UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF ELECTROCHEMICAL SENSOR BASED ON THIOLATED CALIXARENE/GOLD NANOPARTICLE COMPOSITE FOR LEAD AND COPPER IONS DETECTION

CHONG JIN MEI

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By

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Heavy metal pollution is one of the global issues as the presence of excessive heavy metal in environment threaten both aquatic life and human beings. A selective and fast response sensor with a rapid detection method is urgent needed for the detection of heavy metal ions. Hence, this study used a thiolated calix[4]arene modified on gold nanoparticles and a screen-printed carbon electrode (TC4/AuNPs/SPCE) for $Pb^{2+}$and Cu^{2+} determination. The modified electrodes were characterised via Fourier-transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). The modified of thiolated calixarene/gold nanoparticle composite on screen-printed electrode was found enhancing the current response in Pb^{2+} and Cu^{2+} determination. Differential pulse anodic stripping voltammetry (DPASV) was used for the detection of Pb^{2+} and Cu^{2+} under optimum conditions. The limit of detection (LOD) for detecting Pb^{2+} and Cu^{2+} was 0.7982×10^{-2} ppm and 1.3358×10^{-2} ppm, respectively. Except for Zn^{2+} and Hg^{2+}, the presence of competitive ions caused little effect on the current response when detecting Pb^{2+}. However, all competitive ions caused a significant drop in the current response when detecting Cu^{2+}, except Ca^{2+} and Mg^{2+}, suggesting the sensing platform is more selective toward Pb^{2+} rather than Cu^{2+}. The electrochemical sensor demonstrated good reproducibility and excellent repeatability with a low relative standard deviation (RSD) value in detecting Pb^{2+} and Cu^{2+}. Most importantly, the result obtained in the analysis of Pb^{2+} and Cu^{2+} had a good recovery in river water, demonstrating the applicability of the developed sensor for real samples.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk Ijazah Master Sains

PEMBANGUNAN SENSOR ELEKTROKIMIA BERASASKAN TERTIOL KALIKSARENA/NANOPARTIKEL EMAS GUBAHAN UNTUK MENGESAN ION PLUMBUM DAN KUPRUM

Oleh

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Pencemaran logam berat merupakan salah satu isu global kerana kehadiran logam berat yang berlebihan di persekitran mengancam kehidupan akuatik dan manusia. Satu sensor yang berdaya permilihan dan sahutan cepat dengan cara pengesan yang pantas sangat diperlukan untuk megesan ion logam berat. Oleh itu, hasil kerja ini mengunakan tertiol kaliks[4]arena diubahsuai atas nanopartikel emas dan elektrod karbon bercetak skrin (TC4/AuNPs/SPCE) untuk mengesan Pb^{2+} dan Cu^{2+}. Pencirian permukaan pengubahsuaian elektrode telah dijalankan dengan menggunakan spektroskopi inframerah transformasi fourier (FTIR), mikroskop elektron pengimbas pelepasan medan (FESEM), voltammetri kitaran (CV) dan spektroskopi impedans elektrokimia (EIS). Pergubahsuaian tertiol kaliks[4]arena/nanopartikel emas gubahan atas elektrod karbon bercetak skrin dapat meningkatkan tindak balas arus semasa mengesan Pb^{2+} and Cu^{2+}. Perbezaan nadi anodik pelucutan voltammetri (DPASV) telah digunakan untuk mengesan Pb^{2+} dan Cu^{2+} dalam keadaan optimum. Had pengesanan untuk mengesan Pb^{2+} dan Cu^{2+} masing-masing ialah 0.7982×10^{-2} ppm dan 1.3358×10^{-2} ppm. Kehadiran ion persaingan membawa kesan yang kecil kepada tindak balas arus semasa mengesan Pb^{2+}, kecuali kehadiran Zn^{2+} dan Hg^{2+}. Manakala, semua ion persaingan menurunkan tidak balas arus semasa mengesan Cu^{2+}, kecuali kehadiran Ca^{2+} dan Mg^{2+}, mencadangkan TC4/AuNPs/SPCE lebih berkesan dalam mengesan Pb^{2+} daripada ion Cu^{2+}. Sensor elektrokimia ini menujukkan kebolehulangan yang baik dengan sisihan piawai relatif yang rendah dalam mengesan Pb^{2+} dan Cu^{2+}. Yang paling penting, keputusan yang baik telah diperolehi apabila mengesan Pb^{2+} dan Cu^{2+} di dalam air sungai, menunjukkan kebolehan sensor ini untuk mengesan Pb^{2+} dan Cu^{2+} dalam sampel air sungai.

