PREPARATION OF ACTIVATED CARBON FROM MANGROVE PILE LEFTOVER VIA CHEMICAL ACTIVATION USING PHOSPHORIC ACID FOR METHYLENE BLUE ADSORPTION

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By

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LIST OF SYMBOLS

Symbol	Description	Unit
BO	Burn-off	%
C_e	Equilibrium concentration of adsorbate	mg/L
C_o	Initial concentration of adsorbate in the solution	mg/L
IR	Impregnation ratio	-
K_F	Freundlich constants related to the adsorption capacity	$(L/mg)^{1/n}$ (mg/g)
K_L	Constant related to the free energy of the adsorption	L/mg
MW	Molecular weight	g/mol
n	Freundlich heterogeneity factor	-
q_e	Amount of adsorbate adsorbed at equilibrium	mg/g
q_m	Maximal adsorption capacity	mg/g
R^2	Correlation coefficient	-
R_L	Separation factor/Equilibrium parameter for Langmuir isotherm	-
T_a	Activation temperature	˚C
V	Volume of solution	L
w_o	Weight of the original carbon	g
w_1	Weight of activated carbon	g
w_c	Dry weight of final activated carbon	g
w_p	Dry weight of precursor	g
w_{H3PO4}	Weight of phosphoric acid in the solution	g
$w_{precursor}$	Weight of dried precursor	g
Y_1	Yield of activated carbon	%
Y_2	Adsorption capacity	mg/g
λ_{max}	Maximum wavelength	nm

LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
CI	Colour Index
DOE	Department of Environment
EAC	Extruded activated carbon
EDS	Energy Dispersive X-Ray Spectroscopy
FESEM	Field Emission Scanning Electron Microscope
GAC	Granular activated carbon
H_3PO_4	Phosphoric acid
H_2SO_4	Sulphuric acid
IUPAC	International Union of Pure and Applied Chemistry
KOH	Potassium hydroxide
NaOH	Sodium hydroxide
PAC	Powdered activated carbon
rpm	Rotation per minute
SEM	Scanning Electron Microscope
SME	Small medium enterprises
VAA	Volumetric Adsorption Analyzer
ZnCl	Zinc chloride

PENYEDIAAN KARBON TERAKTIF DARIPADA SISA CERUCUK KAYU BAKAU MELALUI PENGAKTIFAN KIMIA DENGAN ASID FOSFORIK UNTUK PENJERAPAN METILENA BIRU

ABSTRAK

Sisa cerucuk kayu bakau yang dianggap sebagai sisa buangan dari tapak pembinaan, digunakan sebagai prekursor lignoselulosa untuk menyediakan karbon teraktif yang mempunyai luas permukaan yang tinggi. Objektif utama kajian ini adalah untuk menyediakan karbon teraktif daripada sisa cerucuk kayu bakau melalui pengaktifan kimia dengan asid fosforik untuk penjerapan metilena biru. Kesan nisbah pengisitepuan asid fosforik ke pelopor dan suhu pengaktifan pada hasil karbon teraktif dan kapasiti penjerapan pada pewarna metilena biru disiasat. Hasil tertinggi sebanyak 44.73 % didapatkan bagi karbon teraktif yang disediakan bawah nisbah pengisitepuan 3 dan suhu pengaktifan 300 ˚C. Nisbah pengisitepuan 5 dan suhu pengaktifan 500˚C didapati berkesan untuk menyediakan karbon teraktif optimum dengan hasil sebanyak 39.13 % dan kapasiti penjerapan biru metilena maksimum sebanyak 298.94 mg/g. Luas permukaan BET, luas permukaan Langmuir dan isipadu mikroliang karbon teraktif optimum masing–masing adalah 1011.7998 m^2/g, 1443.2857 m^2/g dan 0.091286 cm^3/g. Data eksperimen penjerapan metilena biru oleh karbon teraktif optimum didapati berpandanan dengan isoterma Freundlich dengan nilai pekali kolerasi, R^2 sebanyak 0.9478, menunjukkan bahawa penjerapan metilena biru oleh karbon teraktif yang disediakan adalah jenis penjerapan pelbagai lapisan. Keputusan kajian penjerapan menunjukkan bahawa kaedah pengaktifan kimia dengan asid fosforik sesuai digunakan untuk menghasilkan struktur liang dalam karbon teraktif yang disediakan daripada sisa cerucuk kayu bakau untuk penjerapan metilena biru daripada larutan akuas.

