

**ADSORPTION OF BASIC DYE (METHYLENE BLUE) ON  
CORN COB BASED ACTIVATED CARBON (CCAC):  
EQUILIBRIUM, KINETIC AND THERMODYNAMIC  
STUDIES**

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**UNIVERSITI SAINS MALAYSIA**

**2018**

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**by**

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**Thesis submitted in partial fulfilment of the requirement for  
the degree of Bachelor of Chemical Engineering**

**June 2018**

## **ACKNOWLEDGEMENT**

First and foremost, I am grateful to Allah S.W.T, The Almighty God for giving me the strength and healthy health which allows me to complete the research studies successfully.

Next, I would like to place my deep sense of gratitude and huge appreciation to my supervisor, Dr. Muhammad Nazri Murat who in spite of being extraordinarily busy, took his time out to hear, guide and provides me a generous encouragement and useful advice throughout this research studies. Not to be forgotten, thanks to the final year project coordinator, Associate Prof. Dr. Mohd Azmier Ahmad whose make sure every task were completed within the given time.

Apart from that, I also would like to deliver a special thanks to the School of Chemical Engineering, Universiti Sains Malaysia for providing complete facilities and making the EKC 499 - Final Year Project as a part of the course requirements for Bachelor of Chemical Engineering. These provide me an opportunity to expose myself to the research works which helps me in developing the professional and interpersonal skills, knowledge and attitudes. Furthermore, I also would like to thank all the staffs involved throughout this project for their guidance and technical support.

Lastly, I would like to take this opportunity to express my special appreciation to my family members for their understanding and encouragement throughout this research studies. Not to forget, to all my colleagues especially my best friend, Mohd Razif Ramli who always with me start from the beginning until completing this thesis.

*Ahmad Arif Aiman*

*June 1<sup>st</sup>, 2018*

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## LIST OF SYMBOLS

Symbol	Unit
$C_e$	Equilibrium concentration of adsorbate mg/L
$C_o$	Highest initial adsorbate concentration mg/L
$C_t$	Adsorbate concentration at time, t mg/L
$E_a$	Arrhenius activation energy of adsorption kJ/mol
$k_1$	Adsorption rate constant for the pseudo-first-order kinetic 1/min
$k_2$	Adsorption rate constant for the pseudo-second-order g/mg.min
$k_{diff}$	Intraparticle diffusion rate constant mg/g.min <sup>1/2</sup>
$K_F$	Freundlich isotherm constant mg/g (L/mg) <sup>1/n</sup>
$K_L$	Rate of adsorption for Langmuir isotherm L/mg
$M$	Mass of adsorbent g
$n_F$	Constant for Freundlich isotherm -
$q_e$	Amount of adsorbate adsorbed at equilibrium mg/g
$q_m$	Adsorption capacity of Langmuir isotherm mg/g
$q_t$	Amount of adsorbate adsorbed at time, t mg/g
$R$	Universal gas constant 8.314 J/mol K
$R^2$	Linear regression correlation coefficient -
$t$	Time Min or hr
$T$	Absolute temperature K
$V$	Volume of solution L
$\Delta H^\circ$	Changes in standard enthalpy kJ/mol
$\Delta S^\circ$	Changes in standard entropy kJ/mol
$\Delta G^\circ$	Changes in standard Gibbs free energy kJ/mol



## LIST OF ABBREVIATIONS

AC	Activated Carbon
ANOVA	Analysis of Variance
BET	Brunauer-Emmett-Teller
CC	Corn Cob
CCAC	Corn Cob based Activated Carbon
CCD	Central Composite Design
CO <sub>2</sub>	Carbon Dioxide
EA	Elemental Analyzer
FTIR	Fourier Transform Infra-Red spectrometer
IUPAC	International Union of Pure and Applied Chemistry
MB	Methylene Blue
N <sub>2</sub>	Nitrogen gas
RSM	Response Surface Methodology
SEM	Scanning Electron Microscope
STA	Simultaneous Thermal Analyzer
UV	Ultra-Violet
VAA	Volumetric Adsorption Analyzer

# **PENJERAPAN PEWARNA ASAS (METELINA BIRU) PADA KARBON AKTIF BERASASKAN TONGKOL JAGUNG (KATJ): KAJIAN KESEIMBANGAN, KINETIK DAN TERMODINAMIK**

## **ABSTRAK**

Dalam kajian ini, karbon yang telah diaktifkan daripada tongkol jagung (KATJ) disediakan melalui pengaktifan fizikal menggunakan penyinaran gelombang mikro sebagai sumber pemanasan telah diperoleh daripada sisa pertanian dan prestasi penjerapannya dalam penyingkiran pewarna metilena biru (MB) daripada larutan akueus dianalisis dalam sistem kumpulan. Keadaan penyediaan optimum diperolehi pada kuasa radiasi 400W dan masa pengaktifan selama 4minit telah menghasilkan KATJ yang mempunyai luas permukaan BET, kawasan permukaan mesopore, jumlah isipadu liang dan peratusan karbon tetap masing-masing sebanyak  $604.6\text{m}^2/\text{g}$ ,  $458.32\text{m}^2/\text{g}$ ,  $0.4557\text{cm}^3/\text{g}$  dan  $66.84\%$ . Diameter purata liang KATJ ( $5.45\text{nm}$ ) yang diperolehi berada dalam lingkungan julat mesoporous yang berada di antara  $2\text{nm}$  hingga  $50\text{nm}$ . Faktor-faktor yang mempengaruhi penjerapan MB keatas KATJ seperti masa ( $0\text{-}24\text{jam}$ ), kepekatan awal pewarna ( $25\text{mg/L-}300\text{mg/L}$ ) dan suhu larutan ( $30^\circ\text{C-}60^\circ\text{C}$ ) telah dinilai. Keputusan menunjukkan bahawa penjerapan MB keatas KATJ didapati meningkat dengan peningkatan masa, kepekatan awal pewarna dan suhu larutan. Data keseimbangan dinilai menggunakan garis sesuhu Langmuir, Freundlich dan Temkin manakala model kinetik pseudo tertib pertama dan pseudo tertib kedua digunakan untuk menguji data eksperimen. Garis sesuhu Freundlich dan model kinetik pseudo tertib kedua terbaik untuk menerangkan penjerapan MB keatas KATJ. Kajian termodinamik dijalankan untuk menentukan parameter termodinamik seperti tenaga bebas Gibbs ( $\Delta G$ ), entalpi ( $\Delta H$ ) dan entropi ( $\Delta S$ ). Daripada kajian ini, didapati bahawa penjerapan pewarna MB keatas KATJ adalah penjerapan fizikal, bersifat spontan dan endotermik.

