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

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UNIVERSITI TEKNOLOGI MALAYSIA
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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
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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.
Pencemaran air adalah masalah di seluruh dunia yang patut diberi perhatian disebabkan oleh impak negatif terhadap ekosistem, kesehatan 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 akuueus 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 akuueus sebenar. Karbon diperkuatkan grafin oksida-grafit secara penurunan elektrokimia (ErGO-GRC) telah digunakan sempena dengan voltametri pelucutan anod gelombang segiempat (SWASV) bagi penentuan Pb(II). Sementara itu, penentuan selektif dan sensitif Cr(VI) dijalankan menggunakan filem antimon yang dilapisi dengan nafion pada karbon diperkuatkan grafit (NSbFE-GRC) yang disediakan dengan voltametri 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 akuueus ke dalam fasa penerima berasid di dalam lumen beg membran PVDF dengan menggunakan voltan merentasi membran ceair 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 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 akuueus 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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2.16 Schematic illustrations of the equipment used for extraction (A) and for in-situ determination of CLZ by EME-DPV (B) (Rouhollahi et al. 2016)

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4.22 SWVs shows the effect of HCl concentration on Pb(II) ions (6 x 10^{-8} M) with experimental parameters as follows: $E_i = -1200$ mV, $E_f = 0$ mV, S.W. amplitude = 35 mV, step frequency = 50Hz, step height = 1 mV, volume of GO = 10 μl of 0.1% of aqueous colloidal, reduction potential of GO = -0.8 V for 10 min for ErGO modified GRC.

4.23 SWVs shows the effect of HCl concentration on Pb(II) ions (6 x 10^{-8} M) with experimental parameters as follows: $E_i = -1200$ mV, $E_f = 0$ mV, S.W. amplitude = 35 mV, step frequency = 50Hz, step height = 1 mV, volume of GO = 10 μl of 0.1% of aqueous colloidal, reduction potential of GO = -0.8 V for 10 min for ErGO modified GRC.

4.24 Peak potential versus pH with experimental parameters as follows: $E_i = -1200$ mV, $E_f = 0$ mV, S.W. amplitude = 35 mV, step frequency = 50Hz , step height = 1 mV, volume of GO = 10 μl of 0.1% of aqueous colloidal, reduction potential of GO = -0.8 V for 10 min for ErGO modified GRC

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4.27 FE-SEM images of (a) GRC, (b) N-GRC, (c) SbFE-GRC and (d) NSbFE-GRC

4.28 SWASV of 0.5 nM of Pb(II) and Cd(II) using bare GRC, N-GRC, SbFE-GRC and NSbFE-GRC. Plating conditions: 0.01M HCl, 10 mgL\(^{-1}\) of Sb(II), -1200 V plating potential and 240 s of plating time. Detection conditions: \( E_{acc} = -1.0 \) V; \( t_{acc} = 60 \) s; step amplitude: 4 mV, pulse amplitude: 50 mV, and frequency: 25 Hz.

4.29 Effect of HCl concentration on plating and detection of 10 nM of Pb(II) and Cd(II) in 0.1 M HCl. Conditions: \( E_{acc} = -1.0 \) V; \( t_{acc} = 35 \) s; step amplitude: 4 mV, pulse amplitude: 50 mV, and frequency: 25 Hz.

4.30 Effect of concentration of Sb(III) on plating and detection of Pb(II) and Cd(II) in 0.1 M HCl. Conditions: \( E_{acc} = -1.0 \) V; \( t_{acc} = 35 \) s; step amplitude: 4 mV, pulse amplitude: 50 mV, and frequency: 25 Hz.

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4.33 The effect of the accumulation potential ($E_{acc}$) on the
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experimental parameters as follows: $E_i$ = −1200 mV,
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= 50Hz, step height = 1 mV.

4.36 The calibration plot for (a) Pb(II) and (b) Cd(II).
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4.37 SWAdSV of Cr(III)-DTPA (25 nM) using N-GRC,
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Conditions: Concentration of Sb(III): 0.2 – 2.5 mgL$^{-1}$,
concentration of DTPA: 5 mM, concentration of
KNO$_3$: 0.5 M, $E_{ads}$: −0.80 V; $t_{ads}$: 120 s; step
amplitude: 5 mV, pulse amplitude: 25 mV, and
frequency: 25 Hz.
4.38 Effect of concentration of Sb(III) on reduction peak current of Cr(III)-DTPA (50 nM) using SWAdSV in acetate buffer (pH 6). Conditions: Concentration of Sb(III): 0.2 – 2.5 mgL⁻¹, Sb(III) plating time: 150 s, Sb(III) plating potential -1.0 V, concentration of DTPA: 5 mM, concentration of KNO₃: 0.5 M, Eₐₖₖₕₗ: -0.80 V; tₐₖₖₖₕₗ: 120 s; step amplitude: 5 mV, pulse amplitude: 25 mV, and frequency: 25 Hz.

