THE DEVELOPMENT OF INSTRUMENT FOR REAL-TIME MONITORING OF HEAVY METAL DISCHARGE FOR BATIK INDUSTRY

MOHAMMAD NIZAR BIN MOHAMED ZUKRI

UNIVERSITI SAINS MALAYSIA

2019

THE DEVELOPMENT OF INSTRUMENT FOR REAL-TIME MONITORING OF HEAVY METAL DISCHARGE FOR BATIK INDUSTRY

by

MOHAMMAD NIZAR BIN MOHAMED ZUKRI

Thesis submitted in fulfilment of the
requirements for the Degree of
Master of Science

June 2019

ACKNOWLEDGEMENTS

In the name of Allah, the Most Gracious, the Most Merciful.

Praise to Allah SWT, whom giving me strength and perseverance to complete my master research.

I take this opportunity to express my profound gratitude and deep regards to my supervisor, Professor Madya Dr. Elmi Bin Abu Bakar for his exemplary guidance, monitoring and constant encouragement throughout the research of this master project. The blessing, help and guidance given by him from time to time shall carry me through a long way in the journey of life in which I am about to embark.

I also take this opportunity to express a deep sense of gratitude to Professor Dr. Mohd Suffian Bin Yusoff and Dr. Ahmad Zulfaa Bin Mohammed Kassim for their cordial support, valuable information and guidance, which helped me in completing this task through various stages. I also want to express my deepest appreciation to Professor Dr. Naoki Uchiyama for the guidance and facilities prepared during my research work in Toyohashi University of Technology (TUT). I am also gratefully acknowledged the funding received towards my Master studentship from the Research University Grant Top-Down Grant to assist me financially during my research work.

I am obliged to the members of Innovative System and Instrumentation (ISI) laboratory, technicians, colleagues and staff for the valuable information provided by them in their respective fields. I am grateful for their cooperation and support during the period of my research.

Finally yet importantly, I thank Almighty, my parents, brothers, sisters and friends for their constant encouragement without which this research would not be possible.

TABLE OF CONTENTS

CHAPTER ONE: INTRODUCTION

CHAPTER TWO: LITERATURE REVIEW

CHAPTER THREE: METHODOLOGY

CHAPTER FOUR: RESULTS AND DISCUSSION

CHAPTER FIVE: CONCLUSION AND FUTURE WORK

APPENDICES

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATION

AAS	Atomic Absorption Spectrometry
ADC	Analog Digital Converter
AES	Atomic Emission Spectrometry
ASV	Anodic Stripping Voltammetry
BOD	Biological Oxygen Demand
CBF	Clean Batik Initiative
CCM	Computer Color Matching
CFD	Computer Finite Difference
CSTR	Continuous Stirred Tank Reactor
COD	Chemical Oxygen Demand
CVAAS	Cold Vapor Atomic Absorption Spectrometer
DO	Dissolved Oxygen
DOE	Department Of Environment
EC	Electrical Conductivity
GUI	Graphical User Interface
ICP-AES	Inductive Coupled Plasma Atomic Emission Spectrometer
ICP-MS	Inductive Coupled Plasma Mass Spectrometry
IDL	Instrument Detection Limit
IETS	Industrial Effluent Treatment System
MF	Micro Filtration
NF	Nano Filtration

NTU	National Turbidity Unit
P	Proportional
PI	Proportional and Integral
PID	Proportional, Integral and Derivative
PWM	Pulse Width Modulator
RO	Reverse Osmosis
RPD	Relative Percentage Difference
SME	Small and Medium Enterprise
SSE	Steady State Error
TDS	Total Dissolved Solid
TSS	Total Suspended Solid
T-T	Thymine-Thymine
1-D	One Dimensional

LIST OF SYMBOL

α	Temperature coefficient
A	Surface area of electrode
AV	Average voltage
C	Concentration of ion
CV	Coefficient voltage
C_d	Coefficient of discharge
D	Hydraulic diameter
E	Applied potential
G	Conductance
I	Current
Kbps	Kilobits per second
K_c	Cell constant
L	Distance between cell electrodes
Ƞ	Viscosity of solvent
ρ	Pressure drop
P	Poise
$Pa.s$	Pascal second
ppm	Part per million
Q	Flow rate discharge
R_e	Reynold number

R	Solvate radius
S	Siemens
St	Stokes
T	Temperature
u	Mobility of an ion
U	Instantaneous velocity
v_i	Number of ions
Λ	Molar electrolytic conductivity
χ	Conductivity ion
λ_i	Ionic molar conductivity
Z_i	Charge on the ion

