018). Van der Waals Pressure Sensors using Reduced Graphene Oxide Composites. *Chem. Phys. Lett.* 697, 12–16.

Kachoosangi, R. T., and Compton, R. G. (2013). Voltammetric Determination of Chromium(VI) using a Gold Film Modified Carbon Composite Electrode. *Sens. Actuators B Chem.* 178, 555–562.

Kameda, K., Hashimoto, Y., and Ok, Y. S. (2018). Stabilization of Arsenic and Lead by Magnesium Oxide (MgO) in Different Seawater Concentrations. *Environ. Poll.* 233, 952–959.

Kamyabi, M. A., and Aghaei, A. (2016a). Electromembrane Extraction and Anodic Stripping Voltammetric Determination of Mercury(II) using a Glassy Carbon Electrode Modified with Gold Nanoparticles. *Microchim. Acta.* 183(8), 2411–2419.

Kamyabi, M. A., and Aghaei, A. (2016b). Electromembrane Extraction Coupled to Square Wave Anodic Stripping Voltammetry for Selective Preconcentration and Determination of trace levels of As(III) in water samples. *Electrochim. Acta.* 206, 192–198.

Kataoka, H., 2010. Recent Developments and Applications of Microextraction Techniques in Drug Analysis. *Anal. Bioanal. Chem.* 396(1), 339–364.

Kauppila, J., Kunnas, P., Damlin, P., Viinikanoja, A., and Kvarnström, C. (2013). Electrochemical Reduction of Graphene Oxide Films in Aqueous and Organic Solutions. *Electrochim. Acta.* 89, 84–89.

Kawde, A., Ismail, A., Al-Betar, A. R., and Muraza, O. (2017). Novel Ce-Incorporated Zeolite Modified-Carbon Paste Electrode for Simultaneous Trace Electroanalysis of Lead and Cadmium. *Microporous. Mesoporous. Mater.* 243, 1–8.

Kaya, M. (2016). Recovery of Metals and Nonmetals from Electronic Waste by Physical and Chemical Recycling Processes. *Waste. Manage.* 57, 64–90.

Kebiche-Senhadji, O., Mansouri, L., Tingry, S., Seta, P., and Benamor, M. (2008). Facilitated Cd(II) Transport Across CTA Polymer Inclusion Membrane Using Anion (Aliquat 336) and Cation (D2EHPA) Metal Carriers. *J. Membr. Sci.* 310(1–2), 438–445.

Kebiche-Senhadji, O., Tingry, S., Seta, P., and Benamor, M. (2010). Selective Extraction of Cr(VI) Over Metallic Species By Polymer Inclusion Membrane (PIM) Using Anion (Aliquat 336) as Carrier. *Desalination*. 258(1–3), 59–65.

Khan, I., Pandit, U. J., Wankar, S., and Limaye, S. N. (2017). Environmental Nanotechnology , Monitoring and Management Centrifugation assisted digestion for simultaneous voltammetric determination of ultra trace metal ions in water and milk samples. *Environ. Nanotechnol. Monit. Manage*. *7*, 64–72.

Khajeh, M., Pedersen-Bjergaard, S., Barkhordar, A., and Bohlooli, M. (2015). Application of Hollow Cylindrical Wheat Stem for Electromembrane Extraction of Thorium in Water Samples. *Spectrochim. Acta A.* 137, 328–32.

Khodaee, N., Mehdinia, A., Esfandiarnejad, R., and Jabbari, A. (2016). Ultra Trace Analysis of PAHs by Designing Simple Injection of Large Amounts of Analytes Through the Sample Reconcentration on SPME Fiber After Magnetic Solid Phase Extraction. *Talanta.* 147, 59–62.

Kim, J., and Kang, J. (2016). The Chromium Accumulation and Its Physiological Effects in Juvenile Rockfish, Sebastes Schlegelii, Exposed to Different Levels of Dietary Chromium (Cr^{6+}) Concentrations. *Environ. Toxicol.Pharmacol.* 41, 152–158.

Kim, Y., Ha, E. H., Park, H., Ha, M., Kim, Y., Hong, Y. C., Kim, E.J., and Kim, B. N. (2013). Prenatal Lead and Cadmium Co-Exposure and Infant Neurodevelopment at 6 Months of Age: The Mothers and Children's Environmental Health (MOCEH) study. *Neuro. Toxicol.* 35(1), 15–22.

Kjelsen, I. J. Ø., Gjelstad, A., Rasmussen, K. E., and Pedersen-Bjergaard, S. (2008). Low-Voltage Electromembrane Extraction of Basic Drugs from Biological Samples. *J. Chromatogr. A.* 1180(1–2), 1–9.

Kokkinos, C., Economou, A., and Giokas, D. (2017). Paper-Based Device with a Sputtered Tin-Film Electrode for the Voltammetric Determination of Cd(II) and Zn(II). *Sens. Actuators B Chem.* 260, 223–226.

Kokkinos, C., Economou, A., and Speliotis, T. (2014). Tin-Film Mini-Sensors Fabricated by a Thin-Layer Microelectronic Approach for Stripping Voltammetric Determination of Trace Metals. *Electrochem. Commun.* 38, 96–99.

Kokosa, J. M. (2013). Advances in Solvent-Microextraction Techniques. *Trends in Anal. Chem.* 43, 2–13.

Kokosa, J. M. (2015). Recent Trends in Using Single-Drop Microextraction and Related Techniques in Green Analytical Methods. *TrAC - Trends in Anal. Chem.* 71, 194–204.

Konczyk, J., Kozlowski, C., and Walkowiak, W. (2010). Removal of Chromium(III) from Acidic Aqueous Solution by Polymer Inclusion Membranes with D2EHPA and Aliquat 336. *Desalination*. 263(1–3), 211–216.

Korolczuk, M., Tyszczuk, K., and Grabarczyk, M. (2005). Adsorptive Stripping Voltammetry of Nickel and Cobalt at In Situ Plated Lead Film Electrode. *Electrochem. Commun.* 7(12), 1185–1189.

