

**ACTIVATED CARBON ADSORBENT FROM JENGKOL PEEL FOR
DYE REMOVAL: EQUILIBRIUM, KINETIC AND THERMODYNAMIC
STUDIES**

MOHAMAD RAZIF BIN MOHD RAMLI

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THERMODYNAMIC STUDIES**

by

MOHAMAD RAZIF BIN MOHD RAMLI

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LIST OF SYMBOLS

	Symbol	Unit
A	Arrhenius factor	-
B_T	Constant for Temkin equation	-
C	Boundary layer	-
C_e	Equilibrium concentration of adsorbate	mg/L
C_o	Highest initial adsorbate concentration	mg/L
C_t	Dye concentration at time, t	mg/L
E_a	Arrhenius activation energy of adsorption	kJ/mol
K_1	Adsorption rate constant for pseudo-first order kinetic	1/min
K_2	Adsorption rate constant for pseudo-second order kinetic	g/mg.min
K_{diff}	Intraparticle diffusion rate	mg/g.min ^{1/2}
K_F	Freundlich isotherm constant	mg/g(L/mg) ^{1/n}
K_L	Rate of adsorption for Langmuir isotherm	L/mg
n_F	Constant for Freundlich isotherm	-
M	Mass of adsorbent	G
q_e	Amount of adsorbate adsorbed at equilibrium	mg/g
q_m	Adsorption capacity of Langmuir isotherm	mg/g
q_t	Amount of adsorbate at time, t	mg/g
R	Universal gas constant	8.314 J/mol.K
R^2	Correlation coefficient	-
R_L	Separation factor	-
T	Absolute temperature	K
V	Solution volume	L
ΔH^0	Changes in standard enthalpy	kJ/mol
ΔS^0	Changes in standard entropy	kJ/mol
ΔG^0	Changes in standard Gibbs free energy	kJ/mol

LIST OF ABBREVIATIONS

AC	Activated carbon
ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
CCD	Central composite design
FTIR	Fourier transform infrared
IUPAC	International Union of Pure and Applied Chemistry
MB	Methylene Blue
JP	Jengkol peel
JPAC	Jengkol peel activated carbon
SEM	Surface electron morphology
STA	Simulatneous thermal analyzer
Rpm	Rotation per minute
SEM	Scanning electron microscopy
UV	Ultraviolet

PENJERAP KARBON TERAKTIF DARIPADA KULIT JERING UNTUK PENYINGKIRAN PEWARNA METILENA BIRU: KAJIAN KESEIMBANGAN, KINETIK DAN TERMODINAMIK

ABSTRAK

Pada masa kini, industry tekstil telah diiktiraf sebagai sumber pencemaran air sisa yang paling penting yang kebanyakannya berkaitan dengan pewarna yang secara langsung dilepaskan ke dalam takungan air, mengakibatkan pelbagai kesan alam sekitar. Pewarna ini sering dikeluarkan dalam sisa industri, yang membawa kepada masalah pembuangan. Pada tahun-tahun kebelakangan ini, minat penyelidikan yang semakin meningkat dalam penukaran sisa pertanian menjadi karbon teraktif (KT) sebagai penjerap untuk merawat air kumbahan. Tumpuan kajian ini untuk mengkaji prestasi karbon teraktif (KT) daripada kulit jering (KJ) untuk menyingkirkan metilena biru (MB) dengan menggunakan kaedah pengaktifan fizikal yang melibatkan penggasan karbon dioksida (CO_2) dan radiasi gelombang mikro. Keadaan optimum untuk menghasilkan karbon teraktif kulit jering (KTKJ) pada 400 W kuasa radiasi dan 4 minit masa pengaktifan digunakanyang memberi keputusan 92.6% penyingkiran pewarna. Luas optimum permukaan KTKJ Bruneaur-Emmet-Teller (BET), liang meso, isipadu liang, kandungan karbon tetap yang tinggi sebanyak 474.03 m^2/g , 332.64 m^2/g , 0.389 cm^3/g , 70.45 %. Liang diameter bagi KTKJ adalah didapati mengikut jenis liang meso pada 4.28 nm. Kesimbangan penjerapan MB ke atas KTKJ mengikuti garis sesuhu Freundlich. Kajian kinetik pada penjerapan ke atas KTKJ diperhatikan pada data ekperiment yang diperolehi mendapati padanan yang lebih baik untuk model kinetik pseudo tertib kedua. Kajian termodinamik menunjukkan nilai bagi ΔH° adalah negatif yang memberi indikasi bahawa penyerapan adalah process eksotermik .

