METHYL RED REMOVAL USING ACTIVATED CARBON DERIVED FROM ORANGE PEELS AS AN ADSORBENT

by

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DECLARATION

I declare that this thesis entitled 'Methyl Red Removal Using Activated Carbon derived from Orange Peels as an 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 : ____________________________

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LIST OF SYMBOLS

l	Litre
ml	Millilitre
mg	Milligram
g	Gram
°C	Degree Celsius
rpm	Revolutions Per Minute
λ	Wavelengths
μm	Micron Metre
nm	Nanometre
min	Minute
%	Percentage

Methyl Red Removal Using Activated Carbon derived from Orange Peels as an Adsorbent

ABSTRACT

Dye effluents are one of the major concerning problems in wastewater. The operating costs for wastewater treatment are quite high. Therefore, many researchers have identified capability of agricultural wastes as adsorbents to remove many types of pollutants including dyes. This study represents the use of orange peel in removing methyl red dyes and also makes a simple comparison between raw orange peel and activated carbon derived from orange peel. Batch adsorption study was performed to evaluate the effect of various parameters which are the effect of contact time, adsorbent dosage, size particle and pH. All the parameters were conducted at room temperature 27°C with constant shaking at 150 rpm for 80 minutes. The result shows that activated carbon derived from orange peel has the highest removal percentages of methyl red dye which is up to 98% for 80 minutes shaking compared to raw orange peel. This study indicated that activated carbon derived from orange peel can be an attractive option in removing methyl red dye which is low cost and environmental friendly adsorbent.

Penyingkiran Metal Merah Menggunakan Karbon Aktif yang didapati daripada Kulit Oren sebagai Bahan Penjerap

ABSTRAK

Efluen pewarna merupakan salah satu masalah utama berkaitan air sisa. Kos operasi untuk merawat air sisa ini adalah agak tinggi. Oleh itu, ramai penyelidik telah membuktikan sisa pertanian sebagai bahan penjerap untuk mengasingkan pelbagai jenis bahan pencemar termasuk pewarna. Kajian ini menggunakan kulit oren untuk menyingkirkan pewarna metil merah dan juga membuat perbandingan mudah di antara kulit oren mentah dengan karbon aktif yang didapati daripada kulit oren. Penjerapan kelompok telah dilakukan untuk mengkaji kesan daripada beberapa parameter iaitu kesan dari masa sentuhan, kuantiti penjerap, saiz partikel dan pH. Kesemua parameter telah dijalankan pada suhu bilik 27°C dengan pengadukkan yang sekata 150 rpm selama 80 minit. Hasilnya menunjukkan bahawa karbon aktif yang didapati daripada kulit oren mempunyai peratusan lebih tinggi dalam mengeluarkan pewarna metil merah iaitu sehingga 98% untuk 80 minit masa pengadukan berbanding kulit oren mentah. Kajian ini menunjukkan bahawa karbon aktif yang didapati daripada kulit oren boleh dijadikan pilihan yang menarik dalam mengeluarkan pewarna metil merah yang merupakan kos rendah dan penjerap mesra alam sekitar.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The discovery of synthetic dyes make an obvious change from past to present, when things began to change. Scientists have formulated gorgeous new colors and synthetic dyes have become obsolete for most applications. No doubt, this bright colored material has changed the world now days. Due to the characteristics of these new dyes that are cheaper to produce, more color-fast, brighter and easier to apply to fabric, dyes have been chosen by many industries such as textile, paper, cosmetic, plastic, leather, printing and so on to color their product. However, the chemicals used to produce dyes are often toxic, carcinogenic or even explosive and this poses a serious hazard to aquatic living organisms. Among the different pollutants of aquatic ecosystems, dyes are a major group of chemicals. The presences of dye materials greatly influence the quality of water. They can have acute or chronic effects on exposed organisms, which depend on the concentration of the dye and the exposed time (Dash, 2010).

The presence of color and color-causing compounds has always been undesirable in water for any use. Therefore, it is not surprising at all to note that the color in wastewater has now been considered as a pollutant that needs to be treated before discharge. Thus, color removal is one of the most difficult challenges to be addressed by textile finishing, dye manufacturing, pulp and paper industries, among others. These industries are major water consumers and therefore become a source of considerable pollution (Kyzas & Kostoglou, 2014). However, these wastewater containing dyes are difficult to treat with municipal waste treatment operations since the dyes are resistant to aerobic digestion, immune to light, heat and oxidizing agents and also have complicated chemical structures (Sun & Yang, 2003).

There are various biological, chemical and physical methods can be used for the treatment of dyes (Karthik *et al*., 2014). Among the methods, adsorption is found to be most economical and competitive one because it does not need a high operating temperature and several coloring materials can be removed simultaneously (Crini, 2006). Activated carbon is the most widely used adsorbent, because of its high capacity for adsorption of organic matter. But its use is limited because of its high cost (Mckay, 1982). Chitosan also has been classes as one of adsorbent that can be used for the removal of reactive dyes. However, chitosan have several other important applications (Uddin *et al*., 2007).

Therefore various researchers have studied an alternative way in produce activated carbon derived from agricultural waste due to its low cost materials and easy to be found. The agricultural waste products represent unused resources and also they are widely available and environmentally friendly so they have a great potential to be used as adsorbents. In selection for the most appropriate adsorbents, there have some major characteristic properties such as the material is the low-cost along with the satisfactory adsorption properties (capacity, reuse, industrial-scale use *etc.*). It also should be environmentally-friendly nature such as biodegradable and non-toxic which has the lowest impact on environmental balance (Kyzas & Kostoglou, 2014).

1.2 Problem Statement

One of the major problems concerning textile wastewaters is dye effluent. Dyes have been applied to textile and other substances for thousands of years and dyers and their suppliers have continually sought to develop new processes which lead to better result with costs. The dyeing industry effluents contain high Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) value, suspended solids, toxic compounds and the color that is perceived by human eyes at very low concentration (AbdurRahman *et al*., 2013). Moreover, dyes may adversely affect the aquatic life because of the presence of aromatic materials, metals and chlorides (AbdurRahman *et al*., 2013).

There need high operating cost in order to threat this influent water. Therefore, agriculture wastes have been introduced as an alternative adsorbent in removal of dye. Besides, these wastes have disposed in the large amount that may pollute the environment without improper treatment. So that, orange peels have been chosen as one of agriculture waste in this study in order to remove methyl red dye.

1.3 Objective

1. To investigate the potential of orange peel as an adsorbent in removing methyl red from wastewater.
2. To analyze the effect of orange peels as an adsorbent in different particle size, pH, dosage used and the contact time.

1.4 Significance of study

The significance of this study is to give more value added to the orange peel which is regarded as waste product as an efficient and cost-effective bio-adsorbent. Besides, this study will also give some useful information for textile industries and environmental organization in order to help our environment free from pollution.

CHAPTER 2

LITERATURE REVIEW

2.1 Wastewater

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. Wastewater can originate from a combination of domestic, industrial, commercial or agricultural activities, surface runoff or storm water, and from sewer inflow or infiltration. Such wastewater disposal may cause damage to the quality of the receiving water bodies, the aquatic eco-system and the biodiversity of environment (Kyzas & Kostoglou, 2014). Wastewater from textile industries constitutes a threat to the environment in large parts of the world. The degradation products of textile dyes are often carcinogenic. Furthermore, the absorption of light due to textile dyes creates problems to photosynthetic aquatic plants and algae.

