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# Preparation of Raw Oyster Shell For Adsorption of Methyl Red Dye In The Aqueous Solution.

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A thesis submitted in fulfilment of the requirement for the degree of Bachelor of Applied Science (Product Development Technology) with Honours

Faculty of Agro Based Industry

UNIVERSITY MALAYSIA KELANTAN

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# DECLARATION

I hereby declare that the work embodied in this report is the result of the original research and has not been submitted for a higher degree to any universities or institutions.

____________________

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Date:

I certify that the report of this final year project entitled "Preparation of Raw Oyster Shell for Adsorption of Methyl Red Dye in Aqueous Solution" by Norsyafika Binti Mohd Zahari, Matric number F15A0287 has been examined and all correction recommended by examiners have been done for the degree of Bachelor of Applied Science (Product Development Technology) with Honours, Faculty of Agro-Based Industry, University Malaysia Kelantan.

Approved by:

___________________

Supervisor

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Date:

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# Preparation of Raw Oyster Shell For Adsorption of Methyl Red Dye in Aqueous Solution

## ABSTRACT

The raw oyster shell was successfully prepared as an adsorbent for removal of Methyl Red (MR) dye. Adsorption studies were carried out for removal of MR dye from aqueous solution by varying the adsorption parameters such as adsorbent size, adsorbent dosage, initial dye concentration, contact time, pH, agitation speed and agitation time. Optimum conditions for adsorption of MR dye were obtained at 75 µm of adsorbent size with 0.3 g of adsorbent dosage at 2 h as contact time. Initial dye concentration at its optimum level, were found to be 100 mg/L working efficiently at pH 3 and agitation rate of 110 rpm. Orbital shaker was used to reduce the time consumption during the adsorption process and it gives the positive result when the contact time can be reduce from 2 hours to 45 min after process of agitation. The removal efficiency was found out to be 99.2% and this result shows that raw oyster shell has great potential in removing of MR dye from aqueous solution. The experimental data obtained were best fitted by Freundlich isotherm model than Langmuir isotherm model and this define heterogeneous adsorption mechanism of adsorbent.

Keywords: Raw oyster shell, adsorption, methyl red dye, isotherm model

# Penyediaan Cengkerang Tiram Mentah Untuk Penjerapan Pewarna Methyl Red dalam Larutan Akueus

## ABSTRAK

Cengkerang tiram mentah telah berjaya dihasilkan sebagai penjerap untuk penyingkiran pewarna Methyl Red (MR). Kajian penjerapan telah dilakukan untuk menyingkirkan pewarna MR dari larutan akueus dengan mengubah parameter penjerapan seperti saiz penjerap, dos penjerap, kepekatan awal pewarna, masa sentuhan, pH, kelajuan agitasi dan tempoh agitasi. Keadaan optimum bagi penjerapan pewarna MR adalah pada saiz penjerap (75µm), dos penjerap (0.3 g) dengan masa sentuhan selama 2 jam. Kepekatan awal pewarna yang optimum adalah pada 100 mg/L bekerja dengan efektif pada pH 3 dengan kelajuan agitasi, 110 rpm. Shaker orbit digunakan untuk mengurangkan penggunaan masa semasa proses penjerapan dan memberikan hasil yang positif apabila masa sentuhan dapat dikurangkan daripada 2 jam kepada 45 minit selepas proses pergolakan. Kecekapan penyingkiran pewarna MR didapati mencapai 99.2% dan hasil ini menunjukkan bahawa cengkerang tiram mentah mempunyai potensi yang besar untuk menyingkirkan pewarna MR dari larutan akueus. Data eksperimen yang diperolehi telah dipadankan terbaik dengan model isoterma Freundlich daripada model isotherma Langmuir.

*Kata kunci: Cengkerang tiram mentah, penjerapan, pewarna Methyl Red, model isotherma*

# TABLE OF CONTENT

CHAPTER 1 INTRODUCTION

CHAPTER 2 LITERATURE REVIEW

**CHAPTER 3 MATERIALS AND METHODS**

**CHAPTER 4 RESULTS AND DISCUSSION**

# LIST OF TABLES

# LIST OF FIGURES

## LIST OF ABBREVIATIONS

| | |
|---|---|
| ROS | Raw oyster shell |
| MR | Methyl Red |
| UV-Vis | Ultra-Violet Visible |
| Eq. | Equation |
| $C_e$ | final concentration of dye |
| $C_o$ | initial concentration of dye |
| $K_F$ | Freundlich constant |
| $K_L$ | Langmuir constant |
| $q_e$ | Adsorption capacity at equilibrium |
| $q_{max}$ | Maximum adsorption capacity |
| V | Volume of solution |
| W | Mass of dry adsorbent |

# LIST OF SYMBOLS

| | |
|---|---|
| % | Percent |
| & | And |
| ℃ | Degree Celsius |
| g | gram |
| h | hour |
| L | litre |
| M | Molar |
| mL | millilitre |
| nm | nanometre |
| mm | millimetre |
| kg | kilogram |
| $m^3$ | cubic meter |
| mg/L | milligram per Litre |
| mg/g | milligram per gram |
| g/L | gram per litter |
| rpm | Revolutions per minutes |
| $R^2$ | Correlation Coefficient |

# CHAPTER 1

# INTRODUCTION

## 1.1 RESEARCH BACKGROUND

Water pollution occurs when pollutant are directly or indirectly thrown into the water bodies without following any method to remove the harmful compounds. Water pollution will affect the living organisms in the water bodies. Most of the cases reported that the water pollution not only affect the individual species but also the natural biological communities. Water pollution are the leading causes of death and diseases in the world. Dyes are one of the first water contaminant with a varies concentration from 10 to 200 mg $L^{-1}$(Ashrafi, Chamjangali, A., Bagherian, & Goudarzi, 2017).

Dyes are substance that produce colour and has an affinity to the substrate which being applied. It is generally applied in the aqueous solution. Dyes are used in the different industries such as textiles, leather, paper, plastics, food, and rubber in order to colour their product (Ashrafi et al., 2017). It is reported that, annually more than 10,000 tons of dyes utilised and 100 tons are released in water bodies (Ashrafi et al., 2017). Dyes also produce the mutagenic and carcinogenic intermediates through a different reaction which can cause a decrease in level of dissolve oxygen and sunlight diffusion (Ashrafi et al., 2017).

As dyes are one of the most famous group of pollutants as it can be easily identified by human as they are not easily biodegradable. There are a few methods to treat dyes which is by using the biological treatment, chemical treatment, physical treatment and also physicochemical treatment (Ong, Keng, Lee, Ha, & Hung, 2011). Physicochemical treatment including the coagulation method, adsorption on activated carbon, polymer and mineral sorbent, reverse osmosis, chemical oxidation, filtration and electrochemical treatment (Kornaros & Lyberatos, 2006). The biological method display more limitation which is high in cost, low efficiencies and can lead to the secondary pollution (Baccar, Blánquez, Bouzid, Feki, & Sarrà, 2010).

In order to overcome the problem, research found out that the adsorption are one of the best method that can be used due to the effective, economic and easy method (Baccar et al., 2010). Besides that, the adsorption on activated carbon is the best method to adsorb dyes. However, the commercial and conventional carbon are high in cost. Therefore, the researcher find a solution to the problem which by using the renewable and cheaper precursors to form the activated carbon (Baccar et al., 2010). This sources are low in cost and easily to be obtained. Besides, it also help in minimising the amount of solid waste found worldwide.

Food waste thrown by human every day and takes a long time to be disposed. Food waste are produce at the various stage such as the production, processing, retailing and consumption stage. This problem will increase the environmental pollution. Food waste also one of the materials that are suitable to make as adsorbent. Oyster shell are one of the food waste that dumped in landfill need a high disposal cost and cause environmental pollution. Oyster shell are waste product that present a major disposal problem in the coastal regions (Kwon et al., 2004).

Under a define condition which is at 750ºC for 1 hour under a nitrogen atmosphere shows that it will change the oyster shell to the sustainable reagent for the phosphorus removal with higher yield which is up to 98% (Kwon et al., 2004). From the chemical and microstructure analysis shows that the oyster shell are composed of the calcium carbonate with no impurities (Yoon, Kim, Kim, & Han, 2002). Apart from that, this type of waste can be used to produce the value added product such as adsorbent that will help in reducing the concentration of the dyes in the effluent. In this study, the oyster shell were used to prepare the raw oyster shell adsorbent in order to remove Methyl red (MR) dye in the aqueous solution.

## 1.2 PROBLEM STATEMENT

Nowadays, the development of chemical, food and textile industries are growing rapidly and give a big effect to the environment and human. This is caused by the industrial process that produce multi type of waste to the water bodies and did not used the correct method on the treatment of the water. For example the textile industries. Textile industries are industries that used a large amount of dyes in order to colour their product. However, they simply release the excessive dyes into the water body that can cause water pollution and also give the adverse effect to all form of life.

This issues not only rising in the Malaysia but also all around the word as water quality become low and polluted. As a result, it will give various effect to human such as cancer, allergy and also will affect the aquatic life as the sunlight diffusion are low as well as the dissolve oxygen. There are several treatment that can be used for the treatment of dyestuff in the water which is the biological method, chemical method and also adsorption. Adsorption method  are the effective method used to remove the dyestuffs in the effluent. This method also widely being used due the cost needed are low.

Nowadays, most disposal of food waste have been dump to landfill that will lead to the  environmental pollution. For example, the disposal of oyster shell to landfill from the food industries give the negative effect to the human and environment. The disposal of food waste involve a high disposal cost. Apart from that, this type of waste can be used to produce the value added product which is the adsorbent that helps in reducing the concentration of dyes in the effluent. As for this study, oyster shell were used to prepared the raw oyster shell adsorbent to remove MR dye in the aqueous solution.

## 1.3 OBJECTIVE

The objective of this study are :

1. To prepare the raw oyster shell sample as an adsorbent to remove Methyl red dye in the aqueous solution .
2. To optimise the parameter which is the adsorbent size, adsorbent dose, initial dye concentration, contact time pH, agitation speed and agitation time on the MR dye removal in the aqueous solution by using raw oyster shell as an adsorbent.

3. To obtain best-fit model of the adsorption of MR dye in the aqueous solution which is Langmuir adsorption isotherm or Freundlich adsorption isotherm.

## 1.4 SCOPE OF STUDY

This research is to study the adsorption capacity of the oyster shell. In this study, the oyster shell sample were collected at Bachok, Kelantan. The oyster shell was washed by using distilled water in order to remove the impurities and dried using oven to remove the moisture content in the shell. The oyster shell then were crushed and grinded in order to obtain raw powdered adsorbent. The powdery form of raw oyster shell act as adsorbent for the removal of MR dye in aqueous solution. A series of experimental work were conducted in order to optimise the adsorption of MR dye using raw oyster shell. The parameters used are pH, adsorbent dose, adsorbent size, initial dye concentration agitation speed, agitation time and also contact time. Lastly, best-fit model for the adsorption of the MR dye were determined by using Langmuir and Freundlich adsorption isotherm.

## 1.5 SIGNIFICANT OF STUDY

Industries todays, especially textile industries not aware with the method of dye treatment before discharge into water bodies. Dye are one of the pollutants that can be trace by human in the water pollution. Dye can cause an adverse effect to the environment and human health. The aquatic life will die and human will expose to cancer and allergic.

There are several ways for the treatment of dyes in the effluent which is by using biological oxidation, chemical oxidation and also by using adsorption. Adsorption process are the effective method used to reduce the concentration of dye in the aqueous solution.

Nowadays, most of food waste disposal are dump to landfill. Apart from that, food waste can be converted into value added product such as adsorbent. Raw oyster shell can be used as an adsorbent to reduce the concentration of dye in the aqueous solution that is discharged by industries. This can give more value to the oyster shell that normally are dump in landfill. Other than that, this study is conducted to optimise parameters which is adsorbent dose, adsorbent size, initial dye concentration, contact time, pH, agitation speed, agitation time and the best-fit model for the adsorption of dye were determined. This study could be applied to industries to reduce or minimise the discharged of dye by the industries.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 DYE

Dye are the substance that produce colour and has an affinity to the substrate which are applied. Dye are classified according to their chemical structure or their mode of application (Booth, Zollinger, McLaren, Sharples, & Westwell, 2000). Most of dye are organic compound that may be natural or synthetic dyes. The natural dyes are produce by the vegetables, animal or mineral that only need a little processing. Dyes are aromatic compound that have aryl ring structure that have delocalised electron system. The structure have varying wavelengths that responsible for the adsorption of electromagnetic radiation. The chromophore substance that present in the dye does not make the dye coloured. The chromophore cause the energy change in the delocalised electron cloud of the dye. There are many classification of dyes and it has their own way to be classified.

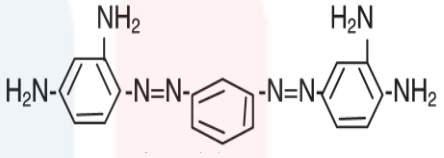
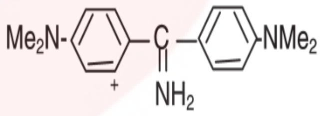
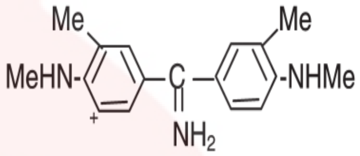
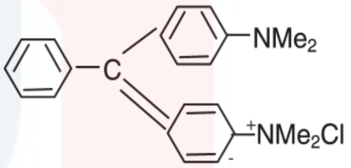
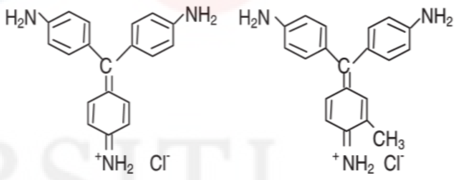
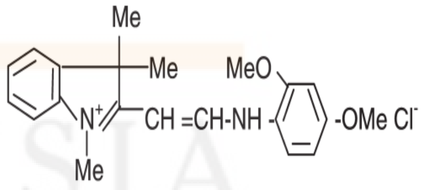
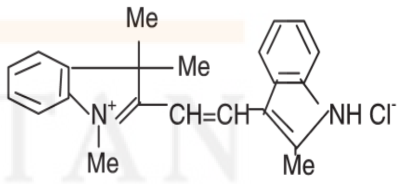
Each classification of dyes has a very unique chemistry, structure and particular ways of bonding. The total dye production per year exceeds 700,000 ton and about 2% of the production are release into the water bodies. Besides, it is about 50% of unused dye are directly entering the wastewater in the dyeing process (González, Villanueva, Piehl, & Copello, 2015). There are many type of dye that commonly used in industries such as the acid dye (Anionic dye), basic dye (Cationic dye), substantive or direct dye, mordant dye, vat dye, reactive dye, disperse dye, azo dye and also sulphur dye. All type of dyes have their own characteristic and also benefits. However, dye give negative effects to the human and environment if exposed in a large dose.

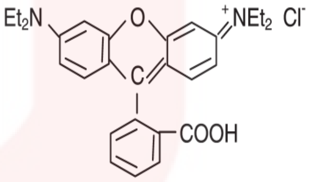
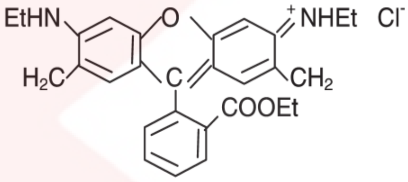
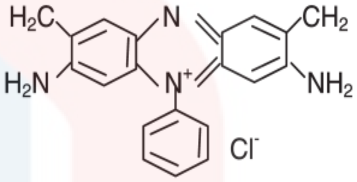
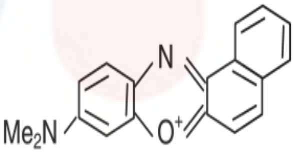
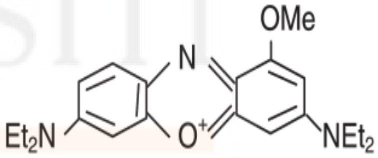
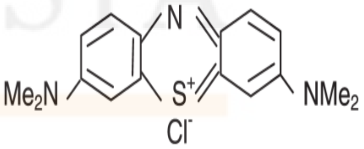
### 2.1.1 Cationic Dye

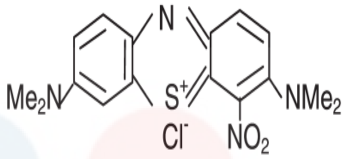
Cationic or basic dyes are the organic based dyes which retain free or will substituted with the amino group for example –$NH_2$, –$N(CH_3)2$ , –$N(C_2H_5)$ ("Dyeing with basic dye," n.d.). This type of dye often referred as the cationic dye. Cationic dye is a group of soluble dye with bright in colour. They can be dissociated into the positively charge ion in the aqueous solution. Cationic dye are alkaline dye but have the different principle of stained alkaline dye which is the cationic dye will dyes the fibre through the binding of cation on the acidic group in the third monomer. There are many type of cationic dye such as azo dyes, triarylmethane dyes, anthraquinone dye and heterocyclic compound.

Basic dye are cheaper and also soluble in the alcohol but did not easily soluble in the water. Basic dye have a cationic nature of dye, so it can precipitate by anionic dye. The basic dye have no affinity for cellulose but it can be applied on it. ("Dyeing with basic dye," n.d.). The specification of the important basic dye are based on the structure and the colour index of the dye. The summarisation are as in the Table 2.1.

Table 2.1 : The structure and colour index of basic dye ("Dyeing with basic dye," n.d.)

| **The structure and colour index of basic dyes.** | | |
|---|---|---|
| **Azo dye** | Bismark brown |  |
| **Diphenylmethane Dyes** | Auramine O |  |
| | Auramine G |  |
| **Triphenylmethane Dyes** | Malachite Green |  |
| | Magenta |  |
| **Methane Dyes** | Astrazon Yollow 3G |  |
| | Astrazon Orange G |  |

| | | |
|---|---|---|
| **Acridine Dyes** | Acridine Orange R |  <br>(zinc chloride double salt) |
| **Xanthene Dyes** | Rhodamine B |  |
| | Rhodamine 6G |  |
| **Azine Dyes** | Safranine T |  |
| **Oxazine Dyes** | Meldola's Blue |  |
| | Acronol Sky Blue 3G |  |
| **Thiazine Dyes** | Methylene Blue |  |

| | |
|---|---|
| Methylene Green |  |

## 2.1.2 Azo dye

Azo dye are organic compound which bearing the functional group of R−N=N−R′, R and R′ are usually from the aryl group. At least one of the carbon atom that linked are belongs to an aromatic carbocycle which is usually benzene or naphthalene derivative or heterocycle (Hunger et al., 2000).

