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GOLD NANOPARTICLES/IONOPHORE MODIFIED SCREEN PRINTED ELECTRODE FOR DETECTION OF PB(II) AND HG(II)

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By

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November 2016

Chair: Prof. Nor Azah Yusof, PhD

Faculty: Institute of Advanced Technology

Contamination of water by toxic metal ions, such as lead and mercury, can lead to serious environmental and health problems. Therefore, monitoring toxic metal ions in natural water supplies requires creation of miniature, low-cost, and highly sensitive detectors that are capable of specifically identifying target substances. In the present work, gold nanoparticles (AuNPs), prepared by citrate reduction method, were combined with ionophore for use as a modifier for disposable screen printed electrodes (SPE) for the detection of Pb(II) and Hg(II) ions. The AuNPs was characterized by different spectroscopic techniques, and the application of AuNPs on surface of the electrode increases the sensitivity of this electrode. due to their excellent electrical conductivity and strong adsorption ability. In addition, Pb ionophore and Hg ionophore are utilized for its excellent selectivity towards Pb(II) and Hg(II) ions.

The screen printed electrode was modified by casting a mixture of AuNPs and ionophore onto the working electrode's surface, Then, (AuNPs/ionophore/SPE) electrode was applied for Hg(II) and Pb(II) detection. The electrochemical studies, using linear sweep voltammetry were performed with AuNPs/ionophore/SPE, gave a high response towards target ions under optimized parametersof some analytical parameters.

A concentration study of lead with AuNPs/lead ionophore/SPE gave linear calibrations and a detection limit of 0.0823 mg L^{-1} was achieved by applying a deposition potential of -1.2 V and a deposition time of 240 s. The electrode showed very good recovery, thus indicating the accuracy of the method. Meanwhile, a concentration study of mercury with AuNPs/mercury ionophore/SPE gave a linear calibration of R^2 = 0.99 and a detection limit of 1.06 µg. L^{-1} was achieved by applying a deposition potential of -1.2 V and a

deposition time of 240 s. Validation of the method, with inductively coupled plasma-mass spectroscopy (ICP-MS), showed a very good correlation.

Furthermore, the selectivity effect of ionophore towards the target ions, studied in the presence of other competitive ions in water samples, such as SO_3^{2-}, SO_4^{2-}, Fe^{3+}, Mg^{2+}, Cu^{2+} and Cd^{2+}, gave an excellent selectivity.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Sarjana sains

ELEKTROD BERCETAK SKRIN YANG DIUBAHSUAIKAN DENGAN NANOPARTIKEL/IONOPHORE UNTUK PENGESANAN Pb(II) DAN Hg(II)

Oleh

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Pencemaran air oleh ion logam toksik, seperti plumbum dan merkuri, boleh menimbulkan masalah serius terhadap alam sekitar dan kesihatan. Oleh itu, pemantauan ion logam toksik dalam bekalan air semula jadi memerlukan penciptaan suatu alat pengesan yang kecil, berkos rendah dan yang sangat sensitif, yang berupaya mengenal pasti bahan sasaran secara khusus. Dalam kajian ini, nanopartikel emas (AuNP) yang disediakan melalui kaedah pengurangan sitrat telah digabungkan dengan ionophore untuk digunakan sebagai pengubahsuai elektrod bercetak skrin pakai buang (SPE) untuk mengesan ion Pb(II) dan Hg(II). AuNP tersebut telah dicirikan melalui berbagai teknik spektroskopi, and aplikasi AuNP itu pada permukaan elektrod telah meningkatkan sensitiviti elektrod ini disebabkan oleh kekonduksian elektrik yang sangat baik and keupayaan penjerapan yang kuat. Di samping itu, ionophore Pb dan Hg telah digunakan sebagai pengubah kerana pemilihan mereka yang sangat baik terhadap ion Pb(II) dan Hg(II).

Elektrod bercetak skrin itu telah diubahsuaikan dengan menuangkan campuran AnNP dan ionophore ke atas permukaan elektrod yang berfungsi. Kemudian, elektrod (AuNP/ionophore/SPE) telah digunakan untuk pengesanan Hg(II) dan Pb(II). Kajian elektrokimia, dengan menggunakan linear menyapu voltametri, telah dijalankan dengan AuNP/ionophore/SPE, dan telah memberi tindak balas yang tinggi terhadap ion sasaran di bawah parameter yang dioptimumkan.