PREPARATION OF ACTIVATED CARBON FROM MANGROVE PILE LEFTOVER VIA CHEMICAL ACTIVATION USING PHOSPORIC ACID FOR METHYLENE BLUE ADSORPTION

ABSTRACT

Mangrove pile leftovers which found as wastes at the construction sites were used as the lignocellulosic precursors to prepare activated carbon with high surface area. The main objective of this research was to prepare activated carbons from mangrove pile leftovers via chemical activation using phosphoric acid for the adsorption of methylene blue. The effects of impregnation ratio of phosphoric acid to precursor and activation temperature on the activated carbon yield and the adsorption capacity on methylene blue were investigated. Highest yield of 44.73% was obtained for the activated carbon prepared at impregnation ratio of 3 and activation temperature of 300 ˚C. An impregnation ratio of 5 and activation temperature of 500 ˚C were found to be effective to produce the optimal activated carbon with a yield of 39.13 % and a maximum adsorption capacity of 298.94 mg/g. BET surface area, Langmuir surface area and micropore volume of this activated carbon were 1011.7998 m^2/g, 1443.2857 m^2/g and 0.091286 cm^3/g respectively. Experimental data of methylene blue adsorption for the optimal activated carbon was found to fit well to Freundlich isotherm with correlation coefficient, R^2 of 0.9478, indicated that the adsorption of methylene blue on the activated carbon prepared was of multilayer adsorption. The results of adsorption study showed that chemical activation method using phosphoric acid was suitable for developing porous structure in the activated carbon prepared from mangrove pile leftover for the removal of methylene blue from aqueous solution.

CHAPTER ONE

INTRODUCTION

1.1 Mangrove

Mangroves, noticed as the distinctive trees that rise from a tangle of roots wriggling out of the mud (Futter, 2004), are generally confined to global tropical and subtropical regions, which is in between approximately 30 °N and 30 °S latitude (Ray and Shahraki, 2016). Growing along shores, coasts, rivers and estuaries in the tropics and subtropics, mangrove are remarkably tough and can live in water up to 100 times saltier that would normally uninhabitable for most other plant species (Futter, 2004). This is due to their desalinisation abilities that allow them to filter out the salt and extract the freshwater as the saltwater enters their roots (Vuuren, 2014). Tough root systems, special bark, unique leaf structures and other distinct adaptations are among few well known specific characteristics of mangrove trees.

In Malaysia, mangrove forests are found mainly along the west coast of Peninsular Malaysia, at the estuaries of Sarawak (1st Division), Rejang (6th Division) and Trusan-Lawas (5th Division) rivers of Sarawak and along the east coast of Sabah (Shukor, 2004). Mangrove forests in Peninsular Malaysia constitute about 17 % of the total mangrove forests in Malaysia of 580,000 ha and the rest are found in Eastern Malaysia, in which 58.6 % are found in Sabah and 24.4 % in Sarawak, as presented in Figure 1.1 (Kanniah et al., 2015).

As mangrove forests are very biological complex and highly productive ecosystems, they not only play vital roles essential to its surrounding habitats ecologically, but also serve as important resources for coastal communities. One of their most significant functions is to protect coastlines against erosive wave action and strong

coastal winds, at the same time act as the natural barrier against tsunamis and torrential storms, which is only realized their importance after the tsunami in 2004 (WWF-Malaysia, 2004).
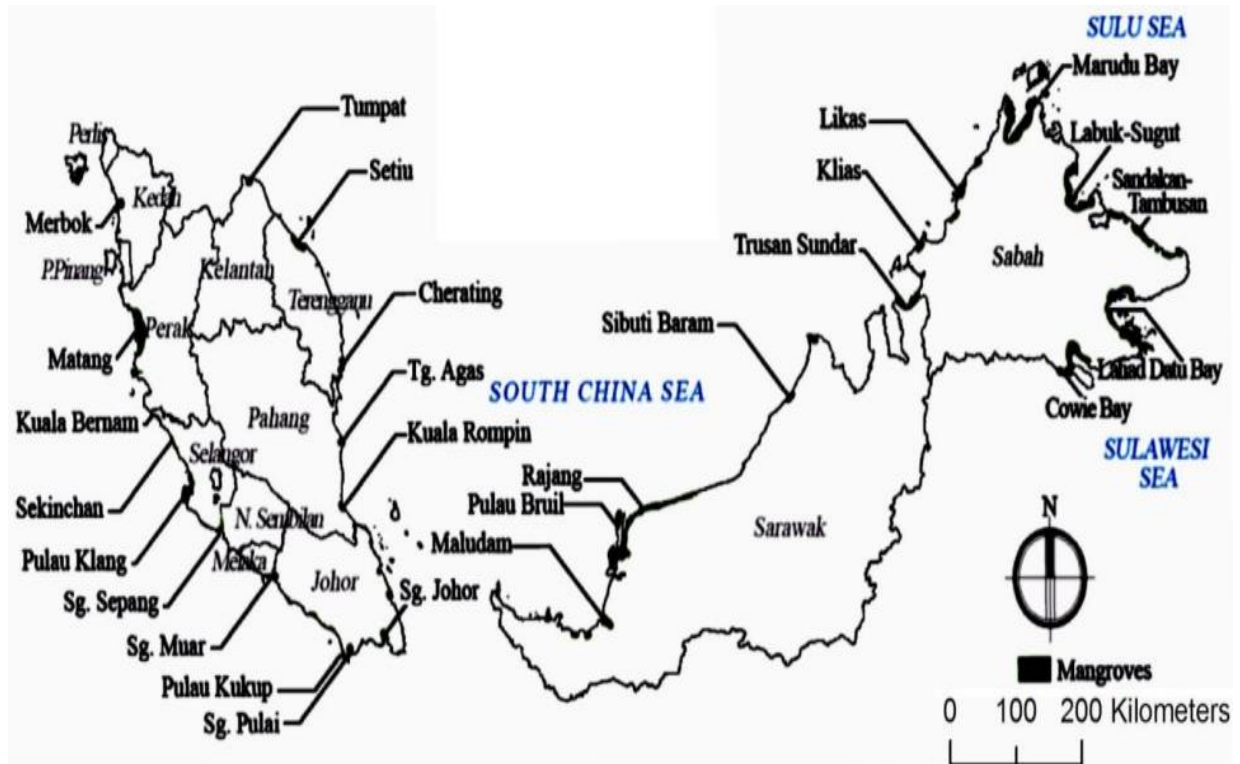
Figure 1.1 : Mangrove forests distribution in Malaysia (Upper left: 7˚22'46''N, 98˚55'48''E and Lower right: 0˚51'10''N, 119˚16'00''E) (Kanniah et al., 2015)