ACTIVATED CARBON ADSORBENT FROM JENGKOL PEEL FOR DYE REMOVAL: EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES

ABSTRACT

Nowadays, textile industry has been recognized as the most significant source of wastewater pollution mostly related to dyes which directly released into water bodies, resulting in various environmental impacts. These dyes are always released in industrial waste, leading to disposal problem. In the recent years, growing research interest in conversion of agricultural waste into activated carbon (AC) as adsorbent for treating dyes wastewater. The aim of this research is to study the performance of AC derived from jengkol peel (JP) for removal of Methylene Blue (MB) dye by using physical activation which involves carbon dioxide (CO₂) gasification and microwave radiation. Optimum conditions for preparation jengkol peel activated carbon (JPAC) were found at 400 W of radiation power and 4 minute activation time which resulted 92.6% MB removal. Optimized JPAC has Brunauer-Emmet-Teller (BET) surface area, mesopore surface area, pore volume, fixed carbon content of 474.03 m²/g, 332.64 m²/g, 0.389 cm³/g, and 70.45 % respectively. The pore diameter of JPAC was discovered to be mesoporous at 4.28nm. Adsorption equilibrium of MB on JPAC followed Freundlich isotherm. Kinetic studies of adsorption onto JPAC fit by pseudo-second order kinetic models. Thermodynamic study shows the value of ΔH° was negative which gave an indication that the adsorption was exothermic process.

CHAPTER 1

INTRODUCTION

1.1 Dyes and textile industries

Textile Industry is one of the industries in Malaysia is vast in term of size due to its variety of products. Product of textile made by thread, yarn, filaments or fibers. Due to sudden changes of technology, industrial products and practices, the textile industry have formed a vital part of manufacturing production, employment and trade in numerous developing countries worldwide. Since textile industry is one of the fastest growing industries and mainly contributes to the economic growth, Malaysia has been known for their man-made textile fiber, which contributes to be one of the major industries in textile dyeing processes (Pang and Abdullah, 2013).

This industry has imparted the economic growth, mainly in Kelantan and Terengganu. Malaysia is the fifteenth largest producer of textile fiber in the 2016 and the ninth largest in Asian region. However, this industry also has high water consumption and subsequently produces high discharge rate of wastewater with high load of contaminants mostly related to the discharge of dyes that are highly recalcitrant and toxic. The high level of dyes production worldwide plus their extensive use in many applications in general has generated coloured wastewaters which caused severe water pollution. Therefore, the appearance of dyes onto streams and rivers are categorized as threatening pollutant that should not be neglected (Dulman and Cucu-Man, 2009)

Dyes a basically substance or chemical compounds used to impart colour of the surfaces and fabrics. The main chemical compounds constituted of two important components are chromophores and auxochromes which responsible dye for producing the

colour and enhance the affinity of the dye towards the fibers respectively. Dyes usually have a synthetic origin and complex chemical structure, which make them very stable to light and oxidation and very difficult to biodegrade (Djilani et al., 2015). Classifications of dyes are according to chemical constitution, application class and end use. Dyes are now classified based on how they are used in dyeing process.

There are several industries which used dyes to provide colour to their products such as dyestuff, textile, paper, printing, carpet, plastic, food and cosmetic. Dyes that are used in the textile industry are basic dyes, acid dyes, reactive dyes, direct dyes, azo dyes, mordant dyes, vat dyes, disperse dyes and sulphur dyes (Djilani et al., 2015). According to the statistics, more than 100,000 different dyes are synthesized on the industrial scale every year, and about 5–15% of dyes are directly released into water, resulting in inestimable disaster to our environment. Moreover, the aromatic structures of the dyes make them toxic and even carcinogenic, which pose a serious threat to both animals and humans (Li et al., 2017). In addition, these dyes molecules hinders the penetration of sunlight into the water, hence reduce the photosynthesis activities of aquatic plants, the producer in aquatic food web. This is especially true for dyes such as Methylene Blue (MB) and Reactive Black 5 (RB5) because they are dark in colour at high concentration.

1.2 Treating Textile Effluent

For the past few decades, the environmental issues created by textile industry have received substantial attention as this industry discharged the largest coloured effluent. Dyes are primarily used in the textile industry, although substantial quantities are consumed for colouring various materials, such as leather, paper, plastics, petroleum products and food (Djilani et al., 2015). Generally, the final effluent from textile wastewater treatment plants has always exhibited a certain degree of colour intensity due to large quantities of dangerous dyes, are emitted into wastewaters. Due to this condition, it makes treating water

contamination become more difficult, because the colour tends to persist even after the conventional removal processes. Traditionally, the conventional methods employed for treating dye effluent includes biological, chemical and physical treatments (Demirbas,2009). Each of these alternatives has its own advantages and drawbacks.

Biological treatment is considered the most economical alternatives as compared to the physical and chemical processes. However, their applications are limited because of technical constraint. Besides biological, chemical treatment under coagulation or flocculation are methods available in order to treat textile effluent for dye removal but it expensive and creates a disposal problem. On the other hand, physical treatment such as adsorption by activated carbon, membrane filtration, ion exchange, irradiation and electro kinetic coagulation have been used to treat the desired wastewater (Yagub et al., 2014). Among type of physical treatments, adsorption process is one of the most powerful and extensively used realistic methods for the removal of wide variety of dye via activated carbon as adsorbent.

