SYNTHESIS OF MnO_2 FOR SURFACE MODIFIED ELECTRODES FOR HEAVY METAL SENSORS

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Synthesis of MnO_2 for Electrode Modification for the Detection of Heavy Metals in Water”. 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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LIST OF SYMBOLS

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

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
A_e	Effective Surface Area
Ag	Silver
AgCl	Silver chloride
Al	Aluminium
APTES	3-Aminopropyltriethoxysilane
As	Arsenic
ASV	Anodic Stripping Voltammetry
Au	Gold
AuNRs	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
CNR	Carbon Nanoparticles

CNT	Carbon Nanotube
Co	Cobalt
Cr	Chromium
Cu	Copper
CV	Cyclic Voltammetry
D	Diffusion Coefficient
DME	Dropping Mercury Electrode
DPASV	Differential Pulse Anodic Stripping Voltammetry
DPV	Differential Pulse Voltammetry
EDX	Energy Dispersive X-Ray
$FeCl_2·4H_2O$	Iron (II) Chloride Tetrahydrate
$FeCl_3·6H_2O$	Iron (III) Chloride Hexahydrate
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
IONRs	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
Mn	Manganese
n	Number of Electron Transfer
NA	Nafion
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide
Ni	Nickel
NR	Nanorods
O	Oxygen
Pb	Lead
ppb	Parts Per Billion
ppm	Parts Per Million
Pt	Platinum

RCA	Radio Corporation of America
Sn	Tin
SnO_2	Tin Oxide
SPCE	Screen Printed Carbon Electrode
SPE	Screen Printed Electrode
SPGE	Screen Printed Gold Electrode
Sr	Strontium
SWASV	Square Wave Anodic Stripping Voltammetry
SWV	Square Wave Voltammetry
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

SINTESIS MNO_2 UNTUK ELEKTROD UBAHSUAI PERMUKAAN UNTUK PENDERIA LOGAM BERAT

ABSTRAK

Pada zaman moden, pencemaran logam berat sumber air telah menjadi masalah besar akibat aktiviti manusia yang berterusan seperti aktiviti perindustrian, perlombongan dan pertanian. Walaupun pengesanan logam berat boleh dilakukan menggunakan cara spektroskopi, yang mana ia tidak sesuai untuk pemantauan masa nyata logam berat kerana memerlukan peralatan mahal, pengendali berpengalaman dan prosedur ujian yang panjang. Penderia elektrokimia tidak mempunyai masalah ini. Walau bagaimana pun, elektrod yang digunakan, seperti elektrod ITO tidak mempunyai kepekaan untuk mengesan kepekatan rendah logam berat. Dalam kajian, kesan menyiasat pengubahsuaian permukaan elektrod ITO kosong dengan nanorod α-MnO_2 untuk meningkatkan 1 ensitivity dan selektiviti elektrod ITO kosong untuk pengesanan logam berat telah dijalankan. Nanorod α-MnO_2 telah disintesis dengan kaedah hidroterma suhu rendah, yang kemudiannya terampai dalam etanol dan titisan tuang pada permukaan ITO kosong, diikuti dengan rawatan haba dan kemudian salutan dengan larutan nafion untuk menghasilkan elektrod Nafion/α-MnO_2NR/ITO. Voltammetri kitaran telah digunakan untuk mengoptimumkan kepekatan ampaian α-MnO_2NR dan kepekatan nafion yang digunakan, di mana parameter optimum didapati ialah ampaian 10 mg/ml α-MnO_2NR dan larutan nafion 0.1%. Limit of Detection (LOD) yang dikira untuk Pb(II) untuk elektrod diubah suai 0.1%Nafion/α-MnO_2NR/ITO ialah 0.393 ppb. Analisis pelucutan serentak Pb^{2+}, Cd^{2+} dan Cu^{2+} tidak menghasilkan puncak, namun ia berkemungkinan disebabkan oleh kebolehulangan yang lemah bagi elektrod. Daripada kajian gangguan elektrod ubah suai 0.1%Nafion/α-MnO_2NR/ITO, menunjukkan bahawa elektrod mempunyai selektiviti

yang cukup tinggi untuk ion Pb^{2+}, Cd^{2+} dan Cu^{2+}, kerana ini adalah satu-satunya puncak yang diperhatikan daripada 23 ion berbeza yang terdapat dalam penyelesaian.

