ENVIRONMENTAL CONTAMINATION BY BATIK WASTEWATER AND THE POTENTIAL APPLICATION OF ACTIVATED CARBON FROM PINEAPPLE WASTE FOR WASTEWATER TREATMENT

NOOR SYUHADAH BINTI SUBKI

UNIVERSITI SAINS MALAYSIA

2017

ENVIRONMENTAL CONTAMINATION BY BATIK WASTEWATER AND THE POTENTIAL APPLICATION OF ACTIVATED CARBON FROM PINEAPPLE WASTE FOR WASTEWATER TREATMENT

by

NOOR SYUHADAH BINTI SUBKI

Thesis submitted in fulfillment of the requirements

for the degree of

Doctor of Philosophy

MAY 2017

ACKNOWLEDGEMENTS

I would like to express my special appreciation and thanks to my main supervisor Dr. Rohasliney Hashim for being a tremendous mentor to me in guiding me through this research. I would like to thank my co-supervisor Dr. Noor Zuhartini Md Muslim for the scientific advice and knowledge and many insightful discussions and suggestions. Not to forget my field supervisor Prof. Dato' Dr. Ibrahim Che Omar for all his ideas and support throughout this research journey and allow me to grow as a researcher.

I would especially like to thank all the laboratory members in School of Health Sciences, Universiti Sains Malaysia, and all the laboratory members in Universiti Malaysia Kelantan for giving me the best cooperation and support during my PhD laboratory work.

A special thanks to my family and friends. Words cannot express how grateful I am especially to my parents, parents-in-law and my sisters who have been supporting me and for all the sacrifices that you have made on my behalf. Your prayer for me was what sustained me this far. Thank you for all my friends who supported me through this journey and incented me to strive towards my goal.

Lastly, I would like to express my appreciation to my beloved husband Saiful Akramin and my two children Daniel and Dayana who always be my strength and my support in the moment when there was no one to answer my queries. These past several years have not been an easy ride, both academically and personally. I truly thank Allah s.w.t that gave me a chance to experience this beautiful journey as PhD candidates.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATE

LIST OF SYMBOLS, ABBREVIATIONS AND ACRONYMNS

°C	Degree Celsius
µm	Micro meter
AC	Activated Carbon
As	Arsenic
BOD	Biological Oxygen Demand
Cd	Cadmium
COD	Chemical Oxygen Demand
Cr	Chromium
DO	Dissolve Oxygen
DOE	Department of Environment
DS	Dissolve solid
EQA	Environment Quality Act
FAAS	Flame Atomic Adsorption Spectrophotometer
Fe	Iron
FTIR	Fourier Transform Infrared
g	Gram
H_2O_2	Hydrogen Peroxide
H_2SO_4	Sulfuric Acid
HCl	Hydrochloric Acid
Hg	Mercury
HNO_3	Nitric Acid
hrs	Hours
Kg	Kilogram

KOH	Potassium Hydroxide
L	litter
mg	Milligram
mL	Milliliter
Mn	Manganese
N	Normality
Na_2O_3Si	Sodium Silicate
NaOH	Sodium Hydroxide
Ni	Nickel
nm	Nanometer
O_2	Oxygen
Pb	Lead
ppm	Part per million
rpm	Revolutions per minute
SEM	Scanning Electron Microscope
SS	Suspended solid
TDS	Total Dissolve Solid
TSS	Total suspended solid
Zn	Zinc
$ZnCl_2$	Zinc Chloride

PENCEMARAN ALAM SEKITAR OLEH AIR LIMBAHAN BATIK DAN POTENSI APLIKASI KARBON TERAKTIF DARIPADA SISA NENAS UNTUK PERAWATAN AIR LIMBAHAN

ABSTRAK

Pertumbuhan industri batik di Malaysia dari awal tahun 1930-an sehingga kini telah menjadi satu industri tempatan yang sangat berdaya maju. Walau bagaimanapun, industri batik menghasilkan sejumlah besar air limbahan yang akhirnya akan mencemarkan alam sekitar. Air limbahan ini perlu dirawat terlebih dahulu sebelum dilepaskan ke alam sekitar. Kajian ini bertujuan untuk menentukan pencemaran logam berat daripada air limbahan kilang batik ke kawasan sekitarnya. Tiga jenis sampel (air limbahan batik, tanah dan tumbuhan) telah dikumpulkan dari tiga kilang batik yang berbeza di sekitar Kota Bharu, Kelantan, Semenanjung Malaysia. Kadmium (Cd), plumbum (Pb), zink (Zn), tembaga (Cu), kromium (Cr) dan besi (Fe) adalah antara logam berat yang telah dipilih sebagai bahan pencemar kajian. Spektroskopi Serapan Atom Nyalaan (FAAS) telah digunakan untuk analisis logam berat. Sifat fizikokimia air limbahan batik juga telah dianalisis di lapangan dengan menggunakan alat pengesan pelbagai parameter. Keputusan daripada analisis ini menunjukkan bahawa kepekatan logam berat dalam air limbahan batik, tanah dan tumbuhan tidak melebihi had kritikal yang telah ditetapkan oleh peraturan antarabangsa dan kebangsaan. Walau bagaimanapun, logam berat seperti Cr dan Cu adalah sangat toksik kepada manusia dan hidupan akuatik walaupun hanya pada kepekatan yang sangat rendah. Dengan itu, rawatan awal untuk air limbahan batik perlu dilakukan sebelum ia di lepaskan ke alam sekitar. Dalam kajian ini, karbon teraktif dihasilkan daripada sisa buah nenas digunakan untuk mengurangkan kepekatan bahan pencemar seperti logam berat di dalam air limbahan batik dan juga dapat membantu mengurangkan sisa buangan nanas yang terhasil daripada pengeluaran nenas secara besar-besaran di Malaysia. Karbon teraktif tersebut telah digunakan bagi menguji kesesuaiannya untuk mengurangkan kandungan logam berat dan permintaan oksigen kimia (POK) di dalam air limbahan batik. Penggunaan karbon teraktif yang dihasilkan daripada jambul, teras dan kulit nenas telah menunjukkan penjerapan maksimum logam berat masing-masing pada 86.5%, 76.73% dan 77.05% Perbandingan antara zink klorida ($ZnCl_2$) dan kalium hidroksida (KOH) juga menunjukkan bahawa karbon teraktif jambul nanas oleh pengaktifan KOH memberi peratusan penjerapan logam berat yang lebih tinggi. Keupayaan karbon teraktif (KOH) untuk mengurangkan POK di dalam air limbahan batik juga menunjukkan peratusan pengurangan antara 69.23% hingga 89.87%. Kajian ini menunjukkan potensi sisa pertanian untuk dijadikan produk tambah nilai seperti karbon teraktif bagi menyelesaikan masalah alam sekitar dan juga membantu untuk menyelesaikan masalah lebihan sisa buangan nenas.

