REMOVAL OF METHYL RED USING ACTIVATED CARBON PREPARED FROM *PARKIA SPECIOSA* POD (PETAI) AS A LOW COST ADSORBENT

by

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A research proposal submitted in fulfilment of the requirements for the degree of Bachelor of Applied Science (Sustainable Science)

FACULTY OF EARTH SCIENCE
UNIVERSITY MALAYSIA KELANTAN

2017

DECLARATION

I declare that this thesis entitled "Removal of Methyl Red Using Activated Carbon Prepared from *Parkia speciosa* Pods as a Low Cost Adsorbent" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : _____

Name : _____

Date : _____

ACKNOWLEDGEMENT

BISMILLAHIRRAHMANIRRAHIM…

First of all, Alhamdulillah and thanks to our creator for allowing me in finishing this final year project in period time given. I would like to express my sincere gratitude to my supervisor, Dr. Rozidaini bt Mohd Ghazi as for her guidance, support, ideas and also assistance from beginning of this final year project until the end the completion of this thesis. Of all her advices, guidance and helping are very useful to me as finishing this final year project.

Besides that, I would like to thanks too to my co-supervisor which is Dr. Nik Raihan bt Nik Yusoff for her advices and coaching during the absence of my supervisor. Not to forget, thanks a lot for both of my examiners which were Madam Nurul Syazana bt Abdul Halim and Madam Nor Shahirul Umirah bt Idris for supporting and correcting my mistakes during FYP 1. From that, all the ideas were compiled and gave me a successful completion in finishing this research.

Besides that, I would like to express too my grateful to our lab assistant which were Mr. Rohanif b. Mohamed Ali and Madam Nur Izzati bt Salleh, and other laboratory lab assistants for allowing and guide me during the experimental activities in environmental lab. Nevertheless, a special thank goes to the Faculty of Earth Science, Universiti Malaysia Kelantan for allowing me to utilize all the facilities and equipment during finishing my final year project.

Last but not least, I would like to extend my humble gratitude to my parents, lecturers and friends who supported me to complete this research successfully.

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LIST OF ABBREVIATIONS

BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
$ZnCl_2$	Zinc Chloride
H_3PO_4	Phosphoric Acid
AC	Activated Carbon
Hg	Mercury
Pb	Lead
Cd	Cadmium
Cu	Copper
Ni	Nickel
Ppm	Concentration
USEPA	US Environmental Protection Agency
EPA	Environmental Protection Agency
OSHA	Occupational Safety and Health Administration
NIOSH	National Institute for Occupational Safety and Health
WHO	World Health Organization
AOAC	Association of Analytical Communities

ABSTRACT

Textile industry is one of the major contributors either in terms of employment or economies. This industry has provided us with variety of daily necessity such as sources of yarn, clothing and the distribution. Extensively use of dyes in this textile industry has created pollutions to occur especially water pollution. The serious problem of this pollution is when the daily water usage, is from the untreated effluents which are discharged directly into water bodies. However, the disposed dyes into environment can be treated with several methods of dyes removal. Due to that, a study was conducted to investigate the capability of adsorbent from agricultural waste to remove methyl red dyes. In this study, *Parkia speciosa* pods were chosen as the raw material from agricultural waste to produce activated carbon. Three kinds of parameters were studied; best adsorbent with chemicals impregnation and carbonization time, contact time and initial dye concentration. From the result, 100% of methyl red was removed by the activated carbon impregnated with zinc chloride solution of 1 hour carbonization time. The optimum time and initial concentration of dye was 30 minutes and 10 ppm respectively with the percentage removal of 100%. Thus, this result can contribute some knowledge on the use of low cost adsorbent from agricultural waste impregnation with specified chemicals in treating textile industrial wastewater.

ABSTRAK

Industri tekstil adalah salah satu penyumbang utama sama ada dari segi pekerjaan atau ekonomi. Industri ini telah menyediakan kita dengan pelbagai keperluan harian seperti sumber benang, pakaian dan pengagihan. Penggunaan pewarna yang meluas dalam industri tekstil ini telah mewujudkan pencemaran terutamanya pencemaran air. Masalah serius pencemaran ini adalah apabila penggunaan air setiap hari, adalah daripada efluen yang tidak dirawat, dilepaskan terus ke dalam sumber-sumber air. Walau bagaimanapun, pewarna yang dilupuskan ke dalam alam sekitar boleh dirawat dengan beberapa kaedah penyingkiran pewarna. Oleh sebab itu, kajian mengenai penyingkiran pewarna telah dijalankan untuk menyiasat penjerap daripada sisa pertanian dengan beberapa parameter untuk mengeluarkan metil merah. Dalam kajian ini, kulit petai telah dipilih sebagai bahan mentah daripada sisa pertanian untuk menghasilkan penjerap. Tiga jenis parameter dikaji; penjerap terbaik dengan rendaman bahan kimia dan masa karbonisasi, masa sentuhan dan kepekatan pewarna awal. Keputusan yang diperolehi dibandingkan dari segi penyingkiran pewarna merah dan parameter yang digunakan. Berdasarkan keputusan itu, 100% pewarna merah boleh dikeluarkan oleh penjerap yang direndam dengan larutan "zinc chloride" bersama masa karbonisasi 1 jam. Di samping itu, masa sentuhan untuk berjaya mengeluarkan pewarna merah adalah selama 30 minit dengan kepekatan pewarna permulaan 10 ppm. Selain itu, keputusan juga menunjukkan hanya 0.5 gram penjerap digunakan oleh kelajuan kacau 100 rpm untuk memperoleh 100% penyingkiran peratusan menggunakan parameter yang dinyatakan di atas. Keputusan ini menyumbang pengetahuan mengenai penggunaan bahan penjerap kos rendah dari sisa pertanian dengan spesifik bahan kimia dalam merawat air sisa industri tekstil.

CHAPTER 1

INTRODUCTION

1.1 Background of study

Industrial textiles consist varies processes such as pretreatment, dyeing, printing and also finishing. In the dyeing operation of textile fibres, cotton is the first in position which occupies more than 50 % of its production is dyed with reactive dyes. From the ecological view, this kind of dyes is also the most unfavorable one as the effluent produced are relatively heavy in colour, high concentrations of salt and exhibit high BOD/COD values. More than 80,000 tonnes of reactive dyes are produced and consumed by people in each year, thus making it possible to estimate the total pollution caused by their use (Allegre *et al*., 2006).

These kinds of operations are not just consuming much amount of water and energy, however chemical pollution has also been occurred. Occurrence of chemical pollution from dyes especially in water bodies such as lake, river and also ocean has contribute to pollute these water sources. Commonly, untreated dyes wastewaters from dyestuff production and dyeing industries have a great variety of colors. Thus, it is difficult to biodegrade due to complex chemical structures (Syafalni, 2012).

Wastewaters from these industrial activities mostly are being dispersed at the end, into the water bodies which are the main sources for human to do their daily activities for household and also agriculture. This wastewater is not only toxic to the biological world, but also contains colour, which blocks sunlight to reach into the water for photosynthesis especially (Abidin *et al*., 2016). For these reasons, it causes many problems for the ecosystem.

There are several methods in removing dyes from industrial wastewater such as coagulation, chemical precipitation, reverse osmosis, ion exchange, electro dialysis, photo-catalysis and adsorption. However, dyes are more difficult to be treated because of their synthetic origin and mainly complex aromatic molecular structures (Mohammed *et al*., 2009). Due to this, among of those methods, adsorption is the most effective and uses less expensive cost. Adsorption is a physical method which removes dyes from the wastewater. Even though biological method such as biodegradation have been proposed, however this conventional biological treatment processes are not very efficient for the treatment of dyes, due to the low biodegradability of dyes (Rahman *et al*., 2012). Adsorption by activated carbon has a greater potential for the removal of dyes without availability of any impurities. Adsorption onto activated carbon is proven to be very effective in treating textile wastewater (Baseri *et al*., 2012). However, the activated carbon used is only low in cost if the source of producing the activated carbon is cheap. Example of cheap sources is agricultural waste which easy to get as they are abundance in nature.

Hence, clean water resources can be produced using agricultural waste as low cost adsorbent. This is due to the quality of clean water is needed in high amount according to the number population of people, plants and also animal. For instance, human body contains from 55% to 78% water, depending on body size. To function properly, the body requires between one and seven litres of water per day to avoid dehydration (Adeyiga *et al*., 1997). Thus, waste water treatment is needed as to remove any contaminants such as heavy metals and dyes in contaminated water, as to get better quality level of water sources for daily usage or disposal.

1.2 Problem Statement

Presence of dyes is one of many factors that lower water quality. These various concentration of dyes cause harmful effects on health, increase environmental toxicity and affect the aesthetic quality of water (Mehla *et al*., 2012). Due to that, loss of biodiversity will increase as the ecosystem services provided by water are damaged. Besides, much affection of diseases may easily expose either to human or animal especially when they are having direct contact with contaminated water of dyes effluent.

Hence, a great deal of interest in the research for the removal of dyes from industrial effluent such as textile industrial wastewater has been focused on the use of agricultural by-products as adsorbents. The use of agricultural by-products in bioremediation of heavy metal ions is known as bio-sorption. This utilizes inactive (non-living) microbial biomass to bind and concentrate heavy metals from waste streams by purely physico-chemical pathways of uptake.

In previous study, new resources such as hazelnut shell, rice husk, pecan shells, jackfruit, maize cob or husk have been proved that they can be used as an adsorbent for dye removal (Momudu & Anyakora, 2010) after chemical modification or conversion by heating into activated carbon. Thus, in this study, *Parkia speciosa* pods is chosen as a low cost adsorbent in removing methyl red in synthetic textile wastewater.

1.3 Objective of research

The objectives of this study are:

i. To produce activated carbon from *Parkia speciosa* pod as a low cost adsorbent.
ii. To identify the optimum parameters affecting methyl red adsorption on *Parkia speciosa* pod such as contact time and initial concentration of dye.

1.4 Significance of Study

Nowadays human activities have increased the economics of each country around the world however, most of the activities may give side effects to our environment. Due to occurrence of environmental pollutions, human health and animal's habitat may be disrupted with the present of heavy metals and dyes especially (Rad *et al*., 2014).

This research on producing activated carbon from agricultural waste is necessary as to provide a low cost adsorbent and reusable of abundancy agricultural waste. By providing low cost adsorbent from this agricultural waste, thus effluents discharged from textiles industries can be treated before the effluents are being channelled into water bodies (Bari & Bhardwaj, 2014). As a result, this research may contribute to agricultural wastes management besides improve the quality of water bodies.