Industrial effluents are one of the largest sources of water pollution and one with the most lethal composition of toxins. The most popular and widespread industrial pollutants include asbestos, mercury, lead, nitrate, phosphates, sulphur, petrochemical and oil. All these pollutants give bad impact to human and environment such as eutrophication, illness, inhibit the action of bodily enzymes and poisoning (Jhansi *et al.*, 2013). Therefore, with increasing population and economic growth nowadays, treatment and safe disposal of wastewater is important to preserve public health, reduce intolerable levels of environmental degradation and preserving the sources of clean water.

2.1.1 Wastewater Treatment

Water is one of the world's most important resources, yet it is under consistent risk because of environmental change and resulting drought, dangerous population growth and waste. One of the most promising efforts to stem the global water crisis is industrial and municipal water reclamation and reuse. Therefore, wastewater treatment is now receiving greater attention from the World Bank and government regulatory bodies (Jhansi *et al.*, 2013).

Conventional wastewater treatment methods for removing dyes include physicochemical, chemical and biological methods, such as coagulation and flocculation, adsorption, ozonation, electrochemical techniques, and fungal decolonization (Robinson *et al*., 2001b). Among the possible techniques for water treatments, the adsorption process by solid adsorbents shows potential as one of the most efficient methods for the treatment and removal of organic contaminants in wastewater treatment (Rashed, 2013). The adsorption processes is widely used for treatment of industrial wastewater from organic and inorganic pollutants and meet the great attention from the researchers. In recent years, the search for low-cost adsorbents that have pollutant –binding capacities has intensified. Materials locally available such as natural materials, agricultural wastes and industrial wastes can be utilized as low-cost adsorbents (Crini, 2005). Table 2.1 shows the comparison for various treatment methods (Foo & Hameed, 2012).

Table 2.1: The comparison for various treatment methods

Treatment method	Method description	Advantages	Disadvantages
Electrochemical destruction	Oxidation reaction using electricity	Breakdown compounds are nonhazardous	High cost of electricity
Electrokinetic coagulation	Addition of ferrous sulphate and ferric chloride	Economically feasible	High sludge production
Fenton reagents	Oxidation reaction using mainly H_2O_2-Fe(II)	Effective decolorization of both soluble and insoluble dyes	Sludge generation
Ion exchange	Ion exchange resin	Regeneration: no adsorbent loss	Not effective for all dyes
Ozonation	Oxidation reaction using ozone Gas	Application in gaseous state: no alteration of volume	Short half-life (20 min)
Membrane filtration	Physical separation	Removal of all dye types	Concentrated sludge production
Photochemical	Oxidation reaction using mainly H_2O-UV	No sludge production	Formation of by-products

(Sources: Foo & Hameed, 2012)

2.2 Dye

A dye is a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber (Booth & Gerald, 2000). Dyes are classified according to their solubility and chemical properties. There are many chemical varieties of dyes, for example acidic, basic and dispersed with structures such as azo-, diazo- and anthraquinone-based and metal-complex dyes. The highest rates of toxicity have been found amongst the basic and diazo direct dyes (Robinson *et al.*, 2001a). Dyes are widely used in various industries such as textiles, leather, plastic, paper and cosmetics for coloring their final products.

The release of colored wastewater from industry may produce an eco-toxic hazard and introduce potential danger of bioaccumulation, which may eventually affect humans through the food chain (Lin *et al*., 2008). The reactive dyes are highly water-soluble polyaromatic molecules, which mean that their adsorption to solids is relatively poor. Some dyes are decolorized under anaerobic conditions. The effluent might, however, be toxic furthermore; there might be a risk for reverse colorization when anaerobic degradation products are exposed to oxygen (Arunachalam & Annadurai, 2011).

2.2.1 Methyl Red

Methyl red (2-(N,N-dimethyl-4-aminophenyl) azobenzenecarboxylic acid), also called C.I. Acid Red 2, is an indicator dye that turns red in acidic solutions. Methyl red solution will turn red at pH below 4.4, yellow for pH over 6.2 and orange in between. In microbiology, methyl red is used in the methyl red test (MR test), used to identify bacteria producing stable acids by mechanisms of mixed acid fermentation of glucose. Methyl red is an anionic azo dye and is dark red crystalline powder.

Azo dyes are the largest group of dyes used in industry. Some azo dyes are toxic and mutagenic. It is well known that methyl red dye has been used in paper printing and textile dyeing and it causes irritation of the eye, skin and digestive tract if inhaled/swallowed (Lachheb *et al*., 2002). Textile wastewater contains residual dyes that are difficult to remove in conventional treatment plants. It is, therefore, essential to remove the dye from wastewater or treat it in such a way so as to minimize the damage to the environment and also to decolorize the water (Muthuraman & Teng, 2009). Figure 2.1 shows the chemical structure of methyl red.

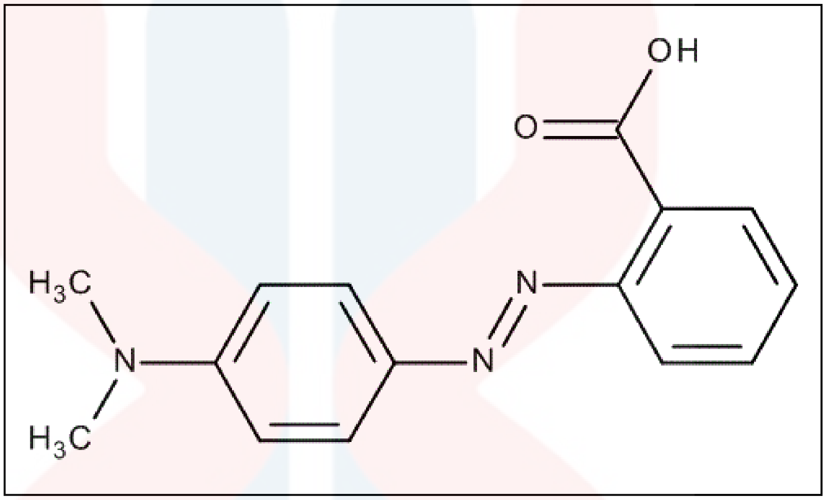

Figure 2.1: Chemical structure of methyl red

2.3 Adsorption

Adsorption is a surface phenomenon with common mechanism for organic and inorganic pollutants removal. When a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure, liquid–solid intermolecular forces of attraction cause some of the solute molecules from the solution to be concentrated or deposited at the solid surface (Rashed, 2013). There are differences in between adsorption and absorption. When a substance is attached to a surface it is called adsorption where the case is the substance is attached to the internal surface of active carbon, while if a substance is absorbed in a different medium it is called absorption.

Adsorption is present in many natural, chemical, biological and physical systems also is widely used in industrial applications such as activated charcoal, capturing and using waste heat to provide cold water for air conditioning and other process requirements adsorption chillers such as synthetic resins, increase storage capacity of carbide-derived carbons and water purification. In water treatment, adsorption has been proved as an efficient removal process for a multiplicity of solutes. Adsorption process has an edge over other methods due to its sludge free operation and complete removal of dyes even from dilute solutions (Foo & Hameed, 2012).

The use of adsorbents in adsorption process is usually in the form of spherical pellets, rods, moldings, or monoliths with a hydrodynamic radius between 0.25 and 5 mm. They must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high capacity for adsorption. The adsorbents must also have a distinct pore structure that enables fast transport of the gaseous vapors (Worch, 2012). Most industrial adsorbents fall into three different classes which is zeolites, silica gel and activated carbon.