1.3 Activated Carbon

Activated carbon also known as activated charcoal is produce from carbonaceous source materials. Activated carbon can be considered as a good adsorbent and is widely used for various applications due to porous and high surface area. Activated carbon originates by a variety source of raw materials from animal, mineral and vegetables. The raw materials is chosen for activated carbon production basically depend on its price, purity, potential extent of its activation and also stability of its supply (Yahya et al., 2015).. In addition, it ability to remove dye from aqueous solutions due to the sorption performance and pore characteristics of activated carbon which depends on the physical and chemical properties of the precursor as well as on the activation technique (Ahmed, 2016). Therefore, activation is an important process because this process will determine the quality of resulting activated carbon both surface area and adsorption power (Azima et al., 2017). Activated carbon is adsorbent

derived from agricultural waste is better to develop due to its accessibility and abundant availability and renewable of raw material.

1.4 Problem Statement

Nowadays, textile industry has been recognized as the most significant source of wastewater pollution mostly related to dyes which directly released into water bodies, resulting in various environmental impacts. These dyes are always released in industrial waste, leading to disposal problems. Their discharges into effluents involve a significant source of pollution due to their recalcitrance nature (Kallel et al., 2016).

MB dyes is commonly used as substance for dyeing cotton, wood and silk. Unfortunately, it can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia (Li et al., 2017). Therefore, developing technologies and focuses on effective dye-removal techniques becomes the matter of vital concern.

Several alternatives have been implemented to remove organic pollutants such as dyes from wastewaters are based on biological, chemical and physical processes. Some of these processes include coagulation–flocculation, filtration, adsorption, advanced oxidation processes, ion-exchange, and biological treatment. Some of these techniques have been shown to be effective in several applications; however they have some limitations such as excess amount of chemical usage, accumulation of concentrated sludge that has serious disposal problems and lack effective in terms of colour reduction. As for dyes removal from wastewater, adsorption technique using AC as adsorbent has shown successfully result. However, the current coal based commercial AC is expensive due to their regeneration and

used non renewable resources. In the recent years, growing research interest in the production of AC derived from agricultural waste has been focused.

Agricultural waste products are available in large quantities and are usually discarded. Conversion of agricultural waste into AC would add considerable economic value, help reduce the cost of waste disposal and most importantly provide a potentially inexpensive adsorbent for treating dyes wastewater.

Generally, preparations of AC by heating and activating the raw materials via either conventional and microwave heating techniques (Ahmed, 2016). Conventional heating is slow heating rate which longer the duration of activation resulting in higher energy consumption and affect the quality of product. Recently, research proposed used microwave heating has advantages of energy transfer, improve activation time, saving energy, and consequently resulted in low cost product. Thus, an attempt was made in this study on producing JPAC via microwave irradiation for MB dye removal.

1.5 Research Objectives

- i. To optimize the preparation conditions microwave power and activation time of jengkol peel activated carbon (JPAC) for adsorption of Methylene Blue (MB) dye using Response Surface Morphology (RSM).
- ii. To characterize JPAC in terms of surface area, surface morphology, proximate analysis and surface chemistry.
- iii. To determine adsorption performance of JPAC through adsorption isotherm, kinetics and thermodynamic studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Dyes

Dye is a coloured organic substance that imparts colour to various substrates (Reddy, Verma et al. 2016). In Malaysia, many industries like textiles, paint, food processing, tanneries, cosmetics, paper and pulp, etc. use dyes to colour their products. The colouring is produced by chromospheres group which is a radical configuration consisting of conjugated double bonds where it holding radiation in UV-visible range. Numerous dyes are linked to surfaces to impart colour and are known to be resistant to the action of detergents (Kallel et al., 2016). The usage of dyes keeps on increases yearly due to their efficacy and easy acquisition (Stagnaro et al., 2015).

Dyeing process uses both organic and inorganic synthetic dye that available in variety of colours. It is first pulled through a chemical agent that helps the dye to bond to the cloth. Based on (Robinson et al., 2001) research more than 100,000 commercial dyes are known with an annual production of over 7×10^5 tonnes/year . According to the Colour Index (C.I.), which is managed by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colourists, currently more than 10,000 various types of dyes are synthesized and available in the world (Moussavi and Mahmoudi, 2009). Normally, the accurate data on the amount of dyes discharged from various processes in the environment are unknown. About 2% of dyes produced annually are discharged in effluent from manufacturing treatments whilst 10% was discharged from textile and associated industries (Demirbas, 2009). Dyes are mainly derived from natural sources without any chemical treatment such as plants, insects, animals and minerals.

2.1.1 Classification of dyes and its applications

There are several ways for classification of commercial dyes. Generally, it can be classified in terms of colour, structure and application methods. However, the classification based on application is often favourable due to the complexities of the colour nomenclature from the chemical structure system. The classification based on chemical structure for the common class of the dyes and their application is presented in Table 2.1 and Table 2.2 respectively.

