UNIVERSITI SAINS MALAYSIA

UNIVERSITI SAINS MALAYSIA

"Determination of heavy metals in batik industry wastewater by using Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)"

Dissertation submitted in partial fulfilment for the Degree of Bachelor of Science in Forensic Science

Fadhilah Binti Abdul Rahman

School of Health Sciences

Universiti Sains Malaysia

Health Campus

16150, Kubang Kerian Kelantan

Malaysia

2011

ACKNOWLEDGEMENTS

I would like to express special thanks to my supervisor, Dr. Noor Zuhartini Md Muslim for her advice and help during final year project progress until it is fully completed. Thanks also to Mr Rosliza and Mr Sahnusi, for guiding me in samples analysis using Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) and Sharmimi Zainudin for providing the data of types of dyes used in batik textile industry. This research work was supported by Universiti Sains Malaysia in the form of analytical facilities. I also want to thanks to my entire friends especially Amirah Che Ahmat and Hafizah Saim. Last but not least, my thanks goes to my close friend Mr. Shahrill Sabarudin and my parents Abdul Rahman Ismail and Hasnah Radzuan for supporting and encouraging me to complete this project. Not forget great appreciation to Dr.Nik Fakhuruddin. Without Dr. Nik Fakhurudin's encouragement, I would not have the strength to complete my study.

CONTENT

ABSTRACT 1

CHAPTER 1: INTRODUCTION 2

1.1 Kelantan's Batik Industry 2

1.2 Environmental Issues 5

1.3 Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) 6

1.4 Heavy Metals Toxicity and Human Health 7

1.4.1 Lead 8

1.4.2 Manganese 9

1.4.3 Cadmium 10

1.4.4 Nickel 11

CHAPTER 2: REVIEW OF LITERATURE

2.1 Heavy Metals in Textile Industry Wastewater 12

2.2 Dyes (Colorant) 16

2.3 Heavy Metals and Wastewater Pollution 18

CHAPTER 3: OBJECTIVES OF THE STUDY 20

CHAPTER 4: SIGNIFICANCE OF STUDY 21

CHAPTER 5: MATERIALS AND REAGENTS 22

5.1 Apparatus 22

5.2 Chemicals 23

5.3 Instrumentation 24

CHAPTER 6: METHODOLOGY 25

6.1 Study Areas 25

6.2 Samples Collection 25

6.3 Samples Preparation for Determination of Total Heavy Metal Concentration 25

6.4 Samples Preparation for Determination of Free Heavy Metals 26

6.5 Preparation of Standard Solution for Quality Control (QC) 27

6.5.1 Preparation of 1000ppb Cadmium, Nickel, Manganase and Lead Standard Solution 27

6.5.2 Preparation of 100ppb Cd, Ni, Mn and Pb Standard Solution 27

6.5.3 Preparation of 20ppb Manganese Standard Solution 28

6.5.4 Preparation of 10ppb Cadmium, Nickel and Lead for Quality Control 28

6.5.5 Preparation of 5ppb Manganese for Quality Control 28

6.5.6 Preparation of Pd-Mg modifier 28

6.6 Samples Analysis by GFAAS 29

CHAPTER 7: RESULTS AND DISCUSSION 30

7.1. Linearity of Standard Calibration Curve 30

7.1.1 Calibration Curve for Lead (Pb) 30

7.1.2 Calibration Curve for Cadmium (Cd) 31

7.1.3 Calibration curve for Manganase (Mn) 32

7.1.4 Calibration Curve for Nickel (Ni) 33

7.2 Limit of Detection (LOD) and Linearity of Standard Calibration Curve 34

7.3 Results and Discussion for Lead (Pb) Concentration 35

7.4 Results and Discussion for Cadmium (Cd) 37

7.4 Results and Discussion for Manganese (Mn) 39

7.5 Result and Discussion for Nickel (Ni) 41

7.6 Comparison of Free and Total Concentration of Pb, Ni, Cd and Mn 42

CHAPTER 8: LIMITATION OF STUDY 44

CHAPTER 9: CONCLUSION 45

REFERENCES 46

LIST OF TABLES AND FIGURES

Tables

Table 2.1: Concentration of heavy metals in textile industry wastewater

Table 2.2: The standard limit allowed by Environmental Quality Act 1974

Table 2.3: Typical metals found in dyes by dye class (Bae and Freeman, 2007)

Table 2.4: The structures of metal complexes acid dyes (Ahn *et al.*, 2009)

Table 5.1: List of apparatus used in the study

Table 5.2: List of chemicals used in the study

Table 6.1: GFAAS parameters

Table 7.1: Limit of detection for lead (Pb), cadmium (Cd), manganese (Mn) and nickel (Ni). All values are mean for five observations each.

