REMOVAL OF METHYLENE BLUE IN TEXTILE INDUSTRY USING ACTIVATED CARBON FROM MANGROVE PILE LEFTOVER VIA CHEMICAL ACTIVATION

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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
k_1	Rate constant of Pseudo-first order kinetic model	$minutes^{-1}$
k2	Rate constant of Pseudo-second order kinetic model	g/minutes$^{\cdot}$ mg
MW	Molecular weight	g/mol
n	Freundlich heterogeneity factor	-
q_e	Amount of adsorbate adsorbed at equilibrium	mg/g
q_t	Amount of adsorbate adsorbed at time, t	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	Weight of adsorbent	g
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
$W_{precusor}$	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

AC	Activated carbon
BET	Brunauer-Emmett-Teller
C	Carbon
Cl	Chloride
CO_2	Carbon dioxide gas
EAC	Extruded activated carbon
EDS	Energy Dispersive X-Ray Spectroscopy
Fe^{2+}	Iron(II) Ion
$Fe(II)/Ca(OH)_2$	Iron (II)/Calcium hydroxide
GAC	Granular activated carbon
H	Hydrogen
H_3PO_4	Phosphoric acid
H_2SO_4	Sulphuric acid
IUPAC	International Union of Pure and Applied Chemistry
KOH	Potassium hydroxide
MATRADE	Malaysia External Trade Development Corporation
N	Nitrogen
NaOH	Sodium hydroxide
O	Oxygen
PAC	Powdered activated carbon
PFEs	Permanent Forest Estates
rpm	Rotation per minute
S	Sulphur

SEM	Scanning Electron Microscope
VAA	Volumetric Adsorption Analyzer
$ZnCl_2$	Zinc chloride
ZnO	Zinc oxide

Penyingkiran Metilena Biru dalam Industri Tekstil dengan Carbon Teraktif Daripada Sisa Cerucuk Kayu Bakau Melalui Pengaktifan Kimia

ABSTRAK

Dalam kajian ini, sisa cerucuk kayu bakau yang kebiasaannya ditinggalkan sebagai sisa sektor pembinaan telah digunakan sebagai prekursor mentah untuk menyediakan karbon teraktif bagi penjerapan metilena biru yang kebiasaannya dijumpai di industri tekstil. Objektif utama kajian ini adalah untuk menyediakan karbon teraktif daripada sisa cerucuk kayu bakau melalui pengaktifan kimia dengan asid fosforik. Kesan pelbagai faktor terhadap hasil karbon teraktif dan kapasiti penjerapan pada pewarna metilena biru terutamanya faktor nisbah pengisitepuan asid fosforik ke pelopor dan suhu pengaktifan telah dikaji. Hasil tertinggi diperolehi bagi karbon teraktif yang disediakan bawah nisbah pengisitepuan 2 dan suhu pengaktifan 400 °C dengan peratusan 34.83 %. Nisbah pengisitepuan 2 dan suhu pengaktifan 600 °C merupakan keadaan penyediaan karbon teraktif yang optimum dengan kapasiti penjerapan biru metilena maksimum sebanyak 388.88 mg/g. Penjerapan metilena biru oleh karbon teraktif optimum yang disediakan adalah jenis penjerapan pelbagai lapis kerana ia didapati berpandanan dengan isotherma Freundlich atas nilai R^2 0.9601. Dari perspektif lain, data eksperimen penjerapan metilena biru oleh karbon teraktif optimum didapati berpandanan dengan model Pseudo-second order dengan R^2 0.9592. Luas permukaan BET, luas permukaan Langmuir dan isipadu keseluruhan karbon teraktif optimum masing–masing ialah 802.3744 m^2/g, 1186.3197 m^2/g dan 0.412336 cm^3/g. Selepas pengaktifan dengan asid, kandungan karbon dalam karbon teraktif didapati meningkat daripada 59.91 ke 84.68 wt % atas pembebasan bahan meruap yang lebih banyak.

Removal of Methylene Blue in Textile Industry Using Activated Carbon from Mangrove Pile Leftover via Chemical Activation

ABSTRACT

In this research, mangrove pile leftovers which were mainly dumped as construction waste were used as the raw precursors to prepare activated carbon for methylene blue removal which could be found mainly in textile industries. The main objective of this research was to prepare activated carbons from mangrove pile leftovers via chemical activation using phosphoric acid. The effects of different factors such as impregnation ratio of phosphoric acid to precursor as well as activation temperature on the yield of activated carbon and the adsorption capacity on methylene blue were studied. Highest yield of activated carbon was obtained for preparation condition of IR of 2 and T_a of 400 °C, with yield of 34.83 %. An impregnation ratio of 2 and activation temperature of 600 °C were found to be the optimum condition for activated carbon preparation since maximum adsorption capacity of 388.88 mg/g was observed. The adsorption of methylene blue on the activated carbon prepared was found to be multilayer adsorption since it fit well to Freundlich isotherm with R^2 of 0.9601. From perspective of kinetic study, the experimental data of adsorption of methylene blue on optimal activated carbon was fit well to Pseudo-second order model with R^2 of 0.9592. BET surface area, Langmuir surface area and total pore volume of the optimally prepared activated carbon were 802.3744 m^2/g, 1186.3197 m^2/g and 0.412336 cm^3/g respectively. After the activation process, the carbon content of activated carbon was found to be increased from 59.91 to 84.68 wt% since more volatile materials were released.

