CHAPTER 1

INTRODUCTION

1.1 Background of Study

1.1.1 Water Crisis

Water is vital for all living things and it is an essential element of life. It is fundamental to maintain the integrity and sustainability of the earth’s ecosystem. However, the availability and accessibility to freshwater has been proved as one of the most severe case effected in recent years (Chun, 2010).

The UN environmental report GEO 2000 proclaims that “the world water cycle seems unlikely to be able to cope with the demands that will be made of it in the coming decades” where global water crisis express a full scale of emergency (Chun, 2010). Besides, World Wide Fund for Nature (WWF) also stresses on freshwater issue where freshwater is important to human health, agriculture, industry and natural ecosystems. However, freshwater is limited in many regions of the world (Chun, 2010). Based on 1st and 2nd United Nations World Water Development Reports, 6,000 people in which mainly children under the age of five are dying from water related diseases every day (Chun, 2010). Moreover, more than a billion people lack of safe drinking water (Chun, 2010). These scenario will become more serious unless effective and correct actions are taken. To make matter worst, the limited supply of freshwater has been seriously threatened with constant discharge of pollutant which include release of industrial effluent from textile industries.
1.1.2 Usage of Dyes in Industry

High level production and usage of dyes worldwide generate coloured water that cause environmental concern. Industries such as textile company, paper and pulp mills, dye manufacturing industries, food companies, electroplating factories and distilleries produced and discharged coloured effluent (Xing et al., 2010). Easton (1995), quoted by Pignon (2006) estimated the industries consume more than 100 tons per year of dyes. It is 90% of the 3,000 compounds registered in the “Colour Index”. Previous study reported approximately 280,000 tons of textile dyes were discharged into the environment per year. Consequently, most of the textile dyes remained in marine ecosystem (Shertate and Thorat, 2013). Table 1.1 shows the loss of dye as effluent after dyeing process for different dye-fiber systems.

Table 1.1: Dye loss as effluent for different dye-fiber systems (Shertate and Thorat, 2013; Chun, 2010).

<table>
<thead>
<tr>
<th>Dye Class</th>
<th>Fiber</th>
<th>Loss as effluent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>Polyamide</td>
<td>5-20</td>
</tr>
<tr>
<td>Basic</td>
<td>Acrylic</td>
<td>0-5</td>
</tr>
<tr>
<td>Direct</td>
<td>Cotton</td>
<td>5-30</td>
</tr>
<tr>
<td>Disperse</td>
<td>Polyester</td>
<td>0-10</td>
</tr>
<tr>
<td>Metal-complex</td>
<td>Wool</td>
<td>2-10</td>
</tr>
<tr>
<td>Reactive</td>
<td>Cotton</td>
<td>10-50</td>
</tr>
<tr>
<td>Vat</td>
<td>Cotton</td>
<td>5-20</td>
</tr>
<tr>
<td>Sulfur</td>
<td>Cellulose</td>
<td>10-40</td>
</tr>
</tbody>
</table>
Malaysian textile and apparel industries has accelerated with about 900 companies throughout the country which employ more than 68,000 workers (Mitchell, 2006). In Malaysia, this industry contributes approximately 2.3% to the country’s total exports of manufactured goods and was the 10th largest export earner in 2011 (Malaysia Investment Development Authority, 2012).

1.1.3 Environmental Impacts of Dyes

The discharged of coloured effluent impose negative result for both toxicological and esthetical reasons. Aquatic communities are impacted upon dyes effluent release as many dyes are toxic. It also impedes light penetration which upset the biological cycle within the stream and decrease the aesthetic value of the environment. Dyes are recalcitrant organic molecules which are resistant to aerobic digestion and stable to light, heat and oxidizing agents (Chun, 2010). The presence of dyes will light penetration in water which can affect photosynthesis process and hamper aquatic life ecosystem. Besides, breakdown of dye’s products might be toxic to some aquatic organisms (Pathiraja, 2014).

Numerous dyes are noticeable in water at concentration as low as 1 mg/L and textile effluent usually contain 10 – 200 mg/L of dye (Pathiraja, 2014). Dyes which are chemically and photolytically stable are highly persistent in natural environment. These two characteristics can cause bioaccumulation of toxic in which may eventually affect human through food chain (Pathiraja, 2014). Hence, it is very crucial to remove dyes from water system.
1.1.4 Methods of Dye Removal

There are a lot of treatment methods available in order to overcome pollution caused by dye effluent, which includes photocatalytic degradation (Sohrabi and Ghavami, 2008 and Sleiman et al., 2007), sonochemical degradation (Abbasi and Asl, 2008), micellar enhanced ultra-filtration (Zaghbani et al., 2008), cation exchange membranes (Wu et al., 2008), electrochemical degradation (Fan et al., 2008), integrated chemical-biological degradation (Sudarjanto et al., 2006), absorption (Argun, 2010 and Argun and Dursun, 2008) and others. Chemical, biological and physical methods for dye removal are discussed in detail as below.

1.1.4.1 Chemical Methods

Breakdown of bonds which aid in decolorization and degradation of dyes is the basic step in removing color and toxicity of dyes. Examples of some chemical methods are coagulation, electro-kinetic coagulation, flocculation combined with floatation, electro-flocculation, electrochemical destruction, irradiation, precipitation, oxidation, ozonation and katox treatment (Pathiraja, 2014). However, these techniques can caused secondary pollution as they will generate a huge amount of sludge at the end of the process and creates environmental problems. Moreover, chemical methods will involve high cost, limited versatility, low efficiency and utilize a significant amount of energy. Toxic derivatives such as primary aromatic amines and heavy metals may still present in treated liquor even after the colors are removed by chemical method.

1.1.4.2 Biological Methods

Biological methods are relatively inexpensive through the use of microorganisms to remove synthetic dyes. The end products of biological methods are fully mineralized through the process of biodegradation (Shertate and Thorat, 2013). The disadvantages
of this method is that they are less flexible in design and operation as they require a large land area and microorganisms are sensitive towards variants. Besides, some of the dyes are resistant to aerobic digestion. The usage of activated sludge for biological treatments do not effectively remove color as the oxidation rate is too low but it can reduce the BOD of the waste water (Pathiraja, 2014).

1.1.4.3 Physical Methods

Filtration, ion-exchange, membrane filtration and adsorption are some of the example of physical methods for dye removal. Membrane use in filtration need to replace consistently and thus costly with limited life time. The membrane also prone to pore clogging problem. The ion-exchange method enable the solvent to be reclaimed after used with no loss of adsorbent on regeneration. However, this method is not widely used for dye removal treatment as it is not effective in removing all dyes. Unlike the others, adsorption method can remove complete molecules without leaving fragments in wastewater. It is very effective and low in cost (Dotto et al., 2012).

Activation method by using activated carbon is an effective and commercially applicable method to remove dyes in effluent. However, it’s wide usage is restricted by the high cost (Xing et al., 2010). Adsorption method is selected for this study to remove basic dyes as it is considered more effective and less expensive as compared to other technologies. It is also well known for its flexibility and simplicity of design, insensitivity to toxic pollutants and the ease of operation (Deans and Dixon, 1992). The most important factor of choosing this method is that it will not produce harmful substances during and after the treatment (Deans and Dixon, 1992).
In recent years, many efforts have been made to study the removal of dye via adsorption using agricultural wastes. Natural materials have potential as low cost adsorbent as they are available in large quantities and environmental friendly. In this study, kenaf, sugarcane bagasse and banana stem were selected to determine their adsorption capability on wastewater of textile industry.

1.2 Problem Statement

Textile industry is very famous in Malaysia. This industry produces wastewater that will contribute to water pollution. Dye removal from textile effluents has been given much attention in the last few years as dye can pose hazards to the environment with the presence of a large number of contaminants, such as toxic organic residues, acids, bases and inorganic contaminants (Ozacar and Sengil, 2003). Some of the dyes were made from hazardous chemicals such as benzidine and metals which are carcinogenic and mutagenic to all form of life (Ozacar and Sengil, 2003).

Dye effluent from textile industries will interfere the transmission of sunlight which will reduce the photosynthetic activity of aquatic life and also affects the aesthetic beauty. This will disturbed the natural equilibrium and affect the aquatic food chain and aquatic life (Hasnain et al., 2007).

Most of the chemical and physical methods used to determine absorbent efficiency are simple in design but the high cost is a disadvantage (Hasnain et al., 2007). Therefore, utilization of agriculture wastes namely kenaf, sugarcane bagasse and banana stem as cheap substitutes can provide a good alternative. These wastes are relatively inexpensive and their reasonable adsorption capacity can be used to remove pollutants such as dye from wastewater effluent.
With this study, it will reduce the pollution intensity of wastewater from textile industry and also identified ‘reuse’ strategy for agricultural waste of which if not utilized will be send off to landfill for disposal.

1.3 Significant of Study

The result of this research is useful due to the following reasons:

1. It can help the textile industry especially those dealing with dye effluent to treat wastewater more efficiently. Dye in wastewater contains high concentration of pollutants. Due to the low cost of agro-wastes such as kenaf, sugarcane bagasse and banana stem, they can be used as an alternative adsorbent to replace existing commercial adsorbents.

2. This study can give contribution to the existing data on wastewater treatment especially in dye adsorption for future research. Adsorbent is very useful as it can remove the dye from the textile.

3. This research can input useful information on the reuse of agricultural wastes as effective agro-wastes dye adsorbent on related industries.

1.4 Objectives of Study

There are four objectives of this study, which include:

1. To study the adsorption capacity of kenaf, sugarcane bagasse and banana stem.

2. To determine the optimal parameters for efficient dye removal, isotherms and thermodynamics.

3. To calculate and compare the cost of each treatment in determining the most cost-effective application.

4. To determine the calorific value of the absorbent used.
CHAPTER 2

LITERATURE REVIEW

2.1 Textile Industry in Malaysia

According to Malaysia Industrial Development Authority (MIDA), textile industry has become the seventh largest contributor of export earnings in manufacturing sector in Malaysia. Malaysia External Trade Development Corporation (Matrade) states that Malaysia produced good quality goods and products include fibers, man-made and natural fiber yarns, woven cotton and man-made fiber fabrics, textile fabrics and related products (Mitchell, 2006).

Malaysian textile industry is very well known for a broad range of activities including polymerization and man-made fiber production, spinning, weaving, knitting, texturizing, dyeing, and printing. Made-up apparel and other textile goods such as home textiles, ropes and carpets, as well as, nonwoven fabrics for personal care, construction, and engineering and furniture applications are also manufactured by most of the Malaysian companies (Mitchell, 2006).

Textile and apparel industry has been foreseen by Third Industrial Master Plan with high forecast of annual growth export of 7.80 % per annum (Lee et al., 2014). Department of Statistics Malaysia has identified that textile and apparel industry in manufacturing sector in year 2012 has contributed 1.70 % to the growth of Gross Domestic Product (GDP) (Department of Statistics Malaysia, 2013). Malaysia’s textile and apparel sector has vast experience as a producer of world known brands such as Brooks Brothers, Ralph, Kohl’s, Calvin Klein, Alain Delon, Gucci, Polo, Lauren,
Adidas, Nike, Yves St. Laurent, Walt Disney, Reebok, Puma, GAP, Oshkosh, Burberry, Ashworth, etc. (Seong, 2007). Most of the imported markets of Malaysian made textile and apparel are China, Taiwan and Japan while major exported countries are Canada, United States, Turkey and Europe (Seong, 2007). Table 2.1 illustrates Malaysian made textile and apparel.

Table 2.1: Malaysian made textile and apparel.

<table>
<thead>
<tr>
<th>Textiles</th>
<th>Apparels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibres</td>
<td>Overcoats</td>
</tr>
<tr>
<td>Yarns (Cotton yarn, CVC yarn, polyester/cotton yarn, polyester/rayon</td>
<td>Skirts</td>
</tr>
<tr>
<td>yarn, spun polyester yarn, texturized nylon yarn, polyester filament</td>
<td></td>
</tr>
<tr>
<td>yarn, acrylic yarn, acrylic/wool blended yarn, worsted and woolen</td>
<td></td>
</tr>
<tr>
<td>yarn, cotton coarse yarn)</td>
<td></td>
</tr>
<tr>
<td>Special yarns, textile fabrics and related products</td>
<td></td>
</tr>
<tr>
<td>Woven cotton fabrics</td>
<td>T-shirts</td>
</tr>
<tr>
<td>Fabrics woven of man-made textile materials</td>
<td>Blouses</td>
</tr>
<tr>
<td>Knitted or crocheted fabrics</td>
<td>Pants undergarments</td>
</tr>
<tr>
<td>Tulles, lace, embroidery, ribbons, trimmings and other small wares</td>
<td>Scarves</td>
</tr>
<tr>
<td>Floor coverings (carpets and rugs)</td>
<td>Handkerchiefs</td>
</tr>
<tr>
<td>Home textiles (bed linen, table linin, towels)</td>
<td>Textile accessories</td>
</tr>
<tr>
<td>Industrial textiles (ropes, cords, car seat fabrics, geo-textiles, dye</td>
<td></td>
</tr>
<tr>
<td>and narrow fabric.</td>
<td></td>
</tr>
</tbody>
</table>

There are an approximately 1,500 textile factories in Malaysia. High concentration of textile projects is mainly found in the southern region namely Johor. The textile city in Malaysia which is Batu Pahat in Johor locates a total of 40% operating textile factories particularly the wet processing plants. There are 15 out of 40 wet processing plants in
Malaysia situated in Batu Pahat (Malaysian Knitting Manufacturers Association, 1998). The amount of exports of textiles and apparel had increased year to year. Table 2.2 shows Malaysian exports of textiles and apparel by years (Malaysian Knitting Manufacturers Association, 2014).

Table 2.2: Malaysian exports of textiles and apparel by years (Malaysian Knitting Manufacturers Association, 2014).