Table 7.2: The linearity of standard calibration curve of Pb, Cd, Mn and Ni

Table 7.3: Concentration of total heavy metal and free heavy metal of Lead (Pb), Cadmium(Cd), Manganese (Mn) and Nickel (Ni) in batik industry wastewater and it's associated with standard limit allowed by Environmental quality (sewage & industrial effluent) regulation 1979. All values are mean ± standard deviation (SD) for three observations each, expressed in µg/l

Figures

Figure 1.1: Schematic diagram of a batik process (Belfer, 1972)

Figure 2.1: Chemical structure of metal complexes of acid dyes (Ahn *et al.*, 2009)

Figure 5.1: Graphite Furnace Atomic Absorption Spectroscopy (GFAAS), Perkin-Elmer® (AAnalyst 800) connected to the computer monitor, Windows® XP operating system

Figure 6.1: Sample preparation for determination of total heavy metal. Ten samples collected from ten different location of batik industry labeled from 1a to 10b

Figure 6.2: Samples preparation for determination of free heavy metal. Ten samples collected from ten different location of batik industry labeled from 1b to 10b

Figure 7.1: Calibration curve of lead (Pb) with correlation factor, R^2=0.997

Figure 7.2: Calibration curve of Cadmium (Cd) with correlation factor, R^2=0.994

Figure 7.3: Calibration curve of Manganese (Mn) with correlation factor, R^2=0.988

Figure 7.4: Calibration curve of Nickel (Ni) with correlation factor, R^2=0.995

Figure 7.5: The graph shows the concentration of total and free Pb at different places of batik industry

Figure 7.6: The graph shows the concentration of total and free Cd at different places of batik industry.

Figure 7.7: The graph shows the concentration of total and free Mn at different places of batik industry

Figure 7.8: The graph shows the concentration of total and free Ni at different places of batik industry.

ABSTRACT

The study was conducted to determine the heavy metals concentration in ten batik textile industries located in several areas around Pantai Cahaya Bulan (Kelantan) and compared to the permissible limit of heavy metals that allowed by Environmental Quality (Sewage & Industrial Effluent) Regulation 1979. The heavy metals analysis was conducted by using graphite furnace-atomic absorption spectroscopy (GFAAS). The samples collection was conducted at 0 m discharge point in order to get the maximum heavy metal contents in batik industry effluent. The results of this study show that concentration of total Lead (Pb), Cadmium (Cd), Manganese (Mn) and Nickel (Ni) ranged from 3.06±0.0012 to 48.5±0.0193, 0.023±0.0029 to 0.677±0.065, 0.344±0.0084 to 20±0.0170 and 0.335±0.0045 to 11.61±0.0082μg/L, respectively. The concentrations of free heavy metals of Pb, Cd, Mn and Ni ranged from 4.78±0.0017 to 43.3±0.0085, 0.0107±0.001 to 0.064±0.0023, 0.01±0.0016 to 16±0.0410 and 0.003±0.0001 to 0.462±0.0057μg/L, respectively. The results of total heavy metals concentration and free heavy metals concentration in this study below the limit set by the Environmental Quality (Sewage & Industrial Effluent) Regulation 1979.

CHAPTER 1: INTRODUCTION

1.1 Kelantan's Batik Industry

The batik industry categorized as a homemade textile industry that become most critical industry among manufacturing industries that contribute to the water pollution because of high percentage of water consumption around 60-400L/kg of fabric and chemicals for wet processing (Ali *et al.*, 2009). Kelantan, especially around Gong Badak and Pantai Cahaya Bulan (PCB), is the most famous batik industry beside Terengganu and Sarawak. Its popularity as a batik industry area becomes the main attraction for foreigners and local people to visit this state until Kelantan itself is recognized as 'Home of Malaysia Batik" (Kheng, 1998). Most of batik industries in Kelantan area was owned by Malay people that stay in villages. This industry become their main source of income and the skill of batik processing starting from waxing; designing until the re-waxing is inherited from one generation to the next generation. They believe that in order to produce a very high quality of batik, the person that conduct the batik process should has a good skill with a long experience in that field (Ahmad *et al.*, (2002)

The creation of batik involves three main stage processes such as waxing, dyeing, and de-waxing. There are also several sub-processes like preparing the cloth, tracing the designs, waxing the area of the cloth, preparing the dye, dipping the cloth into the dye, boiling the cloth to remove the wax and washing the cloth with soap. The process of batik starts with the preparation of fabrics, where the fabrics are bleached with bleaching powder and water and kept overnight for whiteness. Large volume of water was used for washing the fabric and it was dipped in boiling water in order to remove any loose color and to make sure nounexpected color will spread and lastly the fabric was dried under the sun by drying process. Next, cloth ready for the design and the process is continued with waxing of the fabric. The wax is melted before applied to the surface of the fabric and the melted wax will penetrate deeply in the fiber, protecting from dye. The most common wax use is a soy wax, bees wax and paraffin wax. The next step is a dying process, which is the fabric dipped in napthol dye (red). After that, the dye oriented from natural sources like plant and insect were used for fabric batik coloring. Tools like the Tjanting (also known as canting) and stove is used to make outline while paint brush is used to produce interesting pattern. Potassium aluminium sulfate is used in order to get well design on the fabric (Ahmad *et al.*, 2002). The dilute dye can be mix with chemical substances such as ludigol in order to produce more vibrant and lighter color and sodium alginate acts as dyes-thickener to control spreading during painting. Lastly the fabric can be dipped in hot water so that the wax comes off and one gets the required pattern and color. The process of making batik is shown briefly in Figure 1.1