# **ADSORPTION OF BASIC DYE (METHYLENE BLUE) ON CORN COB BASED ACTIVATED CARBON (CCAC): EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES**

## **ABSTRACT**

In this study, the corn cob based activated carbon (CCAC) prepared by physical activation using microwave radiation as a heating source was derived from agricultural waste and its adsorption performance in the removal of methylene blue (MB) from an aqueous solution was analyzed in a batch system. The optimum preparation conditions were obtained at radiation power of 400 W and activation time of 4 minutes which resulted with CCAC of BET surface area, mesopore surface area, total pore volume and percentage of fixed carbon of  $604.6\text{m}^2/\text{g}$ ,  $458.32\text{m}^2/\text{g}$ ,  $0.4557\text{cm}^3/\text{g}$  and 66.84%, respectively. The obtained average pore diameter of the CCAC (5.45nm) lies within the range of mesoporous region which is in between 2nm to 50nm. The factors that influence the adsorption of MB onto CCAC such as contact time (0-24hours), initial dye concentration (25mg/L-300mg/L) and solution temperature (30°C-60°C) were evaluated. The result showed that the adsorption uptake was found to increase with an increase in contact time, initial dye concentration and solution temperature. The equilibrium data were evaluated using Langmuir, Freundlich and Temkin isotherms while pseudo-first order and pseudo-second order kinetic models were applied to test the experimental data. The Freundlich isotherm and pseudo-second order kinetic model were best describes the MB adsorption onto the CCAC. Thermodynamic studies were carried out to determine the thermodynamic parameters such as Gibbs free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ). From the studies, it was found that the MB adsorption on CCAC was physisorption process, spontaneous and endothermic in nature.

# CHAPTER 1: INTRODUCTION

## 1.1 Introduction

Dyes are generally defined as a coloured or chemicals compound that has an affinity towards the substrate in which attach themselves to the surfaces or fabrics to impart a bright and lasting colour. Most of them are basically complex organic molecules and are resistant to many things such as the action of detergents (Seow and Lim, 2016). The colouring is not readily altered by washing, heat, light and other factors to which the material are likely to be exposed (Edward Noah Abrahart, 2018). A dye has a very unique chemistry, structure and particular way of bonding with the substrate depending on its classes. There are several ways for classification of commercial dyes and some of the prominent ways of classification are in term of source of materials, chemical structure, particle charge upon dissolution in aqueous application medium, and methods of application. However, due to the complexities of the colour nomenclature from the chemical structure, the classification based on methods of application is usually favourable (Yagub et al., 2014).

As mentioned earlier, dyes which also known as a coloured compounds with a very unique chemical structure and has an excellent binding ability towards the substrate, it is being widely applied to many fields of advanced technology from industries such as textiles, leather, printing, paper, cosmetics, food industry and etc. to colour their finished products (Yagub et al., 2014). Due to its individual unique chemical structure, different classes of dyes applied to different applications in industry depending on its suitability. As example, because food dyes are classed as food additives, they are manufactured to a higher standard than some others industrial dyes. In other words, various dyes are manufactured to meet the requirement of each type of industries.

According to the current statistics, there are more than 100,000 commercially available dyes (worldwide) with over  $7 \times 10^5$  tonnes of dyestuff produced annually (Yagub et al., 2014). Effluents from dyeing and other related industrial processes are known to contain highly coloured species. Among all the dyes using in industries, textile industries are one of the type of industry which are being considered as the top polluting industry due to it using dyes for coloration of their finished products. This industry are among the industries who are utilizing heavy amount of water in their processes (Maheshwari, 2013). This industry generate both inorganic and organic waste mixed with wastewater from the production processes, which leads to change in both biological and chemical parameters of the receiving bodies (Kaur and Sharma, 2015). It has been projected that, the consumption of dyes in textile industry is more than 10,000 tonnes/year and about 10-15% of these dyes are discharged as wastewater effluents during dyeing processes (Ravi Vital Kandisa, 2016).

As dyes are water soluble and produce very bright colours in water with acidic properties, water pollution caused by industrial effluent discharges has become a worrisome phenomenon due to its impact on environmental safety and health. Due to its utilization of large amount of dyes and water in their processes, the release of dyes into the environment as wastewater effluents contributes to water pollution. Water contamination poses a serious threat of not only for the state of environment but human body causes some chronic diseases (Rahman, 2016). Without a proper treatment, it could exert great impact to the environment because of its toxicity, mutagenicity, and non-biodegradability (Mohamed et al., 2014). In recent years, control of water pollution has gained increasing importance. As example, discharge of these dyes into the water streams will affect the people who may use the effluents for living purposes such as washing, bathing and drinking (Seow and Lim, 2016).