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Declaration by Members of the Supervisory Committee

This is to confirm that:

- the research and the writing of this thesis were done under our supervision;
- supervisory responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2015-2016) are adhered to.

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrometry
ASV	Anodic stripping voltammetry
ATR	Attenuated total reflection
AuNPs	Gold nanoparticles
CA	Chronoamperometry
$CHCl_3$	Chloroform
CNTs	Carbon nanotubes
CV	Cyclic voltammetry
DPASV	Differential pulse anodic stripping voltammetry
DPV	Differential pulse voltammetry
EDX	Energy dispersive X-ray
EIS	Electrochemical impedance spectroscopy
FESEM	Field emission scanning electron microscopy
FL	Fluorescence spectrophotometry
FTIR	Fourier transform infrared spectroscopy
GCE	Glassy carbon electrode
HCl	Hydrochloric acid
HSAB	Hard and soft acids and bases
ICP-MS	Inductively coupled plasma mass spectroscopy
ICP-OES	Optical emission spectrometry
ISEs	Ion-selective electrodes
ITO	Indium tin oxide
$K_4Fe(CN)_6$	Potassium ferrocyanides
KCl	Potassium chloride

LB	Langmuir-Blodgett
LOD	Limit of detection
LSV	Linear sweep voltammetry
MPA	3-mercaptopropionic acid
MWCNTs	Multi-walled carbon nanotubes
NaOH	Sodium hydroxide
NMR	Nuclear magnetic resonance spectroscopy
PBS	Phosphate-buffered saline
PPM	Part-per million
PVC	Poly (vinyl chloride)
RGO	Reduced graphene oxide
RSD	Relative standard deviation
SAMs	Self-assembled monolayers
SPCE	Screen-printed carbon electrode
SPEs	Screen-printed electrodes
SWASV	Square wave anodic stripping voltammetry
SWV	Square wave voltammetry
TC4	Thiolated calix[4]arene
THF	Tetrahydrofuran
WHO	World Health Organization

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

River water quality is important to be monitored in water management as it serves as water sources for a variety of usages (Mokarram, Saber et al. 2020). Heavy metals pollution in surface water is a worldwide environmental issue (Zhou, Yang et al. 2020) and many researchers have reported on the contamination of heavy metal in river basin and confirmed the high rate of anthropogenic released in river basin as the cause of water or sediments pollution (Patel, Raju et al. 2018). It was found that concentrations of Cr^{3+} and Cd^{2+} presented in water and of Mn ion in sediment were higher in the Ganga River in comparison to many other rivers of the world (Siddiqui, Pandey et al. 2019), the Bone River water has been polluted to As^{3+}, Hg^{2+}, and Pb^{2+} that come from artisanal small-scale gold mine activities (Gafur, Sakakibara et al. 2018), and the majority length of Brahmani River contains high to critical value of heavy metal pollution index (HPI) (Swain and Sahoo 2017). In Malaysia, the water quality studies in selected rivers around Tasik Chini were carried out using atomic absorption spectroscopy (AAS). The results illustrated the rivers were slightly polluted with Cd^{2+} and Pb^{2+} that exceed the permissible limit set by World Health Organization (WHO) (Adilah and Nadia 2020). These heavy metals and metalloid are dangerous to environment and humans (Gafur, Sakakibara et al. 2018) and become the main public health concern due to their toxicity (Ali, Khan, & Ilahi 2019, Chiron, Guilet et al. 2003).