<table>
<thead>
<tr>
<th>Year</th>
<th>Textiles (RM Billion)</th>
<th>Apparel (RM Billion)</th>
<th>Total (RM Billion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1996</td>
<td>3.7</td>
<td>3.3</td>
<td>7.0</td>
</tr>
<tr>
<td>1997</td>
<td>4.0</td>
<td>3.6</td>
<td>7.6</td>
</tr>
<tr>
<td>1998</td>
<td>4.7</td>
<td>4.9</td>
<td>9.6</td>
</tr>
<tr>
<td>1999</td>
<td>4.6</td>
<td>4.9</td>
<td>9.5</td>
</tr>
<tr>
<td>2000</td>
<td>5.1</td>
<td>5.3</td>
<td>10.4</td>
</tr>
<tr>
<td>2001</td>
<td>4.3</td>
<td>4.7</td>
<td>9.0</td>
</tr>
<tr>
<td>2002</td>
<td>4.1</td>
<td>4.5</td>
<td>8.6</td>
</tr>
<tr>
<td>2003</td>
<td>4.2</td>
<td>4.3</td>
<td>8.5</td>
</tr>
<tr>
<td>2004</td>
<td>5.0</td>
<td>4.6</td>
<td>9.6</td>
</tr>
<tr>
<td>2005</td>
<td>5.6</td>
<td>4.7</td>
<td>10.3</td>
</tr>
<tr>
<td>2006</td>
<td>6.1</td>
<td>4.8</td>
<td>10.9</td>
</tr>
<tr>
<td>2007</td>
<td>5.5</td>
<td>4.8</td>
<td>10.3</td>
</tr>
<tr>
<td>2008</td>
<td>5.4</td>
<td>5.1</td>
<td>10.5</td>
</tr>
<tr>
<td>2009</td>
<td>5.1</td>
<td>3.8</td>
<td>8.933</td>
</tr>
<tr>
<td>2010</td>
<td>5.76</td>
<td>3.565</td>
<td>9.325</td>
</tr>
<tr>
<td>2011</td>
<td>6.72</td>
<td>4.09</td>
<td>10.81</td>
</tr>
<tr>
<td>2012</td>
<td>5.98</td>
<td>3.48</td>
<td>9.46</td>
</tr>
<tr>
<td>2013</td>
<td>6.35</td>
<td>3.91</td>
<td>10.25</td>
</tr>
<tr>
<td>2014</td>
<td>6.455</td>
<td>4.57</td>
<td>11.025</td>
</tr>
</tbody>
</table>

According to MATRADE (2013), Malaysian Knitting Manufacturers Association (MKMA), Malaysian Textile Manufacturers Association (MTMA) and Malaysian
Garment Manufacturers Association (MGMA) are three main textile and apparel industry associations in Malaysia. There are a vast range of activities that involved textile and apparel industry. The structure of Malaysian textile and apparel industry is separated into two major sectors which is upstream and downstream by MATRADE (Lee et al., 2014). At the earlier stage, upstream comprises of activities before the manufacturing of textile and apparel, for example, fibre, yarn, fabric, wet, spinning, knitting, weaving, dying, printing, silk screening and embroidery processing activities. On the other hand, downstream includes activities after the manufacturing of apparel, textile products, home textiles and clothing accessories (Lee et al., 2014).

One of the main pollution source of textile wastewater in Malaysia is produced from batik industry during dyeing processes. Treatment and removal are hard and difficult to achieve for waste water through processing (Mobarekeh, 2007). There are several batik industries in Selangor which produce and pollute the nearby water sources.

### 2.2 Environmental Aspects

Industrial sectors can pollute the environment through many ways. A large volume of hazardous effluent are usually generated by industrial activity. Dye stuff manufacturing, dyeing and textile industries discharged wastewater containing a variety of dyes into water bodies. The presence of dyes in water will reduce the light penetration, precluding the photosynthesis of aqueous flora (Paven et al., 2007). Some dyes can cause health problem such as allergy, dermatitis, skin irritation and cancer to human and being mutagenic (Paven et al., 2007).

Incomplete degradation of bacteria will produce toxic amines if dyes are broken down in sediment (Hamdaoui, 2006). Besides, formation of toxic carcinogens is a huge
problem when dyes laden wastewater is directly discharged into the municipal wastewater plants and environment (Hamdaoui, 2006). Table 2.3 shows the processes that produced specific pollutants into our environment.

Table 2.3: Specific pollutants from textile wet processing operations (Eglia, 2007).

<table>
<thead>
<tr>
<th>Process</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desizing</td>
<td>Sizes, enzymes, starch, waxes, ammonia</td>
</tr>
<tr>
<td>Scouring</td>
<td>Disinfectants and insecticides residues, NaOH, surfactant, soaps, fats, waxes, pectin, oils, sizes, anti-static agents, spent solvents, enzymes</td>
</tr>
<tr>
<td>Bleaching</td>
<td>H$_2$O$_2$, AOX, sodium silicate or organic stabilizer, high Ph</td>
</tr>
<tr>
<td>Mercerizing</td>
<td>High pH, NaOH</td>
</tr>
<tr>
<td>Dyeing</td>
<td>Color, metals, salts, surfactants, sulphide, acidity/alkalinity, formaldehyde</td>
</tr>
<tr>
<td>Printing</td>
<td>Urea, solvents, colour, metals</td>
</tr>
<tr>
<td>Finishing</td>
<td>Resins, waxes, chlorinated compounds, acetate, stearate, spent solvent and softner</td>
</tr>
</tbody>
</table>

Demand in searching for cheaper method of pollutant removal is initiated with the increase in pollution monitoring, controlling and elimination cost. Hence, an economical way of dye removal is more preferable in which sorption process come out to be an effective and attractive treatment process. Sorption process is easy to operate with simple design, less investment in both initial cost and land required, and no consequences of toxic substances and superior removal of organic waste materials (Lee, 2009).
2.3 Wastewater Treatment in Textile Industry

Textile industries have been investigating to find alternatives to reduce harmful substances for mutagenic, carcinogenic and allergic effects of textile chemicals and dyes. There are a large numbers of technologies invented to remove contaminants in effluent (Pereira and Alves, 2012).

Textile wastes can be divided into hard to treat, high dispersible, hazardous and toxic, and large volume waste (Karmakar, 1999). Selection of appropriate treatment method is crucial to overcome the problems caused by textile discharges. The treatment method chosen will based on factors related to effluent characteristics, including relative costs, level of treatment required and site restriction (Karmakar, 1999).

There are three stages of wastewater treatment in textile industry; primary, secondary and tertiary treatment. Primary treatment consists of physical treatment (equalization, screening and settling) and chemical treatment (neutralization, lime addition, alum addition and iron salt addition). Biological treatment (activated sludge, extended aeration, lagoons) and physical/chemical treatment (powdered activated carbon addition to biological process) are involved in secondary treatment while in tertiary treatment, physical treatment (secondary clarification, mixed media filtration, granular activated carbon, powdered activated carbon) and chemical treatment (ozonation and chlorination) are involved (Lim, 2011).
2.4 Colorant

Colorants tend to be coloured as they have a characteristic to absorb visible light from 400 to 700 nm. Colorant can be divided into natural organic and inorganic. Although colorants has been used since prehistoric times, the discovery of mauve in 1865 by Perkin which initiated the synthetic dye industry (Yasmin, 2004).

Colorant can be either dyes or pigment. An ideal characteristic of pigments is that they are practically insoluble in the media where they are applied. An additional compound need to be added to the attached pigment particles such as by a polymer in paint, in a plastic or in a melt. However, dyes are only applicable to various substrates from a liquid where they are completely or partially soluble and required to possess specific affinity to the substrate for which they are used (Yasmin, 2004).

2.5 Dye

Dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries used dye for a long period of time. The effluent being discharged by these manufacturing and processing industries will pose certain hazards and environmental problems (Pearce, 2003). Dye is a type of colorants which provide a color to the substrate either in the form of aqueous solutions, non-aqueous solution or aqueous suspension. It can be defined by various configurations of unsaturated groups called chromophore groups (Lam, 2005). Chromophore groups is responsible in adsorbing the light of a specific wavelength within the visible light spectrum which results in variety of color that a dye exhibits (Lam, 2005). Figure 2.1 shows some examples of chromophore groups.
According to Pearce (2003), textile industry uses dyes and pigments to colour their products and there are more than 100,000 commercially available dyes with over $7\times10^5$ tonnes of dye stuff which are produced annually. Dye is stable and difficult to biodegrade as it has complex aromatic molecular structures. In addition, dyes are harmful to some microorganisms and may cause direct destruction or inhibition in the catalytic capabilities (Pearce, 2003). Direct dye, reactive dye, acid dye and basic dye are dyes that are used in textile industries where all of them may cause acute disease since they are considered as toxicants and carcinogen. It is found that dyes can cause numeral negative impacts in water through several ways:

- Acute or chronic effect on organisms depends on the dye concentration and exposure time.
- Abnormal coloration of subsurface waters as dyes are highly visible.
- Dramatic effect on bacteria’s growth and influence on their biological activity as dyes can be absorb or reflect sunlight entering the water.
- Dyes are difficult to treat as they have many different and complicated molecular structures.
- Dyes destroy aquatic life as dyes in wastewater undergo chemical and biological changes and consume dissolved oxygen in stream.
2.6 Classification of Dyes

Today, many new types of dyes have been developed and put into regular use with the invention of synthetic materials used in textiles. Dyes and pigments are two basic methods to color textiles. Pigments are resins which mechanically bound to fibers. Dyeing is most conventionally and commonly used colorization technique.

Dyes can be classified in several ways. Color Index is one of the well-known system of classification that being used internationally. Color Index is devised by the Society of Dyers and Colorists in year of 1924 (Chun, 2010). Dyes can be divided into acid dyes, premetalized acid dyes, chrome dyes (mordant dyes), cationic dyes (basic dyes), direct dyes (substantive dyes), direct developed dyes, disperse dyes, napththol dyes, reactive dyes, sulfur dyes, and vat dyes according to the types of fibers they are most compatible with (Price et al., 2005).

2.6.1 Acid Dyes

Acid dyes are most suitable for protein fibers, nylon spandex and special type acid dyeable acrylic fibers. Acid dyes can give bright colors with fabulous fastness, ability to stay on the fabric and not to fade and to dry cleaning (Price et al., 2005).

2.6.2 Premetalized Acid Dyes

Some types of fibers are used for both premetalized acid dyes and chrome dyes. Premetalized acid dyes are less bright with better fastness to light and sweat whereas chrome dyes are dull and have excellent fastness to light, washing and perspiration. Both dyes are good for wool and carpets (Price et al., 2005).
2.6.3 Mordant Dyes (Chrome Dyes)

Mordant is a chemical that have affinity for both fiber and dye. It produces dye-mordant-fiber complex and enhances affinity. Mordants are metal salts and are electrically cationic. All mordant dyes are acid dyes but the reverse is false. Mordant dyes improve fastness, promote dye-metal complex formation and boost acid dye uptake due to cationic nature of chromium salts. Mordant dyeing methods are very useful in cottage industries to dye wool with superior wash fastness (Clark, 2011).

2.6.4 Cationic Dyes (Basic Dyes)

Cationic dyes are used for acrylic, modacrylic, cationic dyeable polyester, cationic dyeable nylon, cellulosic, and protein fibers which produce bright colors with bright colors that have excellent fastness to light, laundering, perspiration, and crocking on synthetics fibers (Price et al., 2005). Example of cationic dyes are Methylene Blue, Malachite Green, Gentian Violet and etc.

2.6.4.1 Methylene Blue

The IUPAC name of methylene blue (MB) is 3,7-bis(Dimethylamino)- phenothiazin-5-i um chloride. Methylene blue is a basic aniline dye with a chemical formula of $\text{CH}_1\text{N}_3\text{SCl}$. It is a cationic thiazine dye which shows deep blue color in oxidized state but colorless in reduced form, leukomethylene blue (LMB) (Cragan, 1999). It inhibits guanylate cyclase and has been used to treat cyanide poisoning and to lower levels of methemoglobin. Methylene blue can be used as a bacteriologic stain and as an indicator. It is also used in coloring paper, temporary hair coloring, dyeing cotton and wools, and coloring of paper stocks (Han, 2007). Methylene blue will dissociate in aqueous solution into methylene blue cation and chloride ion. The serious consequences from methylene blue contamination to human and the environment urge the need to remove
methylene blue from any wastewater (Altaher et al., 2011). The cation $C_{16}H_{18}N_3S^+$ is present in the methylene blue structure. The closest ion to the methyl group which is the chloride ion suggests a distribution of charge between the terminals of amine group to form a stable structure of methylene blue (Cragan, 1999). Figure 2.2 shows the structure of methylene blue.

![Structure of methylene blue](image)

Figure 2.2: Structure of methylene blue (Cragan, 1999).

### 2.6.5 Direct Dyes (Substantive Dyes)

Direct dyes are generally used on cellulosic fibers. They are excellent fastness to perspiration and dry cleaning. Direct developed dyes are good as fastness to laundering. They can apply on same cellulosic fibers (Price et al., 2005).

### 2.6.6 Disperse Dyes

Disperse dyes can be used for acetate, acrylic, modacrylic, nylon, polyester, and olefin fibers. The wash fastness with disperse dyes differ with the types of fibers used. It is good on polyester but poor on acetate. Disperse dyes are good in fastness for perspiration, crocking, and dry-cleaning (Price et al., 2005).
2.6.7 Naphthol Dyes

Naphthol dyes create bright shades of color with varying fastness to light for cellulosic fibers. They have good fastness to washing and perspiration (Price et al., 2005).

2.6.8 Reactive Dyes

Reactive dyes are employed for cellulosic fibers but occasionally on protein fibers and nylon as well. They can give bright shades with excellent fastness in all areas but they are difficult to match shades (Price et al., 2005).

2.6.9 Sulfur Dyes

Sulfur dyes are utilized for cellulosic fibers and create dull shades such as navy, black, and brown. They are weak when exposed to chlorine but excellent fastness in most area (Price et al., 2005).

2.6.10 Vat Dyes

Vat dyes if not properly applied may crock. Vat dyes have fabulous fastness in all areas especially to chlorine and bleach. They are used on cellulosics material (Price et al., 2005).