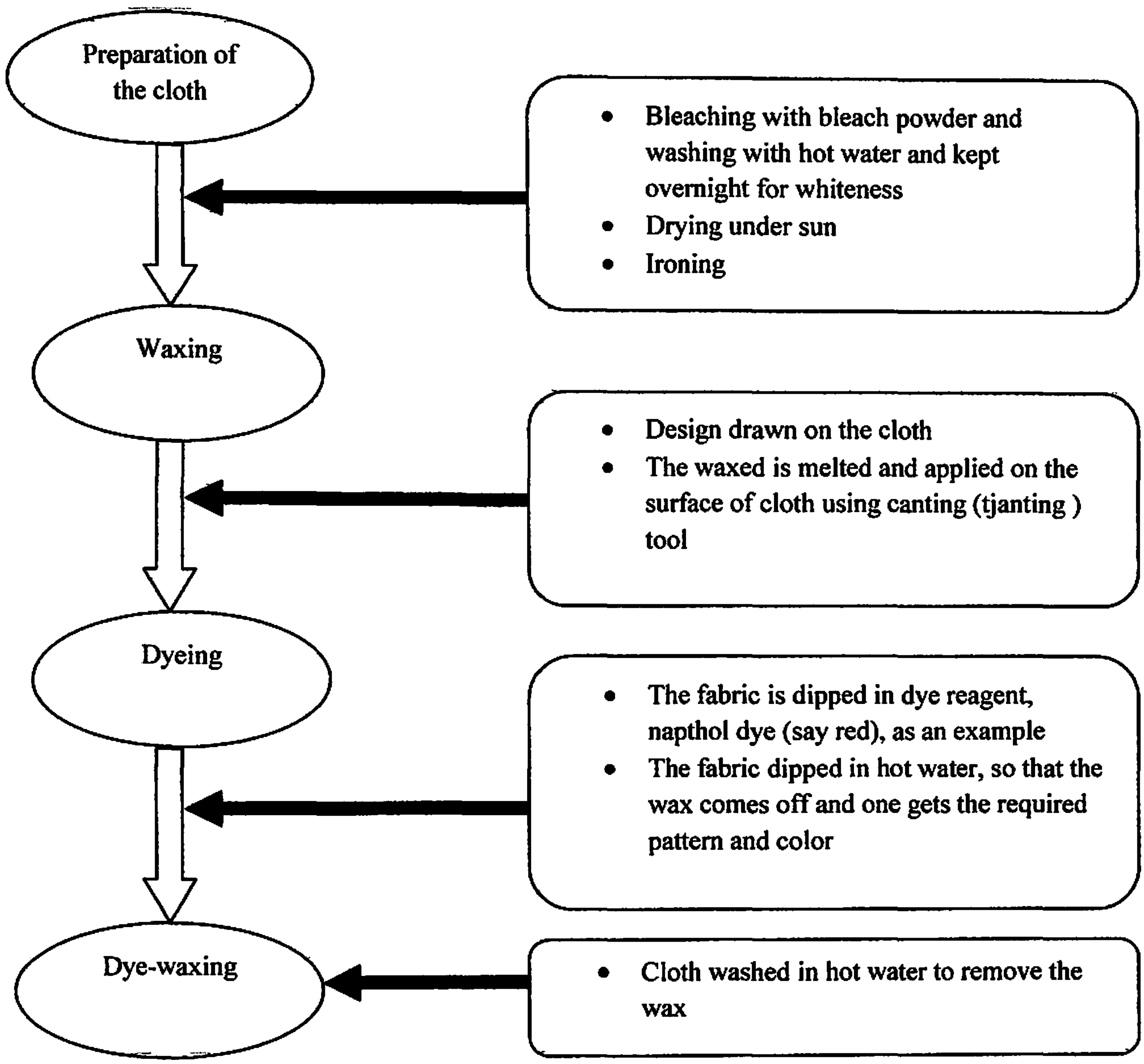

Figure 1.1: Schematic diagram of a batik process (Belfer, 1972)