SYNTHESIS OF MNO_2 FOR SURFACE MODIFIED ELECTRODES FOR HEAVY METAL SENSORS

ABSTRACT

In modern times, heavy metal pollution of water sources has become a huge problem due to ongoing human activities such as industrial, mining and agricultural activities. While detection of heavy metals can be done using spectroscopic means, they are unsuitable for real time monitoring of heavy metals due to requirement for expensive equipment, experienced operators and lengthy testing procedures. Electrochemical sensors do not have these problems. However, the electrodes used, such as ITO electrode lacks the sensitivity to detect low concentration of heavy metals. This work investigates the surface modification of bare ITO electrodes with α-MnO_2 nanorods to increase the sensitivity and selectivity of bare ITO electrodes for heavy metal detection. α-MnO_2 nanorods were synthesized with low temperature hydrothermal method, which is then suspended in ethanol and drop casted on the bare ITO surface, followed by heat treatment and then coating with nafion solution to fabricate Nafion/α-MnO_2NR/ITO electrode. Cyclic voltammetry was applied to optimize the concentration of α-MnO_2NR suspension and nafion concentration used, where the optimal parameters were found to be 10 mg/ml α-MnO_2NR suspension and 0.1% nafion solution. The calculated Limit of Detection (LOD) for Pb(II) for the 0.1%Nafion/α-MnO_2NR/ITO modified electrode is 0.393 ppb. Simultaneous stripping analysis of Pb^{2+}, Cd^{2+} and Cu^{2+} yields no peaks, however it is likely to be due to poor reproducibility of the electrode. From the interference study of 0.1%Nafion/α-MnO_2NR/ITO modified electrode, it is showed that electrode has sufficiently high

selectivity for Pb^{2+}, Cd^{2+} and Cu^{2+} ions, as these are the only peaks observed out of the 23 different ions presence in the solution.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Heavy metals are natural elements present in the earth's crust that only occurs in trace amounts. Heavy metals refer to any metallic element that has a relatively high density, typically greater than 5 g/cm^2 and are toxic to living beings, even at low concentrations (Duruibe, Ogwuegbu & Egwurugwu, 2007). Anthropogenic industrial and agricultural activities have been a big contributor to the emission of heavy metals in water systems such as rivers, which then cause serious health effects on human populations and wildlife present in the area (Dai et al., 2018).

Humans can come into contact with heavy metals mainly through ingestion, inhalation and skin contact of heavy metal contaminants (Kamara et al., 2021). Some examples of heavy metal elements include copper (Cu), lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr) and arsenic (As). Heavy metals tend to accumulate in organs such as the liver, kidneys and bones and have been known to cause serious health effects, such as kidney dysfunction, neurological damage and birth defects (Jamshaid et al., 2018). As heavy metals persist in the food chain and do not degrade, they pose a serious threat to the health of human populations. Thus, detection of these heavy metals is important as it allows for the assessment of environmental and health impacts caused by human activities.

There are many methods to identify or detect the presence of heavy metals in a sample of water. Conventional methods include spectroscopic techniques such as Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), and X-ray fluorescence (Pujol et al., 2014). However, these conventional detection techniques are rather labor intensive, require experienced operators, expensive equipment, have long analysis times and are not suitable for on-field applications. Thus, chemical sensors have been considered quite useful as a replacement for these conventional techniques for the detection and monitoring of heavy metals.

A chemical sensor is defined by the IUPAC as a device to receive and analyze chemical information and consists of two main parts, a receptor to receive chemical information and a transducer, which produces a measurable signal in response to chemical information received (Hulanicki et al., 1991). Chemical sensors are preferred over conventional methods because of the various advantages such as relatively low cost, good response times, excellent heavy metal selectivity, and scalability, and are compact and easy to handle, with minimum sample preparation (Bhardwaj et al., 2015; Stoytcheva et al., 2014). Notable examples of chemical sensors are optical sensors, electrochemical sensors, and biosensors.

Among all types of chemical sensors, electrochemical sensors are favored due to their advantages such as ease of use, high sensitivity and low cost of materials (Li et al., 2013). Electrochemical sensors generally employ a wide range of electrochemical techniques such as potentiometry, voltammetry and conductometry. Potentiometry technique involves measurement of the potential difference in the analyte solution caused by the change in ions concentration under static conditions. As for the conductometry technique, the ionic concentration is measured from the change in electrolytic conductivity of the analyte solution resulting from the chemical reaction. In heavy metal detection, the voltammetry technique are popular over other conventional analytical techniques due to benefits such as high sensitivity, wide range of detection, ease of use, and simple instrumentation as well as capability for on-field applications (Bond et al., 2005). The voltammetry technique involves retrieving information from a solution by measuring the current as a function of the applied electric potential (Eddaif et al., 2019).

Electrochemical sensors detect heavy metal ions through the setup of an electrochemical cell, which consists of three electrodes, working, counter and reference electrodes. The three electrodes are connected to a potentiostat with presence of electrolyte solution. A potentiostat is used to record the electrical signal information resulting from the electrochemical reactions. Redox reactions of oxidation at the anode and reduction at the cathode are induced in the cell during operation (Bansod et al., 2017). In an electrochemical cell, heavy metal detection will happen at the working electrode. When a potential controlled by the reference electrode is passed through the working electrode in an analyte solution containing heavy metal ions, the signal current will be recorded. The signal current produced represents the characteristic of the electrochemical reactions that occur within the analyte solution.