Color Index will divides dyes by referring each dye a generic name determined by its application characteristics. Then, a Color Index constitution number will be refer to the dyes based on its chemical structure if known (Lam, 2005). Dye classes, substrates, method of application and chemical types are summarized in Table 2.4.
<table>
<thead>
<tr>
<th>Classes of dye</th>
<th>Substrates</th>
<th>Method of application</th>
<th>Chemical types</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>Nylon, wool, silk, paper, inks and leather</td>
<td>Usually from neutral to acidic dye baths</td>
<td>Azo including premetalized anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso</td>
</tr>
<tr>
<td>Azoic components and compositions</td>
<td>Cotton, rayon, cellulose acetate and polyester</td>
<td>Fiber impregnated with coupling component and treated with a solution of stabilized diazonium salt</td>
<td>Azo</td>
</tr>
<tr>
<td>Basic</td>
<td>Paper, polyacrylonitrile-modified nylon, polyester and inks</td>
<td>Applied from acidic dye baths</td>
<td>Diazacarbocyanine, cyanine, hemicyanine, diazahemicyanine, azo, azine, xanthene, acridine, oxazine and anthraquinone</td>
</tr>
<tr>
<td>Direct</td>
<td>Cotton, rayon, paper, leather and nylon</td>
<td>Applied from neutral or slightly alkaline baths containing additional electrolyte</td>
<td>Azo, phtalocyanine, stilbene and oxazine</td>
</tr>
<tr>
<td>Disperse</td>
<td>Polyester, polyamide, acetate, acrylic and plastics</td>
<td>Fine aqueous dispersions often applied by high temperature-pressure or lower temperature carrier methods; dye may be padded on cloth and baked on or thermofixed</td>
<td>Azo, anthraquinone, styril, nitro and benzodifuranone</td>
</tr>
<tr>
<td>Fluorescent brighteners</td>
<td>Soap and detergents, all fibers, oils, paints and plastics</td>
<td>From solution, dispersion or suspension in a mass</td>
<td>Stilbene, pryrazoles, coumarin and naphthalimides</td>
</tr>
<tr>
<td>Food, drug and cosmetic</td>
<td>Foods, drugs and cosmetics</td>
<td></td>
<td>Azo, anthraquinone, carotenoid and triarylmethane</td>
</tr>
<tr>
<td>Mordant</td>
<td>Wool, leather and anodized</td>
<td>Applied in conjunction with cleaning Cr salts</td>
<td>Azo and anthraquinone</td>
</tr>
<tr>
<td>Natural</td>
<td>Food</td>
<td>Applied as mordant, vat, solvent or direct and acid dyes</td>
<td>Anthraquinone, flavonols, flavones, indigoids, chroman</td>
</tr>
<tr>
<td>Oxidation bases</td>
<td>Hair, fur and cotton</td>
<td>Aromatic amines and phenols oxidized on the substrate</td>
<td>Aniline black and indeterminate structure</td>
</tr>
</tbody>
</table>
Table 2.4: Application classes of dyes and their chemical types (Chun, 2010) (Continued).

<table>
<thead>
<tr>
<th>Class</th>
<th>Application</th>
<th>Application characteristics</th>
<th>Chemical types</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactive</td>
<td>Cotton, wool, silk and nylon</td>
<td>Reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline)</td>
<td>Azo, anthraquinone, phthalocyanine, formazan, oxazine and basic</td>
</tr>
<tr>
<td>Solvent</td>
<td>Plastics, gasoline, varnish, lacquer, stains, inks, fats, oils and waxes</td>
<td>Dissolution in the substrate</td>
<td>Azo, triphenylmethane, anthraquinone and phthalocyanine</td>
</tr>
<tr>
<td>Sulfur</td>
<td>Cotton and rayon</td>
<td>Aromatic substrate vatted with sodium sulfide and re-oxidized to insoluble sulfur containing products on fiber</td>
<td>Indeterminate structure</td>
</tr>
<tr>
<td>Vat</td>
<td>Cotton, rayon and wool</td>
<td>Water insoluble dyes solubilized by reducing with sodium hydrosulfite, then exhausted on fiber and re-oxidized</td>
<td>Anthraquinone (including polycyclic quinones) and indigoids</td>
</tr>
<tr>
<td>Pigments</td>
<td>Paints, inks, plastics and textiles</td>
<td>Printing on the fiber with resin binder or dispersion in the mass</td>
<td>Azo, basic, phthalocyanine, quinacridone and indigoid</td>
</tr>
</tbody>
</table>

2.7 Existing Approaches of Dye Removal

Many conventional methods in treating dye effluent is not widely applied and practiced in a large scale in paper and textile industry due to its high cost ad disposal problem. They aim to treat effluent or waste stream so it would be suitable and environmental friendly for reuse. Physical and chemical treatments are more favorable in treating industrial effluent as industrial wastewater often consist of pollutants that cannot be removed efficiently by microorganism (Lee, 2009).
2.7.1 Biodegradation

Biodegradation is the most cost effective treatment as compared to other physical and chemical processes. Examples of biodegradation methods are fungal decolourization, microbial degradation, adsorption by living or dead microbial biomass and bioremediation system. Microorganisms such as bacteria, fungi, yeasts and algae are capable to accumulate and degrade different pollutants (Lee, 2006).

Biological treatment are often restricted due to its technical constraints. Some of the organic molecules are recalcitrant because of their complex chemical structure and synthetic organic origin. Besides, this technique uses a large land area and it is restricted by sensitivity toward diurnal variation with the toxicity of some chemicals and less flexibility in design and operation (Crini, 2006).

2.7.2 Coagulation – Flocculation

Coagulation transform finely divided suspension of solid into larger particles to enable settling process (Lee, 2006). Further collisions between the particles formed by coagulation by mixing process which results in the formation of relatively large particles that can be removed easily. It is termed as flocculation (Binnie et al., 2002).

Coagulation happens quickly while flocculation is the term applied indicating a longer process of forming larger particles via the process of coagulation. Coagulant is a chemical that is dosed to cause particles to coagulate (Binnie et al., 2002). Alum, ferric chloride, ferric sulfate, sodium aluminate and various cationic polymers are common coagulants used in conventional water treatment (Pizzi, 2011). Figure 2.3 showed the physical-chemical process involved in coagulation-flocculation.
2.7.3 Adsorption by Activated Carbon

Activated carbon is defined as amorphous carbon-based materials that have an extended interparticulate surface area and high degree of porosity (Bansal and Goyal, 2005). Activated carbon are used widely in many areas especially in the environmental field. Liquid phase applications include purification in the clothing, textile, pharmaceutical industries, food processing, preparation of alcoholic beverages, decolourization of oils and fats, product purification in sugar refining, purification of chemicals (acids, amines, glycerine, glycol, etc.), enzyme purification, decaffeination of coffee, gold recovery, refining liquid fuels, purification of electroplating operations, personal care, cosmetics and application in the chemical and petrochemical industries (Cecen and Aktas, 2011). Among the gas phase applications are recovery of organic solvents, removal of sulphur-containing toxic components from exhaust gases and recovery of sulphur, biogas purification, use in gas masks and others (Cecen and Aktas, 2011). It also contributes in medical and veterinary application, soil improvement, removal of pesticide residues and nuclear and vacuum technologies (Cecen and Aktas, 2011).
Activated carbon can be produced from combustion, partial combustion or thermal decomposition of a number of carbonaceous substances. It can be obtained in granular and powdered forms. Nowadays, they are created in spherical, fibrous and cloth forms for some special applications (Bansal and Goyal, 2005). Granular form of activated carbon possessed larger internal surface area and smaller pores, and the finely divided powdered form come with large pore diameters and a smaller internal surface area. Activated carbon fibres and carbon cloth contain comparatively high coverage of larger pores and have a larger surface area (Bansal and Goyal, 2005).

Adsorption of activated carbon is generally applied in industrial wastewater treatment plant to comply stringent regulations for effluent discharged to receiving water. Activated carbon adsorption can apply as a separate unit process (Bansal and Goyal, 2005). It can be installed after several physiochemical treatment steps, for example, coagulation/clarification, filtration and dissolved air flotation. Another preference is to place activated carbon adsorption prior to biological treatment (Cecen and Aktas, 2011). Almost 300,000 tons/year (nearly 80%) of the total active carbon is consumed for liquid-phase applications and about 20% of the total production of active carbon is used in gas phase application (Bansal and Goyal, 2005). Figure 2.4 showed the different forms of activated carbon.
2.7.4 Ozone Treatment

Ozone is an excellent oxidizing agent (oxidizing potential, 2.07) as compared to chlorine (oxidation potential, 1.36) and H$_2$O$_2$ (oxidizing potential, 1.78) which pioneered used in early of 1970s. Oxidation by ozone can degrade chlorinated hydrocarbons, phenols, pesticides and aromatic hydrocarbons. Total colour and residual COD with no residue or sludge formation and no toxic metabolites are the two variables that should to be considered on deciding the amount of dosage of ozone required to be applied to the dye containing effluent. This method favours double bonded dye molecules. One of the significant advantages of this treatment method is that ozone can be applied in gaseous state and hence it does not raise the volume of wastewater and sludge (Robinson et al., 2001).
Chromophore groups in the dyes are basically organic compounds with conjugated double bonds that can be broken down into smaller molecules in which reduce in colouration. Carcinogenic or toxic properties of these smaller molecules might increase and therefore, ozonation may be used alongside a physical method to hamper this (Robinson et al., 2001). Decolouration can occur in a relatively short time (Robinson et al., 2001).

The detriment of having ozone treatment is its short half-life (typically being 20 minutes) (Robinson et al., 2001). With the present of dye, the time will be further shortened as the stability is affected by the presence of salts, pH and temperature (Robinson et al., 2001). Ozone depletion will accelerate in alkaline conditions, thus, careful monitoring of the effluent pH is a compulsory (Robinson et al., 2001). Irradiation or a membrane filtration technique can be improvised to improve the result (Robinson et al., 2001). Ozone treatment requires an extensive high cost as continuous ozonation is required due to its short half-life (Robinson et al., 2001). Figure 2.5 showed an ozone treatment process.

![Diagram of Ozone Treatment Process](image)

**Figure 2.5: Ozone treatment process.**
2.7.5 Electrochemical Processes

This technique is developed in mid 1990s. It has been proved to be an effective method for dye removal as it required little or no chemicals and no sludge formation. This technique proves to have no hazardous breakdown metabolites leaving the treated wastewater safe to be released back into the water body. It is an economically feasible method with high efficiency in removing and degrading dyes of recalcitrant pollutants. The cost of electricity used is comparable to the price of the chemicals (Robinson et al., 2001). The relatively high flow rates cause a direct decrease in dye removal (Robinson et al., 2001).

2.7.6 Reverse Osmosis

Reverse osmosis (RO) is a membrane-based demineralization technique. The main function of reverse osmosis is to isolate dissolved solids such as ions from aqueous solution. Membrane is used in this technique worked as a permeable selective barrier that enable some species to selectively permeate through and selectively retaining other dissolved species (Kucera, 2011). Reverse osmosis is believed to remove hardness, colour, many kinds of bacteria and viruses, and organic contaminants (Abid et al., 2012). Nataraj et al. (2009) and Abid et al. (2012) had successfully proved that reverse osmosis can efficiently remove dye substances from water body. The water produced by reverse osmosis can be recycled since it is close to pure water (Gupta and Suhas, 2009). Figure 2.6 illustrated the key components in reverse osmosis membrane.
2.7.7 Nanofiltration

Nanofiltration possess approximately 0.0012 - 0.012 µm of pore size for particles and molecules separation with a pressure range of 20 – 40 bar. The dissociation of surface functional groups or adsorption of charge solute caused nanofiltration’s membranes in contact with aqueous solution to be slightly charged. Nanofiltration’s membrane is very useful in separating inorganic salts and small organic molecules. Its properties of low rejection of monovalent ions, high rejection of divalent ions and higher flux enabled it to be applied in many areas especially for water and wastewater treatment, pharmaceutical and biotechnology and food engineering (Mohammad, et al., 2014).

Fundamental factors that affect the performance of the membranes are membrane material (charge of the membrane) (Nada, 2014). Charge synergy plays a role due to the dimension of pores which are less than one order of magnitude larger than the size of ions used to separate ions with different valences (mainly bivalent ions) (Nada, 2014). The concentration of polymers, presence and concentration of additives, and temperature of the polymers (solution) during fabrication, are three major parameters that might affect the performance and morphology of nanofiltration membranes (Nada, 2014). Figure 2.7 showed the types of materials that nanofiltration can filter.
2.7.8 Ultrafiltration – Microfiltration

Ultrafiltration and microfiltration membranes allow particles transportation to occur at their distinct and permanent porous network. These two membranes are unable to reveal intrinsic properties of the polymeric materials and the intrinsic selectivity for the transport species as compared with nonporous membranes (Lawrence et al., 2010).

Both ultrafiltration and microfiltration are classified as low-pressure membranes with larger pore sizes used for the purpose of filtration. Low-pressure membranes focus on physical removal process where the size of the pores justify what contaminants can be removed from the process. Ultrafiltration membranes can filter a portion of fine particles that could pass through microfiltration membranes. One of the disadvantages of ultrafiltration and microfiltration is both membranes are unable to remove dissolved substances (AWWA Staff, 2011).
2.7.9 Ion Exchange

Ion exchange is used in removing cationic and anionic dyes. Wastewater with dye will pass through the ion exchange resin until the vacant exchange sites are saturated (Chun, 2010). Ion exchange resins contain either organic or inorganic network structure with attached functional groups (Eckenfelder et al., 2009). Synthetic resins made by polymerization of organic compounds are used by most ion exchange resins in wastewater treatment. They are usually made into porous three dimensional structure. Ion exchange resins are anionic if they switch negative ions and cationic if they switch positive ions. The disadvantages of this method are it cannot accommodate a wide range of dyes (Chun, 2010) and the usage of expensive solvents for regeneration of the ion exchanger.

2.7.10 Fenton’s Reagent (H₂O₂-Fe²⁺ salts) Treatment

Fenton’s reagent (hydrogen peroxide activated with Fe²⁺ salts) treatment is a chemical process benefits in treating wastewater that are resistant to biological treatment or are hazards to live biomass. This treatment has high efficiency on organics oxidation as the result of the generation of the hydroxyl radicals (Lam, 2005). Hydroxyl radicals will abstract protons to produce organic radical compounds in order to degrade organics. Those organic radical compounds are subject to further oxidation and are very reactive (Chun, 2010). This treatment is best in COD, color and toxicity reduction. However, this method will result in sludge generation via the flocculation of the reagent and the dye molecules. The sludge need to have further disposal option.
2.7.11 Photochemical (H₂O₂-UV radiation)

The end products of this treatment are CO₂ and H₂O via dye molecules degradation by UV treatment in the presence of H₂O₂ (Chun, 2010). Chemical oxidation of organic materials will occur as ultraviolet light invades causes dissociation of hydrogen peroxide into hydroxyl radicals. Ultraviolet light solely has the capability to degrade organic compounds but the combination of ultraviolet light and hydrogen peroxide has the potential to far more enhance the overall oxidation process (Chun, 2010).

