INSTRUMENTATION MONITORING FOR HEAVY METAL DETECTION IN BATIK INDUSTRY

SARAVANAN A/L THUNSH KODI

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INSTRUMENTATION MONITORING FOR HEAVY METAL DETECTION IN BATIK INDUSTRY

by

SARAVANAN A/L THUNSH KODI

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ENDORSEMENT

I, Saravanan A/L Thunsh Kodi hereby declare that I have checked and revised the whole draft of dissertation as required by my supervisor.

(Signature of Student)

Date:

(Signature of Supervisor)

Name:

Date:

ENDORSEMENT

I, Saravanan A/L Thunsh Kodi hereby declare that all corrections and comments made by the supervisor and examiner have been taken consideration and rectified accordingly.

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(Signature of Student)

Date:

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(Signature of Supervisor)

Name:

Date:

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(Signature of Examiner)

Name:

Date:

DECLARATION

This thesis is the result of my own investigation, except where otherwise stated and has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any other degree.

SARAVANAN A/L THUNSH KODI

Date:

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ABSTRACT

A real-time monitoring of heavy metals in water environment is crucial nowadays because it is the biggest contributor to water pollution and leads to many diseases to humans. In contrast with organic pollutants, heavy metals cannot be biologically or chemically degraded at all, and thus may either accumulate locally or be transported over long distances. The wastewater discharge from Batik industries became a significant issue on the sustainability of the environment for the next generation. Heavy metal that exist in wastewater is an extremely dangerous pollutants to ecosystem and toxic to human health. The industry faces difficulty to monitor the waste discharge because the usual practice for analyses heavy metal work in central laboratories causes delay time and contamination of sample during transportation to central of laboratories leads to inaccuracy in data monitoring of heavy metals in water environment. This study proposes the development of instrument device to real-time monitoring heavy metal using an electroanalytical technique. This project introduced mathematical algorithm to represent the existing metal concentration in the solution based on statistical analysis from the data collection using laboratory control sample. In order to ensure the result more robust, the others significant parameter such as temperature and pH were considered during mathematical formulation development. For field work application, the effect of viscosity, pressure drop and condition of pipe for steady flow. The flow changes affect the measurement sensor reading due to the turbulent flow. However, the flow change inside pipe network can change the physical disturbance that can lead to inaccuracy of data measurement.

ABSTRAK

Pemantauan masa nyata logam berat di persekitaran air adalah penting pada masa kini kerana ia merupakan penyumbang terbesar kepada pencemaran air dan menyebabkan banyak penyakit kepada manusia. Berbeza dengan bahan pencemar organik, logam berat tidak dapat secara biologi atau kimia dihilangkan sama sekali, dan dengan itu boleh dikumpulkan secara tempatan atau diangkut dalam jarak jauh. Pelepasan air sisa dari industri Batik menjadi isu penting mengenai kelestarian alam sekitar untuk generasi akan datang. Logam berat yang wujud dalam sisa air adalah bahan pencemar yang sangat berbahaya kepada ekosistem dan toksik kepada kesihatan manusia. Industri menghadapi kesukaran untuk memantau pelepasan sisa kerana amalan biasa untuk menganalisis kerja logam berat di makmal pusat menyebabkan masa kelewatan dan pencemaran sampel semasa pengangkutan ke pusat makmal membawa kepada ketidaktepatan dalam pemantauan data logam berat dalam persekitaran air. Kajian ini mencadangkan pembangunan peranti instrumen untuk pemantauan masa nyata logam berat menggunakan teknik elektroanalitikal. Projek ini memperkenalkan algoritma matematik untuk mewakili kepekatan logam sedia ada dalam larutan berdasarkan analisis statistik dari pengumpulan data menggunakan sampel kawalan makmal. Untuk memastikan hasilnya lebih mantap, parameter lain yang penting seperti suhu dan pH dipertimbangkan semasa pembangunan perumusan matematik. Untuk aplikasi kerja lapangan, kesan kelikatan, penurunan tekanan dan keadaan paip untuk aliran mantap. Perubahan aliran memberi kesan bacaan sensor pengukuran disebabkan oleh aliran turbulen. Walau bagaimanapun, perubahan aliran di dalam rangkaian paip boleh mengubah gangguan fizikal yang boleh menyebabkan ketidaktepatan pengukuran data.

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LIST OF ABBREVIATIONS

DOE	Department of Environment
CVAAS	Cold Vapor Atomic Absorption Spectrometer
AAS	Atomic Absorption Spectrometry
FAAS	Flame Atomic Adsorption Spectroscopy
AES	Atomic Emission Spectrometry
ICP-MS	Inductive Coupled Plasma Mass Spectrometry
ICP-AES	Inductive Coupled Plasma with Atomic Emission Spectrometry
BOD	Biological Oxygen Demand
WHO	World Health Organization
COD	Chemical Oxygen Demand
IDE	Integrated Development Environment
PWM	Pulse Width Modulation
LOD	Limit of Detection
DPV	Differential Pulse Voltammetry
SWV	Square Wave Voltammetry
SCP	Stripping Chronopotentiometry
GND	Ground
VCC	Voltage Common Collector
EC	Electric Conductivity
TDS	Total Dissolved Solid
SEC	Specific Electrical Conductivity
ASV	Anodic Stripping Voltammetry
CSV	Cathodic Stripping Voltammetry

LIST OF SYMBOLS

$\boldsymbol{k}$	Electric conductivity factor
$\boldsymbol{\alpha}$	Temperature compensation factor
mS/cm	Millisiemens per centimeter
$\boldsymbol{T}$	Temperature
ppm	Parts per million
$\boldsymbol{V}$	Voltage
$\boldsymbol{C}$	Concentration
$\boldsymbol{v}$	Volume
$\boldsymbol{\chi}$	Conductivity
$\boldsymbol{R}$	Resistance
$\boldsymbol{\rho}$	Resistivity
$\boldsymbol{L}$	Length of the electrode
$\boldsymbol{A}$	Cross section area
$\boldsymbol{K_c}$	Cell constant

CHAPTER ONE

INTRODUCTION

1.1 Research Background

Malaysian batik is the local craft with the process of drawing fine lines or dots of wax on the surface of fabrics to stimulate its design to avoid absorbing colours during the dyeing process (Akhir and Ismail, 2015). Commonly, batik industry brings out the uniqueness with variety of colours and design that makes it to be an identity to Malaysia and recognize by local people. Furthermore, United Educational, Scientific and Cultural Organization (UNESCO) has recognized batik craft as a living cultural heritage which relates to the traditions inherited form ancestors to the future generations which creates a better opportunity to globalize the Malaysia's batik industry (Akhir et al., 2018).