ENVIRONMENTAL CONTAMINATION BY BATIK WASTEWATER AND THE POTENTIAL APPLICATION OF ACTIVATED CARBON FROM PINEAPPLE WASTE FOR WASTEWATER TREATMENT

ABSTRACT

The growth of the Malaysian batik industry from its early beginning in the 1930s till now has become a viable local industry. However, batik industries produce a large amount of highly polluted discharge water into the environment which required an extensive treatment. This study was aimed to determine the heavy metal contaminant from batik factory wastewater to the surrounding area. Three different types of samples (batik wastewater, soil and plant) were collected from three different batik factories in Kota Bharu, Kelantan, Peninsular Malaysia. Cadmium (Cd), lead (Pb), zinc (Zn), copper (Cu), chromium (Cr) and iron (Fe) were chosen for the study of heavy metal contaminants. Heavy metal concentrations were detected using Flame Atomic Absorption Spectrophotometer (FAAS). The physicochemical properties of the batik wastewater were also analysed *in situ* using the YSI Multiprobe parameter. The results indicated that heavy metal concentration in the batik wastewater, soil and plants did not exceed the critical limits set by international and national regulatory authorities. However, heavy metals, typically Cr and Cu are very toxic to human and aquatic life at relatively low concentrations, requiring extensive treatment for batik wastewater before it is discharged into the environment. In this study, activated carbon derived from different pineapple waste was use to remove contaminants such as heavy metals in batik wastewater and also to reduce the abundance of waste generated from the massive production of pineapple in Malaysia. These activated carbons were used to identify the suitability to reduce heavy metals and chemical oxygen demand (COD) levels in the batik wastewater. The use of activated carbon derived from pineapple crown, peel and core indicated maximum adsorptions of heavy metals of 86.05%, 76.73% and 77.05%, respectively. The comparison between zinc chloride ($ZnCl_2$) and potassium hydroxide (KOH) showed that the pineapple crown activated carbon by KOH activation gave better adsorption value. Capability of activated carbon (KOH) to reduce COD in the batik wastewater showed reduction percentage between 69.23% and 89.87%. This study showed potential of agriculture waste as value added product such as an activated carbon to solve the environmental problems and also helps to solve over abundance pineapple waste altogether.

CHAPTER 1

INTRODUCTION

1.1 Study Background

The textile industry has become a source of income for some countries. Increase in demand for clothing and apparel has brought both positive consequences to some countries, which is in a way an improvement in economy. It is known that textile processing employs a variety of chemicals, depending on the nature of raw materials. Chemical reagents used in textile industry are divers in chemical composition ranging from inorganic to organic. A wide range of chemicals of inputs, if not incorporated in the fabric, will become waste and turn out to be part of water ecology. Therefore, it is obvious that the textile industry contributes to environmental pollution.

Environmental problems from the textile industry are mainly caused by discharge of untreated wastewater. The textile industry is known to be the worst offender of pollution contributor, as it uses more than 2000 types of chemicals and over 7000 types of dyes (Halimoon & Yin, 2010). Once these dye containing chemicals enter water, it is no longer good and sometimes difficult to treat because the dyes have synthetic origin and complex molecular structure which makes them more stable and difficult to be biodegraded (Forgacs *et al.*, 2004).

There are more than 10,000 types of dye that have been used in the textile industry. More than 7×10^5 tonne dyes per year are used in textile industry (Zollinger, 1987). Although most of the colours stay on fabrics, 30 to 40 percent will be washed out and flushed either directly to the environment (land or river) or into the drainage system. Textile wastewater contains different types of dye and heavy metals, for instance, the organo-metallic dye (Visa *et al.*, 2010).

In Malaysia, batik is a very popular traditional handmade textile craft. Batik production in Malaysia started in 1960s and has been developed through time. Until now, batik production is still developing and exerted with modern influence in the fashion industry. In Malaysia, batik is produced as cottage industries, especially in Kelantan and Terengganu. In the past decades, there had been a revival and rejuvenation of the arts and crafts of Malaysia. Under the patronage of the late Y.A.B Datin Paduka Seri Endon Mahmood, for instance, the *kebaya nyonya* and batik has gained international recognition. Her passion for Malaysia's cultural heritage and crafts was reflected in many undertakings projects. Her legacy in promoting and doing more for batik and other Malaysian crafts is still kept alive by passionate parties, namely government and private institutions, batik enthusiasts, and designers. Global exhibitions, workshops, textile conferences, various books, and fashion shows had contributed to batik's popularity and are now attracting new admirers of this ancient art which is given a new life.