CHAPTER 1

INTRODUCTION

1.1 Mangrove

Mangroves are defined as distinctive plants which grow at the interface between land and sea in tropical and sub-tropical latitudes, with location of approximately 30 ˚N and 30 ˚S latitude (Ray and Shahraki, 2016). They could take up water despite of strong osmotic potentials. Because of the harsh growing culture, mangroves normally have the ability to tolerate with high salinity environment since they are managed to filter out the salt and extract the freshwater when the saltwater enters their roots (Vuuren, 2014).

Mangrove forests are among the most productive coastal ecosystems in the world as they give high contribution in enriching of coastal waters, yielding for commercial forest products, protecting coastlines as well as supporting coastal fisheries (Kathiresan and Bingham, 2001). From other perspective, mangroves create unique ecological environments that host rich assemblages of species (Ray and Shahraki, 2016). Their coverage of coastal shorelines and wetlands provides a unique and irreplaceable habitat for many diverse species especially birds, mammals, crustacean, and fish. Undeniably, mangroves forests are extremely productive ecosystems that bring numerous advantages for both of the marine environment and human security.

Malaysia has 645 852 hectare (Azahar et al., 2003) or 2 % of its total land area that rank third after Indonesia and Australia (Kathiresan and Rajendran, 2005). The mangrove forests in Malaysia, occur 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). Out of the total mangrove areas in Malaysia, Sabah covers 58.6 %, followed by Sarawak with 24.4 % coverage and Peninsular Malaysia constitutes about 17 % (Kanniah et al., 2015).

In Peninsular Malaysia, mangrove forests account for about 106,554 ha of land. Of this total, about 88,667 hectare (83.2 %) is gazetted as PFEs while the remaining 17,867 hectare (16.85 %) is state-land mangroves. Among the states, Perak occupied the largest area (47.8 %), followed by Johor (20.6 %), Selangor (17.3 %) and Kedah (9.2 %) (Kanniah et al., 2015; Shukor, 2004).

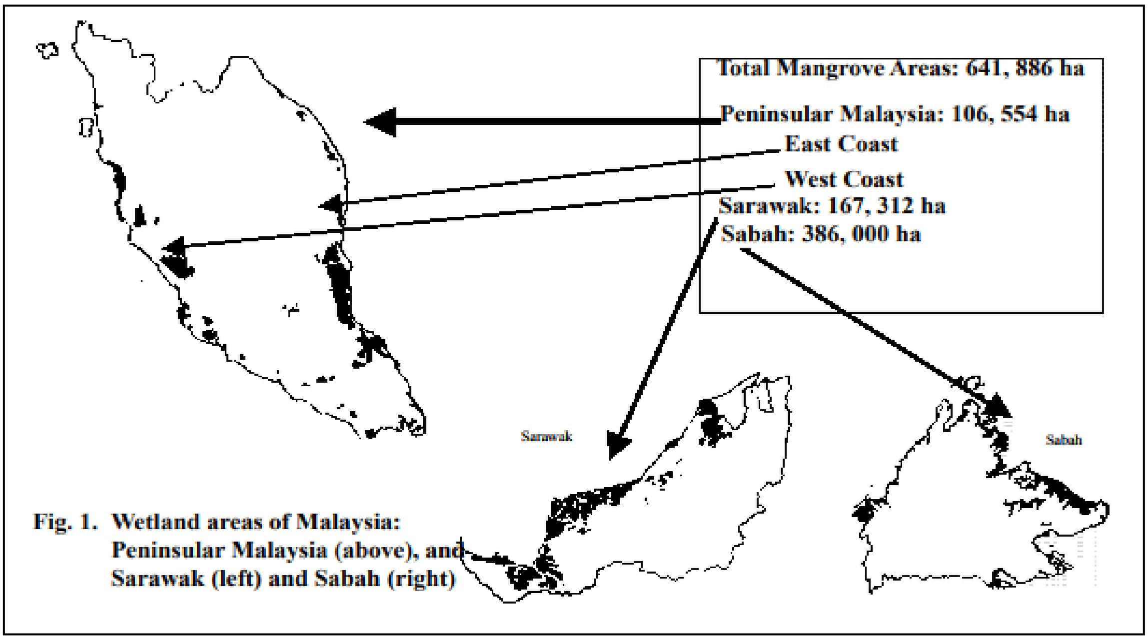

Figure 1.1 Wetland areas in Malaysia (Shukor, 2004)

The uses of mangroves can be divided into two categories, which are the use of the mangrove ecosystem as a whole or its conversion to other uses, and the use of products from the mangrove ecosystem. In Malaysia, mangroves are commonly used as wood for charcoal, poles, firewood and also in the field of building construction. Mangrove forests have been proven to be the most potential economic booster in the country in terms of economic value per hectare per annum of timber. For instance, mangroves trunks are preferable to be used as piles for low-rise buildings and houses due to the mangrove woods' nature density, high strength and also long lasting properties. Also, mangrove piles with lower cost and easier in handling steps in most piling and construction work make them even more preferred by local contractors. Mangrove timber is a dominant source of wood-chips for the manufacture of rayon especially in the states of Sabah and Sarawak (Shukor, 2004).