2.7.12 Photocatalytical (TiO₂-UV radiation)

Titania is a photocatalyst broadly used for generating charge carriers that induced reductive and oxidative processes (Gaya and Abdullah, 2008). Electrons are shifted from the valence band to the conduction band of the TiO₂ particle cut out positively charged holes when the surface of TiO₂ particles in anatase form is exposed to UV light. Dye pollutants can be oxidized by the photogenerated holes directly through the valence band hole before it is captured either within the particle or at the surface of the particle or circumlocutorily through the surface bound hydroxyl radical (i.e., a trapped hole at the particle surface) (Chun, 2010). The photogenerated electrons can trigger the reductive decolourization of dyes (Chun, 2010). The disadvantages of this method include the final products of photocatalytic degradation may not be purely innocuous substances and may not have complete redox reactions with the electron hole recombination process (Gaya and Abdullah, 2008). Escherichiacoli proclaimed that nano-scale TiO₂ water suspension is toxic. However, there has been limited research on the toxicity of the photocatalyst or the complete photocatalytic process.
There are various types of wastewater treatments used in textile industry. It is based on the types of pollutants that need to be treated. Table 2.5 shows the advantages and disadvantages of various types wastewater treatment used in textile industry.

Table 2.5: Advantages and disadvantages of different wastewater treatment used in textile industry.

<table>
<thead>
<tr>
<th>Processes</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biodegradation</td>
<td>Rates of elimination by oxidizable substances about 90%</td>
<td>Low biodegradability of Dyes</td>
<td>Pala and Tokat, 2002; Ledakowicz et al., 2001.</td>
</tr>
<tr>
<td>Coagulation–Flocculation</td>
<td>Elimination of insoluble dyes</td>
<td>Production of sludge blocking filter</td>
<td>Gaehr et al., 1994.</td>
</tr>
<tr>
<td>Ozone treatment</td>
<td>Good decolorization</td>
<td>No reduction of the COD</td>
<td>Adams et al., 1995.</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>Removal of all mineral salts, hydrolyzes reactive dyes and chemical auxiliaries</td>
<td>High pressure</td>
<td>Ghayeni et al., 1998.</td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>Separation of organic compounds of low molecular weight and divalent ions from monovalent salts.</td>
<td>-----</td>
<td>Akbari et al., 2002.</td>
</tr>
</tbody>
</table>
2.8 Adsorption

Kayser first recommended the use the term “adsorption” in 1881 to characterize the condensation of gases on free surfaces which is a phenomenon identified independently by both Scheele in 1773 and Fontana in 1777 (Chun, 2010). Adsorption, similar to surface tension, is a consequence of surface energy that is commonly used to remove substances from liquid phases (gases or liquids). It is also a natural phenomenon that enrich chemical species from a liquid phase on the surface of a liquid or a solid.

Adsorption is capable in removing molecules or ions from aqueous solution and in water treatment field, adsorption has been proved powerful in the removal process for multiple solutes (Worch, 2012). If the concentration of the species in the fluid-solid boundary is larger than that in the bulk of the fluid, a species exist in the fluid phase is consider to be adsorbed on the solid surface (Chun, 2010). Adsorbate is the species that is adsorbed. There can be one or more adsorbates in a given adsorption situation. Adsorbent is the solid substance upon whose surfaces adsorption take place.

Major characteristic of solid surfaces are its active and energy-rich sites. Those characteristics enable interaction with solutes in the adjacent aqueous phase by their specific electronic and spatial properties (Worch, 2012). Generally, active sites have different energies where the surface is energetically heterogeneous (Worch, 2012).

Basic terms of adsorption theory is illustrated in Figure 2.8. Adsorbent is referred as the solid material that serves the surface for adsorption; adsorbate is the species that will be adsorbed (Worch, 2012). Adsorbed species can be released and transferred back from the surface into the liquid phase by changing the properties of the liquid phase, for
example, concentration, pH and temperature (Worch, 2012). The term of this reverse process is desorption (Worch, 2012).

![Figure 2.8: Basic process of adsorption (Worch, 2012).](image)

All adsorption processes can be divided into two categories of physical and chemical adsorption rely upon the strength of the interaction (Lowell et al., 2004). Characteristic of the adsorbate-adsorbent system is the extend of the adsorption of an adsorbate on an adsorbent accomplished under a set of conditions. Characteristics of the adsorbate-adsorbent system also influences by the manner of the adsorbate and adsorbent come into contact with each other. Different chemical species may show diverse adsorptive affinity conductive to a particular adsorbent provides the basis of separating or removing these species from their mixtures by applying this adsorbent.

### 2.8.1 Physisorption

Physisorption is defined as physical adsorption in which adsorbate adheres to the surface through weak intermolecular interactions. Physisorption is commonly considered as an efficient way to rapidly lower the concentration of dissolved dyes in an effluent (Sharifah, 2006).
It is characterized by the:

a) Low temperature, always under the critical temperature of the adsorbate
b) Type of interaction: Intermolecular forces, dipole-dipole interactions, dispersion forces, induction forces (Van der Waals forces)
c) Low enthalpy: $\Delta H < 20$ KJ/mol
d) Adsorption takes place in multilayer, and
e) Low activation energy

2.8.2 Chemisorption

Chemisorption is related to the chemical reactions between the adsorbate and the surface sites (Worch, 2012). According to Sharifah (2006), it is characterized to have:

a) High temperature
b) Type of interaction: Strong; covalent bond between adsorbate and surface
c) High enthalpy: $\Delta H \sim 400$ KJ/mol
d) Adsorption takes place in monolayer
e) High activation energy

Table 2.6 shows the comparison between physisorption and chemisorption.

Table 2.6: Comparison between physical and chemical adsorption (Sharifah, 2006).

<table>
<thead>
<tr>
<th>Physisorption</th>
<th>Chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular condensation in the capillaries.</td>
<td>Monomolecular layer on the surface.</td>
</tr>
<tr>
<td>Without chemical bonding.</td>
<td>With chemical bonding.</td>
</tr>
<tr>
<td>Reversible can be desorption.</td>
<td>Non-reversible.</td>
</tr>
<tr>
<td>Nonselective surface attachment.</td>
<td>Selective surface attachment.</td>
</tr>
</tbody>
</table>
2.8.3 Adsorbent

Adsorbent can be used to define the changes between molecules in a mixture through analysis of adsorption equilibrium and kinetics (Sharifah, 2006). Adsorbent is porous in nature with high surface area that enable adsorption of substances onto its surface by intermolecular forces (Sharifah, 2006).

A solid with fast kinetics but low adsorption capacity and a solid with high adsorption capacity but slow kinetics are both not favorable. Slow kinetics will cause adsorbate molecules to use longer time to reach the particle interior which results in longer residence time in a column and thus low throughput. On the other hand, low adsorption capacity means a huge amount of solid is necessary to attain a given throughput. In short, an effective adsorbent possess great adsorptive capacity by having adequate surface area on a per-unit-mass (or volume) basis and has broad pore network for transfer of adsorbate molecule diffusion which provides good kinetics (Chun, 2010).

Adsorbents such as activated carbon, peat and chitin, have been examined on its possibility to remove dye from aqueous solutions (Sharifah, 2006). Activated carbon has been used widely with a great success in term of adsorption. Activated carbon is popular with high capability of dye removal especially for the adsorption of organic species (Sharifah, 2006). They are widely used for the purpose of unwanted odor, color, taste and other organic and inorganic impurities from industrial and domestic wastewater, solvent recovery, air purification and pollution control plus a variety of gas-phase applications (Bansal and Goyal, 2005). However, due to the high cost production and regeneration of activated carbon, many other resources were investigated on their respective adsorption capability on aqueous solution (Sharifah, 2006).
Commercial types of adsorbents also include silica gel, activated alumina and zeolite. Silica gel and activated alumina are usually used as desiccants and modified form of silica gel and activated alumina are mainly used for special purification process (Yang, 2003). Zeolite, notably synthetic zeolite is another vital class of solid used as broadly as activated carbon. Since they have unique surface chemistries and crystalline pore structure, they are primarily used as adsorbents (Yang, 2003).

### 2.8.4 Adsorption Mechanism

Partitioning, Van der Waals forces, electrostatic interactions, hydrogen bonding and hydrophobic interactions are physical binding and physical interactions involved in adsorption process. Figure 2.9 showed the mechanism of adsorption. According to Sharifah (2006), adsorption process can be divided into three steps as follows:

1. Molecule diffusion process into the thin layer of fluid (called as fluid film) which is attached on the adsorbent.

2. According to developing of diffusion, the surface diffusion process which attached the vapour or gas along the pores. It is called as mixed diffusion because there exist two diffusion of pore diffusion and surface diffusion. The bulk adsorption occurs within the pores of adsorbent where the major available surface area is available. Hence, the adsorbate will migrate from the external surface area into the pores within each adsorbent particle.

3. Adsorption process in the pore adsorption sites.
External diffusion, internal diffusion or mixed diffusion (internal diffusion and external diffusion) regulate the rate of adsorption. The function of external diffusion is to regulate the migration of solute species from solution to the boundary layer of the liquid phase. On the other hand, internal diffusion is responsible in controlling the transfer of solute species from external surface of the adsorbent to the internal surface of the adsorbent material. The rate will governed by particle diffusion if the external diffusion is greater than internal diffusion. A condition may cause molecules to desorb after adsorption. Sometime, adsorbed molecules will react with active sites on the adsorbent pore surfaces and form chemical bonds (Pathiraja, 2014).

Based on Rangabhashiyam et al. (2013), dyes adsorption can be explained as:

1. The dye transfer from the bulk solution to the adsorbent surface.
2. Adsorption on the dye surface.
3. Transport within the adsorbent particle.
Kinetics and isotherms data are crucial to interpret the adsorption process as they will present the adsorption mechanism, for example, the bounding of dye within the adsorbent. There are many factors that can affect the adsorption mechanism such as pH, chemical structures, salt concentration and the present of ligands (Rangabhashiyam et al., 2013).

It have been investigated that basic dyes have higher adsorption capacity than acid dyes due to the ionic charges on basic dyes (Rangabhashiyam et al., 2013). Chemical reaction by using covalent bond formation between the dye molecule and fiber makes reactive dyes attach to the adsorbent (Rangabhashiyam et al., 2013). Film diffusion, pore diffusion and intra-particle transport are the three main steps involved in the adsorption mechanism of adsorbate onto adsorbent (Rangabhashiyam et al., 2013). In batch reactor, pore diffusion and intra-particle diffusion are the factors that limit the rate of diffusion (Rangabhashiyam et al., 2013). However, film diffusion is the limiting factor for diffusion in the case of continuous flow system (Rangabhashiyam et al., 2013).

2.8.5 Factors Affecting Adsorption

There are several crucial factors affecting adsorption process, such as:

i. Surface area of adsorbent

Larger sizes imply a greater adsorption capacity as the amount of surface area increases (Sharifah, 2006).
ii. Contact time / residence time

A complete adsorption can be achieved with a longer contact time (Njoku et al., 2014). At the initial stage of the adsorption process, a higher percentage of textile dyes removal is achieved. Adsorption capability decreases with increasing shaking time until an equilibrium is achieved.

iii. Particle size of adsorbent

Internal diffusion and mass transfer limitation to the penetration of the adsorbate inside the adsorbent can be lowered by having a small particle sizes (i.e. Adsorption capability can be sustained and equilibrium can be easily achieved) (Sharifah, 2006).

iv. Solubility of solute (adsorbate) in liquid (wastewater)

Less soluble substances are more easily and quickly removed from water body (i.e. adsorbate) than substances with high solubility. Non-polar substances are more favorable to remove from aqueous solution than polar substances since latter have better affinity for water (Sharifah, 2006).

v. Degree of ionization of the adsorbate molecule

As compared to neutral molecules, highly ionized molecules are adsorbed in smaller degree (Sharifah, 2006).
vi. pH

pH is one of the most crucial factors that need to be considered as it will affect the capacity of adsorbent in wastewater treatment. Different pH leads to different level of ionization of the adsorptive molecules and the surface properties of the adsorbent (Yagub et al., 2014).

vii. Numbers of carbon atoms

A huge amount of carbon atoms is generally associated with a lower polarity for substances in the same homologous series as a higher potential for being adsorbed will be favored (Sharifah, 2006).

viii. Size of molecule with respect to size of the pores

Large molecules size are not able to enter small pores. This will decrease the ability of adsorption independently of other causes (Sharifah, 2006).

ix. Temperature

Temperature is another important physico-chemical process parameter as it will alter the adsorption capacity of adsorbent. The adsorption is an endothermic process if the amount of adsorption increases with increasing temperature. This is because the mobility of the dye molecules increases and the number of active sites available for adsorption increases with increasing temperature (Yagub et al., 2014). The adsorption is exothermic process when there is a decrease of adsorption capacity with increasing temperature. This occurs as the adsorptive forces between the dye species and the active sites on the adsorbent surface decreases as temperature increases result with the decrease in adsorption (Yagub et al., 2014).
2.9 Adsorption using Agricultural Waste Products

2.9.1 Characteristics of Agricultural Wastes as Adsorbents

Numerous amount of agricultural and wood wastes have been used as adsorbents. For example, coir pith, bagasse, silk cotton hull, sago waste, date piths, banana pith, corn cob, straw, maize cob, rice husk, rice hulls, fruit stones, nutshells, pinewood, sawdust, coconut tree dust, bamboo and cassava peel (Rangabhashiyam et al., 2013). Based on physico-chemical characteristics and the cost of agricultural solid wastes, they are good impending adsorbents (Rangabhashiyam et al., 2013).

Hemicelluloses, cellulose and lignin are three main components of agricultural solid wastes (Rangabhashiyam et al., 2013). They have high molecular weights and the extractives is small in molecular size and available in small quantity. Generally, lignocellulosics is termed as biomass. Lignocellulosic materials are a result of photosynthesis, hence, they also called as photo mass (Rangabhashiyam et al., 2013).

Cellulose is an important pure organic polymer composed of anhydroglucose bound together in a large straight chain molecule (Rangabhashiyam et al., 2013). A microfibril is formed as bundles of linear cellulose chains which are combined and oriented in the cell wall structure. Cellulose is insoluble in most of the solvents in nature. It also proved to have low approachability to acid and enzymatic hydrolysis (Rangabhashiyam et al., 2013).

Hemicellulose is a short molecular chain made up of several monosaccharide units. Hemicellulose is partially soluble in water as the polymer chains consists of short branches and are amorphous. The chains of pentose sugar in hemicelluloses serve as the cement material in order to bind the cellulose micells and fiber together.
Hemicelluloses are easily hydrolyzed and they are highly soluble in alkali (Rangabhashiyam et al., 2013).