Biosorption process is a type of adsorption which utilizes not only plant materials but also a wide variety of micro-organisms in dead, pretreated and immobilized form as adsorbing agents. These materials are cheap to produce and carry wide range of binding sites for dye molecules (Attia *et al*., 2006). Figure 2.2 shows the basic term of adsorption (Worch, 2012).

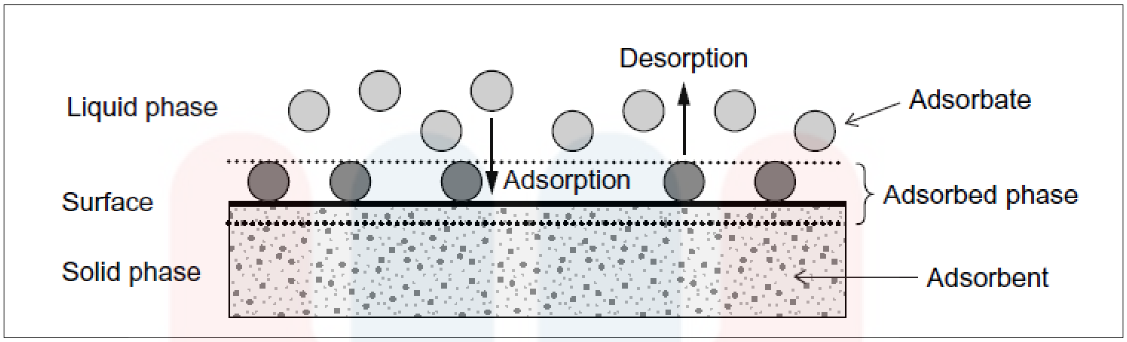

Figure 2.2: The basic term of adsorption (Worch, 2012)

2.4 Activated Carbon

Activated carbon has an inconceivably huge surface area per unit volume and a system of submicroscopic pores where adsorption happens. Activated carbon is a material that is created from carbonaceous source materials, for example peat, coconuts, wood, coal, nutshells, and lignite. The essential crude material utilized for activated carbon is any natural material with high carbon content. The carbon-based material is changed over to activated carbon through physical modification and thermal decomposition physical and in a furnace, under a controlled atmosphere and temperature. The finished product has a large surface area per unit volume and a system of submicroscopic pores where adsorption happens (Attia *et al*., 2006).

Activated carbon can be used to purify liquids and gases in a variety of applications, including odor removal, food and beverage processing, municipal drinking water, point-of-use filters in the home and industrial pollution control. For pollution control, activated carbon is the most commonly used adsorbent, because it has great capacity for adsorbing diverse organic compounds such as dyes, heavy metals, pharmaceutical and surfactants (Da Silva *et al*., 2011). However, the price of activated carbon is relatively high. Due to its relatively high cost, attempts have been made to utilize low cost, naturally occurring sorbents to remove trace contaminants from wastewater.

Many researchers have worked on production of activated carbon from renewable resources, using low cost methods and materials and emphasis also on to decontaminated water in an environmental friendly manner. Agricultural and industrial waste materials were used as activated carbons source by different researchers (Davila *et al*., 2012). The agricultural and forestry waste products represent unused resources and also they are widely available and environmentally friendly so they have a great potential to be used as adsorbents. The example of adsorbents used for dye removal is shown in Table 2.2.

Table 2.2: The example of adsorbents used for dye removal

Dyes	Adsorbent	Adsorption Capacity	References
Methylene Blue	Activated carbon from from Oil palm wood-based	90.9 mg/g	Ahmad *et al*, 2007
Reactive Black 5	Powdered Activated Carbon	58.823 mg/g	Eren & Acar, 2006
Reactive Black 5	Fly ash	7.936 mg/g	Eren & Acar, 2006
Nylosane blue	Orange peel	65.88 mg/g	Benaissa, 2005
Direct red 23	Treated rice husk	4.35 mg/g	Abdel Wahab *et al*, 2005
Basic red 22	Sawdust	20.16 mg/g	Batzias & Sidiras, 2007
Coomassie brilliant blue	Coir pith	31.847 mg/g	Naveen *et al*, 2008

2.4.1 Orange Peel as Adsorbents

Orange peels are one of the agricultural waste materials discarded from juice industry. Since world orange production is estimated in more than 60 million tons and a significant fraction is destined to industrialization, land space occupation and pollution with phenolic compounds due to dumping of the waste, are becoming problematic (Fernandez *et al*., 2014). Orange peel is largely composed of cellulose pectin; hemi-cellulose, lignin and other low molecular weight compounds including limestone. It can be used as an efficient and cost effective bio-adsorbent for removing dyes metals and organic pollutants from industrial wastewater. In addition, orange peel is an alternative as a adsorbent for its abundance in nature, non-toxicity and bio-degradability. This study was performed to utilize the orange peel as a low cost natural adsorbent with respect to various parameters such as different doses, contact time and pH (AbdurRahman *et al*., 2013).

CHAPTER 3

MATERIALS AND METHODS

3.1 Apparatus

Conical flasks (Schott Duran), beaker (Schott Duran), measuring cylinder (Schott Duran), filter paper, pH meter (Hanna), litmus paper, pipette micrometer 100ml (Watson Nexty), vacuum pump, grinder (Elba), sieve (Impact), aluminum foil, weight balanced, oven, mechanical shaker and UV-Vis spectrophotometer (UV-2600) were use throughout this experiment.

3.2 Materials

Distilled water, orange peels, methyl red, 50% phosphoric acid, sodium hydroxide (NaOH) and hydrochloric acid (HCl) were use throughout this experiment.

3.3 Preparations of Raw Materials

The orange peels were collected from fruit stall at Agro Bazaar Ayer Lanas. The peels were washed with tap water to remove dust particles and other inorganic impurities. The orange peels were cut into small pieces then dry under sunlight for two days until the peels become crisp. Then, the peels were crushed using grinder and were sieved through 100 - 600 micron sieve to get the fine powder. The remaining crushed peels and the powder were collected, packed and labeled in the different air-tight container for further use.

3.4 Preparation of Orange Peels Activated Carbon

The orange peels were mixed with 50% phosphoric acid solution (H_3PO_4) in ratio 1:1 acid/materials and were soaked for 2 hours in 110°C (Fernandez *et al*., 2014). Afterwards, the impregnated sample were placed in furnace and heated. The temperature were raised from room temperature up to 475°C at a heating rate of 3°C/min and held for 30 minutes (Basso *et al*., 2002). After cooling to room temperature, the sample were soaked in an alkaline solution for 10 min and subsequently and rinsed with hot water until attain a neutral pH. Then the sample were dried in the oven at 80°C for 24 hours and stored in air-tight container for further use.

3.5 Preparation of Methyl Red Solution

Methyl red (MR) dye has been chosen as a model system because of its intense color in aqueous system and low biodegradability due to the presence of benzene rings (Hassan & Abdulhussein, 2015). A 1000 mg/L stock solution were prepared by dissolving 1000 mg of it in 1000 ml of distilled water and the required standard solutions prepared by dilution method ($V_1M_1=V_2M_2$). The pH was adjusted by adding 0.1M NaOH solution and 0.1M HCl solution (AbdurRahman *et al*., 2013). 100 ml of prepared solution were stored in different beaker as the control of this experiment.