There are three types of reactive dyes that are used in batik industry, namely azo dyes, anthraquinone, and triarylmethane. Azo dyes are diazotised amines coupled to an amine or phenol, with one or more azo bonds (-N=N-) (Chequer *et al.*, 2011). Azo compounds bear the functional group R-N=N-R', in which R and R' can either be aryl or alkyl. But the more stable derivatives contain two aryl groups. The N=N group is called an azo group, even though the parent compound, HNNH, is called diimide. The azo molecule, typically monoazo structure containing a functional group such as hydroxyl, carboxyl or amino, is capable of forming a strong co-ordination complexes with heavy metal ions such as chromium, cobalt, nickel, and copper. In other words, heavy metals present as impurities in a dye or as part of the dye molecule. In metal complex dyes, the metal forms a chemical bond with the organic dye molecule, thus, it is an indispensable constituent of the dye and could govern the fastness to absorb the colours.

The presence of certain heavy metals in the textile dyes will probably lead to direct consequences implication human and environment. Demirizen *et al*., (2007) reported that, textile industries release heavy metals such as cadmium (Cd), copper (Cu), chromium (Cr), nickel (Ni), and lead (Pb) in wastewater production. The possible sources of heavy metals in the textile wastewater are incoming fibre, dyes, plumbing, and chemical impurities. Metals can be presented in dyes as catalysts during dye manufacturing or forming an integral part of the dye molecule. The metallic compound that is bound to the dye molecule is essential for the dye performance as a textile colourant (Bae & Freeman, 2007), see Table 1.1.

Table 1.1 Typical metals found in dyes by dye class (Bae and Freeman, 2007)

Dye Class	**Typical Metals Present in Dye 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 dyes are shown in Figure 1.1 (Ahn *et al.*, 2009) and Table 1.2 (Ahn *et. al.*, 2009). Ramachandra *et. al.* (2010) reported that a wide range of heavy metals such as cadmium (Cd), chromium (Cr), lead (Pb), copper (Cu), manganese (Mn), zinc (Zn) and mercury (Hg) found in wastewater released from industries are very toxic. Heavy metals are not biodegradable and tend to accumulate in living organisms through food chain. They are harmful to living organism and affect productive success whereas in severe contamination, they can be fatal.

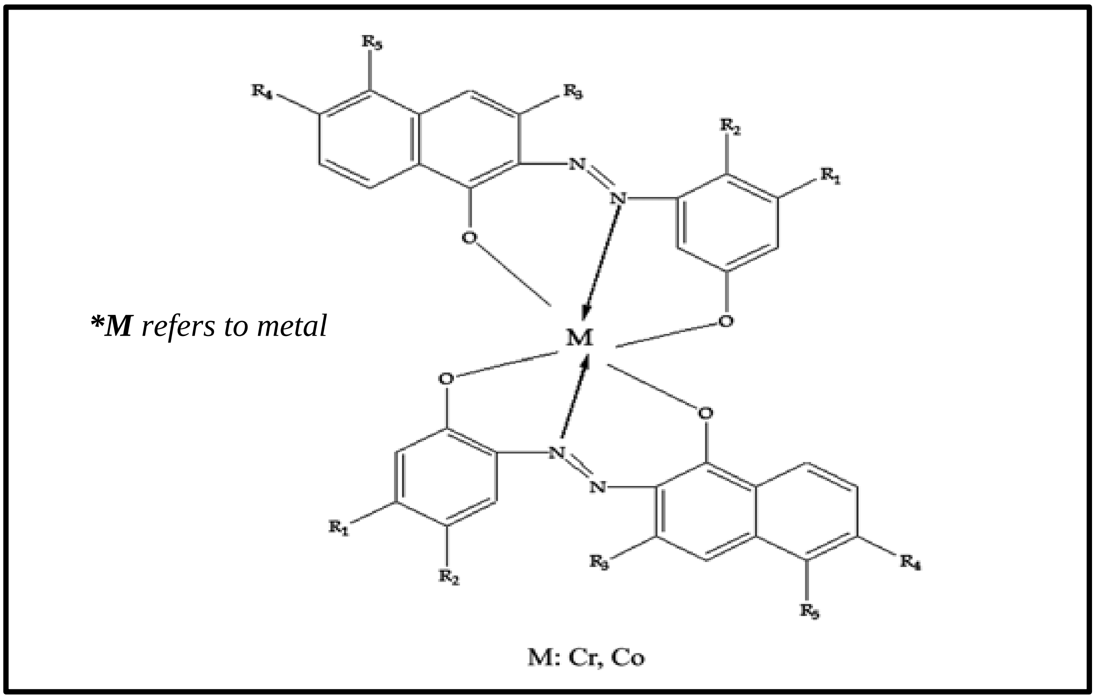

Figure 1.1 Chemical structure of metal complexes of dyes (Ahn *et al.*, 2009)

Table 1.2 Structure of metal complexes of 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

Besides that, high chemical oxygen demand (COD) in the wastewater also gave negative ecological impacts to the water body and environment which directly affect human well-beings. Wastewater with a high COD value (>1600 mg/L) and a strong dark colour is classified as a high strength wastewater (Kobya *et al.*, 2003). A study of the characteristic of batik wastewater in small scale and medium scale batik industries had found that the COD values were 14 500 mg/L and 20 100 mg/L, respectively (Sridewi *et al.*, 2011).

The discharge of the effluents with high COD value to the receiving stream or drainage can lead to the dissolved oxygen depletion and thus creates anaerobic condition (Al-Degs *et al.*, 2000). Under anaerobic condition, foul smelling compound, such as hydrogen sulfides, may be produced, and distress the biological activity especially in the receiving stream.

Unwanted wastewater that is released onto the soil or river will furnish a bad effect to the surrounding environment including to animals and plants. Terrestrial and aquatic plants may absorb pollutants from such release, and then pass on the pollutants into the food chain that is consumed by higher level trophic such as animals and humans. Previous reports have mentioned direct and indirect toxic effects of dyes and metals in the form of tumours, cancer, and allergies besides growth inhibitions on different tropic levels like bacteria, protozoan, algae, plants, and different animals including human beings (Naeem Ali *et al.*, 2009). Besides that, organic dye pollution may also restrict the nitrogen-use-efficiency of plants, thus further reducing the productivity of terrestrial ecosystem (Topaç *et al.*, 2009).