1.2 Environmental Issues

Environmental pollution has been critical issues since the industry become the main activities in developing and developed country. Lee and Stuebing (1990) and Gümgüm *et al.*, (1994) reported that industrial wastes is one of the major contribution of heavy metals in environmental pollution. Güven *et al.*, (1999) reported that accumulation of heavy metals can achieve toxic level based on the environmental condition. Harms (1975), Jefferies and Free-stone (1984) and Freedman (1989) found accumulation of heavy metals at toxic level results in ecological damage. Textile effluents that contains dyes and heavy metals mostly discharged into stream without treatment cause water pollution because textile industry mostly using large quantity of water (60-400l/kg of fabric) during processing such as sizing, resizing, scouring, mercerizing, bleaching, dyeing and finishing (Yusoff and Sonibare, 2004). Contamination of soil, air and water from industry effluent can cause heavy disease burden (World Health Organization, WHO, 2002) and becomes one of the main reasons for the current shorter life among society (WHO, 2003).

Discharge of untreated textile wastewater into streams can cause severe damage to the aquatic biology (Ali *et al.*, 2009). The metals and dyes in wastewater also can accumulate into the food chain and cause severe damage to the human health. The heavy metals in waste water flow out from the industrial site into the stream will results in contamination of water sources nearby the area (Srivastava *et al.*, 2008)

In each country, there are regulations for discharging the wastewater into stream. For example, in Great Britain, the dyes content in textile effluent are fully regulated by the Environment Agency (EA). England and Wales regulated by Scottish Environment Protection

Agency (SEPTA) (Willmott *et al.*, 1998). Meanwhile, in United Kingdom (UK) since September 1997, regulated that concentration of chemicals in wastewater should be zero concentration before discharge into the marine environment (Robinson *et al.*, 2001), and in Malaysia as well, there is regulations on discharges of waste into streams, canals or river has been stated under the Environmental Quality Act (1979). The law that stated by each country as a step to ensure the treatment process applied to the dye-containing effluent before it discharge to the environment.

1.3 Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) (Anonymous, 2011)

Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) have high sensitivity and accuracy for metal detection in the ppb (part per billion) level compared to Flame Atomic Absorption Spectroscopy (FAAS) that can detect metal concentration in ppm (part per million) level with excellent detection limit. The greater sensitivity of GFAAS allows the analyst to use small sample sizes around 1-100µL (microliters, 10^{-6}L). GFAAS system consists of light source, atomizer, monochromator and detector. Light source is usually a hollow-cathode lamp of metal element that is being measured.

Absorption of light energy by ground state atom at a specific wavelength promotes atomization to a higher energy level. The amount of light is absorbed increase as the concentration of heavy metals increase. The number of atoms of a specific metal proportional to the amount of energy absorbed at the specific wavelength. Atomizer (graphite tube) is used to vaporize liquid sample to gaseous phase at high temperature. The furnace can provide thermal energy that can break down chemicals bonding in liquid samples and produce free atom (gas phase). Monochromator is used to isolate the absorption line from background light due to interferences by selecting only one wavelength of interest. The detector will measure the amount of absorption and computer system will display the output.

1.4 Heavy Metals Toxicity and Human Health

Standard levels of heavy metals in living organisms including human being are important for the body biological system to function normally. However, high level of heavy metals will lead to disease (Ward, 1995). According to Lenntech Water Treatment and Air Purification (2004) some heavy metal such as lead, cadmium and mercury do not have function in human body and does not present in human body unless they are brought into body through food that contains the metals. Cell body has a specific enzyme that plays a role in a human biological system and when heavy metals bind to the enzyme, it will destroy the enzyme and disturb the function of cell and lead to disease such as cancers or tumors (Apostoli *et al.*, 2002). Babel and Kurniawan (2004) stated that heavy metals can cause critical health problem when their concentration exceed the standard limit. Heavy metals health-related problem include tumor, decrease development and growth, damaging on the nervous system and organ as well, and in some critical cases can cause death. In addition, high level of heavy metals can give adverse effect to the brain such as irreversible brain damage.

1.4.1 Lead (Pb)

Leads are the most toxic metals among others even though it is non-essential elements that occur in a trace amount (Ferner, 2001). Accumulation of lead in living organism through food that digested in digestive organ will distributed over the body system and deposition of lead typically discovered in bone and it difficult to secrete out from living organism (Ewers and Schlipkoter, 1991). Some of health problems related to this metal include muscle disorders, indigestion and haematogenesis failures (Kyncl, 2008). Exposure of lead among children will decrease their intelligence and slow development (Udedi, 2003). Lead is not carcinogenic to living organisms but teratogenic (Kyncl, 2008; Duruibe *et al.*, 2007). However, according to Radojevic and Bashkin (1999) lead cause carcinogenic to human body system.