PEMBANGUNAN INSTRUMEN UNTUK MEMANTAU PELEPASAN LOGAM BERAT DALAM INDUSTRI BATIK

ABSTRAK

Kajian ini membentangkan pembangunan instrumen untuk mengawasi pelepasan logam berat dalam menghadapi masalah dari kilang batik. Baru-baru ini, pertumbuhan kilang batik yang pesat menjadi isu penting untuk mengekalkan alam sekitar kepada generasi akan datang. Oleh kerana sifat dan komposisinya, logam berat yang wujud dalam air sisa yang dihasilkan oleh kilang batik boleh dikelaskan sebagai bahan pencemar yang sangat berbahaya kepada ekosistem dan kesihatan manusia. Industri Perusahan Kecil dan Sederhana (PKS) menghadapi kesukaran untuk memantau pelepasan air sisa secara kerap kerana biasanya amalan untuk menganalisis kerja logam berat yang dilakukan di makmal adalah tidak secara langsung, mempunyai kelengkapan peralatan yang besar dan memperuntukkan kos yang mahal untuk kerja lapangan. Kajian ini memberi tumpuan kepada pembangunan alatan kos rendah untuk memantau logam berat dengan menggunakan teknik elekrokimia yang dilengkapi dengan komunikasi tanpa wayar (cip rangkaian RFM 95X) untuk mengatasi masalah amalan konvensional. Kerja ini menggunakan algoritma matematik untuk menganalisis kepekatan logam yang sedia ada dalam larutan berdasarkan analisis statistik dari pengumpulan data menggunakan sampel kawalan makmal. Untuk memastikan hasilnya kukuh, beberapa parameter penting seperti suhu dan tahap keasidan (pH) dipertimbangkan semasa pembangunan perumusan matematik. Algoritma kawalan menggunakan gegelung PID dilaksanakan ke dalam sistem peranti untuk menghasilkan input voltan yang mencukupi untuk memberi kuasa kepada penderia. Selepas itu, pemprosesan isyarat digunakan dalam sistem pengumpulan data untuk meningkatkan kualiti data. Akhirnya, instrumen ini menunjukkan prestasi yang baik apabila ketepatan data instrument ini lebih tinggi berbanding dengan kaedah terdahulu. Tambahan pula, pengukuran data yang diperolehi menggunakan instrumen ini hampir sama dengan data yang diperolehi dengan menggunakan alat yang lebih canggih, mahal dan berketepatan tinggi iaitu ICP-MS berdasarkan kaedah regresi linear. Kesimpulannya, sistem yang dibentangkan dalam tesis ini telah berjaya membangunkan alatan kos rendah untuk mengawal pelepasan logam berat secara langsung yang mesra pengguna.

THE DEVELOPMENT OF INSTRUMENT FOR REAL-TIME MONITORING OF HEAVY METAL DISCHARGE FOR BATIK INDUSTRY

ABSTRACT

This study presents the development of instrument for monitoring heavy metal discharge in encountering the problem from batik factories. Recently, the rapid growth of batik factories becomes significant issues to sustain environment for the next generation. Due to its properties and composition, heavy metal that by-produced in wastewater is classified as extremely dangerous pollutants to the ecosystem and human health. This Small and Medium Enterprise (SME) industry faces difficulties to regularly monitor the waste discharge since the conventional practice for analyzing heavy metal work in centralized laboratory are conducted offline, low-portability for field work and is an expensive instrument. This study focuses on the development of low-cost device to monitoring heavy metal using an electroanalytical technique equipped with wireless communication module (RFM 95X network chip) to cope with the problem of the conventional practices. This work had employed mathematical algorithm to analyze the existing metal concentration in the solution based on statistical analysis from the data collection using laboratory control sample. In order to ensure the results are robust, other significant parameters such as temperature and acidity (represented in pH) were considered during mathematical formulation development. The control algorithm using PID loop was implemented in the system devices to generate the sufficient voltage input energizing the conductivity sensor. Subsequently, the signal conditioning was applied in the data acquisition system to increase the data quality. The results show that the system promises a good performance with high accuracy compared to other method implemented on previous literature studies. Based on linear regression method, the results indicated from the research work was also proximate to those indicated in the highly-sophisticated equipment such as inductive coupled plasma mass spectrometry (ICP-MS). In conclusion, the research work presented in this thesis promises a success in development of low-cost instrument for online measurement of heavy metal discharge with user friendly feature.

CHAPTER ONE

INTRODUCTION

1.1 Background of Research

In Malaysia, the textile industry such as batik is one of the industry that contributed an economic growth with an annual income around RM160 million due to high demand from local and also abroad (Diana, 2010). This product has a significant contribution to the economy of Malays as it is manufactured by Malay entrepreneurs, largely dominated by two states on the east coast of Malaysia, Kelantan and Terengganu (Yaacob *et al.*, 2016). This product can be classified as cottage and handicraft industry because it uses traditional method, tools and means. Recently, this industry has expanded beyond traditional domain where the process was developed through the modernization concepts, techniques and philosophy (Yaacob *et al.*, 2015).

Over 1000 batik factories are growing mainly in the east coast of peninsular Malaysia as shown in Figure 1.1 (Rashidi *et al.*, 2012). The major problem that corresponds to this batik industry is the wastewater or the discharge of the industrial effluent produced during soaking, boiling and rinsing without proper treatment. The effluent are produced in large amounts with high concentration of pollutants, hence it require extensive treatment before it can be safely released to the environment (Subki, 2011). If the effluent or wastewater management is not properly conducted, environmental pollution is imminent (Mulyasari *et al.*, 2016).