A high dose of lead exposure will affect human intelligence level, in which an investigation has verified that nervous system is the most prominent target for Pb^{2+} poisoning with the symptoms of headache, memory loss, and lack of attention (Rehman, Fatima et al. 2018). A small dose of Cu^{2+} is significant for health; however, a high dose of Cu^{2+} causes a number of diseases such as Alzheimer's disease, Parkinson's disease, Wilson disease, neurodegenerative disease, kidney damage and amyotrophic lateral sclerosis (Wu, Wang et al. 2019).

In the current literatures, electrochemical sensors have been widely used in numerous applications such as health, biomedical fields and environmental studies owing to their advantages included simple designs, possibility for miniaturization, portability, and relatively inexpensive (Mu, Wang et al. 2012). Subgroups of electrochemical sensor–ion selective or potentiometric sensors have been employed in heavy metal determination. With the developing of new screen-printing technology, these ion selective electrodes can be evolved to sensors with good characteristics of portable, disposable, miniature in size, and excellent selectivity with low limit of detection. Screen-printed electrodes (SPEs) have been gradually introduced because of their mass production and ease of

miniature. The screen-printed electrodes are printed using screen printing techniques with the integration of three electrode system, rather than traditional galvanic cells that contain both independent reference electrode and ion selective electrodes in order to make the operation and measurement convenient (Li, Zhou et al. 2014, Adarakatti, Foster et al. 2017). Chemical modification on electrodes was gained researchers' interest as the selectivity and sensitivity of electrodes in analytes detection could be further improved by chemical modification of electrodes with suitable receptors (Adarakatti, Foster et al. 2017).

Nowadays, host-guest chemistry in molecular recognition has drawn great research enthusiasm (Chen, Zheng et al. 2018). Calixarenes have great potential interests because they form stable host-guest complexes with analytes such as cations, anions and neutral molecules with strong recognition ability as shown in Figure 1.1 ((Nur Abdul Aziz, Zawawi et al. 2018, Wang, Wang et al. 2012). In addition, calixarenes are able to maintain its complexation ability in a mixed monolayer ((De Leener et al., 2016). In spite of its superb recognition ability, these macrocycles have poor conductivity (Chaâbane, Gamoudi et al. 1994, Supian, CHOO et al. 2017). Thus, conductive materials are needed to composite with these macrocycles to enhance their conductivity (Supian, CHOO et al. 2017).

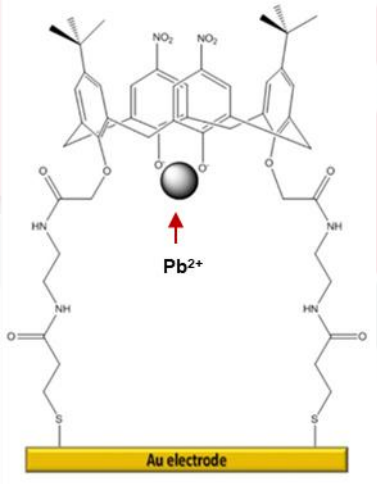

Figure 1.1: The proposed binding interaction of the COOH-C4 electrode with Pb (II) ion (Nur Abdul Aziz, Zawawi et al. 2018)**.**

Gold nanoparticles (AuNPs) were widely used in research because of their remarkable properties such as good conductivity, good biocompatibility, high catalytic activity, effective electron transport, the electrode overpotentials reduction, and large surface area (Zhang, Wang et al. 2010, Pereira, Bertolino et al. 2011, Dechtrirat, Yingyuad et al. 2018). Based on their unique properties,

gold nanoparticles have gained researcher's attention, and were used in fabricating electrochemical sensors and biosensors ((Huang et al. 2019, Tian, Qian et al. 2018).