Lead cause problems in human physiological system especially in immune system because lead stimulate autoimmunity activity, which is one's immune system that attack their own cells and result in damaging of fetal brain (for pregnancy woman), diseases of nervous system, kidney and circulatory system, as well as rheumatoid arthritis, a type of joint disease (Barakat, 2010). Ogwuebgu and Muhanga (2005) also reported similar disease such as kidneys, joints, and reproductive system do not functioning properly and the excess level cause chronic effect particularly on the peripheral nervous system (PNS) and central nervous system (CNS) as well as cease the haemoglobin sysnthesis. Deepali *et al.*, (2010) reported that children was at high risk of getting central nervous system when exposed to excess amount of metals and other diseases related to metal toxicity. These diseases will disturb the immune system and kidney dysfunction. Lead in different forms gives a different effect. For example inorganic lead causes damage on GIT, PNS (peripheral nervous system), and CNS (central nervous system), meanwhile organic lead affect mainly the CNS (McCluggage, 1991; INECAR, 2000; Ferner, 2001; Lenntech, 2004).

1.4.2 Manganese (Mn)

Emsley (2003) classify manganese as an essential substance and their amount occur in a trace level. Brains are the target organ affected when doses of manganese elevated. It also affects the neurological disorder by showing the same sign as the Parkinson's disease (Barbeau, 1984; Inoue and Makita, 1996). The function of manganese in brain development have been proved by Prohaska (1987) and their concentration in adults' brain around 0.25 μg/g wet weight where this level is much higher than infants in age less than one year (Markesbery *et al.*, 1984). Accumulation of manganese in basal ganglia is a primary sign in the development of pathogenesis of chronic hepatic encephalopathy which is associated with the excessive level of manganese in blood. Manganese is also important for growth of bone and the formation of mucopolysaccharides (Keen *et al.*, 1988)

The deficiency of manganese results in abnormality of manganese homeostasis in brain and affects the neuronal system (Hurley *et al.*, 1996). Decreased concentration of manganese also results in improper development of skeleton and growth retardation (Friberg *et al.*, (1986); Priest and Van de Vyver, 1990). Shamberger *et al.*, (1979) listed several effects of manganese deficiency including abnormality of bone, lipid and carbohydrate metabolisms; deficiency in pregnancy women which affect the growth of infant especially skeletal and brain development; and reduce the function of reproductive system, neonatal mortality and intra-uterine.

1.4.3 Cadmium (Cd)

Abnormal level of cadmium results in adverse effect on physiological systems which in turn disturb the embryonic development and reduced the growth rate (Newman and McIntosh, 1991). Chronic toxicity of this metals result in cancer (Waalkes *et al.*, 1988), reproductive failure (Frery *et al.*, 1993; Johnson *et al.*, 2003; Piasek and Laskey, 1999), kidney failure (Barbier *et al.*, 2005) and bone problems (Kazantzis, 1979). Long time of cadmium exposure causes slow accumulation of cadmium in the kidney and result in kidney failure (Deepali *et al.*, 2010). Fowler (2009) discussing several targets organ for cadmium toxicity including kidney, liver, lung, cardiovascular, immune/ hematopoietic systems and reproductive systems and a cancer disease.

Trzcinka-Ochocka *et al.*, (2004) found that excessive accumulation of cadmium in renal system induce the elevated excretion of specific protein such as beta-2 microglobulin, albumin, NAG/NAGB and retinol binding protein. Cadmium toxicity among children has more effects on renal tubular reabsorption than an adult. Toxicity of cadmium in lung induces the activation of lung fibroblast (Li *et al.*, 2008), which is results in pulmonary fibrosis (Kirschvink et al., 2006) and asthma (Willers *et al.*, 2005). The effects of cadmium on cardiovascular systems cause capillary damage and hypertensive effects.

1.4.4 Nickel (Ni)

Nickel activities can stimulate activation of immune systems for allergic and Ni-sensitized humans. Over exposure of nickel brings an adverse effect such as skin irritation, loss of body weight and liver, and heart damage (Akan *et al.*, 2009). Cardiovascular diseases, cancer particularly on the respiratory tract, dermatitis (nickel allergy), kidney failure and lung fibrosis are other adverse effects of nickel toxicity (McGregor *et al.*, 2000; Seilkop and Oller, 2003). Soluble nickel in concentration higher than 1 mg/m^3 and less soluble nickel higher than 10mg/m^3 can result in respiratory cancers (International Committee on Nickel Carcinogenesis in Man, 1990). The normal level of nickel essential for human daily life is about 25-35μg (Anke *et al.*, 1995), 100-300 μg (Barceloux 1999) or 35 μg (International Agency for Research on Cancer, 1990). Elevated level of nickel would affect skin, cardiovascular system, kidney and respiratory systems. Others adverse effect such as hypoxia, inhibit DNA repair activity and damage on oxidative DNA (Denkhaus, 2002). The previous study regarding the nickel and human health had shown that malignant tumors of the lung and the nasal cavities are the most commonly occur in nickel toxicity (Kasprzak *et al.*, 2003).