Azo dye can be classified according to their characteristic of their chemical group or by the colour aspects which is in the application of dye works (Hunger et al., 2000). Azo dye are also important due to their mode of application and also they represent a clearly defined concept (Hunger et al., 2000). Type and characteristic classification of azo dye as in the Table 2.2.

Table 2.2 : The type and characteristic classification of azo dyes (Ajmal, Majeed, Malik, Idriss, & Nadeem, 2014)

| Dye class | Characteristics | Fibre | Dye fixation (%) | Pollutant |
|---|---|---|---|---|
| **Acidic** | Water-soluble anionic compound. | Wool, nylon, cotton blends, acrylic and protein fibres. | 80 – 93 | Colour, organic acids and unfixed dyes |
| **Basic** | Water-soluble, applied in weakly acidic dyebaths, very bright dyes. | Acrylic, cationic, polyester, nylon, cellulosic and protein fibres. | 97 and 98 | NA |

| | | | | |
|---|---|---|---|---|
| **Direct** | Ware-soluble, anionic compound, applied without mordant. | Cotton, rayon and other cellulosic fibres. | 70 – 95 | Colour, salts, unfixed dye, cationic fixing agents, surfactant, defoamer, levelling and retarding agents, finish, diluents. |
| **Dispersive** | Insoluble in water. | Polyester, acetate, mod acrylic, nylon, triacetate and olefin fibres. | 80 – 92 | Colour, organic acids, carriers, levelling agents, phosphates, defoamers, lubricants, dispersants, delustrants, diluents. |
| **Reactive** | Water-soluble, anionic compound, largest dye classes. | Cotton, cellulosic and wool fibres. | 60 – 90 | Colour, salt, alkali, unfixed dye, surfactants, defoamer, diluents, finish. |

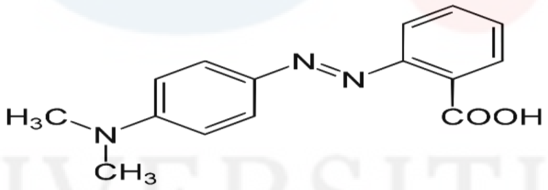
| | | | | |
|---|---|---|---|---|
| **Sulphur** | Organic compound containing sulphur or sodium sulphide. | Cotton and other cellulosic fibres. | 60 – 70 | Colour, alkali, oxidizing agent, reducing agent, unfixed dye. |
| **Vat** | Oldest dyes, chemically complex and insoluble in water. | Cotton, wool and other cellulosic fibres. | 60 – 70 | Colour, alkali, oxidizing agents, reducing agents. |

## 2.2 Methyl Red Dye

Methyl Red (MR) dye is a well-known dye that have widely used in textile dying and paper printing industries (Sahoo, Gupta, & Pal, 2005). MR dye also contain a carboxylic acid functional group which can help in its ability to serve as an acid or hydrogen ion source. MR dye is pH indicator dye which in the form of dark red crystalline powder that turn red in colour when in acidic solution (Ahmad, Z., & Sayyad, 2009). Other than that, it also will change the colour when at the pH of 5.5. MR dye are insoluble in water but soluble in the alcohol and ethanol. Used of MR dye in industry will give the advantages to the environment, animal and people. MR dye are mutagenic under aerobic condition which is its undergoes biotransformation into 2-aminobenzoic acid and also N-N-dimethyl-p-phenylene diamine (Rosemal, Haris, Mas Haris, & Sathasivam, 2009).

For the case of the skin contact, MR dye will cause skin irritation effect. MR dye also will cause the serve pain if eye contact are happened. For the case of inhalation or swallowed, it will cause the irritation of respiratory and digestive tract (Sahoo et al., 2005). MR dye are used as an indicator in 0.1% alcoholic solution. This dye also used for titrating weak organic base. MR dye also an organic semiconductor which have a potential in application of the electronic devices and have a conjugated structure and rich in the 16-µ-electron system (Ahmad & Sayyad, 2009). Table 2.3 listed the physical properties of the MR dye.

Table 2.3 : Physical properties of the MR dye

| **Properties of Methyl Red dye** | |
|---|---|
| **Name** | Methyl Red |
| **IUPAC Name** | 2-[[4-(dimethylamino)phenyl]diazenyl]benzoic acid |
| **Chemical structure** |  |
| **Melting point** | 179–182 °C (354–360 °F; 452–455 K |
| **Boiling point** | 306.8 ºC |
| **Density** | 0.791 g/cm3 |
| **Chemical formula** | $C_{15}H_{15}N_3O_2$ |
| **Molar mass** | 269.304 gmol$^{-1}$ |
| **pH** | 4.8 – 6.0 pH |

## 2.3 Method to treat dye

Dyes are used in the different industries such as textiles, leather, paper, plastics, food, and rubber in order to colouring their product (Ashrafi et al., 2017). It is reported that, annually more than 10,000 tons of dyes utilised and 100 tons are released in water bodies (Ashrafi et al., 2017). There are a few methods to treat dyes which by using the biological treatment, chemical treatment, physical treatment and also physicochemical treatment (Ong et al., 2011). Physicochemical treatment are using the coagulation method, adsorption on activated carbon, polymer and mineral sorbent, reverse osmosis, chemical oxidation, filtration and electrochemical treatment (Kornaros & Lyberatos, 2006).

The biological method display more limitation which is high in cost, low efficiencies and can lead to the secondary pollution (Baccar et al., 2010). Figure 2.1 shows the treatment method for the removal of dye from wastewater effluents and table 2.4 are the summarisation of various physical, chemical, and biological methods for the removal of dye from wastewaters.

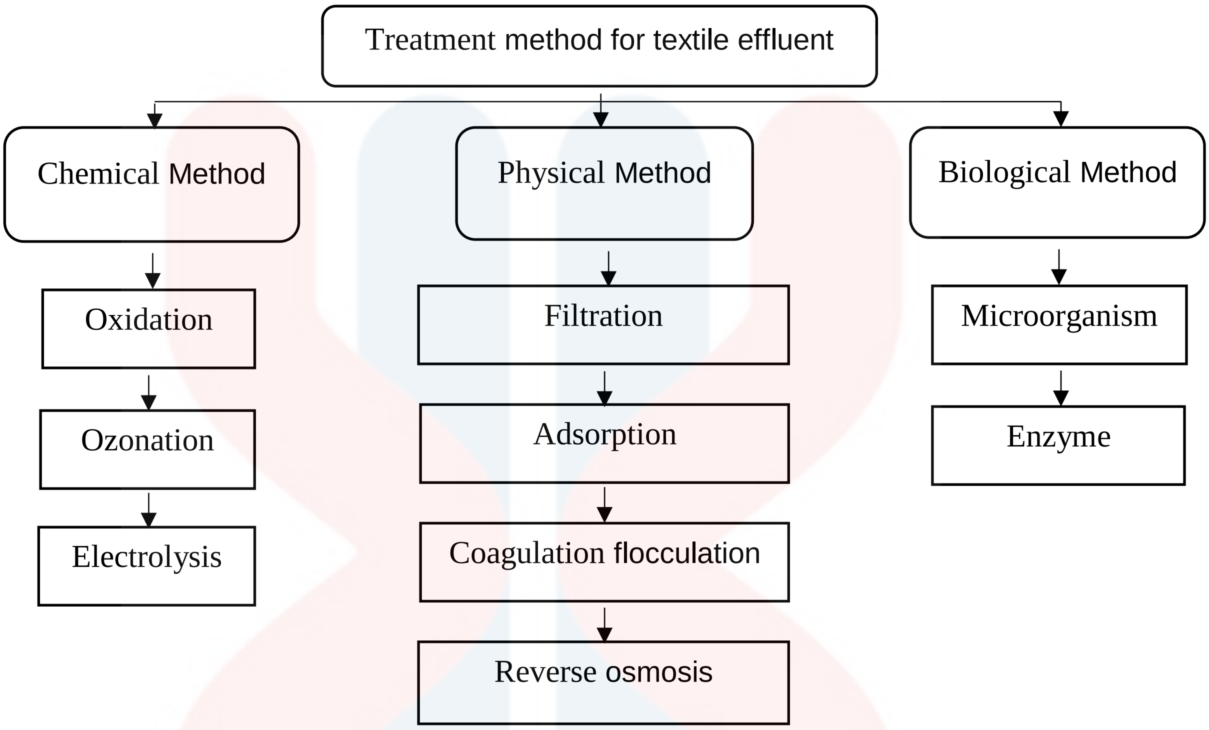


Figure 2.1: Method for removal of dye (Saratale, Saratale, Chang, & Govindwar, 2011)

Table 2.4: The summarisation of various physical, chemical, and biological methods for the removal of dye from wastewaters (Kumar, Agnihotri, Wasewar, Uslu, & Yoo, 2012)

| Type | Method | Advantages | Disadvantages |
|---|---|---|---|
| **Physical** | Adsorption | Good removal in wide range of dye | Nonselective to the adsorbate |
|  | Membrane filtration | Removal of all type of dye | Will produce the concentrated sludge production |

| | | | |
|---|---|---|---|
| | Ion exchange | Do not have any adsorbent loss | Does not effective for all type of dye |
| | Irradiation | The oxidation will effective at the lab scale | Required lot of dissolved oxygen |
| | Electro kinetic coagulation | Economically feasible | High in sludge production |
| | Coagulation-flocculation | Good elimination of insoluble dye | Cost of sludge treatment garbage dump |
| | Adsorption on activated carbon powder coupled with coagulation process | Matter, organic matter and low influence on colour Fast fouling of suspended matter | Cost of activated carbon powder |
| | Reverse osmosis | Retention of mineral salt and hydrolysed reactive dyes and auxiliaries | High pressure process, Fouling with high concentrations |
| | Nano filtration | Separation of mineral salts, hydrolysed | Treatment for complex solution with a high |

| | | | |
|---|---|---|---|
| | | reactive dyes and auxiliaries | concentration of pollutant |
| | Ultrafiltration or microfiltration | Low pressure process | Inadequate quality for reused the permeate |
| **Chemical** | Fenton’s reagent | Effective decolourisation of both soluble and insoluble dyes | Sludge generation |
| | Ozonation | Good elimination of colour | No diminution of COD values Extra costs |
| | Photochemical | No sludge production | Formation of by-product |
| | NaOCl | Initiates and accelerates azo-bond cleavage | release of aromatic amine |
| | Electrochemical destruction | Breakdown compound | High cost of electricity |
| **Biological** | standard biological degradation | Efficiency of oxidizable matter 90% | Low biodegradability of dye, the salt concentration stay constant |

### 2.3.1 Biological Method

Biological method are consist of the fungal treatment, fungal decolourisation, microbial degradation and also bio sorption by using microbes either live or death to treat dyes in water. Biological method are expensive. This is because of the cost of microbs. The bioremediation system are the method that commonly applied to the treatment of the effluent due to many type of microorganisms are able to accumulate and degrade different pollutant (Ramalingam, Harish, & Darmenthirkumar, 2012). This biological treatment does not able to obtain the satisfactory colour elimination with the current conventional process which is biodegradation process (Ramalingam et al., 2012). Due to the present of the recalcitrant and the toxic organic compound, the utilisation of this method may be limited (Kornaros & Lyberatos, 2006).

### 2.3.2 Chemical Method

Chemical method are consist of coagulation, flocculation combined with flotation and filtration, precipitation-flocculation, electro flotation, electro kinetic coagulation, conventional oxidation method which is by using the oxidising agent and also the electrochemical process (Ramalingam et al., 2012). Chemical method did not applied often due to disposal problem and expensive in cost. Flocculation and coagulation is widely applied in wastewater treatment due to their simple operation and also efficient by using the aluminium and iron salt as the coagulants in water which help in removing a broad range of impurities in the effluents including colloidal particles and dissolve organic substance (Khouni, Marrot, Moulin, & Ben Amar, 2011).

### 2.3.3 Physicochemical Method

Physicochemical method consists of the membrane filtration process which is the nano filtration, reverse osmosis, electro dialysis and also the adsorption techniques (Ramalingam et al., 2012). Reverse osmosis are water purification technique that used a semipermeable membrane in order to remove the ions, molecules and also large particles. In this method, the applied pressure is used in order to overcome the osmotic pressure that driven by the chemical potential of the solvent. While the adsorption techniques are the most efficient techniques for the water re-used due to flexibility and simplicity of design, ease of operation, low cost and insensitivity to the toxic pollutants (Ramalingam et al., 2012). The adsorption technique also one of the inexpensive technique that did not need any additional pre-treatment step before the application.

## 2.4 Adsorption

Adsorption is deposition of molecular species onto the surface. Adsorption is also known a phenomenon of accumulation of large number of molecular species at the surface of the liquid or solid phase. The adsorption process involve two component which is the adsorbent and adsorbate. The adsorbent is the substance on the surface at which the adsorption take place while the adsorbate is the substance that being adsorb at the surface of the adsorbent. Adsorption is one of the most and the best technique for the removal of the pollutant either organic or inorganic from the wastewater (Franca, Oliveira, & Ferreira, 2009).

Adsorption are one of the best method can be used because it is the effective, economic and easy method (Baccar et al., 2010). Besides, the adsorption on activated carbon is the best method to adsorb dyes. However, the commercial and conventional carbon are high in cost. Therefore, the researcher find a solution to the problem by which using the renewable and cheaper precursors to form the adsorbent (Baccar et al., 2010). This sources are low in cost and easily obtained. Besides, it also help in minimising the amount of solid waste found worldwide. It also a very useful method.

## 2.5 Adsorbent

The adsorption efficiencies of the process are depending on the chemical and physical properties of the adsorbent used. Therefore, it is important to choose the best adsorbent used in order to obtained a maximum adsorption efficiencies. The selection of the adsorbent are based on their adsorption capacity, the porosity of the adsorbent, the pore structure, the availability and the cost needed. There are various type of adsorbent in the world. The major type of adsorbent used are activated carbon, silica gel, activated alumina, molecular sieve carbon and polymeric adsorbent to remove dyes from the water. Different adsorbent have different characteristic and being used for the different purpose and application.

Through this treatment method, food waste was introduce to be an adsorbent materials for dyes removal. Food waste thrown by human every day and take a long time to be disposed. The causes of food waste are occurs at the various stage such as the production, processing, retailing and consumption stage but the most common stage are at the production and consumption stage. This problem will lead to increasing in environmental pollution. Food waste also one of the materials that are suitable to make as adsorbent for example oyster shell. By using oyster shell as the adsorbent, it will help in reducing the environmental pollution and it also easily to be obtain and low cost. Table 2.5 shows the review of adsorption capacity of different adsorbent.

Table 2.5: The review of adsorption capacity of difference adsorbent

| **Year** | **Type of Dyes** | **Type of Adsorbent** | **Result** | **References** |
|---|---|---|---|---|
| **2018** | Methylene Blue | Lemon Peel activated carbon | • The maximum adsorption capacity are found to be 841.4 mg/g at 24°C.<br>• Langmuir isotherm model. | (Aichour, Zaghouane-Boudiaf, Iborra, & Polo, 2018) |
| **2017** | Malachite green | Orange Peel activated carbon | • Optimal adsorption efficiency are 28.5 mg of dye / g<br>• Combination of Type I and Type II isotherms. | (Lam et al., 2017) |

|  |  |  |  |  |
|---|---|---|---|---|
| **2017** | Methylene Blue | Rice like titanium oxide (TiO2)/graphene hydrogel | • The adsorption capacity of Methylene Blue are 177.3 mg $g^{-1}$. | (Liu, Y., et al., 2017) |
| **2017** | Methylene Blue | Agri-food organic waste | • The adsorption capacity was found to be 285.71 mg $g^{-1}$.<br>• Langmuir isotherm model. | (Anfar et al., 2017) |
| **2016** | Reactive Orange 16 | Fish Scales | • Maximum adsorption capacities are 105.8, 107.2, and 114.2 mg/g at 30 °C, 40 °C, and 50 °C, respectively.<br>• Freundlich equation. | (Marrakchi, Ahmed, Khanday, Asif, & Hameed, 2017) |
| **2016** | Methyl violet and Rhodamine 6G | Walnut Shell | • The maximum adsorption capacity are 332.5 mg $g^{-1.}$<br>• The multiple linear regression model.<br>• The random forest model.<br>• The artificial neural network model. | (Ashrafi et al., 2017) |

| | | | | |
|---|---|---|---|---|
| **2016** | Pb (II) | Pistachio Shell Carbon. | • Maximum adsorption capacity are 24 mg g$^{-1}$ 7.9 mg g$^{-1}$ 7.9 mg g$^{-1}$ of Pb (II) was recorded at pH 6.<br>• Langmuir isotherm model. | (Siddiqui & Ahmad, 2017) |
| **2015** | Methylene Blue | Factory-rejected tea. | • The maximum adsorption capacity was found to be 487.4 mg/g at 30 °C.<br>• Langmuir isotherm model. | (Islam, Benhouria, Asif, & Hameed, 2015) |
| **2014** | Acridine Orange and Rhodamine 6G | Hydrothermal carbonization of urban food waste. | • The maximum adsorption capacity 70.36 mg g$^{1}$ at 313 K for AO while 71.42 mg g1 at 313 K for R6G.<br>• Pseudo-second-order kinetic Model.<br>• Langmuir Isotherm Model. | (Parshetti, Chowdhury, & Balasubramanian, 2014) |
| **2012** | Methylene Blue | Sludge of food processing industries. | • Adsorption capacity are 23.6 mg g$^{-1}$ and 14.2 mg g$^{1}$, respectively.<br>• Langmuir equation. | (Mahapatra, Ramteke, & Paliwal, 2012) |
| **2010** | Lanaset Grey G | Tunisian olive- | • Adsorption capacity was found to be 108.7 mg g$^{-1}$. | (Baccar et al., 2010) |

| | | | | |
|---|---|---|---|---|
| | | waste cakes | - Langmuir Freundlich model. | |
| **2009** | Methylene Blue | Coffee ground | - Temkin models.<br>- The maximum adsorption capacity are 18.71 $mgg^{-1}$.<br>- Langmuir equation model. | (Franca et al., 2009) |

## 2.6 Oyster shell as an adsorbent

Figure 2.2: Oyster shell

*Crassostrea iredalei* are waste product that present a major disposal problem in the coastal regions (Kwon et al., 2004). Under a define condition which is at 750ºC for 1 hours under a nitrogen atmosphere are shows that it will change the *Crassostrea iredalei* to the sustainable reagent for the phosphorus removal with the higher yield which is up to 98% (Kwon et al., 2004). The *Crassostrea iredalei* were characterise of calcium carbonate (Kwon et al., 2004). From the chemical and microstructure analysis shows that the *Crassostrea iredalei* are composed of the calcium carbonate with no impurities (Yoon et al., 2002).