Due to the environmental and health concerns associated with the wastewater effluents, the removal of such coloured compounds from waste effluents becomes environmentally important. Different separation technologies have been used in the removal of dyes from the wastewater effluents in industry and it is being categorized into three categories namely physical, chemical and biological methods. These methods include adsorption, bio-adsorption, coagulation and flocculation, advanced oxidation, ozonation, membrane filtration and etc(Pathania et al., 2017). Each of these methods has their own advantages and disadvantages. However, adsorption has been found to be the most effective method in compare with the other methods in terms of flexibility and simplicity of design, initial cost, insensitivity to toxic pollutants and ease of operation (Yagub et al., 2014).

## **1.2 Problem Statement**

The impact of the pollution in the atmosphere, lithosphere, and hydrosphere poses a constant threat to the environment day by day. A lot of man-made activities such as domestic, industrial, and agriculture are developing the negative impact on the water body by increasing the number of contaminants present in the water (Maheshwari, 2013). Dyes basically a natural or synthetic chemical compounds with an ability to connect themselves to the substrate is used in industries to colour their finished products. Organic dyes are used excessively worldwide and have become serious pollutants to their extensive applications in textile, leather, cosmetic, printing, and paper industries (Zhang et al., 2016).

Discharge of these coloured compounds as wastewater effluents present a major environmental problem for developing countries because of their toxic and carcinogenic effects in living beings (Geçgel et al., 2012). As example, some dyes can cause allergy, dermatitis, skin irritation, cancer, and mutation to humans. Apart from

that, dyes also associated with environmental concern with their absorption and reflection of sunlight entering the water, which will inhibit the growth of bacteria, limiting it to levels insufficient to biologically degrade impurities in the water. In addition, the reduction of sunlight penetration into the water will also affect the growth of aquatic organisms (Seow and Lim, 2016).

Methylene Blue (MB), a typical cationic organic dye that are commonly found in industrial wastewater. Thus, it is necessary to remove this kind of pollutant from wastewater before it is allowed to discharge to the environment. It is because even small amount of dye present in water can be toxic and highly visible. Various physical, chemical and biological methods, including adsorption, bio-sorption, coagulation and flocculation, membrane filtration, ozonation and etc. have been widely used for the treatment of dye containing wastewater in industries (Pathania et al., 2017). Among all the available methods, adsorption has been found to be the most effective methods after considering all the factors like effectiveness, flexibility, simplicity of design, ease of operation and etc. There are various type of available adsorbents used in adsorption, but, among all the available adsorbents in industries, activated carbon is found to be the most potential adsorbent used for dye removal (Rahman, 2016). Commercially, the activated carbon is derived from non-renewable resources material such as petroleum residues, wood, and coal which are very expensive (Yahya et al., 2015). Although commercial activated carbon is a preferred adsorbent for dye removal, its widespread use is restricted due to its relatively high cost which then leads to researches on alternative non-conventional and low cost adsorbents (Kaur and Sharma, 2015). The low cost adsorbent can be developed by utilizing any type of agricultural or industrial waste. In addition, the use of agricultural waste as activated carbon precursors has also been found to be renewable, relatively less expensive and ultimately could utilize the

waste effectively into wealth. Therefore, in recent years, the researchers have been focusing on the production of activated carbon by using agricultural waste due to its effective and inexpensive (Yahya et al., 2015).

In general, there are several ways in the preparation of activated carbon. It can be prepared by two different processes either by physical or chemical activation. Both processes has its own advantages and disadvantages, however, the selection of methods of activated carbon preparation is greatly depends on in suitability of its application. In physical activation, the type and degree of activation could affect the physical and chemical properties of the activated carbon. The purpose of activation is basically to develop further porosity and creating some ordering of the structure which results in a highly porous solid of the activated carbon (Yahya et al., 2015). The activation of precursors by physical activation can be carried out by two different techniques which are by conventional or microwave heating. Recently, the activation by microwave heating has been found to become a viable alternative for the conventional activation in preparation of activated carbon (Ahmed, 2016).



### **1.3 Research Objectives**

The objectives of this research are:-

- i) To prepare the activated carbon (adsorbent) from agricultural waste (Corn Cob) by physical activation.
- ii) To determine the optimum activation parameters (radiation power and activation time) in the production of Corn Cob based Activated Carbon (CCAC) by using microwave radiation.
- iii) To study the adsorption potential of Corn Cob based Activated Carbon (CCAC) for removal of basic dye (Methylene Blue) from an aqueous solution and mechanisms through isotherm, kinetic and thermodynamic studies.

## CHAPTER 2: LITERATURE REVIEW

### 2.1 Dyes

Dyes are coloured or chemicals compound that can be derived either from natural or synthetic resources. The majority of them are synthetic compounds and has an excellent binding affinity towards the substrate to which it is being applied. Due to its capability of being fixed to substrates like surfaces of material or fabrics, dyes are commonly used in an aqueous solution to impart a bright and lasting colour to various substrates in many industries like textile, leather, cosmetics, paper and plastics to colour their finished products. In addition, most of the dyes are complex molecules and are known to be resistant to fading on exposure to light, water, and many chemicals such as the action of detergents (Ahmad et al., 2002). To be use, dyes must possess the following properties namely colour, solubility in water, ability to be absorbed and retained by fibre (substantivity) or to be chemically combined with it (reactivity) and ability to withstand washing, dry cleaning, heat, light and other factors to which the material are likely to be exposed.

