DETERMINATION OF PHYSICO-CHEMICAL PROPERTIES AND HEAVY METAL CONTAMINATION OF BATIK WASTEWATER FROM TEXTILE WORKSHOP, UMK BACHOK CAMPUS

By

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THESIS DECLARATION

I declare that this thesis entitled "Determination of Physico-Chemical Properties and Heavy Metal Contamination of Batik Wastewater from Textile Workshop, UMK Bachok Campus" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ______________________________

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DNA	Deoxyribonucleic Acid
DOE	Department of Environment
EQA	Environmental Quality Act
g	Gram
kg	Kilogram
m^3	Cubic Meter
MCL	Maximum Contaminant Level
mg	Milligram
mg/L	Milligram Per Liter
mL	Milliliter
NTU	Nephelometric Turbidity Units
pH	Potential Hydrogen
ppm	Part Per Million
SS	Suspended Solid
TOC	Total Organic Carbon
TDS	Total Dissolved Solid
TSS	Total Suspended Solid

UMK	University Malaysia Kelantan
USEPA	United State Environmental Protection Agency

LIST OF SYMBOLS

%	Percentage
℃	Degree Celsius
<	Less Than
µm	Micrometer
Ag	Silver
Al	Aluminum
As	Arsenic
Ca	Calcium
Cd	Cadmium
Co	Cobalt
Cr	Chromium
Cu	Copper
H_2O	Water
Hg	Mercury
HNO_3	Nitric Acid
Mn	Manganese
NH_3N	Ammoniacal Nitrogen
Ni	Nickel
Pb	Lead
Sn	Tin

Ti	Titanium
Zn	Zinc

Determination of Physico-chemical Properties and Heavy Metal Contamination of *Batik* Wastewater from Textile Workshop, UMK Bachok Campus

ABSTRACT

Batik industry is the biggest textile industry in the South East of Asia, especially in Malaysia. It provides the handicraft products that contribute greatly to the economy for the Malaysia, but at the same time, it affects human health, aquatic lives and environment. This research investigates the physico-chemical properties and heavy metal concentration of *batik* wastewater discharge from the textile workshop, UMK Bachok Campus. Physical parameters such as total dissolved solids, temperature and turbidity and chemical parameters such as pH, chemical oxygen demand, total suspended solid and ammoniacal nitrogen were also investigated. Furthermore, the concentrations of selected heavy metals of the discharged *batik* wastewater were determined and compared to the Environmental Quality (Industrial Effluents) Regulations 2009 under the Environmental Quality Act 1974. A total of five heavy metals were investigated in this research including zinc, manganese, aluminum, nickel and copper. The concentration of the heavy metals was determined by colorimetric method. The results obtained showed that some of the physico-chemical parameters are exceeding the acceptable conditions for discharge of industrial wastewater for mixed wastewater of standard B set by the Environmental Quality (Industrial Effluents) Regulation 2009 under the Environmental Quality Act 1974. Among them are chemical oxygen demand, total suspended solid, total dissolved solid, turbidity and pH of the *batik* wastewater. While for the selected heavy metals, all of them are within the acceptable conditions for discharge of industrial wastewater for mixed wastewater of standard B set by the Environmental Quality (Industrial Effluents) Regulation 2009. Therefore, all the concentrations of physico-chemical and heavy metal that exceed the standard should be reduced before discharged.

Penentuan Sifat Fiziko-kimia dan Pencemaran Logam Berat Air Sisa Batik daripada Bengkel Tekstil, UMK Kampus Bachok

ABSTRAK

Industri batik merupakan industri tekstil terbesar di Asia Tenggara, terutamanya di Malaysia. Ia menyediakan pelbagai produk kraftangan yang banyak menyumbang kepada ekonomi Malaysia. Walau bagaimanapun, industri batik membawa kesan negatif kepada alam sekitar. Penyelidikan ini mengkaji sifat fiziko-kimia dan kepekatan logam berat air sisa batik daripada bengkel tekstil yang terletak di UMK Kampus Bachok. Parameter fizikal seperti jumlah pepejal terlarut, suhu dan kekeruhan dan parameter kimia seperti pH, permintaan oksigen kimia, zat padat tersuspensi dan ammoniacal nitrogen juga dikaji. Selain itu, kepekatan logam berat air sisa batik yang dilepaskan akan ditentukan dan dibandingkan dengan Peraturan-Peraturan Kualiti Alam Sekeliling (Efluen Perindustrian) 2009 di bawah Akta Kualiti Alam Sekeliling 1974. Terdapat lima logam berat telah dikaji dalam kajian ini termasuk zink, mangan, aluminium, nikel dan kuprum. Kepekatan logam berat ditentukan dengan kaedah kolorimetri. Keputusan yang diperoleh menunjukkan bahawa beberapa parameter fiziko-kimia telah melanggar syarat-syarat yang boleh diterima bagi pembuangan air sisa industri untuk air sisa campuran B standard seperti yang ditentukan dalam Kualiti Alam Sekeliling (Efluen Perindustrian) Peraturan 2009 di bawah Akta Kualiti Alam Sekeliling, 1974. Antaranya ialah keperluan oksigen kimia, jumlah pepejal terlarut, zat padat tersuspensi, kekeruhan dan pH air sisa batik. Manakala, logam berat berada dalam kadar yang selamat bagi pembuangan air sisa industri untuk air sisa campuran seperti yang ditetapkan dalam Standard B di bawah Peraturan-Peraturan Kualiti Alam Sekeliling (Efluen Perindustrian) 2009. Oleh itu, semua parameter yang melebihi standard perlu dikurangkan sebelum disalirkan.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Water is the most abundant and most common liquid on earth. It is unique, ubiquitous substance that is a major component for supporting the living life on earth. Our planet is mostly covered with water which is about 71 % of the Earth's surface, while the other 29 % of the earth surface consists of islands and continents. According to Pennington and Cech (2009), about 96.5 % of all the Earth's water is contained within the oceans, while 1.7 % is the freshwater lake and frozen water which locked up in the glaciers, permanent snow, sea ice and polar ice caps, another 1.7 % freshwater exist as groundwater, rivers, lakes, wetlands, and the soil. Remaining of 0.1 % is contained in the Earth's atmosphere (Pennington & Cech, 2009). This shows that the fresh water has a minor percentage of total water composition which very vital for the living organism on this planet.

In Malaysia, the quality of water is deteriorating due to natural factors and anthropogenic factors. Natural factors are included atmospheric deposition, soil erosion and mineral weathering while anthropogenic factors are human activities such as urban, industries and agriculture residues (Li & Zhang, 2010). Discharge from municipal and industrial wastewater is the main source of water pollution (Al-Badaii & Shuhaimi-Othman, 2014). Improper disposal of wastewater to the surrounding may contribute to the poor quality of the water (Sultana *et al.*, 2009). The water pollution will affect the diversity and growth of flora and fauna, fish survival, recreational activities, private water supply, waste disposal, irrigation, livestock watering and aesthetic values. Hence, one of the hot issues today is the scarcity of fresh drinking water which affects the ecosystem health (Curry, 2010).

Metal ions are among the key nutrients that are necessary for humans in tiny amounts such as copper (Cu), chromium (Cr), manganese (Mn), nickel (Ni) and zinc (Zn). However, the concentration of metal which exceeding the limits are toxic or carcinogenic (Lin *et al.*, 2011). Based on Lin *et al.* (2010), the contamination of heavy metals is mainly caused by human activities and the hot spots of heavy metal are near to the industrial plants and irrigation system.

The wastewater discharged by industry is one of the important sources of water pollution. In developing country, an estimated 90 % of all the industrial wastewater was discharged untreated into the nearby lake, river and coastal areas (Corcoran *et al.*, 2010). Their amount of wastewater depends on the technical level of process in each industry and will be reduced along with the advancement of technologies (Shi & Qian, 2009). The industrial wastewater varies so largely in both the flow and strength of pollution. Table 1.1 shows the types of pollutants based on different industries. Generally, the wastewater released from industries may contain colloidal, suspended and dissolved solids (Alturkmani, 2004). Moreover, they may be either acidic or alkaline, contain high or low concentrations of colored matter, inert, organic or toxic material and pathogenic bacteria (Alturkmani, 2004). This can be resulted in serious water pollution and bring the negative impacts to the ecosystem and human health.

Table 1.1: Water pollutants by the industrial sector (Shi & Qian, 2009)

Type of Industry	Type of Pollutants
Iron and steel	Biochemical oxygen demand (BOD), chemical oxygen demand (COD), oil, metals, acids, phenols and cyanide
Textiles and leather	BOD, solids, sulfates and chromium
pulp and paper	BOD, COD, solids, chlorinated organic compounds
Petrochemicals and refineries	BOD, COD, mineral oils, phenols and chromium
Chemicals	COD, organic chemicals, heavy metals, suspended solid (SS) and cyanide
Non-ferrous metals	Fluorine and SS
Microelectronics	COD and organic chemicals
Mining	SS, metals, acids and salts

1.2 Problem Statement

Textile industry is among the largest polluters in the world (Kant, 2012). The process of textile manufacturing involves large consumption of water, energy and various chemical which become waste as a by-product. Wastewater is one of the by-products that released to the environment (Jaganathan *et al.*, 2014). In addition, this industry produces a huge amount of wastewater from different steps throughout the dyeing and finishing process (Babu *et al.*, 2007). This condition is becoming deteriorated when the amount of wastewater generated by textile industry increasing from year to year (Pang & Abdullah, 2013).

The wastewater produced from textile industry is found that rich in color, containing residues of chemical or reactive dyes, complex components, aerosol, high chroma, biochemical oxygen demand (BOD), chemical oxygen demand (COD) and hard-degradation materials (Wang *et al.*, 2011). The wastewater was discharged directly from the factories in the flowing water or downstream. Then, the presence of these compounds in the wastewater may create serious environmental problems due to its toxicity to aquatic life, causing the river or downstream become sludge and mutagenicity to human (Arora, 2014).

Besides, heavy metal is also one of the chemicals released from the textile industry and it poses a threat to the water quality and ecosystem health (Needhidasan *et al.*, 2013). The heavy metals found in wastewater of textile industry can be very dangerous to the human population (Zeiner *et al.*, 2007). They cannot be degraded or destroyed and high concentration of heavy metals enters to the human body can lead to poisoning (Sarker *et al.*, 2015).

Dyes is a substance that applied to a substrate by a process that alters any crystal structure of the colored substances and it provides the color (Chequer *et al.*, 2013). While the dyeing process is among the crucial factors in the successful trading of textile products and this process involves three steps: preparation, dyeing and finishing. Through the dyeing process, it contributes to the heavy metal production that will have negative impacts to human and environment (Zeiner *et al.*, 2007). The general poisoning signs of heavy metals are the gastrointestinal disorders, diarrhea, stomatitis, tremor, paralysis, vomiting and depression (Duruibe *et al.*, 2007). For example, Cu is toxic to aquatic plants at concentration below 1.0 mg/L while concentration near to this level can be toxic to some aquatic life (Dey & Islam, 2015). Therefore, regular monitoring should be carried out and appropriate treatments should be used to treat the wastewater so that the health of the community and environment are promised.

In this study, the physico-chemical properties and heavy metal contamination of *batik* wastewater from textile workshop, University Malaysia Kelantan (UMK) Bachok Campus was investigated in order to get the preliminary data of *batik* wastewater contamination.

1.3 Objectives

1. To determine the physico-chemical properties [pH, turbidity, temperature, COD, ammoniacal nitrogen (NH_3N), total dissolved solid (TDS), total suspended solid (TSS)] in *batik* wastewater.
2. To determine the concentration of selected heavy metals [copper (Cu) , nickel (Ni), zinc (Zn), manganese (Mn), aluminum (Al)] in *batik* wastewater.
3. To compare the physico-chemicals and heavy metal values with the Environmental Quality (Industrial Effluents) Regulations 2009 Standard B under Environmental Quality Act 1974.

CHAPTER 2

LITERATURE REVIEW

2.1 Textile Industries in Malaysia

Industry is among the largest sources of pollution in the world, it causing more than half of the total water contamination and brings to most deadly pollutants (Joshi & Shrivastava, 2015). There are more than 3600 individual textile dyes are being manufactured by the industry today (Kant, 2012). Textile industries have become the source of income in some countries due to the increasing demand for clothing. This is very helpful in boosting the economy of the country. However, this industry also brings the bad impact to the country, which is degrading the quality of environment. It is estimated as much as 280,000 tons of textile dyes discharged as industrial wastewater every year in the world (Asghar *et al.,* 2015).

There are natural fiber and man-made fiber in the textile industry. For the natural fiber, it includes cotton, linen, wool and silk and it is obtained from natural resources such as flowers, nuts, berries and other plants as well as animal sources. While the man-made fibers are either coming from synthetic polymers or derived from natural polymers. In Malaysia, man-made fiber is important in the textile industry, especially in the east coast of Peninsular Malaysia which is in Kelantan and Terengganu (Pang & Abdullah, 2013). About 400,000 tons of man-made fibers including nylon, polyester filament and staple are produced in Malaysia in 2008. Hence, it also contributed to the generation of huge amount of textile wastewater. Due to this, the textile finishing had accounted for 22 % of the total volume of industrial wastewater production in 2009 (Pang & Abdullah, 2013). This showed that textile industry in Malaysia generate a large amount of wastewater which discharge to the environment.