CHAPTER 2

LITERATURE REVIEW

2.1 Wastewater

Wastewater is any water that has been entirely affected with contamination that is influenced by human activities or natural disaster. Wastewater can be produced from agricultural, mining and industrial activities. Treated water can be used back into the natural environment without adverse ecological impact by removing the contaminants from the polluted water. According to Yahya *et al*., 2015, the main goal of wastewater treatment is to eliminate as much as of the suspended solids as possible before the remaining water called effluent and released back to the environment.

2.1.1 Types of wastewater

Production of wastewater from human activities is unavoidable. This is because human daily life is producing waste during their activities such as eating, development, agriculture which all of these will end up creating a waste. Hence, the quality and quantity of waste products are determined by many factors. The amount and type of waste produced in households is influenced by the behavior, lifestyle and standard of living of the inhabitants as well as the technical and juridical framework by which people are surrounded. For example, in households most waste will end up as solid and liquid waste, and there are significant possibilities for changing the amounts and composition of the two waste streams generated (Algarra *et al*., 2005).

In most developing countries, there are using of separate sewer system functioning as transporting sewage from houses and commercial buildings through pipes for treatment or disposal. Old urban areas might have combined sewer systems

where different types of wastewater are mixed (Table 2.1). In combined systems a part (small or big) of the total wastewater is discharged to local water bodies, often without any treatment (Henze & Comeau, 2008).

Table 2.1: Types of Wastewater

Wastewater from society	**Wastewater generated internally in treatment plants**
Domestic wastewater	Thickener supernatant
Wastewater from institutions	Digester supernatant
Industrial wastewater	Reject water from sludge dewatering
Infiltration into sewers	Drainage water from sludge drying beds
Storm water	Filter wash water
Leachate	Equipment cleaning water

(Source: Srisuwan & Thongchai, 2002)

2.1.2 Wastewater Side Effects to Human and Environment

The constituents in wastewater (Table 2.2) may give awful impacts for the most part to our surroundings and human wellbeing (Husain *et al*., 2014). For human particularly, shift of sicknesses might be contaminated to people effectively if the administration of the wastewater is uncontrolled and inappropriate way is being done. Besides, individuals can get disease easily when they are specifically having contact with the wastewater for instance, in agriculture activities. Skin irritation may happen if precaution steps are not seriously taken for example by wearing the gloves.

Table 2.2: Wastewater Constituent

Wastewater Constituents		Effects
Microorganisms	Pathogenic bacteria, virus and worms eggs	Risk when bathing and eating shellfish
Biodegradable organic materials	Oxygen depletion in rivers, and lakes	Fish death, odours
Other organic materials	Detergents, pesticides, fat, oil and grease, colouring, solvents, phenols, cyanide	Toxic effect, aesthetic inconveniences, bio accumulation in the food chain
Nutrients	Nitrogen, phosphorus, ammonium	Eutrophication, oxygen depletion, toxic effect
Metals	Hg, Pb, Cd, Cr, Cu, Ni	Toxic effect, bioaccumulation
Other inorganic materials corrosion, toxic effect	Acids, for example hydrogen sulphide, bases	Corrosion, toxic effect
Thermal effects	Hot water	Changing living conditions for flora and fauna
Odour (and taste)	Hydrogen sulphide	Aesthetic inconveniences, toxic effect

Wastewater from metal finishing industries contains contaminants, for example, heavy metals, organic substances, cyanides, and suspended solids, at levels which are hazardous to the environment and pose potential health risks to the public (Mara, 2003). Heavy metals, in particular, are of extraordinary concern in light of their poisonous quality to human and other organic life. Substantial metals ordinarily introduce in metal completing wastewater are cadmium, chromium, copper, lead, nickel, silver, tin, and zinc (Ozdemir *et al*., 2009)

The utilization of contaminated water in agriculture, which might be purposeful or unintentional, can be overseen through the execution of different boundaries which lessen the danger to both crop feasibility and human wellbeing. Today an expected 20 million hectares which is seven for every penny of area is inundated utilizing wastewater around the world (Bujang & Ibrahim, 2012),

especially in dry and semiarid districts and urban zones where unpolluted water is a rare asset and the water and supplement estimations of wastewater speak to essential, dry spell safe assets for agriculturists. However, untreated wastewater may contain a scope of pathogens including microorganisms, parasites, infections, harmful chemicals, for example, overwhelming metals and natural chemicals from farming, industry and local sources.

In aquatic ecosystems, heavy metals and dyes greatly depress the number of living organisms. These unfavourable materials have negative effect on the growth of aquatic organisms and can cause serious upsets in biological wastewater treatment plants. The presence of these pollutants serve as great threats to soil and plants growing on such soils, with the consumption of such plants by animals and humans due to their entry into the food chain through biomagnification and bioaccumulation, leading to severe detrimental effects (Akpor, 2014).

2.2 Dyes

Dye is a natural or synthetic colouring material, either soluble or insoluble which impact its colour to a material by staining or being imbibed by, and which is employed from a solution of fine dispersion, sometimes with the aid of mordant. They are widely used in textile, paper, leather, and also mineral processing industries to colour their product (Onukwuli & Okey, 2015). Colour discharged from dyes textiles industries poses certain hazards and environmental problems.

These coloured compounds are aesthetically displeasing, besides inhibit sunlight penetration into the stream and affecting aquatic life. Furthermore, dyes usually have complex aromatic molecular structures which make them more stable

and difficult to biodegrade (Yasin *et al*., 2007). Figure 2.1 shows the molecular structure of dyes.

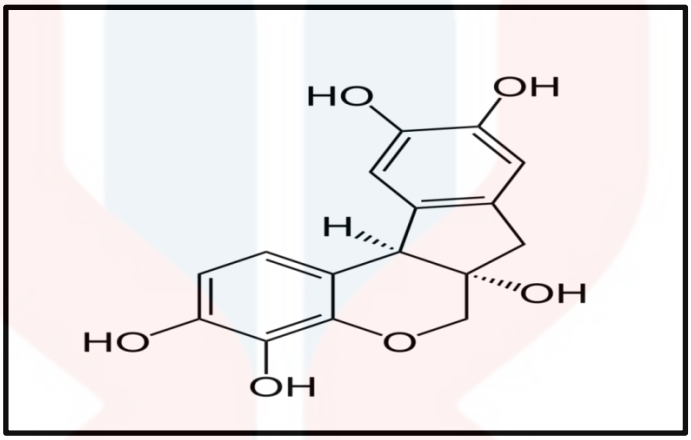

Figure 2.1: Molecular structure of dye

2.2.1 Classification of dyes

Commonly, there are about three kinds of dyes which are most popular. There are natural dyes, synthetic dyes and also reactive dyes. Natural dyes have become a part of human life since time of immemorial. Use of natural dyes in colouration of textile materials and other purpose is just one of the consequences of increased environmental awareness. However, natural dyes exhibit better biodegradability and compatibility with the environment besides, they pose lower toxicity and allergic reactions than synthetic dyes (Alam *et al*., 2007). While synthetic dyes are used widely in textile wastewater and it is generally being treated before it leaves the textile plant. Famous issues on this kind of dyes are colour removal as there are complexities in many types of dyes.

In addition, commercial synthetic dyes have excellent binding ability initiated from the formation of a covalent bond between their reactive group and the surface

groups of textile and cellulose fiber (Maya *et al*., 2014). However, among these three kinds of dyes, reactive dyes are the most dangered and problematic dyes as they can give serious negative impacts to environment and they tend to pass through conventional treatment systems.

2.2.2 Effect of dyes to environment and human health

As textile industry requires various chemicals and dyeing aging in the processing of colouring fibre, thus it contributes large quantity of waste in terms of water, energy and other chemical substances which directly affect the environment to a greater extent. Pollution of this textile industry may be form of water, air and also noise. So these kinds of pollution are considered to be hazardous to health for the surroundings. Among of these three pollutions, water pollution is the most serious and considered one as water supply daily sources for human and other life needs (Jaganathan *et al*., 2014). This is because as scarcity of land has led to many textile industries are located nearby households. Table 2.3 shows the health effects from the effluent discharge from textile industry.

Table 2.3: Effluent discharge from textile industry

Process	Chemical discharge	Pollutants	Health effects
Sizing	Benzene	Resins, fats, waxes, starch and glucose	Carcinogenic, mutagenic and affects central nervous system
Bleaching	Cyanide	Wax, grease, soda ash, sodium silicate	Prolonged exposure will affect kidney and liver
Dyeing	Sulphate	Sulphides, acetic acid, mordant	Eye and respiratory problem
Printing	Nitrate, phosphate	Starch, gums, mordant acids	Eye and respiratory problem

Finishing	Lead	Starch, salts, finishing agents	Suppression of haematological system

(Source: Emigilati *et al*., 2015)

2.2.3 Treatment Methods for Removal of Dyes

Basically, there are several methods to remove dyes. There are biological treatment, physical treatment and also chemical treatment as shown in Table 2.4. Each treatment has its own advantages and disadvantages. Thus, each treatment above has to be evaluated based on cost, application, and performance relative to the removal of dyes (Santos *et al*., 2007). Although there is no treatment technology has universal application, combination of one or two is generally employed depending on wastewater characteristics.

Table 2.4: Treatment methods for removal of dyes

Treatment Methods	Example	Description
Physical	Precipitation, coagulation/flocculation, ion exchange, adsorption and membrane separation	These remove or separate the colour physically and result in need for solid waste disposal
Chemical	Ozonolysis, chemical oxidation/reduction	These technologies remove the colour from the effluent by breaking down the dye into simpler fragments and destroy the chromopore responsible for colour
Biological	Aerobic and anaerobic digestion	Decolourization takes place either by adsorption of dyes on activated sludge or by biological degradation of dye molecules
Electrochemical	Electrodialysis/ion oxidation	It combines the oxidation of the dye and the other polluting

	contaminants by means of the electrolytic process with the physico-chemical precipitation of the sludge.

(Source: Ahmad *et al*., 2007)

Physical and chemical treatment processes which are available for the removal of dyes from waste water such as electro-chemical precipitation, ultrafiltration, ion exchange, electro-dialysis, reverse osmosis, chemical precipitation and adsorption are methods in removing these dyes (Attia *et al*., 2010). However, disadvantages of these processes are high cost, toxic sludge generation or incomplete metal removal. Among of these methods, adsorption using agricultural waste or industrial waste is the lowest cost need and the source is easily to get (Ngoh *et al*, 2015). Besides, this is due to the abundancy of sources which present in our nature.