3.6 Preparation of Blank

30 ml of 100 mg/l methyl red solution were prepared as a blank. The solution was shaken in mechanical shaker with 150 rpm for 80 minutes. The pH was adjusted to pH 7.0 using 0.1M NaOH solution and 0.1M HCl solution. The solution was filtered and analyzed using UV-Vis spectrophotometer.

3.7 Batch Adsorption of Study

Adsorption experiments were performed by the batch technique. The adsorption of a methyl red on orange peels were obtained after stirring the beakers containing 30 ml of 100 mg/l methyl red solution with different adsorbents dosage, different values of pH, different size of adsorbent particles and different contact time at room temperature. The stirring were proceed in constant speed after which the mixture was left to settle and filtered.

3.7.1 Effect of Contact Time

The effect of time on efficient removal of dye from methyl red solution by using activated carbon derived from orange peels as an adsorbent were studied. The contact time is for 0, 20, 40, 60, 80, 100 and 120 minutes. The amounts of adsorbent were 1g/30ml and the pH of the dye solution was adjusted to pH 7.0.

3.7.2 Effect of Adsorbent Dosage

The experiment was carried out to study the effect of amount of adsorbent use. The range of amount of adsorbent was 0, 0.5, 1.0, 1.5 and 2.0 g for 30 ml solution. The pH was fixed at 7.0 and the stirring time for the experiment was 80 minutes.

3.7.3 The Effect of Particle Size

The experiment was carried out using different size of adsorbent to study the effect of the particle size. The different particles size 0, 150, 300 and 500 µm with 1g/30ml amount of adsorbent were mixed into 100 mg/L dilution. The pH was fixed at 7.0 and the stirring time for the experiment was 80 minutes.

3.7.4 Effect of pH

The effect of the amount of color removal for dye solution was analyzed. The pH was adjusted by adding a few drops of 0.1 M NaOH or 0.1 M HCl to get 3.0, 6.0, 7.0 and 9.0. The amount of adsorbent was 1g/30ml and the solution was stirred at the constant speed for 80 minutes.

3.8 UV-Vis Analysis

The absorbance of the filtrate and the blank solution were determined by using UV-Vis spectrophotometer at adjusted 410 nm wavelengths, λ. The absorbent efficiency was calculated using the formula:

$$E = \frac{C_O - C_t}{C_O} \times 100$$

Where, E is the percentages of dye removal (%), C_O is the initial adsorbate concentration (mg/L) and C_t is the adsorbent concentration (mg/L) at time *t*.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Calibration curve

A calibration curve is a mathematical tool that used in analytical chemistry which provides a set of reference points that unknown chemical substances can be compared to. Scientists are often unable to get a completely accurate understanding of the substance's makeup when analyzing certain substances. Therefore, with a calibration curve, chemists can compare known information about unknown substances to make estimates about its makeup and chemical properties (Adeeyinwo *et al*., 2013).

The calibration curve provides a reliable way to calculate the uncertainty of the concentration calculated from the calibration curve. Calibrations curves are usually constructed using standard samples of known chemical substances (Thomas, 2009). The calibration curve can be described by the equation $y = mx + y_0$. The concentration of unknown samples may be calculated from this equation.

For this experiment, calibration curve are made up to set as the control for all of batch adsorption. 100 mg/l methyl red solution was dilute in series for 5, 10, 15, 20 and 25 mg/l. The solutions then were determined by using UV-Vis spectrophotometer at adjusted 410 nm wavelengths, λ. Figure 4.1 shows the calibration curve that have been obtained from the result of dilution. From the calibration curve, the y-value was used to make calculation.

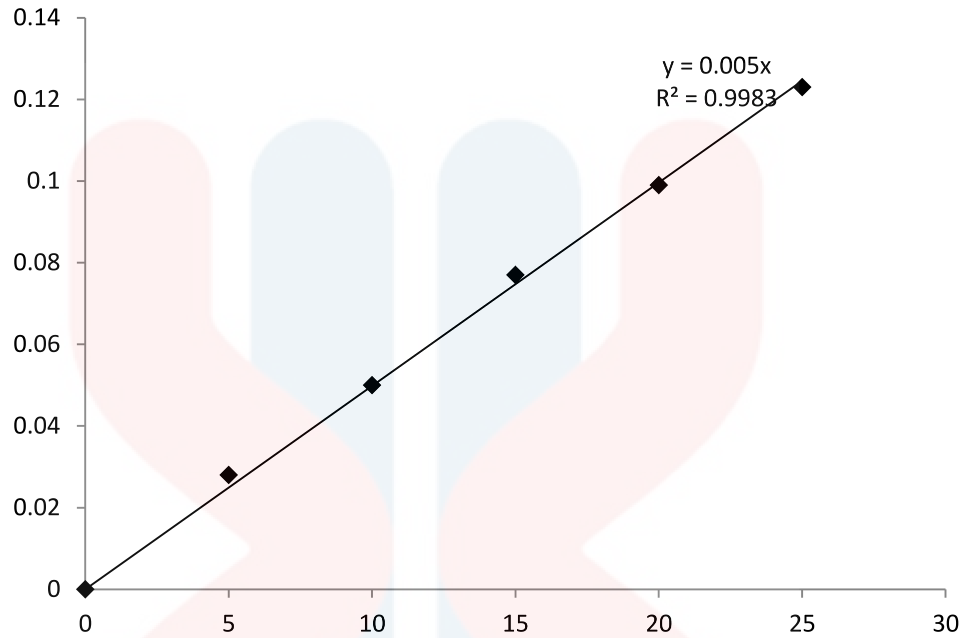

Figure 4.1: Calibration curve

4.2 The effect of contact time on the percentages of methyl red removal using raw and activated carbon orange peel.

Figure 4.2 and Figure 4.3 shows the effect of contact time against the percentages of methyl red removal using raw orange peel and activated carbon derived from orange peel. A series of adsorption experiment was carried out with different time taken (20, 40, 60, 80, 100, 120 min). All the samples were shaken in the mechanical shaker. The concentrations were fixed with 100mg/l at constant volume of dye solution 30ml at constant speed of rotation 150rpm. The temperature was kept constant at room temperature 27°C.

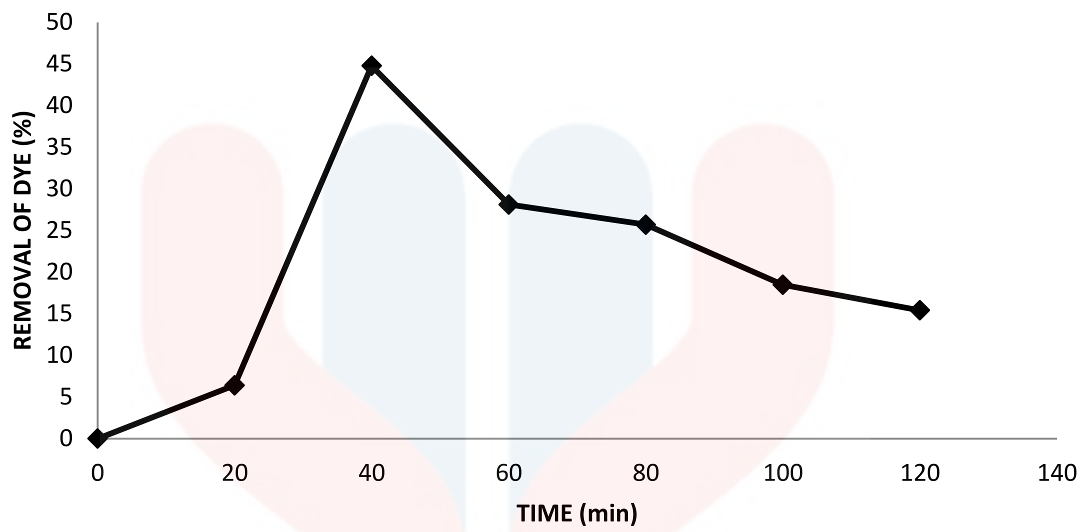

Figure 4.2: The effect of contact time against the percentages of methyl red removal using orange peel (raw)