Heavy metal such as Pb, Cr, Cd and Cu are widely used for the production of color pigments of textile dyes. They exist either naturally in the textile structures or penetrate into fibers of textile during production, dyeing process or through protective agents used during storage. The presence of metals in different dyes is important because they acted as textile colorants (Pang & Abdullah, 2013). The common heavy metal including Cu, Cr, Pb, Mn, Cd, Ni and Zn in different dye classes are summarized in the Table 2.1.

Table 2.1: Common heavy metals in different classes of industrial dye (Verma, 2008)

Dry Classes	**Metals in Dyes**
Acid dyes	Copper, lead, zinc, chromium, cobalt
Basic dyes	Copper, lead, zinc, chromium
Direct dyes	Copper, lead, zinc, chromium
Mordant dyes	Chromium
Pre-metallized dyes	Cobalt, chromium, copper
Reactive dyes	Copper, chromium, lead
Vat dyes	None
Disperse dyes	None

Textile plants are the significant sources of toxic discharges in the aquatic environment (Villegas-Navarro *et al.*, 2001). The textile plant use cotton, synthetic fibers, integrated printing and dyeing operations which applying a wide variety of organic dyes. Hence, the wastewater generated by the textile plant contain dyes and heavy metals and typical sources of metals in textile wastewater is summarized in Table 2.2 (Verma, 2008).

These heavy metals generated will be released to the environment which are high toxicity and bioaccumulate in the human body aquatic life, natural water bodies and also in the soil (Halimoon & Yin, 2010).

Table 2.2: Sources of heavy metals in textile and dye wastewater (Verma, 2008)

Metals	**Sources**
Copper (Cu)	Dyes, fiber wash, source water
Chromium (Cr)	Dyes and laboratories
Zinc (Zn)	Dyes, chemicals, source water
Cobalt (Co)	Dyes
Lead (Pb)	Dyes and plumbing operations
Manganese (Mn)	Use of permanganate strip
Nickel (Ni)	Dyes
Silver (Ag)	Photo operations
Tin (Sn)	Finishing chemicals, plumbing
Titanium (Ti)	Fiber
Arsenic[α] (As)	Fibers, fugitive, source water
Cadmium[α] (Cd)	Impurities in salts used in processing
Mercury[α] (Hg)	Dye/commodity, chemical impurities

[α] AS, Cd and Hg are found in very low concentration

2.1.1 Impact of the Textile Industry

There are a few stages of mechanical processing for the production of fiber in textile industry which are spinning, weaving, yarn preparation, knitting and garment production. These processes make the fiber production become one of the largest consumption of the water (Pang & Abdullah, 2013). Hence, the industry will release a huge amount of wastewater in the end of the process. These textile dyeing wastewater contains concentrated pollutants which are complex composition and low biodegradability, since they contain a large variety of dyes, additives and derivatives that change seasonally (Chequer *et al.*, 2013). The untreated textile wastewater is high in color, COD, BOD, TSS, pH, Total Organic Carbon (TOC), temperature, turbidity and toxicity (Pang & Abdullah, 2013). Hence, the generated wastewater can cause environmental problems and thus it should be treated properly before disposal (Sengupta, 2007). Moreover, the discharge of wastewater from textile industry has to comply with the minimum requirement that stated in Environment Quality Act 1974 in Malaysia (Department of Environment, 2009).

2.2 *Batik* Industry

The term '*batik*' is an Indonesia-Malay word and it is a very ancient form of art. *Batik* is the art of waxing a surface, usually cloth, to make it resist to the dyeing, and removing the wax, re-waxing, and creating intricate designs and patterns (Nagar, 2009). In Malaysia, *batik* had been developed to its own particular aesthetic and design by accommodating the culture of Malaysian in term of the design, motif and color. *Batik* in Malaysia is more preferable by consumers as '*baju kurung*', '*kebaya*' and many more. Moreover, *Batik* has emerged from domestic market to the international recognition nowadays (Ruslan, 2006).

Batik industry is the biggest textile industry in Malaysia and many local people, especially in the east coast of Peninsular Malaysia that earn their living through this industry. They are normally inherited from generation to generation. This industry has become very commercialized and contribute greatly to the economic growth due to high local demands and also from the abroad (Ahmad *et al.*, 2012).

The process of *batik* is started from the preparation of raw materials, cloth and suitable equipment until drying process. For the painting process, the fabrics, dyes, waxes, chemicals and the equipment and tools like canting tool and stove are prepared. This process had a large water consumption. After that, the wax is applied on the fabric and the dyeing process will use both organic and inorganic synthetic dyes that available in various colors. The dye will be reacted with the added chemical agents to bond to the cloth and generate the final color (Ahmad *et al.*, 2012).

The most used dyes in *batik* are remazol and vinyl sulphone fibre reactive dyes (Rashidi *et al*, 2015). Besides, most of the *batik* producers use the plain fabrics that are imported from China, India and Japan. Fabric can be applied with variety of designs by using pencil and stencil. It is always done by the skilled designer in producing attractive and new design from time to time. The design is always based on the natural feature such as trees, flowers and sceneries. This is important since a beautiful design and nice color combination is important to have a good market value (Ahmad *et al.*, 2012).

In Kelantan, most of the entrepreneurs produce *batik* in traditional way, in which the untreated wastewater will be released. The untreated wastewater comprises of dyes, waxes, heavy metals, high COD and TSS content (Noor Syuhadah *et al.*, 2015). *Batik* industry normally involves small family set ups, thus access and ability to treat the wastewater can be considered as very less (Rashidi *et al.*, 2012).

According to DOE Kelantan Report (2011), *batik* industry is said to responsible for water pollution because its compliance rate of the industry is relatively low compared with the other industries and this eventually cause the environmental and health issues. Dyes used in the process of *batik* production are carcinogen and will accumulate in sediments at many sites, especially near to the location of *batik* wastewater discharge, which has an impact on the ecological balance of aquatic system (Intan, 2010). The ground water systems are also affected by these pollutants due to the leaching of soil (Namasivayam & Sumithra, 2005). This shows that the quality of soil and water are affected by the *batik* wastewater. While people will also suffer from skin problem such as allergy, sensitive and itchy skin affected by coloring and waxes of *batik* (Yaacob *et al.*, 2015).

Based on Birgani *et al.* (2016), the *batik* wastewater can be generated in the soaking, boiling and two rinsing processes. These processes have their own pollutants which result in the complexity of wastewater treatment (Birgani *et al.*, 2016). The sequence for the batik and production of wastewater is shown in Figure 2.1. In the coloring process, motifs in the fabric are painted, followed by the background. Then, the fabric is left to dry completely and then submerged in a sodium silicate solution. This is used to fix the coloring and minimize the fading afterward. The fabric is submerged in boiling water to melt and remove the wax from the fabric and reveal the outlines (Birgani *et al.*, 2016). After that, the fabric is rinsed in two times and left to dry. Throughout these processes, the wastewater is released. The released wastewater contains different elements of heavy metals (Widowati *et al.*, 2008). For instance, Zn is one of the heavy metals contained in the *batik* wastewater and it will pollute the environment and can be harmful to aquatic organisms. Consumption of high doses of Zn can cause severe health effect including liver disorders, hematologic and renal (Widowati *et al.*, 2008).

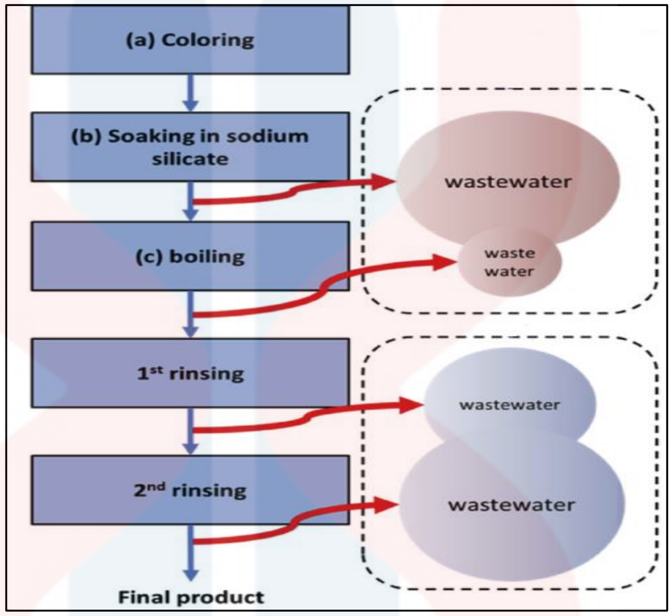

Figure 2.1: Sequence of batik and wastewater production (Birgani *et al.*, 2016)

2.3 Heavy Metal

The term heavy metal is defined as any metallic element that has high density and is toxic even at low concentration (Lenntech, 2004). Generally, they are considered to be those whose density exceeds 5 grams per cubic centimeter (Barakat, 2011). They occur as the natural constituents of earth's crust which are persistent environmental pollutants since they cannot be degraded or destroyed (Duruibe *et al.*, 2007). Besides, they are generally regarded as having atomic numbers of 22 to 92 in all groups from Period 3 to period 7 (Suhaimi *et al.*, 2005). Heavy metals include Pb, Zn, Cd, Hg, As, Ag, Cr, Cu, iron (Fe) and also the platinum group elements (Duruibe *et al.*, 2007). Heavy metals such as Cd, Cr, Cu, Ni, As, Pb and Zn are the most hazardous among the chemical-intensive industries (Barakat, 2011).

The mass of heavy metal is five times greater than the mass of water and thus produce positive ions in solution. These metallic elements can meet the demand of physiological role and provide nutritional requisite (Faudzi *et al.*, 2014). For example, Cu, Cr, Mn, Ni and Zn are necessary for human in minor quantity, while those exceeding the limit will cause the adverse impact to the human (Duruibe *et al.*, 2007). Excess of heavy metals may lead to toxicity and even death (Naja & Volesky, 2009). According to the research of Duruibe *et al* (2007), United State Environmental Protection Agency (USEPA) had set the Maximum Contaminant Levels (MCL) which is the tolerance limits of heavy metals in the drinking water. Table 2.3 shows the maximum contaminant levels for heavy metal concentration in water set by the USEPA.

Table 2.3: The maximum contamination levels for heavy metals concentration in water (Duruibe et al., 2007)

Heavy Metal	Maximum Concentration in Drinking Water (mg/L)	Maximum Concentration in H_2O Supporting Aquatic Life (mg/L or ppm)
Cd	0.005	0.008
Pb	0.01	0.0058
Zn	5.00	0.0766
Hg	0.002	0.05
Ca	50	Tolerable >50
Ag	0.0	0.1
As	0.01	-

With the rapid development of industries including metal plating facilities, mining operations, fertilizer industries, battery industries, paper industries and pesticides, their wastewater containing heavy metals are directly or indirectly discharged into the environment (Fu & Wang, 2011). The heavy metals are also among the waste produced by the textile dyeing and printing industry (Joshi & Shrivastava, 2015).

Heavy metals can be absorbed by the living organisms due to the high solubility in the aquatic environment (Barakat, 2011). Hence, heavy metals are also able to enter into human body through different pathway and cause harmful impacts. They are persistent in all parts of the body due to their inability to be destroyed or damaged (Lin *et al.*, 2011). Toxic effects of heavy metals on human health are well known in affecting the metabolism, harm to the organs, heart disease, damage to the nervous system and allergies. Furthermore, body tissues will be accumulated by the heavy metals and the enzymes are bind with the heavy metals. As a result, the function of the cell will be disrupted by the development of tumors and mutation (Tonetti & Innocenti, 2009). Hence, the *batik* wastewater that contained heavy metals will cause severe impact on the human health.

2.3.1 Zinc (Zn)

Zinc is located in group IIb in the periodic table of the elements, along with the other heavy metals which are Hg and Cd. In ordinary temperatures, it is brittle and crystalline but become ductile and malleable in the temperature of between 110 ℃ and 150 ℃. It can be used as pigment for the plastics, cosmetics, photocopier paper, wallpaper, printing ink and others (Gakwisiri *et al.*, 2012).

Zinc is relatively less toxic to the human health, particularly if taken orally and instances of acute poisoning due to zinc exposure from environmental sources are extremely rare (Nriagu, 2007). There are 2-4 grams of Zn distributed throughout the human body (Wapnir, 1990). Most of the Zn is in the brain, muscle bones, kidney and liver, along with the highest concentrations in the prostate and parts of the eye (Pfeiffer & Braverman, 1982). According to Wapnir (1990), zinc is the only metal which appears in all enzyme classes and it is also second most abundant transition metal in organisms after iron.

Zinc is vital for the human health as it involved in various aspect of cellular metabolism (Classen *et al.*, 2011). Zinc is required for the catalytic activity of more than 200 enzymes and it also plays role in human function including immune function, would healing, protein and DNA synthesis and cell division (Osredkar, 2012). Adequate zinc is required to develop a proper sense of taste and smell, ensure normal and healthy growth during pregnancy, childhood and adolescence (Osredkar, 2012). Therefore, supplemental zinc therapy has been used for the prevention or treatment of conditions such as lower respiratory tract infection in children for symptoms of the common cold and for acne (Porea *et al.*, 2000).

However, the daily doses of elemental zinc used should be ranged from 30 mg to 135 mg and it is harmful to the human if uptake the excess amounts of toxic Zn which cause nausea, epigastric pain, diarrhea, depressed immune function, vomiting, dizziness and lethargy (Porea *et al.*, 2000).

2.3.2 Manganese (Mn)

Manganese is the 5th most common metal and the 12th most common element in the earth's crust. In addition, it is also the fourth most widely used metal in the world, after Fe, Al and Cu (Levy & Nassetta, 2003). Metals present in cotton may cause problems in yarn manufacturing, bleaching and dyeing, even in the processing quality in textile industry (Zeiner *et al.*, 2007). For instance, manganese and ferrous ions are readily air-oxidized and they form compounds causing yellowing of whitewashed denim.