2.3 Methyl Red

In this study, methyl red was chosen as synthetic textiles wastewater. This is due to the presence of its intense colour in aqueous system and low biodegradability for the presence of benzene rings (Hassan & Abdulhussein, 2015). Methyl red is a well-known dye and has been extensively used in textile dyeing and paper printing. It causes skin and eye irritation (Sahoo *et al*., 2005). Methyl red is also known as a pH indicator, which is it will be red in pH under 4.4 and it becomes yellow as the pH is over 6.2, and the colour will be orange in between of both range (Bari & Bhardwaj, 2014). The chemical formula of methyl red is $C_{15}H_{15}N_3O_2$ (Figure 2.2) consisted of carbon, hydrogen, nitrogen and also oxygen bonding with molecular weight of 269.31 g/mole and melting point between 179-182 °C.

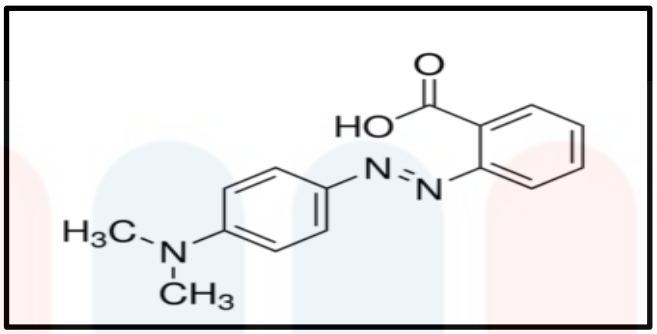

Figure 2.2: Molecular Structure of Methyl Red

2.4 Adsorption Process

Adsorption is always being discussed with absorption. These two terms always give confusion and some people may think both of these process share the same definition.

Over past few decades, adsorption can be seen as one of process which gives lots of importance in industry and environmental protection. Adsorption works on the principle of adhesion (Kandasamy *et al*., 2006). The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. This process can take place either in liquid-gas, liquid-liquid, solid-liquid and solid gas (Mohammed *et al*., 2009). The adsorbing phase is the adsorbent while the material concentrated or adsorbed at the surface of adsorbing phase is the adsorbate.

Due to that, a good adsorbent should have those characteristics which are high porosity, high internal surface, and high adsorption efficiency in a wide range of adsorbate concentrations. In other words, sorption can be happened in two mechanisms, namely absorption and adsorption. Absorbents allow any oil or liquid to penetrate into pore spaces in the material they are made of, whereas adsorbents attract the solution to their surfaces but do not allow it to penetrate into the material (Behnood *et al*., 2013).

2.4.1 Advantages of Adsorption Method

The advantages of using adsorption process, that it is more cheap in cost because usually this method only using agricultural waste or industrial waste as the adsorbent. Adsorption using low cost, readily available agricultural waste materials is a novel technology and has distinct advantages over conventional methods. Its promising results have endeared it to the scientific community as an alternative to traditional methods of wastewater treatment.

Adsorption is one of the most preferred methods for the removal of dyes from textiles industrial effluents due to its ease of operation and insensitivity to toxic substances (Adeyemo *et al*., 2014). However, the applications of activated carbon are restricted due to its high operational costs. Therefore, there is need for an alternative technique, which is economical and efficient. Studies have concentrated on discovering natural, inexpensive and readily available adsorbents with good sorption properties as an alternative for the treatment of textile industrial wastewater.

2.4.2 Physical Adsorption

It is a general incident and occurs in any solid/liquid or solid/gas system. Physical adsorption is a process in which binding of adsorbate on the adsorbent surface is caused by Van der Waals forces of attraction. The electronic structure of the atom or molecule is hardly disturbed upon physical adsorption (Barakat, 2011).

Van der Waals forces originate from the interactions between induced, permanent or transient electric dipoles. Physical adsorption can only be observed in the environment of low temperature and under appropriate conditions, gas phase

molecules can form multilayer adsorption. Commercial adsorbents utilize this physical adsorption for its surface binding (Webb, 2003).

2.4.3 Chemical Adsorption

Chemical adsorption usually occurs opposite to physical adsorption which is the characteristics of this process are not similar. Usually chemical adsorption takes place at high temperature and the heat of adsorption is high. While chemical bonds are the attraction forces that holding the adsorbate (Jeppu & Clement, 2012).

In general, the main steps involved in adsorption of pollutants on solid adsorbent are:

1. Transport of the pollutant from bulk solution to external surface of the adsorbent.
2. Internal mass transfer by pore diffusion from outer surface of adsorbent to the inner surface of porous structure.
3. Adsorption of adsorbate on the active sites of the pores of adsorbent.
4. The overall rate of adsorption is decided by either film formation or intra particle diffusion or both as the last step of adsorption are rapid as compared to the remaining two steps.

2.5 Activated Carbon

Activated carbon is a form of carbon species that is processes and prepared to have high porosity and very large surface area available for adsorption (Joaquin *et al*., 2015). Basically, there are three types of activated carbon used in nowadays industries which are granular activated carbon (GAC), powdered activated carbon (PAC) and extruded activated carbon (EAC). These activated carbons are produced by two main processes of physical reactivation and chemical activation.

Activated carbons can be produced from a number of precursor materials including wood, agricultural wastes, coal and synthetic resins (Sivakumar *et al*., 2012). These precursors are normally exposed to a number of different activation methods such as physical and chemical in an effort to achieve carbon with the high adsorption capacity for a particular application.

2.5.1 Agricultural wastes as a low cost adsorbent

Agricultural wastes as adsorbents for the disposals of waste materials are increasingly becoming a cause of concerning 52,166,167 because these wastes represent unused resources. A large amount of solid wastes are produced in the agricultural sector in most countries of the world. Usually, a major part of this waste is used as a domestic fuel. However, for better utilization of this cheap and abundant agricultural waste, it can be explored as a low cost alternative adsorbent owing to relatively of high fixed carbon content and presence of porous structure (Upadhye & Yamgar, 2016).

In previous study (Iqbaldin *et al*., 2013), there is production of activated carbon from coconut shell as to investigate its potential as an electrode material for supercapacitor. The result has shown that activated carbon produced had high surface area ranging from 1244.0-1768.8 m2/g which is found to be suitable as an electrode for supercapacitor. The Table 2.5 below, shows other study of decolorization percentage of various physical adsorbents from agricultural waste against tested dyes (Noor *et al*., 2008).

Table 2.5: Physical adsorbent with their maximum decolourization percentage

No.	Physical adsorbent	Maximum decolourization percentage (%)	Rank
1.	*Carica Papaya* (seeds)	79	4
2.	*Moringa oleifera* (pods)	76	7
3.	*Moringa oleifera* (seeds)	80	3
4.	*Tamarindus* (seeds)	78	5
5.	*Nigella sativa* (seeds)	85	1
6.	Dried orange (peels)	73	10
7.	*Azadirachta indica* (seeds)	77	6
8.	Dried Coconut (covering)	72	11
9.	Used tea leaves	73	9
10.	Groundnut (hulls)	74	8

2.6 Over view of *Parkia speciosa* (*petai)*

Parkia speciosa is a tropical leguminous tree in the family of *Leguminosae* found in most of South East Asian country. They are huge, 10-15 m in height, and the trees generally grow in harvested from tall rainforest trees that can grow between 15 metres and 45 metres in height (Din & Mohamed, 1993). The fruits are green and

longish while the seeds are in pods, approximately 35 - 45 cm long and 3 - 5cm wide. Usually, the pods contain about 12 to 18 seeds in one of this fruit.

These trees are found in tropical regions like Malaysia, Indonesia, Thailand, and the Philippines. It is known in different countries with different names such as petai in Malaysia, sataw in Thailand, *nejirefusamame* in Japan. The trees of *Parkia speciosa* grow in northern part of Malaysia, in southern part of Thailand and Indonesia (Amarnath, 2004). Figure 2.3 shows some scientific classification of *Parkia speciosa*.

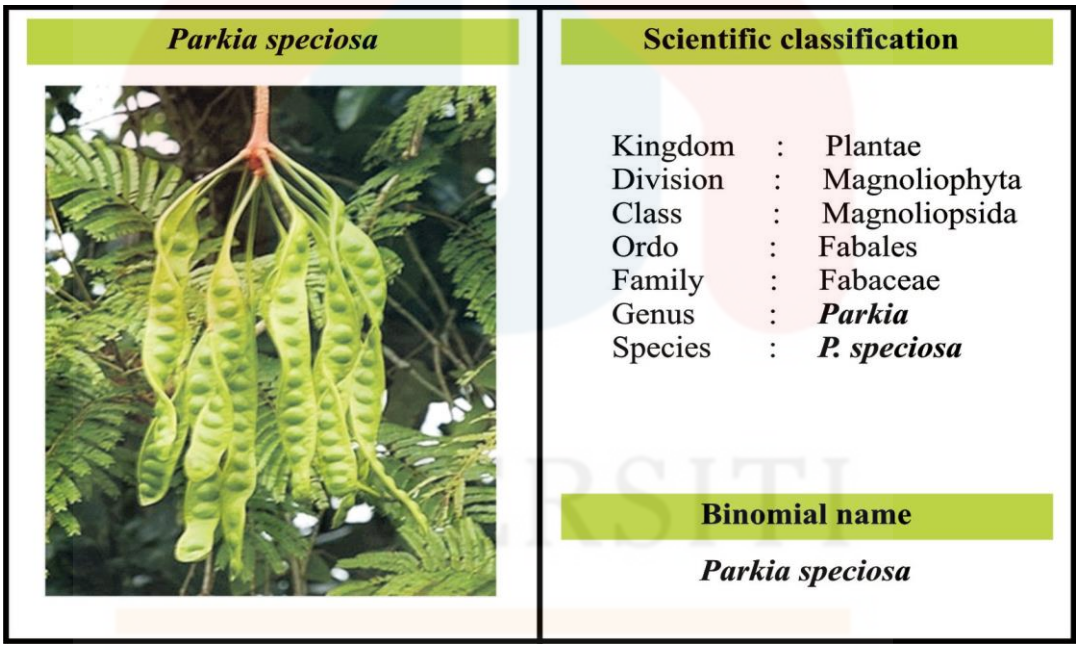

Figure 2.3: Scientific classification of *Parkia speciose*

The seeds have been eaten as food either cooked or raw due to its high nutritional value. It is known to have important chemical and medicinal compounds such as several cyclic polysulfides which are used for treatment of antibacterial activity on kidney, ureter and urinary bladder infections, thiazolidine-4-carboxylic

acid for anticancer activity and have a hypoglycaernic effect due to synergistic action of sitosterol and stigmasterol (Mohd Azizi *et al*.,2008).