Based on the previous study which is in 2005, a study by Namasivayam, C., et al. In this study, the oyster shell powder is prepared by using high pressure steam. From this study, it is concluded that phosphate can be removed by the oyster shell powder (Namasivayam, Sakoda, & Suzuki, 2005). The removal of phosphate by the sorption of oyster shell powder were investigated under the temperature of 24ºC which is at room temperature.

After that, there is also a study on the oyster shell powder which is by Ting-Chu Hsu to the adsorption of $Cu^{2+}$ and $Ni^{2+}$ from aqueous solution by oyster shell powder in 2009. In this study, the oyster shell powder was prepared as an adsorbent for the removal of the $Cu^{2+}$ and $Ni^{2+}$. It is concluded that the oyster shell powder can effectively adsorb $Cu^{2+}$ and $Ni^{2+}$ from wastewater with the higher adsorption capacity (Hsu, 2009). The adsorption isotherm that fitted well are Langmuir, Freundlich, and Dubinin–Kaganer–Radushkevich.

Next in 2012, a study by Wan-Ting Chen, Chiao-Wen Lin, Po-Kang Shih and Wen-Lian Chang about the adsorption of phosphate into waste oyster shell. In this study, the oyster shell powder is prepared with the different dimension. It is concluded that the phosphate removal capacity of an oyster shell will be enhanced with the increase in temperature and decrease in the oyster shell powder dimension (Chen, Lin, Shih, & Chang, 2012).

A study by the Qiong Wu, Jie Chen, Malcolm Clark and Yan Yu (2014) on adsorption of copper to different biogenic oyster shell structures. In this study, the adsorbent that used for the adsorption of copper are from oyster shell powder. From this study, it is concluded that the adsorption behaviour will be different between the prismatic shell layers, nacreous shell layers and whole raw shell (Wu, Chen, Clark, & Yu, 2014). From those study, it is prove that the raw oyster shell have a good adsorption capacity and the main research are more focused on the metal ion removal.

Therefore, in this study the oyster shell was used to prepared the raw oyster shell adsorbent for the removal of MR dye in the aqueous solution. Apart from that, preparation of the raw oyster shell as an adsorbent would provide a potentially cheaper alternative precursor and will reduce the cost of waste disposal. Other than that, it also will reduce the number of food waste disposal that dump in landfill. Table 2.6 listed some past studies on the oyster shell adsorbent.

Table 2.6: Some past study on the oyster shell adsorbent

| **Year** | **Type of metal ion** | **Type of Adsorbent** | **Best-fit model** | **References** |
|---|---|---|---|---|
| **2014** | Copper | Oyster shell powder | • Langmuir adsorption isotherm.<br>• Freundlich adsorption isotherm. | (Wu et al., 2014) |

| | | | | |
|---|---|---|---|---|
| **2012** | Phosphate | Oyster shell powder | • Pseudo-second-order kinetic model | (Chen et al., 2012) |
| **2009** | $Cu^{2+}$ and $Ni^{2+}$ | Oyster shell powder | • Langmuir adsorption isotherm.<br>• Freundlich adsorption isotherm.<br>• Dubinin–Kaganer–Radushkevich adsorption isotherm. | (Hsu, 2009) |
| **2005** | Phosphate | Oyster shell powder | • Freundlich adsorption isotherm. | (Namasivayam et al., 2005) |

## 2.7 Langmuir adsorption model

Langmuir adsorption isotherm equation are the relationship between the number of active sites of the surface that undergoing adsorption and also pressure. The Langmuir isotherm proposed the theory based on the some assumption which is the fixed number of the adsorption are actually available on the surface of the solid. Other than that, the Langmuir isotherm also makes an assumption that each of the cite can hold maximum of one gaseous molecule and have the constant amount of heat energy released during the experiment. Not only that, they also make an assumption that between the adsorbed gaseous molecules and the free gaseous molecules, it have the presence of the dynamic equilibrium.

The Langmuir isotherm are the commonly isotherm being used in order to analyse the sorption of the various compound (Hsu, 2009). The Langmuir equation are as below:

$$\frac{Ce}{qe} = \frac{1}{q_o b} + \frac{C_e}{q_o} \qquad \text{(Equation 2.1)}$$

where $C_e$ (mg $L^{-1}$) is the equilibrium dye concentrations, $q_e$ and $q_o$ (mg $g^{-1}$) are the adsorbed amounts at equilibrium and maximal capacity, and b (L $mg^{-1}$) is the Langmuir constant.

## 2.8 Freundlich adsorption model

Freundlich adsorption model are commonly being used to describe the adsorption characteristic for the heterogeneous surface (State, State, & State, 2012). Not only that, freundlich adsorption also commonly used for describing the adsorption of organic and inorganic compound in the solution (Hsu, 2009). The Freundlich equation can be represent as below:

$$q_e = K_F Ce^{\frac{1}{n}} \qquad \text{(Equation 2.2)}$$

Where the $K_f$ is the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration, the heterogeneity factor is 1/n, and n is a measure of the deviation from linearity of adsorption (Kumar et al., 2012).

# CHAPTER 3

# METHODOLOGY

## 3.1 APPARATUS AND EQUIPMENT

The materials and equipment required in this research are beakers (volume 100 mL, 250 mL and 1000 mL), volumetric flask which is 500 mL, conical flask (50 mL and 250 mL), measuring cylinder (100 mL and 500 mL), filter funnel, pH meter, UV – visible spectrophotometer, weighing scale, glass rod, cuvette (1.5 mL), filter paper for the pore size 0.125 µm, spatula, aluminium foil, sieve, micropipette (1000 µL), grinder and mortar and pestle.

## 3.2 Chemical and reagent

In this research, the experiment were carried out by using the chemical and reagent such as methyl red ($C_{15}H_{15}N_3O_2$), sodium hydroxide (NaOH), sodium bicarbonate ($CHNaO_3$), glycine ($C_2H_5NO_2$), potassium dihydrogen phosphate ($KH_2PO_4$), sodium citrate ($C_6H_5Na_3O_7$) and citric acid ($C_6H_8O_7$).

## 3.3 Preparation of adsorbent

Raw oyster shell were collected at Bachok, Kelantan, Malaysia. The collected oyster shell were washed with distilled water in order to remove all the impurities. The oyster shell then were dried by using oven dry in order to remove the moisture in the oyster shell. The oyster shell then were crushed into a small pieces by using mortar and pastel. The small pieces oyster shell then were grinded by using grinder to obtain powder form. The powder form of raw oyster shell adsorbent was stored in air-tight zipper bag for further used along the research study.

## 3.4 Preparation of dye solution

In order to prepare the dye solution for this research, 0.05 g of MR dye were used. 0.05 g MR dye was weighed by using weighing scale. The MR dye then were mixed with 500 mL of distilled water to obtain a concentration of 100 mg/L. Direct dilution method were used to dilute MR dye solution. The required concentration of the dye solution was prepared freshly each of the time required to be used for the analysis. The outer layer of the volumetric flack that contain the prepared dye solution were wrapped fully with the aluminium foil to prevent the degradation of the dye.

## 3.5 Calibration curve

In order to construct the calibration curve for this experiment, the stock solution were prepared by using 0.05 g of MR dye mixed with 100 mL of distilled water to prepare 100 mg/L solution. Then the MR dye were diluted from the stock solution to 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 mg/L, respectively and marked up with distilled water up to 50 mL by using a 50 mL conical flask. The various concentration of the MR dye solution were measured by using the UV–vis spectrophotometer at the wavelength of 410 nm. The diluted MR dye solution in the conical flask then filled into 1.5 mL cuvette for the UV-Vis test. Distilled water were utilised as blank or act as reference in this experiment. The value that obtained from the adsorbent reading used to construct the MR dye calibration curve.

## 3.6 Optimisation study

### 3.6.1 The effect of the adsorbent size on the MR dye adsorption

The powdered raw oyster shell that prepared and stored in the air-tight zipper bag previously were sieved by using sieving machine with the size of 75 $\mu m$, 150 $\mu m$, 300 $\mu m$, 500 $\mu m$, 710 $\mu m$ and 1000 $\mu m$. A 0.5 g of sieved adsorbent were placed in the six conical flask that contains difference size of adsorbent. The 50 mg/L of dye then added to the conical flask that contain raw oyster shell adsorbent. The mixture then stirred by using a glass rod and left untouched for about 24 hours. After 24 hours, the solution was filtered by using filter paper. The solution were analysed using UV-VIS spectrophotometer with the wavelength of 410 nm.

### 3.6.2 Effect of the adsorbent dosage on the adsorption of MR dye

In this research, the effect of adsorbent dosage also tested. In order to investigate the effect of adsorbent dosage on the MR dye, 9 type of dosage were analyse. The dosage that used were 0.1 g, 0.3 g, 0.5 g, 0.7 g, 1.0 g, 1.3 g, 1.5 g, 1.7 g and 2.0 g of adsorbent. 100 mL MR dye solution at the concentration of 50 mg/L was used and mixed with the different adsorbent dosage in the conical flask. The mixture then stirred using glass rod and left undisturbed at a room temperature for about 24 hours. After 24 hours, the solution were filtered by using filter paper. The solution then were analysed using UV-VIS spectrophotometer at the wavelength of 410 nm.

### 3.6.3 Effect of the initial dye concentration

For the effect of initial dye concentration analysis, the optimum adsorbent size and adsorbent dose that obtained previously were used in order to obtain the best result. 8 different initial concentration of dye solution were tested. The concentration that used are 10 mg/L, 30 mg/L, 50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L, 250 mg/L and 300 mg/L of MR dye solution. The volume used for each of the concentration are 100 mL . The different concentration of the dyes then mixed with the fixed amount of the adsorbent dosage and adsorbent size in the conical flask. The mixture then stirred by using a glass rod and left untouched for about 24 hours. After 24 hours, the solution was filtered by using filter paper. The solution then were analysed by using UV-VIS spectrophotometer at the wavelength of 410 nm.

### 3.6.4 Effect of contact time on the adsorption of the MR dye

The initial concentration of dye that found to have the highest percentage of MR dye removal that obtain from the previous analysis were used for the current and upcoming parameter. The volume that used were maintained at 100 mL for this analysis, the contact time that used was 1 hour for 9 hours. The sample that prepared were filtered at every 1 hours by using filter paper. After required hours, the solution were filtered by using filter paper. The solution then were analysed by using UV-VIS spectrophotometer with the wavelength of 410 nm.

### 3.6.5 Effect of pH on the MR dye adsorption

In this research, the effect of the pH also analysed. The pH that were studied are in the range of acidic, strong acid, base and strong based . Various pH were altered using buffer from 0.1 M citric acid and 0.1 M sodium citrate for acidic pH which is pH 3,4,5 and 6. For 0.1 M potassium dihydrogen phosphate and 0.1 M sodium hydroxide were used for pH 7 and 8. While 0.1 M glycine and 0.1 M sodium hydroxide were used for pH 9 and 10 which is base. For pH 11 which is strong base, 0.1 M sodium bicarbonate and

0.1 M sodium hydroxide used. In this analysis, the pH meter were used in order to get the pH reading of the buffer.

All the chemical prepared then were dissolve in the distilled water in order to reach the required volume which is 100 mL. The mixture then stirred by using a glass rod and left untouched until reach the optimum contact time. The reading of the adsorbent were measured by using UV – Visible spectrophotometer at the wavelength of 410 nm with the optimum parameters of adsorbent size, adsorbent dose, initial dye concentration and also contact time.

### 3.6.6 Effect of agitation speed

The optimum adsorbent size, adsorbent dosage, initial dye concentration, contact time and pH obtained from previous parameters were used. Instead of keeping the sample mixture undisturbed, the mixture was agitation at 5 different speed. The stirring speed was varied up from 90 to 170 rpm which is 90, 110, 130, 150 and 170 rpm. Volume used was maintained at 100 mL.

### 3.6.7 Effect of agitation time

The optimum adsorbent size, adsorbent dosage, initial dye concentration, contact time, pH and agitation speed obtained from previous parameters were used. Instead of keeping the sample mixture undisturbed, the mixture was agitated at 5 different agitation time. The agitation time was varied up from 15 min to 75 min which is 15, 30, 45, 60 and 75 min. Volume used was maintained at 100 mL.

## 3.7 Data analysis

### 3.7.1 Adsorption capacity

For the adsorption capacity analysis, the solutions of the sample were withdrawn at equilibrium in order to find out the concentrations of the residue. UV-Vis spectrophotometer with the wavelength of 410 nm to measure the concentration of dye in the solution after the equilibrium adsorption. The amount of adsorption at equilibrium, $q_e$ (mg/g), were calculated by the following equation.

$$q_e = \frac{(C_o - C_e)V}{M} \qquad \text{(Equation 3.1)}$$

Where $C_e$ are the equilibrium concentrations in the solution (mg/L) while $C_o$ are the initial concentrations in the solution (mg/L); V is the volume of solution (L) and M are the mass of adsorbent (g).

### 3.7.2 Percentage removal of the dye

In this research, the percentage removal of the dye also were determined. The percentage removal of the dye were calculated by using the equation below:

Percentage removal = $\frac{C_o\text{-}C_e}{C_o} \times 100$ (Equation 3.2)

Where $C_o$ are the initial concentration of dye in the solution (mg/L) while $C_e$ are the final concentration of dye in the solution (mg/L) .

### 3.7.3 Langmuir adsorption isotherm

Langmuir isotherm are the most commonly being used to analyse the sorption of the various compound (Hsu, 2009). The Langmuir adsorption isotherm obtained by using the equation below.

$q = \frac{q_{max} b\, C_e}{1+K_L C_e}$ (Equation 3.3)

Where the q = dye uptake; $q_{max}$ = Maximum dye uptake (mg/g); $C_e$ = equilibrium concentration (mg/L); $K_L$ = Langmuir equilibrium constant (L/mg). For the linearized Langmuir isotherm equation are as below.

$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o}$ (Equation 3.4)

Where the $C_e$ = equilibrium concentration (mg/L); $q_e$= amount adsorbed at equilibrium (mg/g); $q_o$= Langmuir constant related adsorption capacity to be determined from slope of $\frac{1}{q_m}$ (mg/g); b = Langmuir constant related to adsorption energy to be determined from intercept of $\frac{1}{b_{qm}}$ (L/mg).

Data obtained were used to construct linear plot of $\frac{C_e}{q_e}$ against $C_e$.

### 3.7.4 Freundlich adsorption isotherm

The Freundlich isotherm are the most commonly being used to describe the adsorption of the organic and inorganic compound in the solution (Hsu, 2009). The equation that used are as below.

$$q_e = K_F Ce^{\frac{1}{n}} \qquad \text{(Equation 3.5)}$$

Where the $q_e$ = amount of dye adsorbed (mg/g); $C_e$ = equilibrium concentration (mg/L); $K_F$ = indicator of adsorption capacity to be determined from intercept (L/mg); $\frac{1}{n}$ = adsorption capacity to be determined from slope (constant) . While for the linearised Freundlich model equation are as below.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad \text{(Equation 3.6)}$$

Where the $q_e$ = amount of dye adsorbed (mg/g); $C_e$ = equilibrium concentration (mg/L); $K_F$ = indicator of adsorption capacity to be determined from intercept (L/mg); $\frac{1}{n}$ = adsorption capacity will be determined from slope (constant).

# CHAPTER 4

# RESULT AND DISCUSSION

## 4.1 PREPARATION OF ADSORBENT

Raw oyster shell were collected at disposal site in Bachok, Kelantan, Malaysia. There a few step need to be taken before preparing the raw oyster shell as adsorbent. Firstly, oyster shell was washed with distilled water in order to remove all the impurities. The oyster shell then was sun dried for 24 hours then dried again using oven at 60ºC in order to remove all moisture content in the oyster shell. The oyster shell then were crushed into a small pieces by using mortar and pastel. The small pieces oyster shell then were grinded by using grinder to powderised them. Powder form were used in this study because they have a higher surface area than the original size of oyster shell. Therefore, maximum adsorption into the pores of adsorbent can be obtained. The powdered raw oyster shell adsorbent then stored in air-tight zipper bag. This is to maintain the quality of the sample and also to prevent the sample from contamination.

## 4.2 ADSORPTION STUDIES

### 4.2.1 CALIBRATION CURVE

A MR dye calibration curve was constructed by using 50 mg/L dye concentration and the adsorbent reading were measured by using UV-Vis spectrophotometer at the wavelength of 410 nm. The stock solution was prepared at the concentration of 50 mg/L and diluted to 8 different concentration by using direct dilution method to concentration of 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 mg/L, respectively. Figure 4.1 shows graph of MR dye calibration curve that measured at the wavelength of 410 nm in the room temperature (25ºC). From the calibration curve obtained, were produce a linear relationship between the absorbance values and the concentration standards. The correlation coefficient of MR dye is $R^2 = 0.9999$. Figure 4.1 shows MR dye calibration curve measured at 410 nm.