4.39 Effect of Sb(III) plating time on reduction peak current of Cr(III)-DTPA (50 nM) using SWAdSV in acetate buffer (pH 6). Conditions: Concentration of Sb(III): 1.0 mgL⁻¹, Sb(III) plating time: 0 - 300 s, Sb(III) plating potential: -1.0 V, concentration of DTPA: 5 mM, concentration of KNO₃: 0.5 M, Eₐₖₖₖₕₗ: -0.80 V; tₐₖₖₖₕₗ: 120 s; step amplitude: 5 mV, pulse amplitude: 25 mV, and frequency: 25 Hz.

4.40 Effect of Sb(III) plating potential on reduction peak current of Cr(III)-DTPA (50 nM) using SWAdSV in acetate buffer (pH 6). Conditions: Concentration of Sb(III): 1.0 mgL⁻¹, Sb(III) plating time: 240 s, Sb(III) plating potential -0.9 to -1.5 V, concentration of DTPA: 5 mM, concentration of KNO₃: 0.5 M, Eₐₖₖₖₕₗ: -0.80 V; tₐₖₖₖₕₗ: 120 s; step amplitude: 5 mV, pulse amplitude: 25 mV, and frequency: 25 Hz.

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4.43 Effect of KNO$_3$ concentration on reduction peak current of Cr(III)-DTPA (20 nM) using SWAdSV in acetate buffer (pH 6). Conditions: Concentration of Sb(III): 1.0 mgL$^{-1}$, Sb(III) plating time: 240 s, Sb(III) plating potential -1.2 V, concentration of DTPA: 15 mM, concentration of KNO$_3$: 0 – 1.0 M, $E_{\text{ads}}$: -0.80 V; $t_{\text{ads}}$: 120 s; step amplitude: 5 mV, pulse amplitude: 25 mV, and frequency: 25 Hz.

4.44 Effect of adsorptive potential on reduction peak current of Cr(III)-DTPA (25 nM) using SWAdSV in acetate buffer (pH 6). Conditions: Concentration of Sb(III): 1.0 mgL$^{-1}$, Sb(III) plating time: 240 s, Sb(III) plating potential -1.2 V, concentration of DTPA: 15 mM, concentration of KNO$_3$: 0.6 M, $E_{\text{ads}}$: -0.5 to -1.1 V; $t_{\text{ads}}$: 120 s; step amplitude: 5 mV, pulse amplitude: 25 mV, and frequency: 25 Hz.

4.45 Effect of adsorptive time on reduction peak current of Cr(III)-DTPA (20 nM) using SWAdSV in acetate buffer (pH 6). Conditions: Concentration of Sb(III): 1.0 mgL$^{-1}$, Sb(III) plating time: 240 s, Sb(III) plating potential: -1.2 V, concentration of DTPA: 15 mM, concentration of KNO$_3$: 0.6 M, $E_{\text{ads}}$: -0.80 V; $t_{\text{ads}}$: 0 - 500 s; step amplitude: 5 mV, pulse amplitude: 25 mV, and frequency: 25 Hz.
SWAdSVs shows the reduction peak current of Cr(VI) for concentration: (a) 0, (b) 0.2, (c) 0.3, (d) 0.4, (e) 0.5, (f) 0.6, and (g) 0.7 nM with experimental parameters as follows: Concentration of Sb(III): 1.0 mgL-1, Sb(III) plating time: 240 s, Sb(III) plating potential: -1.2 V, concentration of DTPA: 15 mM, concentration of KNO3: 0.6 M, Eads: -0.80 V; tads: 200 s; step amplitude: 5 mV, pulse amplitude: 25 mV, and frequency: 25 Hz. The calibration plot is shown in the inset.

The influence of membrane composition (PVDF12, PVDF17 and PVDF22) on extraction voltage of selective EME for (a) Cr(VI)-NSbFE-GRC and (b) Pb(II)-ErGO-GRC and simultaneous EME for (c) Pb(II)-NSbFE-GRC and (d) Cd(II)-NSbFE-GRC. The parameters involved in EME and electrochemical determination stipulated in Table 5.1.

FE-SEM image of (a) PVDF22, (b) PVDF17 and (c) PVDF12 membranes.

The effect of organic solvents (1-octanol, NPOE, toluene) on selective EME for (a) Cr(VI)-NSbFE-GRC and (b) Pb(II)-ErGO-GRC and simultaneous EME for (c) Pb(II)-NSbFE-GRC and (d) Cd(II)-NSbFE-GRC. The parameters involved in EME and electrochemical determination stipulated in Table 5.3.