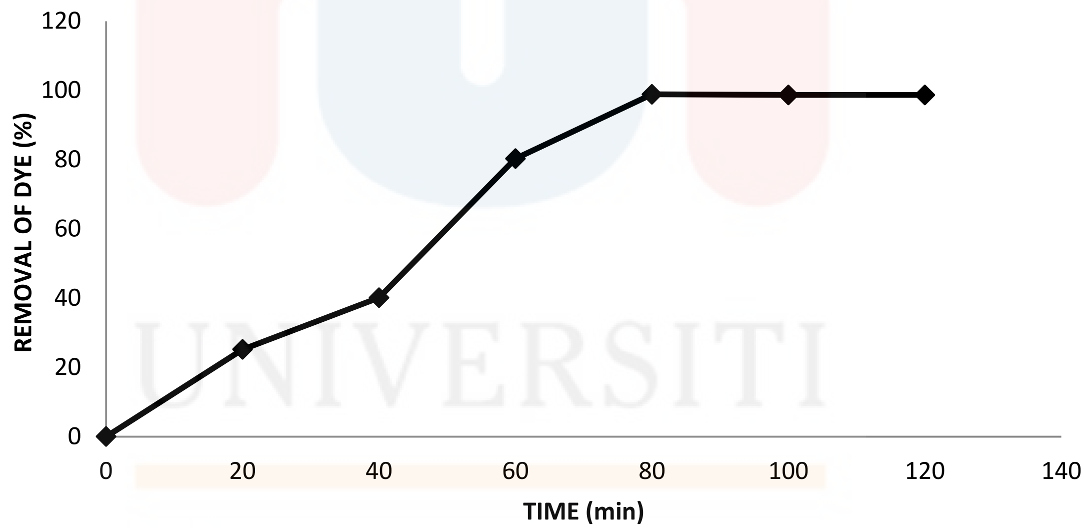

Figure 4.3: The effect of contact time against the percentages of methyl red removal using orange peel (activated carbon)

From Figure 4.2 it can be seen that the highest percentage of methyl red removal by raw orange peel was at 40 minutes shaking which was 44.77 %. The lowest percentage removal of methyl red was at 20 minutes shaking which was 6.39 %. From the graph we can see that the percentage increases and decreases slowly after minutes 40 until minutes 120. This can be concluded that raw orange peel and methyl red should in contact for 40 minutes in order to get maximum removal percentages.

The result in Figure 4.3 shows that the highest rate of time taken for the removal of methyl red using activated carbon derived from orange peel are at minute 80 with the percentages 98.83 %. After the minutes 80, the graph shows the percentages of dye removal are slightly decrease and stop moving which mean that minute 80 was the maximum rate for the removal of methyl red using activated carbon derived from orange peel.

From the Figure 4.2 and 4.3, it can be seen that the graph was increases after the dye and peels in contact, but after that decreases and stop moving where its means that the equilibrium state have achieved. This occurs due to the exposure of methyl red particles to the actives site of the orange peel. When some of the easily available active sites engaged, dye needs time to find out more active sites for building (Fernandez *et al*., 2014).

4.3 The effect of adsorbent dosage on the percentages of methyl red removal using raw and activated carbon orange peel.

Figure 4.4 and Figure 4.5 illustrates the effect of adsorbent dosage against percentages of methyl red removal using raw orange peel and activated carbon derived from orange peel. A series of adsorption experiment was carried out with different dosage of adsorbent (0.5, 1.0, 1.5, 2 g) at fixed concentration 100mg/l with 30ml volume of dye and constant speed of rotation 150rpm for 80 minutes. Similarly, the temperature was kept constant at room temperature 27°C.

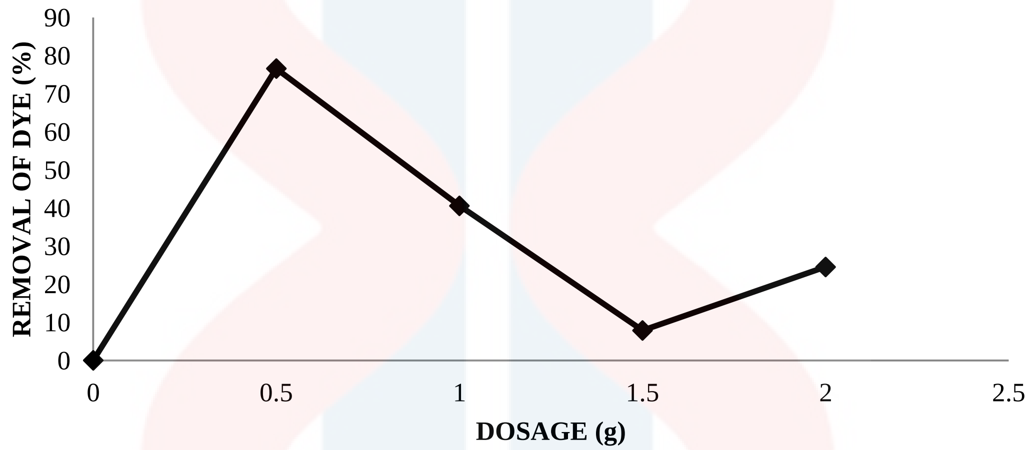

Figure 4.4: The effect of adsorbent dosage against the percentages of methyl red removal using orange peel (raw)

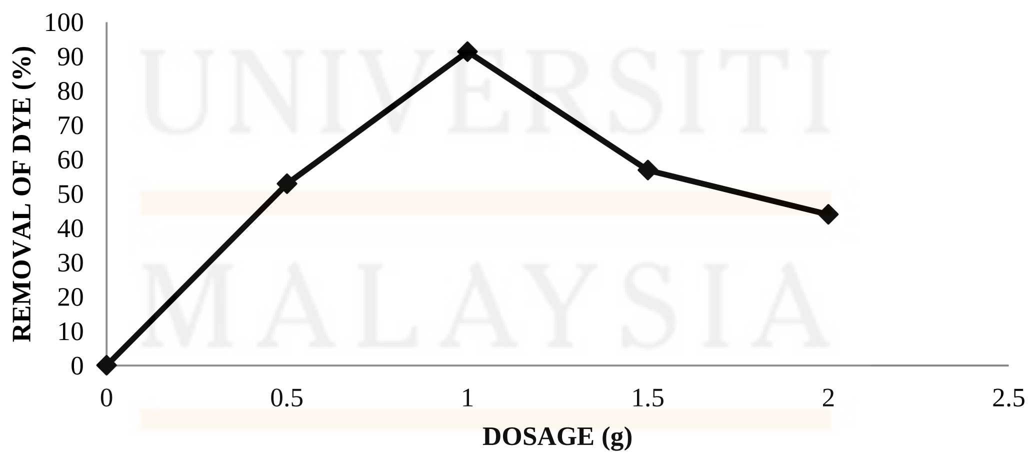

Figure 4.5: The effect of adsorbent dosage against the percentages of methyl red removal using orange peel (activated carbon)

From Figure 4.4, it shows that the percentage of dye removal increases rapidly with the dosage of adsorbent 0.5g with the maximum percentages that is 76.57 %. The percentage of dye removal was decrease to the lowest percentages 7.84 % when the adsorbent dosage is increased to 1.5g. The result indicated that at low amount of adsorbent dosage, higher uptake was obtained.