According to Kallel et al. (2016), dyes are mainly chemical compounds constituted of two important components which are chromophores and auxochromes. The dyescolor is due to the presence of chromospore and its fixed property to the acid and basic group such as OH, SO<sub>3</sub>H, NH<sub>2</sub> and NR<sub>2</sub>. On the other hand, the polar auxochrome are responsible to makes the dyes soluble in water and enhance the affinity of the dye towards the fabrics by the interaction with the oppositely charged groups of fabrics structure. Thus, it is undeniable that the usage of dyes in many industries increases yearly due to their efficacy and easy acquisition (Li et al., 2017). However, a rapid increase in the usage of dyes in industries in the recent years has resulted in the generation of numerous kinds of toxic pollutants (Shakoor and Nasar, 2017). Based on

Isah et al. (2015), the high level of dyes production (worldwide) and their extensive use in many applications, in general, has generated coloured wastewater which caused severe water pollution. So, these pollutants are considered to be the major cause of water pollution (Shakoor and Nasar, 2017).

According to statistics, there are more than 100,000 commercial dyes are known and available with an annual production of over  $7 \times 10^5$  tonnes/year (Yagub et al., 2014). Due to their good solubility, synthetic dyes are common water pollutants and they may frequently be found in trace quantities in industrial wastewater. An indication of the scale of the problem is given by the fact that 2% of dyes that are produced are discharged directly in the aqueous effluent (Crini, 2006). Based on Rafatullah et al. (2010), colour are the first contaminant to be recognized in wastewater and the presence of an even very small amount of dyes in water ( $<1$ ppm) is highly visible and undesirable. Hence, the removal of dyes from waste effluents becomes environmentally important due to its even small quantity of dye present in the water can be toxic and highly visible (Salleh et al., 2011).

## **2.2 Classification of dyes**

There is several numbers of ways for classification of commercial dyes in industries and some of the methods of classification are based on:

### **2.2.1 Source of materials**

One of the very common classification methods of dyes is based on the source from which the dye is made. Many dyes are generally organic compounds which made either from natural or synthetic sources. Natural dyes are dye that derived from natural sources like plants, insects, animals and minerals (Ravi Vital Kandisa, 2016). However, the majority of natural dyes are mainly from vegetable dyes which obtained from plant sources like roots, berries, bark, leaves, wood, and fungi. On the other hand, synthetic

dyes are a man-made dye. These dyes are made from petroleum and sometimes in combination with mineral-derived components. In other words, synthetic dyes are dyes that obtained by adding chemicals to natural dyes.


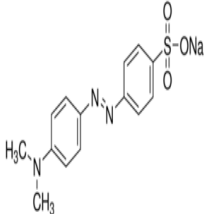
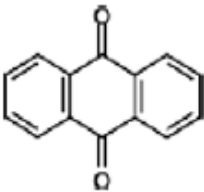
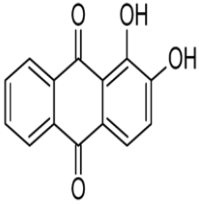
### **2.2.2 Particle charge and its solubility**

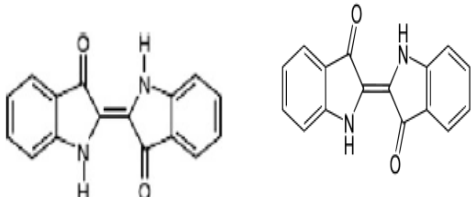
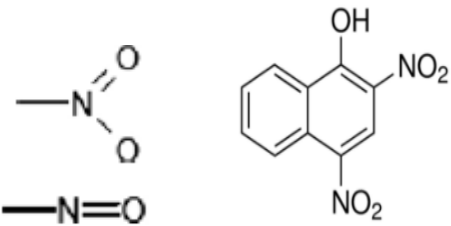
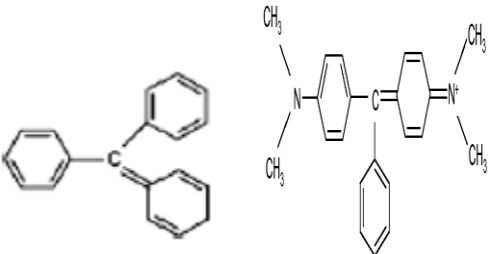
According to Yagub et al. (2014), dyes can be classified based on its particle charge such as cationic, anionic and non-ionic dyes upon dissolution in aqueous application medium. As example, cationic dyes are basic dyes while the anionic dyes include direct, acid and reactive dyes and non-ionic dyes are dispersed dyes (Seow and Lim, 2016). Cationic dyes carry a positive charge in their molecule and soluble in water which yields coloured cation in solution. It is widely used in acrylic, wool, and silk dyeing and also intensely used as a model in dye adsorption studies. On the other hand, anionic dyes depend on a negative ion. It includes many compounds from the most varied classes of dyes which exhibit characteristics differences in structure but possess a common feature such as water-solubilizing and ionic substituents (Salleh et al., 2011). Other than that, dyes may also be classified on the basis of their solubility. Soluble dyes which include acid, mordant, metal complex, direct, basic and reactive dyes while insoluble dyes include azoic, sulfur, vat and disperse dye (Gupta, 2009).

### 2.2.3 Chemical structure

The classification based on chemical structure for the common class of the dyes is presented in Table 2.1.

Table 2.1: Classification of dyes according to the chemical structure (Yagub et al., 2014)

Class	Description	Chromospheres	Example	Application
<b>Azo dyes</b>	Large class of synthetic organic dyes that contain nitrogen as the azo group as primary chromophore their molecular structure.  Highly coloured and are prepared by diazotizing an aromatic amine and coupling with suitable aromatic compound.		 Methyl orange	Used in food and textile manufacture  In theory, azo dye can supply a complete rainbow of colours, but yellow/red dyes are more common as blue/brown dyes.
<b>Anthraquinone dyes</b>	Any of a group of organic dyes having molecular structure based upon that of anthraquinone.		 Alizarin	Alizarin is the main ingredient for the manufacture of the madder lake pigments known to painter as Rose madder and Alizarin crimson.  Alizarin is also used commercially as a red textile dye.