According to the Ministry of Housing and Local Government of Malaysia, in 2007, construction industry generated 26,459 tones of construction waste in Malaysia, contributed to the highest percentage of solid waste which is 37 % (Zuhairi et al., 2016). One of the major contributors of construction waste is from mangrove piling. In mangrove piling, the unused 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. These may contributed to unpleasant environmental issues such as emission of greenhouse gases, global warming and increment of garbage production.

1.2 Activated Carbon

Adsorption is one of the most important percolations processes used in industry for the purification and separation of solutes from a fluid stream onto a surface (Perry, 2003). Activated carbon is the best known general purpose adsorption medium where the system utilizing activated carbon requires little space than many competitive processes and is impervious to toxic wastes.

Activated carbon (AC) is a tasteless, solid, microcrystalline and non-graphitic form of black carbonaceous material with a porous structure (Smisek and Cerney, 1970; Budavari, 1996). It has been identified as a unique and versatile adsorbent due to its extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity (Williams and Reed, 2006; Bansal et al., 1988). No doubt, activated carbon can be prepared in various forms such as powders, pellets, granules, fibers, cloths and others due to its wide range of pore size distributions.

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, and non-hazardous in nature with high carbon or oxygen contents. The precursor for activated carbon can be categorized into two main groups based on the nature of origin, namely 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.

Previously, petroleum residues, natural coal and woods were the main activated carbon precursors. However, since a few years ago, other raw precursors which are lower in cost and easy in accessibility were used to replace the expensive materials. For example, apricot stones (Youssef et al., 2004), barks of palm tree, guava seeds, almond barks and shell of coffee seeds (Baquero et al., 2003) were used as activated carbon precursors. These materials are often considered as wastes, and consequently constitute to environmental problem. The reuse of those solid wastes could be important for the regional economy, because high value products are obtained from low cost materials, and simultaneously brings, solutions to the problem of wastes (Altenora et al., 2009).

1.3 Activated Carbon Preparation

Basically, activated carbon can be prepared through two processes, which are carbonization and activation. Carbonization of the raw material is the step in which raw precursor is heat at elevated temperature in the absence of oxygen to enrich the carbon content of the carbonaceous precursor. This is done by removing the volatile components inside precursor at the mean time turning the precursor into char. On contrary, activation process functions to develop the porosity of the activated carbon in terms of surface area and pore volume.

In principle, the methods for preparing an activated carbon can be divided into two categories: physical or thermal activation and chemical activation (Lu et al., 2016). Physical activation is a two step process that starts with the carbonization of the materials followed by the activation of the resulting char in inert (N_2) or oxidizing atmosphere (CO_2 or O_2) at the elevated temperature range of 600 ℃ to 1000 ℃. Hence, physical activation involves 2 steps, which are carbonization step and activation step.

In chemical activation, a raw material is impregnated with an activating reagent, and the impregnated material is heat-treated under an inert atmosphere. The carbonization step and the activation step simultaneously progress in chemical activation. This method occurs at lower temperature than that of the physical methods. Therefore, it improves the pore development in the carbon structure. The type of chemical agent is selected as a function of the characteristics of the desired activated carbon. It involves the impregnation of materials with dehydrating chemicals such as KOH, $ZnCl_2$, H_3PO_4, and ZnO prior to carbonization at a desired temperature. KOH produces only widening of the microporosity to more heterogeneous micropores, $ZnCl_2$ develops both wide micropores and low mesopores whereas H_3PO_4 produces large mesopores and even macropores (Molina and Rodriguez, 2004).

1.4 Research Background

The discharge of dyes in the environment is worrying for both toxicological and esthetical reasons as dyes impede light penetration, damage the quality of the receiving streams and are toxic to food chain organisms (Padmesh et al., 2006). Various treatment processes such as chemical oxidation, biological treatment, coagulation–flocculation and membrane processes have been proven to be effective in reducing dye concentrations in textile effluent (Juang et al., 1996; Baclioglu and Arslan, 2001). However, these treatment processes are expensive to be applied and often fail to treat the wide range of dyes in wastewaters. Throughout the year, the use of activated carbons prepared from biomass or waste has been widely favored especially in dye industry due to their high adsorption capacities and amphoteric properties which enable the adsorption of both cationic and anionic dyes (Corapcioglu and Huang, 1987; Al-degs et al., 2000).