Result in Figure 4.5 shows that the percentage of dye removal rises about 40 % with the maximum percentage which is 91.35 % when the adsorbent dosages increase from 0.5g to 1.0g. The percentages become the lowest when the adsorbent dosages increase to 2.0g which is 43.96 %. From the result, we can indicate that 1.0g of orange peel activated carbon was the maximum amount for the removal of methyl red.

Figure 4.4 and 4.5 shows that the smaller amount of both raw orange peel and activated carbon derived from orange peel has the higher adsorption rate compare to the larger amount. This result indicated that more surface area was made due to increased mass of adsorbent. Therefore, total number of sites increases (AbdurRahman *et al*., 2013). This is in the agreement with the findings of Yeddou & Bensmaili (2005).

4.4 The effect of particle size of adsorbent on the percentages of methyl red removal using raw and activated carbon orange peel.

Figure 4.6 and Figure 4.7 illustrates the effect of particle size of adsorbent against percentages of methyl red removal using raw orange peel and activated carbon derived from orange peel. A series of adsorption experiment was carried out with different particle size of adsorbent (150, 300, 500 µm) at 100mg/l concentration with

30ml volume of dye and 150rpm speed of rotation for 80 minutes. Similarly, the temperature was kept constant at room temperature 27°C.

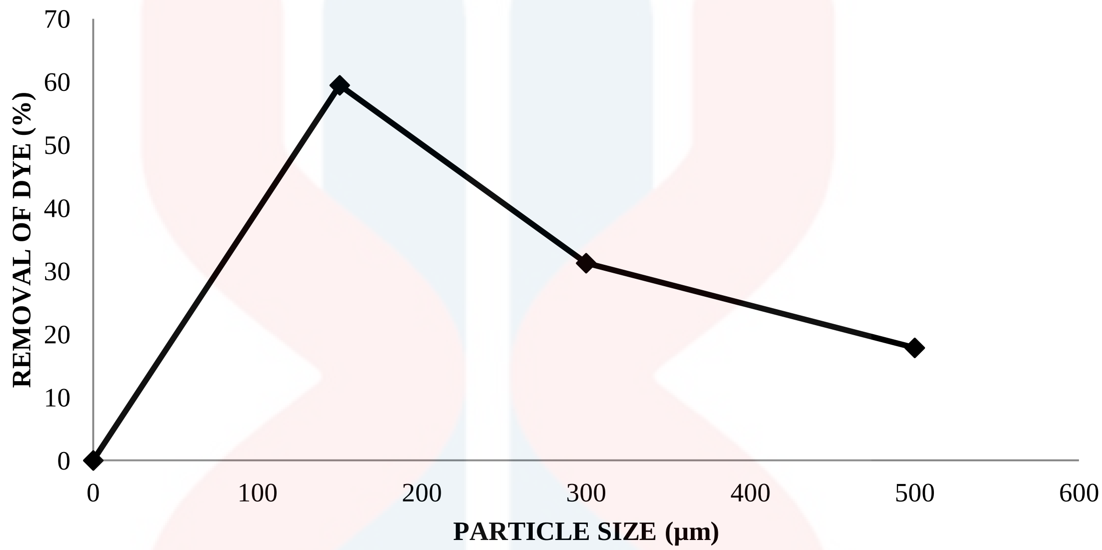

Figure 4.6: The effect of particle size of adsorbent against the percentages of methyl red removal using orange peel (raw)

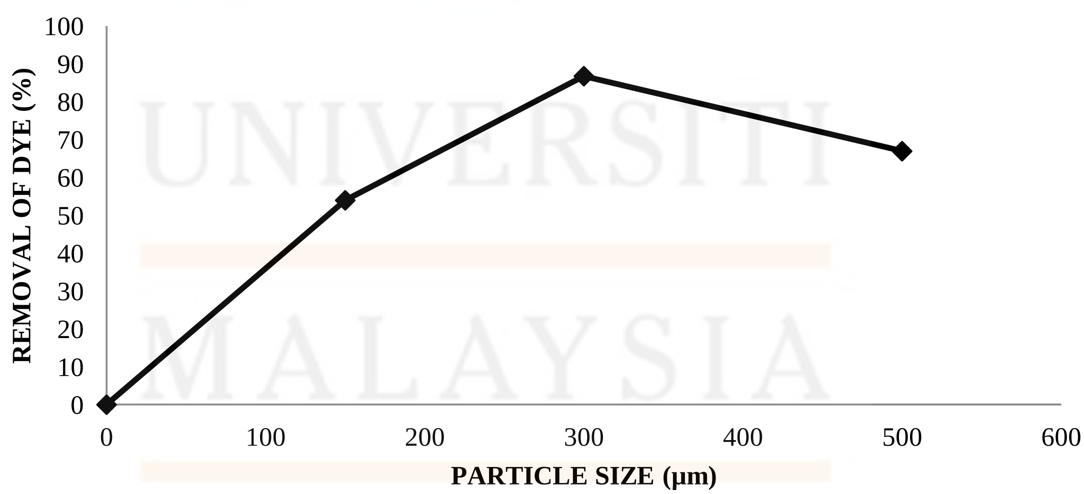

Figure 4.7: The effect of particle size of adsorbent against the percentages of methyl red removal using orange peel (activated carbon)

From the Figure 4.6, it can be seen that the size 150µm of raw orange peel have the highest percentages of dye removal which is 59.45 %. The lowest percentages of dye removal are for the size 500µm which is 17.84 %. This can be concluded that, for the effect of particle size of adsorbent using raw orange peel, 150µm was the effective size for the removal of methyl red.

The result from Figure 4.7 shows that the highest percentage of methyl red removal by activated carbon derived from orange peel was at particle size 300µm which was 86.75 %. From the graph we can see that the percentages were decreased when the particle size of adsorbent was increased to 500µm. This can be concluded that activated carbon derived from orange peel is effective for size 300µm in order to get maximum removal percentages.

From the Figure 4.6 and 4.7, the small size of the adsorbent has the highest adsorption rate compare to the large size of adsorbent. This is because, the small size of adsorbent provide larger surface area for the binding for methyl red molecules. Furthermore, adsorbent with small size can contact faster at the binding site (Azhar *et al.*, 2005).

4.5 The effect of pH on the percentages of methyl red removal using raw and activated carbon orange peel.

Figure 4.8 and Figure 4.9 illustrates the effect of pH against percentages of methyl red removal using raw orange peel and activated carbon derived from orange peel. A series of adsorption experiment was carried out with pH 3, 6, 7, 9 at 100mg/l concentration with 30ml volume of dye and 150rpm speed of rotation for 80 minutes. Similarly, the temperature was kept constant at room temperature 27°C.