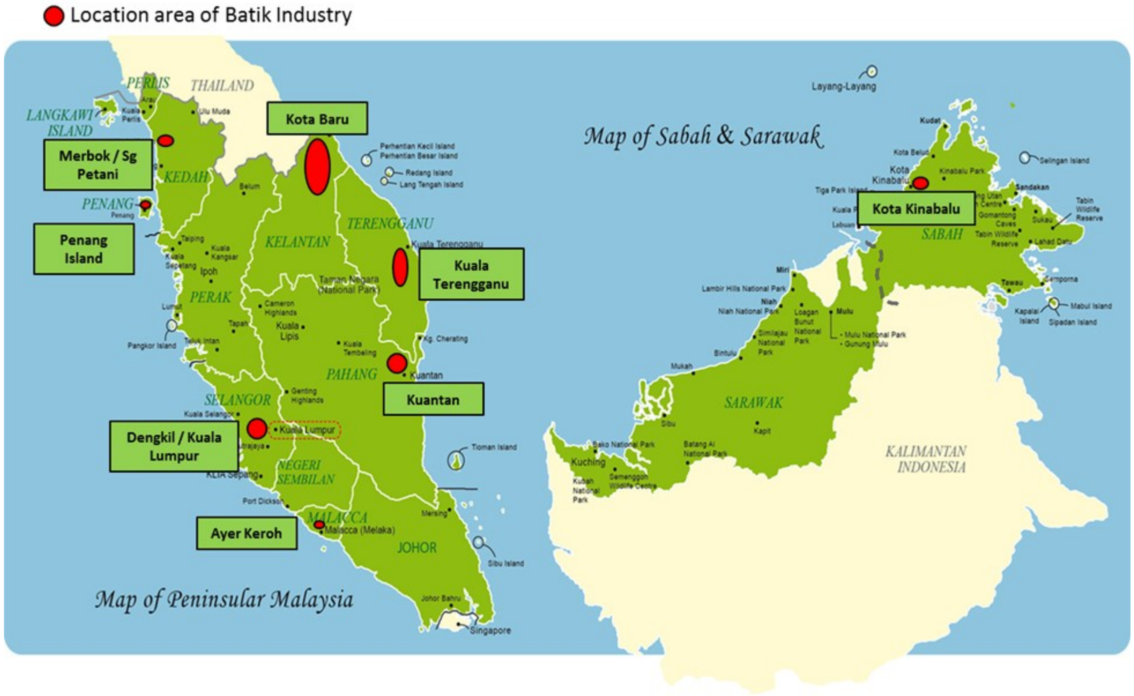

Figure 1.1 Location Batik Factories in Malaysia (Birgani *et al.*, 2016)

In the Malay belts state of Kelantan, batik is mostly produced by small scale industry which is known as the cottage industry as well as Small and Medium Enterprise (SME) (Subki, 2011). According to Clean Batik Initiative (CBI) Project, total batik SMEs cluster in Kelantan is 83 (Kota Baru (41), Pantai Cahaya Bulan (30), Tumpat (10), Bachok (1), and Melor (1)) and 17 from Terengganu (Kuala Terengganu (15), Marang (1), Dungun (1)). However, among the cottage industry, batik industry is the biggest cottage textile in Malaysia and Indonesia (Rashidi *et al.*, 2012). Unfortunately, this industry has poor environmental management record and responsible for the environmental issues due to illegal discharge of large amount effluents during dyeing and finishing process (Khalik *et al.*, 2015). According to the latest report by Kelantan Department of Environment, the compliant rate of the industry was 65% which was relatively low compared to other industry (DOE Kelantan Report, 2011).

1.2 Problem Statement

As generally practiced by either industry or DOE, wastewater was sampled manually at certain timestamp using a sampling bottle, each at four different station such as final discharge point, batik effluent storage tank, untreated batik effluent and environment (Altin *et al.*, 1999). Then, these samples are transported manually to the centralized laboratory to analyse the wastewater content using modern trace method. Unfortunately, heavy metals are sensitive to the exposure of light, dissolved oxygen and precipitation. Hence the parameter-of-interest of the sampled bottles may have been compromised and altered during the process of sampling and transportation. Thus, the data analysed and obtained from the sampled units were prone to be inaccurate and inefficient (Li *et al.*, 2013).

The modernized trace method to analyse the wastewater content is using optical method such as Inductive Coupled Plasma Mass Spectrometry (ICP-MS), Inductive Coupled Plasma with Atomic Emission Spectrometry (ICP-AES), Atomic Absorption Spectrometry (AAS), Atomic Emission Spectrometry (AES), and Cold Vapor Atomic Absorption Spectrometer (CVAAS). These modernized trace analyses are more selective and sensitive compared to the conventional method. However, these methods are not frequently implemented in small scale industry because of the highly specialized technique, long storage time, high cost and bulky for field works application.

1.3 Research Objectives

The proposed study aims to determine the best possible method to be utilized as an analytical instrument for monitoring wastewater status on-site. There are significant features to be highlighted during this work such as data acquisition system, mathematical formulation, signal conditioning, data transmission and graphical user interface. In general, the objectives of this thesis are;

a) To design and develop the algorithm to determine heavy metal ions in the sampled bottle solution.
b) To improve the quality of the communication signal acquired from the sensor meter.
c) To analyse and compare the performance of the portable instrument for detecting heavy metal ions against the established equipment and previous work found in the literature studies.

1.4 Research Scope

This work's primary interest is to develop an integrated process device and control algorithm that monitors heavy metal discharge from batik wastewater. Most of heavy metals that exist in the batik wastewater comes from an application of dyes during batik making process. In this work, the concentration of heavy metals is detected by using an electroanalytical technique based on the amount of ionic charges. Subsequently, as a user-friendly feature, the acquired data is displayed in a GUI to demonstrate the information showing the capability of the treatment system and wastewater characteristics.

The system makes the process more efficient, uncomplicated and had minimized the installation cost. With the sensor meters, communication module, monitoring terminal and integrated board controlled by a computer, the system is developed as a portable instrument for heavy metal discharge monitoring with user-friendly features. The algorithm is developed using Arduino IDE to identify and evaluate heavy metal contents from wastewater. The result is displayed on the GUI window at the monitoring terminal using Microsoft Visual Studio.

This portable instrument consisting of software and algorithms that manage to perform the monitoring, data collecting, processing and transmission. The identification of heavy metals is achieved by using heavy metal sensing unit and several mathematical algorithms alongside the intermediate process. To validate the performance of the monitoring system, the experiment for performance testing is conducted. The final discharge concentration of the solution is analysed and compared with the method used by the previous works and established equipment.

1.5 Thesis Outline

In this thesis, there are 5 main chapters that described the development process of this research work. Starting with the introduction of this project in Chapter 1 which briefly explained the whole project beginning with the background, problem statement, research objectives and research scope. Chapter 2 described brief review and theoretical background from relevant literature source. The theory of the components used in this project are discussed and explained for the basis of fundamental understanding of the project. The research methodology is described in Chapter 3. This chapter is started by illustrating the overall project flow. Further detailed explanations are included which are sample preparation, design and fabrication process, mechanism development performance and the software-hardware integration. Chapter 4 highlighted the experimental results conducted in this project and its corresponding comprehensive discussion and analyses. The development of the instrument's functionality is also shown in this chapter. Finally, this research is concluded in chapter 5. Further recommendations were proposed for future potential development of this work and the contribution of this project is highlighted.

CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy Metal pollution in the batik industry

This section is dedicated to comprehensively explain the heavy metal pollution in batik industry.

2.1.1 Introduction on heavy metal

Heavy metal that persistent in aqueous environment is one of the most critical problem as it poses threat to human health even at low concentration (Long et al. 2013). Heavy metal is generally in a state of cationic form and hazardous when its density is over than 5 gram per cubic meter (March et al. 2015). The dissolved heavy metal ions cannot be degraded as it contaminated a river. This contaminated river is potential to be consumed by human through drinking water, bio-accumulation and food chain (Dexia et al. 2014).

There are about 20 types of metal ion that are classified as toxic metal whereas half of these such as copper, cadmium, chromium, arsenic, nickel and lead are considered most hazardous which pose a major threat to human health (Saifuddin & Kumaran 2005). Detrimental health that affects the human body such as organ and nervous damage, cancer, reduced growth and death are most likely to happen. In fact, children may exposed to higher dose of heavy metals since they consumed more food for their development compared to adults (Barakat 2011).

Heavy metals are extremely dangerous because it is non-degradable, chemically stable and tend to bio-accumulate which are a threat to human health. Exposure to some of the heavy metals such as lead may interfere a fetus growth or a developing child or a reproductive process (reprotoxic) will also affect the learning capacity and neuropsychological growing (Cserfalvi et al. 2010). In general, toxicity of a metal ion form can affect human due to the chemical reactivity of the ion with enzymes, structural protein and membrane system. Long term storage of heavy metal can takes place in hard tissues such as bone and teeth (Mahurpawar 2015). Table 2.1 stated the effects of heavy metal toxicity towards a normal human being.

Table 2.1 Toxicity heavy metal effect on human

Heavy metal	Health Effect
Zinc (Zn)	Lethargy, neurological sign, depression, damage to nervous system and thirst (Department of Environment (DOE) 2009)
Nickel (Ni)	Human carcinogen, dermatitis, nausea, coughing and chronic asthma (Duruibe et al. 2007)
Copper (Cu)	Insomnia, Wilson disease, liver damage, stomach and intestinal irritation (Griswold & Martin 2009)
Manganese (Mn)	Inhalation or contact causes damage to central nervous system (Järup 2003)
Lead (Pb)	Fetal brain damage, congenital paralysis, sensor neural deafness, circulatory system, nervous system and kidney diseases (Tripathi & Rawat Ranjan 2015)
Cadmium (Cd)	Human carcinogen, renal dysfunction, kidney damage, lung disease, bronchitis, gastrointestinal disorder, bone marrow, increase blood pressure and cancer (Tripathi & Rawat Ranjan 2015)

2.1.2 Sources of heavy metals

Generally, industrial effluent discharge from industrial activities can be divided into two categories such as organic compound and inorganic compound. An organic compound does not dissolve in water and existed in covalent bond. This organic compound such as phenol, formaldehyde, and nitrobenzene can be analyzed by measuring the amount of Chemical Oxygen Demand (COD) or Biological Oxygen Demand (BOD) and Total Organic Compound (TOC). An inorganic compound present as ionic bond in water. There are many physical parameters that can be evaluated such as acidity (pH), salt, heavy metal and Sulphur. Thus, heavy metal as discussed in this research was categorized as inorganic compound.

Heavy metal contamination in water is a common problem that is encountered in many countries due to metal leaching or deposition, urban wastes, fertilizer and industrial activity. The industrial activity is one of the primary source that contributed to the existence of heavy metal in aqueous environment (March et al. 2015). Industrial activity such as electroplating, textile, steel fabrication, cement, metal processing, inorganic pigment manufacturing and canning produced a different kind of waste from effluent discharge to the environment (Barakat 2011). The pollution by industrial activity which contains hazardous toxic metals such as mercury (Hg), chromium (Cr), lead (Pb), zinc (Zn), copper (Cu), nickel (Ni), arsenic (As), and cobalt (Co), and tin (Sn) are threatening to human health and ecosystems (Chervin et al. 2016). In Malaysia’s practice, industrial effluent discharge should comply with the regulation of Malaysian Environmental Quality Act, called Environmental Quality (Industrial Effluent) Regulations 2009. The standard effluent discharge limits has been established between 0.1 and 3 milligram per liter (Aziz et al. 2008).

The main source of heavy metal in textile industry is produced from consuming a lot of chemicals in production process (Mustafa Tuzen 2008). Textile industries are the major source of pollution for metal contaminants in the environment (Sarker et al. 2015). Heavy metals are present in different textile process such as metal complex dye, dye stripping agent, odor-preventive agent, antifungal, mordant reactive and oxidizing compound (Rezić & Steffan 2007).

2.1.3 Characteristic of batik wastewater

The production process of a batik product utilized a lot of chemicals such as synthetic dyes which contained of heavy metal (Mulyasari et al. 2016). According to Rashidi *et al.*(2012), wastewater that produced from batik factories was discharged directly into environment without any treatment process. Regrettably, current conventional treatment for removing chemical specifically dyes and fixing reagents are not efficient enough to comply with the standards even with stringent regulations (Diana 2010). The Kelantan Department of Environment (DOE) stated that batik industry has the lowest level of compliance for the regulation and effluent discharge's law. Table 2.2 provides acceptable condition of effluent discharge extracted from Environmental Quality (Industrial Effluents) Regulations 2009, fifth schedule.

Table 2.2 Acceptable limit from Department of Environment (DOE) standard discharge, (Department of Environment 2010)

	Parameter	**Standard B of Effluents**
	Temperature	40 °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

*Seven Schedule, Acceptable condition for effluent containing COD for textile industry

The organic compounds detected on batik wastewater by using GC-MS are benzenes, phenol, esters, hydrocarbons and alkyl halides which can cause unpleasant odor. Effendi, Delima Sari and Hasibuan (2015) stated that the quality characteristics of batik effluent for SME are pH acidity (6.05), turbidity (1306 NTU), Total

Suspended Solid (TSS) (1248 mg/l) and Chemical Oxygen Demand (COD) (3712.5 mg/l). A batik wastewater was previously collected at final discharge in Beseri, Perlis had contained psychochemical characteristics such are BOD (341.25mg/L), COD (4092mg/L), pH (10.77), Temperature (25.3°C), Turbidity (217 NTU) and TSS (303.03).