Malaysia is one of the countries in the world that is well known for its arts and crafts. In Malaysia, textile industry which is more commonly known as Batik Industry, utilizes dyes or colour pigments to increase the economic value of their final products. Batik, having been a cottage industry in Malaysia for centuries, had its profile elevated to a global stage. The batik manufacturing is part of the wider textile industry in Malaysia, with exports projected to grow 5.8 %, from RM 13.4 billion in 2010 to RM 24 billion in 2020 (Nair, 2014).

There are more than 320 batik entrepreneurs registered with Malaysian Handicraft, dominated by two states in the East Coast of Peninsular Malaysia, which are Kelantan and Terengganu (Nordin and Bakar, 2012). It is an industry that is synonymous with the people in East Cost Malaysia. They have provided a big and positive contribution to Malaysia's economic growth. The rapid growing of batik industries in Malaysia that 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. High demand and supply for batik products will contribute to the production of more effluent with high COD value and creating it as one of the main sources of severe pollution in Malaysia (Mohd Rafi et al., 2015).

Textile industry is one of the fastest growing industries and significantly contributes to the economic growth in Malaysia. However, this industry also has high water consumption and subsequently produces high discharge rate of wastewater with high load of contaminants. The release of dyes into the environment during textile fiber dyeing and finishing processes is a main source of water pollution (Yean L. Pang and Abdullah, 2013). For instance, methylene blue which is categorized as cationic dye is the most commonly used substance for colouring among all other dyes of its category. Dyes are normally inert and difficult to biodegrade when discharged into wastewater stream due to their synthetic origin and complex aromatic molecular structures (Ho et al., 2005).

From the environmental point of view, the removal of synthetic dyes is of great concern, since some dyes and their degradation products may be carcinogens and toxic. As consequence, their treatment cannot depend on biodegradation alone (Reife, 1993; Pagga and Braun, 1986). Methylene blue might not be considered as strongly hazardous, but somehow it could bring some harmful effects especially to human being and aquatic life (Vadivelan and Kumar, 2005). Acute exposure to methylene blue can eye burns, and if swallowed, it causes irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea. If inhaled, it may also cause methemoglobinemia, cyanosis, convulsions and dyspnea (Senthilkumaar et al., 2005). Definitely, the removal of such dye from process effluent becomes environmentally important.

Membrane technologies, adsorption, oxidation technique, electrolytic precipitation and foam fractionation, electrochemical processes, ion exchange method, photo catalytic degradation, thermal evaporation are methods used to treat textile effluent (Silvana et al., 2014). However, adsorption is common method used for dye removal effluent due to its ease of operation, lower operating and capital cost with higher efficiency (Damar et al., 2012). It is a phantasm in which molecules of any state (gas or liquid) attached and adsorbed to the surface of adsorbent by either intermolecular bonding or chemical bonding with no reaction. Activated carbon is a big potential for the treatment and used as an adsorbent. 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 (Sulaiman et al., 2015).

In Malaysia, mangrove pile leftover with lignin cellulose structure is normally found to be disposed as waste since it has no commercial value especially in construction site. With high carbon content feature, mangrove pile leftover from the construction sites could be utilized in proper way to produce valuable activated carbon for adsorption process. Hence, in this research, mangrove pile leftover is used as the raw precursor to produce high surface area activated carbon which is then applied for dye removal especially for methylene blue which is normally found in Batik Industry.

1.5 Problem Statement

In Malaysia, mangrove pile leftover was disposed as solid waste especially at construction sites. This leftover was either simply being dumped to the landfill or eliminated via open burning. Actually, mangrove timber leftover from construction site can be recycled and reused in producing charcoal. However, most of the contractors and developers will directly dispose the waste due to its low market value because they are only presented in small quantity.

As mangrove pile leftover is one of the lignocellulosic materials with high carbon content, mangrove pile leftover could be utilized in proper manner for instance as raw precursor to produce activated carbon for adsorption of methylene blue. This approach tends to overcome the disposal problem of mangrove pile leftover. Moreover, it does contribute to the reduction of water pollution issue in textile dyeing industries in Malaysia. According to Malaysia External Trade Development Corporation (MATRADE), textiles are ranked 9th and occupied 2.3 % out of total Malaysia's exportation. The Batik Industry in Malaysia is estimated grew and subsequently contributed to enhancement of the economics of Malaysia due to the high demand of Batik in United State, Japan, Turkey and China.

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 do play dominant roles in developing the porous structure of the activated carbon for adsorption purposes. Yield and adsorption capacity are some of the parameters that are critical for the estimation of the production and the performance of activated carbon. To determine the performance of the activated carbon, adsorption study was hence done using methylene blue as the adsorbate. Besides, 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 research, mangrove pile leftover was used as raw precursor to prepared activated carbon was prepared to remove methylene blue found in textile industries via adsorption. The preparation of mangrove wood based activated carbon was done by single step chemical activation using phosphoric acid.

Two parameters being manipulated throughout the study were activation temperature, T_a and also impregnation ratio, IR. These parameters were manipulated to observe the effects on the activated carbon yield and adsorption capacity. In this research, the range of T_a and IR used were 400 to 600 °C and 2 to 4 with intervals of 100 °C and 1 respectively. All prepared activated carbons were then used in adsorption study on methylene blue. The optimal activated carbon was then figured out and characterized in terms of surface area, surface morphology, pore volume and elemental content. The characteristics studies of the raw precursor such as the element content, surface morphology, surface area and pore volume were also did for comparison purposes.