The effect of pH of donor phase on (pH 1 to 9) on selective EME for (a) Cr(VI)-NSbFE-GRC and (b) Pb(II)-ErGO-GRC and simultaneous EME for (c) Pb(II)-NSbFE-GRC and (d) Cd(II)-NSbFE-GRC. The parameters involved in EME and electrochemical determination stipulated in Table 5.4.
5.5 The effect of carrier concentration in 1-octanol on selective EME for (a) Cr(VI)-NSbFE-GRC and (b) Pb(II)-ErGO-GRC and simultaneous EME for (c) Pb(II)-NSbFE-GRC and (d) Cd(II)-NSbFE-GRC. The parameters involved in EME and electrochemical determination stipulated in Table 5.5.

5.6 The effect of stirring rate on selective EME for (a) Cr(VI)-NSbFE-GRC and (b) Pb(II)-ErGO-GRC and simultaneous EME for (c) Pb(II)-NSbFE-GRC and (d) Cd(II)-NSbFE-GRC. The parameters involved in EME and electrochemical determination stipulated in Table 5.6.

5.7 The effect of extraction time on selective EME for (a) Cr(VI)-NSbFE-GRC and (b) Pb(II)-ErGO-GRC and simultaneous EME for (c) Pb(II)-NSbFE-GRC and (d) Cd(II)-NSbFE-GRC. The parameters involved in EME and electrochemical determination stipulated in Table 5.7.

5.8 The effect of donor phase volume on selective EME for (a) Cr(VI)-NSbFE-GRC and (b) Pb(II)-ErGO-GRC and simultaneous EME for (c) Pb(II)-NSbFE-GRC and (d) Cd(II)-NSbFE-GRC. The parameters involved in EME and electrochemical determination stipulated in Table 5.8.

5.9 Effect of agarose gel as salt bridge (a) without and (b) with on detection of 0.25 nM Cr(VI). The parameters involved in EME and electrochemical determination stipulated in Table 5.9.

5.10 Effect of agarose gel as salt bridge (a) without and (b) with on detection of 1.0 nM Pb(II). The parameters involved in EME and electrochemical determination stipulated in Table 5.9.
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5.12 SWAdSV shows the oxidation peak current of Cr(VI) at different concentrations: (a) 10, (b) 20, (c) 30, (d) 40, (e) 50 and (f) 60 pM; with extraction condition as shown in Table 5.10. The calibration plot is shown in the inset.

5.13 SWASV shows the oxidation peak current of Pb(II) at different concentrations: (a) 0.25, (b) 0.5, (c) 0.75, (d) 1.0, (e) 1.25, (f) 1.5, (g) 1.75 and (h) 2.0 nM; with extraction condition as shown in Table 5.10. The calibration plot is shown in the inset.

5.14 SWV shows the oxidation peak current of Pb(II) and Cd(II) at different concentrations: (a) 0, (b) 2, (c) 4, (d) 6, (e) 8, and (f) 10 pM; with extraction condition as shown in Table 5.10.