<b>Indigoid dyes</b>	<p>Organic compound with a distinctive blue colour.</p> <p>Contains carbonyl chromophore.</p>	 <p>Indigo</p>	<p>Primary use of indigo is as a dye for cotton yarn, which is mainly for the production of denim cloth.</p> <p>Small amount are used for dyeing wool and silk.</p>
<b>Nitro and Nitroso dyes</b>	<p>Dyes that contain nitro or nitroso groups as the chromophore and -OH as auxochrome.</p>	 <p>Acid Yellow 24</p>	-
<b>Triarylmethane dyes</b>	<p>Synthetic organic compounds containing triphenylmethane backbones.</p> <p>A central carbon is bonded to three aromatic rings, one is in the quinod form.</p> <p>Auxochrome are NH<sub>2</sub>, NR<sub>2</sub>, OH.</p>	 <p>Malachite Green</p>	<p>Used as a direct dye for wool and silk.</p>

### 2.3 Applications of dyes

As mentioned, there are several ways of classification of dyes in industries. But, according to literature, the colour nomenclature from the chemical structure system is complex (Seow and Lim, 2016). Hence, the classification in term of methods of application is often preferable. The classification of dyes on the basis of technique employed for their application depends on the nature of both dye and fabric are presented in Table 2.2.

Table 2.2: Classification of dyes based on methods of application (Singh, 2004;Gupta, 2009)

Dye class	Description	Application
<b>Reactive dyes</b>	<ul style="list-style-type: none"> <li>- Dyes with reactive groups that form covalent bonds with OH<sup>-</sup>, NH<sup>2-</sup>, or SH<sup>-</sup> groups in fibers.</li> <li>- Contain chromophoric groups such as azo, anthraquinone, oxazine and etc.</li> </ul>	<ul style="list-style-type: none"> <li>- Generally used for cotton and other cellulose.</li> <li>- Also used to a small extent on wool and nylon.</li> </ul>
<b>Acid dyes</b>	<ul style="list-style-type: none"> <li>- Anionic compounds which are mainly used for dyeing basic groups containing fabrics like wool, polyamide, silk and modified acryl.</li> <li>- Application is generally made under acidic conditions which cause protonation of basic groups.</li> <li>- Contain azo, anthraquinone or triarylmethane type of chromophore groups.</li> </ul>	<ul style="list-style-type: none"> <li>- Used for nylon, wool, silk, modified acrylics, and also to some extent for paper, leather, ink-jet printing, food and cosmetics.</li> </ul>
<b>Direct dyes</b>	<ul style="list-style-type: none"> <li>- Water soluble anionic dyes.</li> <li>- High affinity for cellulose fibers and bind to the fiber through Van der Waals forces.</li> <li>- Contain polyazo compounds, along with some tilbenes, phthalocyanines and oxazines.</li> </ul>	<ul style="list-style-type: none"> <li>- Used in dyeing of cotton and rayon, paper, leather, and nylon.</li> </ul>

<b>Basic dyes</b>	<ul style="list-style-type: none"> <li>- Water soluble cationic compound that are used for dyeing acid group containing fibers, usually synthetic fiber like modified polyacryl.</li> <li>- Contain diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, and oxazine.</li> </ul>	<ul style="list-style-type: none"> <li>- Used for paper, polyacrylonitrile, modified nylons, modified polyesters, cation dyeable polyethylene terephthalate and medicine.</li> <li>- Originally used for silk, wool and tannin-mordanted cotton</li> </ul>
<b>Mordant dyes</b>	<ul style="list-style-type: none"> <li>- Compounds which attach to the fiber and then combine with the dye to form an insoluble complex.</li> <li>- These dyes by themselves have poor affinity for the fiber.</li> <li>- Most mordant dyes are azo, oxazine or triarylmethane compounds.</li> </ul>	<ul style="list-style-type: none"> <li>- Used for dyeing wool, leather, silk, paper and modified cellulose fibers.</li> </ul>
<b>Disperse dyes</b>	<ul style="list-style-type: none"> <li>- Water insoluble non-ionic dyes.</li> <li>- Its diffusion requires swelling of the fiber, either by high temperature (&gt;120°C) or with the help of chemical softener.</li> <li>- Contain small azo or nitro compounds, anthraquinone or metal complex azo.</li> </ul>	<ul style="list-style-type: none"> <li>- Used mainly on polyester, nylon, cellulose, cellulose acetate and acrylic fibers.</li> </ul>
<b>Vat dyes</b>	<ul style="list-style-type: none"> <li>- Water-insoluble dyes.</li> <li>- Applied in their reduced forms which obtained are obtained by treating the compound with some reducing agent such as alkaline sodium dithionite.</li> <li>- Such vat dyes contain indigo and anthraquinone type of chromophore group</li> </ul>	<ul style="list-style-type: none"> <li>- Used for cotton mainly to cellulosic fibers as soluble leuco salts and for rayon and wool.</li> </ul>



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<b>Sulfur dyes</b>	<ul style="list-style-type: none"> <li>- Heterocyclic S-ring containing polymeric aromatic compounds.</li> <li>- Dyeing with sulfur dyes involve reduction and oxidation process, when reduced with sodium sulphide, they become soluble and exhibit affinity for cellulose and upon exposure to air they get oxidized to insoluble dye inside fiber.</li> </ul>	<ul style="list-style-type: none"> <li>- Mainly used for dyeing cellulose fibers.</li> </ul>
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## 2.4 Effects of dyes on environment

The demand for water has increased tremendously with agricultural, industrial and domestic sectors consuming 70%, 22% and 8% of the available fresh water respectively. The usage of fresh water in these sectors has resulted in the generation of large amount of wastewater containing a number of pollutants (Gupta, 2009). Due to their good solubility, one of the very common classes of the pollutant presence in the wastewater is dyes. It is sometimes difficult to treat the dyes containing wastewater as it have a synthetic origin and a complex molecular structure which makes them more stable and difficult to biodegraded.