Types of voltammetry techniques includes Cyclic Voltammetry (CV), Anodic Stripping Voltammetry (ASV) and Square Wave Anodic Stripping Voltammetry (SWASV), which are some of the more popular voltammetric techniques. ASV is a very useful voltammetry technique for heavy metal detection. The reason is because ASV can achieve extremely low limit of detection (LOD) (10^{-10} to 10^{-11} mol/l), in which the LOD may go as low to picomolar range (Daniele, 2005; Bansod et al., 2017).

Additionally, properties of electrochemical sensors such as the sensitivity and specificity are highly dependent on the chosen type of electrode. Electrodes based on mercury have initially been the most popular electrode in the electrochemical detection of heavy metals due to their high sensitivity, low fouling and renewable surface, wide cathodic potential, high affinity for metal cations and high overpotential for hydrogen evolution (Pujol et al., 2014). Some popular examples of mercury electrodes were the hanging mercury drop electrode (HMDE), dropping mercury electrode (DME/SMDE) and mercury film electrode (MFE) (Ariño et al., 2017; Pujol et al., 2014). However, as mercury is itself a heavy metal and contributes to serious environmental and health damage, it has been phased out of usage or outright banned in some countries, and alternative electrodes have been developed to replace it. Several works have reported work on bulk electrodes such as bismuth film electrodes, gold film electrodes and glassy carbon electrodes for electrochemical sensors (Xuan et al., 2016; Waheed et al., 2018). However, these bulk electrodes could not completely replace mercury electrodes as bulk electrodes generally had drawbacks such as large overpotential and coexisting ion interference, which are detrimental for heavy metal detection. Thus, to enhance the electrode performance of bulk electrodes, surface modification of bulk electrodes with nanoparticles has become popular as a way to enhance the properties of bulk electrodes.

While there are many different substrate electrodes that have been used for modification such as the glassy carbon electrode (GCE), screen-printed carbon electrode (SPCE) and indium-tin-oxide (ITO) electrode (Tang & Cheng, 2013), this work will be focusing on the surface modification of the ITO electrode with MnO_2 nanoparticles.

1.2 Problem statement

Heavy metals have significantly impacted the health and wellbeing of human populations as well as the environment, and thus efforts have been taken to detect and monitor the presence of heavy metals in water sources, especially from important water sources such as rivers and lakes. Electrochemical detection techniques are popular for heavy metal detection due to their ease of use, portability, short analysis duration and suitability for continuous and in-field testing. However, bare ITO electrode itself is a bulk electrode, and when used as the working electrode in electrochemical analysis has significant drawbacks in terms of selectivity, specificity, sensitivity, and LOD. Therefore, modification of the ITO electrode surface with nanomaterials has been worked on to improve the electrochemical performance of the ITO electrode. The properties of the working electrode can be improved by modifying the bare working electrode with nanomaterials, which can act as electron mediators due to nanomaterials having increased surface area compared to bulk materials. This increases the effective electrochemical surface area, promising to improve the sensitivity and conductivity of the working electrode.

Metal oxide NRs in particular have been considered a great candidate for electrochemical stripping analysis due to properties such as having low cost and high adsorption capacity to heavy metal ions. Among the metal oxides NRs used, manganese oxide has been a promising candidate as it shows favorable characteristics such as low cost and abundance of raw materials, ease of synthesis, electrochemical stability, low toxicity, presence of different morphologies and polymorphs, and an ability to deliver a high electrical charge in a short time (Bhanjana et al., 2019). Besides that, manganese oxides have already been successfully applied as a catalyst for the redox reactions of compounds such as carbon monoxide and nitrobenzene (Roche & Scott, 2009; Zhao et al., 2017).

Recent work has been done to study the capability of manganese oxides to detect heavy metals. Zhang et al. (2013) has documented the use of α-MnO_2NR/GCE electrode for the detection of heavy metals by SWASV, achieving LOD in the micromolar range for Cu (II), Zn (II), Hg (II), Cd (II), and Pb (II) ions. Mališić et al. (2012) prepared MnO_2NR/Carbon/GCE electrode via hydrothermal synthesis and managed to achieve detection limits of 27 nM for Pb (II) and 52 nM for Cd (II) ions. Bhanjana et al. (2019) reported on the use of Nafion/Mn_3O_4NR/Au electrode for the detection of chromium, achieving an LOD of 9.5 ppb. However, to our knowledge there has not been studies on the performance of Nafion/α-MnO_2NR/ITO electrode for heavy metal detection. MnO_2 NR is interesting to be employed in modification of ITO electrode because it has at least six polymorphic crystalline structures (Daia et al., 2019), which all exhibit semiconductor characteristics with low resistivity. Nafion is a random copolymer with sulfonated tetrafluoroethylene side groups that exhibit ion mobilisation properties (Yusoff, 2018). Nafion acts as a protective film to mechanically stabilize the modified electrode's surface, as well as providing selectivity towards heavy metal ions and may help improve the electrochemical detection performance of α-MnO_2 NR/ITO modified electrode.