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


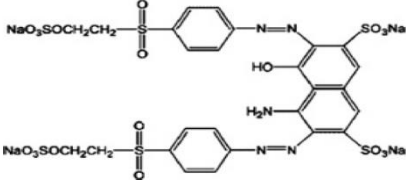
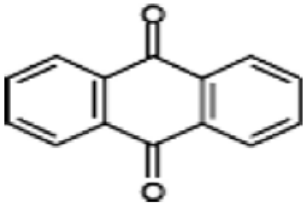
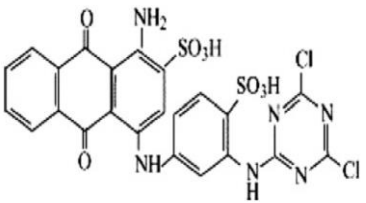
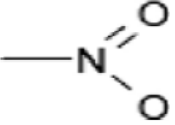
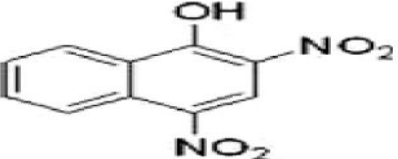

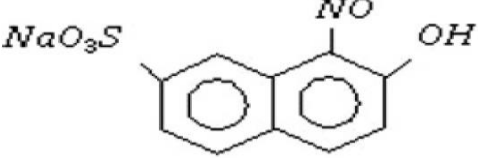
Class	Chromospheres	Example
Azo dye		 Reactive Black 5
Anthraquinone		 Reactive Blue 4
Nitro dye		 Acid Yellow 24
Nitroso dye		 Acid Green 1

Table 2.2: Classification of dye based on their chemical nature (Demirbas, 2009)

Class	Substrate	Method of application	Chemical types
Acid	Nylon, wool, inks, leather and paper	Generally from neutral to acidic bath	Anthraquinone, xanthenes, azo (including nitoso, premetallised)
Basic	Inks, polyacrylonitrile, treated nylon, and polyester	Applied from acidic dye baths	Hemicyanine, azo, cyanine, diazahemicyanine, oxazine, azine
Direct	Rayon, paper, nylon, cotton and leather	Applied from neutral or little alkaline bath containing additional electrolyte	Phthalocyanine, azo, oxazine and stilbene
Disperse	Acetate, polyamide, acrylic polyester, and plastics	Fine aqueous dispersions often applied by high temperature carrier method	Benzodifuranone, nitro, styryl, azo, anthraquinone.
Reactive	Cotton, silk, nylon and wool	Reactive site on dye reacts with functional group on fibre to bind dye covalently under influence of heat and pH	Anthraquinone, azo, oxazine, basic formazan, and phthalocyanine.

There are many structural varieties such as acidic, basic, azo, anthraquinone, disperse and metal complex dyes. From the above table, the major classes of reactive dyes are azo, anthraquinone and phtalocyanine. Reactive dye is a class of highly coloured organic substances, primarily utilized for tinting textiles. The very first fiber reactive dyes were designed for cellulose fibers, and are still used mostly in this way (Demirbas, 2009). Reactive dyes have molecular structure that made up of a chromophoric group and a functional group that can form covalent bonds with cellulosic fibres. Unlike other dyes, it actually forms a covalent bond with the cellulose or protein molecule, as the dye molecule has become an

actual part of the cellulose fiber molecule. Commonly, textile industry used reactive dyes due to their great performance of dyeing process, especially in terms of fastness (Hasan-Al Mamun et al., 2017). Based on studies by (Isah et al., 2015) in view of their colour fastness, ease of application, simple dyeing process together with their superior reproducibility, reactive dyes presently account for about 30% of the synthetic dyes produced globally.

Besides, dyes can also be classified according to their particle charge upon dissolution in the aqueous application medium. For instance, cationic (all basic dyes), anionic (direct, acid and reactive dyes), and non-ionic (disperse dyes) (Hameed et al., 2007). In general, basic dyes are cationic dyes with cationic properties originating from positively charged nitrogen or sulphur atoms. Basic dyes are well-known for their affinity towards textile materials with a net negative charge. For example, Methylene blue (MB) is a cationic dye which is extensively used in dyeing industry. Basic dye demand increases as they are beautiful, shiny crystalline compounds and the most outstanding properties is brilliance. Furthermore, non-ionic dyes refer to disperse dyes because they do not ionise in an aqueous medium. Table 2.3 presents the characteristics of dyes based on different particle charge.

Table 2.3: Characteristics of dyes (Konicki et al., 2015)

Type	Dye	Chemical Formula	Molecular weight	$\lambda_{\max}(\text{nm})$
Anionic dye	Direct Red 23	$\text{C}_{35}\text{H}_{25}\text{N}_7\text{Na}_2\text{O}_{10}\text{S}_2$	813.72	507
Non-ionic dye	Direct Green 97	$\text{C}_{45}\text{H}_{34}\text{O}_3\text{N}_{12}$	790.91	616
Cationic dye	Basic Yellow 28	$\text{C}_{21}\text{H}_{27}\text{N}_3\text{O}_5\text{S}$	433.52	450

2.1.2 Toxicity of dyes

Rapid increase in industrialization and technology in the recent years has resulted in the generation of various kinds of toxic pollutants. These pollutants are considered to be the major cause of water pollution worldwide. Many health related problems such as allergy, dermatitis, skin irritation, cancer, and mutations in humans are associated with dye pollution in water. According to Shakoor and Nasar (2017), the largest wastewater polluters in the world come from textile industry. In this industry, up to 200,000 tons of dyes are lost to effluents every year during the dyeing and finishing operations, due to the inefficiency of the dyeing process. Thus, the effluents from this such industry discharge large amounts of dyes into wastewater without undergo sufficient treatment give negative impacts and creates major problems because of the detrimental effects of dyes to all forms of life such as environment, humans and animals.