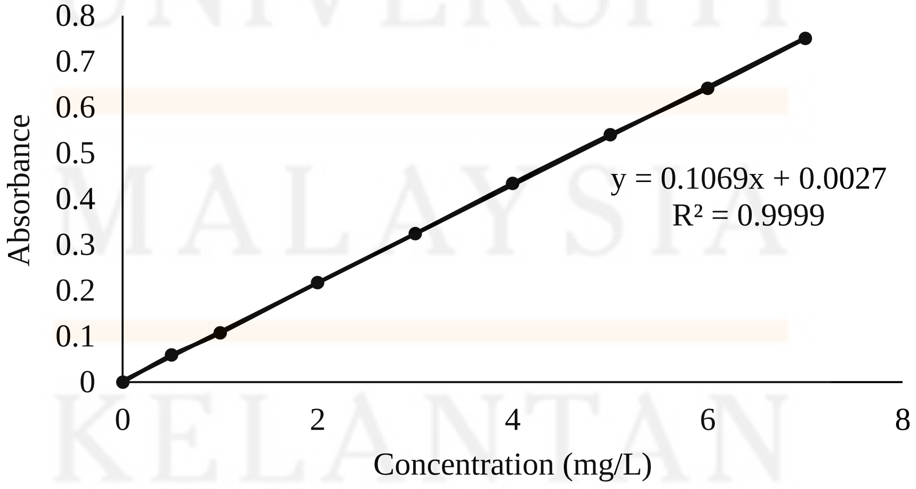


Figure 4.1: MR dye calibration curve measured at 410 nm at room temperature (25ºC)

### 4.2.2 EFFECT OF ADSORBENT SIZE

The effect of adsorbent size are one of the important parameter that influence the rate of adsorption. In order to study the effect of adsorbent size, raw oyster shell (ROS) that were prepared was sieved into six different size which is 75 µm, 150 µm, 500 µm, 710 µm and also 1000 µm. 0.5 g of powder from each size were used to react with MR dye solution. The solution was left untouched for 24 hours. After 24 hours, the solution were filtered by using filter paper and adsorbent reading was obtained by using UV-Spectrophotometer at the wavelength of 410 nm.

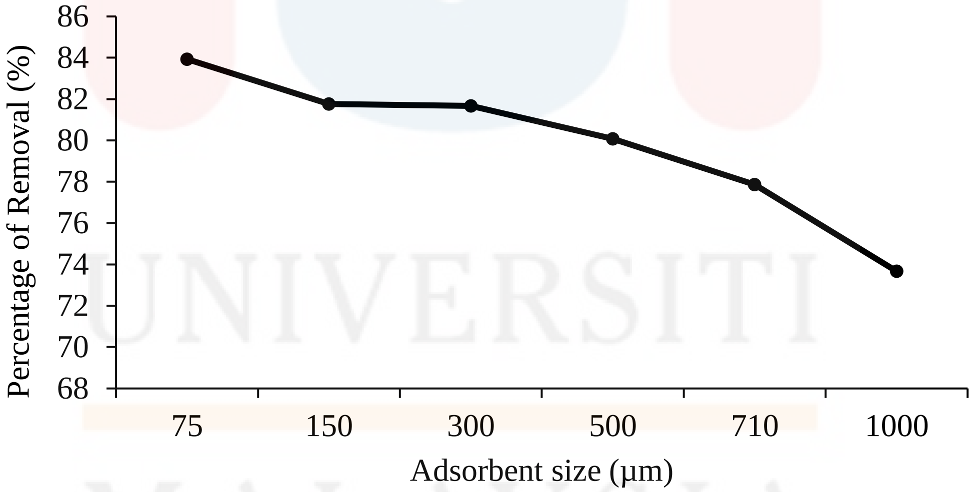


Figure 4.2 : Effect of adsorbent size on MR dye removal, (concentration: 50mg/L MR; volume: 100mL; temperature: 25ºC; adsorbent dosage: 0.5 g; contact time: 24 hour).

Based on Figure 4.2, it shows that the percentage of MR dye removal declined from 75 µm to 1000 µm with the percentage of 83.9% to 73.6%, respectively. From the result obtained, it shows that the highest percentage of MR dye removal were 83.9% at the size of 75 µm and the lowest percentage of MR dye removal obtained were 73.6% with the adsorbent size of 1000 µm. While for the particle size of 50 µm, 300 µm, 500 µm and 710 µm removed 81.7%, 81.6%, 80.0% and 77.8% MR dye, respectively. It can be concluded that, the percentage of MR dye removal will increase with the decreased in adsorbent size.

The smallest particle size which is 75 µm able to remove the highest percentage of MR dye because the smallest the particle size, the larger the surface area of the adsorbent the higher the percentage of MR dye removal. Other than that, higher percentage of MR dye removal that obtained also due to the greater accessibility to pores and the surface area of the adsorbent as the smaller the particle, the larger the surface are (Abdulhussein & Hassan, 2015).

### 4.2.3 EFFECT OF ADSORBENT DOSAGE

Adsorbent dosage also one of the important parameters in the adsorption study. This is because it will determine the capacity of adsorbent for a particular dye concentration (Alagupprathana & Poonkothai, 2017). To determine the adsorbent dosage, nine dosage of raw oyster shell adsorbent were tested which is 0.1 g, 0.3 g, 0.5 g, 0.7 g, 1.0 g, 1.3 g, 1.5 g, 1.7 g and 2.0 g. The different dosage of adsorbent was mixed with MR dye solution with the concentration of 50 mg/L. The volume used are 100 mL for each dosage used. 75 µm adsorbent size which appeared to be the optimum adsorbent size in order to remove MR dye were maintained to be used throughout the experiment.

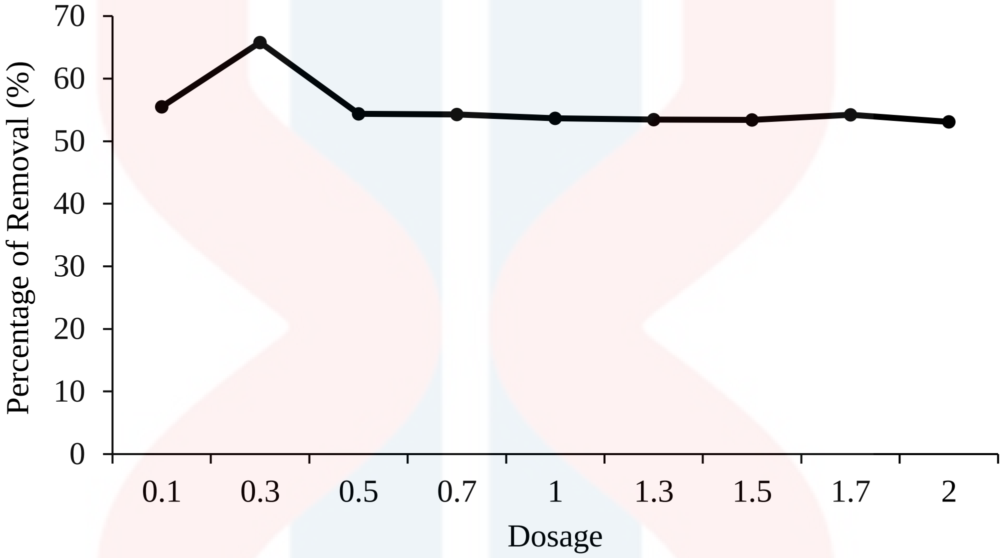


Figure 4.3 : Effect of adsorbent dose on MR dye removal, (concentration: 50mg/L MR; volume: 100 mL; temperature: 25°C; adsorbent size: 75µm; contact time: 24 hour).

Figure 4.3 shows effect of adsorbent dose on MR dye removal. Based on the graph obtained, it shows that the percentage of MR dye removal increased with the increased in adsorbent dosage from 0.1 g to 0.3 g. However the percentage of MR dye removal starts to decrease at the adsorbent dose of 0.5 g to 2.0 g. From Figure 4.3, the highest percentage of MR dye removal which is 65.8% and the lowest percentage of MR dye removal obtained are 53.0% with the adsorbent dosage of 2.0 g. While for the adsorbent dose of 0.1 g, 0.5 g, 0.7 g, 1.0 g, 1.3 g, 1.5 g and 1.7 g removed 55.5%, 54.3%, 54.2%, 53.6%, 53.4%, 53.4% and 54.2% MR dye, respectively. It can be conclude that

0.3 g ROS adsorbent found to be the best adsorbent dosage that give the highest percentage of MR dye removal.

The removal of MR dye was at the higher when the adsorbent dosage are at 0.3 g which due to the MR dye molecules have reacted efficiently with the adsorbent. This can be clearly seen when the adsorbent dose increase, the MR dye surface area also will be increased which can be resulting in increase the availability of more adsorption site (Thirumalisamy & Subbian, 2010). Other than that, when adsorbent dosage increase, it will increase the active site of the adsorbent which can increase the percentage of MR dye removal (Tanzim & Abedin, 2015). At the beginning of the test, the rate of dye removal increased then decreased gradually (Abdulhussein & Hassan, 2015). Besides that, the result shows that the adsorption has reached equilibrium that means all the active site of adsorbent were saturated with MR dye molecules.

### 4.2.4 EFFECT OF INITIAL DYE CONCENTRATION

The effect of initial dye concentration on the removal of the MR dye in the aqueous solution were tested using eight different initial dye concentration. The adsorbent with the size of 75µm and the dosage of 0.3 g were mixed with the different concentration which are 10, 30, 50, 100, 150, 200, 250 and 300 mg/L. Figure 4.4 shows the graph of MR dye percentage removal which obtain from the experiment. From the graph obtained, it shows the percentage of MR dye removal are increased from 84.4% to 92.4% with increase in the initial dye concentration from 10 mg/L to 100 mg/L.

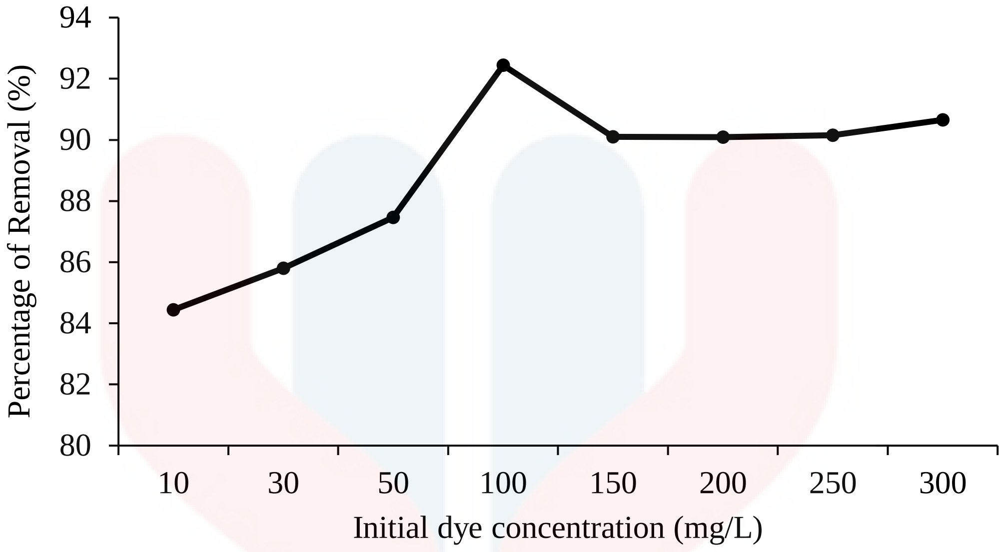


Figure 4.4: Effect of initial dye concentration on MR dye removal, (volume: 100mL; temperature: 25ºC; adsorbent size: 75µm; adsorbent dosage: 0.3g; contact time: 24 hour).

At the concentration of 10 mg/L, it shows the least percentage removal achieved which was 84.4% compared to the 100 mg/L which save the highest percentage removal (92.4%). Not only that, the result that obtained also shows that starting from the concentration of 150 mg/L, there is a reduction on the percentage of MR dye removal which is 90%, followed by concentration of 200 mg/L (90%), 250 mg/L (90.1%) and 300 mg/L (90.6%) that give an almost constant value. The reduction on the percentage removal of MR dye were due to the active site of the adsorbent were saturated with the MR dye molecules. This shows that the adsorption had reached equilibrium at 100 mg/L.

From the observation, it was found out that the concentration of 100 mg/L was the optimum initial dye concentration. When the initial dye concentration increased, the number of dye ion will also increase. Therefore, the collision between dye ions and the surface of the adsorbent also will increase (Rosemal et al., 2009). As a result, it will enhance the interaction between MR dye and adsorbent which also will increase the adsorption process.

### 4.2.5 EFFECT OF CONTACT TIME

The effect of contact time on the removal of the MR dye in the aqueous solution were tested using nine different contact time. By using all the optimum values that obtained from the previous parameter which is adsorbent with the size of 75µm and the dosage of 0.3 g were mixed with 100 mg/L of MR dye solution. Contact time were studied with the interval of 1 hours for 9 hours. Figure 4.5 shows the effect of contact time on MR dye removal.

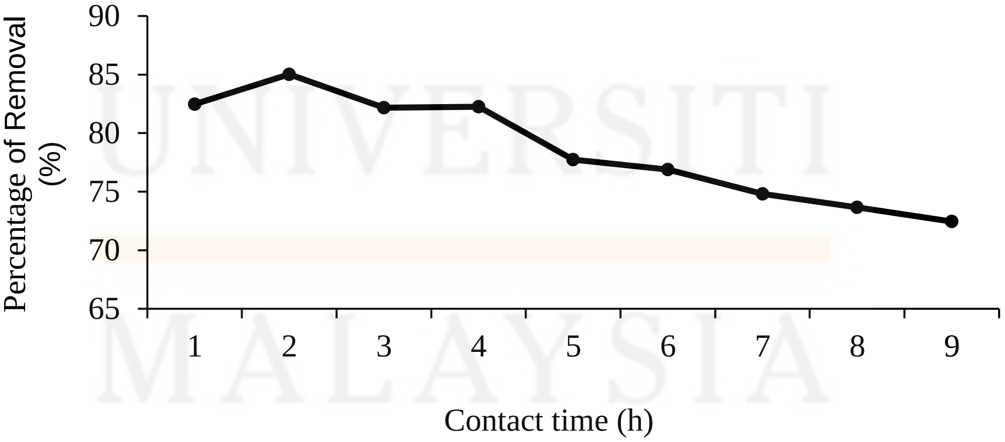


Figure 4.5: Effect of contact time on MR dye removal, (volume: 100mL; temperature: 25ºC; adsorbent size: 75µm; adsorbent dosage: 0.3g; initial dye concentration: 100 mg/L).

Based on Figure 4.5, it shows that the percentage of MR dye removal were increased from 82.47% to 95.02% with the increase in the contact time. Other than that, the result also shows that MR dye were rapidly being adsorbed by the ROS adsorbent for the first 2 hours. While for the next three to nine hours, it shows in slow adsorption on the MR dye. Not only that, the result that obtained also shows that starting from the third hours, there is a reduction on the percentage of MR dye removal which is 82.1%, followed by fourth hours (82.2%), fifth (77.7%), sixth (76.8%), seventh (74.8%), eight (73.6%) and nine hours (72.4%).

The reduction on the percentage removal of MR dye were due to the active site of the adsorbent were saturated with the MR dye molecules. This shows that the adsorption had reached the equilibrium at second hours. This is because, at the initial of the reaction the concentration of dye in the solution were higher and all the active site of the adsorbent surface were vacant. At 100 minutes, the final dye concentration were not very significantly different compared from the start of the adsorption process and it shows that the equilibrium were achieved after 100 minutes (Abdulhussein & Hassan, 2015). Not only that, for the next three to nine hours it shows that the adsorption were slower compared to the first two hours because the adsorbent have slow pore diffusion of the solute ions (Thirumalisamy & Subbian, 2010).

### 4.2.6 EFFECT OF pH

In order to study the effect of pH on the percentage of MR dye removal in the aqueous solution, different buffer concentration ranging from pH 3 to pH 11 were studied. Volume of solution used for this parameter were maintained at 100 mL with the adsorbent size of 75µm and dosage of 0.3 g at the initial MR dye concentration of 100 mg/L. The adsorption were performed at room temperature.

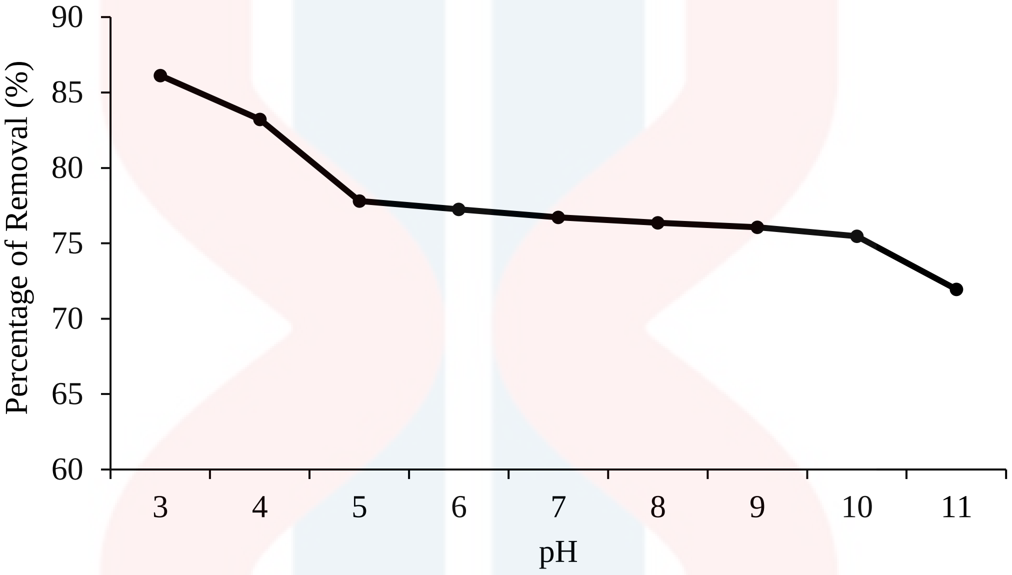


Figure 4.6: Effect of pH on MR dye removal, (volume: 100mL; temperature: 25ºC; adsorbent size: 75µm; adsorbent dosage: 0.3g; contact time: 2 hour).