As the country's eleventh largest exporter, the textile industry has contributed approximately RM15.3 billion which is 16% of the Malaysia's total export of goods in 2017 making USA the leading importer of Malaysia's textile products with RM2.2 billion (14.6%) followed by Japan and Turkey (MIDA, 2019).

The process of making batik is the art of the workmanship making designs on a piece of fabric. The process starts with using melted wax painted or stamped onto a white or a coloured fabric before being dyed because the waxed areas are inaccessible by the dye (WIDIHASTUTI, 2014). Next the stamped fabric undergoes bleaching process to remove the remove the unwaxed regions colour leaving the design of the waxed region. The bleached fabric is then dyed again on the other part of the fabric without wax before smoked to obtain a nuanced background. Finally, the fabric is boiled to remove the wax to get a magnificent result.

The major problem that caused by the batik industry is discharge of wastewater during soaking, boiling and rinsing without proper treatment procedure. The waste discharged are in large amounts with high concentration of pollutants such as heavy metals requires an extra attention on the treatment part before releasing to the environment because the waste discharged to the nearby rivers can cause the underwater aquatic life to be affected (Subki and Rohasliney, 2011).

The figure 1.1 below shows the polluted river in China by textile industry discharging untreated waste water out of secret underground pipes directly into rivers in China exceeding permissible levels of discharge pollutants and failing to use the water treatment facilities (Zimmer, 2012).

Figure 1.1: Polluted river in China (Zimmer, 2012)

1.2 Problem Statement

The general responsibility practice of the industrial wastewater treatment and the Department of Environment (DOE) are to collect the wastewater samples manually at different locations such as the waste storage tank and final discharge point (Altin et al., 1999). After that, the samples are transported to the laboratories to analyse the concentration of effluents present in the wastewater and how much toxic it is. The problem occurs during the transportation process of the samples to the laboratories. It will affect the heavy metal contents in the sample because of the presence of light exposure, precipitation and dissolved oxygen and leads to inaccuracy of data results (Li et al., 2013).

To overcome this problems, modern method analysis was introduced because this method is more selective and sensitive compared to the conventional method which is collecting samples and analysing it at laboratories. There are various techniques introduced as the technology is improving such as Cold Vapor Atomic Absorption Spectrometer (CVAAS), Atomic Absorption Spectrometry (AAS), Atomic Emission Spectrometry (AES), Inductive Coupled Plasma Mass Spectrometry (ICP-MS) and Inductive Coupled Plasma with Atomic Emission Spectrometry (ICP-AES) (Baysal et al., 2013). Due to its complexity to get hands on these devices, small scale industries show less interest to these devices because of high cost, specialized technique requirements and size matters for field work applications.

1.3 Research Objective

This study aims to determine the possible method to be used as an analytical instrument to monitor the content of heavy metal in wastewater at industries for both theoretical and practical work. During this study, several features have been highlighted such as data developing system, mathematical formulation, the characteristics of heavy metals, and the fundamental of the sensors. In general, the objective of this project is:

1. To set up a sub scale heavy metal monitoring instrument in a laboratory scale.
2. To identify the significant parameters in heavy metal monitoring process.
3. To design a parameter control system for optimal and effective heavy metal monitoring.
4. To monitor the heavy metal discharge for real-life application in batik industry.

1.4 Research Scope

The project is about the development of integrated process device and algorithm to monitor the heavy metal discharge form textile industry, for this paper it focuses on batik wastewater. The heavy metals that exist in the wastewater comes from the dyes during the dyeing process.

In this work, the amount of heavy metals content in the wastewater will be detected by using electroanalytical method based on the amount of ionic charges. With sensors and integrated board controlled by computer, the system will be more efficient, easy to operate and lower installation cost because the system can be portable for detection of heavy metal with user friendly accessibility. Besides, the program will be developed using Arduino IDE to evaluate and identify the heavy metal contents from wastewater.

The portable devices can be achieved by software and code to monitor, collect data, process and transmit the data. Heavy metal sensing unit and mathematical algorithm are used to identify the heavy metal present in the intermediate process. The final discharge concentration of the solution will be analysed and compare with the literature survey method and establish equipment method.

1.5 Thesis Outline

The FYP thesis consists of five main chapters that describe the detailed development process from introduction to conclusion of this project. Chapter 1 is started with an introduction of this project. A brief explanation of the whole project is discussed through the project background, problem statement, project scope and project objective. Chapter 2 describes about the brief review and theoretical background from relevant literature source. The theory of components used in this project are discussed and explained for fundamental understanding of the project.

Next, the methodology process is described in Chapter 3. This chapter starts by explaining the overall project flow involved with clear explanation for better understanding about the project. The explanations include the sample preparation, design process, fabrication process, mechanism development performance and the integration software and hardware.

Besides, Chapter 4 provides the results of the analysis done in this project for theoretical and simulation. The results and discussion of the analysis are provided and shows the functionality of the instrument developed. The results are also discussed in detail for each of experiment. In Chapter 5, the conclusion of this project is discussed. This chapter concludes the projects with future recommendations.

