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**Preparation of Raw Oyster Shell for Adsorption of Methyl
Orange Dye in Aqueous Solution**

Wan Anis Syahidah Binti Wan Rosli

F15A0244

**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

UNIVERSITI MALAYSIA KELANTAN

2019

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.

Student

Name: Wan Anis Syahidah Binti Wan Rosli

Date:

I certify that the report of this final year project entitled “Preparation of Raw Oyster Shell for Adsorption of Methyl Orange dye in Aqueous Solution” by Wan Anis Syahidah Binti Wan Rosli, matric number F15A0244 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

Name: Dr. Krishna Veni A/P Veloo

Date:

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Preparation of Raw Oyster Shell for Adsorption of Methyl Orange Dye in Aqueous Solution

ABSTRACT

The development of oyster culture in Peninsular Malaysia nowadays is increasing well due to high demands of oyster from restaurants and hotels especially in tourist spot. However, there is bad consequence through this development which is irresponsible disposal of waste oyster shell to certain areas that create new problems such as delivering an intense scent and pollute surrounding environment. This problem need to be resolved using a creative solution by turning the shell waste into something beneficial and useful. Besides, another problem is to remove dye that has been discharge by industries into water through adsorption technique. The raw oyster shell was successfully prepared as an adsorbent for adsorption of methyl orange dye in aqueous solution. Study on adsorption were carried out for removal of MO dye by varying adsorption parameters such as adsorbent size, adsorbent dosage, initial dye concentration, contact time, pH, agitation speed and agitation time. Based on results, the optimum parameters for the removal of MO dye is using 1.0 g of 75 μm of adsorbent particle size with initial dye concentration of 150 mg/L in acidic condition of pH 3 in 130 rpm agitation speed for 1 hour. Raw oyster shell has great potential in removing MO dye from aqueous solution because it recorded 98.39% of percentage removal. The experimental data obtained were best fitted by Langmuir isotherm model than the Freundlich isotherm model and this prove that monolayer adsorption had happen at specific homogenous site of adsorbent.

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

Penyediaan Cengkerang Tiram Mentah untuk Penjerapan Pewarna Metil Oren dalam Larutan Akueus

ABSTRAK

Perkembangan penternakan tiram di Semenanjung Malaysia kini semakin meningkat dengan baik kerana permintaan tiram yang tinggi dari restoran dan hotel terutamanya di tempat pelancongan. Walau bagaimanapun, terdapat kesan yang buruk melalui perkembangan ini iaitu pelupusan sisa tiram yang tidak bertanggungjawab ke kawasan tertentu yang mewujudkan masalah baru seperti menghasilkan bau yang busuk dan mencemarkan persekitaran sekitar. Masalah ini perlu diselesaikan dengan menggunakan penyelesaian kreatif dengan menjadikan sisa cengkerang tiram sebagai sesuatu yang bermanfaat dan berguna. Di samping itu, masalah yang lain adalah untuk menyingkirkan pewarna yang telah dilepaskan oleh industri ke dalam air melalui teknik penjerapan. Cengkerang tiram telah berjaya disediakan sebagai penjerap untuk penjerapan pewarna metil oren dalam larutan akueus. Kajian tentang penjerapan dilakukan ke atas pelbagai parameter penjerapan seperti saiz penjerap, dos penjerap, kepekatan awal pewarna, masa sentuhan, pH, kelajuan agitasi dan tempoh agitasi. Berdasarkan keputusannya, parameter optimum untuk penjerapan pewarna MO adalah menggunakan 1.0 g dos penjerap dari 75 μm saiz zarah penjerap dengan kepekatan awal pewarna 150 mg/L dalam keadaan berasid pH 3 dengan kelajuan agitasi 130 rpm selama 1 jam. Cengkerang tiram mentah mempunyai potensi yang besar dalam menyingkirkan pewarna MO dari larutan akueus kerana ia mencatatkan penyingkiran peratusan sebanyak 98.39%. Data eksperimen yang diperolehi paling bersesuaian dengan model isoterma Langmuir berbanding model isoterma Freundlich dan ini membuktikan bahawa penjerapan monolayer berlaku pada penjerap di bahagian tertentu.

Kata kunci: Cengkerang tiram mentah, pewarna metil oren, penjerapan, model isoterma

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LIST OF ABBREVIATIONS

ROS	Raw oyster shell
MO	Methyl Orange
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
q_{max}	Maximum adsorption capacity
V	Volume of solution
W	Mass of dry adsorbent

LIST OF SYMBOLS

%	Percent
&	And
°C	Degree Celcius
g	gram
h	hour
L	litre
M	Molar
mL	mililiter
nm	nanometer
mm	milimeter
kg	kilogram
m ³	cubic meter
mg/L	milligram per Litre
mg/g	milligram per gram
g/L	gram per Litre
rpm	rotary per minutes
R ²	Correlation Coefficient

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Water is our main source of life. Water is required for daily activities such as drinking, bath, recreation, manufacturing, and power. However, nowadays most water bodies e.g. lakes, rivers, oceans and aquifers have been contaminated with many sources of pollutant which are very harmful and bring bad consequences to ecosystem balance, human being and other living things. Water contamination happened when pollutants are released directly or indirectly into water bodies without proper treatment to dispose of destructive compounds. Additionally, it could happen when land and air contaminations are passed up by wind or washed by rain into water bodies. The sources of pollutants which bring harm could be from industrial waste that contains a lot of harmful chemicals like heavy metals, dye, leftover foods and garbage (Singh & Gupta, 2016).

Dye is a colouring material that is usually applied in aqueous solution and cling to whatever they are applied to such as fibres, textiles, foods and hair. The main purposes of dye are for aesthetic, decorative and artistic. Dye can be categorised into two main types which are natural and synthetic. Synthetic dyestuffs are widely used in many industries.