In this work, α-MnO_2 NR was synthesized using the low temperature hydrothermal synthesis method. The obtained α-MnO_2 NR was then applied for modification of ITO electrode. Nafion layer is applied on α-MnO_2 NR/ITO modified electrode to improve selectivity and induce mechanical stability. The effect of α-MnO_2 NR concentration and Nafion concentration were observed to obtain the excellent electrochemical performance electrode for heavy metal detection. The modified electrode was analyzed using CV and SWASV for heavy metal detection.

1.3 Objectives

The objectives for this project are:

1. To synthesize and characterize α-MnO_2 NR using low temperature processing
2. To optimize the fabrication of Nafion / α-MnO2 NR / ITO modified electrodes for heavy metal detection

3. To investigate the sensitivity, LOD and specificity of Nafion / α-MnO_2 NR / ITO modified electrode in electrochemical heavy metal detection

1.4 Scope of research

In this project, 19nm α-MnO_2 NRs was synthesized through the low temperature hydrothermal method. Properties of α-MnO_2 NRs were analysed using transmission electron microscopy (TEM), Xray diffraction (XRD) and zeta potential analyser. To fabricate the Nafion/α-MnO_2 NR/ITO electrode, α-MnO_2 NR suspension was drop-casted on ITO electrode, air dried and heat treated in an oven, followed by drop-casting a layer Nafion solution on the α-MnO_2 NR/ITO electrode. Nafion was used to improve the mechanical stability of the surface of the α-MnO_2 NR/ITO electrode, as well as to improve the selectivity of the electrode, to enhance the electrochemical performance. The Nafion/α-MnO_2 NR/ITO electrode was then studied using cyclic voltammetry for modification parameters optimization as well as to electrochemically characterize the electrode. Lastly, electrode properties such as the selectivity and sensitivity of the modified electrode for detection of Pb^{2+} ions was determined using SWASV. Next, interference study of other metal ions on Nafion/α-MnO_2 NR/ITO electrode was done to observe the interference effect of other ions on the detection performance of the Nafion/α-MnO_2 NR/ITO electrode.

1.5 Dissertation outline

This thesis has five chapters. The first chapter covers information such as the research background, problem statement, objectives and scope of research of the project. The second chapter covers the literature review on heavy metals and their health effects, conventional detection and electrochemical detection techniques for heavy metals as well as previous works on modification of the electrodes with various types of nanomaterials, and previous works on MnO_2 modified electrode. The third chapter covers materials, apparatus, and equipment used, experimental procedure, parameters, and characterization methods. The fourth chapter presents the results and discussion of the results, while the fifth chapter outlines the conclusion of the research work and suggestions for future work.

CHAPTER 2

2.1 Introduction

Heavy metals are generally metals and metalloid elements with a density of 5 g/cm^3 or more and is harmful to the human populations, the environment and the ecosystem (Järup, 2003; Jaishankar et al., 2014). Heavy metal pollution is a serious worldwide problem due to anthropogenic activities such as industrial activities, agricultural activities, and rapid urbanization, and is an especially severe problem in developing countries or third world countries where environmental regulations are lax and compliance by private companies are low. Activities associated with mining and ore processing are main contributors of heavy metal pollution in the environment, releasing these heavy metal elements as small particles that settle into the surrounding environment and into the soil and water sources (Fu & Xi, 2019). The heavy metal particulate contaminants persist in the environment for many years and decades to come. Heavy metals accumulate down the food chain in various animals, food crops and livestock. Even small amounts of heavy metals are highly toxic to humans, and can severely impact the ecology, environment and human life expectancy of a population. Exposure to heavy metals can occur in various ways through ingestion of heavy metal contaminated food and water, and inhalation of airborne particles (Rehman et al., 2017). Increasing use of heavy metals in industries such as agriculture, pharmaceutical has caused increasing heavy metal exposure among human populations.

As heavy metals are known to have adverse impacts on human health and the environment, it is important to have effective detection techniques for heavy metals. This project aims to investigate the use of MnO_2 modified electrodes for heavy metal detection. As such, relevant literature on heavy metal pollution and detection is presented. Also, the use of electrochemical sensor electrodes, and the potential of MnO_2 nanoparticles for electrode modification are discussed in this chapter.

2.2 Effects of heavy metal pollution

Heavy metals are known to negatively affect or impair the body's metabolic functions. This is because heavy metals can displace metal ions in protein sites and biological processes, causing the malfunctioning of body cells and leading to toxicity. Heavy metals can also react with certain biological compounds, thus reducing the availability of the original form of the compounds (Rehman et al., 2017; Rusnyiak et al., 2010). Exposure to heavy metals are also known to negatively impact the function of neurotransmitters in the body, resulting in damage to the nervous system. Other effects of heavy metal exposure include generation of free radicals in the body which causes neurological degeneration and disorder, damages DNA and nuclear proteins, and causes inhibition of kidney functions and other endocrine disruptions.