Manganese exposure is a health hazard associated with the mining and processing of Mn ores. Children that live near to the Mn sources may have the chronic toxicity symptoms that are different from adults who experience occupational exposure (Duka *et al.*, 2011). Exposure to the high level of Mn dust of fumes likely to get Parkinson-like syndrome, including weakness, muscle pain, slow speech, less facial expression and clumsy movement of the limbs (World Health Organization, 2011).

2.3.3 Aluminum (Al)

Aluminum has the atomic number of 13 and it is the third most abundant metal found in the earth's crust after oxygen and silicon (Gupta *et al.*, 2013). It is occurring naturally in the air, water and soil. Aluminum can be used to make beverage cans, pots and pans, airplanes, siding and roofing and foil (US Department of Health Human Services, 1999). Aluminum is used extensively in the machinery and equipment for textile industry and in the form of tube, sheet, casting and forgings (Davis & Davis, 1993).

Toxic forms of the aluminum are Al^{3+}, $Al(OH)^{2+}$, $Al(OH)^{2+}$. Chronic exposure to these forms of aluminum is associated with several health impacts. Aluminum affects the nervous system and resulted in the loss of memory, balance problem and loss of coordination (Krewski *et al.*, 2007). Aluminum ions will complete in reaction with other metal ions such as Zn, Fe, Calcium (Ca) and Cr in the human body. It can reach the blood and cross the blood-brain barrier (Sieliechi *et al.*, 2010). Accumulation of Al in the brain will cause the neurodegenerative diseases including Alzheimer's dementia, Parkinson's disease, amyotrophic lateral sclerosis, and dialysis encephalopathy (Gonçalves & Silva, 2007).

2.3.4 Nickel (Ni)

Nickel is the 28th element in the periodic table and it is a silver-white metal found in several oxidation states, but the +2 oxidation state [Ni(II)] is the most common state. It forms nickel-containing alloys easily (Duda-Chodak & Blaszczyk, 2008). The input of Ni to the human environment is about 150,000 and 180,000 metric tons per year from natural and anthropogenic sources respectively in the worlds. This is account of emission from fossil fuel consumption, production of industry and discharge of nickel compound and alloys (Kasprzak *et al.*, 2003).

There are many sources for the Ni, especially textile industries are known as major sources of heavy metal pollutants in water (Akpor *et al.*, 2014). This is because the dyeing process involves the use of compounds such as Ni, Cu, Cr and Pb which is very toxic and carcinogenic (Akpor *et al.*, 2014).

Nickel is distributed to all organs in the human body, mostly presence in the kidney, bone and lungs (Samal & Mishra, 2011). For the elimination of absorbed nickel, urinary excretion is the major route and fecal excretion primarily remove the nickel that is unabsorbed from the diet and passes through the gut (Von Burg, 1997). It is poorly absorbed from diets, typically less than 10 % of ingested nickel is absorbed (Samal & Mishra, 2011).

Nickel plays a well-defined role in the biological system (Sigel *et al.*, 2007). The highest concentrations of nickel in the body is found in the nucleic acids, particularly RNA, and is involved in protein structure or function (Chivers, 2015). Due to this, it probably plays a role in stabilizing the structure of RNA (Kumar & Trivedi, 2016). Besides, it aids in the production of prolactin which has a function in the production of human breast milk. The iron absorption, as well as adrenaline and glucose metabolism, hormones, lipid and cell membrane are also aid by the presence of nickel, which improves bone strength and ensures the production of red blood cells (Kumar & Trivedi, 2016).

2.3.5 Copper (Cu)

Copper is an essential trace element that is vital to the health of all living organisms as it is found in a variety of enzymes and proteins. Copper has an atomic number of 29, which is the first element of group Ib of the periodic table of elements. Copper is the third most important metals used by man and it is mainly used in electrical applications, construction, while other uses are transport and coins, musical instruments, sculptures and cookware (Alloway, 2012).

Copper together with the aluminum and iron show their good light fastness rating for most of the natural dyes (Maulik *et al.*, 2014). They have good complex forming ability to hold molecules of two or more suitable dye together to form insoluble large complex, which improve the light fastness of the dyed substrates (Allen, 1987). Research by Maulik *et al.* (2014) found that copper sulphate, aluminum sulphate and ferrous suphate exhibit high colorfastness to washing due to the formation of insoluble large complex by the coloring component present in colorants besides the presence of these metal ions within the fibre.

Copper is a vital dietary nutrient and it is needed by human well-being in a small amount (Araya *et al.*, 2006). It can be found in every tissue of the body, primarily stored in the liver, and fewer amounts present in the brain, heart, kidney and muscles (Osredkar, 2012). Copper is the third most abundant trace metal in human body after iron and zinc, but the total amount of copper present in body is only 75-100 milligrams (Willis *et al.*, 2005).

Copper is also important in human metabolism, because it allows many critical enzymes to function properly (Harris, 2001). The strength of the skin, blood vessels, epithelial and connective tissue throughout the body can be maintained. In addition, copper can act as both an antioxidant and a pro-oxidant (Osredkar, 2012). As an antioxidant, copper is able to neutralize free radicals in which free radical occurs naturally in the body and damage cell walls, interact with the genetic material and cause health problem. While as a pro-oxidant, copper promotes the damage of free radical and this contribute a lot of the development of Alzheimer's disease (Araya *et al.*, 2006).

Human need approximately 1-2.5 mg of copper daily. Deficiency of Cu in human is always linked to anemia, gastrointestinal disturbances, aortic aneurisms, abnormal bone development and death (Woody & O'Neal, 2012). In contrast, copper is toxic at higher concentration. Overdoses of Cu for 44 mg/L and less can cause gastrointestinal distress, nausea, vomiting, headache, dizziness, and metallic taste in mouth, while higher doses can cause coma and death (National Academic of Science, 2000).

2.4 Heavy Metal Treatment

Since the heavy metals can cause serious health disorder, thus it is necessary to treat metal-contaminated wastewater prior its release to the environment. Concern of the public over the heavy metals contamination to the environment has stimulated the development of treatment technologies in removing heavy metals from wastewater (Ku & Jung, 2001).

Different techniques of treatment for heavy metal in wastewater are carried out in order to improve the quality of the treated wastewater such as chemical precipitation (Fu & Wang, 2011), ion exchange (Peters *et al.*, 1985), membrane filtration (Parmar & Thakur, 2013), coagulation-flocculation (Tzoupanos & Zouboulis, 2008) and others. Each of them has their inherent advantages and limitations respectively in the application of removing the heavy metal from wastewater (Kurniawan *et al.*, 2006).

Chemical precipitation is inexpensive and simple to carry out (Fu & Wang, 2011). This process generates the insoluble precipitates of heavy metals as hydroxide, sulfide, carbonate and phosphate. The most commonly used precipitation is hydroxide treatment due to its simplicity, low cost and ease of automatic pH control (Peters *et al.*, 1985). While ion exchange has high treatment capacity, high removal efficiency and fast kinetics (Kang *et al.*, 2004). As a cost effective method, ion exchange usually involves low cost materials and convenient operations, and it has been proved that effectively remove heavy metals, particularly for treating water with low concentration of heavy metals (Gunatilake, 2015).

Besides, membrane filtration technologies have high efficiency, easy operation and space saving in removal of heavy metal (Fu & Wang, 2011). It is capable of removing organic compound, suspended solid, and also inorganic pollutants such as heavy metal (Gunatilake, 2015). While the major disadvantage of this method is the membrane fouling which can greatly affect the efficiency of filtration. In addition, it is also high operating cost (Sharma, 2014). For the coagulation-flocculation, it is high simplicity and inexpensiveness (Tzoupanos & Zouboulis, 2008). The main disadvantage for coagulation-flocculation is the high operating cost as it involves the consumption of chemical. In addition, the toxic sludge generated must be converted into a stabilized product in order to prevent heavy metals from leaking into the environment (Parmar & Thakur, 2013).

2.5 Colorimetric

Colorimetric analytical methods have been widely used for over 100 years (Simoni *et al.*, 2002). It is concerned with the determination of concentration of a material based on relative absorption of light with respect to a known concentration of a material. Colorimetric tests rely on the generation of color, often by complex formation between an organic ligand and metal ion. A simple definition of colorimetry is the measurement of color and a colorimetric method is any techniques that can be used to evaluate an unknown color in reference to a known color (Steffen, 2001). These color may be measured by using a colorimeter, color comparator and others.

For the colorimeter tubes, if the tubes have been scratched through excessive use must be replaced with new ones. The dirt on the surface of the tubes should be cleaned on both the inside and outside. Besides, fingerprints on the outer surface of the tubes must be wiped in order to prevent excessive light scattering and cause inaccuracy of the result (Steffen, 2001).

Colorimeter is also known as filter photometer. It is the device that used to measure the absorbance of particular wavelengths of light by a specific solution. The color filters used in the colorimeter are changeable so that the wavelength of light can be selected which the solute absorbs the most in order to maximize accuracy (Mukesh & Shinde, 2013). The usual range of wavelength is from 400 to 700 nanometers.

Colorimeter works by passing a specific wavelength of light through a solution, and then measuring the light that comes through on the other side. Normally, the more concentrated the solution is, the more light will be absorbed, which can be seen in the difference between the light at its origin and after it has passed through the solution (Mukesh & Shinde, 2013).

The handheld DR 900 provides the fastest and simplest to most-used testing methods. It stores data for up to 500 tests and can test up to 90 of the most commonly tested water methods. Moreover, it is intuitive user interface which allows for quick selection and easier testing (Hach, 2013).

CHAPTER 3

MATERIAL AND METHOD

3.1 Study area

This study was conducted in UMK Bachok Campus in Kelantan (coordinate: N 05°59’42.7”, E 102°24.1’12.8”). The wastewater used for this study was the *batik* wastewater that generated and released by the textile workshop in UMK Bachok Campus. Total of four sampling points was selected in this study. The coordinates of each sampling points were shown in Table 3.1. Each sampling point was in a distance of about 5 meter and the wastewater will be flowed from first sampling point to the fourth sampling point. After the fourth sampling point, the *batik* wastewater will be flowed into a point which combined with the other wastes. Then, it will flow from the upstream to the downstream through the drainage system and reach the pond and finally flow into the nearest river.

The textile workshop will operate when there are students carry out their final year project and the production of *batik* depend on the final year project by the students.

Table 3.1: Coordinates of sampling points

Sampling Point	Coordinates
First (S1)	N 05°59’42.7”, E 102°24.1’12.8”
Second (S2)	N 05°59’43.5801”, E 102°24’12.3602”
Third (S3)	N 05°59’44.1384”, E 102°24’12.042”
Fourth (S4)	N 05°59’44.3616”, E 102°24’11, 6244”

3.2 Sampling

The samples were collected in May in order to prevent the Northeast Monsoon. This is because the raining season may affect the compositional of wastewater in the drainage. The sampling was conducted three times. The first sampling was conducted before the semester begins. This means that first sampling was before the textile workshop in UMK Bachok Campus generate the wastewater. The result was used as a control. After that, the second and third sampling were conducted after the semester begins and the drainage in UMK Bachok Campus was filled with a lot of *batik* wastewater.

There are three water samples was collected from each sampling point. All of the water samples was collected at each sampling point by using polyethylene bottles that were thoroughly rinsed with 10 % nitric acid (HNO_3) to prevent contamination. Water samples were collected in these 500 mL polyethylene bottles and labeled (Al-Badaii & Shuhaimi-Othman, 2014). Besides, few drops of nitric acid were added to each bottle to acidify the samples to pH < 2 in order to avoid the precipitation of components such as metal oxides and hydroxides and to retard biological activities (American Public Health Association, 1998). After that, the samples was cooled by putting them in a box filled with ices. Then, the samples were transported to the laboratory and stored in the chiller which was maintained its temperature in less than 4 ^{o}C (American Public Health Association, 1998). The proper way of preservation is prior to heavy metals analysis because the physical and chemical characteristics of the samples can be maintained which are truly representing the object under study (Zeiner *et al.*, 2007). All of the samples collected was analyzed for physico-chemical and heavy metals.

3.3 Measurement of Water Parameters

For *in situ* analysis, the physical parameter (temperature, turbidity) and chemical parameter (pH and TDS) were analyzed. All the parameters were analyzed by using YSI Model 556 Multiparameter Meter except for the turbidity which was measured by using 2100P Turbidimeter. While COD, TSS, NH_3N was analyzed in the laboratory by using HACH DR 900 Colorimeter.

3.4 Water Sample Digestion for Heavy Metal Analysis

Heavy metals that were investigated in the wastewater of textile workshop are Cu, Ni, Zn, Al and Mn. All of these elements were analyzed by HACH DR 900 Colorimeter.

Before analysis, USEPA mild digestion was used for the digestion of textile wastewater (Hach, 2007). At first, about 1 liter of the preserved samples was added with 3 mL of 70 % nitric acid. The digestion was generally carried out in conical flasks, covered loosely to avoid atmospheric contamination (Kuboyama *et al.*, 2005). Hence, the 100 mL of acidified sample was transferred to a 250 mL conical flask. Then, about 5 mL of 1:1 hydrochloric acid was added into the sample.