Figure 4.6 shows the effect of pH on MR dye removal. From the Figure 4.6, it shows that the amount of adsorption decreased when the pH were increased. Where by, the percentage of MR dye removal decreased from 86.1% to 71.9% with an increases in pH 3 to 11. Higher percentage of dye removal was observed at pH 3 which was 86.1%. There was gradual drop in percentage of dye removal from pH 4 to pH 11 which was 83.2% to 71.9%. This was due to the electrostatic attraction between the negatively charge dye and the positively charge surface of the adsorbent.

When the pH of the solution were increased, the number of hydroxyl group also will be increased, but the number of positively charged site will be decreased thus reduce the attraction between MR dye and the adsorbent surface (Ahmad, Ahmad, & Bello, 2015). The aqueous chemistry and binding site on the surface of the adsorbents are influenced by the pH of the solution. Not only that, the surface charge of the adsorbent and the functional group of the adsorbate also will be effected by the pH of the aqueous solution (Ahmad et al., 2015).

### 4.2.7 EFFECT OF AGITATION SPEED

The effect of agitation speed on the removal of the MR dye in the aqueous solution were tested using five different speeds. By using all the optimum values that obtained from the previous parameter which is adsorbent with the size of 75µm and the dosage of 0.3 g were mixed with 100 mg/L of MR dye solution with the pH of 3 and the contact time of 2 hours. Five different speeds which is 90 rpm, 110 rpm, 130 rpm, 150 rpm and 170 rpm. Figure 4.7 shows effect of agitation speed on MR dye removal.

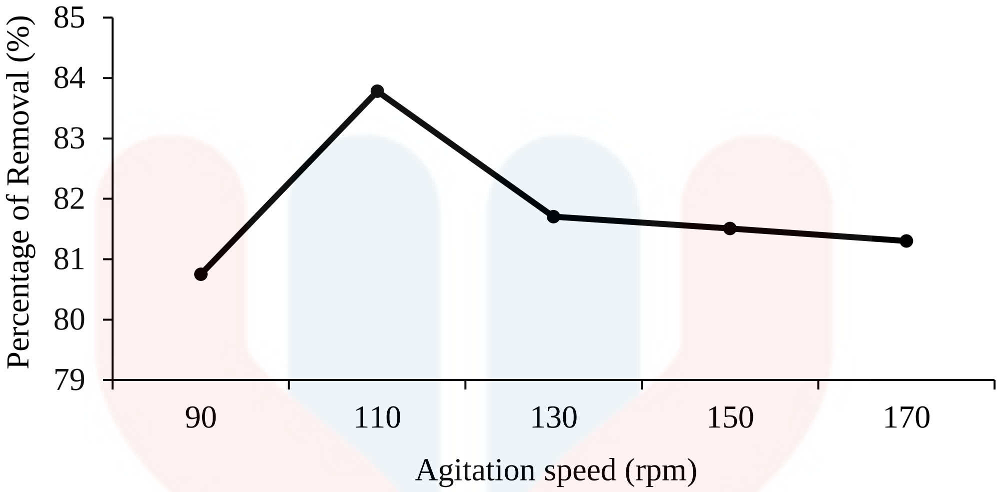


Figure 4.7: Effect of agitation speed on MR dye removal, (volume: 100mL; temperature: 25°C; adsorbent size: 75μm; adsorbent dosage: 0.3g; initial dye concentration: 100 mg/L; contact time: 2 hours).

From Figure 4.7, it shows that the percentage of MR dye removal were increased from 80.74% to 83.77% with increased in the agitation speed. Other than that, the result also shows that MR dye were rapidly being adsorbed by the adsorbent for the speed of 110 rpm. While for 130, 150 and 170 rpm, it shows in slow adsorption on the MR dye. At speed of 90 rpm, the least percentage of MR dye removal which is 80.74% was achieved. This value was increased to 83.77% with the speed of 110 rpm. At 130, 150 and 170 rpm, there was a reduction in the percentage of MR dye removal which were 81.70%, 81.50% and 81.30%, respectively. Agitation speed of 110 rpm is the state where the adsorption capabilities reaches maximum and can be considered as the optimum agitation speed.

The data that obtained indicated that the adsorption capacity increased as the agitation speed increased. The increased the agitation speed, increased the adsorption rate. This effect can be attributed to the increase in the turbulence while decreased in the boundary layer thickness around the adsorbent particles that will give a result of increased in the degree of mixing (Rosemal et al., 2009). At the higher speed which is 130 to 170 rpm, the percentage of dye removal decreased. This due to the increase in kinetic energy of adsorbate and adsorbent particles. Agitation will affect the distribution of the solute in the solution and also the formation of the external boundary film, therefore the adsorption process will be more efficient (Ghaedi et al., 2011).

### 4.2.8 EFFECT OF AGITATION TIME

The effect of agitation time on the removal of the MR dye in the aqueous solution were tested using five different agitation time. MR dye solution were prepared freshly for this experiment. The concentration of MR dye used were 100 mg/L with the volume of 100 mL. MR dye solution then were mixed with 0.3 g adsorbent dosage with the size of 75 µm. Then buffer solution were added in order to reach the pH 3. Then the solution were tested at five different agitation time which were 15, 30, 45, 60 and 75 minutes (min) at the speed of 110 rpm. After reached the desired time, the mixture was filtered by using filter paper and the adsorbent reading was recorded by using UV-Spectrophotometer with the wavelength of 410 nm. Figure 4.8 shows the effect of agitation time on MR dye removal.

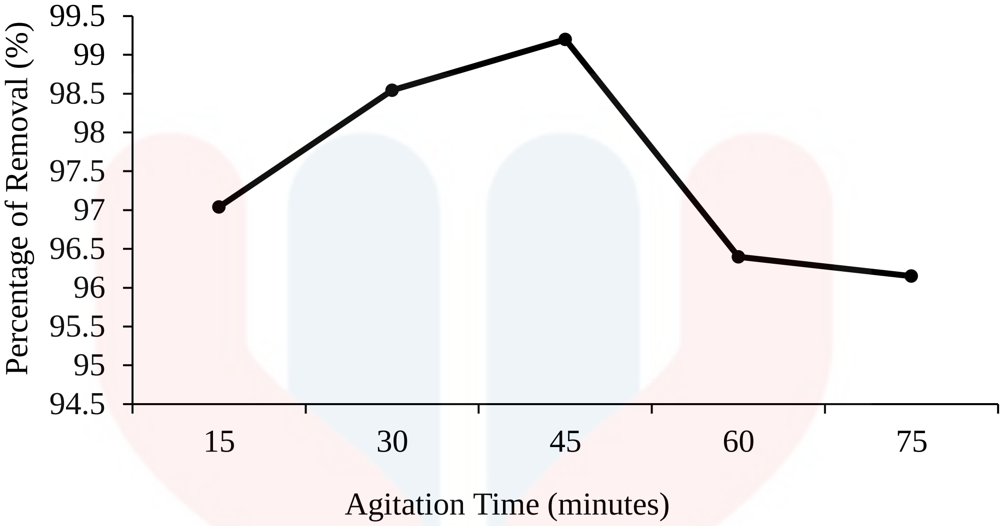


Figure 4.8: Effect of agitation time on MR dye removal, (concentration: 100 mg/L MR dye; volume: 100mL; temperature: 25ºC; adsorbent dosage: 0.3 g; adsorbent size: 75µm; pH: 3; agitation speed: 110 rpm).

From Figure 4.8, it shows that the percentage removal of MR dye were increased from 97.0% to 99.2% with increasing in agitation time. The result obtained also shows that the highest percentage of MR dye removal were at the agitation time of 45 min with the percentage of 99.2% while for the lowest percentage of MR dye removal obtained when the agitation time at the highest which is 75 min with the percentage of 96.1%. The remaining agitation time also being tested which were 15 min, 30 min and 60 min which only obtained the removal of 97.0%, 98.5% and 96.4%, respectively. From the result obtained, it can be concluded that percentage of MR dye removal increased with the increased in agitation time but until reached the optimum agitation time which is 45 min.

Agitation will affect the distribution of the solute in the solution and also the formation of the external boundary film, therefore the adsorption process will be more efficient (Ghaedi et al., 2011). Other than that, the degree of agitation also will reduce the boundary layer resistance and will increase the mobility of the system. Hence, the external mass transfer coefficient also will increase thus, resulting in rapid adsorption of dye molecules (Ghaedi et al., 2011).

## 4.3 ADSORPTION ISOTHERM

As for adsorption isotherm, the equilibrium existence of the adsorbate between the liquid and the solid phase are well describe (Sivakumar & Palanisamy, 2009). Other than that, adsorption isotherm also an invaluable tool for theoretical evaluation and interpretation of thermodynamic parameter which is heats of adsorption (Allen, Mckay, & Porter, 2004). Not only that, under one set of condition, an isotherm may fit the experimental data accurately but fail entirely under another (Allen et al., 2004). The adsorption isotherm study are important to design an adsorption system. Therefore, to analyse the adsorption isotherm, the equilibrium data were analysed by two type of isotherm which is Freundlich and Langmuir model.

### 4.3.1 LANGMUIR ISOTHERM MODEL

Langmuir adsorption isotherm equation are the relationship between the number of active sites of the surface that undergoing adsorption and also pressure. The Langmuir isotherm proposed the theory based on the some assumption which is the fixed number of the adsorption are actually available on the surface of the solid. Other than that, the Langmuir isotherm also make an assumption that each of the cite can hold maximum of one gaseous molecule and have the constant amount of heat energy released during the experiment. Not only that, they also make an assumption that between the adsorbed gaseous molecules and the free gaseous molecules, it have the presence of the dynamic equilibrium.

The Langmuir isotherm are the commonly isotherm used to analysing the sorption of the various compound (Hsu, 2009). Equation 3.4 in the section of 3.7.3 was used to calculate the values of the unknowns. Figure 4.9 shows the adsorption isotherm of MR dye on the raw oyster shell adsorbent due to the effect of adsorbent size. Figure 4.10, 4.11, 4.12, 4.13, 4.14 and 4.15 represent dosage, initial dye concentration, contact time, pH, agitation speed and agitation time respectively. The linear plot of Ce/qe verses Ce suggests the applicability of Langmuir isotherm model for the present system. This demonstrates the development of monolayer coverage of the adsorbate at the external surface of the adsorbent. The values of $q_{max}$ and $K_L$ were determined from the linear plot and their values are given in Table 4.1.

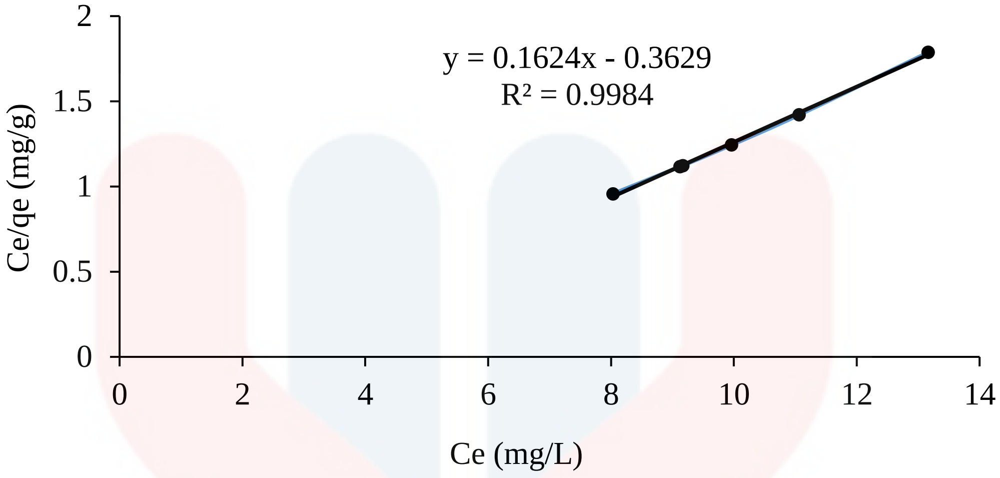


Figure 4.9 : Plot of Langmuir isotherm for effect of adsorbent size on removal of MR dye.

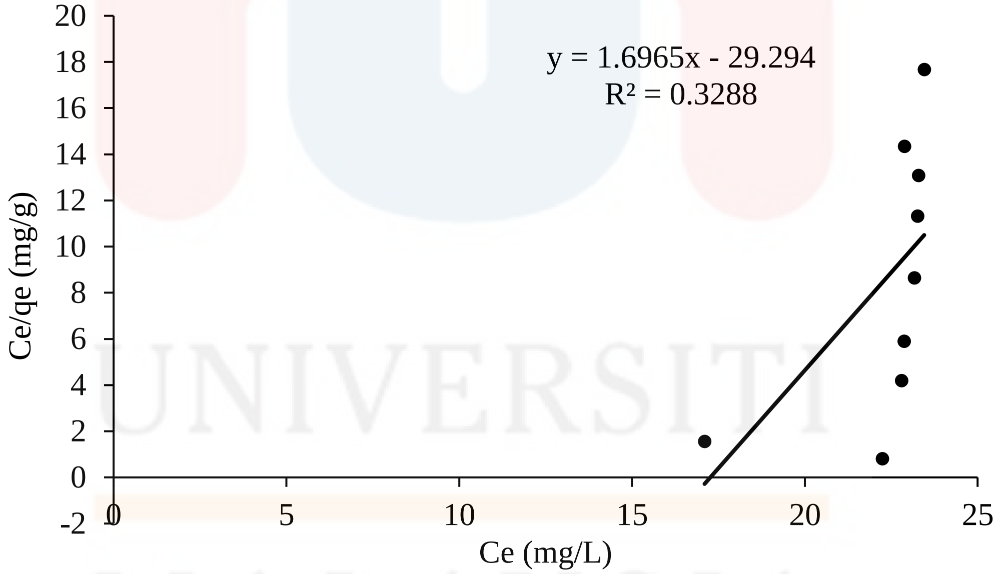


Figure 4.10: Plot of Langmuir isotherm for effect of adsorbent dosage on removal of MR dye.

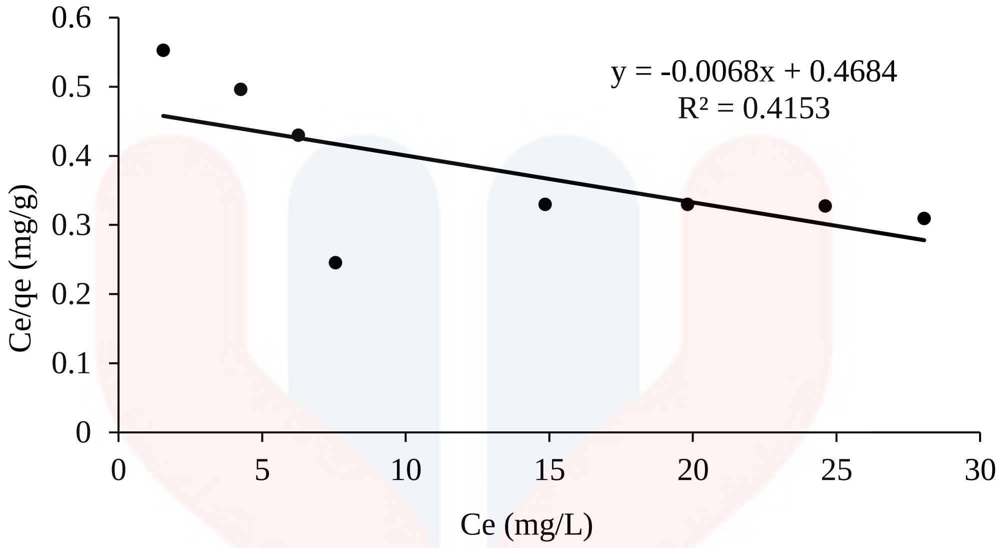


Figure 4.11 : Plot of Langmuir isotherm for effect of initial dye concentration on removal of MR dye.

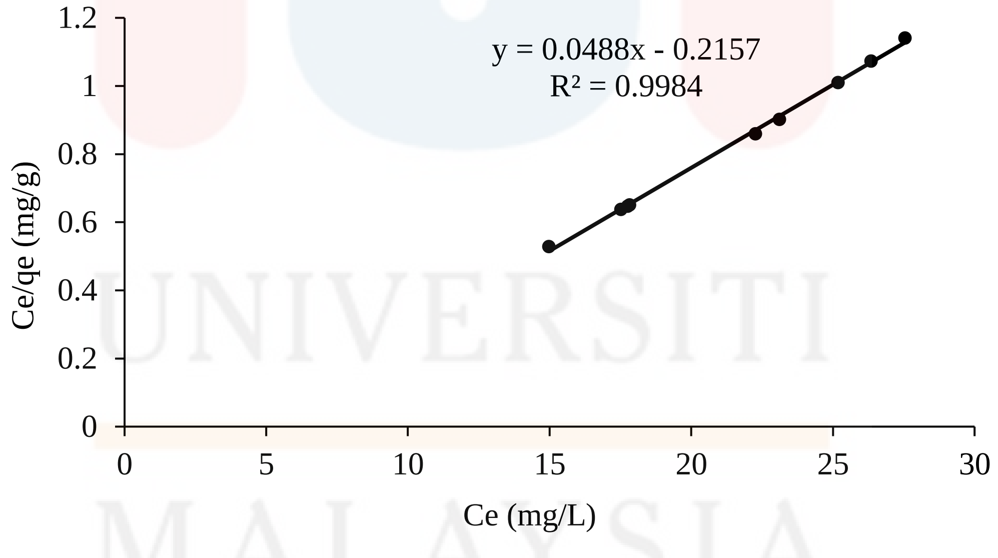


Figure 4.12: Plot of Langmuir isotherm for effect of contact time on removal of MR dye.