This species has very stingy smell. Even though, the seeds are being cooked or boiled, the smell is more obvious to be stinking. The seeds are used as a main ingredient in cooking and have always been a popular local delicacy whereas the pods are usually disposed (Foo & Lee, 2010). Sometimes, people like to make pickled in brine by using the seeds. Furthermore, the plants seeds are also have been used by the locals to treat various diseases and symptoms like diabetes, kidney disorder, and headache.

Hence, *Parkia speciosa* pods can be a potential precursor as a low cost adsorbent as these agricultural wastes are abundance in daily life. Thus, adsorption of this pod is chosen as adsorption of compelling procedure for the evacuation of removing dyes from water (Gupta & Babu, 2009).

2.6.1 Nutritional Value of *Parkia speciosa*

This kind of species is rich in plant protein and essential amino acids, which are building blocks of protein to ensure the proper functioning of the central nervous system (Al Batran *et al*., 2013). Besides, it is a good source of minerals, and is especially high in calcium, phosphorus, potassium, and iron. It is also high in fibre, and contains considerable amounts of vitamin C and E, as well as the vitamins A, B1, B2, and B3. This makes *Parkia speciosa* is one of the most nutritious local vegetables.

In addition, *Parkia speciosa* also plays role as antioxidant which kills harmful radicals and protect the cells from damage. Regularly free radical formation is controlled naturally by various beneficial compounds known as antioxidants (Ko *et*

al., 2014). At the point when there is insufficient of these antioxidants damage because of free radicals can become cumulative and debilitating. Antioxidants are capable of stabilizing, or deactivating, free radicals before they attack cells in the body.

Oxidation is a chemical process which producing free radicals leading to chain reaction that may damage the cells body (Karim & Azlan, 2012). Due to that, the naturally presence of antioxidant in *Parkia speciosa* may prevent those free radicals from damaging the body cells. The antioxidant's compounds usually consist of vitamin E and vitamin C. Both of these vitamins are major contributing to the antioxidants capacity.

Besides, the beans of this species is kindly containing phenols which enhancing the antioxidants activities. Vitamin E that contains in the *Parkia speciosa* has a great function in helping the antioxidant activity. Vitamin E includes four tocopherols and four tocotrienols (Figure 2.4). One form, a-tocopherol, is the most abundant form in nature, has the highest biological activity based on fetal resorption assays (3–5), and reverses vitamin E deficiency symptoms in humans (Hasima *et al*., 2015). The molecular functions fulfilled specifically by a-tocopherol have yet to be fully described, but it is unlikely they are limited to general antioxidant functions.

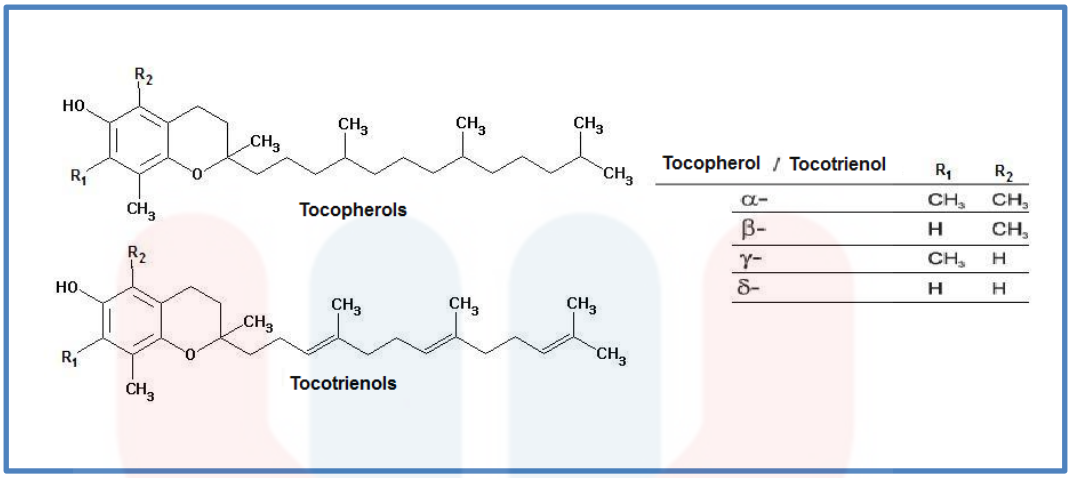

Figure 2.4: Naturally occurring forms of vitamin E in *Parkia speciosa*

The antioxidant activity of vitamin E (Flohe & Traber, 1999) has persuaded many groups to study its ability to prevent chronic diseases, especially those believed to have an oxidative stress component such as cardiovascular diseases, atherosclerosis, and cancer.

CHAPTER 3

MATERIALS AND METHODS

3.1 Study Area

The plant waste which is *Parkia speciosa* pod was collected from supermarket and stalls nearby at Jeli, Kelantan.

3.2 Materials

Parkia speciosa pods acted as raw materials that were used in this experiment to produce the activated carbon. Distilled water was used to wash all the apparatus before starting the experiment and to wash the activated carbon. 30% zinc chloride ($ZnCl_2$) solution and 30% phosphoric acid (H_3PO_4) were prepared as chemicals impregnation with raw materials to produce different characteristics of activated carbon. Besides, methyl red was chosen as dye removal in this experiment and the absorbance was read using UV-vis spectrometer. Orbital shaker was used to stir the methyl red together with activated carbon chosen in specified time of 100 rpm. For dying process, oven was used with adjustable temperature an time (Din & Mohamed, 1993).

3.3 Methods

3.3.1 Pretreatment of *Parkia speciosa* pods

About 3kg of *Parkia speciosa* pods were obtained from a local market and the seeds were taken out from the pods. The pods were repeatedly washed with

distilled water as to remove residues and they were dried in oven at 100°C for 24 hours to reduce moisture content. Then, moisture content of the pods were determined using AOAC standard method (Abdullah *et al*., 2011). Moisture content (wet basis) was calculated as equation (3.1):

MOISTURE CONTENT (wet basis):

$$= 100 \times \left(\frac{wet\ weight - dry\ weight}{wet\ weight}\right) \quad (3.1)$$

The dried pods were ground with a grinder and then they were sieved to a particle size by using 425 mm of siever size.

3.3.2 Preparation of Activated Carbon Impregnating with Zinc Chloride ($ZnCl_2$) solution

Parkia speciosa pods (10 g) were added into a conical flask containing 20 ml of 30 % zinc chloride solution. Then, this sample was shaken about 5 minutes. The sample was then impregnated with the $ZnCl_2$ solution in 24 hours. Later, the sample carbonized in furnace at 400 °C for 5 minutes (Ogugbue & Sawidis, 2011). After the activated carbon was being produced, then it was washed with plenty of deionized water as to get natural pH of 7. In the end, the activated carbon was being dried in oven at 50 °C for 24 hours and then it was kept in a sterile container. The activated carbon was labelled with "$ZnCl_2$ at 5 minutes". The steps above were repeated at 10 minutes, 30 minutes and 1 hour carbonization process.

3.3.3 Preparation of Activated Carbon Impregnating with Phosphoric Acid (H_3PO_4) Solution

Parkia speciosa pods (10 g) were added into a conical flask containing 20 ml of 30 % phosphoric acid solution. Then, this sample was shaken about 5 minutes. The sample was then impregnated with the H_3PO_4 solution in 24 hours. Later, the sample was being carbonized in furnace at 400°C for 5 minutes (Ogugbue & Sawidis, 2011). After the activated carbon was produced, then it would be washed with plenty of deionized water as to get natural pH of 7. In the end, the activated carbon was dried in oven at 50°C for 24 hours and then it was being kept in a sterile container. The activated carbon was labelled with "H_3PO_4 at 5 minutes". The steps above were repeated at 10 minutes, 30 minutes and 1 hour carbonization process.

3.3.4 Preparation of dye (methyl red) solution

The stock solution of the dye was prepared by dissolving 1g of methyl red ($C_{15}H_{15}N_3O_2$) into a reagent bottle and diluted up with 1000 ml of distilled water as to make a stock solution of 1000mg/L (Abdullah *et al.*, 2005). Then, to prepare 100 ppm of stock solution for methyl red, about 25 ml of the stock solution prepared was taken into a 250 ml volumetric flask. After that, it was being diluted up to the mark by addition of distilled water. Then, there was dilution for definite volumes of the stock solution to get the desired concentration of 2 ppm, 4 ppm, 6 ppm, 8ppm, 10 ppm and also 12 ppm. For absorbance reading, a UV-Vis Spectrometer (Model: Spec-20) was used with wavelength setting for methyl red of 410 nm.

Then, percentage of dye removal was calculated using following formula from the equation (3.2):

$$\%\, removal = \frac{initial\ reading - final\ reading}{initial\ reading} \times 100\% \quad (3.2)$$

3.3.5 Adsorption parameters study

There were several parameters (Kandasamy *et al.*, 2006) studied as mentioned in the sub-section below.

3.3.5.1 Best adsorbent from 8 samples produced

For this parameter, all the 8 samples were produced had different carbonization time with specified chemicals soaked. Due to this, each activated carbons produced (5 g) were tested with 25 ml of 10 ppm methyl red solution in conical flasks. After being mixed together, all the conical flaks were shaken in orbital shaker using 100 rpm for 1 hour. After 1 hour, all dyes with activated carbons were filtered into other conical flasks as to get the result for dye removal. The filtered dyes were pipette into cuvettes and the reading read using UV-Vis spectrometer was recorded.

3.3.5.2 Contact times

The best activated carbon from previous experiment was chosen to continue second experiment for contact times. 5 g of activated carbon was tested with 25 ml of 10 ppm methyl red solution in 3 conical flasks. The conical flasks were labelled as 30 minutes, 1 hour and 2 hour. Then, all conical flasks were being shaken using orbital shaker of 100 rpm. After 30 minutes, the first conical flask was removed and

filtered to get the reading of dye removal was recorded using UV-vis spectrometer. This step was repeated for 1 hour and 2 hour tested dye. Then, the best removal time of dye was selected for next test for concentration parameter.

3.3.5.3 Initial dye concentration

From previous test, best activated carbon and best contact time for dye removal was being identified. Then, the best activated carbon with the best contact time was tested for initial dye concentration of 25 ppm and 50 ppm. Due to that, 25 ppm and 50 ppm of methyl red solution were being prepared and diluted up from the stock solution of 100 ppm methyl red solution. Then, 5 g of activated carbon was tested with 25 ml of 25 ppm and 50 ppm of methyl red solution in 2 conical flasks. The conical flasks were labelled as 25 ppm and 50 ppm. Then, both conical flasks were being shaken using orbital shaker of 100 rpm. After 30 minutes, the both conical flasks were removed and filtered to get the reading of dye removal using UV-vis spectrometer.