Khalik *et al.* (2015) studied the effluent wastewater from 5 batik factories in Kota Bharu, Kelantan and presented results as Table 2.3. The samples were collected at dyeing and washing station before the wastewater discharged. The observation showed the information from their correlation analysis where the COD was positively correlated with pH and Temperature and inversely with DO and TDS.

Table 2.3 Data of physicochemical parameter for 5 factories which located in Kota Bharu, Kelantan (Subki 2011)

Physical Parameter	**Industry A**	**Industry B**	**Industry C**	**Industry D**	**Industry E**
Temperature, °C	32.43	30.29	28.15	26.94	29.21
pH	7.92	8.29	8.88	7.65	9.52
TDS, mg/L	5.91	4.11	3.16	9.33	3.22
DO, mg/L	1.77	2.23	2.1	2.05	2.01
COD, mg/L	1473	1423	773	945	4944

Awang *et al.* (2016) studied the toxicology (cytotoxicity and genotoxicity) effect of batik industrial wastewater at Hulu Langat, Selangor. In his study, physicochemical characterization such as pH, COD, BOD, DO, TSS, and TDS are important parameter to evaluate the quality of the wastewater. The results from all the physicochemical measurements had exceeded the limit of Environmental Quality (industrial Effluent) Regulation 2009.

2.1.4 Heavy metals contamination from batik making process

Batik process produces a large volume of wastewater that contains harmful chemical of dyes and auxiliaries into the environment without a proper treatment process (Rashidi et al. 2015). Figure 2.1 shows a traditional process of making batik starting from the preparation of the materials and equipment until the finishing process as described by Nordin (2012), Mirzajani *et al.* (2013), Legino (2012) and Malaysia (2012) .

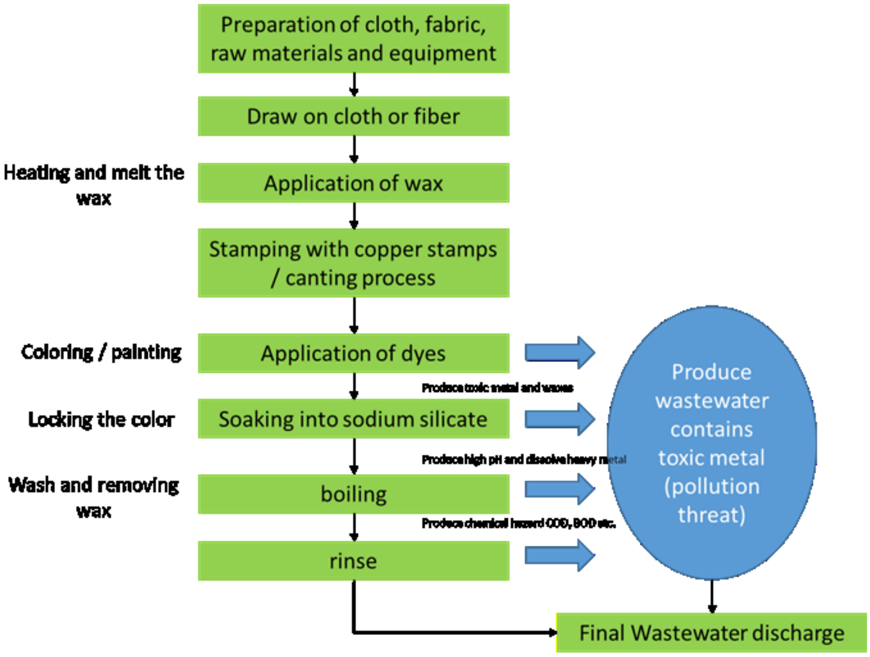

Figure 2.1 Schematic diagram for Batik Processes (Legino 2012)

Usually, painting process used a large volume of water for washing purposes. Subsequently, wax and dye are applied onto the fabric. The art design on the cloth and fabric is created by using canting tool or copper stamps that filled with melted wax. Then, the process continues with applying the dyes before the fabric is boiled into hot water. Conventional practice for dyeing process is by using synthetic or chemical dyes to produce a colour on the plain fabric. Lastly, the fabric is boiled to remove all the waxes that protected the dyes during painting process. This process consumed a lot of water.

Next, the discharging boiled water from the boiling process contains wastewater consists of harmful chemicals and suspended solid. The wastewater is continuously discharged directly into a river or environment without any prior treatment which contributes to environmental pollution.

As previously stated, traditional batik making process uses manual wax-resist dyeing technique using natural and synthetic dyes. Recently, many batik factories preferably use synthetic dyes to colour the fabric. Unfortunately, these synthetic dyes had adversely polluting environment. Hundreds of years ago, natural dyes was used to colour the fabric because it ensures fabric durability and elegance in appearance. Natural dye’s material is organic and made by traditional and manual process, so that it is eco-friendly and does not pollute the environment. However, the disadvantages of this dyes are the colour inconsistency which requires extensive labour work to neatly colour the fabric or cloth, hence natural dyes are not feasible for industrial scale. For this reason, most of batik factories prefer to use synthetic dyes. Synthetic dyes are easier to use for batik colouring and requires minimal time during colouring process. However, the wastewater produced from synthetic dyes may cause health problem such as jaundice, vomiting and increasing of heart rate (Hameed & Ahmad 2009).