CHAPTER TWO

LITERATURE REVIEW

2.1 General View of Heavy Metal Monitoring System

2.1.1 Introduction to Heavy Metal

The transition and post-transition metals are referred as heavy metals because these elements are listed in the Periodic Table from group 3 to 16 that are in periods 4 and greater (Hawkes, 1997). Hawkes stated that these metals are given the name heavy metals because they have high densities of 5 gram per centimetre cubic and above.

Furthermore, metals are found naturally in the earth's crust and their compositions vary among different locations. These metals have the properties like high electrical conductivity, highly malleability, and they donate electrons to form cation ions (Jaishankar et al., 2014). Jaishankar mentioned in his paper that metals become poisonous when they exceed certain amount of concentration because they maintain various biochemical and physiological function in living organisms during low concentration state and that’s why these metals are called unique. Jaishankar also acknowledged that heavy metals have many harmful health effects and can last for a long period of time.

Recently, the exposure of heavy metals has raised exponentially with respect to the development several fields such as industrial, agricultural, domestic and technological applications and it raises these issues of ecological and global public health awareness (Tchounwou et al., 2012).

2.1.2 Source of Heavy Metals Contamination in Environment

Organic compound and inorganic compounds are two classifications that can be related to industrial waste of heavy metals. Organic compound exists as covalent bond because it does not dissolve in water whereas inorganic compound cation ions donates electron to the anion ions and forms ionic bond and dissolves in water.

This paper concerns the main pollution of heavy metal discharged from textile industry because the industry discharges toxic waste containing Cu, Pb, Cr, Fe, Ni and Zn (Phugare et al., 2011). The heavy metal effluent is discharged during the dyeing, bleaching, printing, finishing and cleaning process (Pandey et al., 2017). Dyeing and printing process contributes the main source of heavy metals in textile industries because the waste water consists strong colour with acidic pH, high chemical oxygen demand (BOD), high suspended solids and consists chlorinated organic compounds (Phugare et al., 2011, Verma et al., 2012).

Besides, the heavy metal pollution is also caused by the mining activity and it contributes a big impact to our aquatic ecosystem due to serious pollution of the water resources nearby the mining quarry (Kapusta and Sobczyk, 2015). The increment of sediment level of metal contamination in the nearby streams are caused by the acid mine drainage which leached through the ground and lastly dissolves with the water source (ground water) (Ali et al., 2016).

The chemical separation of metals occurred as the precipitation from the solid materials are transported with high content of toxic elements such as As, Cd, Pb, Zn, Cu, Sb, and Se together during rainfall to the streams (Gabrielyan et al., 2018). Therefore, the acidic drainage and the release of wastewater containing high concentrations of dissolved metals form the mining quarry will pollute the water system, hence affecting the aquatic ecosystem.

Once the heavy metal waste enters the water source, the aquatic life is harmed through chemical adsorption process which later can enter human body and affects human health when they consume the underwater organisms such as fish and plants. Besides, the physical precipitate from the heavy metals will accumulate in the sediments of the water environment (Gao et al., 2014). The content level on the surface sediments are said to be higher compared to the content level in the water body.

2.1.3 Effect of Heavy Metals Exposed to Humans

WHO which is an international body has been regularly reviewing and studying extensively of most of the threats occurred to human health from heavy metals waste that are associated with the exposure of lead, cadmium, mercury and arsenic which brings major impact to the human health (Jarup, 2003). The exposure of heavy metals is increasing in some areas through emissions although the harmful effects of heavy metals have been given awareness to the public.

The toxicity of metal ions is due to chemical reaction between the ions with the internal structure of the human body such as the cellular structural proteins, enzymes and membrane system. The main target of these metal ions are the organs which accumulate the highest concentration of the metal (Mahurpawar, 2015). The target organs and the clinical effects of chronic exposures to the metal are summarized in the table 2.1 below.

Table 2.1: Effect of heavy metals to humans

Metals	Target Region	Primary Source	Clinical Effects
Mercury	Nervous system, Renal	Industrial dust, fumes and polluted food and water	Proteinuria
Tin	Nervous pulmonary system	Medical uses, industrial dust	Central nervous system disorders, visual defects and EEG changes, pneumoconiosis
Nickel	Pulmonary, skin	Industrial dust, aerosols	Cancer, dramatis
Lead	Nervous system, hematopoietic system, renal	Industrial dust and fumes and polluted food	Encephalopathy, peripheral neuropathy, central nervous disorders, anemia
Arsenic	Pulmonary nervous system, skin	Industrial dusts, medical uses of polluted water	Perforation of nasal septum, respiratory cancer, peripheral neuropathy, dermatomes, skin, cancer
Cadmium	Renal, skeletal pulmonry	Industrial dust and fumes and polluted food	Proteinuria, clucosuria, osteomalacia, aminoaciduria, emphysemia
Chromium	pulmonary	Industrial dust and fumes and polluted food	Ulcer, perforation of nasal septum, respiratory cancer
Manganese	Nervous system	Industrial dust and fumes	Central and peripheral neuropathies

Besides the general toxicities of metals, many of us are concerned with the risk of heavy metal that have the potential carcinogenicity of metal compounds. From table 2.1, metals such as Chromium and Nickel have linked with cancers when exposed human populations. Metals have been shown to chronic poisoning to humans and animals. The Table 2.2 below shows the acceptable condition of wastewater discharge extracted from Environmental Quality (Industrial Effluents) Regulations 2009, fifth schedule that every responsibility should take into consider.