Extensive dyes pollution can affect the economy of a country because it is very expensive to be treated upon release to the environment (stream, ocean, soil, and etc). Waste containing dyes are persistent to accumulate in ground water and eventually make their way to the stream or ocean. Nowadays, a lot of techniques were introduced to clean up the pollution in water which cost a lot of money.

Pollution clean-up is generally costly, depending on the location of pollution, contamination size, and the type of the pollution that occurred.

To overcome environmental pollution problems, many research were conducted to explore the most suitable and effective method to remove contaminants, such as heavy metals from industrial wastewater. Methods namely activated carbon adsorption, chemical coagulation, ion exchange, electrolysis, and chemical treatments were developed for removing contaminants from wastewater prior to its release into the environment (Geçgel *et al.*, 2013).

Among the water treatment methods, activated carbon sorption was found to be a better option for adsorption for contaminants, such as heavy metals and dyes, due to its large surface area and pore volume (Gottipati, 2012; Geçgel *et al.*, 2013). According to Syafalni *et al*. (2012), adsorption treatment using activated carbon is more preferable when referring to its efficiency, high adsorption capacity, and low operational cost methods. Coal based activated carbon is widely used but the production of the conventional activated carbon is costly and this limits its usage. As an alternative, scientist has explored the usage of non-conventional and low cost adsorbents from olive-waste cakes (Baccar *et al.*, 2009), coconut shell (Onyeji & Aboje, 2011), cassava peel (Rajeshwarisivaraj *et al.*, 2001), orange peel (Gupta & Nayak, 2012), zeolite (Halimoon & Yin, 2010), fly ash (Visa *et al.*, 2010), and tannery sludge (Reddy *et al.*, 2008) for a lower cost adsorbent applicable for small scale industries.

Activated carbon can be produced from any type of carbonaceous materials or agricultural waste, such as coconut shell (Guo *et al.*, 2009; Cazetta *et al.*, 2011), oil palm (Alam *et al.*, 2007; Tan *et al.*, 2007; E. *et al.*, 2013), banana peels (Reddy &

Yang, 2005; Ali, 2013), bamboo (Kannan & Veemaraj, 2009), rice husk (Gopalakrishnan & Jeyadoss, 2011; Zhang *et al.*, 2011), and many more. Most of the studies on the biosorption of activated carbons were focused on the removal of heavy metals ion (Babel & Kurniawan, 2003) and dyes (Kandisa *et al.*, 2016) from the wastewater. It has been reported that all the low cost biosorbents are capable of removing of heavy metals and dyes in the aqueous solutions (Babel & Kurniawan, 2003; Kandisa *et al.*, 2016).

A good activated carbon is renewable, such as those produced from agricultural waste, contains high carbon content, supply for use in the countries is stable, have higher potential activation extend , and inexpensive. Pineapple waste is a good candidate, since it is widely available in Malaysia. In fact, Malaysia is one of the most successful and potential leading countries in the pineapple industry with more than 6 000 hectares of pineapple plantation, especially in Johor, Selangor, Perak, and Kelantan. According to the data provided by the Malaysia Pineapple Industry Board (2015), the famous pineapple species found in Malaysia are Maspine, Sarawak, Yankee, Gandul, Moris Gajah, Josapine, N36, MD2, and Moris, which all of these types . Because of massive pineapple production, the waste generated from the pineapple industry including pineapple crown, peel, and core have increased. Therefore, turning pineapple waste into activated carbon for the water treatment helps ease the problems for pineapple waste treatment and dispose cost.

Pineapple waste such as peel, core, and crown can also be used in the removal of dyes. This is because pineapple adsorbent is low cost, can prevent disposal cost and prevent off-site burning (Lutpi *et al.*, 2011). Based on the availability of the pineapple waste, pineapple waste namely pineapple crown, peel, and core are chosen for this study to produce activated carbon for the adsorbent of dyes.

Pineapple waste disposal is costly in pineapple industry because of transportation. If it is released untreated, serious environmental problems can result because pineapple waste requires high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) to decompose (Ratna & Padhi, 2012). Thus, in some countries pineapple waste is utilised in various manners, namely as bromelain, ethanol, antioxidant, organic acid, acids, anti-dyeing agent, fibre, removal of heavy metal, animal feed, and energy and carbon source (Maurya *et al*., 2012).

1.2 Problem Statement

A majority of batik production in Kelantan state are operated by small and medium scale factories, often family business, although some factories are operating at a relatively large scale. There is low awareness on the Environmental Quality Act (1974) pertaining to industrial effluent, and is indicated by the poor compliance of the act by batik entrepreneurs as compared to other manufacturing industries (Department of Environment Kelantan, 2009). Even though some batik entrepreneurs are trying to comply with stated environment rules and regulations on the water discharge, batik wastewater treatment is found to be too costly for the treatment system and is unaffordable.

However, if the wastewater is released untreated, heavy metals and dyes in such waste could harm environmental and health consequences. Since there is abundance of pineapple waste generated from the pineapple industry, these waste could be potentially converted into activated carbon, thus serve as a cheap and efficient adsorbent for heavy metals and dye removal, prior to discharge in the batik factory outlet.

1.3 Aim of the study

This research aims to study pollution in batik wastewater, soil and plant in the vicinity of the selected batik factories. Physico-chemical parameters, heavy metals contaminant and COD value were measured in this study. The outcomes of this study could reveal the heavy metal distribution in the batik wastewater soil and plant in the vicinity of the selected batik factories. To remediate such contamination, treatment of batik wastewater using activated carbon made up from pineapple waste was investigated.