The worldwide high level production and extensive use of dyes in industries like textile, leather, paper, cosmetics, food industry and etc generate coloured wastewater which causes environmental pollution. According to Seow and Lim (2016), it is recognized that public perception of water quality is greatly influenced by the colour. Colour is the first contaminant to be recognized in water and has to be removed from wastewater before discharging it into water bodies (Garg et al., 2004). Discharging large amount of dyes into water resources accompanied by organics, bleaches and salts can affect the physical and chemical properties of fresh water. The

colour of the effluent discharged into receiving water affects the aquatic flora and fauna and causes many water borne diseases.

The presence of dyes in wastewater is easily detectable even when released in small concentrations (Robinson et al., 2002). People may use this effluent for living purposes such as washing, bathing and drinking. According to Salleh et al. (2011), it should be noted that even just 1.0 mg/L of dye concentration in drinking water could impart a significant colour, thus making it unfit for human consumption. Upon human consumption, dye may be mutagenic and carcinogenic which may cause severe damage to human beings, such as dysfunction of the kidneys, reproductive system, liver, brain and central nervous system. Based on Pathania et al. (2017), Methylene Blue is a cationic dyes having various applications in chemistry, biology, medical science and dyeing industries. Its long term exposure can cause vomiting, nausea, anemia, and hypertension. On inhalation, it leads to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and causes nausea, vomiting and mental confusion (Ahmed, 2016).

Apart from that, the colouration of the water by the dyes may have an inhibitory effect on photosynthesis affecting aquatic ecosystems. It affects the aquatic plants as the penetration of sunlight through water is reduced. In addition, it will also inhibit the growth of bacteria, limiting it to levels insufficient to biologically degrade impurities in water. According to Kaur and Sharma (2015), dyeing process usually contributes chromium, lead, zinc and copper to wastewater and copper is found to be toxic to aquatic plants at concentration below 1.0 mg/L. Other than that, dyes may also be problematic if they are broken down anaerobically in the sediment, as toxic amines are often produced due to incomplete degradation by bacteria (Robinson et al., 2002). Hence, for protecting the environment and to meet the stringent government law, many

researchers try to find an effective and economical way of dye containing wastewater treatment.

## **2.5 Treatment methods for dye removal**

It is estimated that, around 10-15% of reactive dyes and 0-5% of basic dyes are lost from dyeing processes and being discharged as a pollutant in wastewater. Due to its harmful impacts on receiving waters, many researchers are interested for the treatment of effluent containing such dyes. During the past three decades, several studies have been performed on methods of dye removal from wastewater. It is being categorized into three categories which are physical, chemical and biological methods (Rafatullah et al., 2010). Among all the available methods for dye removal, some of the most highlighted methods in preventing and reducing the adverse effect on our surroundings are clean technology, eco-mark, and green chemistry technologies (Maheshwari, 2013). As example, physical technologies is consisted of several methods such as adsorption, sedimentation, screening, nano-filtration, reverse osmosis, electro-dialysis and so forth while in chemical technologies, it contained some methods like ozonation, neutralization, chloronation and so on (Rahman, 2016). In addition to that, biological technologies provide methods like fungal decolorization, microbial degradation, and bioremediation (Crini, 2006). Each of these methods has its own pros and cons. Table 2.3 shows the advantages and disadvantages of several different dye removal methods.

Table 2.3: Advantages and disadvantages of different dye removal methods (Robinson et al., 2001)

<b>Methods</b>	<b>Advantages</b>	<b>Disadvantages</b>
<b>Physical Treatment</b>		
<b>Adsorption by activated carbon</b>	Good removal of wide variety of dyes	Very expensive
<b>Membrane filtration</b>	Removal all type of dye	Production of concentrated sludge
<b>Ion exchange</b>	No adsorbent loss	Not effective for all dyes
<b>Irradiation</b>	Effective oxidation at lab scale	Require a lot of dissolve O <sub>2</sub>
<b>Electro-kinetic coagulation</b>	Economically feasible	High sludge production
<b>Chemical Treatment</b>		
<b>Oxidative process</b>	Simplicity of application	H <sub>2</sub> O <sub>2</sub> agent needs to activate by some means
<b>Fentons reagent</b>	Fentons reagent is a suitable chemical means	Sludge generation
<b>Ozonation</b>	Ozone can be applied in its gaseous state and does not increase the volume of wastewater and sludge	Short half-life (20 min)
<b>Photochemical</b>	No sludge is produced and foul odors are greatly reduced	Formation of by-products
<b>Sodium hypochloride</b>	Initiates and accelerates azo-bond cleavage	Release of aromatic amines
<b>Electrochemical destruction</b>	No consumption of chemicals and no sludge build up	Relatively high flow rates cause a direct decrease in dye removal
<b>Biological Treatment</b>		
<b>Decolourization by white-rot fungi</b>	Able to degrade dyes using enzyme	Enzyme production has also been shown to be unreliable
<b>Other microbial culture (Mixed bacterial)</b>	Decolourized in 24-30 hours	Under aerobic conditions azo dyes are not readily metabolized
<b>Adsorption by living/dead microbial biomass</b>	Certain dyes have a particular affinity for binding with microbial species	Not effective for all dyes
<b>Anaerobic textile-dye bioremediation system</b>	Allow azo and other water-soluble dyes to be decolourized	Anaerobic breakdown yields methane and hydrogen sulfide

After considering all the factors, in spite of the availability of numerous methods to treat dye containing wastewater, adsorption process has been preferred for the treatment of wastewater due to its cheapness, simple design, ease of operation, less energy intensiveness, insensitive to toxic substances and high quality of the treated effluents (Crini, 2006).