Korolczuk, M., Tyszczuk, K., and Grabarczyk, M. (2007). Determination of Uranium by Adsorptive Stripping Voltammetry at a Lead Film Electrode. *Talanta.* 72(3), 957–961.

Kuban, P., and Bocek, P. (2015). The Effects of Electrolysis on Operational Solutions in Electromembrane Extraction: The Role of Acceptor Solution. *J. Chromatogr. A.* 1398, 11–19.

Kubáň, P., Strieglerová, L., Gebauer, P., and Boček, P. (2011). Electromembrane Extraction of Heavy Metal Cations Followed By Capillary Electrophoresis with Capacitively Coupled Contactless Conductivity Detection. *Electrophoresis*. 32(9), 1025–32.

Kumbasar, R. A. (2010). Selective Extraction of Chromium(VI) from Multicomponent Acidic Solutions by Emulsion Liquid Membranes Using Tributhylphosphate as Carrier. *J. Hazard. Mater.* 178(1–3), 875–882.

Lee, P. M., Chen, Z., Li, L., and Liu, E. (2015). Reduced Graphene Oxide Decorated With Tin Nanoparticles Through Electrodeposition for Simultaneous Determination of Trace Heavy Metals. *Electrochim. Acta*. 174, 207–214.

Lee, S., Park, S. K., Choi, E., and Piao, Y. (2016). Voltammetric Determination of Trace Heavy Metals using an Electrochemically Deposited Graphene/Bismuth Nanocomposite Film-Modified Glassy Carbon Electrode. *J. Electroanal. Chem.* 766, 120–127.

Li, J., Guo, S., Zhai, Y., and Wang, E. (2009). High-Sensitivity Determination of lead and Cadmium Based on the Nafion-Graphene Composite Film. *Anal. Chim. Acta*. 649, 196–201.

Li, W. W., Kong, F. Y., Wang, J. Y., Chen, Z. D., Fang, H. L., and Wang, W. (2015). Facile One-Pot and Rapid Synthesis of Surfactant-Free Au-Reduced Graphene Oxide Nanocomposite for Trace Arsenic (III) Detection. *Electrochim. Acta*. 157, 183–190.

Lin, L., Lawrence, N. S., Thongngamdee, S., Wang, J., and Lin, Y. (2005). Catalytic Adsorptive Stripping Determination of Trace Chromium(VI) at The Bismuth Film Electrode. *Talanta*. 65(1), 144–148.

Liu, H., and Dasgupta, P. K. (1996). Analytical Chemistry in a Drop. *Trends in Anal. Chem.* 15(9), 468–475.

Liu, J., Chen, Y., Gao, D., Jing, J., and Hu, Q. (2014). Prenatal and Postnatal Lead Exposure and Cognitive Development of Infants Followed Over The First Three Years of Life: A Prospective Birth Study in the Pearl River Delta region, China. *Neurotoxicol.* 44, 326–34.

Liu, X., Kim, H., and Guo, L. J. (2013). Optimization of Thermally Reduced Graphene Oxide for an Efficient Hole Transport Layer in Polymer Solar Cells. *Org. Electron.* 14(2), 591–598.

Liu, X., Bouchard, G., Girault, H. H., Testa, B., and Carrupt, P. A. (2003). Partition Coefficients of Ionizable Compounds in o-Nitrophenyl Octyl Ether/Water Measured by the Potentiometric Method. *Anal. Chem.*75(24), 7036–7039.

Locatelli, C. (2010). Mutual Interference Problems in the Simultaneous Voltammetric Determination of Trace Total Mercury(II) in Presence of Copper(II) at Gold Electrode. Applications to Environmental Matrices. *Anal. Methods.* 2(11), 1784.

López-García, I., Vicente-Martínez, Y., and Hernández-Córdoba, M. (2013). Determination of Lead and Cadmium using an Ionic Liquid and Dispersive Liquid–Liquid Microextraction Followed by Electrothermal Atomic Absorption Spectrometry. *Talanta.* 110, 46–52.

Lozano, L. J., Godínez, C., de los Ríos, A. P., Hernández-Fernández, F. J., Sánchez-Segado, S., and Alguacil, F. J. (2011). Recent Advances in Supported Ionic Liquid Membrane Technology. *J. Membr. Sci.* 376(1–2), 1–14.

Lv, M., Wang, X., Li, J., Yang, X., Zhang, C., Yang, J., and Hu, H. (2013). Cyclodextrin-Reduced Graphene Oxide Hybrid Nanosheets for the Simultaneous Determination of Lead(II) and Cadmium(II) using Square Wave Anodic Stripping Voltammetry. *Electrochim. Acta.* 108, 412–420.

Ma, X., Liu, Z., Qiu, C., Chen, T., and Ma, H. (2013). Simultaneous Determination of Hydroquinone and Catechol Based on Glassy Carbon Electrode Modified with Gold-Graphene Nanocomposite. *Microchim. Acta.* 180(5–6), 461–468.

Mafa, P. J., Idris, A. O., Mabuba, N., and Arotiba, O. A. (2016). Electrochemical Co-Detection of As(III), Hg(II) and Pb(II) on a Bismuth Modified Exfoliated Graphite Electrode. *Talanta.* 153, 99–106.

Manzoori, J. L., Amjadi, M., and Abulhassani, J. (2009). Ultra-Trace Determination of Lead in Water and Food Samples by Using Ionic Liquid-Based Single Drop Microextraction-Electrothermal Atomic Absorption Spectrometry. *Anal. Chim. Acta.* 644(1–2), 48–52.

March, G., Nguyen, T., and Piro, B. (2015). Modified Electrodes Used for Electrochemical Detection of Metal Ions in Environmental Analysis. *Biosensors*. 5(2), 241–275.

Martinis, E. M., Berton, P., Altamirano, J. C., Hakala, U., and Wuilloud, R. G. (2010). Tetradecyl(trihexyl)phosphonium Chloride Ionic Liquid Single-Drop Microextraction for Electrothermal Atomic Absorption Spectrometric Determination of Lead in Water Samples. *Talanta.* 80(5), 2034–2040.