According to Denkhaus (2002), low level of nickel can result in poor growth and liver development, and anemia (decrease in hemoglobin). It also affects the absorption of iron in intestine and decreased enzymatic activities particularly enzymes that play a role in metabolism of amino acids and carbohydrates. Study done by Anke *et al.*, (1995) found that excess level of nickel would decrease the levels of the zinc, manganese and magnesium.

CHAPTER 2: LITERATURE REVIEW

2.1 Heavy Metals in Textile Industry Wastewater

Demirizen *et al.*, (2007) found that textile industries release heavy metals such as cadmium, copper, chromium, nickel and lead in wastewater production. Heavy metals is a metallic element that have a specific characteristics such as specific gravity greater than 5.0 and atomic weight in range 63.5 and 200.6 (Srivastava *et al.*, 2008). However, according to Duruibe *et al.*, (2007), heavy metals are group of metals and metalloids having atomic density of more than 4g/cm^3 or 5 times higher than atomic density of water. Meanwhile, Barakat (2010) classify heavy metals as those that posse's density more than 5g per cubic centimeter.

Heavy metals are released to environment in the forms of organic and inorganic (Duruibe *et al.*, 2007). Lenntech Water Treatment and Air Purification (2004) listed different types of heavy metals such as lead (Pb), cadmium (Cd), Zinc (Zn), Mercury (Hg), arsenic (As), Argentum (Ag), chromium (Cr), copper (Cu), and iron (Fe) and platinum (Pt). Oyewo and Don-Pedro (2003) found that the concentration level of heavy metals in various industry situated around Lagos; a West African Coastal Metropolis contain Fe> Zn> Co> Mn> Cu> Cd> Cr> Ni> Pb while mercury not detected.

The concentration of heavy metals in textile industry effluent had been studied by Yusuff *et al.*, (2004), Deepali and Gangwar (2010) and Awomeso *et al.*, (2010). Yusuff *et al.*, (2009) indicates that the heavy in textile effluent are Cr, Al, Cu, Mn, Fe, Zn and Hg. Study done by Deepali and Gangwar (2010) on heavy metals status in effluent of a textile industry, Haridwar, India showed that untreated effluent sample contain high concentration of heavy metals compared to treated effluent. In this study, heavy metal present in textile effluent include Cr, Cd, Fe, Mn and Cu. Awomeso *et al.*, (2010) in their study around Ibeshe, Ikorodu, Lagos state showed types of heavy metals in textile industry wastewater at 0 m discharge point were Cr, Fe, Zn, Pb, K and their concentration 0.01mgL-1, no detected (ND), 0.07mgL-1, not detected (ND) and 0.37mgL-1, respectively.

Yusuff *et al.*, (2004) found various level of heavy metal contained in the textile wastewater in Kaduna (Nigeria). Copper shows the highest concentration in range of 1.96 to 5.14mgL-1 which is above 1.0mgL-1 when compared to standard limit according to Federal Ministry of Environment (FMENV). Chromium and mercury were not detected in their study. Other heavy metals such as Cr, aluminium (Al), Mn, Zn, and Fe have a concentration level below the FMENV.

Deepali and Gangwar (2010) found that chromium have the highest level in the textile wastewater (2.38mgL^{-1}) compared to other heavy metals. The heavy metals concentration show that concentration of Cr> Fe> Mn> Cu> Cd, meanwhile Pb and Ni were not detected in the study. The various types of heavy metals in textile industry wastewater are summarized in Table 2.1

Table 2.1: Concentration of heavy metals in textile industry wastewater

Parameter	Deepali and Gangwar (2010)		Yusuff and Sonibare (2004)	Awomeso *et al.*, (2010)
	Untreated effluent	Treated effluent		
Cr	2.383	0.514	ND	0.01
Fe	1.70	0.780	0.45 to 2.14	ND
Mn	0.570	0.343	0.3 to 1.65	*
Cu	0.011	ND	1.16 to 5.14	*
Pb	ND	ND	*	ND
Cd	0.018	0.006	*	*
Ni	ND	ND	*	*
Zn	*	*	0.19 to 0.36	0.07
Hg	*	*	ND	*

Major contributions of heavy metals in textile industries from coloring process which utilize different types of dyes for coloring. In Malaysia, under the Environmental Quality Act 1974, there are regulations on discharge of wastes in streams (Halimoon *et al.*, 2010). The standard limit of heavy metals concentration in textile wastewater is summarized in Table 2.2

Table 2.2: The standard limit allowed by Environmental Quality Act 1974

Parameter	Environmental quality (sewage & industrial effluent) regulation 1979
Pb	500µg/l
Cr	1000µg/l
As	100 µg/l
Mn	1000µg/l
Fe	*
Zn	2000µg/l
Cd	20µg/l
Ni	1000µg/l
Hg	*