3.3.6 Statistical Analysis

This analysis was being done as to identify the significant difference between optical density of pure dye and treated dye with activated carbon. Generally, T-test was used in statistical analysis to determine either difference in optical density was due to adsorption or due to change of fluctuations from time of testing to another. T-test was conducted by comparing the mean of optical density of pure dye with optical density of treated dye.

In this study, statistical analysis was being determined by using application of Minitab 17 as shown in Appendix B in order to produce one-way ANOVA.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Production of Activated Carbon from *Parkia speciosa* Pods

In this study, *Parkia speciosa* pods were being used as to produce activated carbon. In the beginning, there were 8 samples of activated carbon produced by impregnating with phosphoric acid (H_3PO_4) and zinc chloride ($ZnCl_2$). 8 samples of activated carbon produced were labelled for each as shown in Table 4.1. The category of activated carbon was divided due to chemicals used and carbonization time. Weight loss of raw material was determined in drying process and also sieving process. While for the hardness of *Parkia speciosa* pods were being identified during grinding process of the raw materials.

Table 4.1: Production of Activated Carbon

Types Of Activated Carbon	Acid used	Carbonization time (minutes)	Mass of AC before wash (gram)	Mass of AC after wash (gram)
A	$ZnCl_2$	5	6.94	4.27
B		10	7.49	4.54
C		30	6.81	3.77
D		60	6.55	3.40
E	H_3PO_4	5	9.94	3.67
F		10	10.43	1.97
G		30	11.01	2.54
H		60	9.47	3.01

Figure 4.1 shows the structure and colour of *Parkia speciosa* pods before and after was dried using the oven. The colour of *Parkia speciosa* pods became dark as it was being dried in oven. Due to this, dark colour composed of high carbon content, thus will have low weight loss after carbonization.

Figure 4.1: Structure of *Parkia speciosa* pods before and after drying

After drying process, there was high weight loss of raw material because of high weight at the beginning consisted of large weight of water molecules. Then *Parkia speciosa* pods were ground using grinder machine. In this process, the weight loss of *Parkia speciosa* pods was seen. Then, *Parkia speciosa* pods were sieved by using 425μm siever in obtaining small size of activated carbon. Producing of small activated carbon size may increase its surface area for adsorption process. After sieving, *Parkia speciosa* pods were weighed again and the reading was recorded about 277.75 g.

The prepared raw material was impregnated with chemicals which react as catalyst such as zinc chloride ($ZnCl_2$) and phosphoric acid (H_3PO_4) were being chosen because of its effective activating capabilities, while H_3PO_4 was chosen due to its environmental soundness in meaning of lower environmental and toxicological problem (Khadiran *et al*., 2015). Both of these chemicals were impregnated with raw materials before the carbonization process.

After activated carbons were removed from the furnace, they were weighed for their mass. Then, all of them were washed with a lot of deionized water together with distilled water as to get natural pH. This process of washing was to remove any impurities which attached at the activated carbon. After being washed, activated carbons were dried in an oven at 50℃ for 24 hours. Next, as the activated carbons were dried, their mass (Table 4.1) was weighed again as to determine how much the loss of weight.

From Table 4.1, the result of activated carbon produced showed there was a little loss of weight after the carbonization process. For $ZnCl_2$ impregnation, the range weight of activated after carbonization process was 6.50 to 7.50. While for H_3PO_4 impregnation, the activated carbon weight was range from 9.45 to 11.05 which means the whole weight for activated carbon impregnated with H_3PO_4 was much higher than activated carbon impregnated with $ZnCl_2$. This indicated weight loss was much higher for activated with $ZnCl_2$ impregnation.

However, after the activated carbons were being washed with deionized water and distilled water the loss of weight seemed to be high for H_3PO_4 impregnation. From Table 4.1, the less one activated carbon's mass was activated carbon F with mass of 1.97 g only. This factor would be affected by washing with much of

deionized water and distilled water. During the washing process, activated carbon with H_3PO_4 impregnation seemed need much of water to be washed rather than $ZnCl_2$ impregnation as to get the natural pH.

4.2 Calibration Curve for Methyl Red

Calibration curve in this research was important as to prove either the dilution experiment was correct or not. It was being proved by producing the correlation coefficient (R^2) from the plotting point at the graph as to evaluate the degree of linear association between two variables (Elskens *et al*., 2002). Generally, curves with r $\geq$ 0.995 were considered as linear. Besides that, by producing this calibration curve, the equation gradient produced could determine the unknown reading for calculating of percentage removal.

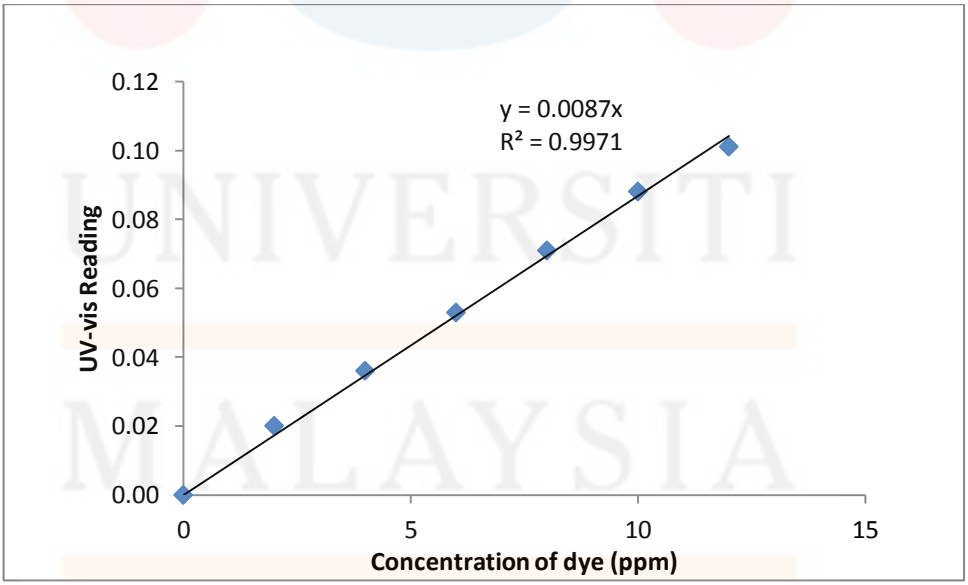

Figure 4.2: Calibration Graph

From the above graph, R^2 value was 0.9971 which proved that the value of dilution for each concentration was definitely correct. In finding the unknown

reading for initial reading by using the equation produced in the graph which was y=0.0087x. This formula used to calculate the initial reading for finding the percentage removal of dyes.

4.3 Comparison between Acid of $ZnCl_2$ and H_3PO_4 Activation for Carbon Activation

Based on this research objective, carbon activation was being conducted using the impregnation of zinc chloride ($ZnCl_2$) and phosphoric acid (H_3PO_4). Both of these chemicals impregnation was to determine the best activating agent for this agricultural waste adsorbent for methyl red removal. From the chemicals used, further parameters were investigated for best adsorbent, contact time and initial dye concentration towards percentage removal of methyl red. The results obtained were graphically represented and being discussed more for the percentage removal of methyl red against parameters.

4.4 Removal of Methyl Red Using Different Type of Adsorbents

Effect of different types of activated carbon on methyl red removal could be seen in Figure 4.3 with calculated percentage removal using the formula of efficiency. Initial dye concentration (10 ppm), contact time (1 hour), adsorbent dose (0.5 g) and stirring speed (100 rpm) were the constant variable used in this parameter.

Based on Figure 4.3, there were 8 types of activated carbon which impregnated with different chemicals and different carbonization time. Activated carbon A, B, C, and D were impregnated with $ZnCl_2$ solution while the other 4 activated carbon of E, F, G, and H were impregnated with H_3PO_4 solution. For

carbonization time in furnace, activated carbon A and E was 5 minutes. Activated carbon B and F were carbonized for 10 minutes while activated carbon C and G carbonization's time was 30 minutes. Last but not least, activated carbon D and G were carbonized for 1 hour in furnace. The main goal of impregnation with different chemical and different carbonization time of these adsorbents was to produce the best activated carbon in removing the methyl red.

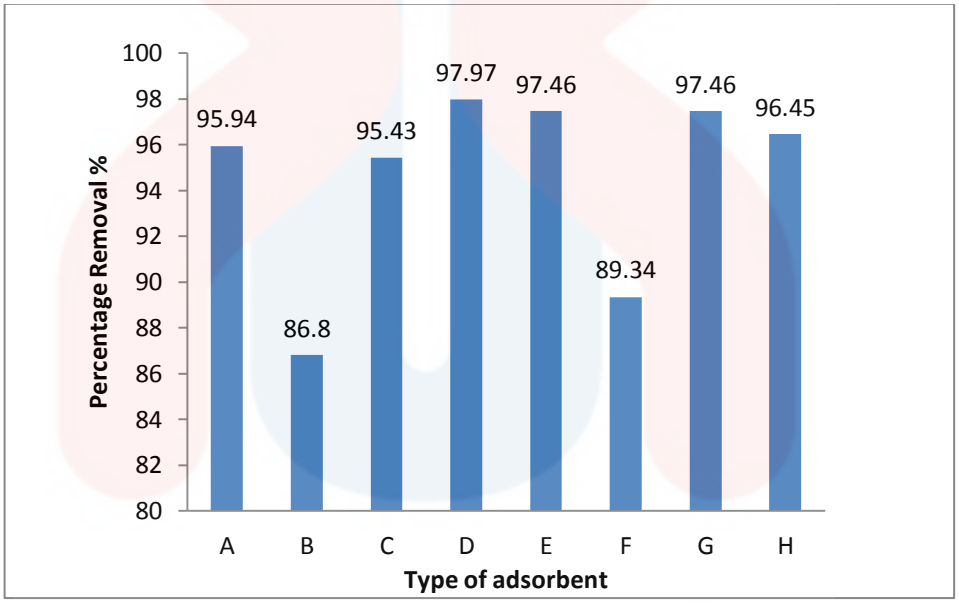

Figure 4.3: Effect of Different Type of Adsorbent

From the experiment, the result showed each activated carbon had different UV-vis reading and percentage removal. Based on Figure 4.3, decreasing of UV-vis reading influenced the increasing of percentage removal for methyl red. Optimum percentage removal of methyl red was 97.97 % by activated carbon D which impregnation of $ZnCl_2$ at 1 hour of carbonization time. This activated carbon recorded the lowest value reading of UV-vis spectrometer with only 0.004.