Mirceski, V., Sebez, B., Jancovska, M., Ogorevc, B., and Hocevar, S. B. (2013). Mechanisms and Kinetics of Electrode Processes at Bismuth and Antimony Film and Bare Glassy Carbon Surfaces Under Square-Wave Anodic Stripping Voltammetry Conditions. *Electrochim. Acta.* 105, 254–260.

Mishra, R. K., Nawaz, M. H., Hayat, A., Nawaz, M. A. H., Sharma, V., and Marty, J. L. (2017). Electrospinning of Graphene-Oxide onto Screen Printed Electrodes for Heavy Metal Biosensor. *Sens. Actuators B Chem.* 247, 366–373.

Moazami, H. R., Hosseiny Davarani, S. S., Mohammadi, J., Nojavan, S., and Abrari, M. (2015). The Effect of Electric Field Geometry on the Performance of Electromembrane Extraction Systems: Footprints of a Third Driving Force Along with Migration and Diffusion. *Anal. Chim. Acta.* 891, 151–159.

Mofidi, Z., Norouzi, P., Seidi, S., and Ganjali, M. R. (2017). Determination of Diclofenac using Electromembrane Extraction Coupled With Stripping FFT Continuous Cyclic Voltammetry. *Anal. Chim. Acta.* 972, 38–45.

Mollema, P. N., Stuyfzand, P. J., Juhász-holterman, M. H. A., Diepenbeek, P. M. J. A. Van, and Antonellini, M. (2015). Metal Accumulation in an Artificially Recharged Gravel Pit Lake Used for Drinking Water Supply. *J. Geochem. Explor.* 150, 35–51.

Morton, J., Havens, N., Mugweru, A., and Wanekaya, A. K. (2009). Detection Of Trace Heavy Metal Ions using Carbon Nanotube Modified Electrodes. *Electroanal.* 21(14), 1597–1603.

Mostafavi, H. A., Mirmajlessi, S. M., and Fathollahi, H. (2016).Graphene-Based Materials Functionalization with Natural Polymeric Biomolecules. *Recent Advances in Graphene*. (pp. 257–297). London : InTechOpen.

Nagles, E., Arancibia, V., Rojas, C., and Segura, R. (2012). Nafion-Mercury Coated Film Electrode for the Adsorptive Stripping Voltammetric Determination of Lead and Cadmium in the Presence Of Pyrogallol Red. *Talanta.* 99, 119–124.

Namieśnik, J., and Rabajczyk, A. (2012). Speciation Analysis of Chromium in Environmental Samples. *Crit. Rev. Environ. Sci. Technol*. 42(4), 327–377.

Narasimharaju, B. L., Bharma, G., Koreboina, V. B., Reddy, U. R., and Ieee. (2015). Modeling and Analysis of Voltage Controlled Positive Output Synchronous Buck-Boost Converter. *2015 Annual IEEE India Conference (INDICON)*, (pp.1–5). Available from: https://ieeexplore.ieee.org/document/7443348/

Navratil, R., Kotzianova, A., Halouzka, V., Opletal, T., Triskova, I., Trnkova, L., and Hrbac, J. (2016). Polymer Lead Pencil Graphite as Electrode Material: Voltammetric, XPS And Raman Study. *J. Electroanal. Chem.* 783, 152–160.

Nojavan, S., and Fakhari, A. R. (2010). Electro Membrane Extraction Combined with Capillary Electrophoresis for the Determination of Amlodipine Enantiomers in Biological Samples. *J. Sep. Sci.* 33(20), 3231–8.

Nomngongo, P. N., and Ngila, J. C. (2014). Determination of Trace Cd, Cu, Fe, Pb and Zn in Diesel and Gasoline by Inductively Coupled Plasma Mass Spectrometry After Sample Clean Up with Hollow Fiber Solid Phase Microextraction System. *Spectrochi. Acta Part B At. Spectrosc.* 98, 54–59.

Noyhouzer, T., and Mandler, D. (2011). Determination of Low Levels of Cadmium Ions by the Under Potential Deposition on a Self-Assembled Monolayer on Gold Electrode. *Anal. Chim. Acta.* 684(1–2), 1–7.

Ouyang, R., Zhang, W., Zhou, S., Xue, Z. L., Xu, L., Gu, Y., and Miao, Y. (2013). Improved Bi Film Wrapped Single Walled Carbon Nanotubes for Ultrasensitive Electrochemical Detection of trace Cr(VI). *Electrochim. Acta.* 113, 686–693.

Ouyang, R., Zhu, Z., Tatum, C. E., Chambers, J. Q., and Xue, Z. L. (2011). Simultaneous Stripping Detection of Zn(II), Cd(II) and Pb(II) using a Bimetallic Hg-Bi/Single-Walled Carbon Nanotubes Composite Electrode. *J. Electroanal. Chem.* 656(1–2), 78–84.

Ouyang, G., and Pawliszyn, J. (2006). Kinetic Calibration for Automated Hollow Fiber-Protected Liquid-Phase Microextraction. *Anal. Chem.*78(16), 5783–5788.

Paneque, P., Morales, M. L., Burgos, P., and Ponce, L. (2017). Elemental Characterisation of Andalusian Wine Vinegars with Protected Designation of Origin by ICP-OES and Chemometric Approach. *Food. Control.* 75, 203–210.

Panda, S. R., and De, S. (2014). Preparation, Characterization and Performance of $ZnCl_2$ Incorporated Polysulfone(PSF)/Polyethylene Glycol (PEG) Blend Low Pressure Nano Filtration Membranes. *Desalination*. 347, 52–65.

Pareja-Carrera, J., Mateo, R., and Rodríguez-Estival, J. (2014). Lead (Pb) in Sheep Exposed to Mining Pollution: Implications for Animal and Human Health. *Ecotoxicol. Environ. Saf.* 108, 210–216.

Park, Y. G. (2012). Effect of Electric Fields for Reducing Membrane Fouling in Dead-End Filtration. *Desalin. Water. Treat*. 33(1–3), 351–358.