1.8 Thesis Organization

This thesis was being divided into five chapters. In chapter one, there will be introduction, research background, problem statement as well as the research objectives of the final year project (FYP). In chapter two, literature reviews about the research title were performed and discussed. For instance, the method of dye removal, preparation methods of activated carbon, parameters affecting the performance of activated carbon, characterization and absorption of activated carbon as well as absorption isotherms and adsorption kinetic were being discussed in detail in this chapter. On contrary, the materials and methods utilized throughout the development of this study were described in chapter three. In this section, detailed experimental procedures were presented in proper way whereas chapter four reported on the results and discussion of the work. Apart from that, chapter five discussed the conclusions deduced from the present work as well as the recommendations for future work. Last but not least, list of references used for this research and appendices that support the accomplished work were attached.

CHAPTER 2

LITERATURE REVIEW

2.1 Dyes

Dye is a substance used to impart colour to textiles, paper, leather, and other materials in a way such that the colouring is not readily and easily altered by washing, heat, light, or other factors. (Edward and Stothers, 2015) Fastness, colour, low cost, and uniformity are essential qualities of dye. Dye must also be soluble in water, attractive to the textile substrate, and reactive with the textile fibers. The colour of a dye depends on its chemical bonds, for instance its pi bonds, multiple bonds as well as unsaturated groups (Hudders, 2014).

Dyes are widely used by textile industries in order to colour their products to become more commercialized and attractive. Textile industry use dyes and pigments to colour their products. According to the World Bank, 17 % to 20 % of textile industry water pollution comes from dyeing and finishing treatments that apply to the fabric (Holkar et al., 2016; Rani et al., 2013). There are more than 100 000 commercially available dyes with over 700 000 tones of dyestuff are produced annually (Alau, 2010). One of the major problems concerning textile wastewaters is coloured effluent (Ramakrishna and Viraraghavan, 1997). This wastewater contains a variety of organic compounds and toxic substances, which are harmful to fish and other aquatic organisms.

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 quite toxic, they may bring to diseases such as allergy, skin irritation and even carcinogenic. These pose a serious hazard to living organisms especially human being and aquatic life. Obviously, it is necessary and crucial to treat these dye effluent prior discharging them to environment.

2.1.1 Types of Dyes

Dyes can be natural or synthetic; they are classified based on the nature of their respective chromophores, the source of materials, and also the method of application of dyes. Each class of dye own an unique chemistry, structure and particular way of bonding (Zemanta, 2011). Their interaction with substrate depends on the nature of the substrate (Hudders, 2014).

Chromophores basically comprise of a group of atoms which gives distinct colour to the dye whereas the colour enhancer named auxochromes is achieved by the electron substitution, either by removing or donating electrons (Christie, 2001). Chromophores contain of functional groups such as $-N{=}N-$, $-C{=}O$, $-NO_2$, and $O{=}(C_6H_4){=}O$) whereas the functional groups are presented in auxochromes such as $-NH_3$, $-COOH$, $-OH$, and $-SO_3H$ (Srinivasan and Viraraghavan, 2010). Dyes are also categorized on the basis of the reactive groups that are in association with OH and -SH groups through the covalent bond formation. Different auxochromes are then classified into different categories of reactants, which could be acid or base, astringic or disperse, pigmented, vat, anionic or in grain form, as well as dissolved or un-dissolved form (Welham, 2000).

Classification of dyes based on the sources which they made of is as shown in Figure 2.1.