About 10,000 different commercial dyes and pigments are being manufactured and over 7×10^8 kilograms are produced annually worldwide (Puvaneswari, Muthukrishnan & Gunasekaran, 2006). Almost 10-20% of these dyes are released as effluents during dyeing process (Saharan et al., 2011; Gomez et al., 2007). The effluents containing dyes are highly coloured and cause water pollution and damage to the environment. Market demand of dye for textile industry is one of the largest sectors globally followed by other industries such as inks and tinting industry, dyestuffs, papers and painting. All these industries consume huge volume of dye thus generating coloured wastewater (Puvaneswari et al., 2006).

Synthetic dyes are widely been used in textile industries because they can be applied to different variety of fibres in dyeing process. The examples of synthetic dyes are acid dyes, basic dyes, azo dyes, direct dyes, vat dyes, reactive dyes, disperse dyes and sulfur dyes (Essawy, Ali & Mottaleb, 2008).

It is difficult to remove synthetic dyes from textile industry effluents because this dye has special characteristics where it is quite stable to reduction and common oxidation processes. Compared to synthetic dyes, natural dyes are biodegradable without use reductant or oxidant, high stability to light, detergent and microbial attack (Couto, 2009). High demands of synthetic dyes in textile industries were because of their synthetic compounds as coloured matters that colour fibres permanently, such that they will not lose this colour when exposed to sweat, light, water and many chemical substances including oxidising agents (Oneill et al., 1999).

In order to overcome the organic dye pollutants problems, there are variety of conventional technique for removal of dyes which are biological method, chemical method and physical method. Adsorption is categorised as physical technique, has wide applicability for decolourisation due to its high efficient and ease of operation. Therefore,

many studies have been conducted recently to search for the low cost adsorbent for dye wastewater treatment (Sawasdee, Jankerd & Watcharabundit, 2017).

Large amounts of low-cost adsorbent are readily available and can be collected from food waste, agricultural waste and industrial by-product and give result as an efficient adsorbent. Besides, the pre-treatment is not too hard to be carried out on raw products, which is cost effective treatment to treat dye. Past investigations have given much proof of low cost adsorbents' efficiency in expelling metal particles from wastewater (Lim & Aris, 2013). Among these several types of low-cost adsorbent, oyster shells also have potential to be an adsorbent to remove dye.

A lot of oyster shell are produced each year. Oyster shells are waste product from marine culture and cause a major disposal problem in most of coastal regions. Some issues of disposing oyster shell waste bring bad consequences such as delivers an intense scent and pollute surrounding environment.

1.2 PROBLEM STATEMENT

Our earth is covered almost 70% with water. Water contamination is one of the global serious issue as it affect human and creature lives and ecosystem in all viewpoints. Water pollution is the contamination of drinking water by the poisonous pollutants generated through food industry, chemical industry, textile industry and others. In Malaysia, the three main sources of river pollution are industrial waste, residential and agriculture (Afroz et al., 2014).

All the pollutants are very harmful and some foreign substances can cause changes in the colour of water that should be colourless. Highly colour water seems to be unsuitable for human activities such as drinking, laundry and industrial use because the

colour of the water affect the quality of the water and prove that the water is unsafe to be use. Dye is a substance that makes the water coloured and cause decrease in light penetration and perturbation in photosynthesis process in water sources (Oneill et al., 1999). Thus, biotic living population will be affected through this problem.

In order to solve water pollution problems, many methods of wastewater treatment were being investigated by researches and one of them is by adsorption method using low-cost adsorbent. According to Jung (2016), many oyster shells were dumped as a by-product of marine aquaculture industry in the southern coast of Korea since it turns to be hard to deal with it adequately because of the issues of securing of landfill sites and gathering or transportation of oyster shells. Waste oyster shell could be utilised as adsorbent because it is easy to get in huge amount. In addition, by producing raw oyster shell as adsorbent, there is no pollution is produced at all because the method used was very eco-friendly, not releasing any harmful gases to the air and cost-efficient.

1.3 OBJECTIVE

The aim of this research is to:

- To prepare raw oyster shell as adsorbent for adsorption of dye.
- To optimise the parameters to adsorb dye (adsorbent size, adsorbent dosage, initial dye concentration, contact time, pH, agitation speed and agitation time) towards the effectiveness of oyster shell as the adsorbent.
- To obtain best-fit model for adsorption of methyl orange dye prepared using raw oyster shell.

1.4 SCOPE OF STUDY

Overall, the purpose of this study is to prepare raw oyster shell as adsorbent for adsorption of methyl orange dye. Oyster shell samples were collected at disposal site in Bachok, Kelantan, Malaysia. After that, the shells were cleaned with water to remove organic residues. In order to eliminate the remaining organic material, the shells were dried by using oven and crushed into a smaller size using mortar and pestle and grinder. Various parameters were studied includes adsorbent size, adsorbent dosage, initial dye concentration, contact time, pH, agitation speed and agitation time to determine the optimum parameters. Then, the optimised parameters were used to develop best-fit models.

1.5 SIGNIFICANT OF STUDY

The significant of this study is to convert waste raw oyster shell into high value added product, biosorbent as an alternative for costly adsorbent. Through this study, an eco-friendly solution for disposal of shell by-products was performed. This research was conducted to remove MO dye from aqueous solution, determined the efficiency of raw oyster shell as biosorbent and identify the best-fit model through the optimisation of various parameters. The developed method will be a cost-efficient and useful technique for treating dye that are discharge by various industries especially textile industries

CHAPTER 2

LITERATURE REVIEW

2.1 DYE

Dye is an organic compound that is broadly utilised for giving colour to materials. It could be either obtained from natural or synthetic sources. An interesting fact about dye is that dissimilar to paint, dye is absorbed into the pores of the material because of molecule size of dye that is smaller than the size of the pores in the fibre. Hence, it does not just develop on the surface of the fibre. In order to resist removal, for instance by washing, dyes must be firmly attached to the textile fibres to which they are applied. The molecules of dyes are designed to provide forces of attraction and affinity for the polymer molecules which constitute the fibre (Christie, 2001).