Dyes are mainly induced by toxicity which synthesized to various metals occupying such as, copper (Cu), chromium (Cr), cadmium (Cd) and zinc (Zn). Molecules of dye consist of two sort of molecule which affect the toxicity of dye-colorant. The toxicity could outcome by the elimination of metals to the nature or symbiotic action to raise the effect of toxics of metals (Rahman, 2016). Most of the dyes delineate severe problems with the ecological system as they are considered as toxic and even have carcinogenic effect and mutagenic properties creating the severe threat to aquatic fauna as well as human health (El Qada et al., 2006). Dye contaminations in water tend to prevent light penetration and resist photochemical and biological attacks to aquatic life. In addition, the safety of seafood is compromised due to biomagnifications and bioaccumulation effects of dyes molecules in the marine ecosystem. Transfer of these compounds into human body though ingestion of seafood could lead to undesirable and irreversible effects to human nervous systems (Wong et al., 2017).Based on Yagub et al. (2014), studies it can also cause severe damage to human

beings such as dysfunction of the kidney, reproductive system, liver, brain and central nervous system.

Among all types of dyes, great attention has been given to the reactive and basic dyes as they were simultaneously existed in the equalization tank of a dye-house. Around 10 – 15 % of reactive dyes and 0 – 5 % of basic dyes were loss from the dyeing process and discharged as polluted effluents. Azo and anthraquinone dyes are major class of reactive dyes which are toxic because of the presence of toxic amines and are most resistant to degradation and remains colour for a large time in effluents. In general, basic dyes have high intensity of colours and are greatly visible even in very little concentration. Methylene Blue (MB) is one example of basic dye is a toxic dye and cause eye burns which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia (El Qada et al., 2006).

2.1.3 Treatment removal of dye

Effluent of industrial wastewater has become a great important issue in scholar research, as the pollutant are emitted into wastewater, when discharge into water bodies, creates negative impacts on the ecosystem and human health. Legislation controlled the used of coloured substances has been implemented in various countries. As the world has become more cautious about the surroundings and also due to ever-increasing and stringent laws, the textile industry all over the world has started using innovative methods for treating dye emission (Rai et al., 2005). Thus, researchers have made several efforts to develop appropriate technologies for the removal of dyes from the effluents. The current strategy applied in treatment of dye can be divided into three categories: biological, chemical and physical. All of these methods have their own advantages and disadvantages in term of dye

removal. Each method portrays different capabilities in terms of colour removal, capital cost and operating condition .Among the numerous techniques designed for dye removal, adsorption is one of the most effective, and it has been successfully employed for the removal of dyes from wastewater (Aljeboree et al., 2017). Table 2.4 shows the advantages and disadvantages of different dye removal methods.

Table 2.4: Advantages and disadvantages of dye removal methods (Yagub et al., 2014)

Methods	Advantages	Disadvantages
Biological treatments		
➤ Decolourisation by white-rot fungi	➤ White-rot fungi are able to degrade dyes using enzymes	➤ Enzyme production has also been shown to be unreliable
➤ Other microbial cultures (mixed bacterial)	➤ Decolourised in 24-30 h	➤ Under aerobic conditions azo dyes are not readily metabolised
➤ Adsorption by living/dead microbial biomass	➤ Certain dyes have a particular affinity for binding with microbial species	➤ Not effective for all dyes
Chemical treatments		
➤ Oxidative process	➤ Simplicity of application	➤ (H ₂ O) agent need to be activated by some means
➤ H ₂ O ₂ + Fe(II) salts (Fenton's reagent)	➤ Fenton's reagent is a suitable chemical means.	➤ Sludge generation
➤ Photochemical	➤ No sludge produce and foul odours are greatly reduce	➤ Short half-life (20 min)
Physical treatments		
➤ Adsorption by activated carbon	➤ Good removal of wide variety of dyes	➤ Very expensive
➤ Membrane filtration	➤ Removal all type of dyes : recovery, and reuse of chemicals and water	➤ Concentrated sludge production and high running cost

2.2 Adsorption

Adsorption is a process of accumulation of a substance at the interface between two phases either gas-solid interface or liquid-solid interface. The substance that accumulates at the interface is called as adsorbate and the solid on which adsorption occurs is the adsorbent which is surface active material (Yagub et al., 2014). The strength between adsorbate molecules are attached with the adsorbents determines the nature of adsorption. According to (Seow and Lim, 2016) adsorption is defined as concentration of materials on the surface of solid bodies. In term of process, adsorption is one of unit operation in the chemical engineering process is utilize to separate wastewater pollutants from industrial effluent. As for environmental remediation purpose, adsorption techniques is based on the transfer of pollutants from the solution to the solid phase, are widely used to remove certain classes of chemical contaminants from waters, especially those that are practically unaffected by conventional biological wastewater treatments. This method is superior and effective for dye removal techniques in terms of simplicity of design, ease of operation, initial cost, and non-toxicity of the utilized adsorbents compared to other conventional wastewater treatment methods (Crini, 2006).

