FABRICATION OF IRON OXIDE NANOPARTICLES/3-AMINOPROPYLTRIETHOXYSILANE MODIFIED ELECTRODE FOR Cd (II) IONS AND Pb (II) IONS DETECTION

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by

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DECLARATION

I hereby declare that, I have conducted, completed the research work and written the dissertation entitled "**Fabrication of Iron Oxide Nanoparticles/3-Aminopropyltriethoxysilane Modified Electrode for Cd (II) Ions and Pb (II) ions**". I also declare that it has not been previously submitted for an award of any degree or diploma or other similar title of this for any other examining body or university.

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Supervisor: Prof. Dr. Khairunisak Abdul Razak Signature:

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LIST OF SYMBOLS

A	Ampere
C	Celcius
g	Gram
Hz	Hertz
L	Liter
M	Molarity
m	Milli
s	Second
V	Volt
Δ	Delta
ϴ	Theta
μ	Micro

LIST OF ABBREVIATIONS

$[Fe(CN)_6]^{3-}$	Ferricyanide
AAS	Atomic Absorption Spectroscopy
A_e	Effective Surface Area
Ag	Silver
Ag/AgCl	Silver/Silver chloride
Al	Aluminium
APTES	3-Aminopropyltriethoxysilane
As	Arsenic
ASV	Anodic Stripping Voltammetry
Au	Gold
AuNPs	Gold Nanoparticles
B	Boron
Ba	Barium
Bi	Bismuth
$Bi(NO_3)\bullet 5H_2O$	Bismuth Nitrate Pentahydrate
Bi_2O_3	Bismuth Oxide
BiFE	Bismuth Film Electrode
BiP	Bismuth Particle
C	Carbon
Ca	Calcium
Cd	Cadmium
CFME	Carbon-Fibre Microelectrode
CNP	Carbon Nanoparticles
CNT	Carbon Nanotube
Co	Cobalt
Cr	Chromium
CT	Chitosan
Cu	Copper
CV	Cyclic Voltammetry
CVG	Cold Vapor Generation
D	Diffusion Coefficient

DME	Dropping Mercury Electrode
DPASV	Differential Pulse Anodic Stripping Voltammetry
DPV	Differential Pulse Voltammetry
EBP	Emeraldine Base Polyaniline
EDX	Energy Dispersive X-Ray
EPA	Environmental Protection Agency
Fe	Iron
γ-Fe_2O_3	Iron Oxide (Maghemite)
Fe_3O_4	Iron Oxide (Magnetite)
$FeCl_2{\cdot}4H_2O$	Iron (II) Chloride Tetrahydrate
$FeCl_3{\cdot}6H_2O$	Iron (III) Chloride Hexahydrate
FePc	Iron Phthalocyanines
FESEM	Field Emission Scanning Electron Microscope
Ga	Gallium
GCE	Glassy Carbon Electrode
HCl	Hydrogen Chloride
Hg	Mercury
HMDE	Hanging Mercury Dropping Electrode
HNO_3	Nitric Acid
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma - Mass Spectroscopy
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
In	Indium
IONPs	Iron Oxide Nanoparticles
I_p	Current Peak
ISE	Ion-Selective Electrode
ITO	Indium Tin Oxide
K	Potassium
$K_4Fe(CN)_6$	Potassium Ferrocyanide
KCl	Potassium Chloride
Li	Lithium
LIBS	Laser Induced Breakdown Spectroscopy
LOD	Limit of Detection
LSV	Linear Sweep Voltammetry

Mg	Magnesium
MMA (III)	Monomethylarsonic Acid
Mn	Manganese
MPTMS	3-Mercaptopropyl Trimethoxysilane
MWCNT	Multiwalled Carbon Nanotube
n	Number of Electron Transfer
NA	Nafion
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide
Ni	Nickel
NMC	Nitrogen Doped Microporous Carbon
O	Oxygen
Pb	Lead
ppb	Parts Per Billion
ppm	Parts Per Million
PSS	Polysodium 4-Styrene-Sulfonate
Pt	Platinum
PVG	Photochemical Vapor Generation
RCA	Radio Corporation of America
SAM	Self-Assemble Monolayer
SERS	Surface-Enhanced Raman Scattering
-SH	Sulfhydryl Group
Sn	Tin
SnO_2	Tin Oxide
SPCE	Screen Printed Carbon Electrode
SPE	Screen Printed Electrode
SPGE	Screen Printed Gold Electrode
SPR	Surface Plasmon Resonance
Sr	Strontium
SWASV	Square Wave Anodic Stripping Voltammetry
SWV	Square Wave Voltammetry
TA	Terephthalic Acid
TEM	Transmission Electron Microscopy
Tl	Thallium