Kumar (2013) stated that dyes possess colour because they absorb light in the visible spectrum (400–700 nm), have a conjugated system (a structure with alternating double and single bonds), have at least one chromophore (colour-bearing group) and exhibit resonance of electrons which is a stabilising force in organic compounds. The colour will be lost if any one of these features is lacking from the molecular structure. Auxochrome (colour helper) is a salt-forming group that contains in most dyes functioned to influence dye solubility and their presence can change colour. The examples of auxochromes are carboxylic acid, sulfonic acid, amino and hydroxyl groups.

2.2 CLASSIFICATION OF DYE

The classification of dye can be based on source of origin whether it is natural or synthetic. Synthetic dye is used widely in food, textile, and other industries is because of cost-efficient during production and easy to apply to fabric. Several groups of synthetic dyes are acid dyes, basic dyes, azo dyes and reactive dyes. Besides, dye also can be classified based on chemical structure, ionic nature, field of application, solubility in water and many more aspects. The classification of dye based on ionic nature is according to the electrical charge that present in its ionised coloured part. Dye can be anionic (direct, acid, reactive, sulphur), cationic which is from basic dye and non-ionic which is disperse dye (Uday et al., 2017).

Other than that, classification of dye could be based on their method of application to the substrate. This includes disperse dyes, azo dyes, direct dyes, reactive dyes, vat dyes and several more types. However, characterisation of dyes by chemical structure is preferable as it has many advantages such as it directly characterise dyes into groups that has similar characteristic properties. For instance, anthraquinone dyes are weak and expensive whereas azo dyes are strong and cost-effective (Pachhade, Sandhya & Swaminathan, 2009). Table 2.1 shows the classification of synthetic dyes. The general classification of dye is summarised in Figure 2.1.

Table 2.1: Classification of synthetic dyes (Barisci et al., 2016)

Dye	Water solubility and other specification	Chemical and bond structure	Chromophoric groups	Application
Azoic Dyes	A type of direct dye	Azo groups – N=N	Stilbene, pyrazoles, coumarin, and naphthalimides	Cotton, other cellulosic materials, soaps, detergents
Basic Dyes	Soluble, cationic	Amino groups to form hydrochlorides and oxalates	Diazahemicyanine, cyanine, hemicyanine, thiazine, oxazine, acridine and xanthene	Silk, wool, and tannin-mordant cotton, paper, leather, and straw
Direct Dyes	Soluble, anionic, polar, high molecular weight	Hydrogen bonds and azo linkage –N=N–	Polyazo compounds, stilbenes, phthalocyanines, and oxazines	Cotton and rayon, paper, leather, cellulose fibers, linen, wool, and silk
Disperse Dyes	Insoluble, nonpolar, nonionic	Van der Waals forces	Azo, anthraquinone, styryl, nitro, and benzodifuranone groups	Polyester, nylon, cellulose, cellulose acetate, and acrylic fibers
Reactive Dyes	Soluble, anionic, polar, smaller molecule size	Chlorotriazine, epoxy, ethyleneimide groups and dye forms covalent bond with fiber polymer	Azo, anthraquinone, triarylmethane, phthalocyanine, formazan, and oxazine	Cotton, yarn and other cellulosic, silk painting, and polychromatic printing
Vat Dyes	Insoluble but soluble with alkali	Redox reactions	Anthraquinone (including polycyclic quinones) and carbazole	Cotton (cellulosic fibers), rayon, linen, silk, and nylon