Activated carbon B and F recorded higher reading of UV-vis spectrometer then made both of the percentage removal were lower than the other activated carbon. The percentage removals were recorded as 86.80 % and 89.34%. While the other 6 activated carbons exceeded 95 % of percentage removal for methyl red were graphically presented as shown in Figure 4.3. This was due to the lower reading of UV-vis spectrometer produced. So, from this experiment activated carbon D was the best adsorbent among the other 7 activated carbons to remove methyl red for 10 ppm at 30 minutes of contact time.

Based on the ANOVA result (Appendix A), this parameter had produced two result of ANOVA using one-way method. Firstly, the result was for ANOVA of percentage removal versus type of adsorbent. The adsorbents were verified their types by comparing with two chemicals activation agent of zinc chloride solution and phosphoric acid solution. Types of adsorbent were recorded as "AC PH" which was activated carbon impregnation with phosphoric acid while "AC ZN" was the activated carbon impregnation with zinc chloride. The null hypothesis for a main effect was that the response mean for all factor levels were equal.

Based on Table 4.2, it showed the significance level was 0.05 indicated a 5% risk of including that an effect exists when there was no actual effect. P-value for types of adsorbent was 0.730 which greater than significance level. This verified that types of adsorbent were not statistically significant. The predictors explained 2.14% of the variation in the response. The adjusted R^2 was 0% which was totally decreasing of 2.14%. The low predicted R^2 value (0%) indicated that the model did not predict new observations as well as it fitted the sample data. This data could be referred in Appendix A.

Table 4.2: Analysis of Variance (ANOVA) for Type of Adsorbent

Source	DF	Adjusted SS	Adjusted MS	F-Value	P-Value
Type of Adsorbent	1	2.611	2.611	0.13	0.730
Error	6	119.520	19.920		
Total	7	122.130			

*Significance level ($p<0.005$), ** non-significance difference ($p> 0.005$)

Secondly, the result was the ANOVA for percentage removal versus time of carbonization. From the Table 4.3, it showed the significance level was 0.05 as same as previous ANOVA for adsorbent. P-value for carbonization time was 0.007 which lower than significance level. This verified that carbonization time were statistically significant. The S value was recorded 1.37810. The predictors explained 93.78% of the variation in the response which mean the higher the R^2 value, the better the models fitted the data. The adjusted R^2 was 89.11% which was decreasing of 4.67%. The low predicted R^2 value (75.12%) indicated that the model did not predict new observations as well as it fitted the sample data. Based on the mean obtained in the ANOVA, it showed that time D which 1 hour of carbonization time had the highest mean of 97.210 among the other time.

Table 4.3: Analysis of Variance (ANOVA) for Carbonization Time

Source	DF	Adjusted SS	Adjusted MS	F-Value	P-Value
Type of Adsorbent	3	114.534	38.178	20.10	0.007
Error	4	7.597	1.899		
Total	7	122.130			

*Significance level ($p<0.005$), ** non-significance difference ($p> 0.005$)

4.5 Removal of Methyl Red Using Different Contact Time

The removal of methyl red with the best adsorbent (Activated Carbon D) obtained from previous experiment was being studied further by varying contact time of 30 minutes, 1 hour and 2 hour. The adsorbent dosage (5 g), initial dye concentration (10 ppm), and stirring speed (100 rpm) were kept constant. The percentage removal of methyl red was given in Figure 4.4, which showed that the percentage of methyl red decreased with increasing contact time. From the table, the result showed activated carbon with 30 minutes had the highest percentage removal which was 100 %. This may be due to the attainment of equilibrium time in adsorption of methyl red at 30 minutes (Alam *et al*., 2007), thus it was being totally removed by the chosen activated carbon with 5 g of adsorbent dosage for 10 ppm initial dye concentration.

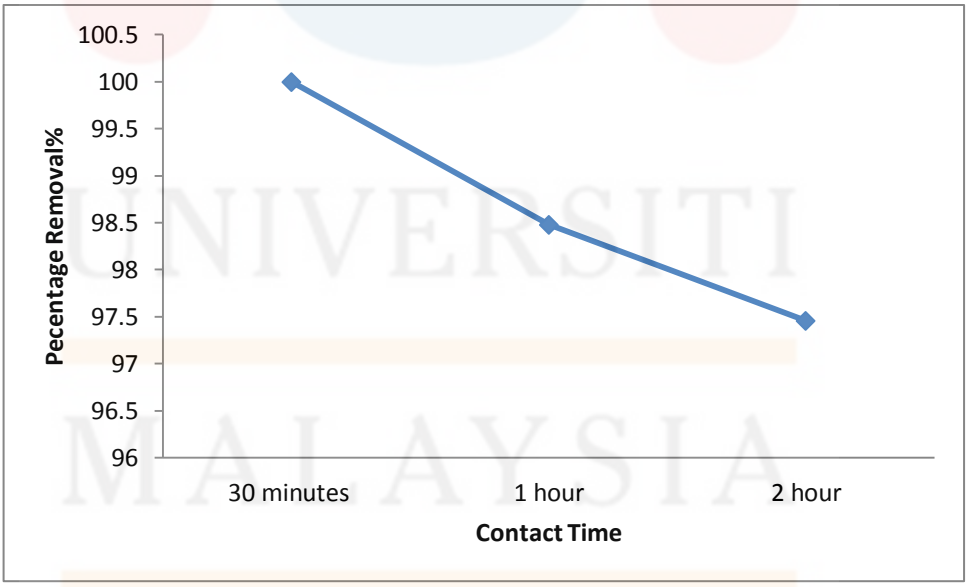

Figure 4.4: Effect of Different Contact Time

Based on Figure 4.4, the graph showed percentage removal of methyl red was inversely proportional to the contact time. This indicated if the experiment was further studied with same parameter and same constant variable, the percentage removal would be decreased influenced by increasing of contact time. As shown in Figure 4.4, after 30 minutes which was at 1 hour, the percentage removal decreased to 98.48 %. While another 1 hour adding of contact time made further decreasing of percentage removal to 97.46 %. The removal adsorption of methyl red decreased as adding of contact time (Table 4.4) could be explained that larger amount of adsorbent dosage or different initial dye concentration may be needed to make the removal was efficient.

Table 4.4: Analysis of Variance (ANOVA) for Contact Time

Source	DF	Adjusted SS	Adjusted MS	F-Value	P-Value
Type of Adsorbent	2	6.45403	3.22702	21523.44	0.000
Error	3	0.00045	0.00015		
Total	5	6.45448			

*Significance level ($p<0.005$), ** non-significance difference ($p> 0.005$)

From the result obtained for ANOVA (Appendix A), it showed the significance level was 0.05. P-value for contact time was 0.000 which lower than significance level. This verified that contact time were statistically significant. The S value recorded was 0.0122474. The predictors explained 99.99% of the variation in the response which mean the higher the R^2 value, the better the model fitted the data. The adjusted R^2 was 99.99% which was same as R^2 value.

The predicted R^2 value (99.97%) which was quite large value indicated that the model had better predictive ability. Based on the mean obtained in the ANOVA, it showed that time A which 30 minutes of contact time had the highest mean of 99.9850 among the other time.

4.6 Removal of Methyl Red Using Different Initial Dye Concentration

Effect of initial dye concentration on removal of methyl red was further studied and discussed by examine three different initial dye concentration (10 ppm, 25 ppm, and 50 ppm). For constant variable, there were adsorbent dose (0.5 g), contact time (30 minutes), and stirring speed (100 rpm). As shown in Figure 4.5, percentage removal of methyl red decreased due to the increasing of initial dye concentration.

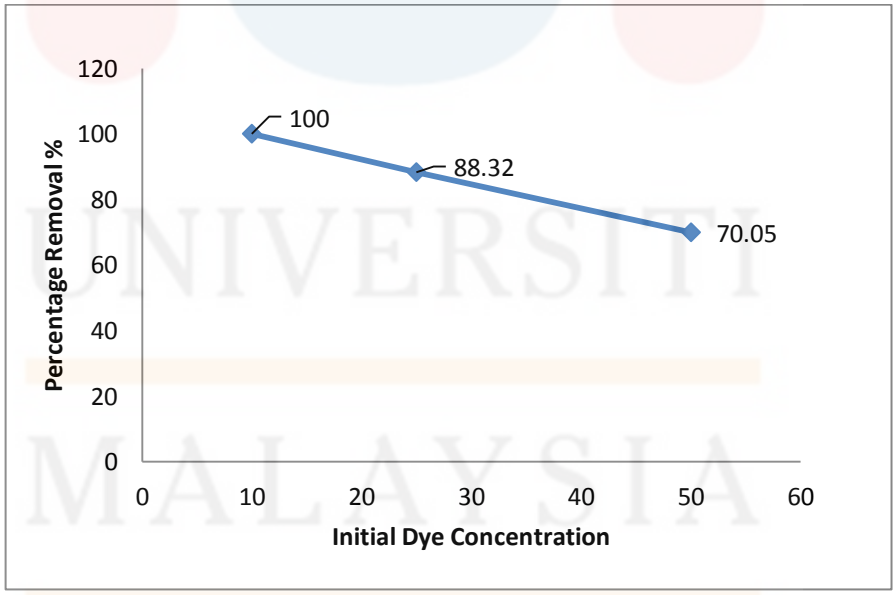

Figure 4.5: Graph for Percentage Removal vs Initial Dye Concentration

This is because at lower concentrations, there are sufficient active sites that the sorbate can easily occupy. However when the concentration became high, active

sorption sites were not sufficiently available for the sorbate to occupy (Attia *et al*., 2010).

Figure 4.5 showed that percentage removal of methyl red was inversely proportional to the initial dye concentration. The size of dye particles in solution usually depends on temperature, concentration of electrolyte and concentration of dyes. The size of dye particles always increased with an increased in dye concentration (Acosta *et al*., 2013). Due to that, adding of adsorbent dosage and contact time may be needed as increasing of initial dye concentration to have an effective dye removal result.

As shown in the Table 4.5, it showed the significance level was 0.05. P-value for initial dye concentration was 0.000 as same as previous parameter which lower than significance level. This verified that initial dye concentrations were statistically significant. The S value recorded was 0.0122474. The predictors explained 100.00% of the variation in the response which mean the higher the R^2 value, the better the models fitted the data. The adjusted R^2 was 100.00% which was same as R^2 value.