Table 2.2: Acceptable limit from Department of Environment (DOE) standard discharge (Environment, 2009)

Parameter	**Standard Requirements of Waste**
Temperature	40 ^{o}C
pH value	5.5 - 9.0
TSS	100*mg/L*
COD	250*mg/L*
BOD	40*mg/L*
Zinc	2.0*mg/L*
Chromium	1.0*mg/L*
Copper	1.0*mg/L*
Iron	5.0*mg/L*
Lead	0.5*mg/L*
Cadmium	0.02*mg/L*

2.2 Hardware Instruments for Heavy Metal Monitoring

2.2.1 Microcontroller

Arduino is an example microcontroller which can be programmed and reprogrammed easily. Arduino platform was introduced in 2015 to connect devices such as sensors and actuators in an inexpensive and easy way (Louis, 2016). Arduino microcontroller has becoming a popular platform especially for students for their projects because it has the access to program mostly any device for them to obtain data and results as it is a user-friendly device. Arduino acts as a minicomputer because it can read the inputs written by the user and control the outputs by constructing algorithms and program the electronic devices through the internet with the help of various Arduino shields.

Arduino IDE (Integrated Development Environment) is the Arduino development board and software for developing algorithms has built in with 8-bit Atmel AVR microcontrollers can be easily programmed with C or C++ language in the Arduino IDE.

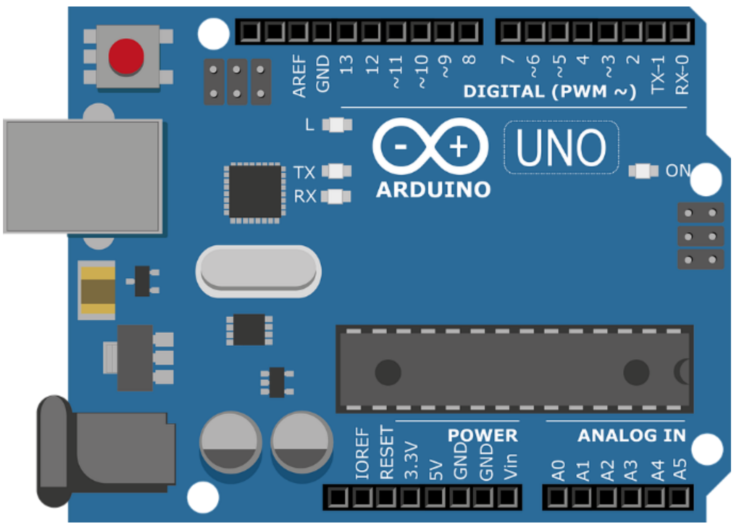

Figure 2.1: Arduino UNO board

From Figure 2.1, the length of the Arduino UNO board is about 68.64*mm* and the width of the microcontroller is about 53.4*mm*. The board also consists of pulse width modulation (PWM). These PWM are used to transmit the entire signal in a pulse modulation to eliminate harmonic and reducing the output of the inverter to achieve a controlled output voltage (Jalnekar and Jog, 2000). There are different PMW techniques available for users such as Square-Wave, Sinusoidal, and Regular-Sampled.

Besides, Arduino UNO consists of 14 input output analog and digital pins which uses ATMEGA-328 microcontroller. The Arduino board can be either powered by power jack cable connected to the computer with USB type cable or connect directly to the power supply. The maximum input voltage supported by the board is 12*V* and the recommended input voltage suggested was 7*V* to power the board efficiently but, the actual operating voltage is 5*V* (Sudhan et al., 2015). The DC current input given to the microcontroller is 40*mA*. From the analog inputs, the users can gain the voltage supply from the range of 0*V* to 5*V* with the addition of resistors to the electronic devices.

2.2.2 Electric Conductivity (EC) Sensor

Electrochemical device is well suited for miniaturization and automatic measurements requiring minimal sample changes be it does not need substance or mixture for the use in chemical analysis and other reactions. Therefore, the contamination by reagents or losses by adsorption can be decreased (Yantasee et al., 2007). Therefore, it just requires simple procedure to operate this electrochemical device as it is compactible to bring elsewhere and user-friendly. Moreover, Yantasee had said in his journal that on-line monitoring of water sample is possible because this electrochemical system helps to gain fast analyses experimental data providing dynamic data of relevance for biogeochemical survey.

As technology develops from day to day, specific developments are required for such applications to improve sensitivity, limit of detection (LOD) and automation. Many electrochemical techniques with different imposed potential or current modulations have been developed such as differential pulse voltammetry (DPV), square wave voltammetry (SWV) or stripping chronopotentiometry (SCP) (Pujol et al., 2014). Another analytical performance with respect to heavy metals detection concerns the selectivity. Pujol stated in his paper that in complex media, the signal of the analytical target often experiences interferences due to the presence of other species (sometimes other heavy metals) and to solve this problem, several surface functionalization strategies have been developed for many years to improve sensors selectivity.

Figure 2.2: Analog electrical conductivity sensor (DFRobot, 2018)

Figure 2.2 shows the analog electrical conductivity meter V2 is specially used to measure the electrical conductivity of the aqueous solution and to evaluate the water quality. It supports 3*V* - 5*V* wide voltage input and it is compatible with 5*V* and 3.3*V* main control board. The output signal filtered by hardware which has low jitter which effectively reduces the polarization effect, improves the precision and prolongs the life of the probe.

The probe uses the conductivity method between the ions in the aqueous solution. Conductivity by definition is the reciprocal of the resistivity, which is related to the ability of the material to carry the current. In the liquid, the reciprocal of the resistance, the conductivity, is the measure of its ability to conduct electricity. Conductivity is the important parameter of water quality. It can reflect the extent of electrolytes present in water.

Table 2.3: Signal Conversion Board (Transmitter) V2 specifications (DFRobot, 2018)

Board dimension (*mm*)	42 x 32
Voltage supply (*V*)	3 - 5
Output voltage (*V*)	0 - 0.34
Probe connector	BNC
Signal connector	PH2.0-3 Pin
Measurement accuracy	±5% F.S.