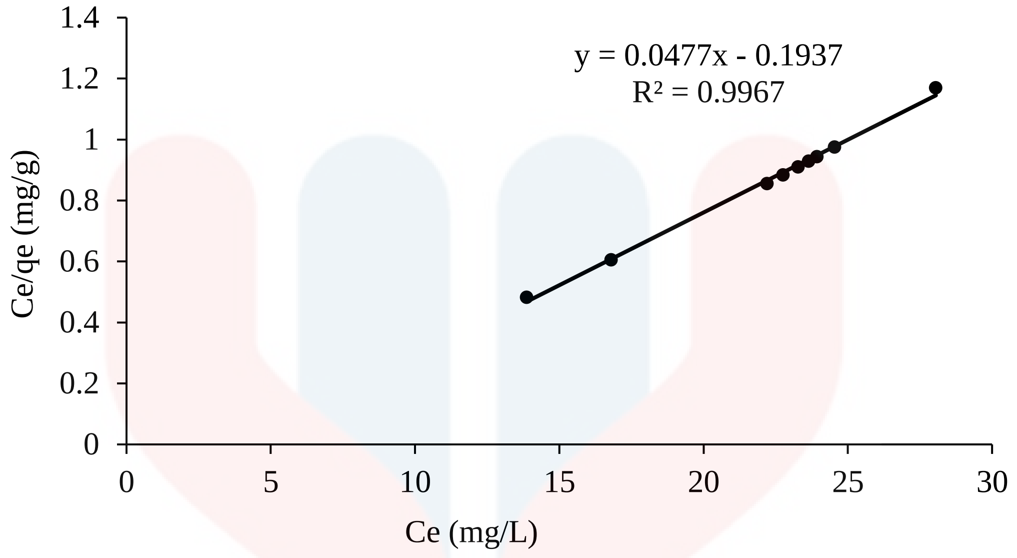


Figure 4.13 : Plot of Langmuir isotherm for effect of pH on removal of MR dye.

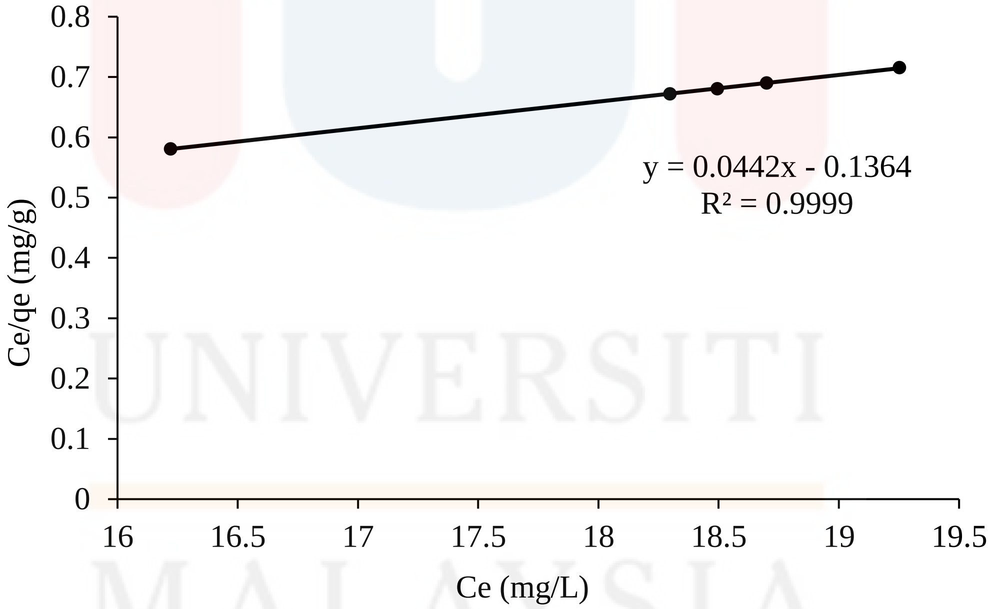


Figure 4.14 : Plot of Langmuir isotherm for effect of agitation speed on removal of MR dye.

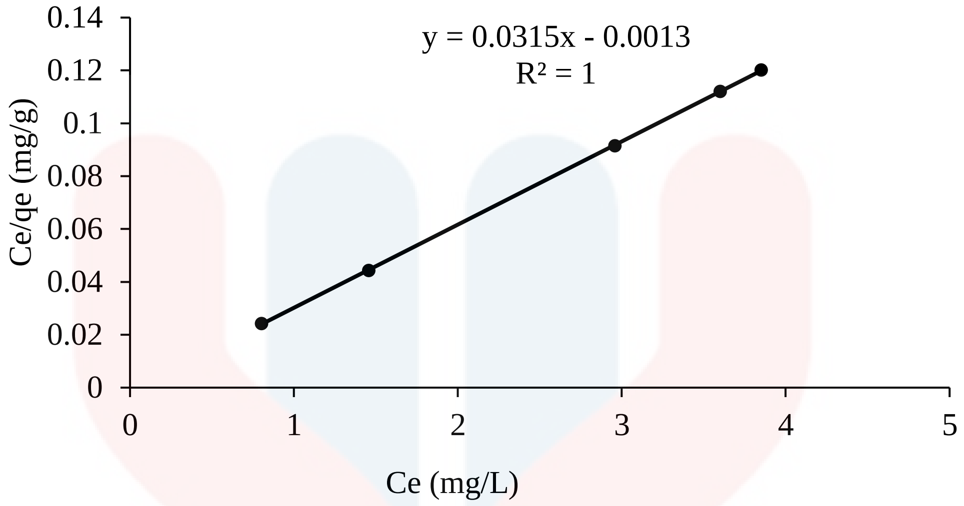


Figure 4.15 : Plot of Langmuir isotherm for effect of agitation time on removal of MR dye.

Table 4.1: Values of constants for Langmuir adsorption model.

| **Parameters** | **$q_{max}$ (mg/g)** | **$K_L$ (L/mg)** | **$R^2$** |
|---|---|---|---|
| Adsorbent size | 6.1576 | -0.4475 | 0.9984 |
| Adsorbent dosage | 0.5894 | -0.0579 | 0.3288 |
| Initial dye concentration | -147.0588 | -0.0145 | 0.4153 |
| Contact time | 20.4918 | -0.2262 | 0.9984 |
| pH | 20.9644 | -0.2463 | 0.9967 |
| Agitation speed | 22.6244 | -0.3240 | 0.9999 |
| Agitation Time | 31.7460 | -24.2308 | 1 |

The result obtained from experimental values and model predicted values was indicated by the correlation coefficient ($R^2$). Models with $R^2$ value close to 1 is considered as best suitable to represent the experimental data. Based on the Table 4.1, $R^2$ value of parameter agitation time which is 1 showed the most best fit value. Value of $q_{max}$ and $K_L$ for agitation time are 31.7460 mg/g and -24.2308 L/mg respectively. $q_{max}$ represent the amount of dye adsorbed per unit weight of adsorbent in the monolayer adsorption process on the adsorbent surface. While for $K_L$ it represent the Langmuir constant. Langmuir constant are evaluated by linearized equation (Allen et al., 2004).

For this Langmuir adsorption, usually it is used for homogeneous sorption, which is sorption activation energy are equal to the sorption of each molecules (Allen et al., 2004). For the second highest $R^2$ values are agitation speed parameter which is 0.9999. Value of $q_{max}$ and $K_L$ for agitation speed are 22.6244 mg/g and -0.3240 L/mg respectively. $q_{max}$ for agitation speed is lower than agitation time while $K_L$ for agitation speed was also lower compared to agitation time. Therefore, it can be conclude that best plot of Langmuir isotherm for removal of MR dye was obtained at agitation time.

### 4.3.2 FREUNDLICH ISOTHERM MODEL

Freundlich adsorption model are commonly used to describe the adsorption characteristic for the heterogeneous surface (State et al., 2012). Freundlich adsorption also commonly being used for describing the adsorption of organic and inorganic compound in the solution (Hsu, 2009). Figure 4.16 shows the adsorption isotherm of MR dye on raw oyster shell on the effect of adsorbent size. While for Figure 4.17, 4.18, 4.19, 4.20, 4.21 and 4.22 are representing dosage, initial dye concentration, contact time, pH, agitation speed and agitation time respectively. Equation 3.6 in the section of 3.7.4 was used to calculate the values of unknowns. The Freundlich equilibrium constants were calculated from the intercept and the slope, respectively of the linear plot of log qe versus log Ce based on experimental data. The values of n and $K_f$ were determined from the linear plot and their values are given in Table 4.2.

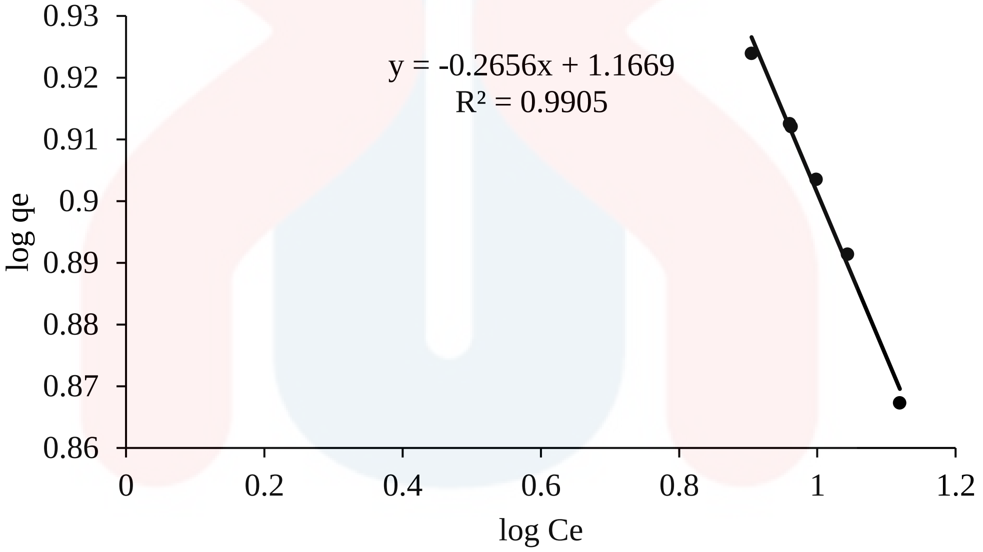


Figure 4.16 : Plot of Freundlich isotherm for effect of adsorbent size on removal of MR dye.

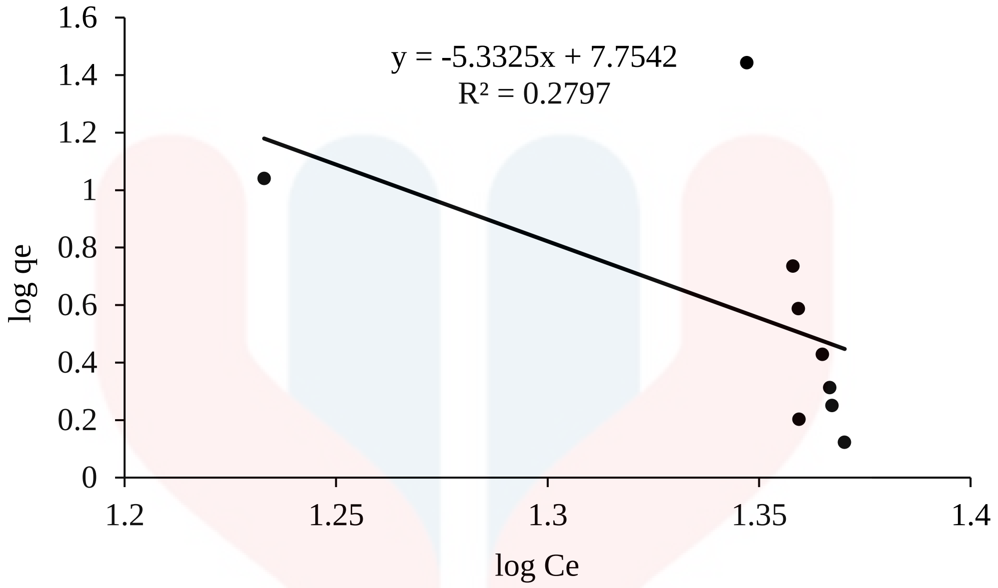


Figure 4.17 : Plot of Freundlich isotherm for effect of adsorbent dosage on removal of MR dye.

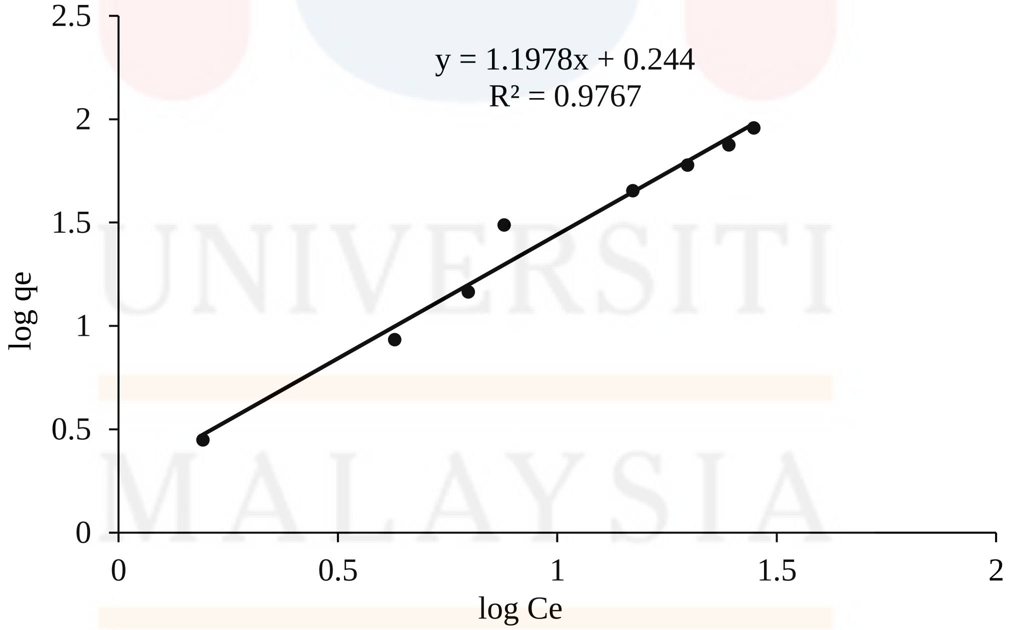


Figure 4.18 : Plot of Freundlich isotherm for effect of initial dye concentration on removal of MR dye.

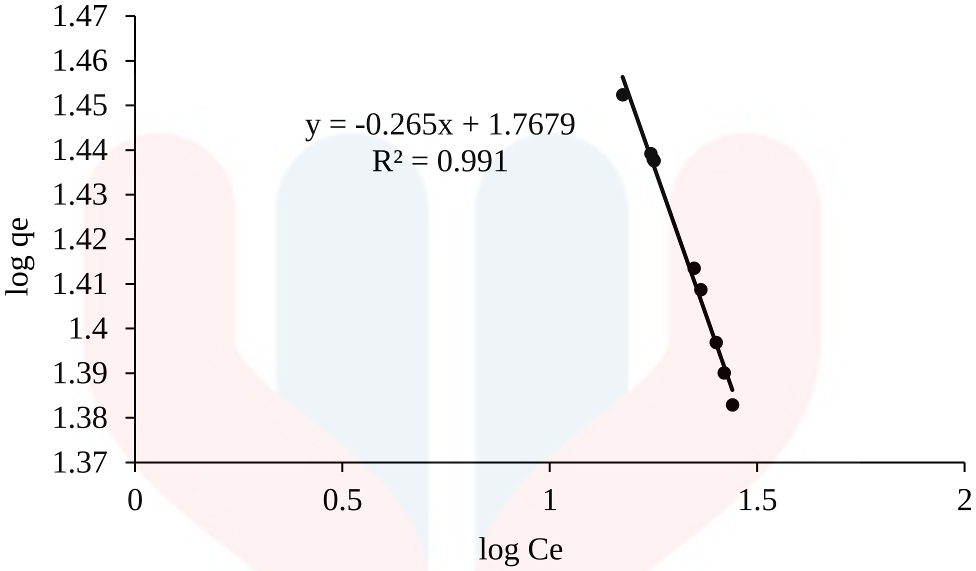


Figure 4.19 : Plot of Freundlich isotherm for effect of contact time on removal of MR dye.

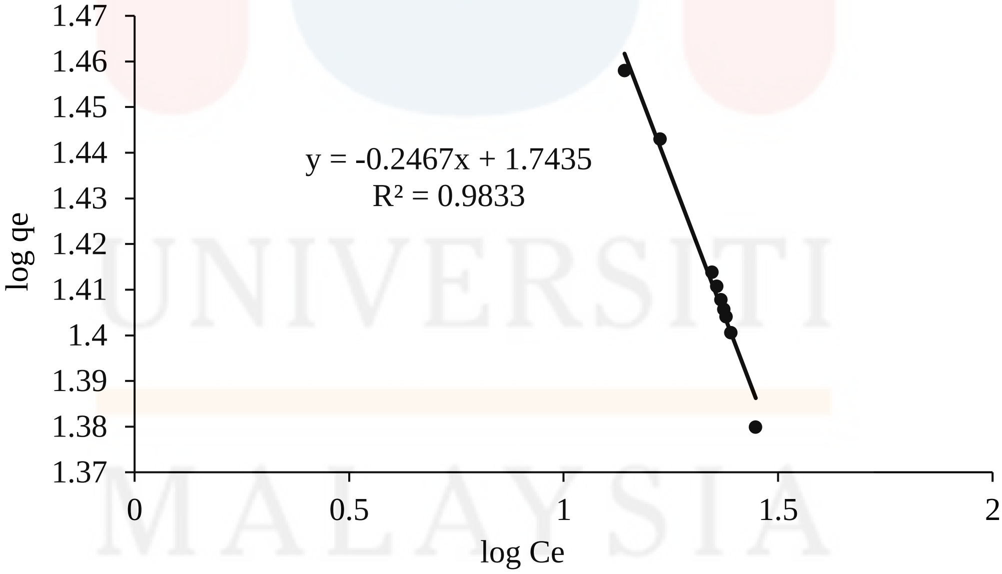


Figure 4.20 : Plot of Freundlich isotherm for effect of pH on removal of MR dye.