The sample was put on a hot plate at 95 ℃ (203 °F) until 15-20 mL of the sample remains. The sample was made sure that do not boil. Then, the cooled sample was put through a 0.45 µm filter to remove any insoluble material. The pH of the digested sample was adjusted to pH 4-5 with 5.0 N sodium hydroxide (NaOH). The pH should not exceed 5 to prevent precipitation. Lastly, the sample was transferred to a 100 mL volumetric flask and diluted to the mark with deionized water.

3.5 Chemical Oxygen Demand Analysis

About 100 mL of water sample was homogenized for 30 seconds in a blender. Then, the homogenized sample was poured into a 250 mL beaker and stirred gently with a magnetic stir plate. After that, about 2 mL of sample was pipetted into the vial for the selected range at an angle of 45 degrees. For the blank vial of selected range, it was added by 2 mL of deionized water. Then, the outside of all the vials should be held over the cap and cleaned with a tissue. The vial was inverted gently several times to mix and then inserted into the preheated DRB200 Reactor. The lid was closed and the sample was heated for two hours at 150 ℃. Then, the vial was left about 20 minutes to cool to 120 ℃ or less. The vial was inverted several times while it was still warm and then was put in a tube rack to cool to room temperature. Then, the blank vial was inserted into the colorimeter and ZERO was pressed. After that, the prepared sample was cleaned and inserted into the colorimeter. READ was pressed and result was shown (Hach, 2007).

3.6 Ammoniacal Nitrogen Analysis

Ammoniacal Nitrogen was analyzed by using HACH DR 900 Colorimeter. For the preparation of blank solution, 0.1 mL of ammonia-free water was added to one AmVer™ Diluent Reagent Test 'N Tube. For the sample preparation, the samples were also added one AmVer™ Diluent Reagent Test 'N Tube. Then, the content of one Ammonia Salicylate Reagent Powder Pillow was added for the 5 mL samples of each vial. After that, the content of one Ammonia Cyanurate Reagent Powder Pillow was added into each vial. The solution was shaken thoroughly in order to dissolve the powder. The solution was waited for 20 minutes to complete the reaction. Lastly, the reading of the sample was taken after the blank solution (Hach, 2007).

3.7 Total Suspended Solid Analysis

Total suspended solid was analyzed by using HACH DR 900 Colorimeter. About 500 mL of wastewater sample was blended at high speed by using a blender for exactly two minutes. Next, about 10 mL of wastewater sample and distilled water was poured into two different sample cell. Then, the sample cell of distilled water was put into colorimeter as the blank solution. After that, the distilled water sample cell was replaced by wastewater sample cell (Hach, 2007).

3.8 Zinc Analysis

The program 780 Zinc of the HACH DR 900 Colorimeter was started. A 25 mL graduated mixing cylinder was filled with 20 mL of sample. The contents of one ZincoVer 5 Reagent Powder Pillow was added to the mixing cylinder. After that, the cylinder was closed and inverted several times to dissolve the powder completely. Inconsistent readings may result if all of the particles are not dissolved.

For blank preparation, about 10 mL of the solution was poured into a sample cell. For the prepared sample, a plastic dropper was used to add 0.5 mL of cyclohexanone to the solution that was still in the mixing cylinder. Then, a 30 second reaction time was started by using instrument timer. During the reaction period, the mixing cylinder was closed and the prepared sample was shaken vigorously. The sample showed reddishorange, brown or blue, depending on the zinc concentration. Then, three minutes reaction time was started and during the reaction period, the prepared sample solution was poured from the mixing cylinder into a second sample cell. When the timer expired, the blank was cleaned and inserted into the cell holder. ZERO was pushed and the display was showed 0.00 mg/L. The prepared sample was cleaned and inserted into the cell holder. READ was pushed and result was shown in mg/L (Hach, 2007).

3.9 Manganese Analysis

The Program 290 Manganese, LP Pan was started. For the preparation of the blank, a sample cell was filled with 10 mL of deionized water. For the preparation of sample, a second sample cell was filled with 10 mL of sample. Then, the contents of one Ascorbic Acid Powder Pillow was added to each sample cell. Both of the sample cells was closed and inverted in order to dissolve the powder. Exact 12 drops of Alkaline Cyanide Reagent Solution were added to each cell. The sample cells were swirled to mix and the solution started to show turbidity. After that, exact 12 drops of 0.1 % PAN Indicator Solution were added to each cell. The sample cells was swirled to mix. Then, a 2 minute reaction time was started by using an instrument timer. When the timer expired, the blank was cleaned and inserted into the cell holder. ZERO was pushed and the display was shown 0.000 mg/L. The prepared sample was clean and inserted into the cell holder. READ was pushed and results were shown in mg/L (Hach, 2007).

3.10 Aluminum Analysis

Program 10 Aluminum Aluminon was started. A graduated mixing cylinder was filled to the 50 mL mark with sample. Then, the content of one Ascorbic Acid Powder Pilow was added. The cylinder was closed and inverted several times to mix. One AluVer 3 Aluminum reagent powder pillow was added. A 1 minute reaction time was started by using instrument timer and the cylinder was inverted repeatedly during the timer. For the preparation of blank, about 10 mL of the reacted sample was poured into a sample cell and one Bleaching 3 Reagent powder pillow was added into the blank. A 30 seconds reaction time was started and the sample cell was swirled vigorously. Then, a 15 minutes reaction time was started. For the preparation of the sample, a 10 mL of solution from the cylinder was poured into a second sample time. After the timer expired, the blank was cleaned and inserted into the cell holder. ZERO was pushed. The display was shown in 0.00 or 0.000 mg/L Al^{3+}. After that, the prepared sample was cleaned and inserted into the cell holder within five minutes after the timer expired. READ was pushed and result was showed in mg/L Al^{3+}. Lastly, the graduated cylinder and sample cells were cleaned with soapy water and a brush immediately after the test. Rinsed with deionized water (Hach, 2007).

3.11 Nickel Analysis

Program 340 Nickel, PAN was started. For the preparation of blank, a sample cell was filled with 10 mL of deionized water. For the preparation of the sample, a second sample cell was filled with 10 mL of sample. The content of one Phthalate-Phosphate Reagent Powder Pillow was added to each cell. The sample cells were closed and shaken immediately to dissolve the reagent. Then, about 0.5 mL of 0.3 % PAN Indicator Solution was added to each cell. The sample cells were closed and inverted several times to mix. Then, a 15 minute reaction time was started by using an instrument timer. The contents of one EDTA Reagent Powder Pillow was added to each cell when the timer expired. After that, the sample cells were closed and shaken to dissolve the reagent powder. The blank was cleaned and inserted into the cell holder. ZERO was pushed and the display was shown in 0.00 mg/L. Next, the prepared sample was also cleaned and inserted into the cell holder. READ was pushed and result was shown in mg/L (Hach, 2007).

3.12 Copper Analysis

The program 135 Copper, Bicinchoninate was started. For the preparation of the sample, a sample cell was filled with 10 mL of sample. Then, the content of one CuVer 1 Copper reagent powder pillow was added. The sample cell was swirled to mix. After that, a 2 minute reaction time was started by using an instrument timer. For the preparation of the blank, a second sample cell was filled with 10 mL of sample. Then, the blank was cleaned and inserted into the cell holder. ZERO was pushed and the display was showed in 0.00 mg/L. After that, the prepared sample was inserted into the cell holder within 30 minutes after the timer expired. READ was pushed and result was shown in mg/L (Hach, 2007).

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Overview

The physico-chemical parameters of batik wastewater were measured by YSI 556 Multiparameter and HACH DR 900 Colorimeter. While the data for heavy metals were measured by HACH DR 900 Colorimeter. The readings of physico-chemical and heavy metal were taken for three times which were one time for control and two times after discharge of *batik* wastewater. The first sampling and second sampling were conducted after the semester begins and the drainage had been filled with the *batik* wastewater released by the students that carry out their final year projects. While the control sampling was taken after the sampling site were not discharged of batik wastewater for more than one month.

4.2 Physico-chemical and Heavy Metal Concentration of *Batik* Wastewater

The physico-chemical properties including COD, TSS, TDS, NH_3N and turbidity were determined for each of the water samples. Data obtained and their mean concentrations were tabulated in Table 4.1. While data from heavy metal tested including Zn, Mn, Al, Ni, and Cu were tabulated in Table 4.2.

Table 4.1: The reading of physico-chemical properties for control, first sampling and second sampling

Parameter	Control				First Sampling				Second Sampling			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
COD (mg/L)	273.00	356.00	43.00	391.00	1086.00	336.00	783.00	102.00	1481.00	594.00	465.00	10.00
TSS (mg/L)	88.00	72.00	77.00	89.00	626.00	564.00	28.00	18.00	329.00	835.00	242.00	161.00
NH_3N (mg/L)	0.31	0.23	0.12	0.30	0.32	0.26	0.12	0.10	0.18	0.32	0.12	0.10
pH	7.02	7.73	7.50	7.26	10.89	11.01	11.17	11.58	10.13	9.73	10.04	10.65
Temperature (^oC)	30.80	31.10	30.72	31.40	33.98	29.35	29.24	29.41	31.32	29.40	30.13	30.06
TDS (mg/L)	280.00	20.00	210.00	240.00	6250.00	6500.00	8830.00	8410.00	5590.00	4020.00	3410.00	5320.00
Turbidity (NTU)	14.00	15.70	29.90	66.90	54.10	60.30	65.00	58.70	159.00	84.70	97.60	67.30

Table 4.2: The reading of heavy metals concentration for control, first sampling and second sampling

Parameter	Control				First Sampling				Second Sampling			
	S1	**S2**	**S3**	**S4**	**S1**	**S2**	**S3**	**S4**	**S1**	**S2**	**S3**	**S4**
Zn (mg/L)	0.240	0.250	0.640	0.670	1.022	1.736	1.667	1.046	0.830	0.720	0.820	0.760
Mn (mg/L)	0.039	0.066	0.084	0.105	0.208	0.235	0.189	0.397	0.090	0.168	0.297	0.078
Al (mg/L)	0.162	0.286	0.545	0.276	5.316	6.659	3.975	4.509	3.043	2.512	2.108	2.063
Ni (mg/L)	0.022	0.013	0.018	0.016	0.009	0.016	0.019	0.015	0.213	0.622	0.253	0.339
Cu (mg/L)	0.190	0.100	0.130	0.030	0.427	0.338	0.267	0.344	0.390	0.200	0.190	0.210

4.3 Comparison of Physico-chemical Content with the Permissible Standard

All of the results were compared to the Environmental Quality Act 1974, Environmental Quality (Industrial Effluents) Regulations 2009, with parameter limits of effluents of standard B except for the TDS and Turbidity which are not included in the list of standard. All of the included parameters were under the Fifth Schedule except the COD parameter which was under the Seventh Schedule in the Environmental Quality (Industrial Effluents) Regulations 2009. The Fifth schedule and Seventh Schedule were shown in Appendix A. There were two standards in Environmental Quality (Industrial Effluents) Regulations 2009 under Environmental Quality Act 1974: Standard A and Standard B. Standard A, as shown in the third column of the Fifth Schedule is used when the industrial wastewater flow into any inland waters within the catchment areas as specified in the Sixth Schedule. While Standard B, as shown in the fourth column of the Fifth Schedule is used when the industrial wastewater flow into any other inland waters or Malaysian waters. Hence, all of the *batik* wastewater were compared with the standard B as the *batik* wastewater discharged did not flow into the catchment area and are not used for the human consumption purpose. Comparison of physico-chemical properties with the permissible standard were shown in Table 4.3.

Table 4.3: Comparison of physico-chemical properties with the permissible standard

Physico-chemical Parameter	Mean Concentration for Control	Mean Concentration for First Sampling	Mean Concentration for Second Sampling	EQA Standard
COD (mg/L)	265.75 ± 156.52	576.75±441.67	637.50±615.60	250.00
TSS (mg/L)	81.50±8.35	309.00±331.24	391.75±303.36	100.00
NH_3N (mg/L)	0.24±0.09	0.20±0.11	0.18±0.10	20.00
pH	7.38±0.31	11.16±0.30	10.14±0.38	5.5-9.0
Temperature (°C)	31.01±0.31	30.50±2.32	30.23±0.80	40.00
TDS (mg/L)	187.5±115.3	7597.5±1311.4	4585±1040.8	-
Turbidity (NTU)	31.6±24.6	59.5±4.50	102.2±39.9	-

4.3.1 Chemical Oxygen Demand Analysis

The comparison of the COD in each sampling points with the standard was shown in Figure 4.1.