5.15 The calibration plot for (a) Pb(II) and (b) Cd(II) ranging from 0 to 10 pM

5.16 Comparative in term of size of commercial DC power supply and PSSD

5.17 (a) Front and (b) side view of portable power supply device (PSSD)
### LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
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<tr>
<td>2-MBT</td>
<td>2-mercaptobenzothiazole</td>
</tr>
<tr>
<td>2-MBT</td>
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<td>4-CNPy</td>
<td>4-cyanopyridine</td>
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<td>4-Cpy</td>
<td>4-cyanopyridine</td>
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<tr>
<td>AAS</td>
<td>Atomic absorption spectrophotometry</td>
</tr>
<tr>
<td>ADDPA</td>
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<td>AdSV</td>
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<tr>
<td>CNTs</td>
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<td>Field emission scanning electron microscopy</td>
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<td>GC</td>
<td>Glassy carbon</td>
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<td>GCE</td>
<td>Glassy carbon electrode</td>
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GF-AAS - graphite furnace atomic absorption spectroscopy  
GRC - graphite reinforcement carbon  
H₂SO₄ - sulphuric acid  
HCl - hydrochloric acid  
HF-LPME - hollow fiber-liquid phase microextraction  
HMDE - hanging mercury drop electrode  
HNO₃ - 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-octylpyridinium 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
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>PF/GCE</td>
<td>polysiloxane film GC electrode</td>
</tr>
<tr>
<td>PDMS</td>
<td>polydimethylsiloxane</td>
</tr>
<tr>
<td>PhACs</td>
<td>pharmaceutical active compounds</td>
</tr>
<tr>
<td>PMMA</td>
<td>poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>ppb</td>
<td>parts per billion</td>
</tr>
<tr>
<td>PPHF</td>
<td>Polypropylene hollow fiber</td>
</tr>
<tr>
<td>PPSD</td>
<td>Portable power supply device</td>
</tr>
<tr>
<td>Pt</td>
<td>platinum</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetra fluoroethylene</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinlidine fluoride</td>
</tr>
<tr>
<td>RE</td>
<td>reference electrode</td>
</tr>
<tr>
<td>rGO</td>
<td>reduced graphene oxide</td>
</tr>
<tr>
<td>Ru(bpy)$_3^{2+}$</td>
<td>Tris(bipyridine)ruthenium(II)</td>
</tr>
<tr>
<td>SAMs</td>
<td>self-assembled monolayers</td>
</tr>
<tr>
<td>SbNP</td>
<td>Antimony nanoparticles</td>
</tr>
<tr>
<td>SCP</td>
<td>Stripping chrono potentiometry</td>
</tr>
<tr>
<td>SDME</td>
<td>single-drop microextraction</td>
</tr>
<tr>
<td>SFFTCCV</td>
<td>stripping fast Fourier transform continuous cyclic voltammetry</td>
</tr>
<tr>
<td>SFOD-ME</td>
<td>Solidified floating organic drop - microextraction</td>
</tr>
<tr>
<td>SLM</td>
<td>supported liquid membrane</td>
</tr>
<tr>
<td>SMDE</td>
<td>static mercury drop electrode</td>
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<tr>
<td>SnNP</td>
<td>Tin nanoparticles</td>
</tr>
<tr>
<td>SPCE</td>
<td>screen printed carbon electrode</td>
</tr>
<tr>
<td>SPE</td>
<td>Screen printed electrode</td>
</tr>
<tr>
<td>SPME</td>
<td>solid-phase microextraction</td>
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<tr>
<td>SWAdSV</td>
<td>Square Wave Adsorptive Stripping Voltammetry</td>
</tr>
<tr>
<td>SWASV</td>
<td>Square Wave Anodic Stripping Voltammetry</td>
</tr>
<tr>
<td>SWCNT</td>
<td>single-wall carbon nanotubes</td>
</tr>
<tr>
<td>TBP</td>
<td>tributhylphosphate</td>
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</tbody>
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UV - ultraviolet
WE - working electrode
WHO - World Health Organization
XRF - X-ray Fluorescence Spectrometry
<table>
<thead>
<tr>
<th>Symbol</th>
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<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>c</td>
<td>Concentration</td>
</tr>
<tr>
<td>$E_{acc}$</td>
<td>Deposition potential</td>
</tr>
<tr>
<td>$E_f$</td>
<td>Final potential</td>
</tr>
<tr>
<td>$E_i$</td>
<td>Initial potential</td>
</tr>
<tr>
<td>$E_p$</td>
<td>Peak potential</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>$I_p$</td>
<td>Peak current</td>
</tr>
<tr>
<td>M</td>
<td>Molar</td>
</tr>
<tr>
<td>mM</td>
<td>Milimolar</td>
</tr>
<tr>
<td>mg</td>
<td>Milligram</td>
</tr>
<tr>
<td>min</td>
<td>Minutes</td>
</tr>
<tr>
<td>mL</td>
<td>Milliliter</td>
</tr>
<tr>
<td>mm</td>
<td>Millimeter</td>
</tr>
<tr>
<td>ppb</td>
<td>Part per billion</td>
</tr>
<tr>
<td>$r^2$</td>
<td>Correlation coefficient</td>
</tr>
<tr>
<td>$mgL^{-1}$</td>
<td>Milligram per liter</td>
</tr>
<tr>
<td>s</td>
<td>Seconds</td>
</tr>
<tr>
<td>$t_{acc}$</td>
<td>Deposition time</td>
</tr>
<tr>
<td>V</td>
<td>Voltage</td>
</tr>
<tr>
<td>$v/v$</td>
<td>Volume per volume</td>
</tr>
<tr>
<td>$^\circ$C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>mA</td>
<td>Micro ampere</td>
</tr>
<tr>
<td>$\mu$L</td>
<td>Micro Liter</td>
</tr>
<tr>
<td>$\mu gL^{-1}$</td>
<td>Microgram per liter</td>
</tr>
<tr>
<td>$\mu M$</td>
<td>Micro molar</td>
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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) (Namiśnik & 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 et al. 2014). However, heavy metal in aquatic environmental samples are usually obtained in extremely 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 difficulties 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 et 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 & Naghd 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 et 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
elecrode 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 study 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 simultaneously 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