The achieve the aims, the following objectives were set;

i. to determine the physic-chemical and COD level in batik wastewater;

ii. to investigate the heavy metals' contamination that occurs in the surrounding of selected batik factories (*i.e.*; batik wastewater, plants, and soil);

iii. to evaluate the potential application of locally produced activated carbon from pineapple waste as one of the treatment method to adsorb heavy metals and to reduce COD value in the batik wastewater;

iv. to establish the optimum condition of pineapple waste activated carbon to reduce the heavy metals and COD in batik wastewater.

CHAPTER 2

LITERATURE REVIEW

2.1 Textile Wastewater

Textile industries have become a source of income for some countries, such as India and China. The increase demand of clothing and apparel has brought both positive consequences to some countries in a way, which is an improvement in economy, or in negative extreme attributed to environmental pollution. In Malaysia, the textile industry was ranked as 11^{th} top export earner and accounted for 1.4% share of Malaysia's export of manufactured goods in 2013 (Malaysian Knitting Manufactures Association, 2013). According to Malaysia External Trade Development Corporation (2015), the total export of Malaysian textiles and apparels/clothing were about RM12.63 billion for the year 2015.

One of the best known textile industries in Malaysia is the batik industry, which is valued by the government at about RM370 to RM400 million per year (Ismail *et al.*, 2013). Most of the batik industries operated as a backyard or a cottage industry throughout the country without proper regulated waste disposal system (Sridewi *et al.*, 2011). The lack of awareness and knowledge from the batik entrepreneurs about the dangerous materials contained in the batik wastewater such as wax, resin, dyes, and fixing agents (sodium silicates) that was directly discharged to the environment (Rashidi, 2015). Without proper treatment of the batik wastewater before being discharged to the environment, it may cause disturbance in physiology and biochemistry of aquatic organisms (Awang *et al.*, 2016).

Chemicals and dye materials used in the textile industries are generally organic compounds of complex structure. Normal sized of textile industries use about 0.51 to 0.58 kg of chemicals per m^3 of water per day (Kant, 2012). High concentration of chemicals and dyes found in the wastewater is due to the large amount of unfixed dyes on the fabrics that get washed away during the finishing process. As for batik making, a lot of water is used in the de-waxing and washing process. It is estimated that about 10 to 15 per cent of the unfixed dyes and chemicals will be released during the process. The process of making batik is shown in Appendix A.

The characteristic of the textile wastewater may differ, depending on the types of manufactured textile products. Wastewater from printing and dyeing units in the textile manufacturing is often rich in colour, containing residues of reactive dyes and chemicals, such as complex components, many aerosols, high chemical oxygen demand (COD), and biological oxygen demand (BOD) concentration as well as much more hard-degradation materials (Wang *et al*., 2010). Wastewater characteristics in the textile industries are presented in Table 2.1 (Soresa, 2011). Meanwhile, batik wastewater contained a large quantity of dyes, wax, and chemicals including ludigol, sodium silicate, sodium carbonate, sodium alginate, and calcium sulphate (Ahmad *et al.*, 2002) involving the '*chanting*', dyeing, fixing, and washing processes.

Table 2.1 Textile industries wastewater characteristics (Soresa, 2011)

Process	**Effluent Composition**	**Characteristics**
Sizing	Starch, wax, carboxy methyl cellulose (CMC), poly vinyl alcohol (PVA), wetting agents	High in BOD, COD
Desizing	Starch, CMC, PVA, fats, waxes, pectins	High in BOD, COD, suspended solids (SS), dissolved solid (DS)
Bleaching	Sodium hypochlorite, sodium hydroxide, acids, surfactants, sodium phosphate, short cotton fiber	High alkalinity, high SS
Mercerizing	Sodium hydroxide, cotton wax	High pH, low BOD, high DS
Dyeing	Dyestuffs urea, reducing agents, oxidizing agents, acetic acid, detergents, wetting agents	Strongly coloured, high BOD, DS, low SS, heavy metals
Printing	Pastes, urea, starches, gum, oil, binders, acids, thickeners, cross-linkers, reducing agents, alkali	Highly coloured, high BOD, oily appearance, slightly alkaline

In Malaysia, all industries that release effluent discharges, including the batik industries must comply with Environmental Quality Act 1974 and subsidiary legislation act, Environmental Quality (Industrial Effluent) Regulations 2009. Table 2.2 shows the acceptable conditions for discharge of industrial effluent or mixed effluent of standards A and B, while Table 2.3 shows the acceptable conditions for discharge of industrial effluent containing chemical oxygen demand (COD) for a specific trade or industrial sector.

Table 2.2 Acceptable conditions for discharge of industrial effluent or mixed effluent of standards A and B (Ministry of Natural Resources and Environment, 2008)

Parameter	Unit	Standard	
		A	B
Temperature	^{o}C	40	40
pH Value	-	6.0-9.0	5.5-9.0
BOD at $20^{o}C$	mg/L	20	50
Suspended Solids	mg/L	50	100
Mercury	mg/L	0.005	0.05
Cadmium	mg/L	0.01	0.02
Chromium, Hexavalent	mg/L	0.05	0.05
Chromium, Trivalent	mg/L	0.20	1.0
Arsenic	mg/L	0.05	0.10
Cyanide	mg/L	0.05	0.10
Lead	mg/L	0.10	0.5
Copper	mg/L	0.20	1.0
Manganese	mg/L	0.20	1.0
Nickel	mg/L	0.20	1.0
Tin	mg/L	0.20	1.0
Zinc	mg/L	2.0	2.0
Boron	mg/L	1.0	4.0
Iron (Fe)	mg/L	1.0	5.0
Silver	mg/L	0.1	1.0
Aluminium	mg/L	10	15
Selenium	mg/L	0.02	0.5
Barium	mg/L	1.0	2.0
Fluoride	mg/L	2.0	5.0
Formaldehyde	mg/L	1.0	2.0
Phenol	mg/L	0.001	1.0
Free Chlorine	mg/L	1.0	2.0
Sulphide	mg/L	0.50	0.50
Oil and Grease	mg/L	1.0	10
Ammoniacal Nitrogen	mg/L	10	20
Colour	ADMI*	100	200

*ADMI-American Dye Manufacturers Institute

Table 2.3 Acceptable conditions for discharge of industrial effluent containing chemical oxygen demand (COD) for specific trade or industrial sector (Ministry of Natural Resources and Environment, 2008)

Trade / Industry	Unit	Standard	
		A	B
(a) Pulp and paper Industry			
(i) pulp mill	mg/L	80	350
(ii) paper mill (recycle)	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

Standard A is used for any effluents discharged into any inland waters within the catchment areas as specified in the Sixth Schedule in Environmental Quality Act, while Standard B is used for any effluents discharged into any other inland waters or Malaysian waters (Ministry of Natural Resources and Environment, 2008).