According to reference 2 in the reference list, mangroves are mainly used to produce charcoal in countries such as Thailand, Peninsular Malaysia, Sumatra (Indonesia), Myanmar and Southern Vietnam. Other possible uses of mangroves include agricultural implements, boat construction (knees and ribs), general heavy construction (rafters, beams and joists), marine and bridge construction (underwater, non-teredo infested waters or above water), fence posts, mining props as well as telegraph and transmission poles.

In Peninsular Malaysia, the features of strong wood strength, superb density and highly resistance to decaying and pests like shipworms enable mangroves to be more preferable to be used as piles for low-rise buildings and houses especially in wet sites than non-treated inland hardwoods. Additionally, mangrove piles with low cost and easier to be handled in most piling and construction work make them even more favoured by local contractors and developers. Moreover, buildings which constructed on mangrove piles as foundation can at least stand for a decade or more. The piles can be easily cleared off when the other type of foundation is to be applied. In Malaysia, Singapore and Hongkong, there is an established demand for mangrove piling poles used in land reclamation and the construction industry as reported in reference 2 in the reference list. Hence, the use of mangroves as piles for construction of low-rise buildings can be widely found in Malaysia.

Mangrove piles are essentially the tubular tree trunk with branches trim off. They are left untreated with the barks which are still attached on the trunks. Before piling work, one end of the mangrove trunk is cut into sharp cone shape for the ease of pile installation into the ground. Small part of the other end of the mangrove pile is cut and flatted in order to allow the use of drop hammer for piling work. The cut off parts of the mangrove piles are left as wastes which either destroyed by open burning or dumped to the disposal site after the construction done.

1.2 Activated carbon

Activated carbon is a porous solid material, consisting primarily of carbon which exhibit appreciable apparent surface area and micropore volume (Radovic, 2008). It is the porosity within the activated carbon which imparts their dominant

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characteristics of adsorption (Marsh and Rodriguez-Reinoso, 2006). With a wide range of pore size distributions, activated carbon can be prepared in various forms for instance powders, pellets, granules, fibers, cloths and others.

Owing to its favourable porosity, special structures and easy availability, activated carbon has widespread applications in various industries for several decades particularly in the effluent treatment for the removal of dyes, heavy metals and pollutants that are not easy to be biodegradable (Chen et al., 2013). In fact, activated carbon becomes the most popular adsorbent used for the removal of dyes from effluents (Kacan, 2016). Moreover, it has also been studied extensively for water and air purification, solvent recovery, metal extraction, energy storage and gas separation specifically due to its high adsorption capacity towards pollutants such as methylene blue, phenolic compound, metallic ions and some volatile organic compounds.

Raw material such as coal of high carbon content has been widely used to produce activated carbon for effluent treatment, however the use of this coal-based activated carbon is limited by its high cost due to expensive starting materials and generation with unjustified pollution control (Selvanathan et al., 2015). Considering the availability of activated carbon has much to do with the accessing resources, it is thus important to develop activated carbon with acceptable specifications using alternative raw materials.

Basically, any cheap raw material with a high carbon content and low inorganics can be used as the precursor to prepare activated carbon (Lu et al., 2016). In alternatives, non-conventional activated carbons which are cheaper and required less maintenance and supervision can be produced from other low cost raw materials or biomass wastes such as coconut shell, sawdust, bottom ash, fly ash, fruit peel, sewage sludge, char fines,

oil mill wastes, wood and so on for the adsorption process (El Shafei et al., 2016). So far, there are many attempts to produce activated carbon from biomass waste reported in the literatures due to the wide availability of the wastes.

1.3 Activated carbon preparation

Activated carbon can be prepared mainly through two processes, which are carbonization and activation. Carbonization of the raw material is first done at elevated temperature in the absence of oxygen to enrich the carbon content of the carbonaceous precursor by removing the volatile components and turning the precursor into char. Carbonization is then followed by activation process, in which activation functions to develop the porosity of the activated carbon in terms of surface area and pore volume.