Azo dyes are considered as the oldest and largest class of synthetic dyes. These dyes are commonly used as dyeing process in batik making such as reactive orange 16, reactive yellow 42 and reactive red 106. In earlier days, natural dyes were used for batik making, but after synthetic dyes were commercialized, the use of natural dyes had decreased. Natural dyes are extracted from flowers, roots, vegetables, insects, minerals, woods and mollusks (Widyatmono & Diponegoro 2015). Synthetic dye can be manufactured consistently and are identical from batch to batch by using computer color matching (CCM) (Maulik et al. 2014).

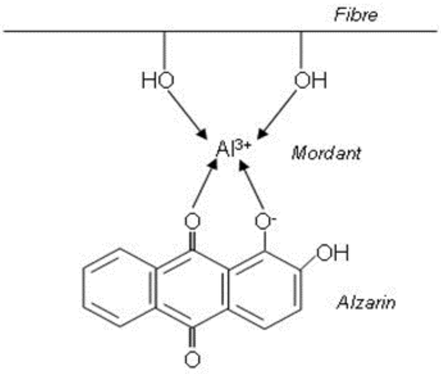

Figure 2.2 Alizarin structure bond with metal ion (Zarkogianni et al. 2012)

Heavy metals present in batik wastewater mostly come from dyes. Metals are used during dye manufacturing as catalyst and present as a part of dye molecules known as impurities. Some of the dyes used metals to bonds chemical structure, forming an integral structure element. In metal complex dyes, metal elements attract to the dye molecule structure and form the chemical bond. For example, chromium is used in metal-complex dyes, copper is used in blue copper-azo-complex reactive dyes. The metallized dyes used for a certain colour shades such as green to increase the speed in which the material absorbs colours and fastness to light (Vijaykumar et al. 2006). The process that used metal ions to color the material is known as mordanting whereas aluminum make the dyes red, tin make the material pink and the iron gives a brown color. Mordanting takes place at high pH conditions, thus the metal hydroxide will precipitate in the fibers (Marshall 1973). Hence, metal ions attach to the cloth and then attract the dye molecules by forming chelate rings as shown in the Figure 2.2 (Emin et al. 2007).

Metallized complex dyes are predominant dye class that improve light fastness after treatment with metals salt compared to non-metallized dyes. The metal ion is introduced into the molecules of dyes to enhance the light fastness by protecting the azo chromophore from ultraviolet degradation. From the studies conducted by Erdem *et al.* (2007), Chromium (Cr), Cobalt (Co), and Copper (Cu) are predominant in metal complex azo dyes in which its application and process tend to create environmental pollution.

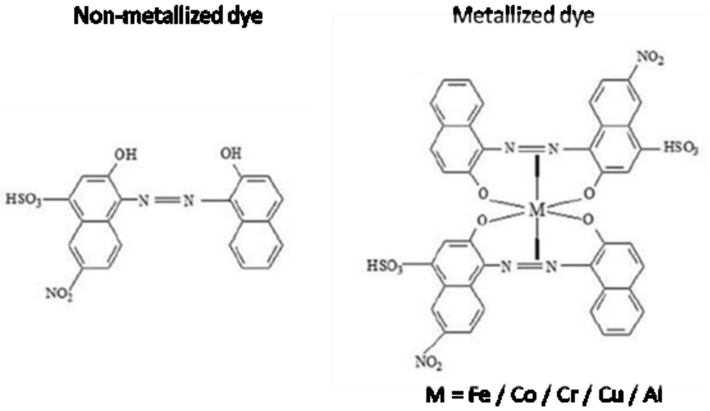

Figure 2.3 Structure of metal complex dyes (Zarkogianni et al. 2012)

Figure 2.3 shows the structure of metal acomplex dyes. In general, the basic process in batik making that produces heavy metals are at three stages (soaking, boiling and rinsing). At first, sodium silicate that applied during the process for colour stabilizer and pH adjustment (pH of dyebath is adjusted to ensure the dye work efficiently) as fixative with dyes produce wastewater during soaking and boiling at very high pH hence dissolved heavy metals. Erturul *et al.* (2009) stated that the discharge level had far exceed the current regulatory limit. The heavy metals (such as Al, Fe, Cu, Zn and Pb) are coming from silicate and dyes (Allègre et al. 2006).

Heavy metals exist as a part of dye component and present as impurities, as shown in Table 2.4. Thus, heavy metal become indispensable in the composition of dyes. The level of heavy metals may slightly increase through boiling as these metals accumulate and deposit during boiling (Birgani et al. 2016).

Table 2.4 Metal present dyes (Verma 2008; Bae & Freeman 2007; Bae et al. 2006)

Class of dyes	**Metals in dyes**
Direct	Copper, lead, zinc, chromium, iron, aluminum
Reactive	Copper, chromium, lead
acid	Copper, chromium, lead, zinc, cobalt
base	Copper, zinc, lead, chromium
mordant	Aluminum, chromium, copper, iron and tin
vat	none
disperse	none

2.1.5 Present technology for heavy metal detection

A variety of inorganic techniques are described in the literature for tracing the elements of heavy metal. Those methods are different based on principle and type of analysis.

Electroanalytical is the technique that focuses on analytic solution by measuring the potential difference (volt) and current (ampere) in interfacial process of chemical or physics species. From this fundamental concept, this technique can be divided to the variety of other method based on aspects of the cell controlled and measured. This method is suitable to develop the field work, real-time and on-line environmental analysis due to high performances such as low detection limits, good stability and wide linear response range (Pei et al. 2014; Tutulea et al. 2012). Potentiometry used potential difference of two electrode to measure the composition of sample. One of electrode is constant potential called reference electrode and another one is indicator electrode which is the potential change with analytic sample. Indicator electrode usually made selective sensitive electrode to the ion of the interest. Potentiometric Stripping analysis (PSA) is one most common electrochemical stripping method which allows the detection of some metals in complex matrices in a wide concentration range compared to other electroanalytical methods (Cerqueira et al. 2014). Coulometry is the method of applying potential difference to convert an analytic from one oxidation state to another. The composition of sample can be determined by knowing the electron passed from the total current passed. Voltammetry is the method of applying a constant and/or various potential to the electrode surface. The resulting current with a three electrodes system is measured and the reduction potential is determined; thus composition of sample can be assessed. Polarography is a subclass of voltammetry where the working electrode used dropping mercury electrode (March et al. 2015). Anodic Stripping Voltammetry (ASV) is a common method used to detect heavy metal in various matrices (Xu et al. 2008; Raj et al. 2013; Legeai & Vittori 2006; Herdan et al. 1998). It can determine 4 to 6 metals simultaneously with inexpensive instrument (Barón-Jaimez et al. 2013)(Farghaly et al. 2014)(Hočevar et al. 2005)(Morton et al. 2009).