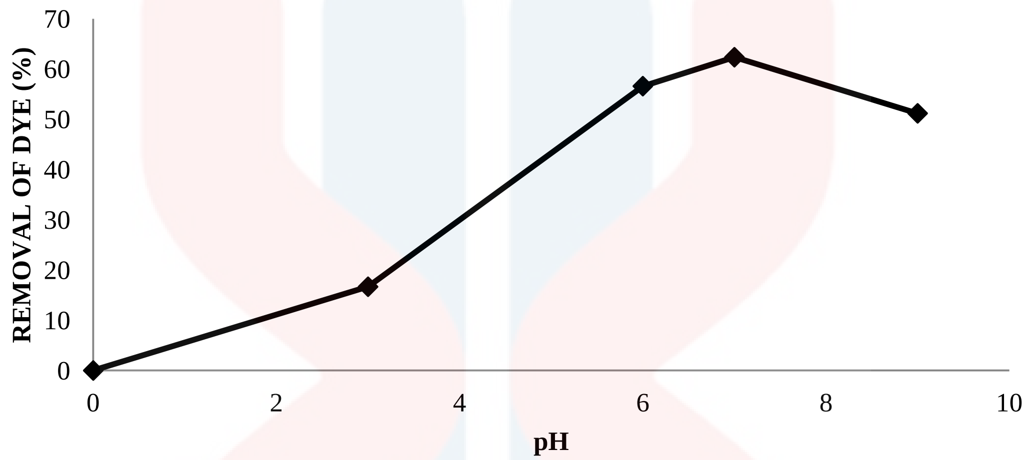

Figure 4.8: The effect of pH against the percentages of methyl red removal using orange peel (raw)

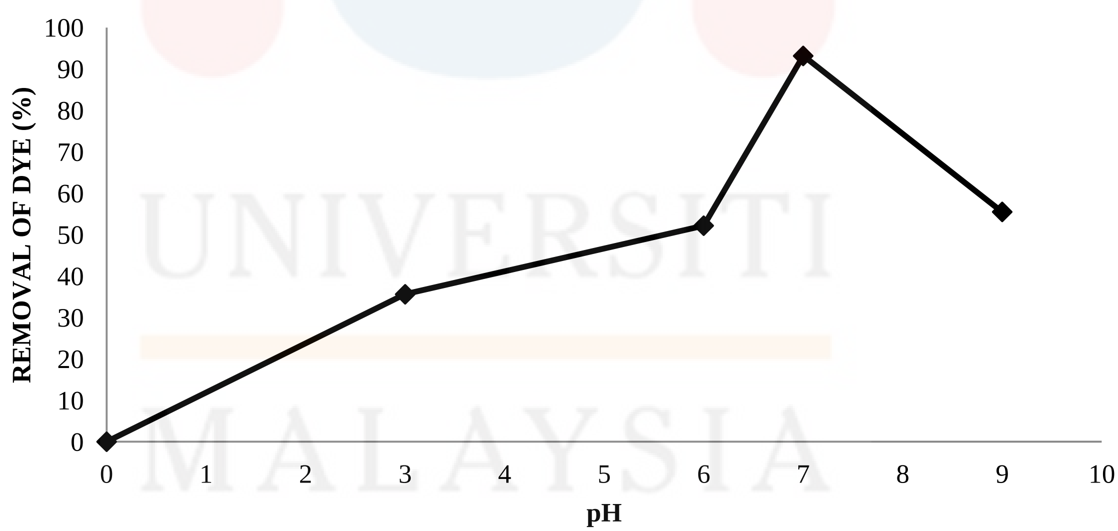

Figure 4.9: The effect of pH against the percentages of methyl red removal using orange peel (activated carbon)

Result in Figure 4.8 shows that the percentage of dye removal increases until the pH 7 and decrease slightly at pH 9. The maximum percentage was at pH 7 with the percentage 62.34 % and the lowest percentage was at pH 3 with the percentage 16.67%. From the result, it can indicate that raw orange peels are effective at pH 7 for the removal of methyl red.

The result from Figure 4.9 shows that the highest percentage of methyl red removal by activated carbon derived from orange peel were at pH 7 which the percentage was 93.15 %. From the graph we can see that the percentages decreased when the pH increased to pH 9. This can be concluded that activated carbon derived from orange peel is effective at pH 7 in order to get maximum removal percentages.

Figure 4.8 and 4.9 shows that the pH of the solution significantly affects the adsorption of dyes by raw and activated carbon orange peels. The more effective dye adsorption capacity of orange peels was observed at normal pH. The optimum adsorption capacity was achieved at pH 7. At lower pH, functional oxidized groups of the peels are promoted and thus active site of orange peels for binding of dye becomes less available (Kadirvelu *et al*., 2003). As a result, removal efficiency decreases.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Orange peel is one of the agricultural wastes which are cheap and easily available that can be used effectively in removing dye. The present study has shown that raw orange peel and activated carbon derived from orange peel can be used in removing methyl red dye. However, the result shows that activated carbon derived from orange peel has the highest removal percentages which is up to 98% compared to raw orange peel.

From this investigation, it can be concluded that activated carbon derived from orange peel is more suitable in removing methyl red dye compared to raw orange peel. Besides, it is also clear that the adsorption of methyl red dye is influenced by the amount of adsorbent, particle size, pH value and contact time. From the study, the adsorption was found to be higher for 80 minutes shaking and the suitable dosage was 1 g with particle size 300µm at pH 7.

Despite the fact that the removal effectiveness of orange peels is a little higher than other bio-adsorbents, it is economically accessible. With this modest and environmental friendly adsorbent considerable dye removal can be accomplished. So it can be substituting other costly bio-adsorbents. With the data obtained in this study, it is possible to design and improve an efficient treatment process for the dye removal from industrial effluents.

5.2 Recommendation

There is a problem occurs during the experiment was carried out where the raw orange peels became moldy. In my observation, this is possibly due to the raw orange peels were not properly stored in airtight container. Therefore, the method in storing the raw material is important in this experiment so that the raw material can last longer.

On other hand, I would like to recommend for the use of activated carbon derived from orange peel in removing heavy metal. Further research can be done in order to investigate the effectiveness of activated carbon derived from orange peel in removing heavy metal.

REFERENCES

Abdel Wahab, O., El Nemr, A., El Sikaily, A., Khaled, A., (2005), Use of rice husk for adsorption of direct dyes from aqueous solution, *A case study of Direct F. Scarlet. Egyptian J. Aqua Res., 31(1)*, 1-11.

AbdurRahman, F., Akter, M., Abedin, M., Z., (2013), Dyes Removal From Textile Wastewater Using Orange Peels, *International Journal Of Scientific & Technology Research*, *2*.

Adeeyinwo, C., E., Okorie, N., N., Idowu, G., O., (2013), Basic Calibration of UV/ Visible Spectrophotometer, *International Journal of Science and Technology, 2 (3)*, 247-251.

Ahmad, A., L., Loh, M., M., Aziz, J., A., (2007), Preparation and characterization of activated carbon from oil palm wood and its evaluation on methylene blue adsorption, *Dyes Pigments, 75*, 263–272.

Arunachalam, R., Annadurai, G., (2011) Optimized Response Surface Methodology for Adsorption of Dyestuff from Aqueous Solution, *Journal of Environment Science And Technology, 4*, 65-72.

Attia, A., A., Rashwan, W., E., Khedr, S., A., (2006), Capacity of activated carbon in the removal of acid dyes subsequent to its thermal treatment, *Dyes and Pigments, 69*, 128-136.

Azhar, S., S., Liew, A., G., Suhardy, D., Hafiz, K., F., Hatim, M., D., I., (2005), Dye Removal from Aqueous Solution by using Adsorption on Treated Sugarcane Bagasse, *American Journal of Applied Sciences, 2 (11)*, 1499-1503.