Generally, there are two main types of activation methods have been used for the preparation of activated carbon, which are physical or thermal activation and chemical activation (Lu et al., 2016). The other type of activation method is physiochemical which combine both physical and chemical activation methods. Physical or thermal activation involves two steps, which is first, the carbonization of precursor at elevated temperature in the absence of oxygen or in the presence of suitable oxidizing gases such as carbon dioxide, steam, air or their mixtures followed by activation whereas for chemical activation, it includes both carbonization and activation in a single step with the use of a chemical agent such as potassium hydroxide, sodium hydroxide, phosphoric acid or zinc chloride (Lu et al., 2016).

According to Vargas et al. (2010), activation temperature (T_a) and impregnation ratio (IR) of activating agent to char are among the two most studied chemical activation parameters for the preparation of activated carbon. In most studies, one factor

is fixed at a certain level and varying another to determine the best condition. This procedure has disadvantages such as the lack of research on the interactive effects of the studied factors and the large number of experiments required, which consequently require more time with a higher cost and consumption of reagents (Vargas et al., 2010).

1.4 Research background

The rapid growing of batik industries in Malaysia that dominated by two states in the East Coast of Peninsular Malaysia, Kelantan and Terengganu, have provided a big and positive contribution to Malaysia's economic growth (Yaacob et al., 2015). However, high production of batik contribute to the release of large amount of effluents that rich in dyes, chemicals, heavy metals and organic pollutants during the wet processing process.

In Kelantan, batik is mostly produced by small medium enterprises (SME) and also by small scale industries which known as cottage industries that still involving the use of traditional methods and tools (Subki and Hashim, 2011). Notwithstanding with current expansion beyond traditional domain and modernization of batik industries, advancement in effluent treatment of the batik industries is still slow (Yaacob et al., 2015). Effluent that produced is mostly discharged directly into the adjoining water channels, streams and estuaries after minimal or without pretreatment, which eventually creates severe water pollution in Malaysia.

According to Kelantan Department of Environment (DOE), the batik industry in the Kelantan state has the lowest level of compliance with the department's law and regulations. Its director, Khairuddin Mohamad Idris revealed that between January and

September 2010, the batik industry in Kelantan only recorded a five per cent level of compliance compares to other manufacturing industries (Subki and Hashim, 2011).

For the past decades, several methods have been developed to remove dyes from effluents prior to discharge into the environment (Gecgel et al., 2012). Physical, chemical and biological treatments are among the three principal technologies for dye removal from effluents. There are several chemical methods can be applied such as coagulation or flocculation combined with flotation and filtration, precipitation-flocculation, electro-flotation, electro-kinetic coagulation, conventional oxidation methods by oxidizing agents, irradiation or electrochemical processes (Archna et al., 2012).

On the other hand, fungal decolourisation, microbial degradation, adsorption by microbial biomass, or bioremediation systems are some biological treatments that available and have been commonly applied to the treatment of industrial effluents (Archna et al., 2012). However, due to high investment and operational costs, chemical and biological methods often found to be limited. Physical methods for instance ion exchange and reverse osmosis are interesting methods because of their effective removal process of pollutants from industrial wastewater but both methods restricts the use in large scale industries due to their high capital and operational costs (Kandisa et al., 2016).

Among all the methods available, adsorption is recognised as the top quality and effective method for removal of dyes and pigments as well as other organic and inorganic pollutants found in the effluents according to Gecgel et al. (2012). Adsorption which follows surface phenomenon found to be more advantageous over the other available methods due to its lower capital, operation costs and simple design (Kandisa

et al., 2016). As activated carbon is an amorphous carbonaceous material with high porosity and extensive surface area, it is a well-known adsorbent among several adsorbents listed in the literature that has been used in the adsorption process (Lim et al., 2015). In fact, activated carbon adsorption is regarded as the better option for adsorption due to the large surface area and pore volume of activated carbon (Selvanathan et al., 2015). Unfortunately, its commercial applications had been limited due to the expensive cost of the raw precursor such as coal. For this reason, other materials are used as replacing precursors to produce activated carbon.

Waste biomasses with high carbon content and low inorganics have proved to be the promising precursors for the production of activated carbon due to their availability from a viewpoint of economy (Ioannidou and Zabaniotou, 2007; Lu et al., 2016). Of all the renewable sources of energy, biomass is unique in that solar energy is effectively stored and it is the only renewable source of carbon that can be converted into convenient solid, liquid and gaseous fuels (Demirbas, 2001). The energy and material production from biomass will thus result in a net reduction of greenhouse gas emissions and the replacement of a non-renewable energy source as reported by Lu et al. (2016).

In recent years, widely available, cheap and environmental friendly lignocellulosic biomass becomes the ideal raw material to produce activated carbon. This kind of biomass is characterized by a low ash and sulphur content, a high volatile matter yield and highly reactive fixed carbon content (Yorgun and Yıldız, 2015). In order to fill the gap of slow advancement in effluent treatment of the batik industries in Malaysia, especially in Kelantan state, it is crucial to draw attention and research interests on developing these cheap lignocellulosic biomasses into activated carbon for the treatment of liquid effluent from these batik industries.