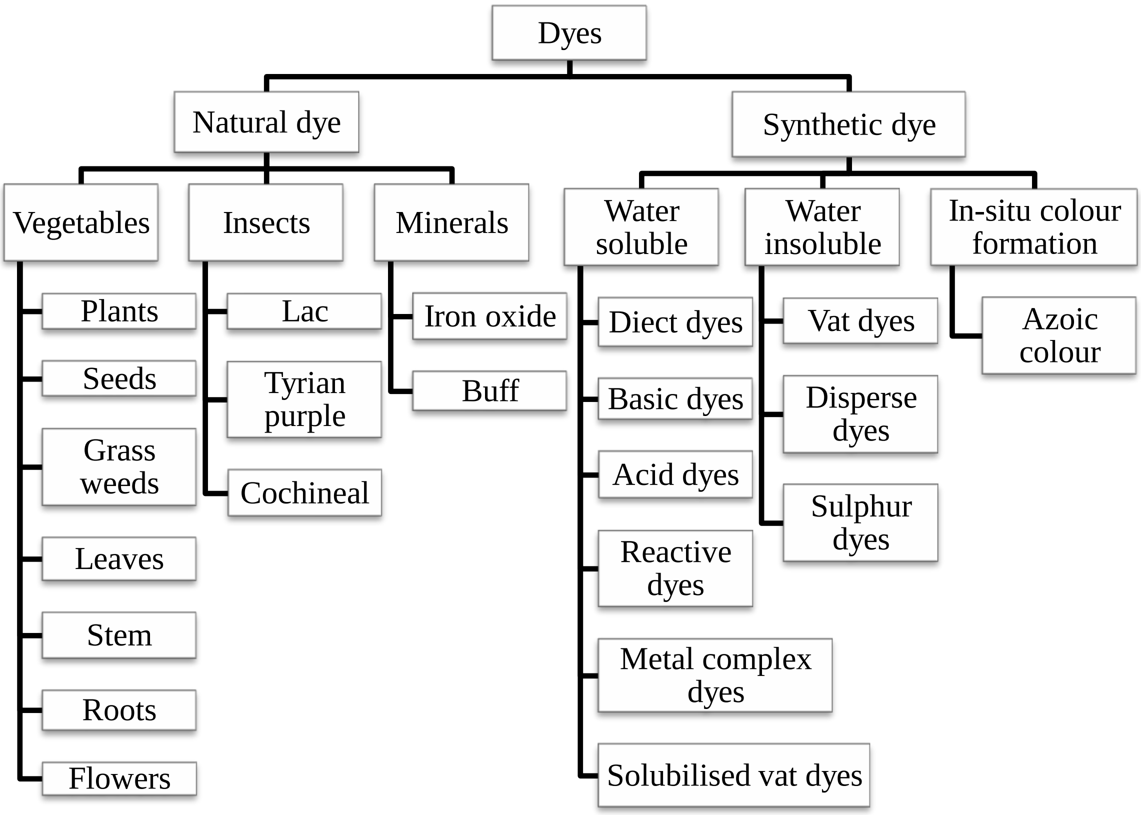

Figure 2.1 Types of dyes (Ajmal et al., 2014)

Natural dyes are derived from natural resources and based upon their source of origins; these are broadly classified as plant, animal, mineral, and microbial dyes although plants are the major sources of natural dyes. Natural dyes are considered eco-friendly as these are renewable and biodegradable; are skin friendly and may also provide health benefits to the wearer. Natural dyes can be used for dyeing almost all types of natural fibers (Sujata and Raja, 2014). Throughout the year, plants have been used for the extraction of a majority of natural dyes. Various plant parts including roots, leaves, twigs, stems, heartwood, bark, wood shavings, flowers, fruits, rinds, hulls, husks, and the like serve as natural dye sources. Natural dyes are widely use in the coloration of textiles, foods, drugs, and cosmetics. Small quantities of dyes are also been applied in colouration of paper, leather, shoe polish, wood, cane, candles and many others (Yagnesh, 2015).

Apart from that, synthetic dyes are those derived from organic or inorganic compound. Examples of class of synthetic dyes include direct, acid, basic, reactive, metal complex, vat, azoic and many others (Sujata and Raja, 2014). Synthetic dyes usually have a complex aromatic molecular structure such as benzene, naphthalene, anthracene, toluene and xylene. Synthetic dyes are extensively used in textile dyeing, paper printing, colour photography, pharmaceutical, food, cosmetic, and leather industries (Kuhad et al., 2004; Couto, 2009). Synthetic dyes offer some advantages over natural dyes, for instance, they are lower in cost, producing brighter colour and also easy to be applied on fabrics (Yagnesh, 2015).

When considering the general structure of dye, dyes do group into anionic, nonionic and cationic dyes. Direct, acid and reactive dyes are the major anionic dyes. They are the bright in colour, water soluble, reactive and acidic dyes. Such kinds of dyes are quite problematic since they are unable to be removed through conventional treatment systems. On the other hand, the major nonionic dyes are disperse dyes which does not ionized in the aqueous environment while the major cationic dyes are the azo basic, anthroquinone disperse as well as reactive dyes. Among these 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 objection to aromatic ring structure (Suteu and Zaharia, 2012).

2.1.2 Methylene Blue

Methylene blue is a synthetic chemical cationic dye employed by industries such as textile industry for a variety of purposes. It is a heterocyclic aromatic chemical compound with a molecular formula $C_{16}H_{18}N_3SCl$ with molecular weight of 319.85 g/mol. It is a dark green crystals or crystalline powder with bronze luster. Methylene blue is odorless and stable in air. Once dissolves in water or alcohol, it forms deep blue solution together with the formation of double salts. (PubChem, 2013)

Methylene blue widely used as dyes and have a number of biological uses. It is used in human and veterinary medicine for several therapeutic and diagnostic procedures, including as a stain in bacteriology, REDOX colourimetric agent, targeting agent for melanoma as well as be an antiseptic and disinfectant (O'Neil et al., 2006). It was the first synthetic compound ever used as an antiseptic in clinical therapy, and the first antiseptic dye to be used therapeutically. From other perspective, it has been used for decades in the field of textile industry for instance in Batik industry in Peninsular Malaysia. Theoretically, methylene blue dissociates in aqueous solution into methylene blue cation and chloride ion. The coloured cation is adsorbed by several adsorbents preferentially to a very great extent (Walker et al., 2006). As a result, methylene blue was selected to be the adsorbate in this research.