Lead is highly toxic but a common heavy metal pollutant which has seen widespread usage in many industries, such as lead-based paints (Rehman et al., 2017), production of lead-acid batteries, production of ceramics with lead content, various manufacturing processes such as welding and soldering, mining processes such as ore smelting (Fu & Xi, 2019) and manufacturing of military arms and ammunitions (Goyer & Clarkson, 2001). Lead serves no biological purpose, and is toxic to most living organisms as it leads to generation of reactive oxygen species (ROS) within cells, such as hydroperoxides and O^{2+} (Jaishankar et al., 2014). Lead has been shown to raise ROS levels and Ca^{2+} within cells, which causes cell death (Moreira, Vassilieff & Vassilieff, 2001; Fu & Xi, 2019). Lead also increases the oxidative stress in cells by affecting enzymes that react with free radicals in the cells. Lead has a number of recorded effects on the human body, including lead-induced neuropathy, blood iron deficiency, renal disease, immunotoxicity, and cancer.

Cadmium is a by-product of zinc and lead production (Goyer & Clarkson, 2001) as they are naturally found in ores (Rehman et al., 2017). However, cadmium is a heavy metal with many modern applications. Cadmium is currently used in alkaline batteries as a component of the battery electrode, coatings, pigments, electroplating and galvanizing processes of metals and as a plastic stabilizer (Jaishankar et al,. 2014). Cadmium has also been found in phosphate fertilizers that are used in agricultural activities. Incineration of cadmium-containing wastes heavily contaminates the surrounding environment. Exposure of cadmium in humans is mainly through contaminated food and water, and inhalation. Studies in humans and animals have shown that osteoporosis, calcium metabolism disorders, kidney stone formation and hypercalcemia are linked to cadmium exposure (Kamara et al., 2021). Ingesting large amounts of cadmium can cause stomach irritation, vomiting, and diarrhoea. Cadmium and zinc share the same oxidation state, and readily replaces zinc in the metal sulphur protein, causing metabolic disorders (Flora, Mittal & Mehta, 2008; Fu & Xi, 2019). Cadmium is also highly toxic to the kidney and causes bone mineralization and renal dysfunction. Cadmium bioaccumulates inside the body throughout life, with an estimated half-life as long as 30 years.

Mercury is a common heavy metal that exhibits a liquid state in its pure form at room temperature. Mercury exists in 3 major forms, metallic elements, organic compounds and inorganic salts, with different toxicity and bioavailability (Jaishankar et al., 2014). Mercury is mainly generated in deposits around the world as cinnabar. Mercury are found naturally in the environment in the form of elemental mercury vapour from volcanoes and the release of inorganic mercury due to weathering and movement of water (Bose-O'Reilly, McCarty, Steckling & Lettmeier, 2010). Anthropogenic sources such as burning of fossil fuels, mining and refining processes, manufacturing of electrical and automotive parts, waste disposal and emissions from industrial activities also add to mercury pollution. Like lead, mercury has no biological purpose and only brings negative effects to the body. Organic mercury compounds such as methylmercury are neurotoxic and will impair the nervous system in high enough doses. Methylmercury significantly increases the level of free calcium ions in nerve cells in the brain affecting the cellular processes. It induces oxidative stress by interfering with mitochondrial breathing chains, affects DNA repair and causes cell death in the brain (Ho et al., 2013; Fu & Xi, 2019). Aside from the brain, organic mercury compounds can disrupt any organ or tissue in the body, leading to malfunction of nerves, kidneys and muscles and even impair immune cells .

Chromium is mainly used in production of metal alloys and ceramics and is used in the chrome plating process. Chromium occurs in two stable forms in the environment: Cr (VI) and Cr (III). Cr (III) is less toxic and insoluble, while Cr (VI) is very toxic and easily soluble. Cr (III) is a micronutrient that is essential for the body to metabolise fats and carbohydrates, as well as synthesise fatty acids and cholesterols in the body, while Cr (VI) compounds have been known to be toxic, mutagenic, and carcinogenic (Kamara et al., 2021). Chromium compounds coming in contact with an open wound will cause severe ulcers which are difficult to heal (Jaishankar et al., 2014).

Arsenic is a metalloid element whose compounds are generally toxic and carcinogenic (Jaishankar et al., 2014). Human exposure to arsenic comes from drinking water and consuming food contaminated with arsenic compounds either through agricultural waste or pesticides, or industrial wastes (Fu & Xi, 2019). Industrial activities like ore mining also release arsenic particles into the air, affecting the quality of nearby water sources and groundwater. Natural arsenic minerals can also contaminate the water supply in certain areas. Arsenic compounds are carcinogenic and have been known to cause cancer in the lungs, liver, bladder and skin. Chronic arsenic exposure may also cause skin lesions, damage to the bone marrow, neurological problems and cardiovascular disease (Smith et al., 2000). Table 2.1 shows a summary of the heavy metals discussed and their long term health effects on exposed human populations (Tchounwou, 2012).