Lignins are aromatic compounds. They provides the sealing of water conducting system that links roots with leaves and prevent the plant from degradation. Lignins also gives structural strength to the plant. Lignin has a complex three dimensional structure consists of alkyl phenols (Rangabhashiyam et al., 2013). Lignin is covalently bound with xylans in hardwoods and covalently bound with galactoglucomannans in softwoods (Rangabhashiyam et al., 2013). As a result of huge quantities of wastes being rejected, agricultural waste productions are available in large quantities throughout the world (Rangabhashiyam et al., 2013).

2.9.2 Studies of natural form of agricultural waste adsorbents

There are numerous amount of studies proved on the successful dye adsorption using raw adsorbents prepared from agricultural wastes and used plant parts (Rangabhashiyam et al., 2013). In order to avoid the usage of chemicals, expenditure and its complicated steps of modification, several agricultural wastes were tried in its natural form since they are readily available and economical for dye removal (Rangabhashiyam et al., 2013).

Indian Jujuba Seeds (IJS) (Zizyphus maruritiana) is successfully subjected for the removal of dye (Congo red) from aqueous solution (Somasekhara et al., 2012). The dried seed of Indian Jujuba Seeds were crushed and sieved to desired mesh sizes ranging from $<53 \ \mu m$ to $<150 \ \mu m$ (Somasekhara et al., 2012). The Langmuir adsorption isotherm present the best fit to the experimental data with a maximum
adsorption capacity of 55.56 mg g⁻¹ (Somasekhara et al., 2012). The adsorption kinetics follows pseudo-second order kinetics (Somasekhara et al., 2012).

Whole Canola stalks were used as an adsorbent for Acid Orange 7 and Remazol Black 5 dyes from aqueous solution (Hamzeh et al., 2012). It is capable of removing > 90% of dyes with minimal contact times (less than 20 minutes) (Hamzeh et al., 2012). Both Acid Orange 7 and Remazol Black 5 dyes best fits Langmuir isotherm model and the adsorptions kinetics obeys the pseudo second order model (Hamzeh et al, 2012).

Khatod (2013) studied the removal of Methylene Blue using raw orange peel powder. The experimental data fits well in first order kinetic model. Equilibrium was obtained at 18 min with an initial concentration of 2.5 x 10⁻⁵ mg/L dye (Boumediene et al., 2014). Due to the agglomeration of biosorbent, the dye adsorption process decreased with increasing dye concentration resulted by less surface area involved in adsorption process (Khatod, 2013). It was also studied by Boumediene et al. (2014) on the ability of orange peel to remove Methylene blue. Batch experiments were conducted with biomass of 1 g, 1 L of known dye solution, 400 rpm agitation rate under 25 ± 1°C to determine kinetic, isotherms and thermodynamic studies (Boumediene et al., 2014).

The removal of Methylene Blue with adsorption into potato peels was also examined by Öktem et al. (2012). The kinetic experiments were done and the equilibrium achieved after 60 min with optimal pH of pH 8 (Öktem et al., 2012). Hydroxyl and carboxylic functional groups were found to aid in dye adsorption through FTIR spectra (Öktem et al., 2012). The adsorption of AR37 was also carried out through the use of potato husks. Maximum color removal observed at pH 5.3 and the optimum time and adsorbent dosage were found to be 60 min and 1.0 g/L, respectively (Hilal et al., 2012).
Banana peel powder was employed for the removal of Methylene Blue from spent textile dyeing wastewater. The effect of particle size ($d < 80 \mu m$ and $80 \mu m < d < 2 \ mm$), solution temperature ($22^\circ C$ and $50^\circ C$) and biosorbent’s mass were determined (Pishgar et al., 2013). Optimum adsorption was found for $d < 80 \mu m$ using $0.1 \ g$ mass of adsorbent (Pishgar et al., 2013). Temperature was found to have no significant effect on the amount of dye uptake (Moubarak et al., 2014). Banana peels were also being utilized for the removal of BB159 dye (Pishgar et al., 2013). Batch experiments were applied as a function of pH (3-10), mass of adsorbent ($0.2 – 0.8 \ g$), contact time (5 – 120 min), initial dye concentration (50 – 400 mg/L) and agitation speed (100 – 400 rpm) (Pishgar et al., 2013). The total removal of BB159 was achieved at the optimal conditions of pH 9 using 0.4 g of adsorbent when the equilibrium was reached after 60 min (Pishgar et al., 2013).

A new biosorbent almond shell ($Prunus dulcis$) has been investigated in a batch biosorption technique for the removal of Rhodamine 6G (Sentruk et al., 2010). The biosorption kinetics follows pseudo second order model for all the investigated initial concentration of Rhodamine 6G (Sentruk et al., 2010). Equilibrium data fits well with both Langmuir and Freundlich isotherm models. By looking at the best fit of Langmuir isotherm model, it showed a monolayer biosorption capability of almond shell to be as 32.6 mg g$^{-1}$ (Sentruk et al., 2010).

The assessment of the Methylene Blue dye adsorption by lotus leaf showed equilibrium data perfectly illustrated by Koble-Corrigan isotherm (Han et al., 2011). The maximum equilibrium capacities of lotus leaf found to be as 2217 mg g$^{-1}$ at 293 K (Han et al., 2011). The mechanism follows a pseudo second order mode and might be a chemisorption process. A large number of carbonyl and hydroxyl groups was found to
distribute on the surface of the material according to the result of Fourier transform infrared spectroscopy analysis (Han et al., 2011).

Coconut coir dust were used for the removal of Methylene Blue from aqueous solutions in a batch system (Etim et al., 2012). The adsorption process varied non-linearly with pH but varied linearly with the amount of adsorbent and concentration with time (Etim et al., 2012). Langmuir, Freundlich and Temkin models were found to fit well in the adsorption process with correlation, $R^2 \geq 0.90$ (Etim et al., 2012). The adsorption kinetics well described by pseudo second order kinetic model. Temperature effect proves that the adsorption was endothermic with a mean change in enthalpy and spontaneous in nature with a mean free energy change (Etim et al., 2012). The results of Fourier transform infrared spectroscopy analysis showed that dye adsorption happened by the means of chemical interaction of the functional groups on the adsorbent surface (Etim et al., 2012).

Pomelo peels was utilized in the removal of RB114 dye (Argun et al., 2014). The experiments were carried out in a pH range in between 2 – 11 (Argun et al., 2014). According to the result shown, the zeta potential values increased with increasing pH of the solution (approximately from $-3 \text{ mV}$ to $-30 \text{ mV}$) (Argun et al., 2014). The repulsive forces resulted from negatively charged dye molecule onto negatively charged surface caused the adsorption process to be retarded (Argun et al., 2014). Kinetic studies indicated that equilibrium was reached in about 90 min (Argun et al., 2014).
CHAPTER 3

MATERIALS AND METHODS

3.1 Characteristics of Textile Effluent

For the purpose of this study, textile wastewater sample was collected from a selected textile industry. Textile wastewater was collected during wash out process for excess methylene blue dye on fabric. Wastewater was analyzed according to Standard Method for wastewater. The analysis conducted includes Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS), Total Suspended Solids (TSS), pH, total solid and turbidity.

3.1.1 Biological Oxygen Demand (BOD)

3.1.1.1 Reagents and Standards

**Phosphate buffer:** 8.5 g KH₂PO₄, 21.75 g K₂HPO₄, 33.5 g Na₂HPO₄·7H₂O and 1.7 g NH₃·C were dissolved in distilled water and diluted to 1L. The pH is 7.2 without further adjustment.

**Magnesium sulphate**: 22.5 g MgSO₄·7H₂O was dissolved in distilled water and diluted to 1L.

**Calcium chloride**: 27.5 g anhydrous CaCl₂ was dissolved in distilled water and diluted to 1L.

**Ferric chloride**: 0.25 g FeCl₃·7H₂O was dissolved in distilled water and diluted to 1L.
3.1.1.2 Preparation of Solution

One mL each of phosphate buffer, magnesium sulphate, calcium chloride and ferric chloride solutions were added into 1 L of distilled water and was mixed well.

3.1.1.3 Sample Preparation

The effluent was diluted 100x with the prepared BOD dilution water. Textile effluent was neutralized to pH 7. BOD bottles were filled and DO\textsubscript{0} was determined by using DO meter (YSI Pro Plus multi-probe meter). BOD bottles were filled to the rim and trapped gas bubbles were avoided. The BOD bottles were incubated at 20°C for 5 days in BOD incubator. DO\textsubscript{5} were determined after 5 days. Following equation was used to determine the BOD value:

\[ \text{BOD}_5 = \text{DO}_0 - \text{DO}_5 \times \text{dilution factor} \]  \hspace{1cm} (Equation 3.1)

3.1.2 Chemical Oxygen Demand (COD)

HI 839800 COD reactor and HI 83099 COD meter were used for COD test. The reactor was preheated to 150°C. The supplied syringe was used and 0.2 mL of textile sample was added into the vial. The cap of the vial was replaced tightly and mixed by inverting the vial. Another reagent vial was added with deionized water as control. The vials were inserted into the reactor and heated for 2 hours at 150°C. The vials were allowed to cool to room temperature. The value of COD was determined by using HI 83099 COD meter.

3.1.3 Total Dissolved Solids (TDS)

TDS was determined by using YSI Pro Plus multi-probe meter.

3.1.4 Total Suspended Solids (TSS)

TSS was determined by using Hach DR 5000 UV-Vis spectrophotometer.
3.1.5 pH

pH is measured by using Hanna GLP pH meter HI 111. Varied pH of the effluent samples were adjusted using 0.1 M of NaOH and 0.1 M of HCL.

3.1.6 Total Solid

The mass of an empty porcelain dish was determined. 1mL of textile effluent was filled into the porcelain dish. The content was evaporated at 80°C for 48 hours in an oven. The porcelain dish was weighed after it cooled to room temperature in a desiccator.

\[
\text{Total Solid} = \text{Porcelain dish with 1 mL textile effluent} - \text{porcelain dish with 1 mL textile effluent after evaporation} \quad \text{(Equation 3.2)}
\]

3.1.7 Turbidity

Turbidity was determined by using Hach DR 5000 UV-Vis spectrophotometer.

3.2 Preparation of Adsorbent

Kenaf (FH 990) was collected from National Kenaf and Tobacco Board, Selangor while sugarcane bagasse and banana stem was collected from a sugarcane and banana plantation. The supplied adsorbent samples was washed with distilled water and dried in an oven at 40°C for 48 hours to a constant weight. Then, it was grounded into powder and sieved through 1 mm siever.

3.3 Characteristics of Adsorbents

The surface area of the adsorbents were analyzed by using BET surface area analyzer and the surface morphology of three adsorbents was visualized by a scanning electronic microscope. FTIR spectroscopy (Perkin Elmer Frontier FT-IR/FIR Spectrometers) was used to identify the presence of certain functional groups in the adsorbent. Infra spectra
of the adsorbents were obtained by accumulating 8 scans at spectral resolution of 1 cm\(^{-1}\) from 4000 cm\(^{-1}\) to 600 cm\(^{-1}\).

3.4 Adsorption Studies

Adsorption studies were carried by using synthetic methylene blue to determine the maximum parameters for adsorption treatment. Different absorbance was identified by calibrating synthetic methylene blue at 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 50 mg/L, 60 mg/L and 70 mg/L.

3.4.1 Effect of pH

50 mL of textile effluent was poured into conical flasks. Varied pH of the effluent samples (pH 2, pH 4, pH 6, pH 8 and pH 10) were adjusted using 0.1 M of NaOH and 0.1 M of HCL in different conical flasks. 0.5 g of adsorbents was added and the conical flasks were shaken in a water bath shaker under 150 rpm for 300 min. Temperature (60°C) and concentration (70 mg/L) of the adsorbents was maintained. After reaching the equilibrium, the mixtures was filtered using syringe filter. Three replicates of dyes that had been filtrated were analyzed by using Shidmadzu UV-1800 spectrophotometer after centrifuged.

3.4.2 Determination of Optimum Agitation Time

50 mL of textile effluent was poured into conical flasks. 0.5 g of adsorbents was added into the conical flasks. Conical flasks was put into the water bath shaker (Daihan Wisebath WSB-30) for various time period ranging from 5 min to 300 min under 150 rpm. Temperature (60°C), initial concentration (70 mg/L) and pH (pH 8) of the adsorbent was maintained. After reaching the equilibrium, the mixtures was filtered.
using syringe filter. Three replicates of dyes that had been filtrated were analyzed by using Shidmadzu UV-1800 spectrophotometer after centrifuged.

3.4.3 Effect of Initial Concentration

50 mL of textile effluent was poured into conical flasks. 0.5 g of adsorbents was added into the conical flasks. Varied concentration of adsorbate (50 mg/L, 100 mg/L, 150 mg/L and 200 mg/L) was added and the conical flasks were shaken under optimum agitation time. Temperature (60°C) and pH (pH 8) of the adsorbents was maintained. After reaching the equilibrium, the mixtures was filtered using syringe filter. Three replicates of dyes that had been filtrated were analyzed by using Shidmadzu UV-1800 spectrophotometer after centrifuged.

3.4.4 Effect of Temperature

50 mL of textile effluent was poured into conical flasks. 1g of adsorbents was added into the conical flasks. Various temperature was used to determine the effect of temperature on adsorbents such as 20°C, 40°C, 60°C and 80°C. Initial concentration (70 mg/L) and pH (pH 8) were adjusted and the mixtures were shaken under 60°C at optimum agitation time. After reaching the equilibrium, the mixtures was filtered using syringe filter. Three replicates of dyes that had been filtrated were analyzed by using Shidmadzu UV-1800 spectrophotometer after centrifuged.