However, it is dominant to remove methylene blue from the textile effluent of batik industries since it brings various harmful effects on the human beings. Methylene blue can cause eye burn which may be responsible for permanent injury to the eyes of human as well as aquatic animals. Methylene blue also causes irritation to the skin once in contact with it (Umoren et al., 2012).

2.1.3 Methods of Dyes Removal

Recently, the primary concern is focused on developing economical and effective methods to treat textile effluent to protect the aquatic life in water bodies. The dyes removal methods could be physical, chemical, biological methods or even physiochemical which provide effective technologies in removing contaminants from wastewater coming from the textile industries.

Membrane-filtration processes for example reverse osmosis, electro-dialysis, nano-filtration and various adsorption techniques are examples of physical treatment process. The major disadvantage associated with the membrane filtration processes is that they have a limited life time as well as the problem of membrane fouling. As a consequence, cost of periodic replacement of membrane has to be considered in any analysis of their economic viability (Kharub, 2011).

Chemical methods includes a number of processes such as coagulation or flocculation combined with flotation and filtration, precipitation-flocculation with $Fe(II)/Ca(OH)_2$, electro-kinetic coagulation, irradiation and many others. These chemical techniques are helpful in the removal of dyes from the wastewater. Nevertheless, these methods are quite expensive to be practiced since they consume large amount of chemical reagents. They are efficient for waste water treatment purposes contaminated with different pollutants in them (Kharub, 2011).

Biological methods involve the degradation of dyes with the biological phenomena. For example, bioremediation is an environmental friendly and green technique to remove dye from textile effluent (Ekambaram et al., 2016). This biological degradation method is economically feasible, environmental-friendly besides generating less volume of sludge as compared with other techniques (Ali, 2010). Bioremediation do cause the degradation of synthetic dyes to a comparatively less toxic inorganic compound as a result of breaking down of chemical bond by biological material such as algae, bacteria, fungi and yeasts (Babu et al., 2015). However, biological process is relatively slow and an optimum favorable environmental is necessary to be created to grow the biological materials. By then, operating and maintenance costs increase.

Among all the techniques, it was reported that adsorption is the best process for the removal of decontaminants such as dyes from industrial textile 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 2.1 summarizes the advantages and limitations of different dye removal technologies.

2.2 Activated Carbon

Activated carbons (AC) have been widely applied depending on the industrial, medical or environmental purpose. They have been developed in terms of their specific surface area, diverse pore structure as well as size through the changes of a number of associated physical and chemical characteristics, for instance the type of raw material and the activation procedure applied (Lim et al., 2010).

Activated carbon is a group of porous carbons manufactured by the treatment between a char and oxidizing gases or by carbonization of carbonaceous materials which are impregnated with dehydrating chemicals. It is treated physically or chemically to generate microfissures that vastly increase its adsorptive surface area. The large electrical charged surface area which ranges between 500 to 1500 m^2/g enable the adsorption of a wide range of polar compounds, notably phenols and their derivatives (Jackson, 2014). Activated carbon has the strongest physical adsorption forces or the highest volume of adsorbing porosity of any material known to mankind (Arvanitoyannis et al., 2008). 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).

Activated carbon is often used for remediation of pollutants in soil and water due to porous structure, large surface area and high adsorption capacity (Sabir et al., 2015). Basically, activated carbon can be utilized to remove soluble and insoluble organic pollutants with the removal capacity up to 99.9 % through adsorption process (Imran et al., 2012). Over decades, it has been widely used for the separation of gases, recovery of solvents, removal of organic pollutants such as Fe^{2+} from drinking water, as super-capacitors electrodes and so on (Chmiola et al., 2006; Elmouwahidi et al., 2012; Ridder et al., 2012).

The demand for activated carbon is growing in fast trend due to the water pollution issues that are increased rampantly from decade to decade (Lee et al., 1999). As mentioned before, adsorption is considered as the best effluent treatment method due to its inexpensiveness and also its ease of operation. Unluckily, the production and regeneration of commercial activated carbons are quite expensive. Recently, there are still a number of researches in figuring out alternative raw materials which are both economically attractive and give similar or even better characteristics and performances than that of the conventional ones (Gurses et al., 2014).

Table 2.1 Different technologies for colour removal (Banat et al., 1996)

Process	**Technology**	**Advantages**	**Disadvantages**
Physical	Membrane separations	Removes all dye types, high-quality treated effluent.	Requires high pressures, expensive, incapable of treating large volumes.
	Adsorption on activated carbons	The most effective adsorbent, high loading 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.
Chemical	Ion-exchange	No loss of adsorbent on regeneration, effective.	Economic constraints and not effective for disperse dyes.
	Oxidation	Rapid and efficient process.	High energy cost, chemicals are required.
	Advanced oxidation process	No production of sludge, little or no consumption of chemicals, efficiency for recalcitrant dyes.	Economically un-feasible, formation of by-products.
	Coagulation & Flocculation	Simple, economically feasible	High sludge production, handling and disposal problems.
	Biodegradation	Economically	Slow process, necessary to

		attractive publicly accepted treatment.	create an optimal favorable environment, maintenance and nutrition requirements.
Biological	Selective	Economically attractive, high selectivity, regeneration is not necessary.	Requires chemical modification, non-destructive process.
	Bio-adsorbents 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).