High dyes visibility in textile wastewater even in a very small concentrations may affect their transparency and aesthetics and this colour is very difficult to deal with (Dhas, 2008). The high concentration of chemicals and colour in the textile wastewater may cause a critical environmental problem if not treated properly before being discharged to the environment.

2.2 Pollution by Textile Wastewater

Environmental problems of the textile industry are mainly caused by discharge of a large amount of wastewater without proper prior treatment. Its manufacturing process consumes a large amount of water mainly in the dyeing, washing, and finishing process. Wastewater from the textile industry is classified as the most polluting of all the industrial sectors, considering the volume generated as well as the effluents' composition. Textile processing employs a variety of chemicals, depending on the nature of the raw materials. The chemical reagents used in the textile industry are divers with organic and inorganic composition (Yogalakshmi & Balakrishnan, 2013) such as dyes and heavy metals. These, if not incorporated in the fabric, will become waste and turn out to be part of water ecology if discharged untreated. Once they enter the water, it is no longer good and sometimes difficult to treat these chemicals such as dyes which have a synthetic origin and a complex molecular structure that makes them very stable and consequently difficult to be biodegraded (Forgacs *et al.*, 2004).

Approximately 40,000 different dyes and pigments are used in the textile industry. It was estimated that 10 to 15 per cent of the dyes used in the textile processing were lost in the wastewater and 2 to 20 per cent are directly discharged as aqueous effluents in different environment components (Zaharia Carmen & Suteu Daniela, 2012). The most significant sources of pollution produced in textile industries are from pre-treatment, dyeing, printing, and finishing of textile materials (Dhas, 2008). Dyeing and finishing processes which require the input of a wide range of chemicals and dyestuffs were the main processes that contribute to pollution in textile wastewater (Savin & Butnaru, 2008). This is because the dyeing process will contribute to the largest portion of the total wastewater from dye preparation, spend dye bath and washing processes which contain high salt, alkalinity and colour, while the finishing process will generate pollutants such as gums, glucose, waxes, resins, softeners, and others (Dhas, 2008; Soresa, 2011).

A complex mixture of pollutants (dispersants, acids, levelling agents, carriers, alkalis, and various dyes) in textile wastewater will change the pH, increase the biochemical oxygen demand (BOD) and chemical oxygen demand (COD), and release intense colourations in the river or any water body. Table 2.4 shows the range for textile wastewater for pH, BOD, and COD.

Table 2.4 Range for pH, BOD and COD for textile wastewater (Eswaramoorthy *et al.*, 2008)

	Parameters		
	pH	**BOD**	**COD**
Range	6 - 10	80 – 6000 mg/L	150 – 12000 mg/L

Apart from that, this textile wastewater usually have high level of COD, BOD, acidity, chlorides, sulphates, phenolic compounds, and heavy metals (Lanciotti *et al.*, 2003). The content of heavy metals in dyes concerns with a serious bad impact on natural water bodies and land in the surrounding area in future. Heavy metals are present as impurities in a dye or as part of the dye molecule. In metal complex dyes, the metal forms a chemical bond with the organic dye molecule. Thus, it is an indispensable constituent of the dye and governs the fastness to absorb the colours. But the presence of the heavy metals later in the wastewater will give many bad consequences to the environment and human health because of their cumulative effect and has high possibilities for entering into the food chain and endanger living organisms. The common metals found in different class of dyes are summarised in Table 2.5.

Table 2.5 Common metals found in different dye class (Verma, 2008)

Dye class	Metals in Dyes
Acid dyes	copper, lead, zinc, chrome, cobalt
Basic dyes	copper, zinc, lead, chromium
Direct dyes	copper, zinc, lead, chromium
Mordant dyes	chrome
Pre-metallized	cobalt, chrome, copper
Reactive dyes	copper, chromium, lead
Vat dyes	none
Disperse dyes	none

Previous study reported that the average value for a few metal ions such as Cu^{+}, Fe^{+}, Mn^{+}, Zn^{+}, Cd^{+} and Cr^{+} in the batik wastewater were 5.54, 4.83, 3.57, 2.69 0.52, and 1.65 mg/L, respectively (Siddiqui *et al.*, 2011). Kristijanto *et al.* (2011) detected a small amount of Cr (0.05 mg/L) and Pb (0.45 mg/L) in batik wastewater in one of the batik factories in Central Java, Indonesia. Even the concentrations of heavy metals present in wastewater is low or even at undetectable quantities, their recalcitrance and consequent persistence in water bodies imply that through natural process such as bio-magnifications, concentration may become elevated to such an extent that they begin exhibiting toxic characteristics (Mohan & Sreelakshmi, 2007).

Due to the mobility of heavy metals in food chain, aquatic ecosystems, and their toxicity to higher life forms, heavy metals in surface water and groundwater supplies have been prioritised as major inorganic contaminants in the environment. Heavy metals enter the environment mainly via three routes: (i) deposition of atmospheric particulate, (ii) disposal of metal enriched sewage sludge and sewage effluents, and (iii) by-products from metal mining process (Begum *et al.*, 2009). These heavy metals which have been transferred to the environment are highly toxic and can bio accumulate in the human body, aquatic life, natural water-bodies, and also possibly trapped in the soil (Mathur *et al.*, 2005).