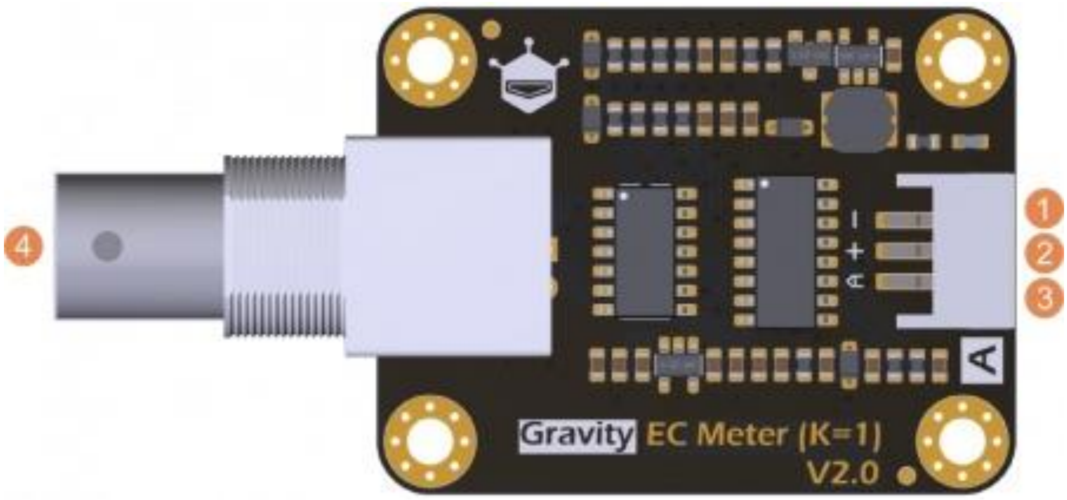

Figure 2.3: Signal Conversion Board (Transmitter) V2 (DFRobot, 2018)

Table 2.4: Board connection (DFRobot, 2018)

Number	Label	Description
1	-	Power GND (0*V*)
2	+	Power VCC(3.0~5.0*V*)
3	A	Analog Signal Output(0~3.4*V*)
4	BNC	Probe Connector

Table 2.5: Electrical Conductivity Probe specifications (DFRobot, 2018)

Probe type	Laboratory grade
Cell constant	1.0
Support detection range (*mS/cm*)	0-20
Recommended detection range (*mS/cm*)	1-15
Temperature range (*°C*)	0-40
Probe life	More than 0.5 year (depending on frequency of use)
Cable length (*cm*)	100

2.2.3 Temperature Sensor

The temperature measurement with the combination of DS18B20 waterproof sensor and Arduino contributes to user-friendly and relatively low cost to be used for data acquisition system (Koestoer et al., 2019). It is widely used to measure temperature at extreme conditions like in chemical solutions, mines or soil etc and the constriction of the sensor is rugged with waterproof option making the mounting process easy. The Figure 2.4 shows the temperature sensor's pinout labelling.

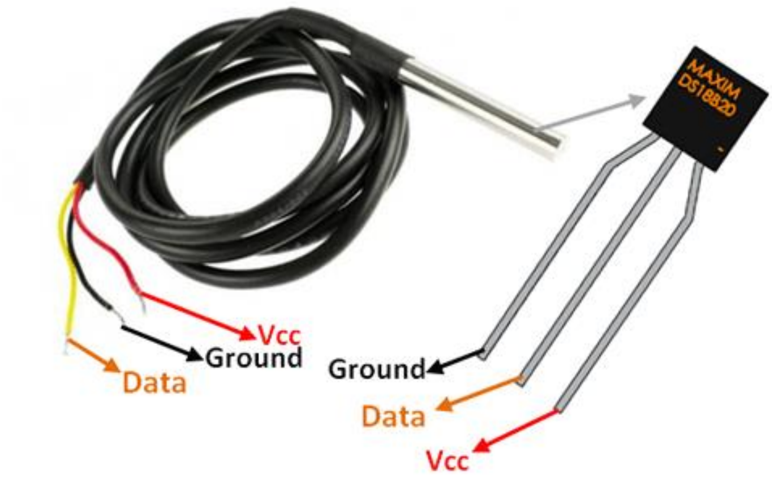

Figure 2.4: DS18B20 Temperature Sensor (Components101, 2018)

Table 2.6: Temperature sensor pin configuration (Components101, 2018)

No	Pin Name	Description
1	Ground	Connects to the ground
2	Vcc	Connects to the power ($3.3V$ or $5V$)
3	Data	Gives output value which reads using 1-wire method

DS18B20 Waterproof sensor operates in range of temperature -55°C to +125°C with ± 0.5°C error at -10°C to +85°C and has an 0.0625°C accuracy and the linear scale of voltage and temperature of the sensor is +10.0mV/° C (Integrated, 2015).

2.3 Relatedness of Parameters Relates to Heavy Metals Monitoring

2.3.1 Relationship Between EC and TDS

Electrical conductivity (EC) is defined as the measure of the liquid capacity to conduct electric charge and it depends on the dissolved ion concentration and temperature. The dissolved ion concentration is measured as total dissolved solid (TDS) because each of them are interrelated (Patil. et al., 2012).

EC can be measured easily with less cost by using a portable water quality checker probe but the analysis of TDS is hard and expensive because it requires high technological equipment and consumes some time (Rusydi, 2018). Hence, researchers have done investigations to relate these two terms with a precise mathematical correlation so that TDS can easily calculated from the EC value. The relationship between the two parameters has been estimated by the following equation:

$$\boldsymbol{TDS\ (mg/L) = k\ x\ EC\ (\mu S/cm)} \qquad (2.1)$$

The value of *k* acts as a factor and will increase with the respect to the concentration of ions in the liquid but the relationship between EC and TDS are not directly proportional because it relates with the ionic strength (Hayashi, 2004).