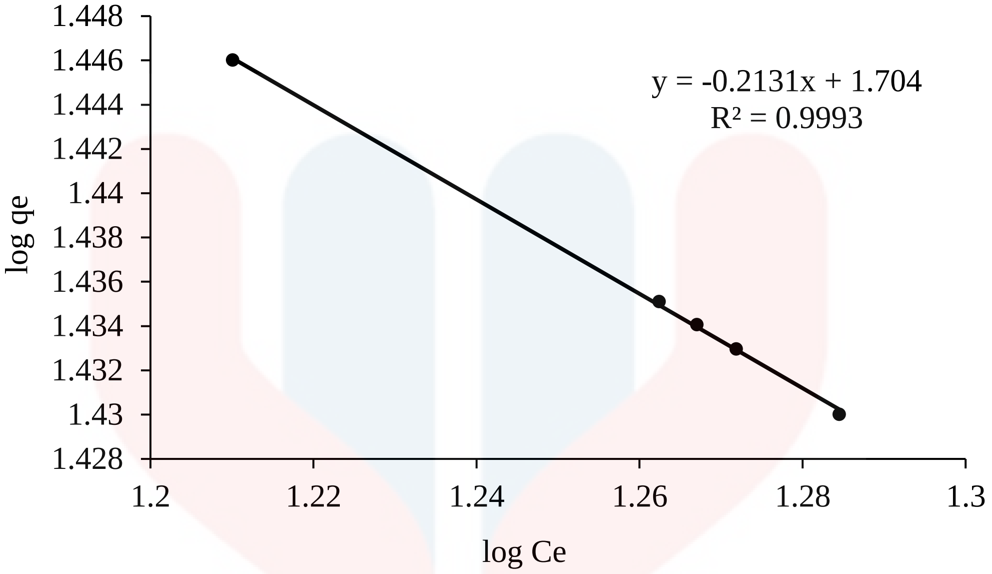


Figure 4.21 : Plot of Freundlich isotherm for effect of agitation speed on removal of MR dye.

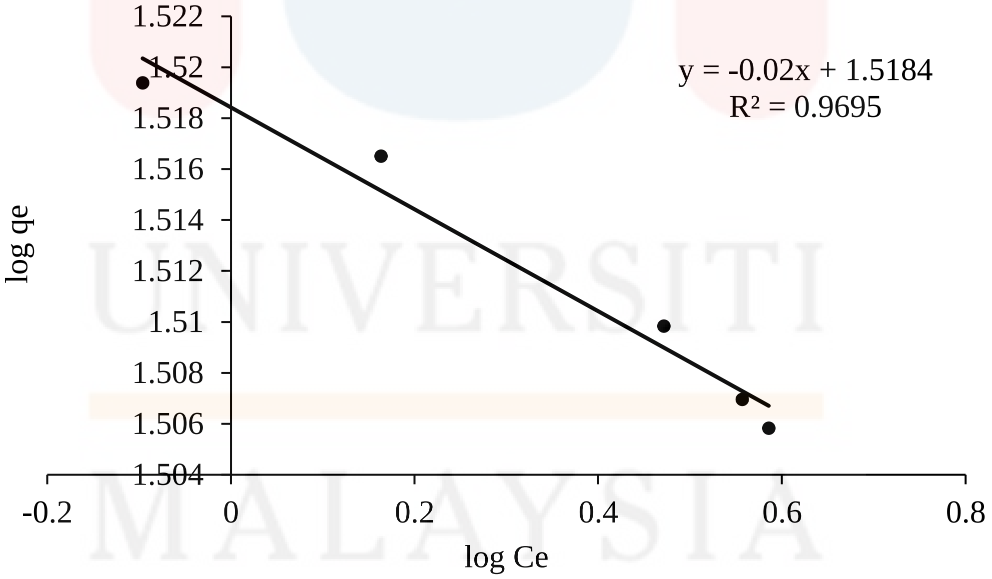


Figure 4.22 : Plot of Freundlich isotherm for effect of agitation time on removal of MR dye.

Table 4.2: Values of constants for Freundlich adsorption model.

| **Parameters** | **n** | **$K_f$ (L/mg)** | **$R^2$** |
|---|---|---|---|
| Adsorbent size | -3.7651 | 14.6859 | 0.9905 |
| Adsorbent dosage | -0.1875 | 56780602.95 | 0.2797 |
| Initial dye concentration | 0.8349 | 1.7539 | 0.9767 |
| Contact time | -3.7736 | 58.6003 | 0.9910 |
| pH | -4.0535 | 55.3988 | 0.9833 |
| Agitation speed | -4.6926 | 50.5825 | 0.9993 |
| Agitation time | -50 | 32.9913 | 0.9695 |

Based on the table 4.2, the result obtained shows that the correlation coefficient, $R^2$ of agitation speed are 0.9993. Value of n and $K_f$ for agitation speed showed are -4.6926 and 50.5825 respectively. The value of n and $K_f$ are the Freundlich constant that related to the adsorption intensity and adsorption capacity respectively (Q. S. Liu, Zheng, Wang, Jiang, & Li, 2010). This adsorption are characterized by the heterogeneity factor, thus it can be applied to described the heterogeneous system (Allen et al., 2004). If the value of n is between 0 and 1 it describe favourable sorption while if n equals to 1 it represent the boundary between two layers is independent of the concentration.

Base on the Table 4.2 that obtained, it shows that n value was less than 1 which describe that it is unfavourable for sorption process. Other than that, the result obtained are in the negative value. If the value of $\frac{1}{n}$ obtained are below than one, it describe an ordinary Freundlich isotherm while $\frac{1}{n}$ obtained are above one it represented by corporative adsorption. $K_f$ can be defined as the adsorption or the distribution coefficient, therefore it represent the quantity of dye adsorbed onto activated carbon for a unit equilibrium concentration (Hameed, Tan, & Ahmad, 2008). The higher the maximum capacity, the higher the value of $K_f$.

Based on Table 4.1 and 4.2, it can be concluded that the experimental data suited Freundlich adsorption isotherm better that Langmuir adsorption isotherm. By comparing the correlation regression coefficient, $R^2$ of initial dye concentration of Freundlich adsorption isotherm was higher than Langmuir adsorption isotherm which marked 0.9767 and 0.4153 respectively. Thus, it also shows that the $R^2$ for Freundlich isotherm are higher than Langmuir isotherm. Maximum adsorption capacity was recorded at 0.8349 mg/g and Freundlich constant was 1.7539 L/mg. Therefore, Freundlich isotherm can be said to have taken place for adsorption of MR dye by raw oyster shell adsorbent and the adsorption energy of raw oyster shell adsorbent is constant and independent to the surface coverage.

# CHAPTER 5

# CONCLUSION AND RECOMMENDATIONS

Raw oyster shell was successfully prepared and being used as adsorbent for removal of MR dye in this study. For the adsorption study, all the parameter was successfully optimised. The optimum value for each parameter such as adsorbent size, absorbent dosage, initial dye concentration, contact time, pH, agitation speed and agitation time were determined.

The highest percentage of MR dye removal in this study was found to be 99.2% that perform well in the optimum parameter that obtained. Thus, the raw oyster shell adsorbent were found to give the best result at the adsorbent size of 75 µm with 0.3 g of adsorbent dosage in 100 mg/L initial dye concentration at pH 3 with 110 rpm agitation speed of orbital shaker at 45 min. Orbital shaker were used to reduce the time consumption during the adsorption process and it gives the positive result when the contact time can be reduces from 2 hours to 45 min after the process of agitation.

The highest percentage removal achieved was 99.2% and this shows that the raw oyster shell adsorbent has a great potential in removing MR dye in the aqueous solution.

Therefore, to study the characteristic of adsorption, adsorption isotherm were carried out. The plot of experimental values that obtained shows that the adsorption are inclined towards the Freundlich adsorption isotherm model.

In order to improve the adsorption process further to obtained higher percentage removal, the porosity of the adsorbent need to be higher. This is because porosity are one of the main factor for an adsorption process to occur. Thus, the raw oyster shell adsorbent can be converted into activated carbon. This is to improve the surface area of the pores on the adsorbent.

Other than that, the oyster shell could be treated with chemical in order to increase the surface are as well as increased the porosity of the adsorbent. So that the adsorption process can rapidly occur. Not only that, the adsorption process also should be done under a controlled temperature. So that, the adsorption process occur simultaneously. As the temperature increased, the adsorptive site of the adsorbent will be increased. Thus, it make the condition are more favourable for dye molecules to sit in the adsorptive site. Other than that, the characterisation of raw oyster shell also can be done.

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# APPENDIX

Figure A1: Oyster shell were collected at Bachok, Kelantan, Malaysia.

Figure A2: Oyster shell was washed to remove all impurities.

Figure A3: Washed oyster shell were placed in oven for drying process.

Figure A4: Oyster shell were break into small pieces.

Figure A5: Dried oyster shell were blended to powder form.

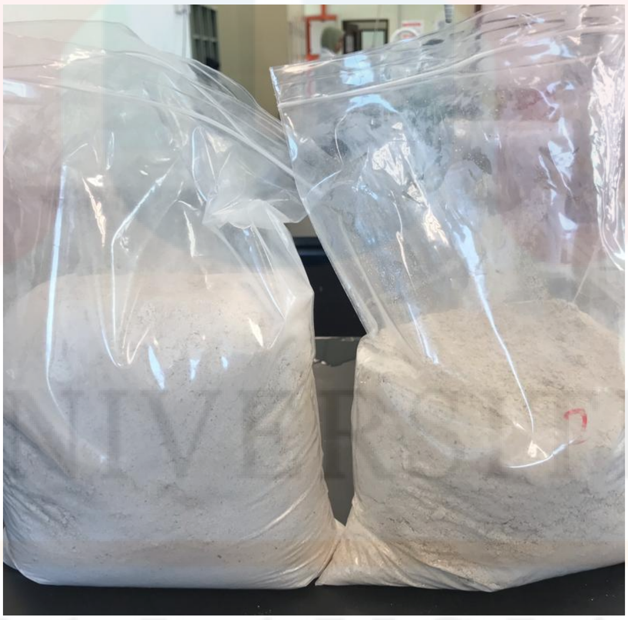

Figure A6: Powdered raw oyster shell.

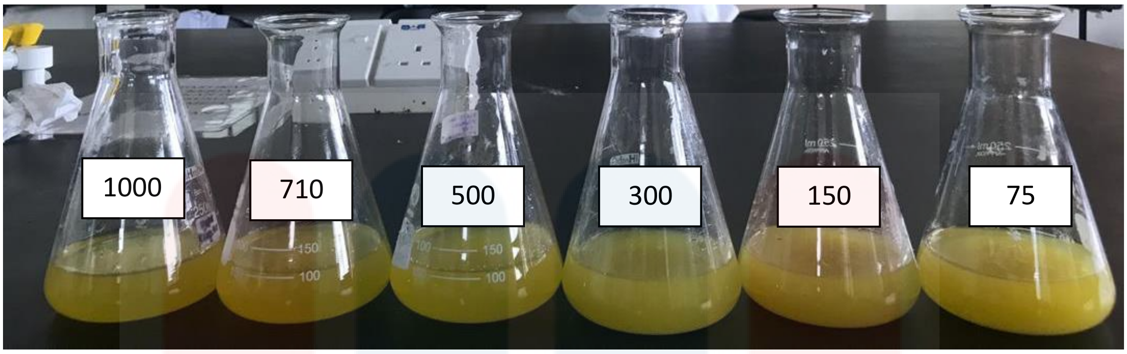

Figure B1: Colour change of MR dye with various adsorbent size before 24 hours.

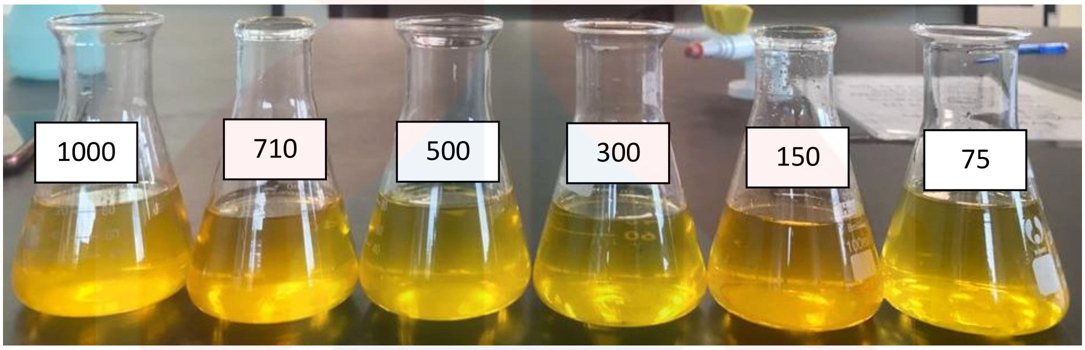

Figure B1.1: Colour change of MR dye with various adsorbent size after 24 hours.

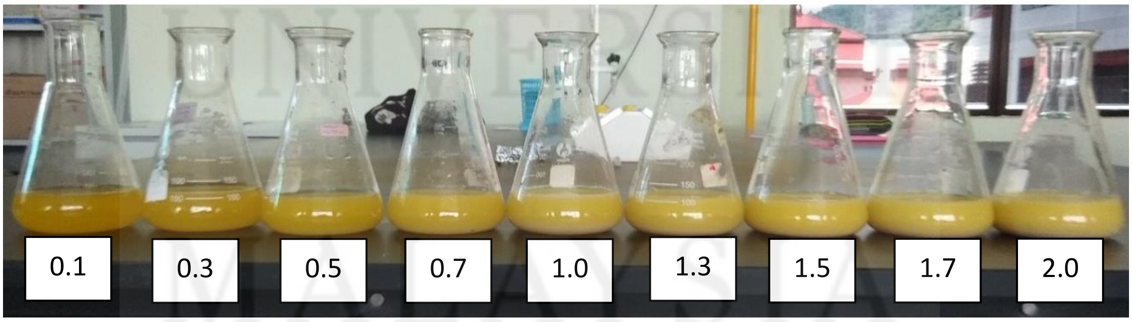

Figure B2: Colour change of MR dye with various adsorbent dosage before 24 hours.

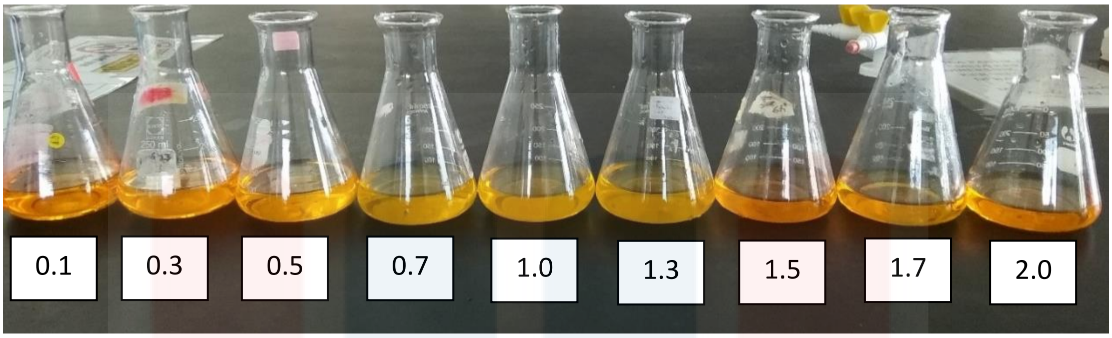

Figure B2.1: Colour change of MR dye with various adsorbent dosage after 24 hours.

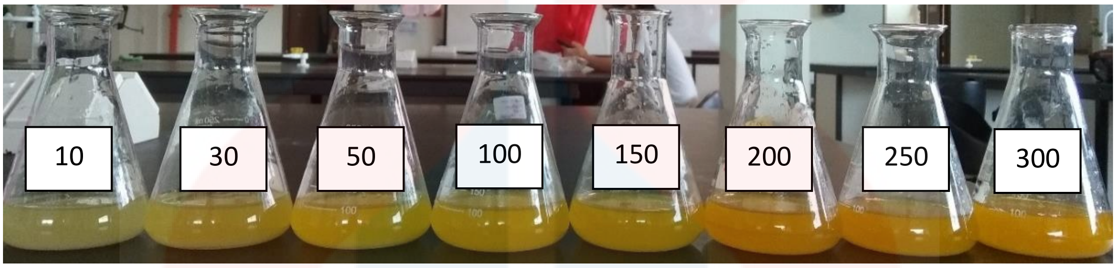

Figure B3: Colour change of MR dye with various initial dye concentration before 24 hours.

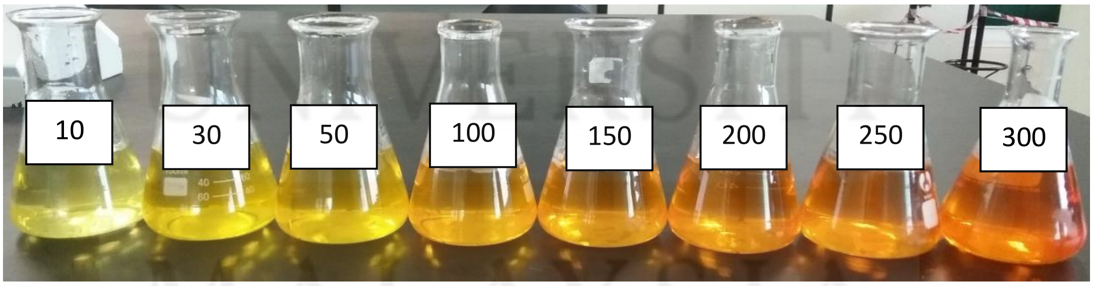

Figure B3.1: Colour change of MR dye with various initial dye concentration after 24 hours.