Pearson, D., Chakraborty, S., Duda, B., Li, B., Weindorf, D. C., Deb, S., Brevik, e., and Ray, D. P. (2017). Water analysis Via Portable X-Ray Fluorescence Spectrometry. *J.Hydrol.* 544, 172–179.

Pedersen-Bjergaard, S., and Rasmussen, K. E. (1999). Liquid-Liquid-Liquid Microextraction for Sample Preparation of Biological Fluids Prior to Capillary Electrophoresis. *Anal. Chem.* 71(14), 2650–2656.

Pei, S., and Cheng, H.-M. (2012). The Reduction of Graphene Oxide. *Carbon*. 50(9), 3210–3228.

Peng, X.-Y., Liu, X.-X., Diamond, D., and Lau, K. T. (2011). Synthesis of Electrochemically-Reduced Graphene Oxide Film with Controllable Size and Thickness and Its Use in Supercapacitor. *Carbon.* 49(11), 3488–3496.

Pérez-Ràfols, C., Trechera, P., Serrano, N., Díaz-Cruz, J. M., Ariño, C., and Esteban, M. (2017). Determination of Pd(II) using an Antimony Film Coated on a Screen-Printed Electrode by Adsorptive Stripping Voltammetry. *Talanta.* 167, 1–7.

Pérez-Ràfols, C., Serrano, N., Díaz-Cruz, J. M., Ariño, C., and Esteban, M. (2016). New Approaches to Antimony Film Screen-Printed Electrodes using Carbon-Based Nanomaterials Substrates. *Anal. Chim. Acta.* 916, 17–23.

Pérez-Ràfols, C., Serrano, N., Díaz-Cruz, J. M., Ariño, C., and Esteban, M. (2015). Mercury Films on Commercial Carbon Screen-Printed Devices for the Analysis of Heavy Metal Ions: A Critical Evaluation. *Electroanal.* 27(6), 1345–1349.

Petersen, N. J., Jensen, H., Hansen, S. H., Rasmussen, K. E., and Pedersen-Bjergaard, S. (2009). Drop-to-Drop Microextraction Across a Supported Liquid Membrane by an Electrical Field Under Stagnant Conditions. *J. Chromatogr. A.* 1216(9), 1496–1502.

Petersen, N. J., Jensen, H., Hansen, S. H., Foss, S. T., Snakenborg, D., and Pedersen-Bjergaard, S. (2010). On-chip Electro Membrane Extraction. *Microfluid. Nanofluidics.* 9(4–5), 881–888.

Petersen, N. J., Foss, S. T., Jensen, H., Hansen, S. H., Skonberg, C., Snakenborg, D., Kutter, J. P., and Pedersen-Bjergaard, S. (2011). On-Chip Electro Membrane Extraction with Online Ultraviolet and Mass Spectrometric Detection. *Anal. Chem.* 83(1), 44–51.

Pillai, K. P. P. (1970). Fringing Field of Finite Parallel-Plate Capacitors. *Proc. Inst. Electr. Eng*. 117, 1201–1204.

Ping, J., Wang, Y., Wu, J., and Ying, Y. (2014). Development of an Electrochemically Reduced Graphene Oxide Modified Disposable Bismuth Film Electrode and its Application for Stripping Analysis of Heavy Metals in Milk. *Food. Chem.* 151, 65–71.

Pokpas, K., Zbeda, S., Jahed, N., Mohamed, N., Baker, P. G., and Iwuoha, E. I. (2014). Electrochemically Reduced Graphene Oxide Pencil-Graphite in situ Plated Bismuth-film Electrode for the Determination of Trace Metals by Anodic Stripping Voltammetry. *Int. J. Electrochem. Sci.* 9, 736–759.

Poon, W. C., Herath, G., Sarker, A., Masuda, T., and Kada, R. (2016). River and fish pollution in Malaysia: A green ergonomics perspective. *Appl. Ergon.* 57, 80–93.

Pourreza, N., and Naghdi, T. (2014). Silicon Carbide Nanoparticles as an Adsorbent for Solid Phase Extraction of Lead and Determination by Flame Atomic Absorption Spectrometry. *Ind. Eng. Chem. Res.* 20(5), 3502–3506.

Pumera, M. (2013). Electrochemistry of Graphene, Graphene Oxide and Other Graphenoids: Review. *Electrochem. Commun.* 36, 14–18.

Rahmani, T., Rahimi, A., and Nojavan, S. (2016). Study on Electrical Current Variations in Electromembrane Extraction Process : Relation Between Extraction Recovery and Magnitude Of Electrical Current. *Anal. Chim. Acta.* 903, 81–90.

Rahmani, T., Rahimi, A., and Nojavan, S. (2016). Study on Electrical Current Variations in Electromembrane Extraction Process : Relation Between Extraction Recovery and magnitude of Electrical Current. *Anal. Chim. Acta.* 903, 81–90.

Ramesha, G. K., and Sampath, S. (2007). Exfoliated Graphite Oxide Modified Electrode for the Selective Determination of Picomolar Concentration of Lead. *Electroanal.* 19(23), 2472–2478.

Ramesha, G. K., and Sampath, S. (2011). In-situ Formation of Graphene-Lead Oxide Composite and Its Use in Trace Arsenic Detection. *Sens. Actuat. B*, 160(1), 306–311.

Rasool, A., Xiao, T., Farooqi, A., Shafeeque, M., Masood, S., Ali, S., Fahad. S., and Nasim, W. (2016). Arsenic and Heavy Metal Contaminations in the Tube Well Water of Punjab , Pakistan and Risk Assessment : A case study. *Ecol. Eng.* 95, 90–100.

Reyes-Aguilera, J. a., Gonzalez, M. P., Navarro, R., Saucedo, T. I., and Avila-Rodriguez, M. (2008). Supported Liquid Membranes (SLM) for Recovery of Bismuth from Aqueous Solutions. *J. Membr. Sci.* 310(1–2), 13–19.