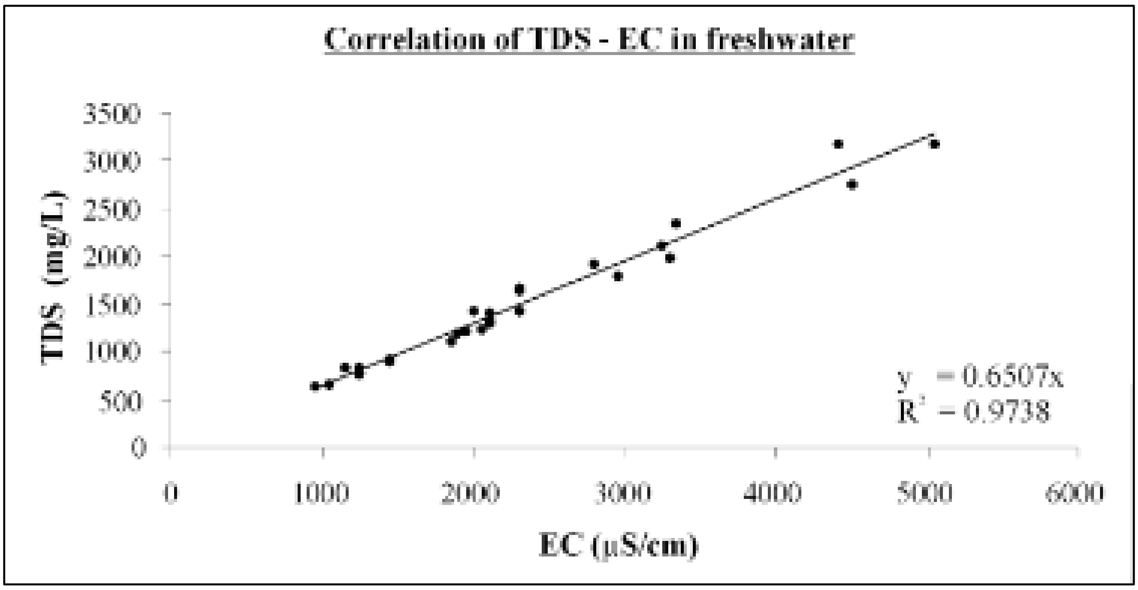

Figure 2.5: Relationship between EC and TDS in freshwater (Rusydi, 2018)

From the research paper, the value of k has been calculated and written as the following equation:

$$\boldsymbol{TDS\ (mg/L) = 0.65\ x\ EC\ (\mu S/cm)} \tag{2.2}$$

2.3.2 Relationship Between EC and Temperature

EC values are dependent to temperature of a solution because the movement of ions becomes faster when there is an increment in the temperature value. The values of EC are technically referred as specific electrical conductivity (SEC) because the EC data are corrected to $25°C$ (Hayashi, 2004).

Hayashi also mentioned that the EC–Temperature correlation of natural water is basically nonlinear but due to the degree of nonlinear is very small in range from $0°C$ to $30°C$ and as arbitrary constant is used for temperature compensation assuming the relationship between EC and temperature is linear. The linear equation that represent the relation stated by Sorenson and Glass, 1987 is:

$$\boldsymbol{EC_t = EC_{25}[1 + \alpha(t - 25)]} \tag{2.3}$$

where EC_t is the electrical conductivity at specific temperature, EC_{25} is the electrical conductivity at 25°*C* and α is the temperature compensation factor with the unit (°C^{-1}).

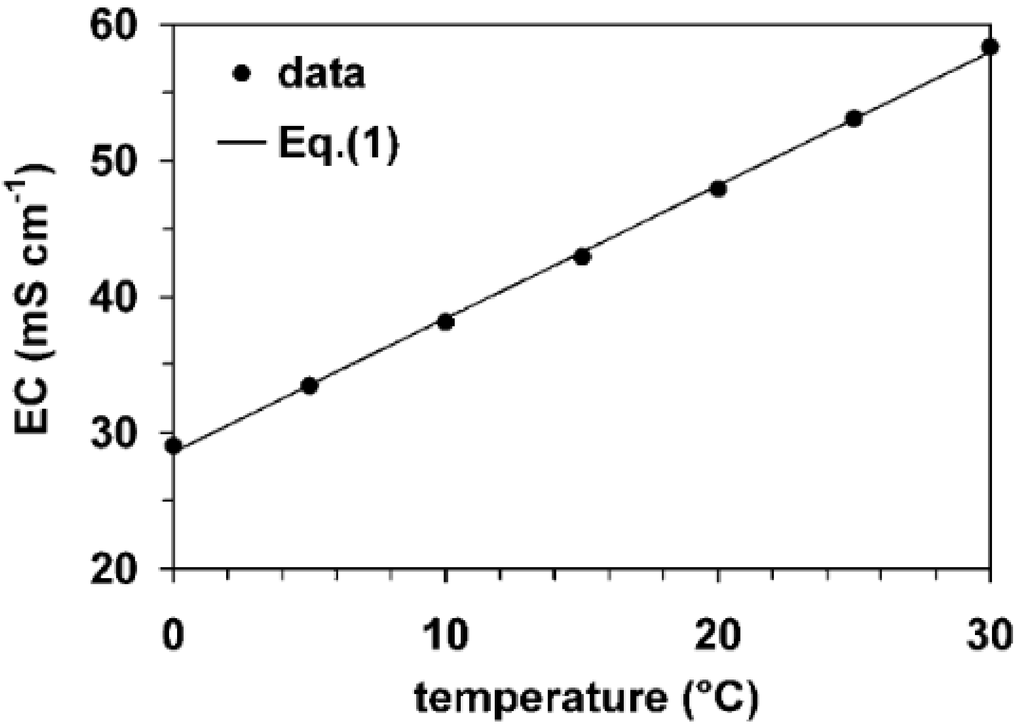

Figure 2.6: Relationship between EC and temperature of standard seawater (Hayashi, 2004)

2.4 Electroanalytic Method of Monitoring Heavy Metals in Liquid Solutions

2.4.1 Voltammetry Technique

The current response with respect to the potential voltage applied to the voltammetric cell is known as voltammetry. The voltammetric method compromising the combination of voltage and amperometry (Fischer and Fischerová, 1995). In another words, it is the measurement of electric current flowing through the cell that carried by the ions in a liquid solution. In the electroanalytic chemistry, stripping voltammetry (SV) is one of the important techniques that has an extremely low limit of detection (LOD).