TMFE	Thin Mercury Film Electrode
UV/Vis spectrometry	Ultraviolet Visible Spectrometry
UV-Vis NIR	Ultraviolet-Visible Near Infrared Spectrophotometer
WHO	World Health Organization
XRD	X-Ray Diffraction
Zn	Zinc
E_p	Peak Potential

FABRIKASI DAN PENGUBAHSUAIAN ELEKTROD MENGGUNAKAN NANOPARTIKEL BESI OKSIDA/3-"AMINOPROPYLTRIETHOXYSILANE" SEBAGAI PENGESAN UNTUK Cd (II) ION DAN Pb (II) ION

ABSTRAK

Pencemaran logam berat telah menjadi kebimbangan besar pada masa kini kerana ia menyebabkan pelbagai masalah kesihatan. Kebanyakan analisa telah dijalankan di makmal menggunakan "Inductively Coupled Plasma Spectrometry" dan "Atomic Absorption Spectrometry" yang mahal, memerlukan kakitangan yang terlatih dan tidak sesuai untuk analisa di tapak. Pengesan elektrokimia mengatasi kelemahan ini, tetapi elektrod untuk pengesan ini perlu diubahsuai untuk meningkatkan kepekaan dan pemilihan itu. Dalam kajian ini, nanopartikel besi oksida (IONPs) telah disintesis menggunakan kaedah "co-precipitation". Bismut partikel (BIP) telah disintesis dengan menggunakan kaedah hidroterma. IONPs telah dipasang sendiri di atas oksida indium timah (ITO) elektrod dengan bantuan 3-"aminopropyltriethoxysilane" (APTES). Kesan masa rendaman APTES/ITO di dalam IONPs (30, 60, 90, 120 dan 150 min) telah dikaji. Sifat elektrokimia IONPs/APTES/ITO telah dikaji dengan menggunakan analisa voltammetri berkitar (CV) dan gelombang anodik persegi - pelucutan voltammetri (SWASV). 90 min IONPs/APTES/ITO elektrod dipilih sebagai optimum kerana ia memberikan kekonduksian yang tinggi dan luas permukaan berkesan, A_e. Julat linear untuk Cd (II) dalam pengesanan individu adalah 1 - 10 ppb dengan kepekaan 110.59 μA ppb^{-1} dan had pengesanan (LOD) 2.5 ppb. Kepekaan untuk Pb (II) adalah 7.01 μA ppb^{-1} dalam julat linear 50-70 ppb dengan LOD 2.09 ppb. Untuk pengesanan serentak, julat linear untuk Cd (II) adalah 30 ppb - 70 ppb dengan

kepekaan 5.69 μA ppb^{-1} dan LOD 9.15 ppb. Manakala bagi Pb (II) puncak itu hanya diperhatikan untuk kepekatan 80 dan 100 ppb. Puncak yang jelas telah dihasilkan dalam kajian ganguan, menandakan elektrod yang diubah suai itu sangat sensitif dan selektif terhadap pengesanan Cd (II). Akhir sekali, IONPs/APTES/ITO telah digunakan untuk sampel air laut, Cd (II) dikesan dengan kepekatan 14.13 ppb dan 26.84 ppb untuk sampel dari pantai Seagate dan Pantai Jerejak masing-masing. Hasil kajian menunjukkan bahawa elektrod IONPs/APTES/ITO boleh digunakan sebagai sensor logam yang berat.

FABRICATION OF IRON OXIDE NANOPARTICLES/3-AMINOPROPYLTRIETHOXYSILANE MODIFIED ELECTRODE FOR Cd (II) IONS AND Pb (II) IONS DETECTION