Table 2.1: Long term health effect of various heavy metal elements (Tchounwou, 2012).

Heavy metal element	**Long term health effects**
Lead	Lead poisoning, neurodegenerative disorders and neurodevelopmental abnormalities in offspring
Cadmium	Changes in pulmonary function, emphysema, decrease in olfactory function, decrease in bone mineral density and osteoporosis
Mercury	Gastrointestinal toxicity, neurotoxicity, and nephrotoxicity
Chromium	Multiorgan toxicity such as renal damage, allergy and asthma, and cancer of the respiratory tract, irritation to the lining of the nose and nose ulcers, and severe respiratory, cardiovascular, gastrointestinal, hematological, hepatic, renal, and neurological effects as part of the sequelae, leading to death.
Arsenic	Cardiovascular and peripheral vascular disease, developmental anomalies, neurologic and neurobehavioral disorders, diabetes, hearing loss, portal fibrosis, hematologic disorders (anemia, leukopenia, and eosinophilia), and carcinoma

While it may be difficult to reduce heavy metal pollution in the short term, effort should be made to detect heavy metals in food and water sources that are most likely to cause the most contamination and ill health to humans. Research that aims for continuous improvements in the effectiveness of heavy metal detection in water sources is needed to ensure that the health of the general populace as well as the environment is not compromised. The current study sought to extend work in this direction by evaluating the use of MnO_2 nanoparticles for electrode modification for heavy metal detection in water.

2.3 Detection of heavy metal presence in water samples

There are many techniques that have been used to detect the presence of heavy metals. Spectroscopic methods such as Atomic Absorption Spectrometry, Atomic Emission Spectroscopy and X-ray fluorescence analysis methods have been used to detect the presence of heavy metals.

Atomic absorption spectroscopy (AAS) is an old analytical method that has been around since the 1960s. The sample is atomized by flame, plasma or electrothermal atomizer (Malik et al., 2019) into an atomic vapor state. A hollow cathode lamp is used to emit a beam of light, which passes through a monochromator and the atomic vapor and finally onto a detector, which records the wavelengths of light received (Van Loon, 2012). A specific wavelength is used to excite specific single atoms of an element to the excited state, from its ground state. The energy absorbed during this process is determines the concentration of the atoms of the specific element present in the sample. The cloud of atomized particles absorbs the emission spectra that correspond to its elemental constituents, and the beam is then recorded by the detector. AAS method is sensitive to metals and semimetal elements and have low detection limits in part per million range. For an Electrothermal Atomization AAS, the detection limit is even lower in the part per billion range. However, AAS can only characterize a single element at a time (Holcombe, 2005), but modern equipment may allow for analysis of up to 8 elements simultaneously. Figure 2.1 shows the general schematic of an AAS equipment setup.

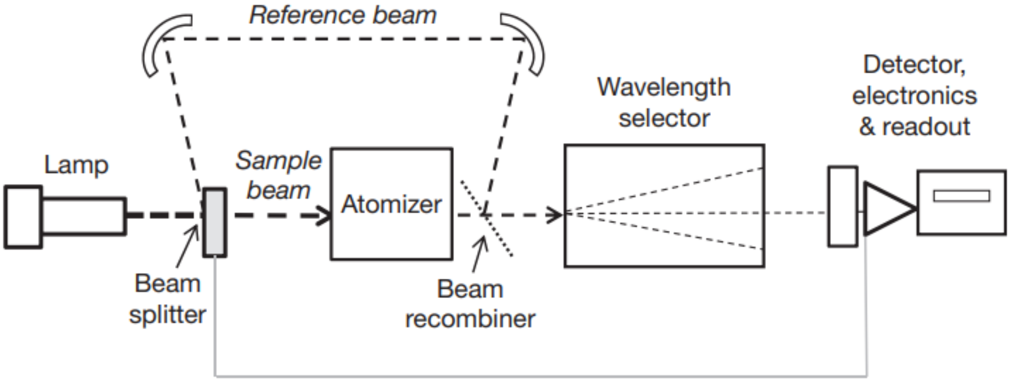

Figure 2.1: General schematic of an AAS equipment setup (Fernández, 2018)

Atomic Emission Spectroscopy (AES) is a similar technique to AAS where the sample is atomized to produce a cloud of free atoms. However the detector detects the emission spectra of the excited atoms in the sample instead of using a lamp. Inductively coupled plasma (ICP) has been used as an excitation source in AES method (Sperling, 2005). AES limit of detection is in the ppb range, and is highly sensitive to most metal elements.