Suatu kajian kepekatan plumbum dengan AuNP/ionophore plumbum/SPE telah memberikan penentukuran linear, dan had pengesanan 0.0823 mg L^{-1} telah dicapai dengan menggunakan potensi pemendapan -1.2 V dan masa pemendapan 240 saat. Elektrod itu menunjukkan pemulihan yang sangat baik dan, dengan itu, menandakan ketepatan kaedah tersebut. Sementara itu, satu kajian kepekatan merkuri dengan AuNP/ionophore merkuri/SPE memberikan penentukuran linear R^2 = 0.99, dan had pengesanan 1.06 µg L^{-1} telah dicapai

dengan menggunakan potensi pemendapan -1.2 V dan masa pemendapan 240 saat. Pengesahan kaedah, dengan spektroskopi plasma-jisim ditambah secara induktif (ICP-MS), menunujukkan korelasi yang sangat baik.

Tambahan pula, kesan pemilihan ionophore terhadap ion sasaran yang dikaji dengan kehadiran ion lain yang berdaya saing dalam sampel air, seperti SO_3^{2-}, SO_4^{2-}, Fe^{3+}, Mg^{2+}, Cu^{2+} dan Cd^{2+}, telah memberi pemilihan yang sangat baik.

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I certify that a Thesis Examination Committee has met on 2nd of November 2016 to conduct the final examination of Samira Ashour Bilgasim Shoub on his her thesis entitled "Gold Nanoparticles/Ionophore Modified Screen Printed Electrode for Detection of Pb(II) and Hg(II)" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the (insert the name of relevant degree).

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Scienc. The members of the Supervisory Committee were as follows:

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

A	electrode surface area
ASV	anodic stripping voltammetry
AuNP	gold nanoparticles
C	concentration of analyte or reactant in the bulk solution
CNT	carbon nanotubes
CSV	cathodic stripping voltammetry
CV	cyclic voltammetry
DPASV	differintial pulse anodic stripping voltammetry
GCE	glassy carbon electrode
I	current
LSV	linear sweep voltammetry
MWCNT	multi wall carbon nanotubes
N	numbers of electrons
ppb	part per billion
ppm	part per million
SPE	screen printed electrode
SWASV	square wave anodic stripping voltammetry
v	scan rate
WHO	world health organization
A	absorbance
AdSV	adsorptive stripping voltammetry
AgNPs	silver nanoparticles
AuNPs	gold nanoparticles
AuNs/CSPE	gold nanostructures carbon screen printed electrode
BiNPs	bismuth nanoparticles
C.E	counter electrode

CHAPTER 1

INTRODUCTION

1.1 Heavy metals

The definition of heavy metals is usually based on their chemical properties such as malleability, and ductility with metallic lustre. They are also characterised by their ability to conduct heat and electricity, along with the ability to lose the outermost electrons to form cations with basic oxides (Duffus, 2002). This group of metals generally have a high density that is greater than 5 g cm^{-3} (Järup, 2003; Oves *et al*., 2012) and atomic weights between 63.5 and 200.6 g (Gumpu *et al.,* 2015).

The heavy metals are known to form stable complexes with a variety of ligands and their average stability decreases with electronegativity of the metal they get attached to in the following order Pd > Cu > Ni > Co > Zn > Cd > Mn (Rühling & Tyler, 1973). This order is further influenced by several other factors such as pH.

There are hundreds of sources that induce heavy metal contamination in the environment. Some of the major sources of heavy metal pollution include emission from industries (such as dust released due to industrial processes or waste released into rivers), farming activities, domestic activities and vehicle emission. Figure (1.1). Earlier studies of environmental pollution caused by heavy metals attributed the source of this pollution to be the anthropogenic and natural weathering, industrial activities and mining (Hu *et al*., 2013), and continuous urbanisation and industrialisation in developing countries (Järup, 2003). Furthermore, heavy metal waste generated from agricultural activities and industries can accumulate into sludge, which could pollute cultivated soil, and easily get transferred to the food chain (Li, 2010; Oves *et al.,* 2012; Zhao *et al.,* 2013).