Basically, adsorption is categorized into two types which are chemical and physical adsorptions. Chemical adsorption or chemisorptions is characterized by the formation of a strong chemical association between ions or molecules of adsorbate to adsorbent surface, which normally is due to the exchange of electrons and thus results in irreversible process in majority cases while physical adsorption or physisorption occurs for most particles in contact with a solid or liquid surface and its characterised by weak van der Waals intraparticle bonds between adsorbate and adsorbent and thus reversible in most cases (Allen and Koumanova, 2005). In addition, Table 2.5 present the difference between chemisorption and physisorption in detailed.

Table 2.5: Difference between physical and chemical adsorption (Allen and Koumanova, 2005)

PHYSICAL ADSORPTION	CHEMICAL ADSORPTION
The forces operating are weak van der Waal's forces	The forces operating are similar to those of chemical bond.
Low heat of adsorption (20- 40 kJ/mol)	High heat of adsorption (40-400 kJ/mol)
Not require any activation energy	Requires any activation energy
Forms multi-molecular layer	Form uni-molecular layer
Adsorption decrease with increase of temperature	Adsorption increase with increase of temperature
No compound formation takes place	Surface compounds are formed
Reversible process	Irreversible process

Normally, major type of adsorbent used for adsorption process are activated alumina, molecular sieve carbon, molecular sieve zeolites, polymeric adsorbents, activated carbon and silica gel. Each of material has its own characteristics in term of pore structure, porosity, and nature of its adsorbent surface. Among several adsorbents proposed, activated carbon is well-known popular adsorbent that has been used effectively for removal of pollutants, because it is highly porous material and possess an extensive surface area (Georgin et al., 2016). Recently, many researchers focused on development of adsorbent derived from agricultural based due to its availability and cheapness.

2.2.1 Adsorption via activated carbon

Activated carbon or activated charcoal is carbonaceous materials which provide high porosity, high adsorptive capacity, high physicochemical stability, high surface area, high mechanical strength, and high degree of surface reactivity. As stated by (Yahya et al., 2015)

its tasteless, amorphous, microcrystalline, non graphite, form of carbon and a black solid substance which resemble powder or granular charcoal. According to Cuhadaroglu and Uygun, (2008) activated carbon cannot be characterized by any distinctive chemical formula. However, it can be categorized into several classifications; granulated activated carbon (GAC), powdered activated carbon (PAC), fibrous activated carbon and extracted activated carbon (EAC) and etc.

Activated carbon has been well-known for the removal of organic and inorganic pollutants dissolve in aqueous media, or from the gaseous environment among all types of other sorbent materials and widely used for various applications due to its effectiveness and great performance. According to (Hameed, Din et al. 2007) activated carbon are widely used for adsorption processes to remove pollutants especially in the textile industry, the effectiveness of adsorption onto activated carbon for removal of large variety of dyes from waste water has made in ideal alternative to other treatment options. adsorption of dye can be represented in four consecutive steps which include (Noroozi and Sorial, 2013):

1. Diffusion of dye molecules via the bulk of solution
2. Diffusion of dye molecules via a diffusion boundary layer
3. Diffusion of dye molecules from the surface into the interior of the adsorbent materials
4. Diffusion of dye molecules on the surface of the materials through molecular interactions.

Normally, the concentration of the dye and agitation may affect step 2. On the other hand, step 3 is usually considered as the rate determining stage, which certainly should affect the adsorption of dyes on the substrate. Whereas, step 4 is dependent on the nature of the dye molecules, such as anionic and cationic structures.

In terms of adsorption capacity, activated carbon usually depends not only on its surface area, but also its internal pore structure, surface characteristics and the presence of functional group on pore surface. The porous structure of activated carbons is tridisperse, comprises of micro-, meso-, and macropores. Each of these pores plays a significant role in the adsorption process and depends both on the precursor used and the method of preparation. The classes of pores together with their respective dimensions and characteristics are summarized in Table 2.6.