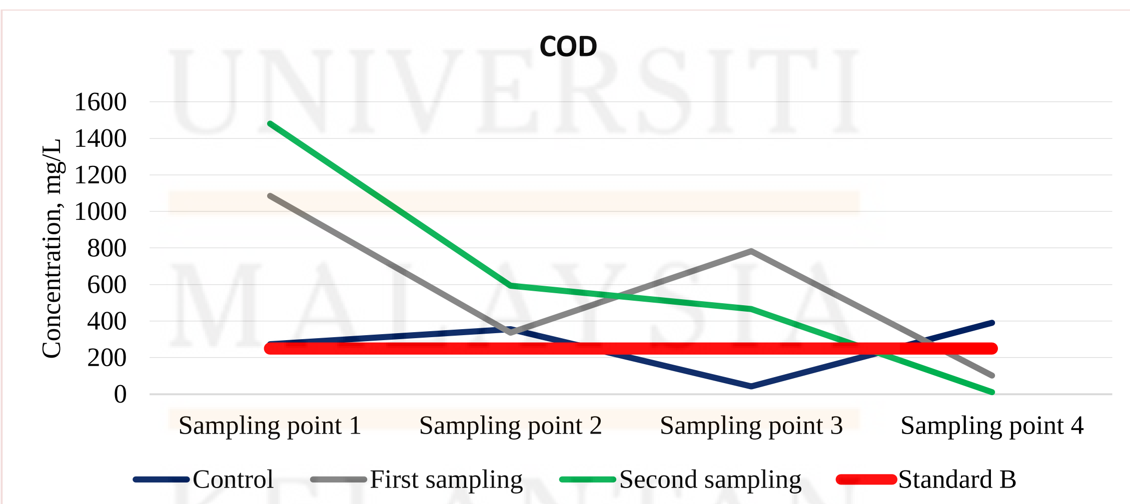

Figure 4.1: Reading of COD for the control, first sampling and second sampling

From the Figure 4.1, it can be seen that most of the concentration in each point were higher than standard. The control reading of sampling site was also a bit higher than the standard except for the third sampling point which was within the standard. The COD value of first sampling point for the second sampling was apparently higher than the other sampling points. Based on observation, this happened because there were leftover and food waste that discharged in the first sampling point of second sampling. These kind of organic matter increase the COD value (Qasim & Mane, 2013). However, it is also shown that all of the COD concentration in fourth sampling point has reached a concentration which is near to the standard. This means that the wastewater discharge did not cause much harm to the environment since the COD concentration had been reduced in the last sampling point.

COD is a measure of capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic matter and the oxidation of inorganic chemicals such as nitrogen and nitrite. High value of COD in the samples indicates a high degree of water pollution (Joshi & Santani, 2012). The dyeing and finishing operations involve the dyestuffs, chemicals and textile auxiliaries which vary from day to day (Mustapha, 2015). It contains variety types of waste chemical pollutants such as sizing agents, wetting agents, complexing agents, fluorocarbon, surfactants, oils, wax and other additives which are used throughout the processes. These pollutants contribute to high COD, TSS, BOD and others (Arumai Dhas, 2008). The high level of COD in this research is also supported by Hussein (2013) who stated that the wastewater of textile industry is characterized by highly visible color, high value of BOD, COD and pH.

A high value COD cause the pond require high amount of oxygen to completely oxidize the organic matter in the water body to carbon dioxide and water (Boyd, 1973). As a result, the discharge of the effluents with high COD value to the environment can lead to the depletion of dissolve oxygen and thus creates anaerobic condition (Subki & Rohasliney, 2011).

Measurement of COD is very useful to the people who concerned with water quality since they represent the necessary amount of oxygen for the aerobic biological oxidation of the organic matter in water body. With the aerobic biological oxidation, the pollution and amount of organic substance in the wastewater can be reduced (Eckenfelder, 1990).

4.3.2 Total Suspended Solid Analysis

Based on Table 4.3, the average concentration of TSS discharge in first sampling and second sampling were about triple than the value of EQA standard. The comparison of the TSS in each sampling point with the standard was shown in Figure 4.2.

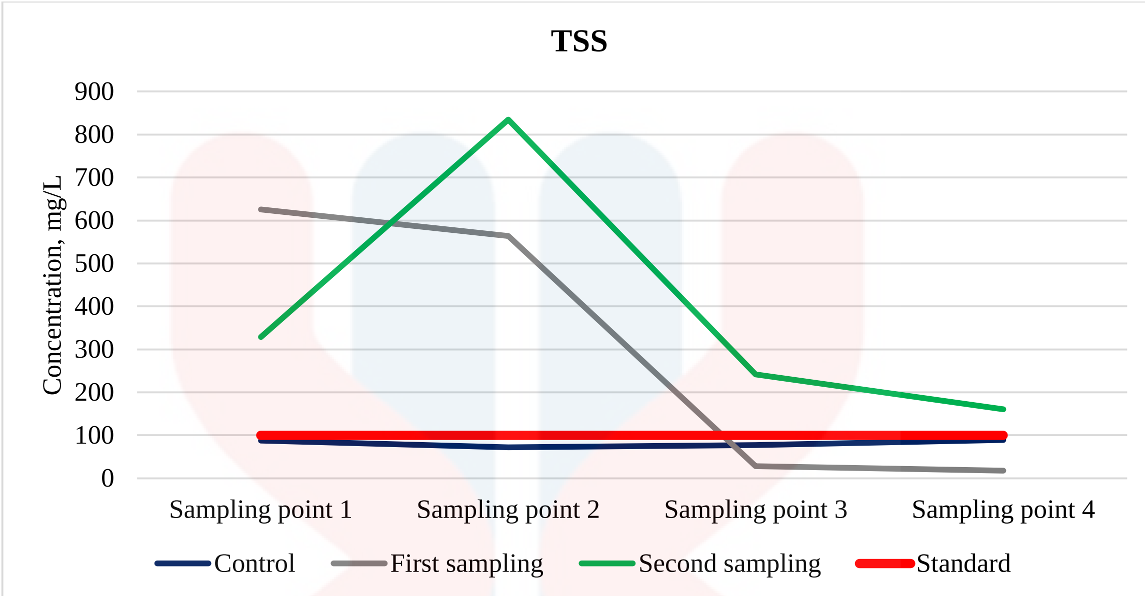

Figure 4.2: Reading of TSS for the control, first sampling and second sampling

From the Figure 4.2, it showed that the control reading of TSS were within the acceptable condition for discharge of industrial wastewater or mixed wastewater of standards B. While first sampling and second sampling were much higher than the standard, especially in the first and second sampling point. However, the concentrations of TSS had been reduced sharply in the third and fourth sampling point which was near to the standard value. The TSS of the textile workshop presented due to the undissolved solid particles remove from the cloth (Hussain *et al.*, 2004). Based on my observation at the sampling site, the source of TSS may come from the erosion of nearby land and sometimes accelerated by the flow of wind and running of rain water. Sometimes, the chemicals used in the processes of *batik* get precipitated due to change in pH, which increases the suspended particles (Hussain *et al.*, 2004).

Total suspended solid includes wax particles in the *batik* wastewater which will not able to pass through a filter. A high content of TSS affects the survival of aquatic life in a water body. This is because the suspended solids absorb the heat energy from sunlight, which causes the temperature of water increase. Due to this, the amount of dissolved oxygen in the water body will be reduced as warm water holds less oxygen than cool water (Akan *et al.*, 2012). The low amount of dissolved oxygen has a detrimental effect on aquatic life.

Besides, TSS can cause physical and abrasive damage to the fishes by clogging their gills and respiratory passages and affect their resistant to the diseases. Moreover, the suspended solid cover and blanket the bottom of the water body, smother the spawning beds and screen out the sunlight which is essential in the process of photosynthesis for the aquatic plants (Akan *et al.*, 2012).

4.3.3 Ammoniacal Nitrogen Analysis

The concentration of HN_3N in each sampling point was shown in Figure 4.3.

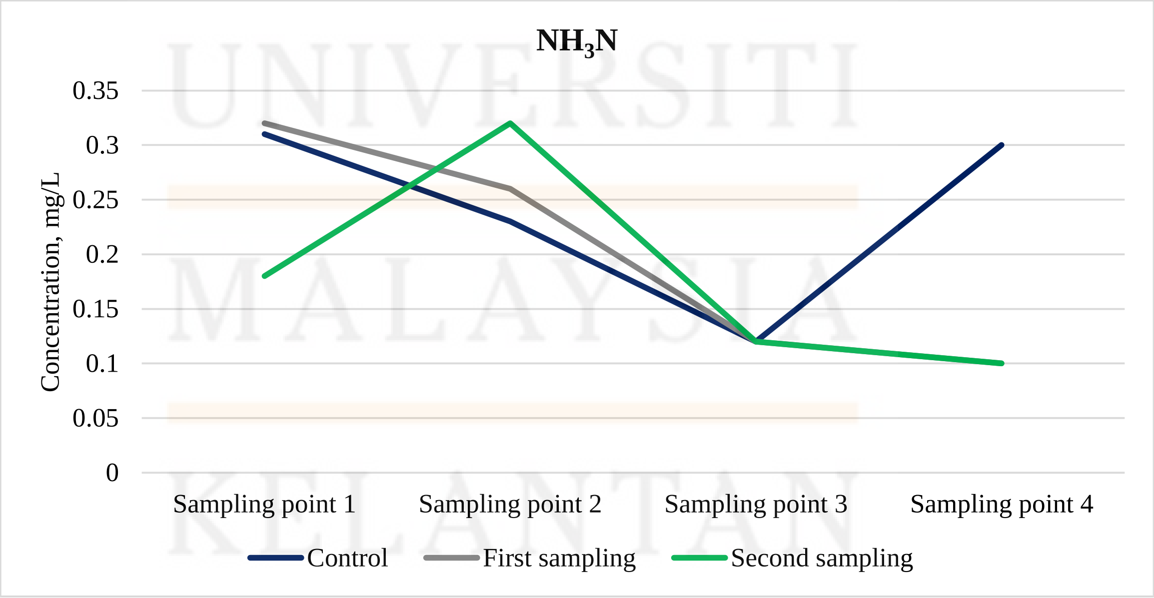

Figure 4.3: Reading of NH_3N for the control, first sampling and second sampling

Ammoniacal nitrogen is always related to nitrification and hypoxia, which result in fish poisoning and affect the water purification capacity (Luo *et al.*, 2015). Based on Figure 4.3, the concentrations of HN_3N for the control, first sampling and second sampling were significantly very low compare to the EQA standard which was 20 mg/L. Hence, the line of standard was high enough and did not show in the Figure 4.3. This also indicates that ammoniacal nitrogen does not have a clear impact on the water environment in this research.

4.3.4 pH Analysis

The comparison of the pH in each sampling point with the standard was shown in Figure 4.4.

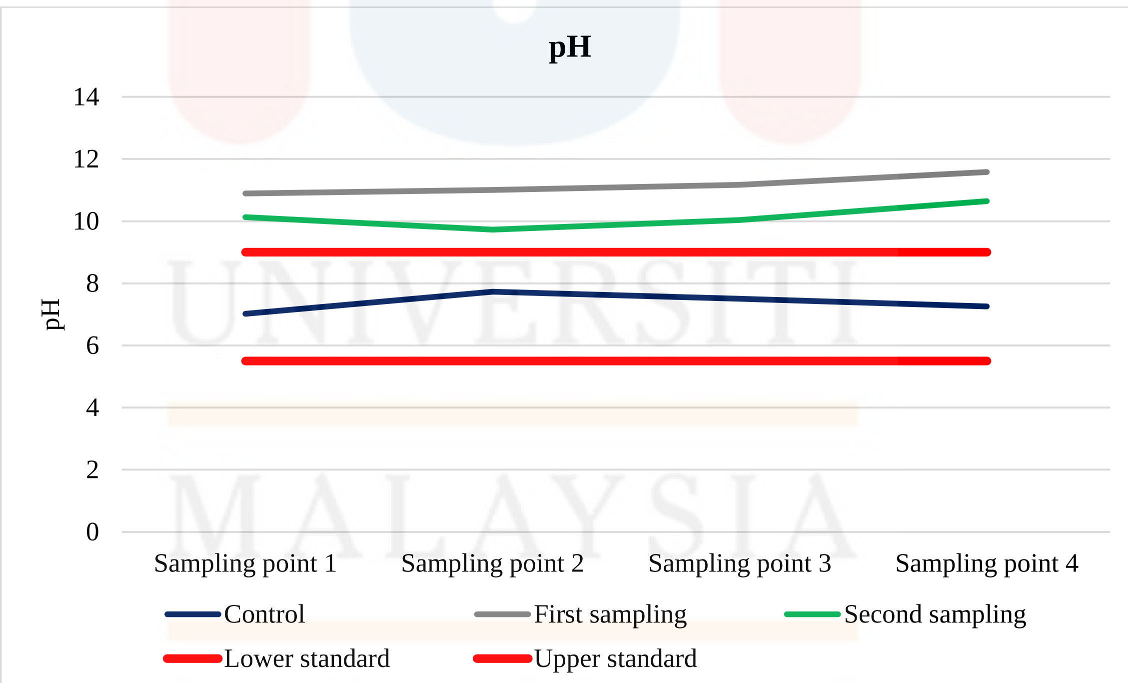

Figure 4.4: Reading of pH for the control, first sampling and second sampling

pH is the measurement of acidity and alkaline. In the textile processing units, pH is important factor in dyeing step as the solubility of the dyes depends on it. The pH also changes with the type of cloth processed (Hussain *et al.*, 2004). The acceptable pH for the industrial effluent is in the range of 5.5 to 9.0 because this range is likely not to harm the fish. A high pH value will be harmful to the various biochemical processes (Luklema, 1969). From the Figure 4.4, the control concentration of *batik* wastewater was within the range of standard. However, all of the pH values for the samplings after the discharge of *batik* wastewater were more than 9.0 which exceed the acceptable conditions for discharge of industrial wastewater.

In this research, *batik* wastewater showed a high value of pH. Most of the value of pH for the first and second sampling was in between 10 to 11. According to Nordin *et al.* (2013), the pollutants in textile wastewater are either organic acid or base which influence the property of pollutants available in the wastewater. The pH of dyeing water is between 10 to 11 when it is treated by alkali at high temperature in the process of desizing, scouring and mercerization. This is because the process mainly uses sodium hydroxide and its pH is also 10 to 11. Hence, the *batik* wastewater is alkaline (Wang *et al.*, 2011).

pH is an important factor in the chemical and biological system of the water as pH value of the wastewater has a direct impact on organisms and indirect impact on the toxicity of certain pollutants in the water (Subki & Rohasliney, 2011). Many heavy metals from hydroxides or basic carbonates that are relatively insoluble will tend to precipitate when pH is greater than 9 (Islam *et al.*, 2016). They remain suspended in the water as fine particles (Stiff, 1971). The suspended hydroxide of metal is toxic based on the particular situation.