Reza, M., Zanjani, K., Yamini, Y., Shariati, S., and Ake, J. (2007). A new Liquid-Phase Microextraction Method Based on Solidification Of Floating Organic Drop. *Anal. Chim. Acta*. 585(2), 286–293.

Rocha, D. L., Batista, A. D., Rocha, F. R. P., Donati, G. L., and Nóbrega, J. A. (2013). Greening Sample Preparation in Inorganic Analysis. *Trends in Anal. Chem.* 45, 79–92.

Rodríguez de San Miguel, E., Vital, X., and de Gyves, J. (2014). Cr(VI) Transport Via a Supported Ionic Liquid Membrane Containing CYPHOS IL101 as Carrier: System Analysis and Optimization Through Experimental Design Strategies. *J. Hazard. Mater.* 273, 253–262.

Rojas-Romo, C., Serrano, N., Ariño, C., Arancibia, V., Díaz-Cruz, J. M., and Esteban, M. (2016). Determination of Sb(III) Using an Ex-Situ Bismuth Screen-Printed Carbon Electrode by Adsorptive Stripping Voltammetry. *Talanta.* 155, 21–27.

Rouhollahi, A., Kouchaki, M., and Seidi, S. (2016). Electrically Stimulated Liquid Phase Microextraction Combined With Differential Pulse Voltammetry: A New and Efficient Design for In Situ Determination of Clozapine from Complicated Matrices. *RSC Adv.* 6(16), 12943–12952.

Ruecha, N., Rodthongkum, N., Cate, D. M., Volckens, J., Chailapakul, O., and Henry, C. S. (2015). Sensitive electrochemical Sensor Using A Graphene-Polyaniline Nanocomposite for Simultaneous Detection of Zn(II), Cd(II), and Pb(II). *Anal. Chim. Acta.* 874, 40–48.

Safari, M., Nojavan, S., Davarani, S. S. H., and Morteza-Najarian, A. (2013). Speciation of Chromium in Environmental Samples by Dual Electromembrane Extraction System Followed by High Performance Liquid Chromatography. *Anal. Chim. Acta.* 789, 58–64.

Sang, F., Li, X., Zhang, Z., Liu, J., and Chen, G. (2018). Recyclable Colorimetric Sensor of Cr^{3+} and Pb^{2+} Ions Simultaneously Using A Zwitterionic Amino Acid Modified Gold Nanoparticles. *Spectrochim. Acta* . 193, 109–116.

Sander, S., Navrátil, T., Bašová, P., and Novotný, L. (2002). Electrosorption of Chromium-Diethylenetriaminepentaacetic Acid on Mercury Electrode Under Voltammetric Conditions. *Electroanal.* 14(15–16), 1133–1137.

Sander, S., Navrátil, T., and Novotný, L. (2003). Study of the Complexation, Adsorption and Electrode Reaction Mechanisms of Chromium(VI) and (III) with DTPA Under Adsorptive Stripping Voltammetric Conditions. *Electroanal.* 15(19), 1513–1521.

Saputro, S., Yoshimura, K., Takehara, K., and Matsuoka, S. (2011). Oxidation of Chromium(III) by Free Chlorine in Tap Water during the Chlorination Process Studied by an Improved Solid-Phase Spectrometry. *Anal. Sci.* 27(6), 649.

Schneider, M., Pereira, É. R., de Quadros, D. P. C., Welz, B., Carasek, E., de Andrade, J. B., Menoyo, J. D. C., and Feldmann, J. (2017). Investigation of Chemical Modifiers for the Determination of Cadmium and Chromium in Fish Oil and Lipoid Matrices Using HR-CS GF-AAS and a Simple “Dilute-And-Shoot” Approach. *Microchem. J.* 133, 175–181.

Schmitz, H. A., Maher, W. A., Taylor, A. M., and Krikowa, F. (2015). Effects of Cadmium Accumulation From Suspended Sediments and Phytoplankton on the Oyster Saccostrea Glomerata. *Aquat. Toxicol.* 160, 22–30.

Schlosser, S., and Kossaczky, E. (1980). Comparison of Pertraction Through Liquid Membranes and Double Liquid-Liquid Extraction. *J. Membr. Sci.* 6, 83–105.

Sebez, B., Ogorevc, B., Hocevar, S. B., and Veber, M. (2013). Functioning of Antimony Film Electrode in Acid Media Under Cyclic and Anodic Stripping Voltammetry Conditions. *Anal. Chim. Acta.* 785, 43–49.

Segura, R., Pradena, M., Pinto, D., Godoy, F., Nagles, E., and Arancibia, V. (2011). Adsorptive Stripping Voltammetry of Nickel with 1-Nitroso-2-Napthol Using a Bismuth Film Electrode. *Talanta.* 85(5), 2316–2319.

Seip, K. F., Faizi, M., Vergel, C., Gjelstad, A., and Pedersen-Bjergaard, S. (2014). Stability and Efficiency of Supported Liquid Membranes in Electromembrane Extraction-A Link to Solvent Properties. *Anal. Bioanal. Chem.* 406, 2151 - 2161.

Seidi, S., Yamini, Y., and Rezazadeh, M. (2011). Electrically Enhanced Microextraction for Highly Selective Transport of Three Β-Blocker Drugs. *J. Pharm. Biomed. Anal*. 56(5), 859–866.

Senol, A. (2017). Extractive Removal of Cr (VI) from Aqueous Acidic Media by Aliquat 336 / Xylene System : Optimization and Modelling of Equilibrium. *Indian J. Chem. Technol.* 24, 269–283.

Serrano, N., Díaz-Cruz, J. M., Ariño, C., and Esteban, M. (2016). Antimony- based Electrodes for Analytical Determinations. *Trends Anal. Chem.* 77, 203–213.

Serrano, N., Díaz-cruz, M., Esteban, M., and Ari, C. (2017). Voltammetric Determination of Metal Ions Beyond Mercury Electrodes . A Review. *Anal. Chim. Acta.* 990. 11-53.