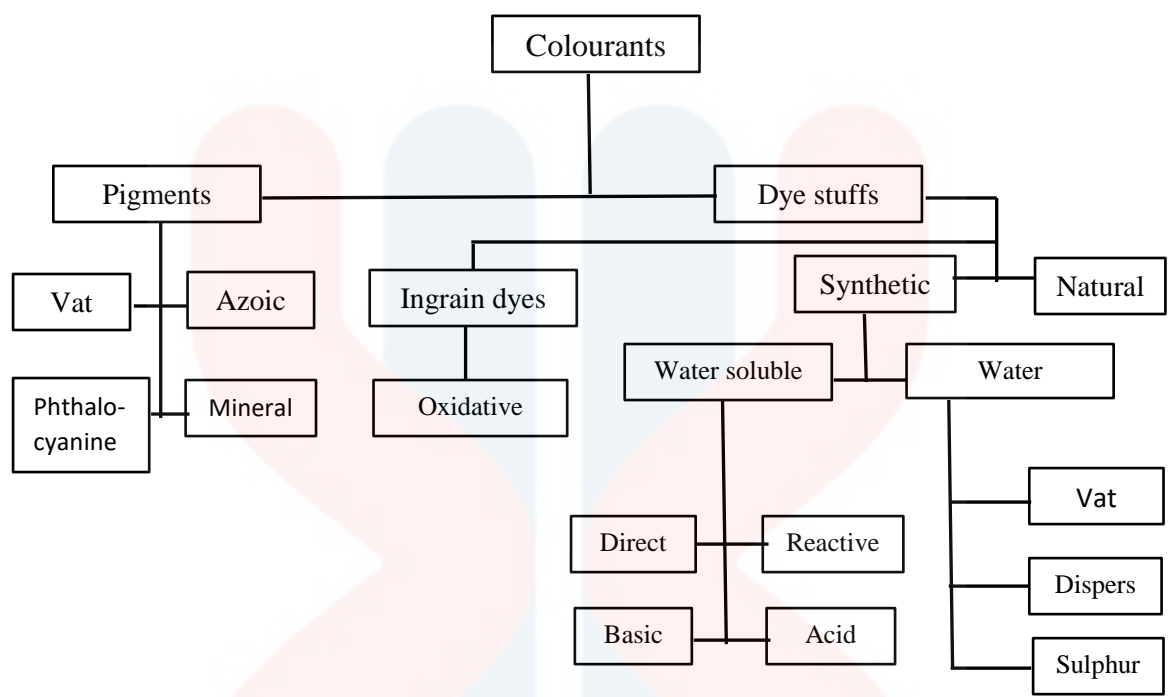


Figure 2.1: General classification of dye (Sivashankar, Sathya, Vasantharaj & Sivasubramanian, 2014)

2.2.1 Azo Dye

Azo dye class constitute the largest class of synthetic dyes that is about 60-70% and has physical characteristic of vivid colour. Azo compounds chemically structured as $R-N=N-R'$, where $-N=N-$ is the azo group, and the R or R' can be either aryl or alkyl compounds (Chudgar, 2012). For the past few decades, rapid industrialisation in some parts of the world like synthetic dyes in industrial effluents poses a major threat to environment since synthetic dyes especially azo dyes are stable, non-biodegradable and potentially carcinogenic and toxic. There are approximately 3,000 azo dyes available in the past and were used in pharmaceutical, textile, printing, dyeing and paper industries (Meyer, 1981). For more than 50% of dyes produced globally consist of azo dye and it is

estimated that over 7 x 10⁵ tons of these dyes are produced worldwide (Puvaneswari et al., 2006).

Chronic effects of azo dyes have been investigated for several decades. Benzidine is one of type of azo dye components that has been recognised as a human urinary bladder carcinogen and tumorigenic in a variety of laboratory animals. This compound is linked to human cancers and dye workers that were exposed to azo dye have higher potential of getting bladder cancer. Hence, it is proven that azo dye impose lethal effects, genotoxicity, mutagenicity, and carcinogenicity to humans and also animals (Puvaneswari et al., 2006).

2.3 METHYL ORANGE

Methyl orange (MO) is categorised as water soluble azo dye and it is anionic which commonly used in industries like textile, printing, pharmaceutical, food industries and also in research laboratories. MO has a molecular formula of C₁₄H₁₄N₃NaO₃S and molecular weight of 327.33 g/mol. It is a common azo dye with features of both a dye and an acid-base indicator in aqueous solutions due to its ability to function as weak acid. In acidic medium in which pH less than 3.1, MO shows red colour and yellow colour in basic medium (pH > 4.4) (Alzaydien, 2015). Methyl orange, congo red, and bismarck brown record for roughly 60-70% of all dyes utilised in textiles and food industries (Anirudhan, Radhakrishnan & Vijayan, 2013). According to Kim and Son (2011), the presence of nitrogen in the azo group –N=N– as primary chromophore of their molecular structure characterise the azo dyes. These highly coloured dyes are prepared by diazotising an aromatic amine and coupling with suitable aromatic compound. There are several techniques introduced for MO dye removal. However, adsorption is a more

preferable technique because of simple technique and require small cost (Rattanapan, Srikrum & Kongsune, 2017). Table 2.2 shows the physical and chemical properties of MO dye.

Table 2.2: Physical and chemical properties of MO dye (MERCK, 2018)

Physical and chemical properties of MO dye	
Name	Methyl orange
IUPAC Name	Methyl Orange; 547-58-0; Orange III; Gold Orange; Eniamethyl Orange; Helianthine
Molecular Formula	$C_{14}H_{14}N_3NaO_3S$
Molecular Weight	327.33 g/mol
pH value	3.1 (Red)- 4.4(Orange)
Bulk Density	1000 kg/m ³
Solubility in water	0.5 g/mL at 20°C
Melting point	>300°C
Storage temperature (°C)	Room temperature

Methyl orange dye usually applied in dyeing industry and printing textile. Thus, MO production that used for textiles may result in its release to the environment through various waste streams. MO has given no evidence of carcinogenic potential in limit oral and injection studies in the rats but it still brings some destructive impacts since it

has mutagenic properties. Based on statistics, 23,943 workers (14% female) are potentially exposed to MO in the US as estimated. Occupational exposure may be through inhalation of dusts and dermal contact with MO compound during its production at workplace (National Institute for Occupational Safety and Health [NIOSH], 1983). Besides that, MO dye can also accidentally entering the body through ingestion, metabolites into aromatic amines by intestinal microorganisms. Reductive enzymes in the liver can also catalyse the azo linkage to produce aromatic amines and can even lead to intestinal cancer (Kocukosmanoglu, Gezici & Ayer, 2006). Therefore, it is crucial to do treatment of dye from wastewater for the sake of ecological and animal wellbeing concern. Figure 2.2 shows the structure of MO dye.

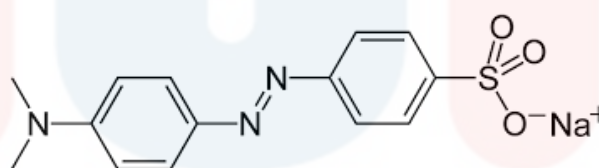


Figure 2.2: Structure of MO (Bazrafshan, 2014)

Table 2.3 presents the previous study on the removal of MO dye using various types of adsorbents. The first one is by using activated carbon of sea mango (*Cerbera odollam*) with microwave-assisted technique that gives 97 mg/g adsorption capacity (Azmi et al., 2016). In year 2013, removal of MO dye was carried out by Dniz using *Prunus amygdalus L.* (almond) shell waste. It give result of 38.63 mg/g maximum adsorption capacity. In 2012, a modified halloysite nanotubes was used as adsorbent to remove MO dye and it gives 91.74 mg/g adsorption capacity. In 2010, a natural and

treated almond skin was utilised as adsorbent and each give 15 mg/g and 31.3 mg/g maximum adsorption capacity respectively.