Table 4.5: Analysis of variance (ANOVA) for initial dye concentration

Source	DF	Adjusted SS	Adjusted MS	F-Value	P-Value
Type of Adsorbent	2	911.347	455.674	3037823.44	0.000
Error	3	0.000	0.000		
Total	5	911.347			

*Significance level ($p<0.005$), ** non-significance difference ($p> 0.005$)

The predicted R^2 value (100.00%) which was as same value as both previous R^2 that indicated the model had better predictive ability. Based on the mean obtained in the ANOVA, it showed that initial dye concentration A which 10 ppm had the highest mean of 100.00% among the other concentration. Further details of this ANOVA could be seen in Appendix A.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

In this research, several parameters were studied to obtain the optimum conditions for the removal of methyl red by producing activated carbon from *Parkia speciosa* pods as a low cost adsorbent.

The percentage removal of 10 ppm methyl red with 1 hour of contact time has shown the highest removal (97.97%) by activated carbon D among the other seven adsorbents. This activated carbon is impregnated by zinc chloride solution with 1 hour of carbonization time. Due to this, activated carbon D has been chosen in removing methyl red for next parameter. For second parameter of percentage removal against contact time, the result obtained shows that 30 minutes is the best contact time for the methyl red to be fully removed by the activated carbon D.

Further experiment has been studied for initial dye concentration of methyl red using the best adsorbent and the best contact time. Based on the result observation, 10 ppm methyl red is the best initial dye concentration with 100% removal of methyl red.

These three parameters have been conducted using same dosage of adsorbent (0.5 g), stirring speed of 100 rpm and 25 ml of methyl red. Due to these results and discussion, it can be concluded that 0.5 g of activated carbon D is the best removal for 25 ml of 10 ppm methyl red in 30 minutes of contact time.

In this study, it can be concluded that 0.5 g of activated carbon D was the best removal for 25 ml of 10 ppm methyl red with 30 minutes contact time.

5.2 RECOMMENDATION

Based on this research, it can be identified that activated carbon from *Parkia speciosa* pods can be produced as a low cost adsorbent and it can remove or adsorb methyl red with certain parameters as discussed in previous result and discussion. However, within the scope of this research, there are several recommendations that can be taken as to improve the efficiency of removal methyl red in future research by this low cost adsorbent by considering a few matters.

Firstly, it is essential to alert that 0.5 g of activated carbon D which is chosen as the best adsorbent, is only can fully remove 25 ml of 10 ppm methyl red within 30 minutes. However, if the initial dye concentration and contact time are being changed, the same adsorbent cannot fully remove the methyl red as showed in the result. Thus, for further research, dosage of adsorbent should be tested too in having more efficiency for removal of methyl red.

Secondly, future research can focus too on identifying functional group of the agricultural waste. Functional group can help in understanding of potential mechanism of adsorption besides electrostatic attraction. This identification of functional group can be carried out by using Fourier-Transform Infrared Spectroscopy (FTIR).

Furthermore, there should be identification of physical characteristics for activated carbon produced such as surface area and porosity. Due to this, future research may obtain results in comparing physical characteristics of each activated carbon thus can identify the best character of adsorbent for adsorption. Brunauer-Emmett-Teller (BET) can be used as to determine the pore surface area of activated carbon for further discussing high capacity of adsorption.

REFERENCES

Abdullah, A. G. L., Salleh, M., Mazlina, M. K. S., Noor, M. J. M. M., & Osman, M. R. (2005). Azo Dye Removal By Adsorption Using Waste Biomass : Sugarcane Bagasse Adsorbents. *Journal of Engineering and Technology*, *2*(1), 8–13.

Abdullah, M. H. R. O., Ch'ng, P. E., & Lim, T. H. (2011). Some Physical Properties of Parkia speciosa seeds, *9*, 43–47.

Abidin, Z. A., Fahmi, Ong, S. ., Makhtar, S. N. . M., Rahmat, N. R., & Ahmad, R. (2016). Decolourization and COD Reduction of Textile Wastewater by Ozonation in Combination with Biological Treatment. *Journal of Automotive and Mechanical Engineering (IJAME)*, *13*(1), 3141–3149.

Acosta, I., Cardenas, J. F., Moctezuma, M. D. G., & Martinez, V. M. (2013). Removal of Hexavalent Chromium from Solutions and Contaminated Sites by Different Natural Biomasses. *Applied Bioremediation - Active and Passive Approaches*, (Vi), 209–226.

Adeyemo, A., Adebowale, K., & Olu-Owolabi, B. (2014). Adsorption of Copper by Raw Pinecone. *American Chemical Science Journal*, *4*(6), 992–1000.

Adeyiga, A. A., Hu, L., & Greer, T. (1997). Removal of Metal Ions From Wastewater With Natural Wastes. *Water*, 1–8.

Ahmad, A. L., Harris, W. A. N. A., & Seng, O. O. I. B. (2007). Removal Of Dye From Wastewater Of Textile Industry Using Membrane Technology Homemade textile industry is very well known in Malaysia especially in the East Coast of Peninsular Malaysia and Sarawak . This industry is traditionally inherited from generatio. *Journal of Technology*, *36*, 31–44.

Akpor, O. B. (2014). Heavy Metal Pollutants in Wastewater Effluents: Sources, Effects and Remediation. *Advances in Bioscience and Bioengineering*, *2*(4), 37.

Al Batran, R., Al-Bayaty, F., Jamil Al-Obaidi, M. M., Abdualkader, A. M., Hadi, H. A., Ali, H. M., & Abdulla, M. A. (2013). In Vivo Antioxidant and Antiulcer Activity of Parkia speciosa Ethanolic Leaf Extract against Ethanol-Induced Gastric Ulcer in Rats. *PLoS ONE*, *8*(5), 2–12.

Alam, M. M., Rahman, M. L., & Haque, M. Z. (2007). Extraction of Henna Leaf Dye and its Dyeing Effects on Textile Fibre. *Journal of Science*, *42*(2), 217–222.

Algarra, M., Jiménez, M. V., Rodríguez-Castellón, E., Jiménez-López, A., & Jiménez-Jiménez, J. (2005). Heavy metals removal from electroplating wastewater by aminopropyl-Si MCM-41. *Chemosphere*, *59*(6), 779–786.

All, C., Moulin, P., Maisseu, M., & Charbit, F. (2006). Treatment and reuse of reactive dyeing effluents. *Journal of Membrane Science*, *269*, 15–34.

Amarnath, B. (2004). a Study on Antioxidant Nature. *Journal of Science*, *3*(2), 161.

Attia, A. A., Khedr, S. A., & Elkholy, S. A. (2010). Adsorption of chromium ion (VI) by acid activated carbon. *Brazilian Journal of Chemical Engineering*, *27*(1), 183–193.

Bari, Q., & Bhardwaj, N. (2014). Role of Bio-sorbents in the decolorization of some commonly used dyes. *Journal of Science*, *4*(10), 637–642.

Baseri, J. R., Palanisamy, P. N., & Sivakumar, P. (2012). Preparation and characterization of activated carbon from Thevetia peruviana for the removal of dyes from textile waste water. *Journal of Applied Science*, *3*(1), 377–383.

Behnood, R., Anvaripour, B., Jaafarzade, N., & Fard, H. (2013). Application of Natural Sorbents in Crude Oil Adsorption. *Iranian Journal of Oil & Gas Science and Technology*, *2*(4), 1–11.

Bujang, M., & Ibrahim, N. A. (2012). Physicochemical Quality of Oily Wastewater from Automotive Workshop in Kota Bharu, Kelantan Malaysia. *Australian Journal of Basic and Apllied Sciences*, *6*(9), 748–752.

Din, F., & Mohamed, S. (1993). Hypoglycemic Effect of Extracts of Petai Papan (Parkia speciosa, Hassk), *16*(3), 161–165.

Elskens, M., Van Loco, J., Croux, C., & Beernaert, H. (2002). Linearity of calibration curves : use and misuse of the correlation coefficient. *Journal of Scientific Institute*, *7*, 281–285.

Emigilati, M. A., Ishiaku, I., Usman, B. Y., & Kuta, G. I. (2015). Assessment of effluents discharged from textiles industries in selected villages in Kaduna State , Nigeria. *Journal of Environmental Science and Technology*, *9*(May), 385–389.

Flohe, R. B., & Traber, M. G. (1999). Vitamin E: function and metabolism. *Journal of Human Nutrition & Food Management*, *13*(10), 1145–1155.

Foo, P., & Lee, L. (2010). Preparation of activated carbon from Parkia Speciosa Pod by chemical activation. *Proceedings of the World Congress on Engineering ...*, *II*, 1–17.

Gupta, S., & Babu, B. V. (2009). Removal of toxic metal Cr(VI) from aqueous solutions using sawdust as adsorbent: Equilibrium, kinetics and regeneration studies. *Chemical Engineering Journal*, *150*(2-3), 352–365.

Hasima, Faridah, D. N., & Kurniawati, D. A. (2015). Antibacterial activity of Parkia speciosa Hassk. peel to Escherichia coli and Staphylococcus aureus bacteria. *Journal of Chemical and Pharmaceutical Research*, *7*(4), 239–243.

Hassan, A. A., & Abdulhussein, H. A. (2015). Methyl Red Dye Removal From Aqueous Solution by Adsorption on Rice Hulls. *Journal of Babylon University/Engineering Sciences*, *23*(2).

Henze, M., & Comeau, Y. (2008). Wastewater Characterization. *Biological Wastewater Treatment: Principles Modelling and Design.*, 33–52.

Iqbaldin, M. N. M., Khudzir, I., Azlan, M. I. M., Zaidi, A. G., Surani, B., & Zubri, Z. (2013). Properties Of Coconut Shell Activated Carbon. *Journal of Tropical Forest Science*, *25*(4), 497–503.

Jaganathan, V., Busi, I., Mgt, M. P., Int, M. P., Mba, B., Premapriya, M. S., & Phil, M. (2014). Environmental Pollution Risk Analysis And Management In Textile

Industry : A Preventive Mechanism. *Scientific Journal*, *2*(September), 323–329.

Jeppu, G. P., & Clement, T. P. (2012). A modified Langmuir-Freundlich isotherm model for simulating pH-dependent adsorption effects. *Journal of Contaminant Hydrology*, *129-130*, 46–53.

Joaquin, A., Hamad, S., Al, A., & Namdeti, R. (2015). Water Analysis Using Activated Carbon From Coconut Shell Present Of Salts In Fog Water. *International Journal of Latest Research in Science and Technology*, *4*(5), 5–7.

Kandasamy, J., Vigneswaran, S., Hoang, T. T. L., & Chaudhary, D. N. S. (2006). Adsorption and Biological FIltration in Wastewater Treatment. Waste Water Treatment Technologies. *Encyclopedia of Life Support System*, *2*(56), 100–120.