In Malaysia, mangrove pile leftover with lignin cellulose structure is normally found to be as waste and has no commercial value at the construction sites. According to the case study by Conservation and Development of the Biosphere Reserve of Kien Giang, a typical mangrove tree may increase in dry biomass by greater than 5 times with every doubling of its trunk diameter of which about half is carbon. This indicates that mangrove pile actually has high carbon content.

Owing to this high carbon content feature, mangrove pile leftover from the construction sites can be utilised to produce valuable activated carbon for adsorption process instead of leaving as wastes with no economical applications. Therefore, in this research, mangrove pile leftover is to be used as the precursor to produce activated carbon. The high surface area porous activated carbon prepared using mangrove pile leftover will then be used for the treatment of dye, specifically methylene blue as it is the most important basic dye discovered by Caro in 1878 (Ahmad et al., 2011) that widely applied in most of the batik industries, via adsorption.

1.5 Problem statement

Recently, there are growing research interests on the production of activated carbon from low cost lignocellulosic materials to replace the expensive and non-renewable commercial precursors such as coal and lignite. In Malaysia, mangrove pile leftover with high carbon content was found as solid waste at construction sites. This leftover was simply been dumped to the landfill or eliminated via open burning by the contractors due to small amount. As mangrove pile leftover is one of the lignocellulosic material and also to reduce the disposal problem of this leftover, an attempt was hence

made to use this mangrove pile leftover as the precursor to produce activated carbon for adsorption of methylene blue.

Over the years, there were studies done on the production of activated carbon from mangrove wood for characterization and adsorption of iodine, from mangrove bark for the removal of direct red 23 and from propagule waste for the removal of lead as reported by Zulkarnain et al. (1993), Tan et al. (2010) and Astuti et al. (2017) respectively. However, there is no study reported in the literature on the preparation of activated carbon from mangrove pile for methylene blue adsorption. Thus, this research work was mainly conducted to synthesize and explore the potential use of high carbon-content mangrove pile leftover as activated carbon for the removal of methylene blue via adsorption.

For the preparation of activated carbon from mangrove pile leftover via chemical activation using phosphoric acid, parameters such as chemical impregnation ratio and activation temperature played vital roles in developing the porous structure of the activated carbon for adsorption process. Yield and adsorption capacity are some of the parameters that are critical for the estimation of the production and the performance of activated carbon. Adsorption study was hence done using methylene blue as the adsorbate to determine the performance of the activated carbon. Besides that, characterization study was done to have better investigation and understanding on the surface morphology, structures and contents of the activated carbon.

1.6 Research objectives

The objectives of this research are:

i.   To prepare activated carbon from mangrove pile leftover via single step chemical activation using phosphoric acid (H_3PO_4).

ii. To determine the effects of activation temperature (T_a) and impregnation ratio (IR) on the yield and adsorption capacity of activated carbon.

iii. To study the adsorption of methylene blue on the activated carbon prepared.

iv. To characterize the raw precursor and the optimal activated carbon.

1.7 Scope of study

In this work, activated carbon was prepared by using mangrove pile leftover as the precursor for the removal of methylene blue via adsorption. The preparation of mangrove wood based activated carbon was done by single step chemical activation using phosphoric acid.

T_a and IR were the two parameters being manipulated to observe the effects on the activated carbon yield and adsorption capacity. In this work, the range of T_a and IR used are 300 ˚C to 500 ˚C and 3 to 5 with intervals of 100 ˚C and 1 respectively. All the prepared activated carbons were then used in adsorption study on methylene blue.

The optimal activated carbon was characterized in terms of surface area, surface morphology, pore volume and elemental content. The characteristics of the raw precursor such as the element content, surface morphology, surface area and pore volume were also included for comparison purposes.

1.8 Thesis Organization

This thesis was organized into five chapters, in which this was the first chapter, presenting the introduction, research background and objectives of the project. In chapter two, review from literature were performed and discussed, for example the dye removal methods, preparation methods of activated carbon, parameters affecting the preparation of activated carbon, characterization and absorption of activated carbon as well as absorption isotherms. The materials and methods used throughout the development of this work were described in chapter three. In this section, detailed experimental procedures were presented. Chapter four reported on the results and discussion of the work whereas chapter five included the conclusions deduced from the present work and the recommendations for future work. At the last part, list of references used for this work and appendices that support the accomplished work were presented.

CHAPTER TWO

LITERATURE REVIEW

2.1 Dyes

Dyes by definition is a natural or synthetic coloured material that been used to add or change colour of something. Generally, dyes are derived from natural sources without any chemical treatment such as plants, insects, animals and minerals. Dyes derived from plant sources are indigo and saffron, insects are cochineal beetles and lac scale insects whereas animal sources are derived from some species of mollusks or shellfish, and minerals are ferrous sulphate and ochre (Kandisa et al., 2016). However, there are also synthetic dyes available in the market. Synthetic dyes usually have a complex aromatic molecular structure such as benzene, naphthalene, anthracene, toluene and xylene.