## **2.6 Adsorption**

The history of adsorption in the purification of water dates back to ancient times (Cheremisinoff, 2001). Adsorption on porous carbons was described as early as 1550 B.C. in an ancient Egyptian papyrus and later by Hippocrates and Pliny the Elder, mainly for medicinal purposes. However, on scientific records the phenomenon of adsorption (Tien, 1994) was observed by C.W. Scheele in 1773 for gases exposed to carbon. This was followed by observations made by Lowitz in 1785 of the reversible removal of colour and odour producing compounds from water by wood charcoal. Larvitz in 1792 and Kehl in 1793 observed similar phenomenon with vegetable and animal charcoals, respectively.

The term adsorption refers to the accumulation of a substance at the interface of two different phases (liquid-solid interface or gas-solid interface). The substance that accumulate at the interface is called as adsorbate and the solid on which the adsorption take place is known as adsorbent (Yagub et al., 2014). According to KayserGupta (2009), a person who introduced for the first time in 1881 the term adsorption to differentiate surface accumulation from intermolecular penetration. He postulated that the basic feature of an adsorption process is surface accumulation material. However, it is now customary to differentiate between two types of adsorption. Adsorption can be classified into two types which are physical adsorption and chemical adsorption (Yagub et al., 2014). Generally, in physical adsorption, the attractive forces between adsorbate

and adsorbent are Van der Waals forces and they being weak in nature result in reversible adsorption (Gupta, 2009). On the other hand, chemical adsorption is illustrated by the formation of strong chemical associations between molecules or ions of adsorbate to adsorbent surface, which generally due to the exchange of electrons (Yagub et al., 2014). Thus, due to its higher strength of bonding in chemical adsorption, it is difficult to remove chemisorbed species from the solid surface. According to Yagub et al. (2014), adsorption on most of the adsorbent is controlled by physical forces with some exception of chemical adsorption. The main physical forces controlling adsorption are Van der Waals forces, hydrogen bonds, polarity, and dipole-dipole interaction (Ali, 2010).

Recently, it is well known that adsorption process is a preferred and extensively used method for removal of organic pollutants such as dyes from aqueous solution in comparison with other available conventional methods due to its effectiveness and some economic reasons. Some of the main commercial adsorbent used in adsorption process includes activated carbon, decolorizing carbon, bone char, alumina, silica, bauxite, bentonite, fuller's earth, molecular sieve, peat, lignite, chitin, chitosan, and ion exchange resin (Tsai et al., 2001). Among all of these available solid adsorbent used in industries, most of the commercial technologies used activated carbon as adsorbent due to its excellent adsorption ability and other few reasons. In addition, activated carbon adsorption has been cited by the US Environmental Protection Agency (EPA) as one of the best available control strategies (Crini, 2006).

## **2.7 Activated carbon**

Activated carbon, also called as activated charcoal or sometimes being called as a solid sponge is basically referred to a carbon-based material that has been processed and being widely used as adsorption media or adsorbent. According to Yahya et al.

(2015), it is widely used as adsorbent due to its high porosity with extremely large surface area, high physicochemical stability, high adsorptive capacity, high mechanical strength and high degree of surface reactivity. However, although activated carbon is a preferred adsorbent, its widespread use is restricted due to its presents several disadvantages. According to Crini (2006), it is quite expensive, non-selective and ineffective against removal of several types of dye like disperse and vat dyes, and its regeneration process are not straightforward and may results in loss of the adsorbent. After considering all the factors in choosing type of adsorbent, the cost are actually plays an important role for the comparison and selection of adsorbent. An adsorbent can be considered as low cost if it requires little processing, abundant in nature (Rafatullah et al., 2010) and can be obtained from by-products or waste material from other industry (Crini, 2006). In order to reduce the cost of treatment and increase the effectiveness of adsorption on commercial activated carbon for removal of wide variety of dyes from wastewater (Demirbas, 2009), there is a need for the development of low cost and easily available materials which can be used more economically on large scale (Rafatullah et al., 2010).

Activated carbon can be produced by a variety of raw materials from animals, vegetables, and minerals. In general, there are two main sources in the production of activated carbon namely coal and agricultural wastes or lignocellulosic materials (Yahya et al., 2015). Commercially, activated carbon is derived from non-renewable resources starting material such as petroleum residues, wood, coal, peat and lignite which are very expensive. Due to it is obtained from non-renewable resources and very expensive, the uses of agricultural waste are preferable as a starting material for activated carbon production. This is because the use of agricultural by-products as activated carbon precursors has also been found to be renewable and relatively less

expensive. There are several factors to be considered in choosing the starting materials used in the production of activated carbon such as its price, purity, potential extent of its activation and also stability of its supply. Other than that, the starting materials also have to be easily activated and have properties of low degradation by aging. Low yield of activated carbon derived from agricultural by-products are expected due to its low carbon contents available as compared with coal or peat. However, due to its low cost, it gives significant impact more than its lower yield.