Shin, H.J., Kim, K. K., Benayad, A., Yoon, S.M., Park, H. K., Jung, I.S., and Lee, Y. H. (2009). Efficient Reduction of Graphite Oxide by Sodium Borohydride and Its Effect on Electrical Conductance. *Adv. Funct. Mater.* 19(12), 1987–1992.

Shokri, M., Beiraghi, A., and Seidi, S. (2015). In Situ Emulsification Microextraction Using a Dicationic Ionic Liquid Followed By Magnetic Assisted Physisorption for Determination of Lead Prior to Micro-Sampling Flame Atomic Absorption Spectrometry. *Anal. Chim. Acta.* 889, 123–129.

Sikanen, T., Pedersen-Bjergaard, S., Jensen, H., Kostiainen, R., Rasmussen, K. E., and Kotiaho, T. (2010). Implementation of Droplet-Membrane-Droplet Liquid-Phase Microextraction Under Stagnant Conditions for Lab-On-A-Chip Applications. *Anal. Chim. Acta.* 658(2), 133–140.

Silwana, B., Horst, C. Van Der, Iwuoha, E., and Somerset, V. (2015). Synthesis , Characterisation and Electrochemical Evaluation of Reduced Graphene Oxide Modified Antimony Nanoparticles. *Thin Solid Films*. 592, 124–134.

Silwana, B., van der Horst, C., Iwuoha, E., and Somerset, V. (2016). Reduced Graphene Oxide Impregnated Antimony Nanoparticle Sensor for Electroanalysis of Platinum Group Metals. *Electroanal. 28*(7), 1597–1607.

Texas Instrument (2011). Characteristics of Rechargeable Batteries. *Texas : National Semiconductor.*

Šlampová, A., Kubáň, P., and Boček, P. (2016). Additional Considerations on Electrolysis in Electromembrane Extraction. *J. Chromatogr. A.* 1429, 364–368.

Šlampová, A., Kubáň, P., and Boček, P. (2012). Electromembrane Extraction Using Stabilized Constant D.C. Electric Current-A Simple Tool for Improvement of Extraction Performance. *J. Chromatogr. A.* 1234, 32–37.

Song, W., Zhang, L., Shi, L., Li, D. W., Li, Y., and Long, Y. T. (2010). Simultaneous Determination of Cadmium(II), Lead(II) and Copper(II) by Using a Screen-Printed Electrode Modified with Mercury Nano-Droplets. *Microchim. Acta.* 169(3), 321–326.

Sopha, H., Baldrianova, L., Tesarova, E., Hocevar, S. B., Svancara, I., Ogorevc, B., and Vytras, K. (2010). Insights into the Simultaneous Chronopotentiometric Stripping Measurement of Indium (III), Thallium (I) and Zinc (II) in Acidic Medium at the In Situ Prepared Antimony Film Carbon Paste Electrode, *Electochim. Acta*. 55, 7929–7933.

Sopha, H., Jovanovski, V., Hocevar, S. B., and Ogorevc, B. (2012). In-Situ Plated Antimony Film Electrode for Adsorptive Cathodic Stripping Voltammetric Measurement of Trace Nickel. *Electrochem. Commun.* 20(1), 23–25.

Sosa, V., Barcelo, C., Serrano, N., Arino, C., Diaz-Cruz, J. M., and Esteban, M. (2015). Antimony Film Screen-Printed Carbon Electrode for Stripping Analysis of Cd(II), Pb(II), and Cu(II) in Natural Samples. *Anal. Chim. Acta.* 855, 34–40.

Srivastava, P., and Angove, M. (2004). Competitive Adsorption of Cadmium (II) onto Kaolinite as Affected by pH. *Australian New Zealand Soils Conference.* 5 – 9 December 2004. Sydney, Australia: 1-6.

Stanisz, E., Werner, J., and Zgoła-Grześkowiak, A. (2014). Liquid-Phase Microextraction Techniques Based on Ionic Liquids for Preconcentration and Determination of Metals. *Trends Anal. Chem.* 61, 54–66.

Stankovich, S., Piner, R. D., Chen, X., Wu, N., Nguyen, S. T., and Ruoff, R. S. (2006). Stable Aqueous Dispersions of Graphitic Nanoplatelets Via the Reduction of Exfoliated Graphite Oxide in the Presence of Poly(Sodium 4-Styrenesulfonate). *J. Mater. Chem.* 16(2), 155 - 158.

Sun, J. N., Chen, J., and Shi, Y. P. (2014). Ionic Liquid-Based Electromembrane Extraction and Its Comparison with Traditional Organic Solvent Based Electromembrane Extraction for the Determination of Strychnine and Brucine in Human Urine. *J. Chromatogr. A.* 1352, 1–7.

Svobodova-Tesarova, E., Baldrianova, L., Stoces, M., Svancara, I., Vytras, K., Hocevar, S. B., and Ogorevc, B. (2011). Antimony Powder-Modified Carbon Paste Electrodes for Electrochemical Stripping Determination Of Trace Heavy Metals. *Electrochim. Acta.* 56(19), 6673–6677.

Tavares, P. H. C. P., and Barbeira, P. J. S. (2008). Influence of Pencil Lead Hardness on Voltammetric Response of Graphite Reinforcement Carbon Electrodes. *J. Appl. Electrochem.* 38(6), 827–832.

Tesarova, E., Baldrianova, L., Hocevar, S. B., Svancara, I., Vytras, K., and Ogorevc, B. (2009). Anodic Stripping Voltammetric Measurement of Trace Heavy Metals at Antimony Film Carbon Paste Electrode. *Electrochim. Acta.* 54(5), 1506–1510.

Thordarson, E., Jonsson, J. A., and Emneus, J. (2000). Immunologic Trapping in Supported Liquid Membrane Extraction. *Anal. Chem.* 72(21), 5280–5284.

Toh, S. Y., Loh, K. S., Kamarudin, S. K., and Daud, W. R. W. (2014). Graphene Production via Electrochemical Reduction of Graphene Oxide: Synthesis and Characterisation. *Chem. Eng. J.* 251, 422–434.