Hence, the intergration of gold nanoparticles and thiolated calix[4]arene as electrode modifiers were introduced. Gold nanoparticles provide an effective electron transport and also a support surface for binding of thiols-containing compound. Calixarene has unique 3D structure and functionalized calixarenes are highly attractive to selective and sensitive compounds. The calixarene with thiol groups attached at the lower rim will induce self-assembly on gold nanoparticles and form a well arrangement of modifier layer on electrode. The integration of AuNPs and calixarene enables to improve the electrochemical performance in Pb^{2+} and Cu^{2+} detection. Moreover, the capability of our thiolated calix[4]arene (TC4) to detect Pb^{2+} and Cu^{2+} has not yet been explored and established. Therefore, in this study, the electrochemical performance of TC4/AuNPs/SPCE in Pb^{2+} and Cu^{2+} detection was tested.

1.2 Problem Statement and Research Motivation

The anthropogenic activities such as fossil fuels combustion, mining, lead acids batteries manufacturing and synthesis of oxides for paints and pigments increased the lead exposure (Koki, Low et al. 2018, Rehman, Fatima et al. 2018). The detection of Pb^{2+} is significant as children absorb Pb^{2+} more rapid than adults due to their smaller body size. Researchers investigated Pb^{2+} would pass to the fetus from pregnant women who exposed to Pb^{2+} and may lead to premature baby birth, low weight fetus, and the children will suffer from brain developmental abnormalities (Rehman, Fatima et al. 2018). High-level of lead poisoning in children will cause seizures, coma, multi-organ damage, anaemia and even death. Whereas, chronic low-level of Pb^{2+} poisoning will affect psychological and neurobehavioral development, bringing harmful effect on cognition and sleep disturbance (Wang, El-Fahmawi et al. 2019). Copper, as one of the most abundant metal and essential trace elements, has vital role in various biological processes (Liu, Ding et al. 2017, Ranee, Sivaraman et al. 2018). Despite categorized as heavy metal, it is essential to human health with permissible daily intake varies between 0.9 – 2.2 mg for adults. However, Cu^{2+} becomes toxic at high concentration, above 1.3 mg L^{-1}, and may cause the changes in nervous system, depression, lung cancer and gastrointestinal irritation (Moreira, Lebron et al. 2019). Furthermore, exposure to Cu^{2+} may also lead to hypertension, lethargy, gastrointestinal bleeding and DNA damage (Mahdi, Yu et al. 2018). Considering the adverse effects caused by the heavy metals, development of a simple and rapid detection approach is urgently needed.

There are various analytical methods for heavy metal ions detection included atomic absorption spectrometry (AAS) (Safari, Karimaei et al. 2018), fluorescence spectrophotometry (FL) (Yarur, Macairan et al. 2019) and inductively coupled plasma mass spectroscopy (ICP-MS) (Shen, Chen et al.

2018). However, great challenges still exist as these techniques need pre-treatment processes, long analysis time, qualified operator to handle and costly instrumentation (Nur Abdul Aziz, Zawawi et al. 2018, Erdemir and Malkondu 2020).

A rapid and sensitive analytical method such as electrochemical method is needed urgently to monitoring them. Electrochemical approaches have advantages of fast with short analysis time, simple, low cost, sensitive, good selectivity, portable and provide insitu analysis without any sophisticated instrumentation, ease of operation and low maintenance cost (Adarakatti, Foster et al. 2017, Adarakatti, Siddaramanna et al. 2019). In electrochemical approaches, electrochemical sensor is introduced as an alternative solution to detect Pb^{2+} and Cu^{2+}. The bare electrode can modify with selective functionalities in order to improve the sensitivity and selectivity toward Pb^{2+} and Cu^{2+}.

1.3 Objectives of Study

1.3.1 Aim

The main objective of this research is to develop an electrochemical sensor for Pb^{2+} and Cu^{2+} determination based on TC4/AuNPs/SPCE.

1.3.2 Specific Objectives

I. To fabricate and characterize the thiolated calix[4]arene/gold nanoparticle-modified screen printed carbon electrode by physical, morphological and chemical methods.
II. To perform analytical measurement of developed sensor (TC4/AuNPs/SPCE) for Pb^{2+} and Cu^{2+} detection by electrochemical method.
III. To investigate the applicability of developed sensor in real sample (river water) and compare with the conventional method (ICP-OES).

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