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) uses a plasma source to excite the atoms in the samples to emit light with specific wavelength, which is then measured by the detector to determine the concentration of the elements detected (Kaur et al., 2016). ICP-MS can achieve low LOD levels for several elements. However, there is limitation of the matrix effect which can reduce the intensity of the signal of the tested element and deposit on the sampling cone which reduces the amount of ions present in the sample, making results less reliable (Kaur et al., 2016). Figure 2.2 shows the schematic diagram of ICP-MS.

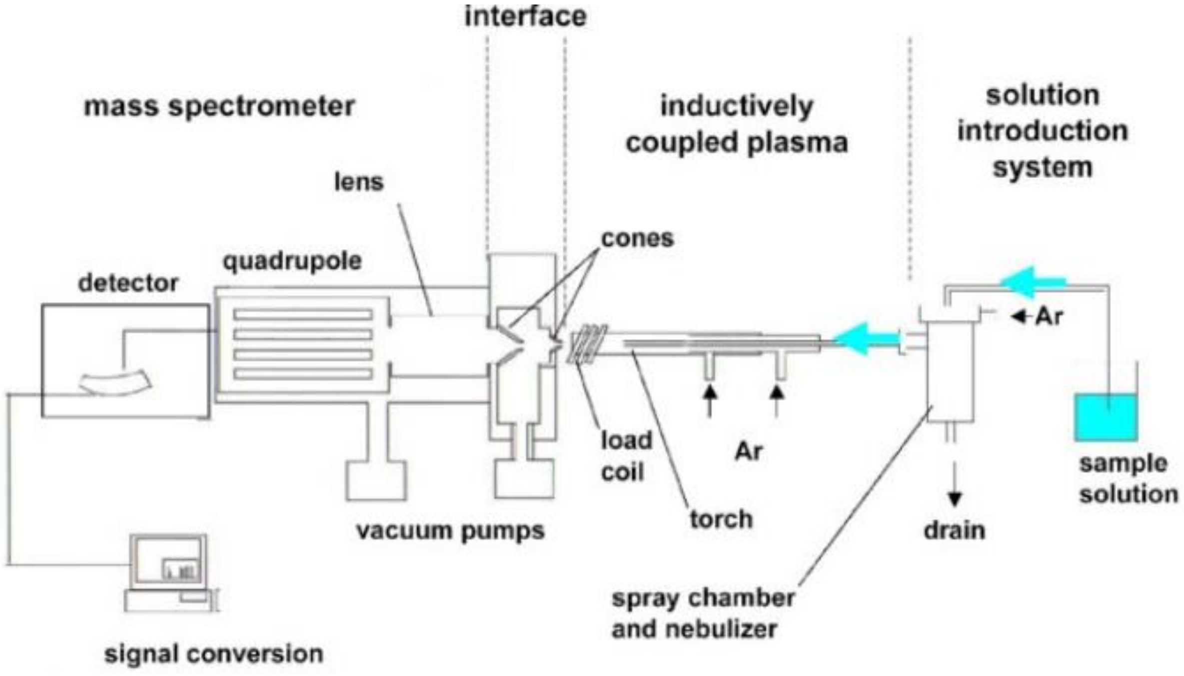

Figure 2.2: Schematic diagram of ICP-MS (Gilstrap, 2018)

X-Ray Fluorescence Spectroscopy uses X-rays to bombard the sample to produce a unique fluorescence spectra to identify the elemental composition of a sample. This is due to the inner orbital electrons of atoms in the sample getting excited by the bombardment of X-rays, which causes the atom to emit fluorescence in response. Figure 2.3 shows a typical setup for X-Ray Fluorescence Spectroscopy.

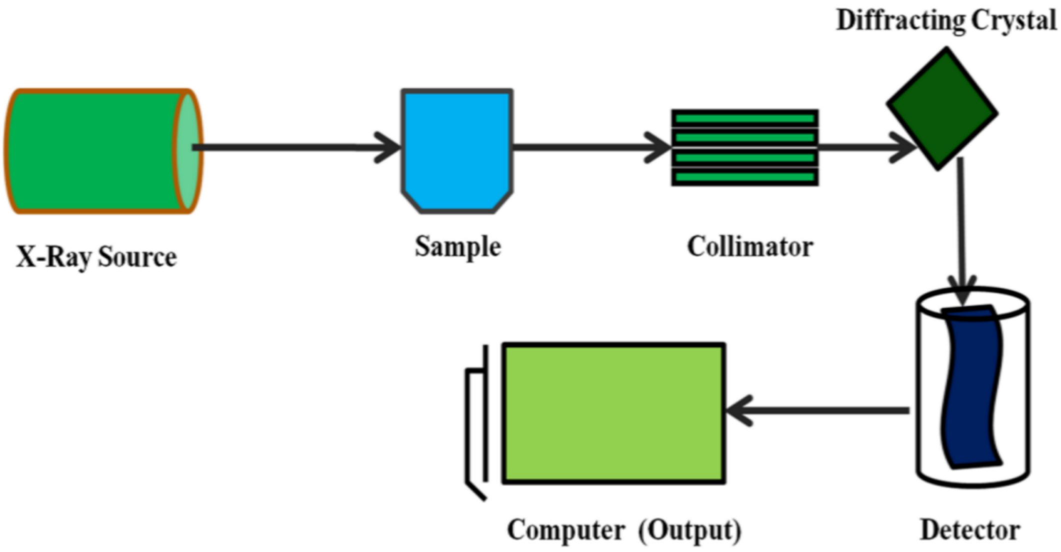

Figure 2.3: X-Ray Fluorescence Spectroscopy schematic (Malik et al., 2019)