3.5 Isotherms

3.5.1 Removal Efficiency of Adsorbents

The following formula that was used to determine the decolouration efficiency of each experiments in percentage by calculating the difference concentration of the dye before and after the treatment (Torres et al., 2009).
Where,

\[ Ab_1 = \text{Initial concentration of dye} \]

\[ Ab_2 = \text{Concentration of dye after treatment} \]

### 3.5.2 Adsorption Capacity

This equation was used to calculate the adsorption capacity of the adsorbents by involving the weight and volume of the adsorbents (Deng et al., 2011).

\[
q_e = \frac{(C_0 - C_e)}{M} \times V 
\]

(Equation 3.4)

Where,

\[ q_e \text{ (mg g}^{-1}\text{)} = \text{Adsorption capacity} \]

\[ V \text{ (L)} = \text{Volume} \]

\[ M \text{ (g)} = \text{Weight of the adsorbent} \]

\[ C_o \text{ (mg L}^{-1}\text{)} = \text{Initial Concentration of adsorbate} \]

\[ C_e \text{ (mg L}^{-1}\text{)} = \text{Equilibrium concentration of substrates in the solution} \]

### 3.5.3 Langmuir Isotherm

The Langmuir isotherm assumes that adsorption occurs on a homogeneous monolayer surface containing sites with uniform energy with a finite number of identical sites. It also assumes there is no interaction between the adsorbed molecules (Xing et al., 2010).

\[
\frac{1}{q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m}
\]

(Equation 3.5)
Where,

\( q_s \, (\text{mg g}^{-1}) = \text{Adsorption capacity} \)

\( Q_m \, (\text{mg g}^{-1}) = \text{Maximum amount of adsorption} \)

\( b \, (\text{L mg}^{-1}) = \text{Adsorption equilibrium constant} \)

\( C_e \, (\text{mg L}^{-1}) = \text{Equilibrium concentration of substrates in the solution} \)

### 3.5.4 Freundlich Isotherm

The Freundlich expression is for a multilayer sorption to occur and it is an empirical equation for adsorption on heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface (Xing et al., 2010).

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{(Equation 3.6)}
\]

Where,

\( q_s \, (\text{mg g}^{-1}) = \text{Adsorption capacity} \)

\( K_F \, (\text{mg/L})(\text{L/mg})^{1/n} = \text{Freundlich constant related to adsorption capacity of adsorbent} \)

\( n = \text{Freundlich exponent related to adsorption intensity} \)

\( C_e \, (\text{mg L}^{-1}) = \text{Equilibrium concentration of substrates in the solution} \)
3.6 Adsorption Thermodynamic

Energy and entropy are key elements to be evaluated in any interaction process design. Thermodynamic parameters including Gibbs free energy change (\(\Delta G^\circ\)), enthalpy change (\(\Delta H^\circ\)) and entropy change (\(\Delta S^\circ\)) were calculated using the following equations to evaluate the feasibility and endothermic nature of the adsorption process (Zhang et al., 2011).

\[
\Delta G^\circ = -RT\ln K_d
\]

(Equation 3.7)

\[
\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}
\]

(Equation 3.8)

Where,

- \(R\) (J K\(^{-1}\) mol\(^{-1}\)) = Gas constant (8.3145 J K\(^{-1}\) mol\(^{-1}\))
- \(T\) (K) = Temperature
- \(K_d\) (m\(^3\) mol\(^{-1}\)) = Equilibrium constant

3.7 Determination of Calorific Value by using Bomb Calorimeter (Parr 1341 Plain Jacket Calorimeter)

Adsorbates were weighted (1 g). The bomb was set on an A38A support stand and a 10 cm length of Parr 45C10 nickel alloy wire was fasten between the two electrodes. Fuel capsule with its weighed adsorbate was placed in the electrode loop and the wire was bend downward towards the surface of the charge. 1 mL of distilled water was placed at the bottom of the bomb as a sequestering agent. The bomb head with adsorbate was then moved from support stand to the bomb cylinder. The bomb was next filled with oxygen to 30 atm and placed into the calorimeter bucket filled with 2000 mL of distilled water. Two ignition lead wires were pushed into the terminal sockets on the bomb head while the stirrer was left to run for 5 minutes to reach equilibrium before a measured run. Calorimeter was fired after 5 minutes by pressing the ignition button. Temperatures
were recorded at one-minute intervals until the temperature reached a maximum and dropped very slowly. The motor was stopped and the bomb was lifted out of the bucket by removing the ignition leads. The gas pressure was released from the bomb and the head was lifted out of the cylinder. Interior surfaces was washed with a jet of distilled water. Unburned pieces of fuse wire was then measured. Finally, bomb washing was titrated using standard sodium carbonate solution using methyl red indicator.

### 3.7.1 Calculation for Temperature Rise

\[
 t = t_c - t_a - r_1(b - a) - r_2(c - b) \quad \text{(Equation 3.9)}
\]

Where,

- \( t_a \) = Temperature at time of firing
- \( t_c \) = Temperature at equilibrium
- \( r_1 \) = Rate at which the temperature was rising during the 5 minute period before firing
- \( r_2 \) = Rate at which the temperature was rising during the 5 minute period after time of equilibrium
- \( a \) = Time of firing
- \( b \) = Time when the temperature reaches 60\% of the total rise
- \( c \) = Time at the beginning in which the rate of temperature changes has become constant
3.5.2 Calculation for Gross Heat of Combustion

\[ H_g = \frac{tW - e_1 - e_2 - e_3}{m} \]  

(Equation 3.10)

Where,

\( t \) = Temperature rise

\( W \) = Standardization of benzoic acid

\( e_1 \) = Correction in calories for heat of formulation of nitric acid

\( e_2 \) = Correction of calories for heat of formulation of sulphuric acid

\( e_3 \) = Correction in calories for heat of combustion of fuse wire

\((2.3)(cm)\)
CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characteristics of Textile Effluent

4.1.1 Characteristics of Textile Effluent before the Treatment

Pt-Co method is a common comparison method used to compare the intensity of yellow-tinted samples in order to evaluate pollution levels in wastewater. Since this research only targeted on methylene blue, hence, this method is not suitable to be used in this research. Table 4.1 showed the characteristics of textile effluent as compared to wastewater discharged effluent of Standard A and Standard B. pH of wastewater effluent was alkaline which displayed pH 11.12. This might due to the present of methylene blue dye in the wastewater which caused the wastewater to be alkaline.

Table 4.1: Characteristics of textile effluent.

<table>
<thead>
<tr>
<th></th>
<th>Effluent</th>
<th>Standard A</th>
<th>Standard B</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>11.12</td>
<td>6.0-9.0</td>
<td>5.5-9.0</td>
</tr>
<tr>
<td>Total Solid</td>
<td>1.05 g</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total Suspended Solid</td>
<td>1.05 mg/L</td>
<td>50 mg/L</td>
<td>100 mg/L</td>
</tr>
<tr>
<td>Turbidity</td>
<td>354 FAU</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TDS</td>
<td>96.9 ppm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BOD</td>
<td>206 mg/L</td>
<td>20 mg/L</td>
<td>50 mg/L</td>
</tr>
<tr>
<td>COD</td>
<td>25500 mg/L</td>
<td>80 mg/L</td>
<td>250 mg/L</td>
</tr>
</tbody>
</table>

Total solid and total suspended solid of the wastewater effluent were 1.05 g and 1.05 mg/L, respectively. Low value in both total solid and total suspended solids indicated that the amount of solid and suspended particles in the wastewater effluent are lower than the standard allowed. The turbidity of wastewater effluent was 354 FAU. Turbidity
is a good parameter to measure the status of polluted water because higher concentration of dyes, ions and other polluting agents will caused the wastewater becomes turbid and polluted.

The amount of total dissolved solids in wastewater effluent was 96.9 ppm. Total dissolved solids display the pollution strength of the wastewater. Higher concentration of total dissolved solids will convey odors of wastewater effluent. BOD₅ and COD of wastewater effluent sample were 206 mg/L and 25500 mg/L, respectively. By comparing with Standard A and Standard B, value of both BOD₅ and COD were extremely high. High reading of BOD₅ and COD indicated that the amount of organic matter in wastewater effluent is high.

### 4.1.2 Characteristics of Effluent after the Treatment

Table 4.2 showed the characteristics of textile effluent before and after the treatment process for dye removal using kenaf, banana stem and sugarcane. Based on the results, water quality of the effluent improved after the treatment process. The textile wastewater was highly alkaline (pH = 11.12) before the treatment due to the presence of sodium hydroxide and silica during dyeing process. pH of the textile effluent decreased to neutral pH after the dye removal process which display a pH value of 7.68, 7.70 and 7.65 for kenaf, banana stem and sugarcane bagasse, respectively. Methylene blue is a basic dye, hence, the reduction of methylene blue present in effluent will reduce the pH value.
Table 4.2: Characteristics of textile effluent before and after treatment.

<table>
<thead>
<tr>
<th>Analyst</th>
<th>Initial</th>
<th>After Treatment</th>
<th>Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Kenaf</td>
<td>Banana Stem</td>
</tr>
<tr>
<td>pH</td>
<td>11.12</td>
<td>7.68</td>
<td>7.70</td>
</tr>
<tr>
<td>Total Solid (g)</td>
<td>1.05</td>
<td>1.03</td>
<td>1.01</td>
</tr>
<tr>
<td>Total Suspended</td>
<td></td>
<td>1.05</td>
<td>0.09</td>
</tr>
<tr>
<td>Solid (mg/L)</td>
<td>Turbidity (FAU)</td>
<td>354</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>TDS (ppm)</td>
<td>96.90</td>
<td>96.20</td>
</tr>
<tr>
<td>TDS (ppm)</td>
<td>BODs (mg/L)</td>
<td>206</td>
<td>163</td>
</tr>
<tr>
<td>BODs (mg/L)</td>
<td>COD (mg/L)</td>
<td>25500</td>
<td>10640</td>
</tr>
<tr>
<td>Percentage of</td>
<td></td>
<td>-</td>
<td>96.96</td>
</tr>
<tr>
<td>Dye Removal (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Besides, total solid and total dissolved solid (TDS) also showed slight improvement after adsorption treatment of less than 12%. There is no significant change as compared to the initial values. This probably due to the fact that after the dyeing process, most of the solid such as wax will be filtered and removed before the wastewater is discharged into water bodies. Thus, the remaining total solid and total dissolved solid in the wastewater were very minimum.

Total suspended solids and turbidity were two parameters that showed significant improvement with the applied adsorption treatment. These two parameters showed percentage differences of more than 90%. The amount of suspended solids was reduced from initial value of 1.05 mg/L to 0.09 mg/L, 0.08 mg/L and 0.09 mg/L by kenaf, banana stem and sugarcane bagasse, respectively. This contributes to a decrease in turbidity of wastewater effluent from 354 FAU to 22 FAU, 19 FAU and 21 FAU in treatment with kenaf, banana stem and sugarcane bagasse, respectively. Removal of dye after adsorption treatment caused the total suspended solids and turbidity of the wastewater to decrease. Mahmoued (2010) stated that there is a relationship between amount of suspended solids and turbidity. Turbidity is the measure of water clarity influenced by the amount of suspended solid in the water body. Thus, dyes and pigments, binder, solvents and other inorganic substances may produce turbidity in the water which caused by different types of suspended materials such as colloidal and sub colloidal (Mahmoued, 2010).

$\text{BOD}_5$ and COD are the two important parameters to indicate the degree of pollution in the textile effluent. From Table 4.3, $\text{BOD}_5$ values for the wastewater effluent was reduced from 206 mg/L to 163 mg/L, 142 mg/L and 171 mg/L by kenaf, banana stem and sugarcane bagasse, respectively. The higher $\text{BOD}_5$ value at the initial stage was
mainly contributed to the presence of organic matter since dye consists of a lot of organic compounds. These organic materials will then decomposed by bacteria and caused high BOD$_5$ level. High BOD$_5$ reading indicates low dissolved oxygen (DO) level in water body which is unfavorable for aquatic ecosystem. Hence, a decline in BOD$_5$ value of the wastewater via adsorption process is necessary to improve the wastewater quality. BOD$_5$ value can be reduced through the removal of excess organic compounds such as dyes and pigments from the wastewater.

COD is used to measure the amount of organic pollutants present in water body. The textile effluent after treatment showed lower COD value which were 10640 mg/L, 10312 mg/L and 10937 mg/L for kenaf, banana stem and sugarcane bagasse, respectively, as compared to the raw wastewater effluent which was 25500 mg/L. COD value reduced after adsorption treatment as dyes (organic compounds) had been removed from wastewater. Low concentration of organic compounds will give low COD value. BOD$_5$ and COD value could be further reduced by incorporate with other wastewater processes within a wastewater treatment plant.

Table 4.3 showed the percentage of pollutant reduction for all the analysts. Total dissolved solids (TDS) was the least reduced after adsorption treatment which is in between 0.62 % - 11.76 %, followed by total solid and BOD$_5$ with reduction at 1.90 % - 3.81% and 16.99 % - 31.07 %, respectively. pH and COD was better reduced at 30.76 % - 31.21 % and 57.11 % - 59.56 %, respectively. Two parameters that showed significant improvements at 91.43 % - 92.38 % and 93.79 % - 94.63 %, were total suspended solid and turbidity, respectively.
Table 4.3: Percentage reduction of pollutant in textile effluent.

<table>
<thead>
<tr>
<th>Analyst</th>
<th>Minimum (%)</th>
<th>Maximum (%)</th>
<th>Mean (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>30.76</td>
<td>31.21</td>
<td>30.99</td>
</tr>
<tr>
<td>Total Solid (g)</td>
<td>1.90</td>
<td>3.81</td>
<td>2.86</td>
</tr>
<tr>
<td>Total Suspended Solid (mg/L)</td>
<td>91.43</td>
<td>92.38</td>
<td>91.91</td>
</tr>
<tr>
<td>Turbidity (FAU)</td>
<td>93.79</td>
<td>94.63</td>
<td>94.21</td>
</tr>
<tr>
<td>TDS (ppm)</td>
<td>0.62</td>
<td>11.76</td>
<td>6.19</td>
</tr>
<tr>
<td>BODs (mg/L)</td>
<td>16.99</td>
<td>31.07</td>
<td>24.03</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>57.11</td>
<td>59.56</td>
<td>58.34</td>
</tr>
<tr>
<td>Percentage of Dye Removal (%)</td>
<td>96.96</td>
<td>97.82</td>
<td>97.39</td>
</tr>
</tbody>
</table>

Based on Table 4.2 and Table 4.3, all agro-wastes were able to remove more than 95 % of methylene blue dye from wastewater. Percentage of methylene blue dye removal were 96.96 %, 97.82 % and 97.42 % for kenaf, banana stem and sugarcane bagasse treatments, respectively. The sequence of dye removal ability according to percentage of dye removal was banana stem > sugarcane bagasse > kenaf.