Table 2.3: Previous study on removal of Methyl orange dye using various type of adsorbent

Year	Type of adsorbent	Maximum adsorption capacity	References
2016	Activated carbon using sea mango (<i>Cerbera odollam</i>) with microwave-assisted technique	97 mg/g	(Azmi et al., 2016)
2015	Granular activated carbon	46.1 mg/g	(León et al., 2015)
2013	<i>Prunus amygdalus</i> L. (almond) shell waste	38.63 mg/g	(Deniz, 2013)
2012	Modified Halloysite Nanotubes	91.74 mg/g	(Liu et al., 2012)
2012	Activated papaya leaf	333.34 mg/g	(Ahmaruzzaman, 2012)
2011	Coal fly ash	374 mg/g	(Matheswaran, 2011)
2010	Natural and treated almond skin	15 mg/g and 31.3 mg/g for natural and treated skin almond respectively	(Atmani et al., 2010)

2.4 TECHNIQUES FOR DYE TREATMENT

Dyes are generally utilised within food, cosmetics, pharmaceutical, printing, textiles and many more industries. This causes the discharge of highly coloured effluents that influence transparency of water and gas solubility in water bodies. Moreover, they represent an issue because of carcinogenicity and lethality. Thus, suitable treatment technologies to remove dye are crucial and required before releasing them into water stream (Saratale, Chang & Govindwar, 2010). There are numerous techniques that are relevant for dye removal for industrial wastewater treatment. This technique are classified into three major groups which are biological method, chemical method and physical method. It is important to identify the most suitable technique for dye treatment and it must consider the advantage and disadvantage as well (Rahman, 2016).

2.4.1 BIOLOGICAL METHOD

Biological treatment mostly utilise bacteria in the biochemical disintegration of wastewaters to stable final products. The successful biological treatment depends on the development and maintenance of an appropriate, active, mixed microbial population in the system. Based on dissolved oxygen availability, biological treatment can be divided into aerobic and anaerobic technique (Mittal, 2011). Both aerobic and anaerobic techniques have advantage and disadvantages. For instance, almost 98% of organic contaminants can be removed by aerobic technique efficiently. However, large amount of electrical energy needed by aerobic digestion that may lead to greenhouse gases production because of fossil fuels burning to generate that energy. For anaerobic technique, it is more environmental friendly compared to aerobic because produce less

gas (Saratale et al., 2010). Biochemical oxygen demand (BOD) is the measure of organic matter capabilities to consume oxygen. The higher level of BOD in water indicates the presence of decomposing organic matter followed with high bacterial counts that downgrade water quality and other potential uses. Chemical oxygen demand (COD) is the measures of wastewater sample requirement for overall oxygen, including oxidisable components which not determined in the BOD analysis (Lee & Nikraz, 2014). According to Rathi (2002), there are limits for BOD and COD that should be followed by textile industry before discharging the effluents.

2.4.2 CHEMICAL METHOD

Kharub (2012) stated that chemical methods includes many processes such as coagulation or flocculation combined with flotation and filtration, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation, electro-flotation or electrochemical processes. However, because of expensive cost (high electrical energy demand and huge consumption of chemical reagents), these efficient techniques of dye removal are rarely used. Accumulation of the concentrated sludge is also one of the other disadvantage of these techniques. According to Chenna et al., (2015), one of the chemical method of removal of dye used flocculating and coagulating agent but this process is not applicable to all dye especially for highly soluble dyes.

2.4.3 PHYSICAL METHOD

Physical method includes several techniques such as reverse osmosis, sedimentation, filtration, coagulation flocculation and adsorption. Coagulation

flocculation technique is effective for removing sulphur and disperse dyes but not for acid, direct, reactive and vat dyes. Physicochemical technique also can be utilised for dye removal. However, this method resulting inefficiency of the colour removal and limit its application when sludge is produced (Saratale et al., 2010). Filtration method has the ability of expelling particles due to high efficiency by moving on a membrane called semi-permeable membrane with very small pores (about 0.6 nm) and its function at a high rate of operation in this method (Akbari,2007).

2.5 ADSORPTION

Adsorption is a surface phenomenon which happen when a film of adsorbate (the molecules or atoms being accumulated) is created on the surface of adsorbent when adhesion of atoms, or molecules of gas, liquid, or dissolve solids to a surface. In other word, substance of a liquid phase are pulled into the surface of a solid adsorbent (Kumar, 2013). Adsorption is commonly applied in wastewater treatment for removal of toxic or organic pollutants, inorganic pollutants or any substance that will cause accumulation in water. Adsorption is the most efficient process in the physical treatment of wastewater. This method has advantages such as their higher productivity for the expulsion of an extensive variety of dyes.

In addition, this technique is cost-efficient because we can use low cost bio adsorbent wastes like agriculture waste, food waste and seafood waste for the colour removal of dye wastewater. The choice of an adsorbent depends on qualities, for example, target compound capacity, high affinity and likelihood of adsorbent generation (Saratale et al., 2010).