Trindade, A. S. N., Dantas, A. F., Lima, D. C., Ferreira, S. L. C., and Teixeira, L. S. G. (2015). Multivariate Optimization of Ultrasound-Assisted Extraction for Determination of Cu , Fe , Ni and Zn in Vegetable Oils by High-Resolution Continuum Source Atomic Absorption Spectrometry. *Food. Chem.* 185, 145–150.

Tyszczuk-Rotko, K., Sadok, I., and Barczak, M. (2016). Thiol-Functionalized Polysiloxanes Modified by Lead Nanoparticles: Synthesis, Characterization and Application for Determination of Trace Concentrations of Mercury(II). *Microporous. Mesoporous. Mater.* 230, 109–117.

Tyszczuk, K., Korolczuk, M., and Grabarczyk, M. (2007). Application Of Gallium Film Electrode for Elimination of Copper Interference in Anodic Stripping Voltammetry of Zinc. *Talanta.* 71(5), 2098–2101.

Venkateswaran, P. (2007). Di(2-ethylhexyl)phosphoric Acid-Coconut Oil Supported Liquid Membrane for the Separation of copper Ions From Copper Plating Wastewater. *J. Environ. Sci.* 19, 1446–1453.

Vukomanovic, D. V., Vanloon, G. W., Nakatsu, K., and Zoutman, D. E. (1997). Determination of Chromium (VI) and (III) by Adsorptive Stripping Voltammetry with Pyrocatechol Violet. *Microchem. J.* 57(1), 86–95.

Wang, D., Sun, H., Wu, Y., Zhou, Z., Ding, Z., Chen, X., and Xu, Y. (2016). Tubular and Glomerular Kidney Effects in the Chinese General Population with Low Environmental Cadmium Exposure. *Chemosphere*. 147, 3–8.

Wang, G., Yang, J., Park, J., Gou, X., Wang, B., Liu, H., and Yao, J. (2008). Facile Synthesis and Characterization of Graphene Nanosheets. *J. Phys. Chem. C.* 112(22), 8192–8195.

Wang, H., Liu, L., Hu, Y.-F., Hao, J.H., Chen, Y.H., Su, P.Y., Fu, L., Yu. Z., Zhang, G. B., Wang, L., Tao, F. B., and Xu, D.X. (2016). Maternal Serum Cadmium Level During Pregnancy and Its Association with Small for Gestational Age Infants: a Population-Based Birth Cohort Study. *Sci. Rep.* 6, 1-7.

Wang, L., Paimin, R., Cattrall, R. W., Shen, W., and Kolev, S. D. (2000). The Extraction of Cadmium(II) and Copper(II) from Hydrochloric Acid Solutions Using an Aliquat 336 / PVC membrane. *J. Membr. Sci.* 176, 105–111.

Wang, Y., Chen, L., Gao, Y., Zhang, Y., Wang, C., Zhou, Y., Shi, R., and Tian, Y. (2016b). Effects of Prenatal Exposure to Cadmium on Neurodevelopment of infants in Shandong, China. *Environ. Poll.* 211, 67–73.

Wang, Z., Zhou, X., Zhang, J., Boey, F., and Zhang, H. (2009). Direct Electrochemical Reduction of Single-Layer Graphene Oxide and Subsequent Functionalization with Glucose Oxidase. *J. Phys. Chem. C.* 113(32), 14071–14075.

Wang, Z., Wang, H., Zhang, Z., and Liu, G. (2014). Electrochemical Determination of Lead and Cadmium in Rice by a disposable Bismuth/Electrochemically Reduced Graphene/Ionic Liquid Composite Modified Screen-Printed Electrode. *Sens. Actuators B Chem.* 199, 7–14.

Way, J. D., Noble, R. D., Flynn, T. M., and Sloan, E. D. (1982). Liquid Membrane Transport: A Survey. *J. Membr. Sci.* 12(2), 239–259.

Wei, Y., Gao, C., Meng, F., Li, H., Wang, L., Liu, J., and Huang, X. (2012). SnO_2/Reduced Graphene Oxide Nanocomposite for the Simultaneous Electrochemical Detection of Cadmium (II), Lead (II), Copper (II), and Mercury (II): An Interesting Favorable Mutual Interference. *J. Phy. Chem.* 116, 1034–1041.

Willemse, C. M., Tlhomelang, K., Jahed, N., Baker, P. G., and Iwuoha, E. I. (2011). Metallo-Graphene Nanocomposite Electrocatalytic Platform for the Determination of Toxic Metal Ions. *Sensors.* 11(4), 3970–87.

Williams, G., Seger, B., and Kamat, P. V. (2008). UV-Assisted Photocatalytic Reduction of Graphene Oxide. *ACS. Nano*. 2(7), 1487–1491.

Xia, W., Hu, J., Zhang, B., Li, Y., Sr, J. P. W., Bassig, B. A., Zhou, A., Savytz, D. A., Xiong, C., Zhao, Y., Pan, X., Yang, J., Wu, C., Jiang, M., Peng, Y., Qian, Z., Zheng, Y., and Xu, S. (2016). A Case-Control Study of Maternal Exposure to Chromium and Infant Low Birth Weight in China. *Chemosphere*. 144, 1484–1489.

Xie, Y. L., Zhao, S. Q., Ye, H. L., Yuan, J., Song, P., and Hu, S. Q. (2015). Graphene/CeO_2 Hybrid Materials for the Simultaneous Electrochemical Detection of Cadmium(II), Lead(II), Copper(II), and Mercury(II). *J. Electroanal. Chem.* 757, 235–242.

Xu, L., Basheer, C., and Lee, H. K. (2007). Developments in Single-Drop Microextraction. *J. Chromatogr. A.* 1152(1–2), 184–192.

Xu, Y., Zhang, W., Shi, J., Zou, X., Li, Y., Tahir, H. E., Xianwei, H., Zhihua, L., Xiandong, Z., and Xuetao, H. (2017). Electrodeposition of Gold Nanoparticles and Reduced Graphene Oxide on an Electrode for Fast and Sensitive Determination of Methylmercury in Fish. *Food. Chem.* 237, 423–430.