4.2 Characteristics of Adsorbent

Characterization of kenaf, banana stem and sugarcane bagasse were carried out by using FTIR (Fourier transform infrared spectroscopy) analysis, field emission scanning electron microscopy (FESEM) and surface area and pore size analysis (BET analysis). It is crucial to determine the characteristic of adsorbents as their physical and chemical properties can influence the adsorption behavior.
4.2.1 FTIR (Fourier transform infrared spectroscopy) Analysis

FTIR spectra was employed to ascertain the bond types, structures and functional groups in three agro-wastes and to determine the groups responsible for the adsorption of the dye. Figure 4.1 showed the FTIR spectra of kenaf, banana stem and sugarcane bagasse. Kenaf showed broadband at 3338.47 cm\(^{-1}\) which typically attributed to hydroxyl group (O-H group). The adsorption band at 1028.40 cm\(^{-1}\) and 1240.80 cm\(^{-1}\) are attributed with C-O groups. Besides, the other adsorption at 1421.23 cm\(^{-1}\) and 1596.07 cm\(^{-1}\) are attributed to aromatic compounds with C=C bond.

![Figure 4.1: FTIR spectra of kenaf, banana stem and sugarcane bagasse.](image)

In the case for banana stem, the common and large band located at 3328.01 cm\(^{-1}\) can be attributed to O-H group. On the other hand, the adsorption band at 1028.61 cm\(^{-1}\) and 1243.80 cm\(^{-1}\) can be assigned to C-O groups while 1513.54 cm\(^{-1}\) and 1631.64 cm\(^{-1}\) were attributed to C=C bond in aromatic compounds.
Sugarcane bagasse showed an intense band at 3335.33 cm\(^{-1}\) attributed to O-H group. The region of spectrum at 1033.67 cm\(^{-1}\), 1102.25 cm\(^{-1}\) and 1157.45 cm\(^{-1}\) are attributed to ethers groups (C-O groups). Meanwhile, an adsorption band at 1425.65 cm\(^{-1}\) could be attributed to C=C bond as in aromatic compounds.

The function of infrared (IR) spectroscopy is to judge the adsorption of IR radiation by materials as the atoms vibrate about their bonds (Kelesoğlu, 2007). According to Aseel et al. (2014), the existence of hydroxyl groups, ethers groups and aromatic compounds proved to help in physical adsorption. Hence, it can be concluded that all agro-wastes adsorbents would be able to perform high adsorption properties due to the presence of hydroxyl groups, ethers groups and aromatic compounds.

### 4.2.2 Morphology Observation via FESEM (Field Emission Scanning Electron Microscopy)

Morphology observation via field emission scanning electron microscopy of kenaf, banana stem and sugarcane bagasse were shown in Plate 4.1, Plate 4.2 and Plate 4.3, respectively. As shown in Plate 4.1, kenaf displayed a rigid and highly ordered fibrils. The result of this study is in agreement with the findings of Yousif et al. (2012) that reported the morphology of untreated kenaf (Yousif et al., 2012).
Plate 4.1: Field emission scanning electron microscopy for kenaf.

Plate 4.2 and Plate 4.3 display the FESEM images of banana stem and sugarcane bagasse, respectively. Both banana stem and sugarcane bagasse have rough and irregular surfaces. However, banana stem is apparently rougher than sugarcane bagasse with some micropores on the surface. Based on the research done by Baek et al. (2010), rough and porous surface offer better adsorption process. Hence, based on the morphology of all the adsorbents, banana stem would have the most favourable morphological conditions for adsorption.
Plate 4.2: Field emission scanning electron microscopy for banana stem.

Plate 4.3: Field emission scanning electron microscopy for sugarcane bagasse.
4.2.3 BET Surface Area Analysis of Agro-wastes

The specific surface area of kenaf, banana stem and sugarcane bagasse were determined by BET method from adsorption – desorption isotherm of nitrogen. Table 4.4 showed the result of BET surface area, pore volume and average pore size analysis of kenaf, banana stem and sugarcane bagasse. The values of BET surface area, pore volume and pore size of kenaf was 1.2630 m$^2$/g, 0.0029 cm$^3$ and 91.6521 Å, respectively while the value for banana stem was 0.9613 m$^2$/g, 0.0032 cm$^3$/g and 132.0609 Å, respectively. Comparatively for sugarcane bagasse, the corresponding values are 0.3438 m$^2$/g, 0.0007 cm$^3$/g and 79.6355 Å, respectively.

In line with the results showed in Table 4.4, kenaf, banana stem and sugarcane bagasse showed micropore characteristics. Kenaf showed highest surface area followed by banana stem and lastly sugarcane bagasse. Kenaf exhibits surface area of 1.2620 m$^2$/g followed by banana stem and sugarcane bagasse which are 0.9613 m$^2$/g and 0.3438 m$^2$/g, respectively.

Moreover, by comparing the pore size of all the agro-waste adsorbents, banana stem showed the largest pore size (132.0609 Å) followed by kenaf (91.6521 Å) and sugarcane bagasse (Å). Hence, larger pore size are able to enhance the adsorption process for dye removal.

<table>
<thead>
<tr>
<th></th>
<th>Surface area (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kenaf</td>
<td>1.2630</td>
<td>0.0029</td>
<td>91.6521</td>
</tr>
<tr>
<td>Banana Stem</td>
<td>0.9613</td>
<td>0.0032</td>
<td>132.0609</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>0.3438</td>
<td>0.0007</td>
<td>79.6355</td>
</tr>
</tbody>
</table>

Table: 4.4: BET surface area characterization.
4.3 Adsorption Studies

Various operational parameters were selected to investigate adsorption characteristics of kenaf, banana stem and sugarcane bagasse for methylene blue dye adsorption from aqueous solution. These parameters include pH, agitation time, initial concentration and temperature.

4.3.1 Calibration Curve of Methylene Blue

Different absorbance was identified by calibrating the methylene blue dye at various concentrations namely 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 50 mg/L, 60 mg/L and 70 mg/L. Figure 4.2 showed the graphical representation of the calibration of methylene blue dye. The coefficient values of the calibration curves was 0.9961 for methylene blue dye. The calibrated results were referred to identify respective dye removal capability of adsorbents.

![Graph showing calibration curve of methylene blue dye](image)

Figure 4.2: Calibration of methylene blue dye using various dye concentrations.
4.3.2 Effect of pH

The pH of the aqueous solutions is one of the vital controlling parameter in the adsorption process. Chemical nature of the adsorbate and adsorbent decide the optimal pH value of the absorption process (Viera et al., 2011). Hence, the determination of optimum pH was carried out in an aqueous solution of 70 mg/L concentration with constant temperature (60°C), absorbent dosage (0.5 g) and a fixed agitation time in methylene blue dye in different range of pH (pH 2 – 10).

In Figure 4.3, the maximum removal of methylene blue dye was noted at pH 8 for the three adsorbents (kenaf, banana stem and sugarcane bagasse) were 95.84 %, 97.69 % and 95.48 %, respectively. pH 2 showed 62.51 % to 82.04 % dye removal percentage in while pH 4 removed 94.09 % to 95.24 % dye for kenaf, banana stem and sugarcane bagasse. On the other hand, pH 6 displayed a range of 94.72 % to 97.42 % of dye removal capability and a range of 94.78 % to 95.57 % dye removal percentage for pH 10. Therefore, optimum pH 8 was selected for further studies.

![Figure 4.3: Determination of optimum pH of adsorbents for methylene blue dye in 70 mg/L concentration.](image)

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The adsorption capacity of the absorbent is affected by pH of the dye solution through modification of the state of ionization of the binding groups either by increasing or decreasing the competition between the protonated species and adsorbate molecules for the active sites (Viera et al., 2011). The pH values were selected by considering the electrostatic attraction that exists between the negatively charged surfaces of absorbent mainly due to cationic dye (Pavan et al., 2008). Preliminary tests were carried out to obtain the most favorable pH. Dye removal percentage under slightly alkaline condition using banana stem found the most effective with the highest removal percentage (97.69 %) of methylene blue dye. This is due to the present of charged species that influence the adsorption process. With dominated negatively charged species responsible for acquiring negative charge on the surface of the sample, the increasing electrostatic attraction between positively charged adsorbate species and negatively charged adsorbent particles would lead to an increased in dye adsorption (Khatrri et al., 2009). Similar trends were reported for the adsorption of methylene blue onto Fe(III)/Cr(III) hydroxide (Namasivayam and Sumithra, 2005) and adsorption of methylene blue onto yellow passion fruit peel (Pavan et al., 2008).

4.3.3 Determination of Optimum Agitation Time

Optimum agitation time were conducted to evaluate the time at which equilibrium was reached for three different agro-wastes adsorbents. The results of optimum agitation time for removing methylene blue dye using kenaf, banana stem and sugarcane bagasse is presented in Figure 4.4. The effect of agitation time (5 – 300 min) on the adsorption capacity of kenaf, banana stem and sugarcane bagasse for methylene blue dye were studied at pH 8, 0.5 g adsorbent dose, 70 mg/L initial dye concentration and at 60 °C.
Figure 4.4: Determination of optimum agitation time for removing methylene blue dye.

The results showed a rapid increase of dye removal percentage at the initial stage and then reached the equilibrium. This trend is observed as high number of vacant binding active sites were available for dye at the initial stage and these binding sites were covered slowly that caused a decrease in adsorption rate to finally attain the equilibrium (Noreen et al., 2013). The equilibrium agitation time required for removing methylene blue using kenaf was 25 minutes with 93.81 % of dye removal efficiency. However, banana stem and sugarcane bagasse were slower to reach equilibrium with higher removing efficiency of 96.60 % and 95.62 % at 200 minutes of agitation time. Kenaf was able to reach equilibrium within a shorter time (25 minutes) as compared to banana stem and sugarcane bagasse (200 minutes). This was due to the larger surface area of kenaf as according to BET surface area analysis. Larger surface area enable kenaf to perform rapid adsorption process which result in rapid equilibrium.
The agitation time is one of the influential factors for the development of surface charges at solid solution interface (Tiong, 2013). It was indicated that maximum agitation time plays an important role for removing dyes from aqueous solution by adsorption at a fixed concentration, pH and temperature. The result of present study for methylene blue dye removing ability is in agreement with the findings of Khattri et al. (2009) who reported that an establishment of equilibrium in dye adsorption in a short time and a sharp uptake of dyes indicate the efficiency of the adsorbent. The rest of the experiments were conducted using these optimum agitation times for kenaf, banana stem and sugarcane bagasse, respectively, to remove methylene blue dye from aqueous solution.

4.3.4 Effect of Initial Concentration

The adsorption potential of kenaf, banana stem and sugarcane bagasse were determined at several different initial concentrations (10 – 70 mg/L) conducted under equilibrium condition of 60 ºC, pH 8, adsorbent dosage of 0.5 g and a fixed agitation time of 25 min (kenaf) and 200 min (banana stem and sugarcane bagasse), respectively. The results were shown in Figure 4.5.

![Figure 4.5](image)
As illustrated in Figure 4.5, dye removal efficiency increases with increasing initial dye concentration to reach an equilibrium state. Kenaf, banana stem and sugarcane bagasse showed highest removal percentage at the concentration of 70 mg/L with 96.96 %, 97.82 % and 97.42 %, respectively. In order to overcome the diffusive mass transfer resistance of all molecules between adsorbents and adsorbate, initial dye concentration is an important driving force (Khataee et al., 2013). Hence, a higher initial concentration gives a crucial driving force to overcome all resistances of dye between aqueous and solid phases thus increased the dye uptake.

Based on Amel et al. (2012), an increase in the initial ions concentrations of methylene blue will enhance the number of collisions resulted between the dye ions and the adsorbent, thus, improves the adsorption process. Similar trends was noticed for the adsorption of basic dye onto neem sawdust which concluded that the amount of surface sites available for adsorption will reduced after a lapse of time which will then repulse the solute molecules of solid and bulk phases (Khatttri and Signh, 2009).

4.3.5 Effect of Temperature

Present study considered a series of experiment using different temperature such as 40°C, 60 ºC, 80 ºC and 100 ºC at pH 8, 0.5 g adsorbent dosage, initial dye concentration of 70 mg/L and respective agitation time (25 minutes for kenaf and 200 minutes for banana stem and sugarcane bagasse). The result as illustrated in Figure 4.6 indicated that kenaf, banana stem and sugarcane bagasse showed an optimum dye removal capability of 96.96 %, 97.82 % and 97.42 %, respectively at 60 ºC. The order of effective temperature for methylene blue dye removal was 60ºC > 40 ºC > 80ºC > 20 ºC > 100 ºC for all types of adsorbents.
Temperature has a pronounced effect on the adsorption capacity of the adsorbents. An alteration in chemical potentials might explain the differences occurred in the extent of adsorption with temperature. It is interlinked to the solubility of the adsorbate species that increase with a rise in temperature, while decreases in chemical potential. Both temperature and solubility of adsorbate species work in the same direction. An equilibrium process can be referred to the adsorption reaction at any interface between two phases (Khattri and Singh, 2009).

Figure 4.6 shows that 60 °C was a better temperature as compared to lower temperature, 40 °C. Jayarajan et al. (2011) stated that an elevation in the mobility of the large ions would due to an increase in temperature and produce a swelling effect within the internal structure of the nano-porous material hence, enable further penetration of large size molecules. However, 60 °C showed the highest adsorptive capacity as compared to 80 °C and 100 °C. This may be due to the reason that 80 °C and 100 °C is an extreme temperatures that will alter and destroy the structure of kenaf, banana stem and sugarcane bagasse and caused a reduction in adsorption capability. High temperature will destroy the covalent bond, thus, reduce the holding capacity of the adsorbents to trap dye molecules. The adsorption capacity largely rely on the chemical reaction between the functional groups of the adsorbent surface and adsorbate (Jayarajan et al, 2011).
4.3.6 Maximum Adsorption Capacity under Optimum Condition

After conducting a series of adsorption batch mode studies, the optimum condition such as pH, time, initial concentration and temperature were obtained. The optimum pH for kenaf, banana stem and sugarcane bagasse was pH 8 whereas the optimum agitation time for kenaf was 25 min while optimum agitation time for banana stem and sugarcane bagasse were 200 min. All three agro-wastes adsorbents were able to performed best at an initial concentration of 70 mg/L. Due to the relatively high adsorption capacity of the dye, temperature of 60 °C is of interest for further application in treating dye.

Under the optimum conditions, all three agro-wastes adsorbents were able to remove more than 95 % of dye in the aqueous solution. As shown in Figure 4.7, kenaf was able to remove 67.87 mg/L of methylene blue while for banana stem and sugarcane bagasse, it was 68.47 mg/L and 68.19 mg/L, respectively.
4.4 Isotherm Studies

4.4.1 Langmuir Isotherm

Adsorption isotherms provide the capacity of the adsorbent and the equilibrium relationships between adsorbent and adsorbate that normally are the ratio between the quantity adsorbed and the remains in solution at fixed temperature at equilibrium (Igwe and Abia, 2007). Langmuir isotherm and Freundlich isotherm are two simplest isotherms used to describe the adsorption behaviour by using adsorption equation (Igwe and Abia, 2007).