2.6 ADSORBENT

Adsorbent is a material that has a capacity to contain a definite amount of liquid in small chambers similar to a sponge. Utilisation of agriculture wastes as adsorbent are recommended because of relatively cheap or no cost at all, readily available in large amount, prove high affinity to dyes and renewable. However, to enhance the efficiency of adsorption, a further investigation of biosorption process is required in the direction of modeling, regeneration of biosorbent and immobilization of the waste materials. Many studies have been conducted for the removal of various dyes by using different types of adsorbents. A wide different of waste materials , for example, orange peel, rice husk, date pit and pomelo peel are being utilised (Bharati & Ramesh, 2013). Table 2.4 shows the past studies on adsorption of various dye using waste.

Table 2.4: Past studies on adsorption of various dye using waste

Year	Type of waste	Dye	Maximum adsorption capacity	References
2018	Coffee grounds waste	Rhodamine B (RhB)	50.59mg/g	(Medina et al., 2018)
2017	Rice husk	Synthetic dye	14.9mg/g	(Sawasdee et al., 2017)
2015	Oyster shell	Congo red	91.33 mg/g	(Duthala et al., 2015)
2014	Raw chitin shrimp shell	Acid blue 25	211.00 mg/g	(Daneshvar et al., 2014)

2010	Sea shell	Malachite green	42.33 mg/g	(Chowdhury and Saha., 2010)
2010	Sawdust carbon (SDC) and rice husk carbon (RHC)	Acid yellow 36	183.8 mg/g for SDC and 86.9 mg/g for RHC	(Malik and P.K.,2003)

2.6.1 Oyster shells

Oyster is one of the main species in the aquaculture industry in Malaysia. Oyster is known as bivalve molluscs and the species are different according to their distribution. The four most commercial species of oysters that have been identified in Malaysia are *Crassostrea* (*C. beichei* and *C. iredalei*), *Saccostrea* (*S. echinata* and *Saccostrea spp*), *Ostrea* (*O. folium*) and *Hyotissa* (*Hyotissa hyotis*). In east coast region of Terengganu and Kelantan, oyster culture is widely practised by small-scale producers (Devakie and Ali, 2000; Najiah *et al.*, 2008). Based on observation, *C. iredalei* is the species of oyster shell that was used for this project. This species is usually found in brackish water lagoons in the east coast states of Malaysia and its range is known to extend into southern Thailand and Philippines (Nair *et al.*, 1993).

Usually, oysters are harvested mainly to be sold as fresh live oysters in hotels and restaurants. Statistics by the Department of Fisheries Malaysia showed an increasing

oyster production over the past 10 years. The highest production of oyster was recorded in year 2009. Sabah contributed 98% of the total oyster production and 97% of the total wholesale value. The number of culturists in Sabah also higher which is 344 compared to the number of culturists in Peninsular Malaysia (Devaki & Ali,2000).

Based on previous study by Hamester, Balzer and Becker (2012), microstructure analysis stated that oyster shell is a hard tissue mainly composed of 96% calcium carbonate and the remainder is organic matter and other compound. The hardness level of oyster shell depends on the concentration of silica in the shells. The higher the silica concentration, the hard the shell is. The high percentage of calcium carbonate component in the shells make it suitable to be utilised for adsorption of dye. Besides, for adsorption of large molecule like anionic dye, high mesoporosity substance is desired. Oyster shell is considered as naturally occurring, plentiful, cheap and powerful material. The structural component of oyster shell called chitin is located in the cuticles of crustacean shells, where it is complex with calcium carbonate, lipids, pigments and proteins (Hyun, Dong & Jin, 2010).

High demand for the use of oyster as an ingredients in food industry causing more factories doing suckling process which lead to the illegally disposal of more shells in the surrounding areas. It will become a problem to be exact 'pollutant' because shells take a long time to decay. In coastal regions of Southeast Korea, oyster shells are a waste product from marine-culture that presents a major disposal problem (Kwon et al., 2004). Thus, a creative solution was proposed by turning waste oyster shell into something beneficial and useful which was a bio-adsorbent to adsorb dye in water pollution.

Oyster shell was chosen as bio-adsorbent in this study because of its availability, rigidity, extraordinary chemical constitutes, characteristic shape and biological stability. When oyster shell releases calcium carbonate (CaCO_3) into wastewater, the calcium

content increased the pH and supply sufficient alkalinity. Oyster shell is likewise useful for expelling phosphorus from wastewater by creating calcium phosphate precipitation (Lim & Aris, 2013).

Many research have been done to make use of oyster shell in different application to prevent it from wasted. Oyster shell has been examined for few of application including supplant limestone as a source of calcium carbonate, which is a typical ingredient in cement and can be utilized to treat wastewater. Additionally, crushed shells can be fed to hens as a calcium supplement on farmer's fields to control soil acidity (Cimons, 2017). Based on experimental results shows that oyster-shells can be resources of pure calcareous materials and can be used to substitute sand as reusable construction materials (Yoon, Kim & Han, 2003). Duthala, Sen and Ouchi, (2015) which studied on adsorption of Congo red (CR) by using oyster shell as adsorbent stated that the increasing of initial dye concentration and contact time between dye and adsorbent resulting the increasing of adsorption rate.



Figure 2.3: Oyster shell (Nair et al., 1993)

2.7 ADSORPTION ISOTHERM

Adsorption isotherm is a graph or a relation between the amounts of adsorbate adsorbed on the surface of adsorbent and pressure where temperature is constant. Adsorption also can be defined as a separation process in which some materials (adsorbate) is concentrated from a bulk vapour or liquid phase on to the surface of a porous solid (adsorbent). Usually, a fraction of monolayer only formed as the result of adsorption. In order to adsorb huge amount of materials, a large specific surface area of adsorbent is compulsory so that the rate of adsorption can be increased. Adsorption isotherm is used for porous solids characterization and industrial adsorption process design (Keller, 2005). A simple application of adsorption is silica gel packets to adsorb moisture from packaged electronic or optical equipment.