Most dyes containing heavy metals will affect the aquatic life and living organisms due to their non-degradability and toxicity (Gopalakrishnan & Jeyadoss, 2011). Dyes and chemicals in the textile wastewater prevent photosynthesis in aquatic plants by blocking penetration of sunlight into water and cause alteration in aquatic habitat (Wang *et al*., 2010). More than 600,000 tons of dyes, mostly from the textile industries, are discharged into the environment every year, and more than 80% of which are azo dyes (Wenrong & Haiyan, 2001). Azo dyes have complicated structures, high chemical stability, and poor biodegradation. The azo dyes are considered recalcitrant xenobiotic compounds due to the presence of an N=N bond and other possible groups that are not easily biodegraded. The azo dyes are toxic and harmful to the environment by affecting the aesthetic and a transparency aspect of the water received, and also involves some possible environmental concerns on the toxic, carcinogenic, and mutagenic effects of some azo dyes (Spadaro *et al.*, 1992; Lu *et al.*, 2010; Modi *et al.*, 2010).

In 2007, a study in the Cristais River in Brazil detected a mutagenic activity which was linked an Azo dyeing plant as one of the sources. Cristais River was a drinking water sources in Brazil. Though the drinking water was treated in a plant located 6 km downstream of the discharge site, testing confirmed the presence of carcinogenic aromatic amines. Effluents from the Azo dyeing plant was then tested as drinking water on the laboratory rodents. When laboratory rodents consumed the effluent at 1-10% concentration, an increase in pre-tumour lesions of the colon was observed (Alves de Lima *et al.*, 2007).

Most of the batik industry used azo dyes or reactive dyes for the colouring process. The final process of making batik left wastewater that contains the remaining colouring dyes. Colour is imparted to textile effluents because of various dyes and pigments used. Many dyes are visible in water at concentration as low as 1 mg/L. Textile wastewaters, typically with dye concentration with a range of 10 – 200 mg/L, are therefore highly coloured (Ali & Suhaimi, 2009). Prolonged exposure to textile dyes may cause harm to human health, such as dermatitis, ulceration of skin, irritation of lungs and skin, headaches, nausea, and even cancer in some of the cases have been reported (Jain *et al.*, 2003; Mathur & Bhatnagar, 2007; Tufekci *et al.*, 2007).

Chemical oxygen demand (COD) test can be used to estimate the pollution (that cannot be oxidised biologically) level in the surface water and wastewater. COD value easily helps to estimate the organic matter in surface water or wastewater. COD test needs no sophistication and it is time saving. The result of a COD test indicates the amount of water-dissolved oxygen (expressed as parts per million or milligrams per litter of water) consumed by the contaminants, during two hours of decomposition from a solution of boiling potassium dichromate. The higher the COD value, the higher the amount of pollution in the test sample.

Previous study proved that COD value for batik wastewater is increasing from time to time. This may be due to the increasing demand for the batik product. More batik production, more wastewater is produced. In 1993, Rakmi A. Rahman reported that COD value in batik wastewater is between 139 mg/L to 358 mg/L in two different batik factories in Kuala Lumpur. But in 2011, the value of COD recoded in one of the batik factories in Pahang was 2334 mg/L. A research on the characterisation of the batik wastewater in the small and medium scale of batik industry was carried out in Penang and had reported that the COD value that was directly measured in the batik wastewater were 14 500 mg/L and 20 100 mg/L respectively (Sridewi *et al.*, 2011).

COD value that was directly measured in batik wastewater were between 817 mg/L to 10 061 mg/L (Kristijanto *et al.*, 2011; Kasam *et al.*, 2012; Kusumawati *et al.*, 2012). The COD value in the batik wastewater showed a massive increase from time to time and this trend could contribute to environmental pollution. Besides that, the COD value that were recorded before in the batik wastewater was higher than the standard limit in Standard A (50 mg/L) and Standard B (100 mg/L) in Environmental Quality Act 1974 and subsidiary legislation act, regulation 6: Prohibition of discharge of effluent containing certain substance into inland water.

Some of the Malaysian batik industry entrepreneurs release their wastewater to the environment either directly to the land/soil or river. The wastewater that was released without prior treatment to the soil or river may furnish bad effect to the surrounding environment (including to the animals and plants). The wastewater that contains some pollutants such as dyes and heavy metals may alter the characterisation of the soil of the batik factory area either directly or indirectly. This is because soil can be a major sink for heavy metals when being released into the environment. The heavy metals concentration can persists for a long time after being introduced into the soils, with lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni) are most commonly found in contaminated soil (Wuana & Okieimen, 2011). Terrestrial and aquatic plants may absorb pollutants from the water in the polluted soil (as their main nutrient sources) and pass the up the food chain to be consumed by animals and humans.

The long term effect posed by heavy metal uptake in the human health is very crucial. Previous study reported that the direct and indirect toxic effects of dyes and heavy metals contamination are in the form of tumors, cancer, and allergies besides growth inhibitions on different tropic levels like bacteria, protozoan, algae, plants, and different animals including human being (Ali & Suhaimi, 2009). Besides that, organic dye pollution may also restrict the nitrogen-use-efficiency of plants, thus further reducing the productivity of terrestrial ecosystem (Topaç *et al.*, 2009).

2.3 Wastewater Treatment

The environmental and human health effects of dyes released in textile industry wastewater has gotten attention from most of the scientists. A study on cytotoxic effect of batik wastewater on V79 cells showed that the wastewater is hazardous to human and environment. This is because the results of cytotoxicity assessment towards V79 cells showed that the batik wastewater exhibited the cytotoxic effect in various concentrations (Awang *et al.*, 2016). Various treatment techniques for textile wastewater have been developed which can fall into three main categories, namely biological, chemical and physical methods, depending on the size, type of waste and degree of treatment needed (Dhas, 2008).