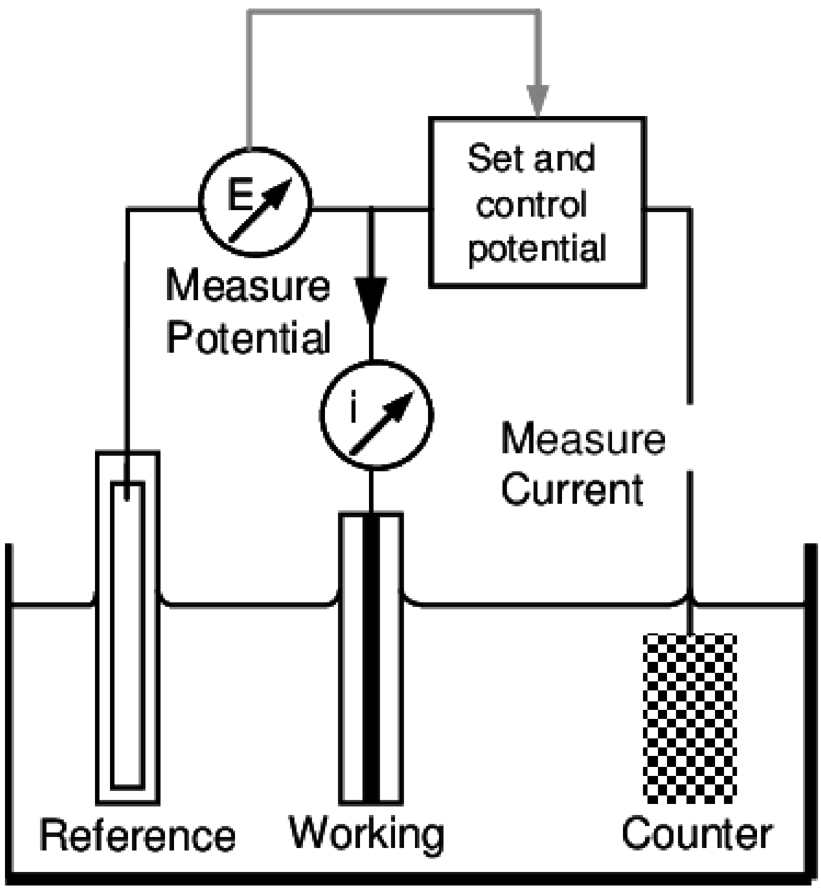

Figure 2.7: Schematic drawing of the voltammetry with 3 electrodes (Patel et al., 2007)

The current response is proportional to the analyte concentration when subsequent stripping steps where the preconcentrated analyte was stripped back into the solution making it to have an excellent sensitivity and well suited for automated online measurements (Pujol et al., 2014). In addition, it utilizes low cost instrumentation because it offers multielement and evolution capabilities for monitoring system purpose.

Stripping voltammetry can also be divided into two categories which are anodic stripping voltammetry (ASV) and cathodic stripping voltammetry (CSV) but they differ in functions such as preconcentration and stripping steps. For ASV, it is more favourable towards more positive potentials to determine anodic currents and cathodic preconcentrating step is taken but, for CSV it is the vice versa.

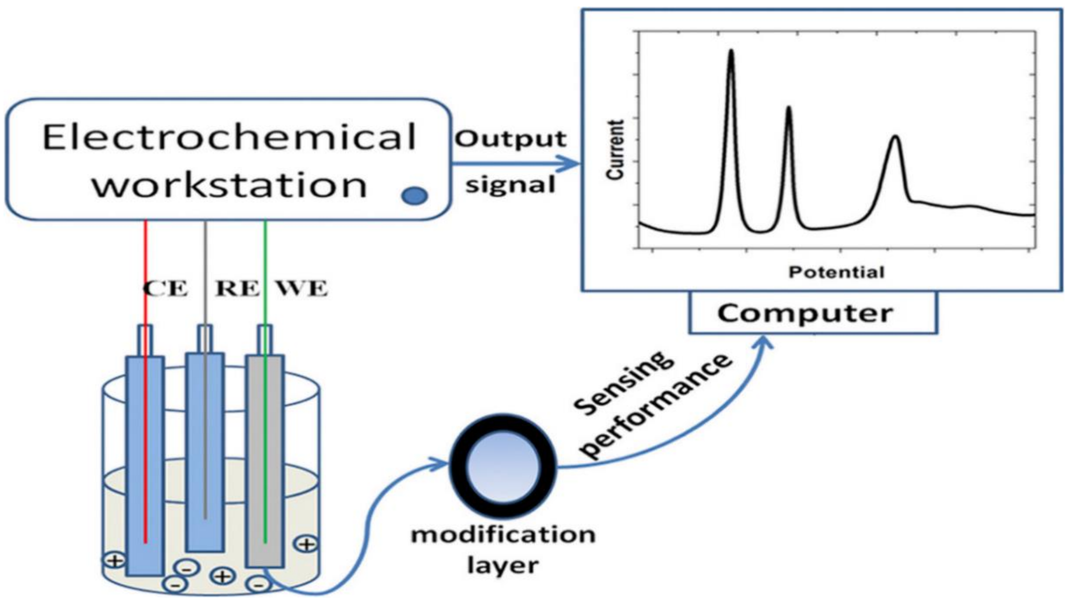

Figure 2.8: Working principle of voltammetry

From the published journal by Thipnet et al., 2016, a portable cyclic voltammetry sensor containing electrode that uses gold wire (for working electrode), silver wire (for counter electrode) and platinum wire (for reference electrode) was invented for the simultaneous determination of lead (Pb), cadmium (Cd) and copper (Cu). In his result and discussion, Thipnet mentioned that a portable system is possible to trace heavy metal contamination due to the high sensitivity and good reproducibility of the unharmful gold, silver and platinum wire. During his experiment by Thipnet, the successive voltammograms of the gold electrode has the ability to read the voltage range from -1.30V to 1.30V as shown in Figure 2.9 and the electrode showed a linear analytical response ranged from 10$\mu g/L$ to 50$\mu g/L$ as shown in Figure 2.10.