Besides, characteristics of adsorbent is important to determine the efficiency to remove dye waste in a short period. An adsorbent must be small in size, have to be porous which contribute to larger surface area, and time needed to reach equilibrium is low so that dye can be removed faster. The isotherm models which are Langmuir and Freundlich commonly will be tested to discuss the adsorption behaviour (Belhachemi, & Addoun, 2011).

2.7.1 LANGMUIR ADSORPTION MODEL

Langmuir adsorption model used to quantify amount of adsorbate that will be adsorbed by adsorbent as a function of partial pressure at given temperature. Regarding to Langmuir adsorption, there are four assumptions or theories which is first, only one adsorbate molecule will occupied to one active sites of adsorbent surface that are identical

and equivalent. Second, the heat of adsorption is constant as no lateral interaction between adsorbed molecule happen and adsorption energy in all sites is equal (Ghosal & Gupta, 2016). Besides, adsorbed molecule will stay at adsorption site unless it is localized and no interaction and transmigration between nearby molecule will happen. Langmuir adsorption represent for a monolayer model which means only a monolayer is formed that adsorbate molecule only being adsorbed on free surface of adsorbent and not stacking on other molecule. Equilibrium saturation point is achieved when a molecule occupies a site and no further adsorption can take place (Foo & Hameed, 2010). Langmuir isotherm equation is as follow;

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o} \quad (2.1)$$

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.

2.7.2 FREUNDLICH ADSORPTION MODEL

Freundlich isotherm model is reversible adsorption and unlike Langmuir model, it not restricted to the formation of monolayer which means it is applicable to multilayer adsorption, disuniformity in distribution of adsorption heat and affinities over heterogenous surface. The equation Freundlich adsorption regarded as the mathematical equation is widely utilized in heterogeneous systems especially for organic compounds. There is a limitation of Freundlich adsorption isotherm which is it explain more to adsorption qualitatively and only applicable within certain limits of pressure. At higher pressure, it failed to predict value of adsorption. This relation is called as the Freundlich adsorption isotherm (Mittal & Kurup, 2007).

Freundlich equation is represent as;

$$q_e = K_F C_e^{\frac{1}{n}} \quad (2.2)$$

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.

CHAPTER 3

METHODOLOGY

3.1 APPARATUS AND EQUIPMENTS

The apparatus and equipments that were used for this study are beaker (250 mL & 1000 mL), conical flask (50 mL & 250 mL), volumetric flask (500 mL), measuring cylinder (100 mL & 500 mL), filter funnel, pH meter, weighing scale, glass rod, cuvette (1.5 mL), filter paper (0.125 μm), spatula, aluminum foil, micropipette, sieving machine, grinder, mortar and pestle, UV-visible spectrophotometer and orbital shaker.

3.2 CHEMICALS AND REAGENTS

The chemicals and reagents used for this study were methyl orange dye ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$), citric acid ($\text{C}_6\text{H}_8\text{O}_7$), sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$), hydrochloric acid (HCl), sodium bicarbonate (CHNaO_3), potassium hydrogen phosphate (KH_2PO_4), glycine ($\text{C}_2\text{H}_5\text{NO}_2$) and sodium hydroxide (NaOH).

3.3 PRE-TREATMENT AND PREPARATION OF ADSORBENT

Raw oyster shells (*C. iredalei*) were collected from disposal site in Bachok, Kelantan. Before preparing oyster shells as adsorbent, there were few steps that need to be carried out as pre-treatment. Firstly, the shells was washed thoroughly with water, scrubbed clean and rinsed to remove residual meat and sediments, adhering dirt and organic residue. Next, the shells were air-dried in oven at 60°C for 24 hours to ensure complete dryness to remove moisture content within the shells. Besides, drying also being carried out to eliminate the remaining organic material. After that, the shells were crushed with mortar and pestle and were ground with grinder to obtain fine powders. The powdered oyster shell was stored in air-tight zipper bag for further use.

3.4 PREPARATION OF DYE SOLUTION

Stock solution of methyl orange (MO) dye was prepared by dissolving 0.05 g of MO dye powder in 500 mL of distilled water to obtain a concentration of 100 mg/L. Direct dilution method was conducted freshly each time when required.

3.5 CALIBRATION CURVE

Stock solution was prepared to construct calibration curve using 0.05 g of dye to 500 mL of distilled water to prepare 100 mg/L. Then, the MO dye was diluted from the stock solution to eight different concentrations (0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 mg/L and distilled water were added up to 50 mL using a 50 mL conical flask. All the concentrations of MO dye solutions were filled into 1.5 mL cuvette respectively to

measure wavelength of 465 nm using UV-visible spectrophotometer. Distilled water was utilised as blank or reference. Values that were obtained from the absorbance reading were used to construct MO calibration curve.

3.6 OPTIMISATION STUDIES

3.6.1 EFFECT OF ADSORBENT SIZE

The powdered raw oyster shell that was stored in air-tight zipper bag was sieved using siever of the sizes of 75 μm , 150 μm , 300 μm , 500 μm , 710 μm and 1000 μm . 50 mg/L of dye solution was mixed and placed in a conical flask containing 0.5 g of sieved adsorbent of each of the 75 μm , 150 μm , 300 μm , 500 μm , 710 μm and 1000 μm particle sizes, respectively. Then, all mixtures were stirred by using a glass rod and were left undisturbed until the next 24 hours. After 24 hours, the solution were filtered with filter paper. The residual concentration of MO were analysed using UV-vis spectrophotometer at wavelengths of 465 nm.