Residual dyes from different sources for examples textile industries, paper and pulp industries, dye and dye intermediates industries, pharmaceutical industries, tannery and craft bleaching industries are considered a wide variety of organic pollutants introduced into the natural water resources or wastewater treatment systems (Carmen and Daniela, 2012). In textile industry, it is estimated that 10 % to 15 % of the dye is lost during the dyeing process and released with the effluent (Tan et al., 2010). These pollutants are toxic, causing allergy, skin irritation and even carcinogenic, posing a serious hazard to living organisms. Therefore, it is necessary and crucial to treat them prior discharge to environment.

2.1.1 Types of dye

Commercially, there are more than 100,000 available dyes namely acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulphur dyes with a production of more than 105 metric tons per year (Wong et al., 2013). In particular, textile dyes are mainly classified in two ways based on its application characteristics like "Colour Index (CI) Generic Name" such as acid, basic, direct, disperse, mordant, reactive, sulphur dye, pigment, vat and azo insoluble as summarized in Table 2.1 and according to its chemical structure like "CI Constitution Number" such as nitro, azo, carotenoid, diphenylmethane, xanthene, acridine, quinoline, indamine, sulphur, amino- and hydroxy ketone, anthraquinone, indigoid, phthalocyanine, inorganic pigment and so on as tabulated in Table 2.2 (Carmen and Daniela, 2012). A "CI Generic Name" describes a commercial product by its recognised usage class, its hue and a serial number, which simply reflects the chronological order in which related colorant types have been registered with the Colour Index, for example (refer Table 2.1) CI Acid Unmetallised Azo 20, CI Basic Thiazole 5, CI Direct Stilbene 98, CI Solvent Methine 5 and so on.

Almost two-third of all organic dyes are azo dyes (R1-N=N-R2) used in a number of different industrial processes such as textile dyeing and printing, colour photography, finishing processing of leather, pharmaceutical and cosmetics excluding the colorant precursors such as azoic component, oxidation bases and sulphur dyes (Carmen and Daniela, 2012).

Table 2.1 : Distribution of each chemical class between major application ranges

(Carmen and Daniela, 2012)

Chemical class	Distribution between application range (%)								
	Acid	Basic	Direct	Disperse	Mordant	Pigment	Reactive	Solvent	Vat
Unmetallised azo	20	5	30	12	12	6	10	5	-
Metal complex	65	-	10	-	-	-	12	13	-
Thiazole	-	5	95	-	-	-	-	-	-
Stilbene	-	2	98	-	-	-	-	-	-
Anthraquinone	15	2	-	25	3	4	6	9	36
Indigold	2	-	-	-	-	17	-	-	81
Quinophthalene	30	20	-	40	-	-	10	-	-
Aminoketone	11	-	-	40	8	-	3	8	20
Phtalocyanine	14	4	8	-	4	9	43	15	3
Formazan	70	-	-	-	-	-	30	-	-
Methine	-	71	-	23	-	1	-	5	-
Nitro, nitroso	31	2	-	48	2	5	-	12	-
Triarylmethane	35	22	1	1	24	5	-	12	-
Xanthene	33	16	-	-	9	2	2	38	-
Acridine	-	92	-	4	-	-	-	4	-
Azine	39	39	-	-	-	3	-	19	-
Oxazine	-	22	17	2	40	9	10	-	-
Thiazine	-	55	-	-	10	-	-	10	25

When considering only the general structure, textile dyes are also grouped into anionic, nonionic and cationic dyes according to Carmen and Daniela (2012). Direct, acid and reactive dyes are the major anionic dyes in which the most problematic ones are the brightly coloured, water soluble reactive and acid dyes as they unable to be removed through conventional treatment systems. The major nonionic dyes are disperse dyes that does not ionised in the aqueous environment whereas the major cationic dyes

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are the azo basic, anthraquinone disperse and reactive dyes. The most hazardous dyes are those which are made from known carcinogens such as benzidine and other aromatic compounds for instance anthroquinone-based dyes that are resistant to degradation due to their fused aromatic ring structure (Carmen and Daniela, 2012). Table 2.3 presents the principle characteristics of some textile dyes.

Table 2.2 : Colour index classification of dye chemical constituents

(Carmen and Daniela, 2012)

Chemical class	C.I. Constitution Number	Chemical class	C.I. Constitution Number
Nitroso	10000-10299	Indamine	49400-49699
Nitro	10300-10099	Indophenol	49700-49999
Monoazo	11000-19999	Azine	50000-50999
Disazo	20000-29999	Oxazine	51000-51999
Triazo	30000-34999	Thiazine	52000-52999
Polyazo	35000-36999	Sulphur	53000-54999
Azoic	37000-39999	Lactone	55000-56999
Stilbene	40000-40799	Aminoketone	56000-56999
Carotenoid	40800-40999	Hydroxyketone	57000-57999
Diphethylmethane	41000-41999	Anthraquinone	58000-72999
Triarylmethane	42000-44999	Indigoid	73000-73999
Xanthene	45000-45999	Phthalocyanine	74000-74999
Acridine	46000-46999	Natural	75000-75999
Quinoline	47000-47999	Oxidation base	76000-76999
Methine	48000-48999	Inorganic pigment	77000-77999
Thiazole	49000-49399		

2.1.2 Methylene blue

Methylene blue is the most important basic dye, discovered by Caro in 1878, which appears as a dark green powder or crystalline solid (El Qada et al., 2006). By definition, basic dyes are cationic dyes with cationic properties originating from positively charged nitrogen or sulphur atoms. Hence, methylene blue is also a cationic dye. The charge is generally delocalized throughout the chromophoric system, although it is probably more localized on the nitrogen atoms. In fact, basic dyes are so named because of their affinity to basic textile materials with net negative charge.