Karim, A. A., & Azlan, A. (2012). Fruit pod extracts as a source of nutraceuticals and pharmaceuticals. *Molecules*, *17*(10), 11931–11946.

Khadiran, T., Hussein, M. Z., Zainal, Z., & Rusli, R. (2015). Textural and Chemical Properties of Activated Carbon Prepared from Tropical Peat Soil by Chemical Activation Method. *Bioresources Journal*, *10*, 986–1007.

Ko, H.-J., Ang, L.-H., & Ng, L.-T. (2014). Antioxidant Activities and Polyphenolic Constituents of Bitter Bean Parkia Speciosa. *International Journal of Food Properties*, *17*(9), 1977–1986.

Mara, D. (2003). Domestic wastewater treatment in developping countries (p. 310).

Maya, R., Radin, S., Nanyan, N. M., Rahman, N. A., A, N. M., Kutty, I., … Kassim, M. (2014). Colour Removal of Reactive Dye from Textile Industrial Wastewater using Different Types of Coagulants. *Journal of Applied Science*, *02*(05), 650–657.

Mehla, R., Guha, D., & Ayyavoo, V. (2012). Chemokine Deregulation in HIV Infection: Role of Interferon Gamma Induced Th1-Chemokine Signaling. *Journal of Clinical and Cellular Immunology*, *7*(4), 1–12.

Mohammed, W. T., Farhood, H. F., Hassoon, A., & Al-mas, B. (2009). Removal of Dyes from Wastewater of Textile Industries Using Activated Carbon and Activated Alumina. *Journal of Chemical and Petroleum Engineering*, *9*(4), 43–52.

Mohd Azizi, C. H., Salman, Z., Nik Norulain, N. ., & Mohd Omar, a. . (2008). Extraction and Identification of Compounds from Parkia Speciosa Seeds by Supercritical Carbon Dioxide, 153–163.

Ngoh, Y. Y., Leong, Y. H., & Gan, C. Y. (2015). Optimization study for synthetic dye removal using an agricultural waste of Parkia speciosa pod: A sustainable approach for waste water treatment. *International Food Research Journal*, *22*(6), 2351–2357.

Noor, A. Bin, Asri, M., & Mohd, B. (2008). Textural Characteristics of Activated Carbons Prepared from Oil Palm Shells Activated with ZnCl 2 and Pyrolysis Under Nitrogen and Carbon Dioxide. *Journal of Physical Science*, *19*(2), 93–104.

Ogugbue, C. J., & Sawidis, T. (2011). Bioremediation and Detoxification of Synthetic Wastewater Containing Triarylmethane Dyes by Aeromonas hydrophila Isolated from Industrial Effluent. *Journal of Biotechnology*, *2011*.

Onukwuli, C. A., & Okey, D. (2015). Adsorptive Removal Of Dyes From Synthetic Wastewater Using Activated Carbon From Tamarind Seed. *Journal of Chemical Engineering*, *11*(18), 190–221.

Ozdemir, C., Karatas, M., Sahinkaya, S., & Argun, M. E. (2009). Physico-chemical studies of enamel cover industry wastewater. *Asian Journal of Chemistry*, *21*(2), 964–970.

Rad, M. S., Irandoust, M., Amri, S., Feyzi, M., & Ja, F. (2014). water samples using silica coated magnetic nanoparticles. *Journal of Applied Research in Water & Wastewater*, *1*, 6–12.

Rahman, M. A., Amin, S. M. R., & Alam, A. M. S. (2012). Removal of Methylene Blue from Waste Water Using Activated Carbon Prepared from Rice Husk. *Journal of Chemistry*, *60*(2), 185–189.

Sahoo, C., Gupta, A. K., & Pal, A. (2005). Photocatalytic degradation of Methyl Red dye in aqueous solutions under UV irradiation using Ag + doped TiO 2. *Journal of Civil Engineering*, *181*, 91–100.

Santos, B., Cervantes, F. J., & Lier, J. B. Van. (2007). Review paper on current technologies for decolourisation of textile wastewaters : Perspectives for anaerobic biotechnology. *Journal of Bioresource Technology*, *98*, 2369–2385.

Sivakumar, B., Kannan, C., & Karthikeyan, S. (2012). Preparation And Characterization Of Activated Carbon Prepared From Balsamodendron Caudatum Wood Waste Through Various Activation Processes. *Journal of Engineering and Technology*, *5*(3), 321–327.

Srisuwan, G., & Thongchai, P. (2002). Removal of heavy metals from electroplating wastewater by membrane. *Journal of Chemical and Pharmaceutical Sciences*, *24*(3), 965–976.

Syafalni, S. (2012). Treatment of Dye Wastewater Using Granular Activated Carbon and Zeolite Filter, *6*(2), 37–51.

Upadhye, G. C., & Yamgar, R. S. (2016). Analytical study of agricultural waste as non- conventional low cost adsorbent removal of dyes from aqueous solutions. *International Journal of Chemistry Studies*, *4*(1), 128–133.

Webb, P. a. (2003). Introduction to Chemical Adsorption Analytical Techniques and their Applications to Catalysis. *MIC Technical Publications*, *13*(January), 1–4.

Yahya, M. A., Al-Qodah, Z., & Ngah, C. W. Z. (2015). Agricultural bio-waste materials as potential sustainable precursors used for activated carbon production: A review. *Renewable and Sustainable Energy Reviews*, *46*(2), 218–235.

Yasin, Y., Hussein, M. Z., & Ahmad, F. H. (2007). Adsorption Of Methylene Blue Onto Treated Activated. *Journal of Analytical Science*, *11*(11), 400–406.

APPENDIX A

One-way ANOVA: Percentage Removal versus Type of adsorbent

```
Method

Null hypothesis         All means are equal
Alternative hypothesis  At least one mean is different
Significance level      α = 0.05

Equal variances were assumed for the analysis.


Factor Information

Factor             Levels  Values
Type of adsorbent       2  AC PH, AC ZN


Analysis of Variance

Source             DF   Adj SS  Adj MS  F-Value  P-Value
Type of adsorbent   1    2.611   2.611     0.13    0.730
Error               6  119.520  19.920
Total               7  122.130


Model Summary

      S   R-sq  R-sq(adj)  R-sq(pred)
4.46318  2.14%      0.00%       0.00%


Means

Type of
adsorbent  N   Mean  StDev       95% CI
AC PH      4  94.03   4.95  (88.57,  99.50)
AC ZN      4  95.18   3.92  (89.72, 100.64)

Pooled StDev = 4.46318
```

Tukey Pairwise Comparisons

```
Grouping Information Using the Tukey Method and 95% Confidence

Type of
adsorbent  N   Mean  Grouping
AC ZN      4  95.18  A
AC PH      4  94.03  A

Means that do not share a letter are significantly different.
```

Tukey Simultaneous 95% CIs

One-way ANOVA: Percentage Removal versus Time

```
Method

Null hypothesis         All means are equal
Alternative hypothesis  At least one mean is different
Significance level      α = 0.05

Equal variances were assumed for the analysis.


Factor Information

Factor  Levels  Values
Time         4  A, B, C, D


Analysis of Variance

Source  DF   Adj SS  Adj MS  F-Value  P-Value
Time     3  114.534  38.178    20.10    0.007
Error    4    7.597   1.899
Total    7  122.130


Model Summary

      S    R-sq  R-sq(adj)  R-sq(pred)
1.37810  93.78%     89.11%      75.12%


Means

Time  N    Mean  StDev        95% CI
A     2  96.700  1.075  (93.994, 99.406)
B     2   88.07   1.80  ( 85.36,  90.78)
C     2   96.44   1.44  ( 93.74,  99.15)
D     2  97.210  1.075  (94.504, 99.916)

Pooled StDev = 1.37810
```

Tukey Pairwise Comparisons

```
Grouping Information Using the Tukey Method and 95% Confidence

Time  N    Mean  Grouping
D     2  97.210  A
A     2  96.700  A
C     2   96.44  A
B     2   88.07    B

Means that do not share a letter are significantly different.
```

Tukey Simultaneous 95% CIs

One-way ANOVA: Removal versus Contact time

```
Method

Null hypothesis         All means are equal
Alternative hypothesis  At least one mean is different
Significance level      α = 0.05

Equal variances were assumed for the analysis.


Factor Information

Factor        Levels  Values
Contact time       3  A, B, C


Analysis of Variance

Source        DF   Adj SS   Adj MS   F-Value  P-Value
Contact time   2  6.45403  3.22702  21513.44    0.000
Error          3  0.00045  0.00015
Total          5  6.45448


Model Summary

        S    R-sq  R-sq(adj)  R-sq(pred)
0.0122474  99.99%     99.99%      99.97%


Means

Contact
time     N     Mean   StDev         95% CI
A        2  99.9850  0.0212  (99.9574, 100.0126)
B        2    98.48    0.00  (  98.45,    98.51)
C        2    97.46    0.00  (  97.43,    97.49)

Pooled StDev = 0.0122474
```

Tukey Pairwise Comparisons

```
Grouping Information Using the Tukey Method and 95% Confidence

Contact
time     N     Mean  Grouping
A        2  99.9850  A
B        2    98.48    B
C        2    97.46      C

Means that do not share a letter are significantly different.
```

Tukey Simultaneous 95% CIs

One-way ANOVA: Removal versus Initial Dye Concentration

```
Method

Null hypothesis         All means are equal
Alternative hypothesis  At least one mean is different
Significance level      α = 0.05

Equal variances were assumed for the analysis.


Factor Information

Factor                     Levels  Values
Initial Dye Concentration       3  A, B, C


Analysis of Variance

Source                     DF   Adj SS   Adj MS     F-Value  P-Value
Initial Dye Concentration   2  911.347  455.674  3037823.44    0.000
Error                       3    0.000    0.000
Total                       5  911.347


Model Summary

        S     R-sq  R-sq(adj)  R-sq(pred)
0.0122474  100.00%    100.00%     100.00%


Means

Initial Dye
Concentration  N     Mean   StDev        95% CI
A              2    100.0     0.0     ( 100.0,   100.0)
B              2     88.3050  0.0212  (88.2774, 88.3326)
C              2     70.05    0.00    (  70.02,   70.08)

Pooled StDev = 0.0122474
```

Tukey Pairwise Comparisons

```
Grouping Information Using the Tukey Method and 95% Confidence

Initial Dye
Concentration  N     Mean  Grouping
A              2   100.0      A
B              2    88.305    B
C              2    70.05     C

Means that do not share a letter are significantly different.
```

Tukey Simultaneous 95% CIs