Yamini, Y., Seidi, S., and Rezazadeh, M. (2014). Electrical Field-Induced Extraction and Separation Techniques: Promising Trends in Analytical Chemistry-A Review. *Anal. Chim. Acta.* 814, 1–22.

Yi, W. J., Li, Y., Ran, G., Luo, H. Q., and Li, N. B. (2012). Determination of Cadmium(II) by Square Wave Anodic Stripping Voltammetry Using Bismuth–Antimony Film Electrode. *Sens. Actuators B Chem.* 166–167, 544–548.

Yuanyuan, L., Xinqiang, L., Niyungeko, C., Junjie, Z., and Guangming, T. (2017). A Review of the Identification and Detection of Heavy Metal Ions in the Environment by Voltammetry. *Talanta.* 178, 324–338.

Zaheri, P., Abolghasemi, H., Ghannadi Maraghe, M., and Mohammadi, T. (2015). Intensification of Europium Extraction Through a Supported Liquid Membrane Using Mixture of D2EHPA and Cyanex272 as Carrier. *Chem. Eng. Process*. 92, 18–24.

Zaouak, O., Authier, L., Cugnet, C., Castetbon, A., and Potin-Gautier, M. (2010). Electroanalytical Device for Cadmium Speciation in Waters. part 1: Development and Characterization of a Reliable Screen-Printed Sensor. *Electroanal.* 22(11), 1151–1158.

Zaouak, O., Authier, L., Cugnet, C., Normandin, E., Champier, D., Rivaletto, M., and Potin-Gautier, M. (2010). Electroanalytical Device for Cadmium Speciation in Waters. part 2: Automated System Development and Cadmium Semicontinuous Monitoring. *Electroanal.* 22(11), 1159–1165.

Zbeda, S., Pokpas, K., Titinchi, S., Jahed, N., Baker, P. G., and Iwuoha, E. I. (2013). Few-layer Binder Free Graphene Modified Mercury Film Electrode for Trace Metal Analysis by Square Wave Anodic Stripping Voltammetry. *Int. J. Electrochem. Sci.* 8, 11125–11141.

Zhang, N., and Hu, B. (2012). Cadmium (II) Imprinted 3-Mercaptopropyltrimethoxysilane Coated Stir Bar for Selective Extraction of Trace Cadmium from Environmental Water Samples Followed by Inductively Coupled Plasma Mass Spectrometry Detection. *Anal. Chim. Acta.* 723, 54–60.

Zhang, Q. X., Wen, H., Peng, D., Fu, Q., and Huang, X. J. (2015). Interesting Interference Evidences of Electrochemical Detection of Zn(II), Cd(II) and Pb(II) on Three Different Morphologies of MnO_2 Nanocrystals. *J. Electroanal. Chem.* 739, 89–96.

Zhang, W., Xiong, B., Chen, L., Lin, K., Cui, X., Bi, H., Guo, M., and Wang, W. (2013). Toxicity Assessment of Chlorella Vulgaris and Chlorella Protothecoides Following Exposure to Pb(II). *Environ. Toxicol. Pharmacol.* 36(1), 51–7.

Zhang, X., Zhang, Y., Ding, D., Zhao, J., Liu, J., Yang, W., and Qu, K. (2016). On-Site Determination of $Pb^{2+}$and Cd^{2+}in Seawater by Double Stripping Voltammetry with Bismuth-Modified Working Electrodes. *Microchem. J.* 126, 280–286.

Zhang, Z., and Yin, J. (2014). Sensitive Detection of Uric acid on Partially Electro-Reduced Graphene Oxide Modified Electrodes. *Electrochim. Acta.* 119, 32–37.

Zhao, D., Guo, X., Wang, T., Alvarez, N., Shanov, V. N., and Heineman, W. R. (2014). Simultaneous Detection of Heavy Metals by Anodic Stripping Voltammetry Using Carbon Nanotube Thread. *Electroanal.* 26(3), 488–496.

Zhong, W. S., Ren, T., and Zhao, L. J. (2016). Determination of Pb (Lead), Cd (Cadmium), Cr (Chromium), Cu (Copper), and Ni (Nickel) in Chinese Tea with High-Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry. *J. Food. Drug. Anal.* 24(1), 46–55.

Zhou, M., Wang, Y., Zhai, Y., Zhai, J., Ren, W., Wang, F., and Dong, S. (2009). Controlled Synthesis of Large-Area and Patterned Electrochemically Reduced Graphene Oxide Films. *J. Eur. Chem.* 15(25), 6116–20.

Zhou, Q., Zhao, N., and Xie, G. (2011). Determination of Lead in Environmental Waters with Dispersive Liquid-Liquid Microextraction Prior to Atomic Fluorescence Spectrometry. *J. Hazard. Mater.* 189(1–2), 48–53.

Zhou, S. F., Han, X. J., and Liu, Y. Q. (2016). SWASV Performance Toward Heavy Metal Ions Based on a High-Activity and Simple Magnetic Chitosan Sensing Nanomaterials. *J. Alloys. Compd.* 684, 1–7.

Zhou, S., Rosenthal, D. G., Sherman, S., Zelikoff, J., Gordon, T., and Weitzman, M. (2014). Physical, Behavioral, and Cognitive Effects of Prenatal Tobacco and Postnatal Secondhand Smoke Exposure. *Curr. Probl. Pediatr. Adolesc. Health. Care.* 44(8), 219–241.

Zhu, W. W., Li, N. B., and Luo, H. Q. (2007). Simultaneous Determination of Chromium(III) and Cadmium(II) by Differential Pulse Anodic Stripping Voltammetry on a Stannum Film Electrode. *Talanta.* 72(5), 1733–1737.

Zhu, Y., Cai, W., Piner, R. D., Velamakanni, A., and Ruoff, R. S. (2009). Transparent Self-Assembled Films of Reduced Graphene Oxide Platelets. *Appl. Phys. Lett.* 95(10), 103104.