2.2 Dyes (Colorant)

There are two types of dyes (organic and inorganic synthetic) that are commonly used during dyeing processes. Ahmad *et al.*, (2002) states that improper treatment of heavy metals may results in toxicity when release into streams. During textile process various heavy metals presents in the form of metal complex dyes (Rezić and Steffan., 2006). Raw textile materials may also contain heavy metals. In textile wet processing, metals for example chromium is used as a based dyes with other dyes to color the fibers in a short period. Other heavy metals that used as a base dyes include cobalt, chromium, copper and nickel. This heavy metals based dyes were used for wool, nylon and leather materials. Rezić and Steffan (2006) in their study found that Al and Mn in extracted textile materials contain in range of 0.11-0.29mg/l and <0.002-2.17mg/l, respectively. Meanwhile, As, Cd, Cr, Cu and Ni present in the amount higher than was allowed.

According to Wagner (1993), dyes and chemicals become the major sources of heavy metals in textile wastewater. Similar to the Australian Environmental Protection Authority (AEPA) that described dyes that used in textile wastewater contains some of heavy metals. This dyeing process usually contributes chromium (Cr), Lead (Pb), Zinc (Zn) and copper(Cu) to wastewater (Benavides,1992). Barclay et al., in their study performed the level of heavy metals concentration in dyes as follow 3.0-32.0 (Zn), 1.0 to 1.4 (As), 3.0-83.0 (Cr), up to 1.0 (Cd), 33.0-110.0 (Cu), 0.5-1.0(Hg), 1.0-3.2 (Co) and 6.0-52.0 (Pb). Zinc and trace level of mercury, cadmium and arsenic usually found in the cationic dyes (Leonas *et al.*, 1994).

Bae and Freeman (2007) state that metals that bound to dyes were needed for a textile colorant. The typical metals commonly found in dyes were summarized in Table 2.3.

Table 2.3: Typical metals found in dyes by dye class (Bae and Freeman, 2007)

Dye class	Typical metals in structure
Direct	Copper
Fiber reactive	Copper and nickel
Vat	None
Disperse	None
Acid	Copper, chrome and cobalt
Premetalized	Copper, chrome and cobalt
mordant	Chrome

The structures of metal complexes in acid dyes were shown in Figure 2.1 and Table 2.4 (Ahn *et al.*, 2009)

Table 2.4: The structures of metal complexes acid dyes (Ahn *et al.*, 2009)

	R_1	R_2	R_3	R_4	R_5
Cr				NH_2	H
Cr				$NHCOCH_3$	H
Cr				NH_2	SO_3H
Co	H	NO_2	SO_3H	NH_2	H
Co				$NHCOCH_3$	H
Co				NH_2	SO_3H

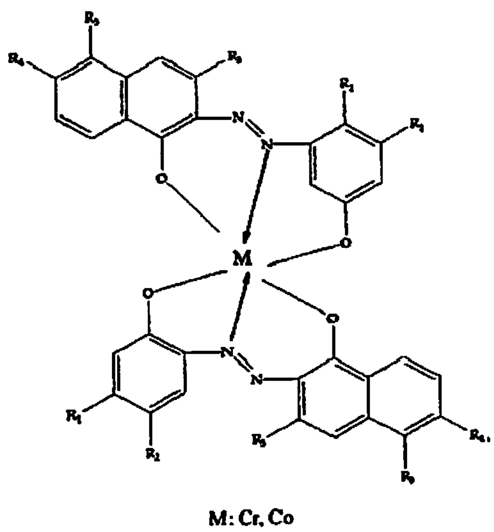

Figure 2.1: Chemical structure of metal complexes of acid dyes (Ahn *et al.*, 2009)

2.3 Heavy Metals and Wastewater Pollution

Water is the most important component in human life, animal and plant consumption (Rai, 2009). Physicochemical characteristics of water altered by the industrial waste that usually contain the heavy metals and the amount of concentration of their contents which based on the nature of waste that is being charged (Singh *et al.*, 2005; Rai 2008a, b). According to Rai and Tripathi (2006) metals in waste will change the physicochemical property of water and become toxic for human use. Wastewater that flow out into the river without going through water treatment process will result in poor quality of water and unsafe for human uses. Heavy metals is one of the parameters that was set by EPA (1974) to measure the degree of pollution in textile wastewater because heavy metal like Cr, Cu, Zn, and Hg can contaminate water.