2.2.1 Activated Carbon Precursors

Nowadays, the utilization of commercial activated carbon is limited because they are costly. In order to overcome this problem, agricultural wastes such as hardwood, spent coffee, lignin, coconut husk, pomegranate leaves and olive waste with lower cost could be used as precursors for preparation of activated carbon (Enaime et al., 2016). They could be used as alternative adsorbents for the wastewater treatment.

Basically, precursor for activated carbon can be grouped into two main categories based on their nature of origin, namely organic and inorganic. Organic precursors include plants, animals and other materials with high carbon contents.

Fruit waste, rice husks, bark, seaweed, algae, peat moss, hair and keratin are some examples of organic precursors. Whereas, the inorganic precursors include soil, clay, mud, zeolites, ore materials, metal oxides and hydroxides (Imran et al., 2012).

The selected raw material for the production of activated carbon should be easily accessible, inexpensive, non-hazardous in nature and easily activated. Precursor with a high carbon and oxygen contents but low in inorganic contents (ash) is more preferable to be used as a raw material for the production of AC (Tsai et al., 1997). Hence, mangrove pile leftovers with high carbon content are definitely a suitable raw precursor for activated carbon preparation.

2.2.2 Types of Activated Carbon

Activated carbons are classified into different types according to their sizes and shapes. They are primarily presented in three forms or shapes, which are powdered, granular and extruded.

2.2.2 (a) Powdered Activated Carbon

Powdered activated carbon, PAC typically has an average diameter of 15 μm to 25 μm with the size less than 0.1 mm. They present a large surface to volume ratio with a small diffusion distance. PAC has an apparent density ranging between 23 and 46 lb/ft^3. PAC is made from organic materials with high carbon contents such as wood, lignite and coal. It is normally added early in the treatment process and is subsequently removed either by sedimentation or by the filter beds during backwashing. PAC is usually added at the head of the plant to provide the longest contact time possible before applying other treatment chemicals (Westerhoff et al., 2005).

Coating of PAC with coagulants or other water treatment chemicals should be avoided before the PAC has had sufficient contact time with the source water. Besides, PAC should not be added concurrently with chlorine or potassium permanganate as these chemicals will adsorb to the PAC. PAC dosages can range between 1 to 100 mg/L depending on the type and concentrations of organic compounds present (EPA, 2014).

The presence of PAC improves sludge sedimentation. However, sludge production is increased proportionately with the addition of PAC. The presence of activated carbon could possibly influence the disposal possibilities for the excess sludge. Appropriate amount of PAC should be utilized to overcome such environmental problem.

2.2.2 (b) Granular Activated Carbon

Granular activated carbon, GAC has a relatively larger particle size as compared to powdered activated carbon. Consequently, it presents a smaller external surface. They have the size range of 0.2 mm to 5 mm. They are irregular shaped particles formed from milling and sieving with apparent density ranging between 25 and 31 lb/ft^3. They are longer lasting and harder compared to powdered activated carbon. Smaller GAC is particularly suited to liquid phase applications, while larger GAC is better for vapors and gases.

The two most common options for locating a GAC treatment unit in water treatment plants are at post-filtration adsorption and filtration-adsorption unit. In post-filtration, the GAC unit is located after the conventional filtration process (post-filter contactors or adsorbers). Whereas, for filtration-adsorption unit, some or all of the filter media in a granular media filter is replaced with GAC. Due to environmental issues, spent GAC must be disposed of recognizing that contaminants can be desorbed, which can potentially result in leaching of contaminants from the spent GAC when exposed to percolating water, contaminating soils or groundwater. Due to contamination concerns, spent GAC regeneration is typically favored over disposal (EPA, 2015).

2.2.2 (c) Extruded Activated Carbon

Extruded activated carbon, EAC combines powdered activated carbon with a binder, which are fused together and extruded into a cylindrical shaped activated carbon block. Typically, they are a cylindrical pellet product ranging in size from 1 mm to 5 mm. They are normally used for gas phase applications due to their low pressure drop, high mechanical strength as well as low dust contents (Seidel and Mickey, 2004).

2.3 Preparation of Activated Carbon

There are two main steps for the preparation of activated carbons; they are the carbonization of the carbonaceous raw material below 800 °C in the absence of oxygen and also the activation of the carbonized product which is either by physical or chemical mean (Ioannidou and Zabaniotou, 2007). Carbonization is an inert thermal process to convert raw material into solid char and leaving other liquids and gaseous as by products (Chattopadhyaya et al., 2006). Meanwhile, activation is a sequence process to enhance the char porosity and to clean out the tar-clogging pores; thus increasing the total surface area of the produced activated carbon (Turmuzi et al., 2004).