Agricultural by-products offer an inexpensive and renewable additional source of activated carbon. These by-products have little or no economic value and often present a disposal problem. Therefore, there is a need to valorize these low cost by-products. Thus, conversion of agricultural by-products into activated carbons would add considerable economic value, and help reduce the cost of waste disposal and most importantly provide a potentially inexpensive alternative to the existing commercial activated carbon (Demirbas, 2009). In other word, it could ultimately utilize the waste effectively into wealth. Therefore, in recent years, many researchers have been focusing on the production of activated carbon by using agricultural by-products such as corncob, hazelnut shell, olive stone, coconut shell, wood, bamboo, rice husk, coconut husk, and sugarcane bagasse.

Based on Rafatullah et al. (2010), the adsorption capacities are greatly depends upon the sources of raw materials used, the method of its preparation and treatment conditions such as the temperature and time of its activation. Different starting material and activation treatment process produces different quality, characteristics and properties of resulting activated carbon. Thus, the selection of starting material and activation treatment for production of activated carbon for its specific applications in industries are considered crucial.



## **2.8 Preparation of activated carbon**

Based on literature, there are several factors that would influence the adsorption performance of resulting activated carbon. Some of the factors include type of starting materials or precursors, methods used for the preparation of activated carbon and treatment conditions such as temperature and time of its activation. Although type of precursors is known to be the most important thing in influencing the quality, characteristics and properties of activated carbon, other factors like methods used for the preparation of activated carbon and treatment conditions also need to be consider as it also plays an important role in affecting the properties and quality of resulting activated carbon. Based on Ahmed (2016), the adsorption performance and pore characteristics of activated carbon are greatly depends on the physical and chemical properties of precursors as well as on the activation technique. In general, there are two different methods in the production of activated carbon. According to Kazmierczak-Razna et al. (2015), it can be either by physical activation or chemical activation. Both of these methods have its own advantages and disadvantages and are responsible in the production of good quality activated carbon. In physical activation, it is basically realised in two stage processes which are carbonization of precursors in neutral gas atmosphere followed by the activation by steam or carbon dioxide of the carbonized obtained. On the other hand, according to Yahya et al. (2015), chemical activation is usually realised in one stage process which are impregnation of precursors with an activating agent which then subjected to thermal treatment in neutral gas atmosphere.

### **2.8.1 Physical activation**

As mentioned, physical activation involved in two step processes; carbonization and activation of precursors. According to Yahya et al. (2015), it is basically referred to dry oxidation which involves the reaction between the samples and gaseous ( $\text{CO}_2$  and

air), steam or mixture of gaseous and steam at temperature reaching above 700°C. CO<sub>2</sub> gas has been commonly used due to its clean, easy to handle and the activation process can be easily controlled at temperature around 800°C due to its slow reaction rate (Ioannidou and Zabaniotou, 2007). In addition, a greater uniformity of pore also can be achieved with the activation of CO<sub>2</sub> as compared to steam. Based on Ioannidou and Zabaniotou (2007), carbonization temperature usually in the range between 400-850°C while activation temperature generally around 600°C -900°C. According to literature, the purpose of carbonization is to obtain charcoal from precursors. In other words, carbonization is carried out to reduce the volatile content of the precursors to convert the resulting char with higher content of fixed carbon for activation purpose (McDougall, 1991). It is reported that, through this carbonization process, it releases most of the non-carbon elements particularly hydrogen, oxygen and nitrogen in the form of gases and tars. It is also intended to create initial porosity in the char. According to Martinez et al. (2003), the porosity development in this treatment occurs through the selective elimination of the more reactive carbon of the structure. In general, carbonization is basically involved the pyrolytic decomposition of the precursor and non-carbon species elimination. The low molecular weight volatiles will be first released and followed by light aromatics and hydrogen gas which led to the production of fixed carbonaceous char (Yahya et al., 2015). This carbonaceous form is then activated by activation process. The purpose of activation is basically to develop further porosity and creating some ordering of the structure which results in a highly porous solid of the activated carbon.

### **2.8.2 Chemical activation**

Basically, chemical activation or also called as wet oxidation requires catalyst to be impregnated into the precursors and washed to produce the activated carbon

(Yahya et al., 2015). This activation process are usually involved a relatively low temperature range from 300-700°C and basically depends on the action of the inorganic additives to degrade and dehydrate the cellulosic materials found in the precursors (Bello and Ahmad, 2011). According to Yahya et al. (2015), activating agents basically act as dehydrating agents and oxidants which could influence the pyrolytic decomposition. It also could prevent the formation of the tar or ash hence developing the carbon yield. This process is then followed by the washing step. Through this step, it would remove the chemical components in the activated carbon by washing it with acid or alkali and followed by washing with water. Thus, the porosity of the resulting activated carbon is occupied by the chemicals in the carbon structure.

## **2.9 Heating techniques**

In addition to the type of precursors and preparation methods, the treatment conditions such as the temperature and time during activation are also one of the important parameter that can strongly affect the physical and chemical properties of activated carbon structure. Previously, it is common that the synthesis of activated carbon with the help of conventional heating. However, according to Kazmierczak-Razna et al. (2015), this method of heating has many disadvantages in term of non-uniform heating of the sample or the necessity to perform pyrolysis and activation in high temperature (>800°C). Thus, it led to the search for new, economical, and more effective methods for the synthesis of activated carbon. Recently, activation by microwave radiation in preparation of activated carbon has the potential to become a viable alternative for the conventional activation due to its several advantages like uniform interior heating, high heating rate, lower time, selective heating, no direct contact between the heating source and heated materials, reduced equipment size and