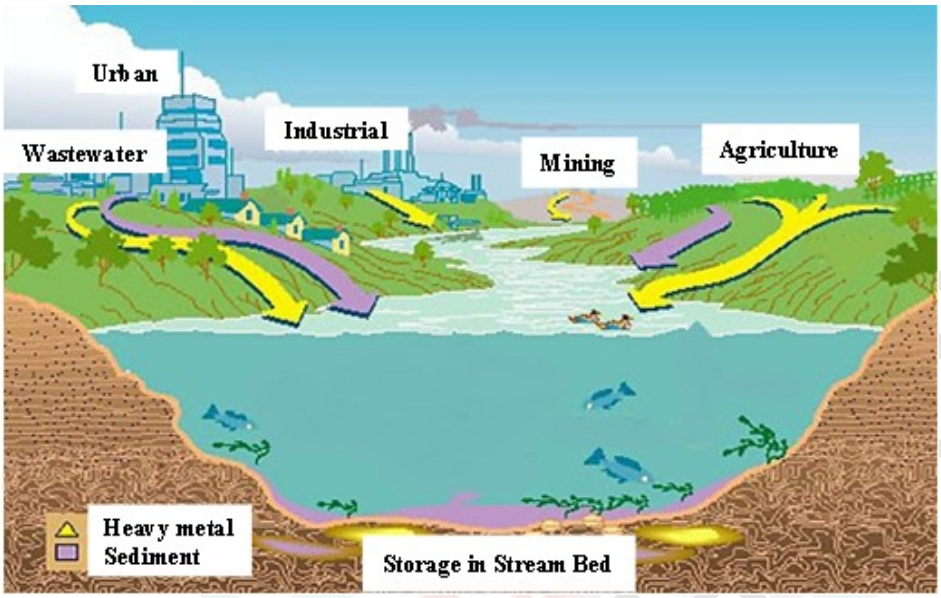

Figure 1.1: Source of heavy metal pollution to aqueous system (Li, 2010)

In many developing countries around the world, an increasing concentration of heavy metals in the environment is becoming a serious threat to both human and animal health, and is causing disruption in food protection and production.

Heavy metals might enter the human body through inhalation, oral intake, and dermal contact (Zheng *et al.,* 2013), which could lead to occasional biological effects or chronic diseases, especially in children (Hu *et al*., 2013). Prolonged exposure to heavy metals might even lead to many types of cancer (Zhao *et al.,* 2013). The rise of heavy metal pollution is a considerable threat to the environment and human health, due to its widespread presence everywhere, such as soil, dust, water and sediments. Therefore, the monitoring of these pollutants is paramount in order to improve the environmental health.

1.2 Problem statement

The rise of heavy metal pollution in natural waters is increasingly becoming a significant environmental problem throughout the world. This rise is mainly because of the increased use of heavy metals in industrial processes and products. Heavy metal poisoning may cause numerous disorders in plants and animals, and their accumulation may lead to various systemic diseases of nervous and other systems (Tchounwou *et al.,* 2012)

Of all the heavy metals studied, lead Pb(II) is of particular importance and concern as its compounds can be tremendously toxic. Lead is widely used in solders, cable sheaths, storage batteries, and as a petrol additive. It moves in the environmental biogeochemical cycle and is deposited on the surface and in the ground waters (Jan *et al*., 2015).

Mercury is a common and persistent environmental contaminant which is widely released to the environment by industrial activities (for example, gold mining and combustion of fossil fuels and wastes). It exhibits extreme toxicity mainly on renal and nervous systems through the disruption of enzyme activity. The solvated divalent mercuric ion Hg(II) is one of the most common and stable forms of mercury pollution due to its high water solubility (Du *et al.,* 2012). According to the toxicity data and scientific studies, the World Health Organisation (WHO) as well as the European Water Quality Directive has fixed a maximum allowable level of lead and mercury as 10 ppb and 1 ppb, respectively. Water with concentrations of lead and mercury that exceed these levels are considered to pose a health risk (Li, 2010).