Basso, M., C., Cerrella, E., G., Cukierman, A., L., (2002), Activated carbons developed from a rapidly renewable biosource for removal of cadmium(II) and nickel(II) ions from dilute aqueous solutions, *Ind. Eng. Chem. Res., 41*, 180–189.

Batzias, F., A., Sidiras, D., K., (2007), Dye adsorption by pre-hydrolysed beech sawdust on batch and fixed-bed systems, *Biores. Technol., 98*, 1208-1217.

Benaissa, H., (2005), Removal of azo dyes from aqueous solutions using orange peel as a sorbent material, *Ninth International Water Technology Conference,* 1175-1187.

Booth, Gerald, (2000), Dyes, *General Survey, Wiley-VCH,* 1-38.

Crini, G., (2006), Non-conventional low cost adsorbents for dye removal: a review, *Bioresour, Technol., 97*, 1061-1085.

Crini, G., (2005), Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, *Prog. Polym Sci., 30*, 38–70.

Da Silva, L., G., Ruggiero, R., Gontijo, P., D., Pinto, R., B., Royer, B., Lima, E., C., Frnandes, T., Calvete, T., (2011), *Chem. Eng. J, 168*, 620–628.

Dash, B., (2010), Competitive adsorption of dyes (congo red, methylene blue, malachite green) on activated carbon, *B.Tech thesis*.

Davila, P., A., Facultad de Ciencias, O., L., Ramos, R., L., Perez, R., O., (2012), Clean-Soil, Air, Water *40 (1)*, 45–53.

Eren, Z., Acar, F., N., (2006), Adsorption of reactive black 5 from an aqueous solution : equilibrium and kinetic studies, *Desalination*, *194*, 1-10.

Fernandez, M., E., Nunell, G., V., Bonelli, P., R., Cukierman, A., L., (2014), Activated carbon developed from orange peels: Batch and dynamic competitive adsorption of basic dyes, *Industrial Crops and Products, 62*, 437–445.

Foo, K., Y., Hameed, B., H., (2012), Desalination and Water Treatment An overview of dye removal via activated carbon adsorption process, *Desalin. Water Treat.*, 37–41.

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

Jhansi, S., C., Shah, M., Mishra, S., K., (2013), Wastewater Treatment and Reuse : Sustainability Option, *The Journal of Sustainable Development, 10,* 1-15.

Kadirvelu, K., Kavipriya, M., Karthika, C., Radhika, M., Vennilamani, N., Pattabhi, S., (2003), Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions, *Bioresource Technology, 87*, 129–132.

Karthik, V., Saravanan, K., Bharathi, P., Dharanya, V., Meiaraj, C., (2014), An overview of treatments for the removal of textile dyes, *Journal of Chemical and Pharmaceutical Sciences*, *7*, 301-307.

Kyzas, G., Z., Kostoglou, M., (2014), Green Adsorbents for Wastewaters: A Critical Review, *Materials, 7*, 333-364.

Lachheb, H., Puzenat, E., Houas, A., (2002), Photocatalytic degradation of various types of dyes (alizarin S, crucein orange G, methyl red, Congo red, methylene blue) in water by UV-irradiated Titania, *Catalysis B Environ*, *39*, 75–90.

Lin, J., X., Zhan, S., L., Fang, M., H., (2008), Adsorption of basic dyes from aqueous solution onto fly ash, *J Environ Manag, 87*, 193–200.

Mckay, G., (1982), Adsorption from dyes stuff from aqueous solutions with activated carbon. Part 1. Equilibrium and batch contact time studies, *J. Chem. Technol. Biotechnol*, *32*, 759-772.

Muthuraman, G., Teng, T., T., (2009), Extraction of Methyl Red from Industrial Wastewater Using Xylene as an Extractant, *Progress in Natural Science, 19(10),* 1215–1220.

Naveen, P., R., Viswanathan, S., Renuka, D., J., Rajkumar, J., Parthasarathy, N., (2008) Kinetics and equilibrium studies on biosorption of CBB by coir pith, *American-Eurasian J. Sci. Res., 3(2)*, 123-127.

Pavan, F., A., Mazzocato, A., C., Gushikem, Y., (2008), Removal of methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent, *Bioresource Technology, 99,* 3162–3165.

Uddin, M., T., Islam, M., S., Abedin, M., Z., (2007), Adsorption of phenol from aqueous solution by water hyacinth Ash: ARPN, *Journal of Engg. & Appl. Sci, 2*, 11-17.

Rashed, M., N., (2013), Adsorbtion Technique for The Removal of Organic Pollutants From Water and Wastewater, *InTech*, 168-194.

Robert, B., (2006), Ultraviolet/Visible (UV – Vis) Spectroscopy of potassium permanganate, *CH EN*, 4903.

Robinson, T., Chandran, P., Nigam, P., (2001a), Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. *Water Res*., *36*, 2824.

Robinson, T., McMullan, G., Marchant, R., Nigam, P., (2001b), Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative, *Bioresour. Technol., 77*, 247–255.

Sun, Q., Yang, L., (2003), The adsorption of basic dyes from aqueous solution on modified peat-resin particle, *Water Res*., *37*, 1535–1544.

Tanzim, K., Abedin, M., Z., (2015), A Novel Bioadsorbent for the Removal of Methyl Red from Aqueous Solutions, *Journal of Environmental Science, Toxicology and Food Technology, 9,* 87-91.

Thomas, G., (2009), Evaluating goodness of fit for linear instrument calibration through the origin, *Journal of Environmental Analytical Chemistry, 89*, 383 – 388.

Worch, E., (2012), Adsorption Technology in Water Treatment, *De Gruyter*, 98.

Yeddou, N., Bensmaili, A., (2005), Kinetic models for the sorption of dye from aqueous solution by clay-wood saw dust mixture, *Desalination*, *185*, 499-508.

APPENDIX A

<u>Result for effect of contact time</u>

Raw

Contact Time (min)	UV-Vis Reading	Percentages Dye Removal (%)
20	1.039	6.39
40	0.613	44.77
60	0.798	28.10
80	0.825	25.68
100	0.905	18.47
120	0.939	15.41

Activated carbon

Contact Time (min)	UV-Vis Reading	Percentages Dye Removal (%)
20	0.831	25.16
40	0.665	40.09
60	0.219	80.27
80	0.013	98.83
100	0.015	98.65
120	0.015	98.65

Result for effect of adsorbent dosage

Raw

Adsorbent dosage (g)	UV-Vis Reading	Percentages Dye Removal (%)
0.5	0.260	76.57
1.0	0.660	40.54
1.5	1.023	7.84
2.0	0.838	24.50

Activated carbon

Adsorbent dosage (g)	UV-Vis Reading	Percentages Dye Removal (%)
0.5	0.523	52.88
1.0	0.096	91.35
1.5	0.479	56.85
2.0	0.622	43.96

Result for effect of particle size

Raw

Particle size (µm)	UV-Vis Reading	Percentages Dye Removal (%)
150	0.450	59.45
300	0.763	31.26
500	0.912	17.84

Activated carbon

Particle size (µm)	UV-Vis Reading	Percentages Dye Removal (%)
150	0.511	53.96
300	0.147	86.75
500	0.367	66.94

Result for effect of pH

Raw

pH value	UV-Vis Reading	Percentages Dye Removal (%)
3	0.925	16.67
6	0.482	56.58
7	0.418	62.34
9	0.542	51.17

Activated carbon

pH value	UV-Vis Reading	Percentages Dye Removal (%)
3	0.715	35.59
6	0.531	52.16
7	0.076	93.15
9	0.494	55.49