Table 2.6: Pore classification (Rai et al., 2005,)

Type of pore and dimensions	Characteristics
Micropores (pore diameter less than 2 nm)	<ul style="list-style-type: none"> ➤ Adsorption occurs through volume filling and capillary condensation does not take place 0.15 to 0.70 cm³/g pore volume ➤ Characterized by adsorption of gases and vapors
Mesopores (pore diameter between 2 to 50 nm)	<ul style="list-style-type: none"> ➤ Specific surface area does not exceed 5% of the total surface area of activated carbon ➤ to 0.2 cm³/g pore volume ➤ Characterized by capillary condensation of the adsorbent with formation of meniscus of the liquefied adsorbate
Macropores (pore diameter larger than 50 nm)	<ul style="list-style-type: none"> ➤ Surface area of adsorbate is very small which does not exceed 0.5 m²/g. ➤ Process is consider not important to the process adsorption of active carbons

Besides, characteristics of raw materials for activated carbon production need to be considered to achieve higher performance sorbent in adsorption process. Based on Peláez-Cid

and Teutli-León (2012), the material for activated carbon must fulfil the requirements as listed below :

1. High carbon content and low inorganic compound level of raw materials in order to obtain high yield during carbonization process.
2. Low-cost adsorbents materials that generally require little processing and are abundant in nature, or are by-products or waste materials from other processes(Demirbas, 2009)
3. Economical and effective resources material to be used as an adsorbent for pollutants removal from liquid system.

Based on requirement above, commercial activated carbon normally uses precursors such as petroleum residues, coal, wood, peat and lignite which are non renewable and very expensive. Thus, it's contributed into several problems in terms of high cost, necessity of regeneration and loss adsorbent during regeneration. Recently, there is a growing interest in finding inexpensive and effective alternatives in order to replace the existing commercial activated carbon which may contribute to environmental sustainability. The use of agricultural waste as activated carbon precursors have been found to be renewable and relatively less expensive and ultimately could utilize the waste effectively into wealth (Yahya et al., 2015). In addition low cost adsorbents derived from agricultural wastes have demonstrated outstanding capabilities for the removal of dyes from wastewater.

2.2.2 Agricultural waste materials

By definitions, agricultural waste is waste release from agricultural operations such as waste from poultry houses, farms, and slaughterhouses. The agricultural by-products are easily obtainable in most of the tropical countries as they constitute a huge volume of total waste materials that threats both environment and society (Rashidi et al., 2012). Main

structures of agricultural waste are divided into three structural components: cellulose, hemicelluloses and lignin. These three main components have high molecular weight and contribute to mass, while the extractives is much smaller in molecular size, and available in little quantity. In general, lignocellulosics have been termed as biomass and photomass as they are a results of photosynthesis process (Demirbas, 2009).

Furthermore, the carbon content from agricultural waste such as corn cob, bamboo, coconut shell, jackfruit peel and many others are lower than commercial activated carbon which derived from coal, peat and anthracite. Thus, resulting in lower yield from these type of precursors. Since agricultural waste is inexpensive and renewable additional source of activated carbons, its lower cost gives significant impact more than its lower yield (Yahya et al., 2015). Thus, conversion of waste materials into activated carbons would add considerable economic value and off-set the costs of treatment and disposal. In addition, provide a potentially inexpensive alternative to the existing commercial activated carbons. Table 2.7 listed the various form of agricultural wastes used as an economical adsorbent.

Table 2.7: Various form of agricultural wastes based AC

Activated Carbon	Adsorption Capacity(mg/g)	References
Mango seed kernel	142.90	(Kumar and Kumaran 2005)
Wheat straw	312.50	(Gong et al., 2005)
Rice husk	40.588	(Vadivelan and Kumar, 2005)
Rambutan peel	329.49	(Ahmad and Alrozi, 2011)
Lotus stalks	564.97	(Huang et al., 2011)
Oil plum fibers	312.5	(Foo and Hameed, 2011)
Walnut saw dusk	59.17	(Ferrero, 2007)
Peanut hull	68.03	(Gong et al., 2005)
Guava leaf powder	95.10	(Ponnusami et al., 2008)
Jack fruit peel	285.71	(Hameed, 2009)
Barley husk	8.30	(Robinson et al., 2002)
Rattan sawdust	294.14	(Hameed et al., 2007)
Tree fern	408	(Ho et al., 2005)
Neem leaf powder	0.55	(Bhattacharyya and Sarma, 2003)
Pineapple peels	462.1	(Foo and Hameed, 2012)
Coffee husk	66.67	(Ahmad and Rahman, 2011)
Pamelo skins	501.1	(Foo and Hameed, 2011)

2.2.3 Preparations of activated carbon

Activated carbon can be prepared under physical or chemical activation. These mechanisms undergo to vary the shapes and sizes of starting material. Physical activation or sometimes called as thermal treatment involves two main steps: carbonization of material

under high temperature and activation. It refer to dry oxidation which reaction between precursors as sample and gaseous such as carbon dioxide (CO₂), air, steam or mixture at high temperature. The advantages of CO₂ are clean gas, easy to handle, easy to control activation process and promote uniform pore size.

The carbonization process is to obtain charcoal from starting material. The purpose of carbonization is to reduce volatile content for conversion of char with high carbon for activation and create initial porosity in the char (Yahya et al., 2015). Then, the carbonaceous form will be activated under activation process. Pores and vessels are form under this process because of entering oxidizing gases into char surface resulting in remove of reactive carbon atom hence generate porous structure.