Therefore, monitoring of these toxic metal ion levels in water (drinking, sea, river, etc.) is very important in terms of waste management, environmental analysis, toxicology, water safety, and water quality. A variety of analytical techniques have been used for metal ion analysis – for instance, atomic absorption spectrometry (Bannon *et al.,* 1994; Kenawy *et al.,* 2000), inductively couple plasma mass spectroscopy (Dressler *et al*., 1998; Gao *et a*l., 2002), x-ray fluorescence spectrometry (Prange *et al.,* 1985), and surface-enhanced Raman scattering (Tan *et al.*, 2012). Even though these methods provide good limits of detection and wide linear ranges, these require intense technical training because of their complicated procedures and high cost of analytical instruments. Furthermore, these techniques do not allow onsite analysis due to non-portability of the equipment. Hence, the application of these methods is not very feasible.

This led to the advent of disposal screen printed electrodes (SPE) and electrochemical techniques that are portable, cost-effective, and easy to operate. These techniques have received great attention from researchers, while electrochemical techniques have paved the way for reliable new methods. Among the various electrochemical methods for heavy metals determination, anodic stripping analysis offers many advantages over other analytical techniques, such as high sensitivity, favourable portability, suitability for automation, high speed of analysis, low power requirement, and inexpensive equipment (Jiang *et al*., 2010).

Nanomaterials are an attractive choice for development of the SPEs, as they can improve the sensitivity of electrodes for a particular group and also enhance the sensor performance (Li *et al.,* 2012). The size, chirality, and composition of the nanomaterials are responsible for their use in many applications. Hence, incorporating the surface-active nanomaterials on the SPEs for improving the chemical marker analysis enhances the SPE signals and their incorporation for detection of pollutants in the environment. Furthermore, it could be noted that modifying the SPE with a surface plasmon resonance material like gold nanoparticles improves its detection sensitivity (Li *et al.,* 2010).

To date, many electrodes have been reported for heavy metal ions detection in environmental samples. However, it should be noted that most electrodes for stripping voltammetry are subject to interferences from other heavy metal ions, such as the formation of intermetallic compounds and peak overlapping

problems, that affect its accuracy and precision, which are specific and relate to the nature of the stripping measurement (Pan *et al.,* 2009). Such problems can be alleviated by modifying the surface of electrode with a suitable macrocyclic compounds (Guziński *et al*., 2013). Electrodes modified with macrocyclic compounds have been employed recently for heavy metal detection, where the selective detection of analyte molecules is achieved by employing the ionophores that provide binding sites for suitable metal ions. Ionophore selection has been made based on the complexing ability and crown cavity size, suitable for a particular analyte molecule (Jiang *et al.,* 2010).

In this study, the unique properties of AuNPs (that is, enlarged active surface area and strong adsorptive capability) are combined with the specific complexing ability of ionophores and SPE to fabricate a selective and sensitive electrochemical sensor for trace determination of Pb(II) and Hg(II) ions in natural water.

1.3 Objectives

1.3.1 General objective

The objective of this research is to develop a sensor system for selective and sensitive detection for Pb(II) and Hg(II) in aqueous solution based on AuNPs/ionophore modified SPE.

1.3.2 Specific objective

Specific objectives for this research are

1. To modify and characterize the screen printed electrode (SPE) with gold nanoparticles (AuNPs).

2. To electrochemically characterized modified screen printed electrode with AuNPs and ionophore.

3. To characterize the sensing capability of the modified screen printed electrodes in Pb(II) and Hg(II) detection.

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LIST OF PUBLICATIONS

Paper

B. Shoub, S. A, Yusof, N. A., & Hajian, R. (2017). Gold Nanoparticles/Ionophore- Modified Screen Printed Electrode for Detection of Pb(II) in River using Linear Sweep Anodic Stripping Voltammetry, Sensors and Materials.

Poster

Samira Ashour, Nor Azah Yusof**,** Modified Screen Printed Electrode for Determination of Pb(II) using Gold Nanoparticles and Ionophore, WAMN 2015.

Oral Presentation

Samira Ashour, Nor Azah Yusof, Modified Screen Printed Electrode for Determination of Lead Ions Using Gold nanoparticles and Ionophore, The Fundamental Science Congress 2015, UPM

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