Table 2.3 : Principle characteristics of different textile dyes (Carmen and Daniela, 2012)

Types of textile dye	C.I. Constitution numbers	Molecular weight, MW (g/mol)	Maximum wavelength, λ_{max} (nm)	Characteristics of dye
Reactive Orange 16	18097	617.54	495	Anionic monoazo reactive dye
Brilliant Red HE-3B	25810	530	530	Anionic, bifunctional azo reactive dye
Crystal Violet	42555	407.99	590	Cationic triphenylmethane dye
Rhodamine B	45170	479.2	550	Cationic, Xantenic dye
Methylene Blue	52015	319.85	660	Cationic, phenothiazine dye

Methylene blue widely used as a stain and has a number of biological uses. It dissociates in aqueous solution like electrolytes into methylene blue cation and chloride ion. The coloured cation is adsorbed by several adsorbents preferentially to a very great extent according to El Qada et al. (2006). For that reason, methylene blue was selected to be the adsorbate in this research. Moreover, it is of utmost importance to be removed from the effluent of batik industries as it causes various harmful effects on the human beings. By nature, it can cause eye burns in humans and animals, irritation to the skin, and if ingested, irritation to the gastrointestinal tract, nausea, vomiting and diarrhea (Senthilkumaar et al., 2005). In addition, the extent of adsorption of methylene blue from an aqueous solution is a convenient indicator in the evaluation of active carbons (Barton, 1987).

2.1.3 Methods of dye removal

There are basically three separation techniques that been used in dye removal, which are physical, chemical and biological methods. Table 2.4 summarizes the advantages and limitations of different dye removal technologies.

Among all the techniques, adsorption is proven as the most effective physical treatment method for the removal of dissolved organic pollutants like dyes from industrial effluent (Kandisa et al., 2016). This process consists in the transfer of soluble organic dyes as the solutes from effluent to the surface of highly porous solid particles, the adsorbent.

Table 2.4 : Advantages and limitations of different dye removal technologies

(Kharub, 2012)

Method	Technology	Advantages	Limitations
Physical	Adsorption on activated carbons	The most effective adsorbent, great, capacity, produce a high-quality treated effluent.	Ineffective against disperse and vat dyes, the regeneration is expensive and results in loss of the adsorbent, non-destructive process.
	Membrane separations	Removes all dye types, produce a high-quality treated effluent.	High pressures, expensive, incapable of treating large volumes.
Chemical	Oxidation	Rapid and efficient process.	High energy cost, chemicals required.
	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes.	Economically unfeasible, formation of by-products, technical constraints.
	Ion-exchange	No loss of sorbent on regeneration, effective.	Economic constraints, not effective for disperse dyes.
	Coagulation/ Flocculation	Simple, economically feasible.	High sludge production, handling and disposal problems.
Biological	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on micro-organisms.	Slow process, performance depends on some external factors (pH and salts).
	Selective bioadsorbents	Economically attractive, regeneration is not necessary, high selectivity.	Requires chemical modification, non-destructive process.
	Biodegradation	Economically attractive publicly acceptable treatment.	Slow process, necessary to create an optimal favourable environment, maintenance and nutrition requirements.

Activated carbon is the most used adsorbent due to bearing high surface area, well-developed internal pore structure and surface chemical functional groups located at the outer and inner surfaces. Apart from activated carbon, some commercial low-cost adsorbents from industrial or agricultural wastes such as peat, coal ashes, refused derived coal fuel, clay, bentonite and modified bentonite, red soil, bauxite, rice husk, tree barks, neem leaf powder, wood chips, ground nut shell powder, rice hulls, bagasse pith, wood sawdust, grounded sunflower seed shells, other ligno-cellulosic wastes are also used for removal of dye and organic coloured matter from textile effluents (Carmen and Daniela, 2012).

Referring to Carmen and Daniela (2012), using activated carbon as the adsorbent, high removal rates of about 60 % - 90 % are obtained for cationic mordant and acid dyes and a slightly lesser extent for dispersed, direct, vat, pigment and reactive dyes with consumable doses of 0.5-1.0 kg adsorbent/m^3 wastewater.

2.2 Activated carbon

Activated carbon is a water industrial standard adsorbent with highly developed porosity, specific surface area of more than 400 m^2/g, surface functional groups especially oxygen groups and relatively high mechanical strength (Acikyildiz et al., 2014). The internal porosity and its related properties such as surface area, pore volume, pore size distribution and the presence of functional groups on pore surfaces play the significant role in the adsorptive capacities of activated carbon (Kumar and Jena, 2016).