The effect of pH also involves the synergy (Mara & Horan, 2003). Synergy is the interaction of two or more elements that combined and produce the effect greater than their sum. The low value of pH will be reacted with certain chemical and metals, which increase the toxicity than the normal. For example, fish can withstand pH as low as 4.8 but they will die at pH 5.5 in the water present as low as 0.9 mg/L of iron (Younger & Wolkersdorfer, 2004).

4.3.5 Temperature Analysis

The comparison of the temperature in each sampling point with the standard was shown in Figure 4.5.

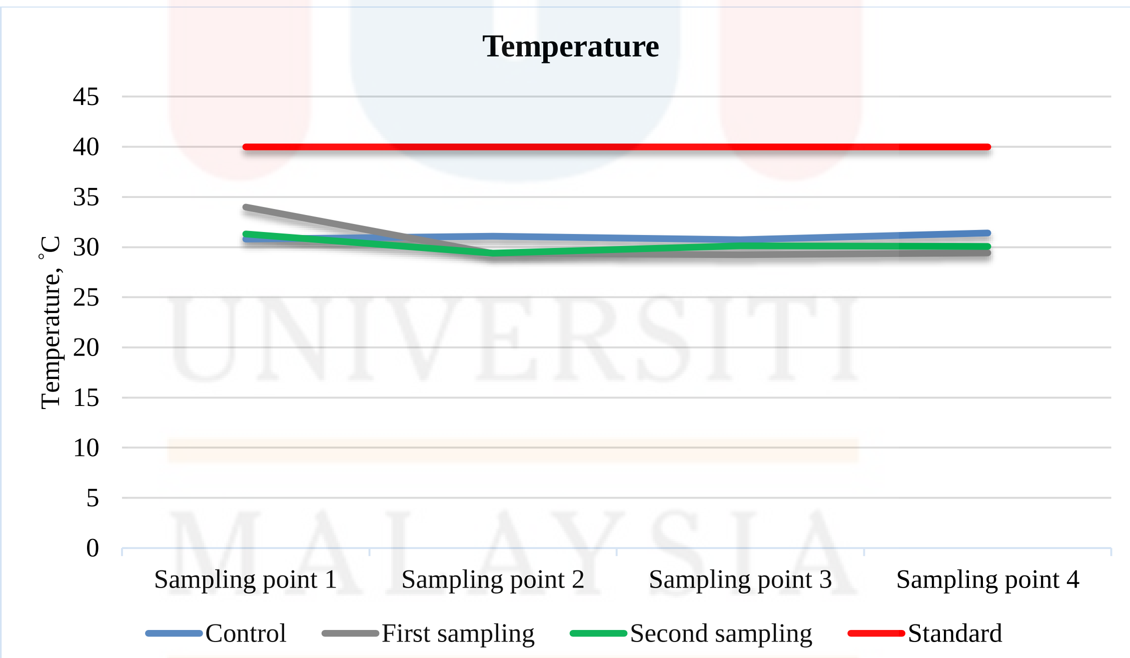

Figure 4.5: Reading of temperature for the control, first sampling and second sampling

The *batik* workshop removed the wax on the surface of the *batik* with boiling water, thus released the boiled water to the environment. From the Figure 4.5, the temperature for the control reading, first sampling and second sampling of *batik* wastewater were in the range of 29.2 ℃ to 34 ℃. These value of temperature were considered low when compare to the Environmental Quality (Industrial Effluents) Regulation 2009 standard B which is 40 ℃. The mean concentration of temperature for control reading was high due to the time for sampling was in the afternoon which was around 1.00 pm. High temperature changes can damage to the aquatic plants and wildlife and accelerate the biological degradation, corrosion of concrete pipe and odor production from anaerobic decomposition (Yeboah, 2015).

4.3.6 Total Dissolved Solid Analysis

The concentration of TDS in each sampling point was shown in Figure 4.6.

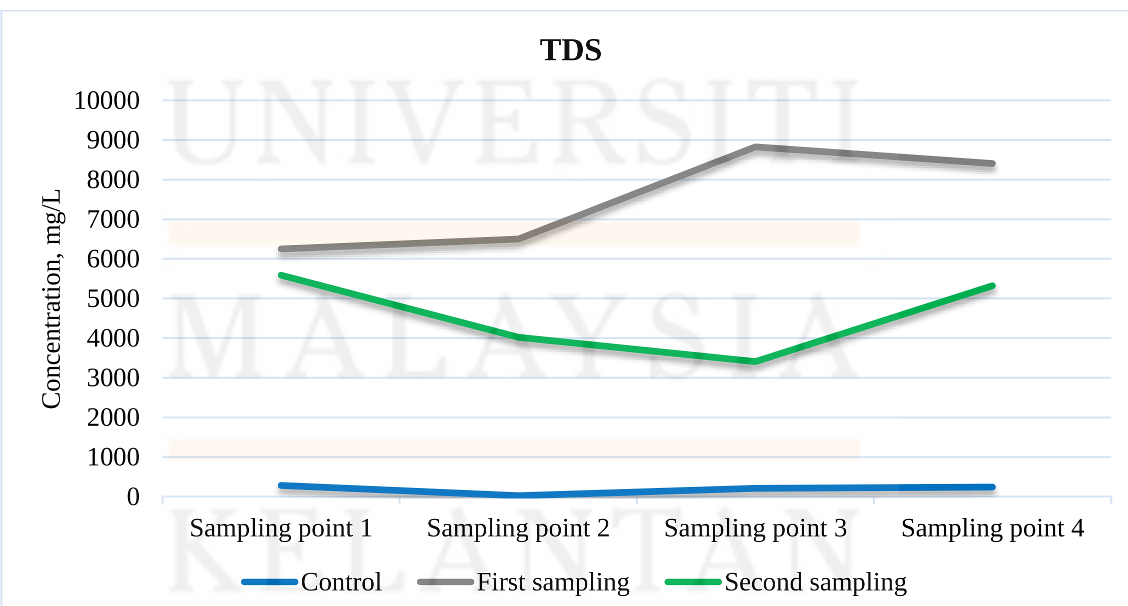

Figure 4.6: Reading of TDS for the control, first sampling and second sampling

TDS is not considered in Environmental Quality (Industrial Effluents) Regulations 2009. From the Figure 4.6, the control of the TDS concentration was relatively low compare to first sampling and second sampling. TDS was not considered in acceptable condition for the discharge of industrial effluent for mixed wastewater in Environmental Quality (Industrial Effluents) Regulations 2009 standard because TDS was not of health concern at all levels.

4.3.7 Turbidity Analysis

The concentration of turbidity in each sampling point was shown in Figure 4.7.

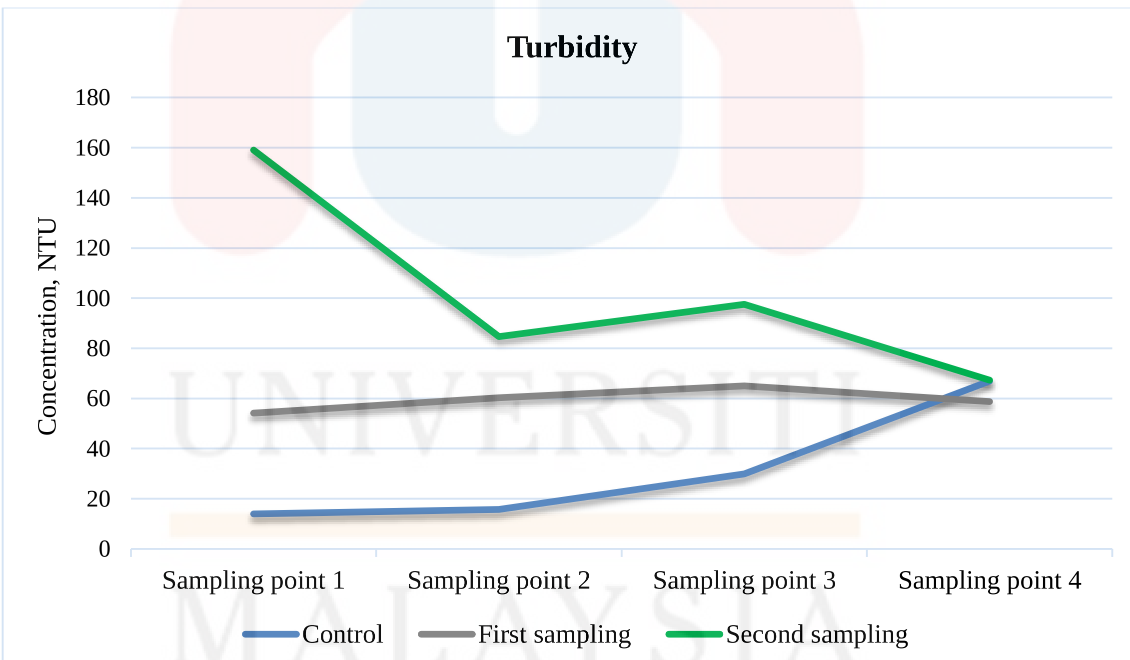

Figure 4.7: Reading of turbidity for the control, first sampling and second sampling

Turbidity was not considered in the standard of Environmental Quality (Industrial Effluents) Regulations 2009. It is a measure of the degree to which the water loses its transparency due to the presence of the suspended particulates (Wong *et al.*, 2015). This research showed that the turbidity concentration of control was increasing gradually from first sampling point until last sampling point which was 66.9 NTU. Based on observation, the increasing of the turbidity from first sampling point to last sampling point is due to the presence of suspended sediments in the last sampling point.

The first sampling of turbidity concentration showed that the turbidity was constant in each sampling points and the average concentration was 59.5 NTU. For the second sampling, the turbidity was decreased from first sampling point of 159.0 NTU to the 67.3 NTU of the fourth sampling point. The average concentration of the second sampling was 102.2 NTU. The high turbidity in the sampling can be caused by the presence of phytoplankton or suspended sediments in water (Pennington & Cech, 2009). As a consequence, turbidity blocks out the sunlight that is vital for the submerged aquatic vegetation and causes low level of dissolved oxygen in the water body.

Due to usage of dyes and chemicals, *batik* wastewater is dark in color, which increases the turbidity of water body. This in turn reduces the photosynthesis process and causing an alteration in the habitat (Aslam *et al.*, 2004).

4.4 Comparison of heavy metal concentration with the permissible standard

Heavy metal concentrations in *batik* wastewater were compared with the Environmental Quality (Industrial Effluents) Regulations 2009 Standard B. The comparison of heavy metals with the standard is tabulated in the Table 4.4.

Table 4.4: Comparison of heavy metal concentration with the permissible standard

Heavy Metal Concentration	Mean Concentration for Control (mg/L)	Mean Concentration for First Sampling (mg/L)	Mean Concentration for Second Sampling (mg/L)	Mean Concentration for All Samplings (mg/L)	EQA Standard B (mg/L)
Zinc (Zn)	0.450±.237	1.368±0.387	0.783±0.052	0.867±0.465	2.0
Manganese (Mn)	0.074±0.028	0.257±0.095	0.183±0.085	0.171±0.0921	1.0
Aluminum (Al)	0.317±0.162	5.115±1.168	2.432±0.455	2.621±2.405	15.0
Nickel (Ni)	0.017±0.004	0.015±0.004	0.357±0.184	0.130±0.197	1.0
Copper (Cu)	0.113±0.067	0.344±0.065	0.248±0.095	0.235±0.116	1.0

According to Cook (1998), the major problems associated with the textile wastewater are the presence of heavy metals, which generate from dyeing process and use of metal-containing dye in large quantity. There are mainly two sources of metal in textile wastewater including caustic soda, sodium carbonate and salts which are used in the different stages of textile industry (Hussein, 2013). The dyes used in batik industry mostly contain synthetic chemicals which are generally metal-based and these metals are harmful to the human health above the permissible limits (Orebiyi *et al.*, 2010).

All of the heavy metal tested were detected present in the *batik* wastewater by comparing the control reading and the readings after the discharge of *batik* wastewater. From the Table 4.4, the average concentration of heavy metal present in wastewater for all the samplings were found in the order Ni (0.130 mg/L) < Mn (0.171 mg/L) < Cu (0.235 mg/L) < Zn (0.867 mg/L) < Al (2.621 mg/L). This showed that the concentration of Ni was the lowest, while Al had the highest concentration in *batik* wastewater. The median concentration was the Cu which was always used to fix direct dyes and improve the light fastness on nylon fiber (Zeiner *et al.*, 2007). Zinc together with other trace concentration of heavy metals were the impurities that contained in the cationic dyes. The Zn and Cu were also used in wool dyeing or oxidizing agents in the sulfur dyeing (Chavan, 2001).

These heavy metal form metal-complex dyes which offer excellent fastness properties (Houser, 1986). They present in the textile wastewater as free ionic or complex metals due to their widespread applications (Zeiner *et al.*, 2007). Metals are most used in textile wet processing, but the concentration of *batik* wastewater will be vary in composition over time and from factory to factory due to the different materials used. (Wynne *et al.*, 2001). In future, the dyes used will probably be replaced by newly developed dyes which contain less toxic metals (Zeiner *et al.*, 2007).

4.4.1 Zinc Analysis

The comparison of zinc in each sampling point with the standard was shown in Figure 4.8.