Halimoon *et al.*, (2010) had stated that the textile industries became the major contributors of pollution because this industry consumed more than 200 types of chemicals and beyond 7000 types of dyes. On each stages of textile industry release different types of chemicals and dyes and most of the wastewater does not follow proper treatment before discharged to the water body which consequently lead to water pollution. Other than that, heat that released from the textile industry can increase the pH and others materials that used during the operation such as dyes, de-foamers, bleaches, detergents, optical brighteners and equalizers can cause water saturation. Li *et al.*, (2005) suggest wastewater treatment before discharge is necessary in order to prevent damaging on the natural environment and implication on human health.

Halimoon *et al.*, (2010) had reported Pb, Cr, Cd and Cu mostly used for the production of color pigments in textile dyes. During dyeing process, these heavy metals can penetrate through the fibers and become toxic to human body and aquatic life, and can accumulate and trapped in soil when released into the environment (Marthur *et al.*, 2005).

CHAPTER 3: OBJECTIVES OF THE STUDY

The purpose of this project was study the level of heavy metals in batik industries wastewater by using Graphite Furnace-Atomic Absorption Spectroscopy (GFAAS). The heavy metals content in textile wastewater should follow the standard limit regulated by government under Environmental Quality (Sewage and Industrial Effluents) Regulations 1979. The aims of the study were listed as follow:

1) To study and analyze various types of heavy metal contents in batik industries' wastewater.

2) To determine the concentration of total and free heavy metals in batik industries' wastewater.

3) To compare the heavy metals concentration in Batik industries' wastewater with standard limits allowed by Environmental Quality (Sewage & Industrial effluent) Regulation 1979.

CHAPTER 4: SIGNIFICANCE OF STUDY

1) This study provides information about the level of heavy metals contents in batik industries' wastewater.

2) To suggest for wastewater treatment if heavy metal concentration exceed the standard limit allowed by Environmental quality (sewage & industrial effluent) regulation 1979

CHAPTER 5: MATERIALS AND REAGENTS

5.1 Apparatus

All apparatus used in this study were summarized in Table 5.1

Table 5.1: List of apparatus used in the study

Apparatus	**Brand**
Beakers 200ml, beakers 100ml, , Erlenmeyer flask, volumetric flask 50ml, volumetric flask 10ml, dropper, watch glass, 500ml polyethylene plastic bottle, measuring cylinder 100ml	SCHOTT DURAN
Hot plate	DRAGON
Glass funnels	SCHOTT DURAN
pH paper	Merck KGaA
Whatman filter paper (diameter 11cm)	Whatman ®
Pipette 25µL, 100 µL, 1000 µL	Gilson, France

5.2 Chemicals

All chemicals used in this study were analytical grade reagents and were summarized in Table 5.2

Table 5.2: List of chemicals used in the study

Chemicals	Description	Brand
Conc. nitric acid (HNO_3)	0.5% v/v nitric acid	AnalaR grade, BDH 69%
Matrix modifiers	• Atomic absorption modifier solution Pd $(NO^3)^2$ in 15% HNO^3, conc. 10000mg/L (20°C) (conc. 1%) • Atomic absorption modifier solution Mg $(NO^3)^2$, conc. 10000mg/L (20°C) (conc. 1%) • Matrix Modifier 10% $NH^4H^2PO^4$	PerkinElmer™ Instruments PerkinElmer™ Instruments PerkinElmer Pure Atomic Spectroscopy Standard
Standard solutions	• Nickel standard solution (1000mg/L), solute: Nickel (II) nitrate $[Ni(NO_3)_2.6H_2O]$, Matrix: Nitric acid, $c(HNO^3)$= 0.5 mol/L, c(Ni)=1001 ± 5mg/L • Manganese standard solution (1000mg/L), solute: magnesium nitrate $[Mg(NO^3)^2.6H^2O]$, Matrix: Nitric acid, $c(HNO^3)$= 0.5 mol/L, c(Mg)= 1000± 5 mg/L • Cadmium standard solution (1000mg/L), solute: Cadmium nitrate $[Cd\ (NO^3)^2.4\ H^2O]$, Matrix: Nitric acid, $c(HNO^3)$ = 0.5 mol/L, c (Cd)= 1000 ± 5mg/L • Plumbum standard solution (1000mg/L), solute: Plumbum nitrate $[Pb\ (NO^3)^2.4\ H^2O]$, Matrix: Nitric acid, $c(HNO^3)$ = 0.5 mol/L, c (Pb)= 1000± 5mg/L	BDH SpectrosoL® BDH SpectrosoL® BDH SpectrosoL® BDH SpectrosoL®

5.3 Instrumentation

The Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) used was a Perkin-Elmer (AAnalyst 800). The instrument was equipped with an auto sampler and hollow cathode lamp (PerkinElmer®). The GFAAS connected to the computer monitor, Windows® XP operating system as shown in Figure 5.1.

Figure 5.1: Graphite Furnace Atomic Absorption Spectroscopy (GFAAS), Perkin Elmer® (AAnalyst 800) connected to the computer monitor, Windows® XP operating system