The experimental data from Table 4.5 did not fit the Langmuir isotherm as it give negative slopes and intercepts for all three adsorbents. Langmuir isotherm plots were shown in Figure 4.8, Figure 4.9 and Figure 4.10. All the graphs showed negative slopes and negative interceptions. Negative $Q_m$ caused the actual adsorption value cannot be calculated.
Table 4.5: Langmuir isotherm constants and regression data for adsorption of methylene blue.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Isotherm Constant</th>
<th>Temperature (K)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>313K</td>
<td>333K</td>
<td>353K</td>
<td></td>
</tr>
<tr>
<td>Kenaf</td>
<td>$Q_m$ (mg/g)</td>
<td>-7.2254</td>
<td>-4.1563</td>
<td>-8.3126</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$b$ (L/mg)</td>
<td>-0.1099</td>
<td>-0.1461</td>
<td>-0.0962</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9598</td>
<td>0.9252</td>
<td>0.9537</td>
<td></td>
</tr>
<tr>
<td>Banana stem</td>
<td>$Q_m$ (mg/g)</td>
<td>-7.4794</td>
<td>-8.3195</td>
<td>-8.058</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$b$ (L/mg)</td>
<td>-0.1093</td>
<td>-0.1016</td>
<td>-0.1021</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.7892</td>
<td>0.9623</td>
<td>0.9046</td>
<td></td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>$Q_m$ (mg/g)</td>
<td>-14.684</td>
<td>-5.9102</td>
<td>-17.301</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$b$ (L/mg)</td>
<td>-0.0653</td>
<td>-0.1246</td>
<td>-0.0376</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9489</td>
<td>0.9858</td>
<td>0.9394</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.8: Langmuir plot for methylene blue dye by using kenaf.
Figure 4.9: Langmuir plot for methylene blue dye by using banana stem.

Figure 4.10: Langmuir plot for methylene blue by using sugarcane bagasse.
The Langmuir isotherm suggests that adsorbates are chemically adsorbed at a fixed number of well-defined sites in which each site can only hold one adsorbate species and all sites are generically equivalent (Prola et al., 2013). This theory assume no interactions between the adsorbate species where the adsorption process occurs on a homogeneous surface to obtain maximum adsorption capacity (Prola et al., 2013). This leads to a conclusion in which the adsorption behavior did not follow the assumptions according to Langmuir isotherm. Kiurski et al., (2012) and Kiurski et al., (2011) also showed similar results with negative slope and intercept of Langmuir isotherm.

4.4.2 Freundlich Isotherm

The Freundlich isotherm was found to fit the experimental data for methylene blue sufficiently in accordance with the linear correlations ($R^2$). Freundlich isotherm model follow the principles where as the adsorbate concentration increases, the concentration of adsorbate on the surface will also increases. This model assumes the occurrence of an infinite amount of adsorption which is by having heterogeneous adsorption with different energy of active sites and eversible adsorption (Freundlich, 1906). The linear plot of Freundlich isotherms were shown in Figure 4.11, Figure 4.12 and Figure 4.13. All the graphs showed positive slopes and positive interceptions.
Figure 4.11: Freundlich plot for methylene blue using kenaf.

Figure 4.12: Freundlich plot of methylene blue using banana stem.
The value of $K_F$, n and regression correlation coefficients were calculated from the slope and intercept of these plots, and reported in Table 4.6. $K_F((\text{mg/g})(\text{L/mh})^{1/n})$ indicates the relative adsorption capacity of the adsorbent related to bond energy where n is the heterogeneity factor representing the deviation from linearity of adsorption. If the n value is lower to unity, this shows that the adsorption process is chemical and if the value is above unity, this implies a favourable physical process (Aljebrori et al., 2014). Hence, the adsorption process performed was a physical process. The $R^2$ values of Freundlich isotherm at 333K (60°C) was the highest among all temperatures ($R^2 = 0.9179$ (kenaf), $R^2 = 0.9845$ (banana stem) and $R^2 = 0.9863$ (sugarcane bagasse)). Based on $K_F$ value, the adsorption equilibrium data fitted Freundlich isotherm model in the order of banana stem $>$ sugarcane bagasse $>$ kenaf.
Table 4.6: Freundlich isotherm constants and regression data for adsorption of methylene blue.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Isotherm Constant</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>313K</td>
</tr>
<tr>
<td>Kenaf</td>
<td>$K_F$ ((mg/g)(L/mg)1/n)</td>
<td>0.7679</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>6.8027</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9087</td>
</tr>
<tr>
<td>Banana stem</td>
<td>$K_F$ ((mg/g)(L/mg)1/n)</td>
<td>2.2735</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>10.345</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9824</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>$K_F$ ((mg/g)(L/mg)1/n)</td>
<td>2.3094</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>10.6496</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9861</td>
</tr>
</tbody>
</table>

4.5 Adsorption Thermodynamic

Table 4.7: Thermodynamic parameters for kenaf, banana stem and sugarcane bagasse.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperature (K)</th>
<th>$\Delta G^\circ$ (kJ/mol)</th>
<th>$\Delta H^\circ$ (J/mol)</th>
<th>$\Delta S^\circ$ (J/K mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kenaf</td>
<td>313</td>
<td>Negative</td>
<td>-0.43</td>
<td>3.72</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>Negative</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>353</td>
<td>Negative</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Banana</td>
<td>313</td>
<td>Negative</td>
<td>-0.2</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>Negative</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>353</td>
<td>Negative</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sugarcane</td>
<td>313</td>
<td>Negative</td>
<td>-2.56</td>
<td>-3.01</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>Negative</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>353</td>
<td>Positive</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4.7 presents the thermodynamic parameters at various temperatures. Enthalpy of adsorption ($\Delta H^\circ$), Gibb’s free energy ($\Delta G^\circ$) and entropy of adsorption ($\Delta S^\circ$) for the determination of thermodynamics parameters are crucial as they contributes features on the final state of the system. Figure 4.14 show the van’t Hoff plots in $\ln K_d$ versus $1/T$. These parameters enable the justification whether the process is favourable under the thermodynamic point of view, the spontaneity of the system and if the adsorption process occurs with adsorption or release of energy (Vieira et al., 2012).

Figure 4.14: Van’t Hoff plot for the estimation of thermodynamic parameters.

The negative values of $\Delta G^\circ$ confirmed the spontaneity of methylene blue adsorption onto kenaf, banana stem and sugarcane bagasse. It also suggests that the process is thermodynamically feasible. Negative $\Delta H^\circ$ proves the exothermic nature for the adsorption process. Positive value of $\Delta S^\circ$ indicates good affinity of methylene blue towards adsorbents (kenaf and banana stem). Positive value of $\Delta S^\circ$ showed an increased randomness at the solid/solution interface during methylene blue adsorption process.
(Zhang et al., 2011). Meanwhile, the negative value of $\Delta S^\circ$ was caused by the lack of randomness at solid/solution interface (Muggundha et al., 2013).

### 4.6 Calorific Value

Calorific value is the heating value of a substance. Industrial sectors require a lot of combustion materials for combustion process. Combustion materials such as coal, charcoal and briquettes require high calorific value to ensure efficient and effective combustion. Hence, determination of calorific value is crucial. Table 4.8 shows the calorific value before and after the treatment for methylene blue removal. Experiment was conducted under optimum conditions ($\text{pH} = \text{pH} 8$, agitation time = 25 minutes (kenaf) and 200 minutes (banana stem and sugarcane bagasse), initial concentration = 70 mg/L and temperature = 60 °C).

Table 4.8: Calorific value before and after the treatment for kenaf, banana stem and sugarcane bagasse.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Before treatment (Calories/gram)</th>
<th>After Treatment (Calories/gram)</th>
<th>Percentage of differences (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kenaf</td>
<td>5418.76</td>
<td>7272.70</td>
<td>18.54</td>
</tr>
<tr>
<td>Banana Stem</td>
<td>4796.50</td>
<td>6689.66</td>
<td>18.93</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>5517.11</td>
<td>9315.25</td>
<td>37.98</td>
</tr>
</tbody>
</table>

All of the three adsorbents showed an increase in calorific value after they were used to remove methylene blue dye from the wastewater. This might due to the presence of methylene blue dye molecules attached on the surface of the adsorbents. Sugarcane bagasse showed the highest calorific value after being used for ethylene blue removal which is 9315.25 calories/gram. Sugarcane bagasse showed a significant difference in calorific value of 3798.12 calories/gram before and after the methylene blue dye
removal. This might due to the advantage of sugarcane bagasse for its composition. The ascending sequence of calorific value for these three agro-wastes is sugarcane bagasse > kenaf > banana stem.

Higher calorific value proved to provide an advantage in combustion process. Hence, there is a potential to utilise all the three agro-waste adsorbents after their use for methylene blue dye removal in cement industry. As compared to commercialized agro wastes briquettes available, kenaf, banana stem and sugarcane bagasse exhibit higher calorific value. Table 4.9 showed the comparison of calorific value of agro wastes.

Table 4.9: Calorific value of agro wastes (AZEUS, 2012).

<table>
<thead>
<tr>
<th>Agro Wastes Briquettes</th>
<th>Cal./kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundnut shell*</td>
<td>4524</td>
</tr>
<tr>
<td>Palm kernel*</td>
<td>4985</td>
</tr>
<tr>
<td>Sawdust*</td>
<td>3898</td>
</tr>
<tr>
<td>Cotton stalks*</td>
<td>4252</td>
</tr>
<tr>
<td>Coffee husk*</td>
<td>4045</td>
</tr>
<tr>
<td>Tea waste*</td>
<td>4237</td>
</tr>
<tr>
<td>Paddy straw*</td>
<td>3469</td>
</tr>
<tr>
<td>Mustard stalk*</td>
<td>4200</td>
</tr>
<tr>
<td>Wheat straw*</td>
<td>4100</td>
</tr>
<tr>
<td>Sunflower stalk*</td>
<td>4300</td>
</tr>
<tr>
<td>Palm husk*</td>
<td>3900</td>
</tr>
<tr>
<td>Soya bean husk*</td>
<td>4170</td>
</tr>
<tr>
<td>Wood chips*</td>
<td>4785</td>
</tr>
<tr>
<td>Forestry waste*</td>
<td>3000</td>
</tr>
<tr>
<td>Banana Stem</td>
<td>6689.66</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>9315.25</td>
</tr>
<tr>
<td>Kenaf</td>
<td>7272.70</td>
</tr>
</tbody>
</table>

* references from AZEUS, 2012.
4.7 Economic Feasibility

In this research, economic feasibility for three agro-wastes adsorbents were calculated. A rough assessment of the capital cost of kenaf, banana stem and sugarcane bagasse for dye was made based on the saturation capacity of the adsorbents alone without considering other factors such as regeneration or spent adsorbent disposal cost. The cost involved in using kenaf, banana stem and sugarcane bagasse as adsorbents is shown in Table 4.10.

Table 4.10: Cost of using kenaf, banana stem and sugarcane bagasse as adsorbents.

<table>
<thead>
<tr>
<th>Kenaf</th>
<th>Banana</th>
<th>Sugarcane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process</td>
<td>Charge</td>
<td>Charge</td>
</tr>
<tr>
<td>Agro-Waste</td>
<td>1.70</td>
<td>FOC</td>
</tr>
<tr>
<td>(per kg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(National Kenaf and Tobacco Board, 2014)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drying (Air Dry)</td>
<td>FOC</td>
<td>FOC</td>
</tr>
<tr>
<td>Grinding Process (1 hour x 7.5 Kw/h x 0.210)</td>
<td>1.60</td>
<td>1.60</td>
</tr>
<tr>
<td>Total (RM)</td>
<td>3.30</td>
<td>1.60</td>
</tr>
</tbody>
</table>

*FOC = Free of charge

With reference to the cost, agro-wastes can be an effective option to reduce the cost of adsorbents. Although activated carbon is very effective in removing dye from aqueous solution, the high price of activated carbon in the market (approximately RM6548 per tonne) make the utilization of agro-wastes as adsorbents a good alternative.
Adsorption process showed many advantages as follow:

1. Easy to operate, convenience and simple in term of it’s design (Bhatnagar and Minocha, 2006).

2. Low operational cost, easy automation, lack of sensitivity to toxic pollutants, high flexibility and potential of operation at low concentration, less investment of initial capital and environmental friendly (Auta and Hameed, 2013).

3. Low cost adsorbents (agro-waste adsorbents) used in this technique

4. Agro-waste adsorbents are abundance with potential adsorption capacity.

5. Low detrimental effect on treated water (Altaher, 2014).

6. Agro-based adsorbents are environmental friendly.

7. The use of agro-waste adsorbents can reduce the amount of wastes disposed in landfill.
This study proves the potentials of some agro-waste to be utilized as low cost adsorbants for dye effluent. The results from this study shows that kenaf, banana stem and sugarcane bagasse exhibit more than 95% adsorption capacity at concentration of 70 mg/L methylene blue dye. The optimum parameters for the best adsorption capacity were achieved at pH 8, initial concentration of 70mg/l methylene blue and 60°C. The agitation time needed for kenaf was 25 minutes while for banana stem and sugarcane bagasse, it was 200 minutes.

Among all of the adsorbents, banana stem is the best in removing methylene blue dye as it can achieved maximum percentage (97.82%) of removal with an adsorption capacity of 68.48 mg/L. The results obtained are well fitted in the linear form of Freundlich adsorption isotherms. The calculated values of different thermodynamics parameters indicate that the ongoing adsorption process is feasible, spontaneous and exothermic in nature.

Based on the rough assessment of capital cost for agro-wastes production, the cost involved ranged between RM 1.60 to RM 3.30. As compared to activated carbon, agro-wastes as adsorbents are more economical. Besides, the calorific value of all the agro-wastes showed an increase in their calorific value after adsorption treatment process. Hence, it can be used as combustion materials for energy conversion in cement industry.
From the current research, it clearly proved that the use of agro-wastes (kenaf, banana stem and sugarcane bagasse) as adsorbent is economical, effective and more viable. It can efficiently be used to remove methylene blue dye.
REFERENCES


LIST OF PUBLICATIONS AND PAPERS PRESENTED

19th Biological Science Graduate Congress Singapore (19th BSGC Singapore)
Adsorption Studies of Methylene Blue on Banana Stem
Poster Presentation