ABSTRACT

Heavy metal pollution has become the biggest concern nowadays as it causes various health issues. Most analysis have been carried out in laboratory using Inductively Coupled Plasma Spectrometry and Atomic Absorption Spectrometry that are expensive, requires trained personnel and not suitable for on site analysis. Electrochemical sensors overcome these drawbacks, but the working electrode needs to be modified to enhance its sensitivity and selectivity. In this work, iron oxide nanoparticles (IONPs) was synthesized using co-precipitation method and bismuth particles (BiP) was synthesized by using hydrothermal method. The IONPs was self-assembled on indium tin oxide (ITO) electrode with the aid of 3-aminopropyltriethoxysilane (APTES). The effect of soaking time of APTES/ITO in IONPs (30, 60, 90, 120 and 150 min) was investigated. Electrochemical properties of IONPs/APTES/ITO were studied using cyclic voltammetry (CV) and square wave anodic stripping voltammetry (SWASV) analysis. The 90 min IONPs/APTES/ITO electrode was chosen as the optimum as it showed high conductivity and effective surface area, A_e. The linear range for Cd (II) in individual detection was 1 – 10 ppb with sensitivity of 110.59 µA ppb^{-1} and limit of detection (LOD) of 2.5 ppb. The sensitivity for Pb (II) was 7.01 µA ppb^{-1} in the linear range of 50 – 70 ppb with LOD of 2.09 ppb. For simultaneous detection, the linear range for Cd (II) was 30 ppb – 70 ppb with sensitivity of 5.69 µA ppb^{-1} and LOD of 9.15 ppb. While for Pb (II) the peak was only observed for 80 and 100 ppb. A well-defined peak was produced from interference study, signifying the modified electrode was highly sensitive and selective towards detection of Cd (II). Finally, the IONPs/APTES/ITO electrode was applied for seawater samples, where by Cd (II) was detected with concentration 14.13 ppb and 26.84 ppb for samples from Seagate beach and Pantai Jerejak, respectively. The findings revealed that the IONPs/APTES/ITO electrode can be used as a heavy metal sensor.

CHAPTER 1

INTRODUCTION

1.1 Introduction

The term heavy metal is defined as chemical elements with atomic weight in between 63.5 to 200.6 and metal density greater than 5 g/cm^3 (Srivastava and Majumder, 2008). Usually, heavy metal enters the environment by natural (volcanic activity) or anthropogenic (manmade) means. The discharge of waste from vast industrial activity, mining and agriculture contains a certain amount of heavy metals as well, if the waste was not managed before discharging to the environment. The most commonly found heavy metals in waste water effluents are arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), silver (Ag) and zinc (Zn) (Akpor, 2014). Studies performed in Penang reported the presence of Cd, Cr, Cu, Fe and Pb in surface water of major rivers in Penang namely, Sungai Muda, Sungai Jarak, Sungai Kerian, and Sungai Kongsi (Alsaffar et al., 2016).

Frequent exposure of this heavy metals, either directly (workplace) or indirectly (ingestion of contaminated food and water) can cause severe health issues. Singh et al. (2011) have summarized the effect of heavy metals to human's health as in Table 1.1. These heavy metals exhibit high toxicity even in trace amount. Thus, it is important for us to monitor the concentration of heavy metal in surface water to avoid contamination in living organisms. Aragay et al. (2011b) have summarized the permissible limit guideline for heavy metal contamination in drinking water as tabulated in Table 1.2 according to World Health Organization (WHO) and Environmental Protection Agency (EPA).

Table 1.1: Heavy metals and its effect to human health (Singh et al., 2011).

Heavy Metals	Sources	Health issues
Arsenic	Pesticides, Fungicides, Metal smelters	Bronchitis, Dermatitis, Poisoning
Cadmium	Welding, Electroplating, Pesticides, Fertilizers, Cd & Ni batteries, Nuclear fission plant	Renal dysfunction, Lung disease, Lung cancer, bone defects, gastrointestinal disorder, kidney damage
Chromium	Mines, Mineral sources	Nervous system damage, fatigue, irritability
Copper	Mining, pesticides production, chemical industry, metal piping	Anaemia, liver and kidney damage, stomach and intestinal irritation
Lead	Paint, pesticides, smoking, automobile emission, mining, burning of coal	Mental retardation in children, developmental delay, fatal infant encephalopathy, congenital paralysis, nervous system damage, liver, kidney, gastrointestinal damage
Manganese	Welding, fuel addition, ferromanganese production	Inhalation or contact causes damage to central nervous system
Mercury	Pesticides, batteries, paper industry	Tremors, gingivitis, minor psychological changes, nervous system damage, protoplasm poisoning
Zinc	Refineries, brass manufacture, metal plating, plumbing	Zinc fumes have corrosive effect on skin, nervous system damage

Table 1.2: Guideline value for heavy metals in drinking water (Aragay et al., 2011b).

Heavy metal	**Provisional Guideline value (ppb)**	
	WHO	**EPA**
Arsenic, As	10	10
Cadmium, Cd	3	5
Copper, Cu	2000	1300
Lead, Pb	10	15
Mercury, Hg	1	2
Nickel, Ni	70	40
Zn	3000	5000