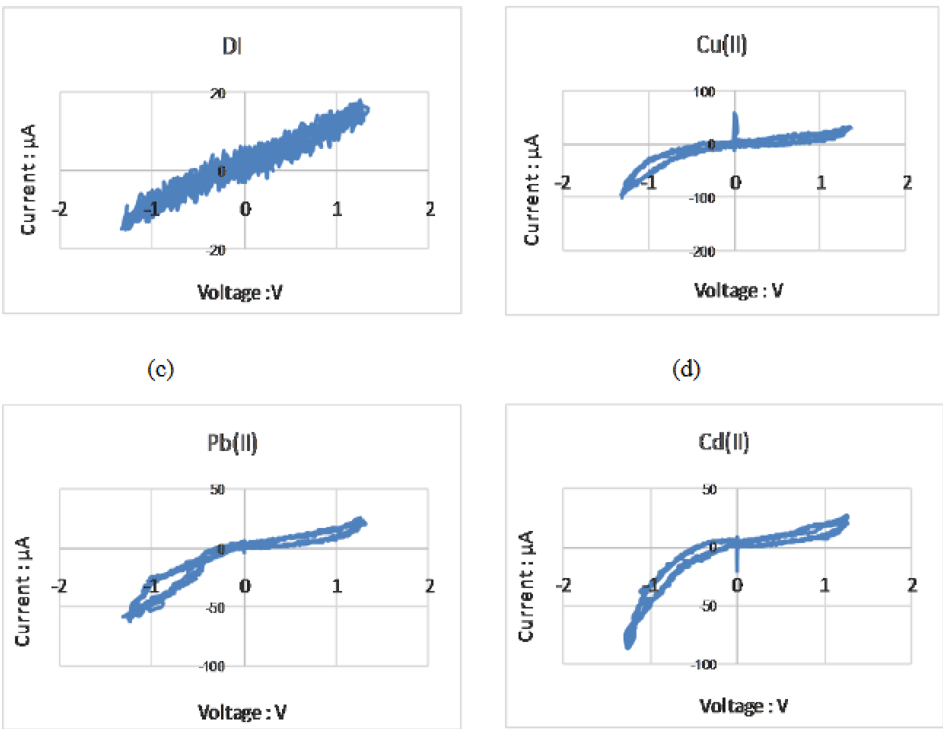

Figure 2.9: Successive voltammograms of deionized water (DI), copper (Cu), lead (Pb) and cadmium (Cd) at 20$\mu g/L$ (Thipnet et al., 2016)

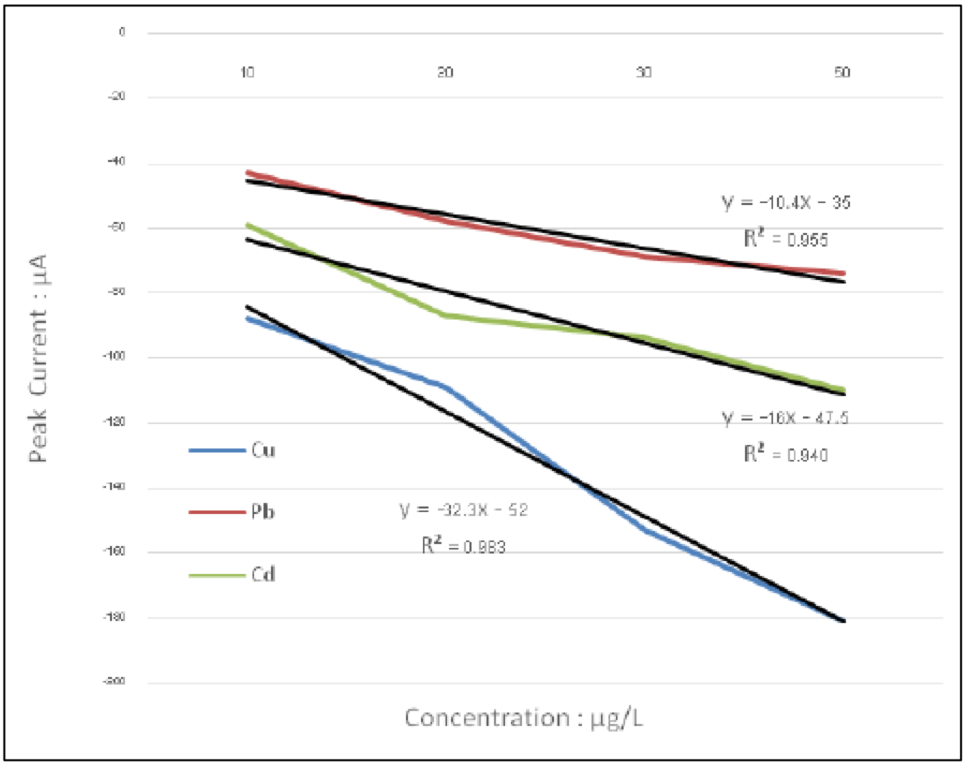

Figure 2.10: Peak current against concentration of copper (Cu), lead (Pb) and cadmium (Cd) (Thipnet et al., 2016)

2.4.2 Atomic Absorption Spectroscopy (AAS) Technique

AAS plays an important role in analytical method to estimate different atoms through the measurement of light energy with emits specific wavelength which helps to detect the concentration of different elements with a higher degree of sensitivity and precision (Sudunagunta et al., 2012). Sudunagunta also added that AAS can be classified as a modern analytical laboratory equipment which can be used in many fields such as food, biological, geological metallurgical, environmental forensic and marine application.

Furthermore, AAS is used to measure the absorbed radiation of the chemical quantities present in the environmental samples by reading the spectra produced when