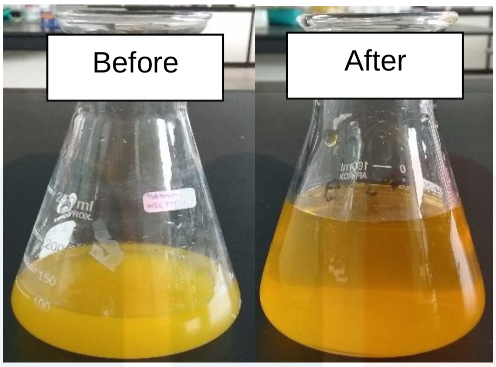

Figure B4 : Colour change of MR dye before and after for the first hour.

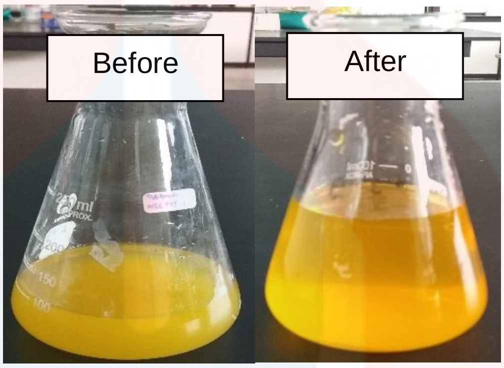

Figure B4.1: Colour change of MR dye before and after for the second hour.

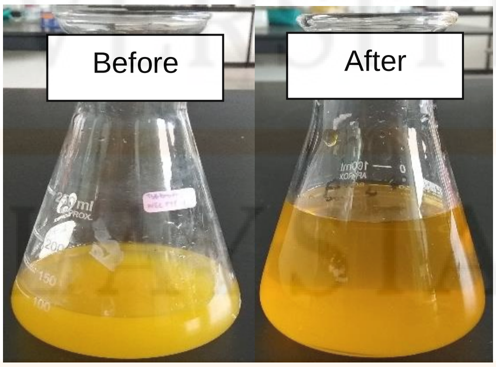

Figure B4.2: Colour change of MR dye before and after for the third hour.

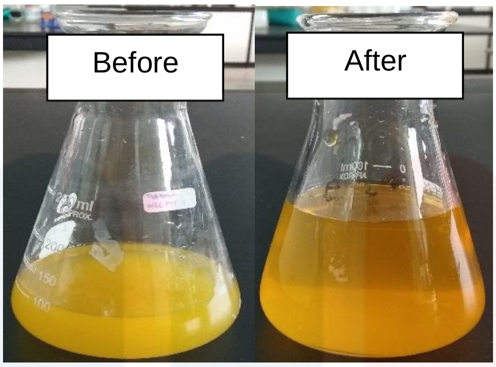

Figure B4.3: Colour change of MR dye before and after for the fourth hour.

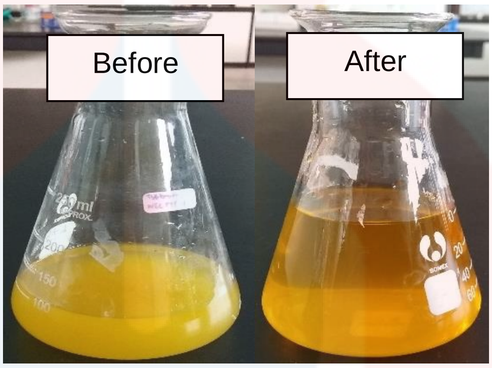

Figure B4.4: Colour change of MR dye before and after for the fifth hour.

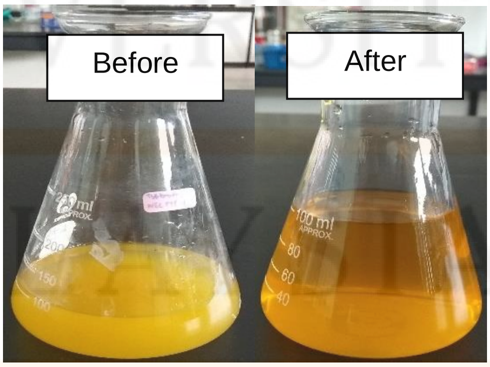

Figure B4.5: Colour change of MR dye before and after for the six hour.

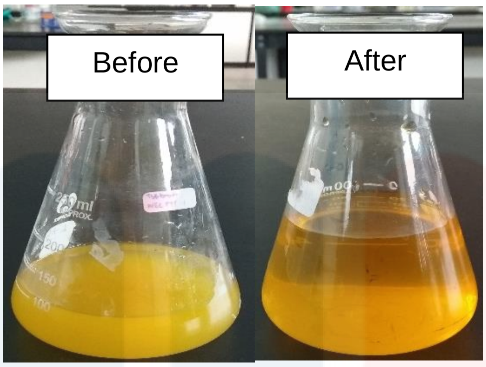

Figure B4.6: Colour change of MR dye before and after for the seventh hour.

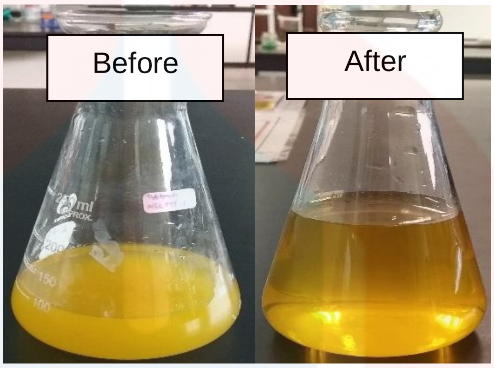

Figure B4.7: Colour change of MR dye before and after for the eight hour.

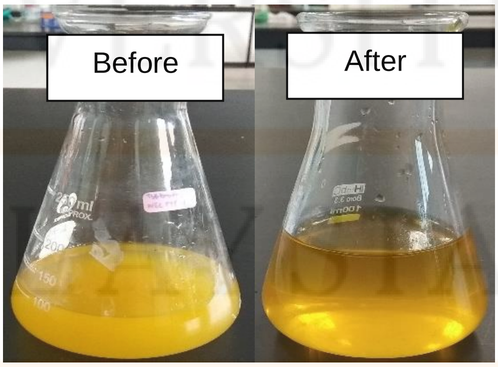

Figure B4.8: Colour change of MR dye before and after for the nine hour.

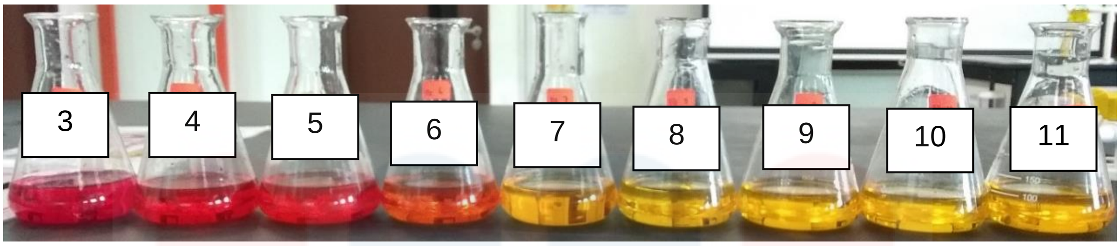

Figure B5: Colour change of MR dye with various pH before.

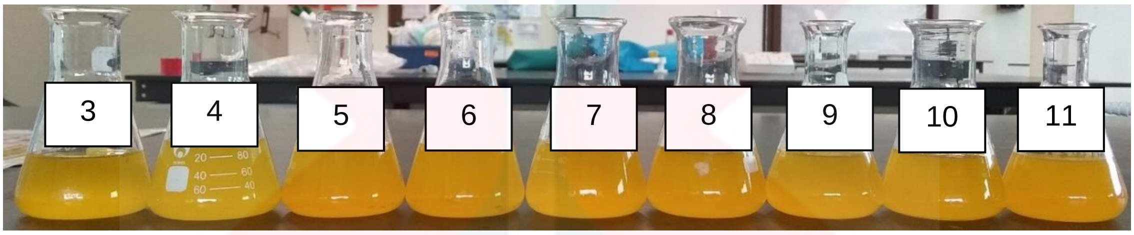

Figure B5.1: Colour change of MR dye with various pH after .

Figure B6: Dye preparation before adding adsorbent.

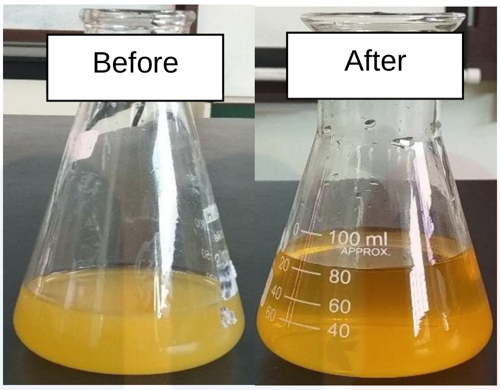

Figure B6.1: Colour changes of MR dye before and after for speed of 90rpm.

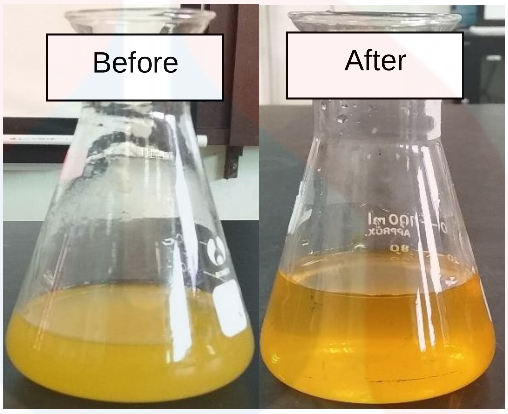

Figure B6.2: Colour changes of MR dye before and after for the speed of 110rpm.

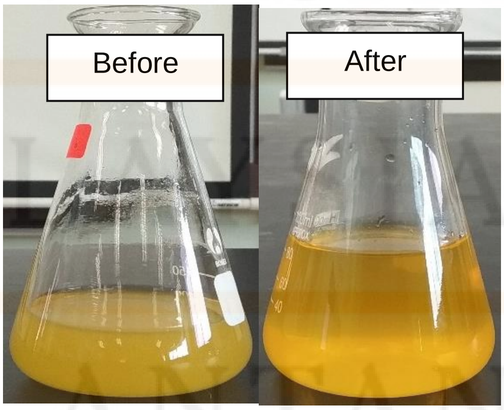

Figure B6.3: Colour changes of MR dye before and after for the speed of 130rpm.

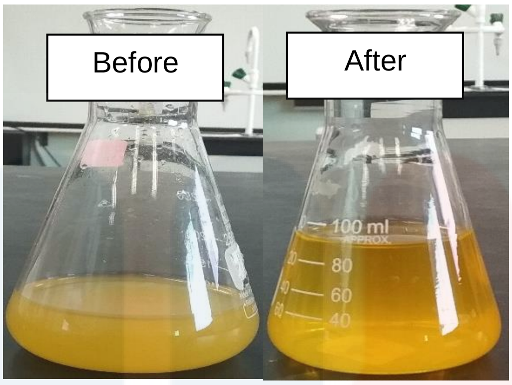

Figure B6.4: Colour changes of MR dye before and after for the speed of 150rpm.

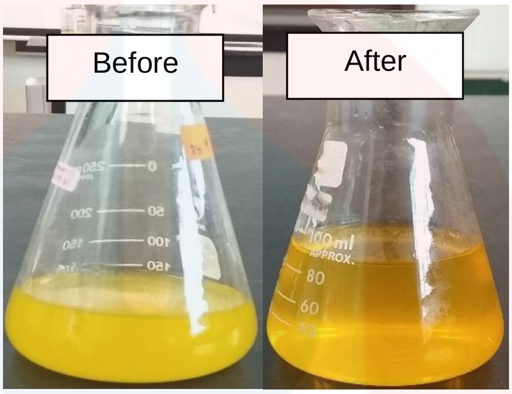

Figure B6.5: Colour changes of MR dye before and after for the speed of 170rpm.

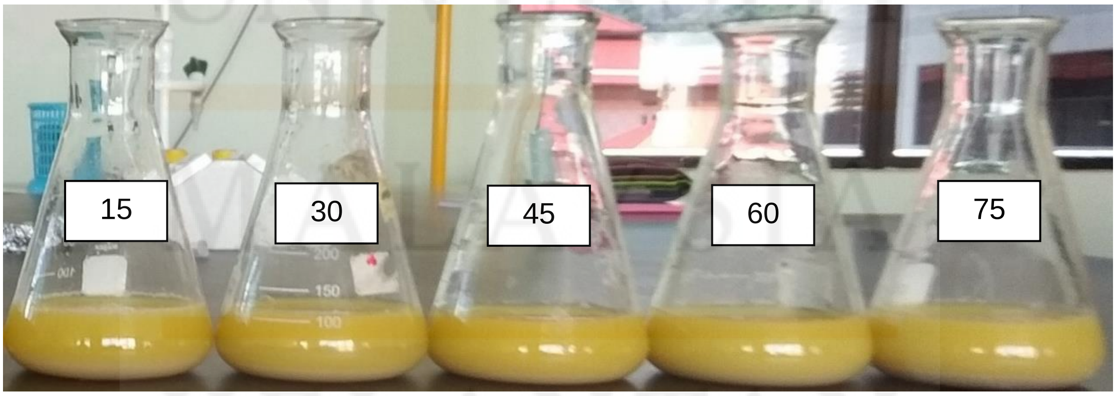

Figure B7: Colour change of MR dye with various agitation time before.

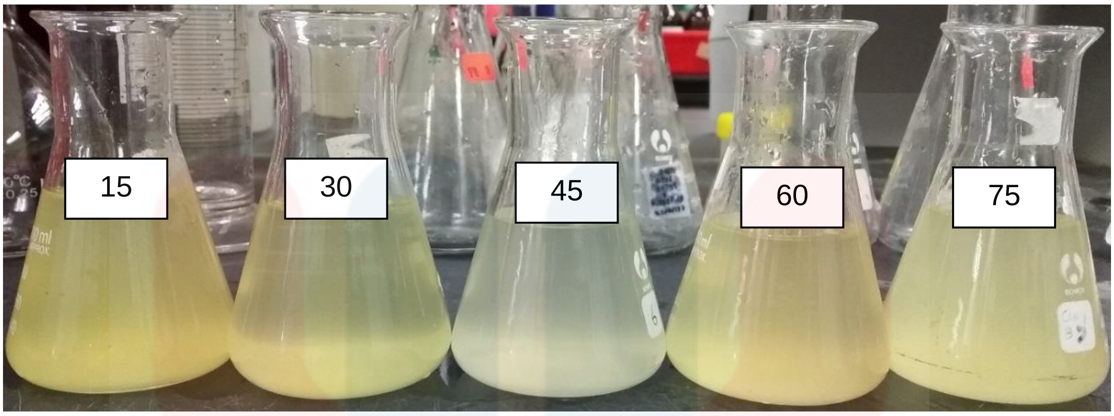

Figure B7.1: Colour change of MR dye with various agitation time after.

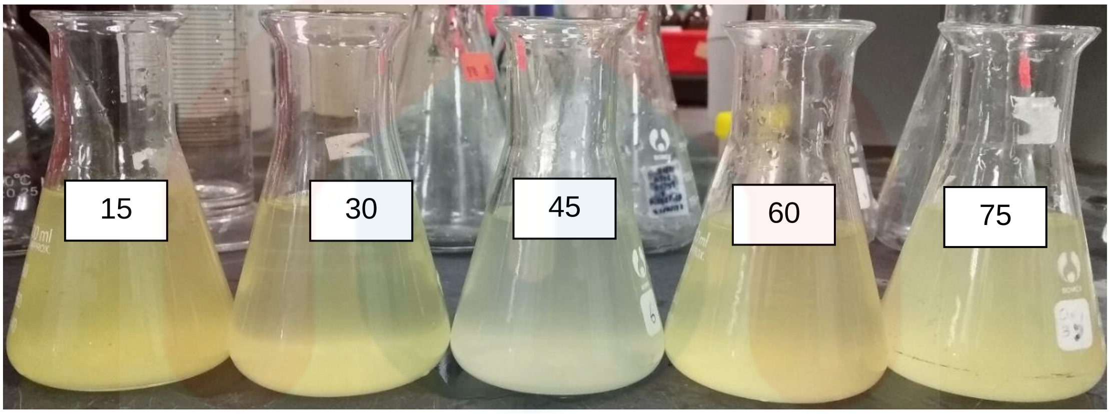

Figure B8: Colour change of MR dye before run membrane filtration.

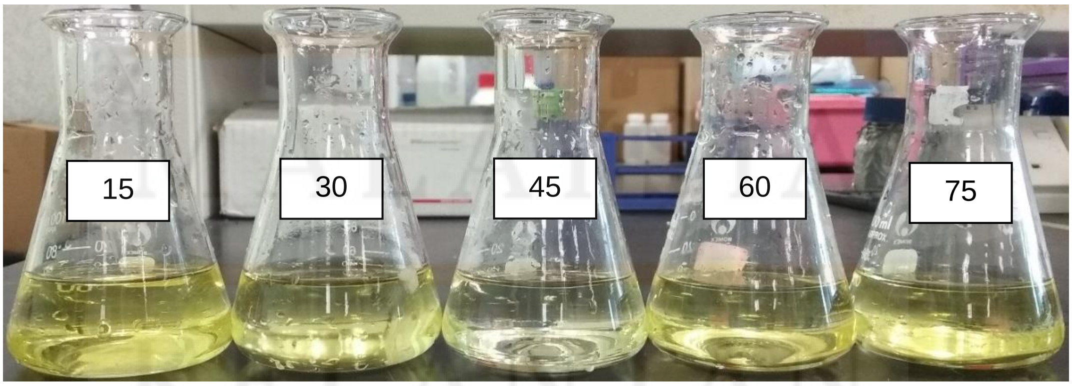

Figure B8.1: Colour change of MR dye after run membrane filtration.