In fact, activated carbon can remove soluble and insoluble organic pollutants with the removal capacity up to 99.9% through adsorption as reported by Imran et al. (2012). Activated carbon adsorption has been used for the removal of a variety of

pollutants, for instances dyes (Senthil Kumar et al., 2010; Wong et al., 2013), toxic heavy metal ions such as mercury, lead, cadmium, nickel and copper (Kadirvelu et al., 2001; Astuti et al., 2017) as well as phenol (Altenor et al., 2009) from various contaminated water sources.

As environmental pollution particularly water pollution is becoming a more serious problem, the need for activated carbon is growing due to the fact that adsorption is considered as the best effluent treatment method for its universal nature, inexpensiveness and ease of operation. However, production and regeneration of commercial activated carbons are still expensive and there are many continuing researches for potential materials and methods to manufacture activated carbon by using low-cost raw materials and methods (Acikyildiz et al., 2014). Hence, it has drawn the attention to search for suitable alternative raw materials which are economically attractive to produce activated carbon and at the same time present similar or even better characteristics and performances than that of the conventional ones.

2.2.1 Selection of activated carbon precursor

There are few factors need to be considered when selecting the precursor for the development of low cost activated carbon. The precursor should be freely available, inexpensive, non-hazardous in nature and consists of high carbon or oxygen contents (Imran et al., 2012). Apart from those, high thermal stability, high abrasion resistance and small pore diameters are the other preferable characteristics which can result in higher exposed surface area of activated carbon and hence high surface capacity for adsorption.

2.2.2 Types of activated carbon precursors

The precursor for activated carbon can be categorized into two main groups based on the nature of origin, which are inorganic and organic. Organic precursors include plant, animal and other materials with high carbon content. Meanwhile, the inorganic precursors include soil, clay, mud, zeolites, ore materials, metal oxides and hydroxides (Imran et al., 2012). Fruit waste, rice husks, bark, seaweed, algae, peat moss, hair and keratin are some examples of organic precursors. Other than that, petroleum and fertilizer products are also considered as industrial organic products. Some of the waste products used in producing low cost activated carbon either organic or inorganic are tabulated in Table 2.5.

Table 2.5 : Waste products used for generating low cost activated carbons

(Imran et al., 2012)

Class	Classification	Example
A	House hold wastes	Fruit waste, coconut shell, scrap tyres
B	Agricultural products	Bark and other tannin-rich materials, saw dust and other wood type materials, rice husk, other agricultural waste
C	Industrial waste	Petroleum wastes, fertilizer wastes, fly ash, sugar industry wastes, blast furnace slag
D	Sea materials	Chitosan and seafood processing wastes, sea weed and algae, peat moss, miscellaneous waste
E	Soil and ore materials	Clays, red mud, zeolites, sediment and soil, ore minerals
F	Metal oxides and hydroxides	-

2.2.3 Types of activated carbon

Activated carbon is primarily present in three forms or shapes, which are powdered, granular and extruded. Each form is available in variety of sizes depends on the specifications and requirements of industry applications.

2.2.3 (a) Powdered activated carbon (PAC)

Powdered activated carbons usually have an average diameter of 15 μm to 25 μm with the size less than 100 μm. Generally, they are applied in liquid phase adsorption. Powdered activated carbons are added into the liquid to be treated and mixed with the liquid, which are then been removed by sedimentation or filtration after the adsorption. Their flexibility in operation enables their dosage to be altered easily as the process conditions change. They have comparatively lower processing costs.

2.2.3 (b) Granular activated carbon (GAC)

Granular activated carbons with the size range of 0.2 mm to 5 mm are irregular shaped particles formed from milling and sieving. They are longer lasting and harder compared to powdered activated carbon. As they can purify large volumes of gas or liquids of a consistent quality and be reactivated and reused for many times, they are used widely in both liquid and gas phase applications and in both fixed and moving systems. Practically, granular activated carbons have the advantage of having sufficient flow with an acceptable pressure drop through the carbon bed in gas phase applications.

2.2.3 (c) Extruded activated carbon (EAC)

Extruded activated carbons as the cylindrical pellets have diameter ranging from 1 mm to 5 mm. High volume activity, low pressure drop and high stock resistance of extruded activated carbons make them to be favourable in solvent recovery, automotive emission control and gas purification fields. Type of raw material and the extrusion process are the two factors that ensure the end product is hard and applicable for heavy duty applications.

2.3 Preparation of activated carbon

Activated carbon can be prepared by three different methods, which are physical, chemical and physicochemical activations to develop optimum pore-size distributions that meet the broad range of industrial requirements. The differences between them lie mainly in the preparation procedures and the activating agents used. Physical activation is a two-stage process with carbonization process precedes the activation process whereas chemical activation is a much simpler process as the carbonization and activation processes occur simultaneously in a single stage. Meanwhile, physicochemical activation is the combinations of both physical and chemical activations. Among these methods, chemical activation is a widely used method to produce activated carbon from carbon-containing materials (Yorgun and Yıldız, 2015).

2.3.1 Physical activation

Physical activation for the preparation of activated carbon comprises of two steps which are carbonization of the precursor in an inert atmosphere followed by