While these spectroscopic methods are effective in detecting heavy metal ion presence in samples, they generally require expensive and heavy equipment, experienced operators and lengthy sample preparation and testing procedures. Thus, these spectroscopic methods are unsuitable for conducting on-site analysis and real-time monitoring of the presence of heavy metals in water sources. The long analysis procedures associated with these methods increase the risk of errors in the analysis (Pujol et al., 2014). These properties make the methods unsuitable for scaling up to real-time monitoring of heavy metal concentration in water sources. To overcome these weaknesses, methods that utilize chemical sensors have been developed.

Chemical sensors are defined by the IUPAC as devices to receive and analyze chemical information (Hulanicki et al., 1991). Chemical sensors consist of two main parts, a receptor to receive chemical information and a transducer, which produces a measurable signal in response to chemical information received. Chemical sensors are preferable to traditional spectroscopic methods due to various advantages associated with them, such as its relative low cost, good response times, selectivity and scalability (Bhardwaj et al., 2015), and being compact and easy to handle with minimum sample preparation (Stoytcheva et al., 2014). Notable examples of chemical sensors are optical sensors, electrochemical sensors and biosensors.

Optical sensors are chemical sensors that detect chemical information through its optical properties. Optical sensors can be categorized into two general categories, which are direct optical sensors and reagent-mediated optical sensors (McDonagh et al., 2008). Direct optical sensors measure chemical concentration via intrinsic optical property of the chemical, while reagent-mediated optical sensors detect the optical response of the detected chemical and a reagent, such as a dye, to measure the concentration of the chemical. Direct optical sensors are used whenever the analyte (detected chemical) has intrinsic optical properties, and reagent-mediated optical sensors are used for analytes without useful optical properties. Optical sensors such as Fiber Optic Chemical Sensors (FOCS), Planar Waveguide-Based Chemical sensors (PWCS), Optical Fluorescent Chemosensors and Optical Chemical Mesosensors have been developed for use in detection of heavy metals with some success (El-Safty et al., 2012). However, the optical sensors also face disadvantages such as interference from ambient light sources, photobleaching or indicator leaching of analytical reagent and poor selectivity (Lobnik et al., 2012).

Electrochemical sensors, by IUPAC definitions and classification, are a type of chemical sensor (Stoytcheva et al., 2014; Hulanicki et al., 1991). The transducer in the sensor collects information from the electrochemical reaction between the analyte and the electrode, and emits a measurable electrical signal, which can then be analyzed. These electrochemical sensors are further divided into different types, which are voltammetric sensors, potentiometric sensors, and conductometric sensors. These sensors are generally subjected to electrochemical methods such as amperometry, voltammetry, electrogenerated chemiluminescence techniques and electrochemical impedance spectroscopy (EIS) (Bakirhan et al., 2021). Generally, electrochemical methods measure the current generated as a potential is scanned across the solution in an electrochemical cell. These techniques are further explained in Section 2.3.

A biosensor is an analytical device that has an immobilized biocomponent such as enzymes connected with a transducer (Neelam et al., 2005). Biosensors are a diverse group of chemical sensors, encompassing many transduction mechanisms such as electrochemical, electrical, optical, thermal and piezoelectric (Turdean et al., 2011). Many types of biosensors have been developed, namely enzyme-based biosensors, protein-based biosensors, DNA-based biosensors, antibody-based biosensors (immunosensors), whole cell biosensors, and genetically engineered microorganism biosensors. However, while biosensors are generally versatile and have been developed to detect a wide range of environmental contaminants, it is still a developing field and current biosensors still face challenges such as poor commercial scalability and low specificity (Wang et al., 2014; Saidur et al., 2017).

2.4 Electrochemical detection of heavy metal presence in water samples

Electrochemical measurement techniques for the characterization of chemical systems and materials have been greatly expanded with the advancement of more complex electronics in recent decades, especially for the application of heavy metal ions detection. These techniques are important as the efficiency of electrochemical sensors greatly depends on the electroanalytical technique used.

Potentiometry is an old technique, which involves the application of an electromotive force without the application of current on the analyte to determine the concentration of the analyte (Malik et al., 2019). Potentiometry is based on liquid or polymer membrane materials and has been an established method since as early as the