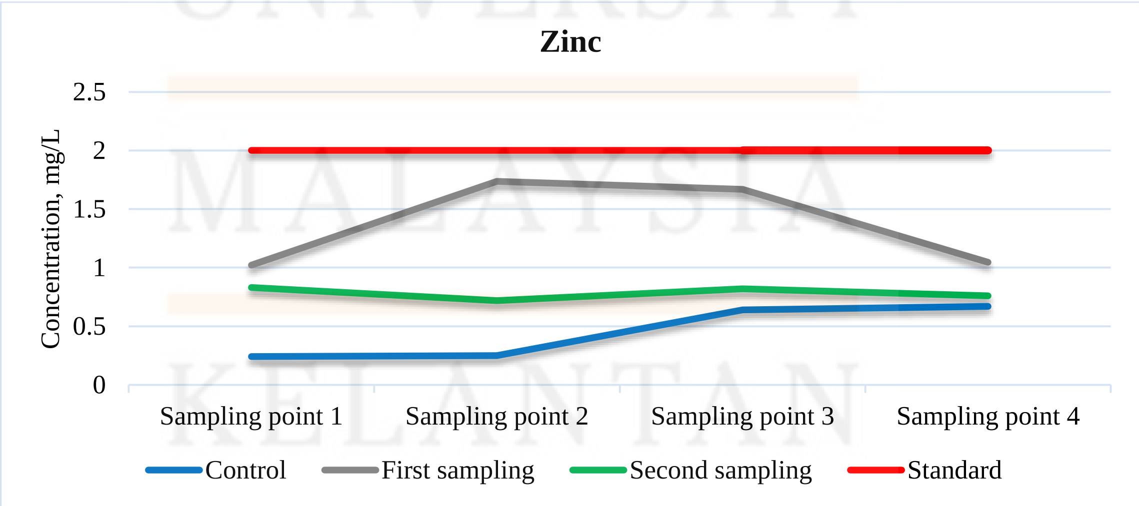

Figure 4.8: Reading of Zn for the control, first sampling and second sampling

For control reading, the first sampling point of 0.24 mg/ L increased a little to the fourth sampling point of 0.67 mg/L. While the concentration of zinc for the first sampling and second sampling were clearly higher than the control reading but they were still within the acceptable condition of Environmental Quality (Industrial Effluents) Regulations 2009 Standard B which was 2.0 mg/L. Zinc element had found to be the highest concentration in the first sampling in which the mean concentration was 1.368 mg/L. While the average reading of second sampling was 0.783 mg/L. Based on observation, the reading of first sampling was higher than the reading of second sampling because of the used of different dyes by the final year project students in UMK Bachok. Based on the research by Hussain *et al.* (2004), Zn presented in textile workshop was also due to the impurities of chemicals used.

Zinc have the potential to cause negative impact to the human health. A minor quantity of zinc in the human body can affect considerably human health. According to (Gakwisiri *et al.*, 2012), Human can handle large extent of zinc, but too much of zinc can still cause severe health problems. This is also supported by the research of Eckenfelder *et al.* (2008) who report that high zinc concentration cause serious poisoning in human.

According to Wuana and Okieimen (2011), the water body is polluted with Zn due to the presence of large quantities in the wastewater of industrial plants. A serious adverse synergistic effect can occur when Zn is presented with other heavy metals such as cadmium and copper, in which Zn had been known to biomagnifying through the specific marine food chain (Cardwell *et al.*, 2013). For instance, some fish can accumulate Zn in the body if they live in Zn-contaminated water body (Wuana & Okieimen, 2011). The toxicity of Zn will depend on the total hardness of the water because Zn ions are complexed by the presence of anions that contribute to total water hardness (Eisler, 1986).

4.4.2 Manganese Analysis

The comparison of the manganese in each sampling point with the standard was shown in Figure 4.9.

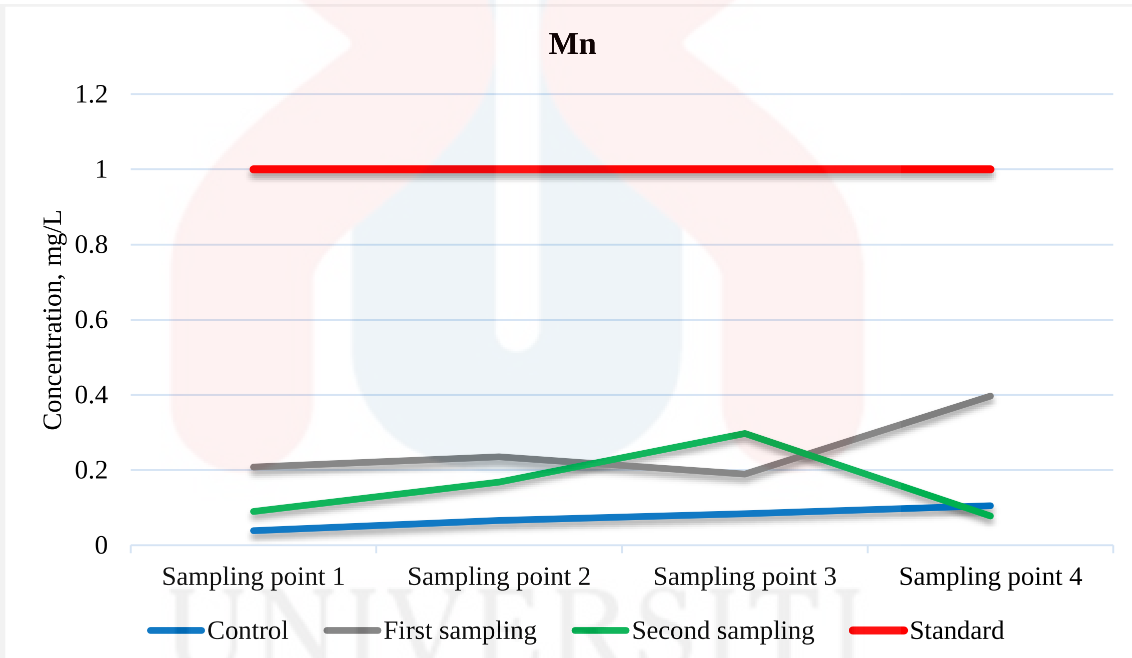

Figure 4.9: Reading of Mn for the control, first sampling and second sampling

The acceptable condition for discharge of industrial wastewater of Mn is 1.0 mg/L. It was clear that all the concentration of Mn was within the EQA standard. From the Figure 4.9, the control reading of Mn was quite constant from the first sampling point to the fourth sampling point and the average reading was 0.074 mg/L. For the first sampling and second sampling, it showed that there was presence of a little manganese as their mean concentration was higher than that of control reading.

Mn is an essential element to the growth of animals and plants when present in a minor quantity (Soetan *et al.*, 2010). Nevertheless, exposure to high concentration of Mn are associated with increase mental retardation and reduced intelligence in children and chronic exposure to high level of Mn can cause motor disturbance (Bouchard *et al.*, 2011). According to Javed and Usmani (2013), High level of Mn released from the textile workshop that exceeds 1.0 mg/L can affect fish by causing disturbances of lung, liver and vascular, declination of blood pressure, failure of animal fetuses development and brain damage. Permanganates is the chemical compound containing manganate (VII) ion (MnO^-) and it have been reported to kill fish in 8 to 18 hours at concentration of 2.2 to 4.1 mg/L (Sujatha *et al.*, 2013). In this research, the peak concentration of Mn was about 0.4 mg/L. This is still in the safe zone to be discharged to the environment which do not kill fish.

4.4.3 Aluminum Analysis

The comparison of the aluminum with the standard was shown in Figure 4.10.

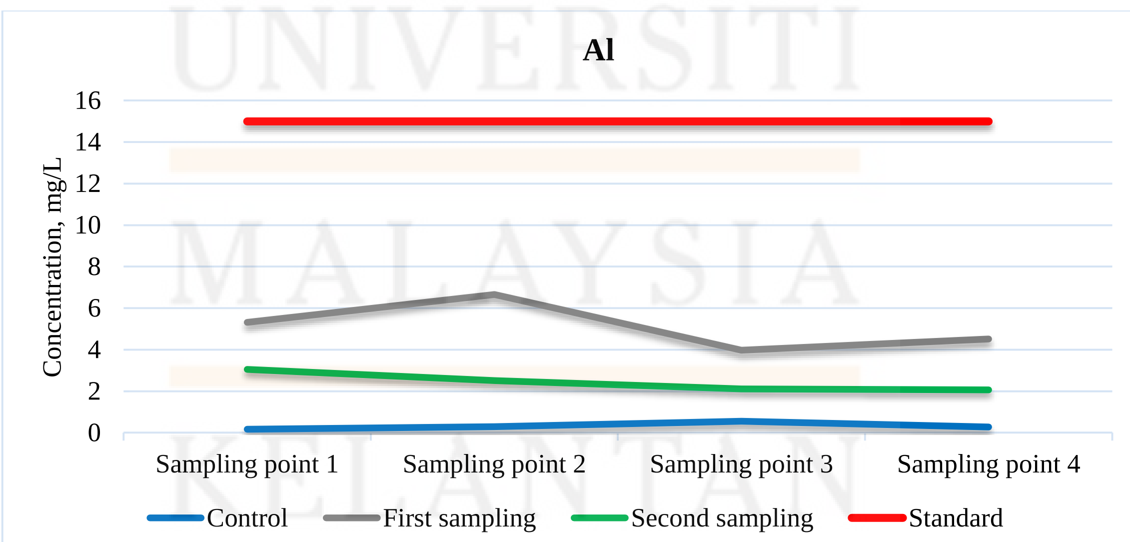

Figure 4.10: Reading of Al for the control, first sampling and second sampling

From the Figure 4.10, all of the control reading of Al concentration were lower than 1.0 mg/L. This showed that the concentration of Al was very low and nearly not exist before the discharge of *batik* wastewater.

For the first sampling and second sampling, their average concentration of Al were 5.115 mg/L and 2.432 mg/L respectively. This showed that the batik wastewater contained a lot of Al but it was within the acceptable condition for discharge of industrial wastewater set by the Environmental Quality (Industrial Effluents) Regulations 2009.

4.4.4 Nickel Analysis

The comparison of the nickel in each sampling point with the standard was shown in Figure 4.11.

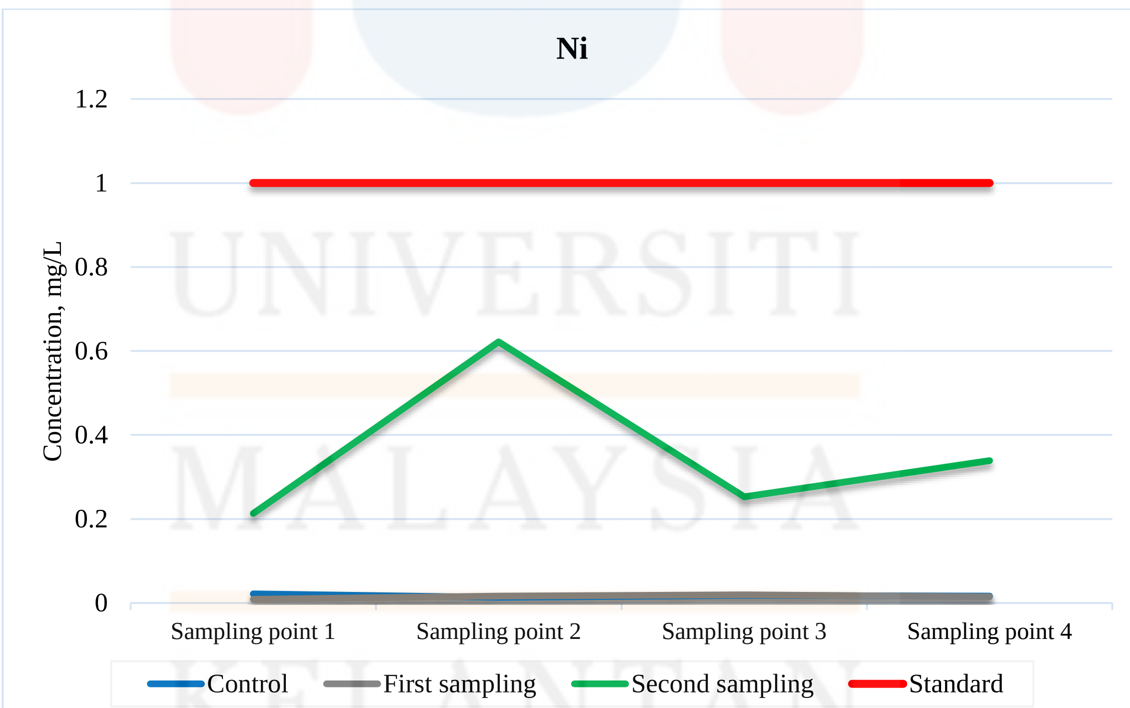

Figure 4.11: Reading of Ni for the control, first sampling and second sampling

For the Figure 4.11, the control reading and first sampling reading of Ni concentration were very close. The average of control concentration for Ni was 0.017 mg/L and average Ni concentration of the first sampling was 0.015 mg/L. This indicates that the first sampling does not contain much of the Ni concentration.

For the second sampling, the readings were fluctuated for these four sampling points. The first sampling point of 0.213 mg/L increase to 0.622 mg/L in the second point. After that, Ni concentration dropped to 0.253 mg/L in the next point and increase to 0.339 mg/L in the last point. The Ni concentration of second sampling was higher significantly than the first sampling. The presence of Ni is because it form part of the most commonly used dyes, such as leather materials, nylon and wool (Zeiner *et al.*, 2007).