Optical detection is an alternative method for metal trace determination. The most predominant techniques are Inductive Coupled Plasma Mass Spectrometry (ICP-MS), Inductive Coupled Plasma with Atomic Emission Spectrometry (ICP-AES), Atomic Absorption Spectrometry (AAS), Atomic Emission Spectrometry (AES), and Cold Vapor Atomic Absorption Spectrometer (CVAAS). These modern trace analyses are more selective and sensitive compared to conventional method. However, these methods were not frequently used because of the sophisticated technique, long process time, high cost, and bulky for field works. The argon plasma is used in ICP-MS as ion source to distinguish ion based on their mass-to-charge ratio. For ICP-AES, ion metal detection is based on optical emission measurement from excited atoms (Nham & Monitoring 2006; C. Voica, M. H. Kovacs 2012). Both method is widely used in environmental analysis which has high detection limits compares to others and can analyses multi-element of heavy metal ion simultaneously (Gayla 2009). The metal concentration for AAS is based on passing light absorption of radiant energy produced by a special radiation source through cloud of atoms from a sample (Sanders 2012; Farey & Nelson 1982; Kojuncu et al. 2004; Rafiquel et al. 2016). In AES technique, a spectrometer detects each element of light emission at a characteristic wavelength. High energy promotes the atom to excitethe state of electron that emit light when returned to the ground electron state (Tareen et al. 2014; Prevedello et al. 2008). The CVAAS is flameless AAS procedure for metal detection based on absorption of radiation at 253.7nm by mercury vapour (Helaluddin et al. 2016).

Recently, the development of bioanalytical technique for metal detection is applicable for food and clinical application. Biomolecules such as nuclei acid measures the heavy metal through DNA probes. These two main methods are well-established by using DNA hybridization and the fact that thymine-thymine (T-T) mismatches the complementary sequences and binds heavy metal ions (Wang et al. 2003; Knecht & Sethi 2009; Turdean 2011).

2.2 Rapid method for detection of heavy metal ions in the solution

This subchapter will be describing the rapid method for detection of heavy metal ions in the solution. It includes the formulation of electroanalytical technique, an electrical conductivity for the detection of ion metals and the turbidity detection.

2.2.1 Formulation of electroanalytical technique

Electroanalytical technique has be proven successful in measuring free metal ion concentration in a relatively short time. It is easy to be interpreted, operator-friendly and can be done on-line (Li et al. 2012). Most of the principles and methods were presented in Section 2.1.5. The conductance measurement for trace metal analysis in the solution is topic-of-interest in order to prepare the simple instrument for field work application.

Measurement of solution conductance can be classified as classical electroanalytical techniques as conducted in previous works. For recent application, conductance as well as conductivity are measured to know the salinity of the field. Salinity is the amount of salts in water and the total dissolved ions. Khodari et al. (2001) used conductance measurement to study the corrosion process of copper in nitric acid HNO_3 (Assaf et al. 2003). By knowing the fundamental theory of signal application, it is important to acknowledge that conductance value can extensively provide more information than a simple total ion concentration. Sarojini et al. (2013) studied nanofluids containing metallic and ceramic particles by evaluating the conductance measurement. In addition, conductance measurement is also useful in food industry to detect the contamination of water, monitoring of microbial growth and metabolic activity. Mabrook & Petty (2003) measured the contribution of various component of milk since the distribution of salt fraction in a soluble and colloidal iron may affect the conductivity measurement.

Two electrodes are immersed in electrolytic solution and a potential voltage is applied between two cells. This principle followed Ohm’s law (Sas 2004) as shown in equation 2.1.

$$E = IR \qquad (2.1)$$

Where E is the applied potential (Voltage), I is the measured current and R is the resistance of the electrolyte solution between two electrodes.

Resistance measurement is an important parameter to extensively analyse the industrial effluent laden with heavy metals. The concentration of ions present in the solution is inversely proportional to the resistance value.

The electrical conductance, G is the reciprocal of solution's resistance (S.I units: S Siemens). However, the measurement of conductance or resistance depends on distance, L between cell electrode and microscopic surface area (geometric area x roughness factor), A of the electrode (Area for both electrode are identical). These parameters correlated through conductivity formula (Prieto García et al. 2005);

$$conductance, G = \frac{1}{R} \qquad (2.2)$$

$$conductivity, \chi = G\frac{L}{A} \qquad (2.3)$$

$$G = \frac{1}{R} = \chi\frac{A}{L} \qquad (2.4)$$

2.2.2 An electrical conductivity for the detection of ion metals.

Conductivity, χ can be classified as a significant parameter to evaluate water characteristic (SI unit: Sm^{-1} and μScm^{-1} because mostly measurement give low values). From the measurement, the information such as concentrations and ion mobility can be further analysed. Conductivity is directly proportional to the ratio of distance against area, L/A. Therefore, in a particular measurement and instrumentation, the ratio of L-A is usually fixed. L/A is called as constant, (K_c) (Toledo 2010). Thus,