Biological method utilises naturally occurring micro-organisms to remove pollutants, basically by oxidising organic waste (Gray, 2005; Dhas, 2008). Conventional biological process may not be effective for treating dyestuff wastewater because many commercial dyestuffs are toxic to treating organisms being used and result in the problems of sludge bulking, rising sludge, and pin flock (Ahn *et al.*, 1999). For example, bacterial granule was used in wastewater treatment (Cheunbarn *et al.*, 2008) to remove dyes and reduce chemical oxygen demand (COD). Previous study had reported that bacterial granule was able to decolourise 96.9% of the dyes and 66.7% reduction of COD (Cheunbarn *et al.*, 2008). Although the granule bacterial is able to treat the textile wastewater, it takes two to ten days for the granule bacterial to maximum reduce dyes and COD in the wastewater, indicating that it requires more time and is cost consuming. Apart from low biodegradability of many textiles chemicals and dyes, biological treatment is not always effective for textile industry wastewater (Pala & Tokat, 2002).

For chemical method, it normally includes coagulation or flocculation, oxidation, and precipitation. Some researchers used chemical methods on their research such as Ahn *et al.* (1999); Al-Kdasi, Idris, Saed, & Guan (2005); John & Shaughnessy (2004) on chemical oxidation, Ahn *et al.*, (1999); Al-Kdasi *et al.*, (2004); Aguinaldo (2009); Baysal, Ozbek, & Akman (2013) on chemical precipitation, Ledakowicz, Bilińska, & Żyłła (2012) on application of Fenton's Reagent, Allison (2005) on electro dialysis, and many more.

Among all the chemical methods used, chemical oxidation is the most common technique used to treat the textile wastewater (Dhas, 2008). Chemical oxidation is the most commonly used method for decolourisation by chemical owing to its simplicity. Chemical oxidation uses strong oxidising agents such as hydrogen peroxides, chlorine, and others to force degradation of resistant organic pollutant. The strongest oxidation agent commonly used is hydrogen peroxide.

Three common types of physical methods for textile wastewater treatment are nano filtration, reverse osmosis, and adsorption. Adsorption has been suggested as the best type among all three physical methods due to its sludge free clean operation and complete removal of dye even from dilute solutions (Kanawade & Gaikwad, 2011). Due to these reasons, activated carbon, which contains of extended surface area, micro porous structure, high adsorption capacity and high degree of surface reactivity, is found to be the best adsorbent (Wahab *et al*., 2005). Commercially available activated carbons are very expensive. In view of this reason, more researchers have started to use low commercially available materials for the adsorption of colour, such as coconut shell (Alif, 2010; Onyeji & Aboje, 2011), palm oil shell (Bakhtiar *et al*., 2010; Nik *et al*., 2006; Rahman & Yusof, 2011), rice husk (Sharma & Singh, 2009; Wahab *et al*., 2005; Yahaya, Pakir, Abustan, & Ahmad, 2010), mangrove bark (Seey *et al*., 2012), and other carbonaceous materials.

Several research were conducted for the batik wastewater treatment using coagulation technique (Lee *et al.*, 2015), electrochemical oxidation technique (Nordin *et al.*, 2013), ceramic membrane (Kasam *et al.*, 2012), ultrafiltration membrane (Kusumawati *et al.*, 2012), anaerobic baffled reactor (Kristijanto *et al.*, 2011), indigenous bacteria (Siddiqui *et al.*, 2011), nano-composite films (Sridewi *et al.*, 2011), nano filtration membrane (Ali & Suhaimi, 2009), and membrane technology (Ahmad *et al.*, 2002; Mansor, 2010). Physical treatment was also applied on synthetic or simulated batik wastewater in order to remove wax and to reduce COD (Rashidi *et al.*, 2013a; Rashidi *et al.*, 2013b). Table 2.6 summarises the various studies on batik wastewater treatment.

Table 2.6 Summarised of batik wastewater treatment

Type of Treatment	Application	Result	Reference
Locally Fabricated Asymmetric Nanofiltration Membrane	Mn, Cd, Cu, COD	Removal efficiency up to 90% Removal efficiency up to 80%	(Ali and Suhaimi, 2009)
Solar Photocatalytic by using P(3HB)-TiO2 Nanocomposite Films	Colour COD	Removal efficiency up to 100% Removal efficiency up to 80%	(Sridewi *et al.*, 2011)
Anaerobic Baffled Reactor & Rotating Biological contractors.	Colour Turbidity TDS COD Sulphate, $N\text{-}NH_3$	2.7% removal 4.1% removal 12.6% removal 19.8% removal 38.6% removal 8.8% removal	(Kristijanto *et al.*, 2011)
Fenton Oxydation and Ultrafiltration Membrane	COD	Removal efficiency up to 97.60%	(Kusumawati *et al.*, 2012)
Ceramic membrane	TSS COD	Removal efficiency up to 62.63% Removal efficiency up to 49.81%	(Kasam *et al.*, 2012)
Electrochemical Oxydation Technique using metal plate	Colour COD	Removal efficiency up to 96%	(Nordin *et al.*, 2013)
Physical Pretreatment System	pH Wax COD	Decrease slightly 88% decrease Decline to 100mg/L	*(Rashidi *et al.*, 2013a)
Baffle Tank Pretreatment	pH Wax COD	Decrease to 0.1-0.2 98% decrease Decline to 150mg/L to 350mg/L	*(Rashidi *et al.*, 2013b)

*For synthetic batik wastewater

Ahmad *et al*. (2002) used microfiltration membrane separation technology to remove the suspended solid in the batik wastewater that was produced from dyes in the painting and colouring process. The filtration process was controlled by the dye concentration, pH of dye, and the operating pressure. At higher feed concentration, cake formation on the surface of the filter was found to be more dominant and contributed to the membrane fouling. However, membrane technology has been