Nickel is sensitive bio-indicator of water pollution and it is easily accumulated in the biota, particularly in the phytoplankton or other aquatic plants (Cempel & Nikel, 2006). It can be deposited in the sediment after the processes such as precipitation, complexation and adsorption on clay particles (Nriagu & Pacyna, 1988). Exposure to high quantities of nickel is toxic to fish and it can cause various kinds of cancer on different sites within the bodies of animals (Javed & Usmani, 2013).

For the human health, exposure to highly nickel-polluted environment has the potential to produce several pathological effects including skin allergies, lung fibrosis, respiratory tract cancer and iatrogenic nickel poisoning (Clarkson *et al.*, 2012). Based on Cempel and Nikel (2006), exposure of human to Ni had associated with the haematological effects, but no reproductive effects found.

4.4.5 Copper Analysis

Comparison of pH in each sampling point with the standard was shown in the Figure 4.12.

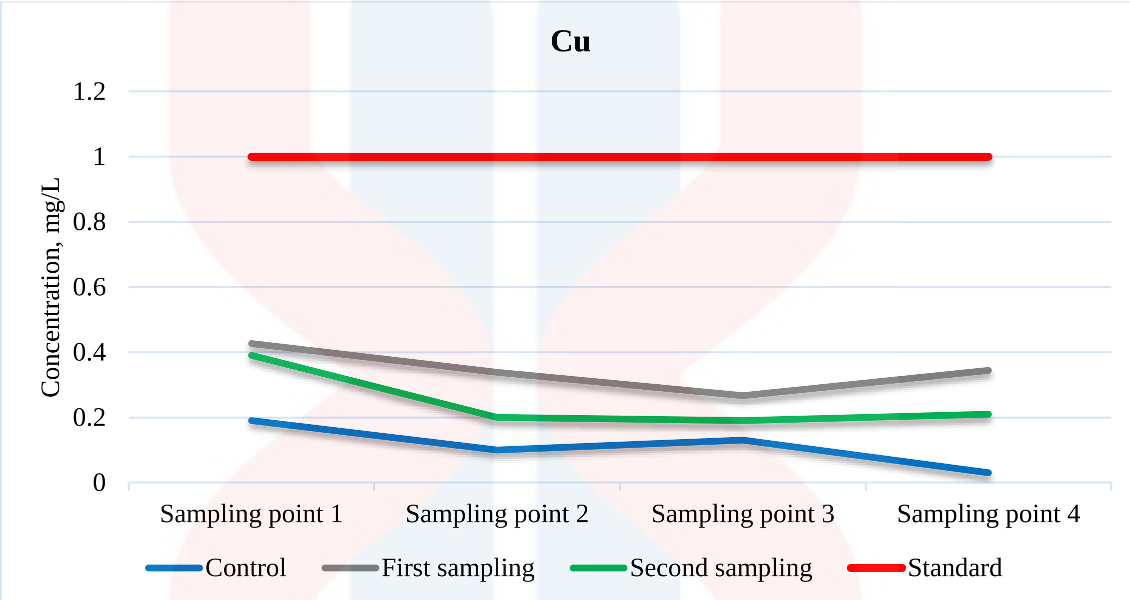

Figure 4.12: Reading of Cu for the control, first sampling and second sampling

From Figure 4.12, the acceptable condition for discharge of industrial wastewater was 1.0 mg/L. For the control reading, the average of the Cu concentration was 0.113 mg/L. the average concentration of Cu for first and second sampling were 0.344 mg/L and 0.248 mg/L respectively. The concentration of Cu was considered less as compared to the standard which was 1.0 mg/L. This presence of Cu was due to the impurities in the chemicals used and the process involving using of copper complex dyes (Hussain *et al.*, 2004). Besides, heavy metal such as Cu and Zn may come from chromium salts used in wool dyeing or as oxidizing agents in the process of sulfur dyeing (Chavan, 2001).

Copper present as an essential trace element that is necessary for the growth of plant and animal. It is used in agriculture and is vital for health of human, flora and fauna (Wuana & Okieimen, 2011). Conversely, exposure to high concentration of Cu can result in severe health impact. Exposure to water polluted with Cu lead to the development of anemia, damage of liver and kidney, abdominal pain, vomiting, headache and nausea in children (Akpor *et al.*, 2014). Besides, it also creates a kind of disease similar to the flu. Copper can be bio-accumulated in human bodies and it had been proved that intake of 30 g copper ion is fatal and 1.3 mg/L of Cu can cause common diarrhea, abdominal cramps and nausea (Wuana & Okieimen, 2011). The storage of excessive copper in the body such as in brain, liver, kidney and cornea can cause genetic disease which is Wilson' disease which is autosomal recessive illness (Osredkar, 2012). According to Adriano (2001), aquatic life are potentially at risk from exposure to Cu. While Cu concentration greater than 1.0 mg/L is toxic to aquatic plants and fish (Sawyer & McCarty, 1978). Hence, the direct discharge of *batik* wastewater without proper treatment have a potential to cause negative impact to the environment.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Batik industry is the largest textile industry in Malaysia and the released wastewater is said to responsible for water pollution. Hence, this research is vital to investigate whether the *batik* wastewater discharge from the workshop is complying with the EQA 1974 standard. The physico-chemical properties of *batik* wastewater including COD, TSS, NH_3N, pH, temperature, TDS and turbidity were determined. The result showed that the *batik* wastewater contained high value in most of these physico-chemical parameters especially the COD concentration. This is supported by Şahinkaya (2013) who found that most of the textile wastewater contain high salinity, high COD and pH as well as strong color.

Besides, the concentration of selected heavy metals including Cu, Ni, Zn, Mn and Al in the *batik* wastewater were also determined. All of the heavy metals of *batik* wastewater are within the standard and they are discharged under the acceptable conditions for discharge of industrial effluent for mixed effluent of standard B.

In this research, the physico-chemical content of *batik* wastewater discharged from the workshop in UMK Bachok Campus is exceed to the standard, but all of the concentration for heavy metal is totally comply with the standard. These preliminary data of batik wastewater pollutant is important for the further research and as the guideline for the workshop before discharge of *batik* wastewater to the environment. The level of physico-chemical properties and heavy metal concentration of the wastewater were accessible. The result showed that there is urgent need to carry out efficient treatment methods on the physico-chemical of *batik* wastewater before discharge to the environment.

5.2 Recommendation

After completing the research, there are a few recommendations that can be carried out in order to obtain a better result for the further research. More details and proper research on the physico-chemical and heavy metal concentration of wastewater from different industries that involves the use of dye should be conducted so that the impact of the dyes to the environment can be determined. The investigation of heavy metals should be included with more elements as *batik* wastewater are not merely contain Cu, Ni, Zn, Mn and Al, but also other elements such as chromium, cobalt, lead and mercury (Verma, 2008). Hence, the information of heavy metals that included in the *batik* wastewater can be more comprehensive.

Besides, the sampling period of *batik* wastewater should be extended to a longer duration. Since the textile workshop only operate when there are students carry out their final year projects, hence the sampling period can be extended to two years because the dyes in each semester are different and thus the discharged wastewater will have different physico-chemical properties and heavy metals concentration. The extended sampling period make sure all of the possible heavy metals in different dyes and chemicals can be investigated and determined.

For the conduction of the research, sampling methods, testing equipment method, preservation and measuring method will have impact on the accuracy of the result. Hence, the researcher must have a correct handling skill throughout all the processes. Besides, the university must always monitor and improve the equipment and apparatus in order to ensure the smoothness of the researches. The spoiled instrument should be repaired immediately so that the researchers can continuous conduct their research and done before the deadline.

Besides, atomic absorption spectrophotometer (AAS) can be used in determining the concentration of heavy metal instead of using colorimeter. Atomic absorption determines the presence and concentrations of heavy metals in liquid samples. AAS is widely used to determine the trace and ultra-trace elements in all kinds of samples. It can be used to analyze the concentration over 62 different metals in a solution (García & Báez, 2012). There is a beam of light passes the samples in AAS and a certain quantity of the light will be absorbed depends on the concentration of the element. Then, the concentration of the element can be determined by comparing the intensity of the original beam and the intensity of the beam after passing the sample (Zeiner *et al.*, 2007). Hence, it is suitable for monitoring studies of a certain element such as Cd, Cr, As and Pb, even when present in very low mass concentration. One of the advantages of using AAS is due to its fully automated procedure and this reduce the labor-intensive (Zeiner *et al.*, 2007). It is also relatively inexpensive and easy to use especially for the beginners or learners. This can reduce the cost of determination of heavy metals instead of using colorimeter which involves the expensive regents and tedious procedure for each element.

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APPENDIX A

Table A.1: Acceptable Conditions for Discharge of Industrial Effluent for Mixed Effluent of Standard A and B (Fifth Schedule)

ACCEPTABLE CONDITIONS FOR DISCHARGE OF INDUSTRIAL EFFLUENT FOR MIXED EFFLUENT OF STANDARDS A AND B

	Parameter	Unit	Standard	
			A	B
	(1)	(2)	(3)	(4)
(i)	Temperature	°C	40	40
(ii)	pH Value	-	6.0-9.0	5.5-9.0
(iii)	BOD_5 at 20°C	mg/L	20	40
(iv)	Suspended Solids	mg/L	50	100
(v)	Mercury	mg/L	0.005	0.05
(vi)	Cadmium	mg/L	0.01	0.02
(vii)	Chromium, Hexavalent	mg/L	0.05	0.05
(viii)	Chromium, Trivalent	mg/L	0.20	1.0
(ix)	Arsenic	mg/L	0.05	0.10
(x)	Cyanide	mg/L	0.05	0.10
(xi)	Lead	mg/L	0.10	0.5
(xii)	Copper	mg/L	0.20	1.0
(xiii)	Manganese	mg/L	0.20	1.0
(xiv)	Nickel	mg/L	0.20	1.0
(xv)	Tin	mg/L	0.20	1.0
(xvi)	Zinc	mg/L	2.0	2.0
(xvii)	Boron	mg/L	1.0	4.0
(xviii)	Iron (Fe)	mg/L	1.0	5.0
(xix)	Silver	mg/L	0.1	1.0
(xx)	Aluminium	mg/L	10	15
(xxi)	Selenium	mg/L	0.02	0.5
(xxii)	Barium	mg/L	1.0	2.0
(xxiii)	Fluoride	mg/L	2.0	5.0
(xxiv)	Formaldehyde	mg/L	1.0	2.0
(xxv)	Phenol	mg/L	0.001	1.0
(xxvi)	Free Chlorine	mg/L	1.0	2.0
(xxvii)	Sulphide	mg/L	0.50	0.50
(xxviii)	Oil and Grease	mg/L	1.0	10
(xxix)	Ammoniacal Nitrogen	mg/L	10	20
(xxx)	Colour	ADMI*	100	200

ADMI- American Dye Manufactures Institute

Source: Extracted from Environmental Quality (Industrial Effluents) Regulations 2009 (PU(A)434)

Appendix A2

Table A.2: Acceptable Conditions for Discharge of Industrial Effluent Containing Chemical Oxygen Demand (COD) for Specific Trade or Industrial Sector

(1) Trade/Industry	(2) Unit	(3) Standard	(4) Standard
		A	B
(a) Pulp and paper industry			
(i) pulp mill	mg/L	80	350
(ii) paper mill (recycled)	mg/L	80	250
(iii) pulp and paper mill	mg/L	80	300
(b) Textile industry	mg/L	80	250
(c) Fermentation and distillery industry	mg/L	400	400
(d) Other industries	mg/L	80	200

Source: Extracted from Environmental Quality (Industrial Effluents) Regulations 2009 (PU(A)434)

APPENDIX B

Figure B.1: Reading of sample by using colorimeter

Figure B.2: Heating of samples by DRB200 Reactor for COD reading

Figure B.3: Blending process to homogenize the suspended solid

Figure B.4: Process of adding 0.1 % PAN indicator solution

Figure B.5: Taking reading of YSI 556 Multiparameter in UMK Bachok

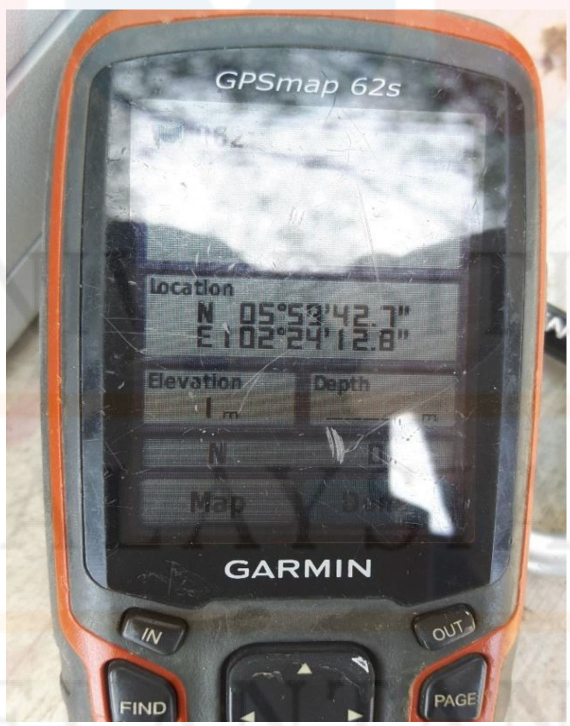

Figure B.6: Coordinate of sampling site by using GPS

Figure B.7: Map of University Malaysia Kelantan Bachok Campus