Chemical activation or known as wet oxidation undergo under single stage which precursor impregnated by activating agent followed by heating under inert atmosphere. This activation usually operates at lower temperature range. Chemical activation commonly done at temperature 450-600°C (Molina-Sabio and Rodriguez-Reinoso, 2004). Normally, it depends on the action of the inorganic additives to degrade and dehydrate the cellulosic materials found in the precursor. Typical chemical agents such as KOH, NaOH, Na₂CO₃, AlCl₃ and etc are commonly used for preparing activated carbon. Advantages of chemical activation are it produces higher yield, produce high surface area of activated carbon. However, there are some limitations which require washing step for activated carbon to eliminate the chemical agent and inorganic reaction products.

2.2.4 Heating technique

Physical and chemical characteristics of activated carbon are mainly affected by heating technique during preparation methods. Recently, heating techniques can be applied into two ways: conventional and microwave heating. Conventional and microwave heating

techniques represent two different types of activation methods. Conventional heating where location of the heat source is located outside the carbon bed and energy is transferred to the samples from the surface to the interior through the convection, conduction, and radiation mechanisms (Ahmed, 2016). Thus, thermal gradient from the hot surface of the sample to its interior until it achieve steady state conditions. In order to avoid thermal gradient, slower rate of heating with isothermal holding was used because when increasing slow heating rate the longer duration of the activation process which results in greater energy consumption and contribute to high cost (Ahmed, 2016). In addition, conventional heating lead to in homogeneous where the surfaces, edges and corners being much hotter than the inside of the material. Thus, it affects the quality of product.

Nowadays, a researcher focused on preparations of activated carbon by using microwave heating which leads to more efficient carbonization process. Based on microwave heating is both internal and volumetric, where the materials receive energy through dipole rotations and ionic conduction (Ahmed, 2016). Microwave irradiations interact directly with the particles inside the pressed compact material and convert electromagnetic energy into heat transfer inside the dielectric materials. It is not conducted into the sample from an external heat source, providing quick volumetric heating (Thakur et al., 2007). By using microwave heating provide shorter processing time, less energy consumptions and generate low cost product. The advantages using microwave radiation are lower activation temperature, improved safety, simplicity of operations, smaller equipment size and less automation (Ji et al., 2007).

2.3 Adsorption isotherm

Adsorption isotherm is used to study on how the adsorption molecules are distributed between liquid phase (adsorbate) and the solid phase (adsorbent) as the adsorption process reached an equilibrium state (Gimbert et al., 2008). Generally, the curve from adsorption use

to describe the equilibrium concentration of solute on the surface of adsorbent, q_e to the concentration of solute in the liquid C_e when it is in contact. Many isotherms have been developed in order to study the adsorptions system. In this research, isotherm models such as Langmuir, Freundlich, Temkins are used and linear regression is used to determine the correlation coefficient, R^2 to show the best-fitting isotherm between the isotherms.

2.3.1 Langmuir isotherm

The langmuir isotherm, which is monolayer adsorption is developed on the assumption that the adsorption process will only take place at specific homogenous sites within the adsorbent surface with uniform distribution of energy level where intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent (El-Bindary et al., 2015).

The linearized equation of Langmuir isotherm is shown as below

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \quad (2.1)$$

where C_e is the equilibrium concentration of adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), q_m is the adsorption capacity of the adsorbent (mg/g) and K_L is the Langmuir adsorption constant related to the free energy adsorption (L/mg). The constant value can be evaluated from intercept and slope of the linear plot of experimental data of (C_e/q_e) versus C_e . The essential characteristics of the Langmuir equation can be expressed in terms of dimension separation factor, R_L , defined as:

$$R_L = \frac{1}{(1+K_L C_o)} \quad (2.2)$$

where C_o is the highest initial solute concentration (mg/L) whereas R_L value implies the adsorption to be unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

2.3.2 Freundlich isotherm

The Freundlich isotherm is an often used for heterogeneous surface system developed on the assumption that the adsorption process occurs on a heterogeneous surface through a multilayer adsorption mechanism and the adsorbed amount increases with the concentration according to the following equation. Besides, energy distribution on each active sites are not equivalent and binding force between adsorbate molecules and active sites decreasing with increasing of degree of site occupations.

Linearized Freundlich isotherm can be expressed as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (2.3)$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), K_f is the Freundlich isotherm constant [(mg/g).(L/mg)^{1/n}], which indicates the relative adsorption capacity of the adsorbent related to the bonding energy, C_e is the equilibrium concentration of the adsorbate (mg/L) and n is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient.

A plot of ($\ln q_e$) against ($\ln C_e$) yields a straight line that indicates the confirmation of Freundlich isotherm for adsorption. The constant can be obtained from the slope ($1/n$) and intercept ($\ln K_f$) of the linear plot of experimental data. The n parameter indicated whether the adsorption is linear ($n = 1$), chemical process ($n < 1$), or physical process ($n > 1$). The slope of $1/n$ ranging between 0 and 1 is a measurement of adsorption intensity, it becomes more heterogeneous as the value gets closer to zero (Haghseresht and Lu, 1999).