$$\chi = G\frac{L}{A} = GK_c \tag{2.5}$$

Bolan et al. (2014) stated the measurement of conductivity for solution of 1 Molar HCl is different than 1 Molar KCl due to the facts that protons are much more mobile in solution than potassium ions. The difference occurred because of quantifying parameter namely mobility, u which is independent of concentration. In ideal case, mobility of an ion can be describe as function of mobility of an ion (u), charge on the ion (Z), solvate radius (R), viscosity of solvent (Ƞ), and elementary charge constant (Coury & Ph 1999; Panote Thavarungkul 1995) given in equation 2.6;

$$u_i = \frac{|Z_i|e}{6\pi\eta R_i} \tag{2.6}$$

In order to determine the ionic solution, contribution of all ion that are mobile in the solution can support the current flow. In terms of mobility, conductivity can be expressed as Faraday constant or F (96 485 C/mol) and C is the concentration of ion in mol per cubic cm as shown in equation (2.7);

$$\chi = F\sum_i u_i C_i = F\sum_i |Z_i|\left(\frac{|Z_i|e}{6\pi\eta R_i}\right)C_i \tag{2.7}$$

The electrical conductivity measurement varies with temperature change. As thermal energy increases, Brownian motion increase (Icier & Ilicali 2005). Ensuring the stability of temperature in the test sample is critical because it can affect the accuracy of conductivity measurement (Icier & Ilicali 2005). The temperature coefficient (α) can be expressed as;

$$\alpha = \frac{d\chi/dt}{\chi} \tag{2.8}$$

Where α is temperature coefficient, *t* is a temperature, χ_i is the measured conductivity values, and χ_{25} is conductivity measurement at temperature of 25 degree (Barthel et al. 1980). Thus,

$$\chi_i = \chi_{25}\,[1 + \alpha(t - 25)] \tag{2.9}$$

Molar electrolytic conductivity, Λ is a measure of the capability of the electrolyte solution to carry electric current (unit S m^2 mol^{-1}) and as described by Son et al.(2017);

$$\Lambda = \frac{\chi_t}{C}\, X\, 10^{-3} \tag{2.10}$$

Where χ_t is the difference of conductivity of solution and solvent (χ solution - χ solvent) (Sm^{-1}) and *C* is electrolyte molar concentration (M). Molar electrical conductivity of electrolyte is determined by the total number of ions present and is shown as follows;

$$\Lambda = \sum v_i \lambda_i \tag{2.11}$$

Where v_i is the number of ions (anions and cations) and λ_i is the ionic molar conductivity (units: Sm^2mol^{-1}). The ionic molar conductivity is a significant parameter that provides quantitative information on the contribution of a given ion type to the solution conductivity.

2.2.3 Turbidity detection

The clarity and transparency of fluid can be measured by physical characteristic of fluid clarity. Turbid fluid decreases fluid clarity as the fluid visibility might turn to opaque, colored or cloudy. Turbidity level can be used to estimate the water clarity as the total suspended of solid can be estimated. Total suspended solid is defined as the number of particles that has size larger than 2 microns. Otherwise, the solid is a dissolved solid. Both particles contributed to the clarity of water.

Turbid water is caused by the existence of particle suspended in the water. It can be evaluated by knowing the amount of light scattered from the particles in water. Turbid meter is an electronic instrument utilised to measure the turbidity due to the scattering of light passing through a water or solution containing suspended solid particle. Turbidity also can be used to determine the changes of suspended solid concentration in the solution. Unit for turbidity measurement is NTU. At 5 NTU, the solution is classified as clear and transparent, turned cloudy at 55 NTU and became opaque at 515 NTU.

2.3 The hardware for monitoring instrument

This subchapter of literature review will be discussing about the hardware for the monitoring instrument of wastewater discharge.

2.3.1 Instrument controller

There are few significant differences between microcontroller and microprocessor. Microprocessor is developed to do a task as similar as a CPU in microcomputer system such as Intel's Pentium 1,2,3,4 Core 2 Duo, i3, i5, and i7. To make them functional, a system designer requires to integrate other modules such as RAM, ROM and other peripheral devices on the chip. For example, it is used to apply on desktop PC's, laptops, and notepads. In contrast, microcontroller is developed to do a specific task, in which the input and output are defined. It has a CPU and fixed amount of RAM, ROM and other peripherals embedded on a single chip.

Generally, microcontroller is used in industrial control devices such as industrial instrumentation devices and process control devices. There are many types of microcontroller where it can be categorized according to their architecture, memory, instruction sets and bits. There are examples for microcontrollers which are ATmega 2560 used in Arduino Mega, Raspberry Pi, MSP430 LaunchPad, PIC32MX440F256H used in Pinguino PIC32 and many others which offer similar functionality. In this project, the Arduino Mega with ATmega 2560 microcontroller is used as the embedded system.

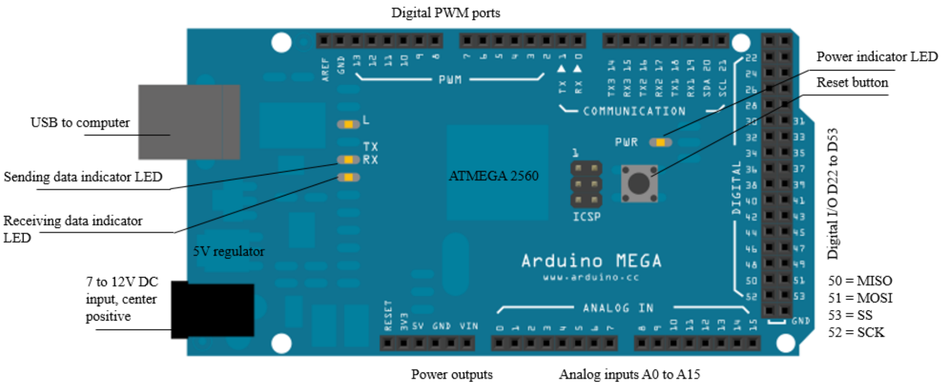

Figure 2.4 Arduino MEGA Single-Board Microcontroller (John 2018)