3.6.2 EFFECT OF ADSORBENT DOSAGE

The best result from adsorbent size was used to continue for the next parameter. The effects of adsorbent dosage was conducted by varying nine sets of adsorbent amount from 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. Then, they were mixed respectively, with 100 mL of MO at the concentration of 50 mg/L. The mixture were stirred and left at room temperature until the next 24 hours. After 24 hours, the solution

were filtered with filter paper. The solution was analysed using UV-vis spectrophotometer at wavelength of 465 nm.

3.6.3 EFFECT OF INITIAL DYE CONCENTRATION

Optimum size and dosage of adsorbent obtained from previous parameters was used to study the effect of initial dye concentration. Different dye concentrations which were 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 were prepared. The volume used was 100 mL for each concentration. These different concentrations of dyes were mixed with the fixed amount of adsorbent size and dosage in a conical flask. The mixture were stirred using a glass rod before left untouched until it reach 24 hours. After 24 hours, the solution were filtered with filter paper. The solution were analysed using UV-vis spectrophotometer at wavelength of 465 nm.

3.6.4 EFFECT OF CONTACT TIME

Initial dye concentration which was found to have the highest MO removal percentage was used for this parameters. The volume of MO was maintained at 100 mL. Contact time used was 1 hour interval for a maximum of 9 hours. The mixtures were stirred only at the start of the experiment. Each of solution was filtered for each 1 hour interval until 9th hours with filter paper. The solutions were analysed using UV-vis spectrophotometer at wavelength of 465 nm.

3.6.5 EFFECT OF pH

Effect of pH was studied in this research to identify whether it is highly pH dependent process or otherwise. pH is one of an important parameter for adsorption of ions from aqueous solution because it affects the structure of dye molecules, the degree of ionisation of the adsorbate during reaction and charge on surface of adsorbent (Gong et al., 2013). Various pH were altered to values in range of 3-6 using buffer of 0.1 M citric acid and 0.1 M sodium citrate for pH 3, 4, 5 and 6. For pH 7 and 8, buffer of 0.1 M potassium dihydrogen phosphate and 0.1 M sodium hydroxide were used. 0.1 M glycine and 0.1 M sodium hydroxide were used as buffer for pH 9 and 10. For pH 11, 0.1 M sodium bicarbonate and 0.1 M sodium hydroxide were used. A pH meter was used to measure the pH of each buffer. 100 mL volume of MO dye were filled into nine different conical flasks for each pH buffer respectively. Few drops of each buffer were dropped in each conical flask contain MO dye solution until the solution reached the required pH. Then, optimum amount of adsorbent were put in each conical flask for the adsorption to start.

The mixture were stirred with a glass rod and left undisturbed until it reached the optimum contact time found earlier from previous parameter. The absorbance reading were measured using UV-visible spectrophotometer at wavelength of 465 nm.

3.6.6 EFFECT OF AGITATION SPEED

By using the optimum adsorbent size, adsorbent dosage, initial dye concentration, contact time and pH that were obtained from previous tests, the effect of agitation speed were studied by using different agitation speed which are 90 rpm, 110 rpm, 130 rpm, 150 rpm, and 170 rpm. The solution was left in the orbital shaker for 3 hours in room temperature.

3.6.7 EFFECT OF AGITATION TIME

Effect of agitation time was studied by using the optimum adsorbent size, adsorbent dosage, initial dye concentration, pH and agitation speed that were obtained from previous tests. Agitation time was set in the interval of 15 minutes until 75 minutes. Then, the solutions were filtered, and absorbance reading were measured using UV-visible spectrophotometer at wavelength of 465 nm.

3.7 DATA ANALYSIS

3.7.1 ADSORPTION CAPACITY

The effects of adsorbent size, adsorbent dosage, initial dye concentration, contact time, pH and agitation speed on the adsorption uptake were studied. The solutions of the sample were withdrawn at equilibrium to find out the concentrations of the residue. UV-vis spectrophotometer were used to measure the concentration of dye in the solution after equilibrium adsorption. The adsorbed amount of MO at equilibrium, q_e (mg/g), were calculated by the following equation:

$$q_e = \frac{(C_o - C_e)V}{M} \quad (3.1)$$

C_e = equilibrium concentrations in the solution (mg/L); C_o = initial concentrations in the solution (mg/L); V = volume of solution (L); M = mass of adsorbent (g)

3.7.2 PERCENTAGE REMOVAL OF DYE

Percentage removal of MO dye were calculated by using equation 3.2:

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

C_o = initial concentration of dye in the solution (mg/L); C_e = final concentration of dye in the solution (mg/L)

3.7.3 LANGMUIR ADSORPTION ISOTHERM

Langmuir isotherm was developed by Irving Langmuir in 1916 is equation used to describe the amount of gas adsorbed on a plane surface, as a function of the pressure of the gas in equilibrium with the surface (Daintith, 2008). The Langmuir adsorption isotherm were obtained through all the parameters using equation 3.3.

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

where q = dye uptake; q_{\max} = Maximum dye uptake (mg/g); C_e = equilibrium concentration (mg/L); K_L = Langmuir equilibrium constant (L/mg)

For Linearised Langmuir isotherm equation, the equation that were used was

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}KL} + \frac{1}{q_{\max}} C_e \quad (3.4)$$

Where C_e = equilibrium concentration (mg/L); q_e = amount adsorbed at equilibrium (mg/g); q_0 = 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 $\frac{1}{bq_m}$ (L/mg).

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

3.7.4 FREUNDLICH ADSORPTION ISOTHERM

According to Daneshvar et al., (2014), Freundlich model is an empirical model that describes monolayer adsorption with heterogenous surface. Freundlich adsorption isotherm were obtained by using equation;

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3.5)$$

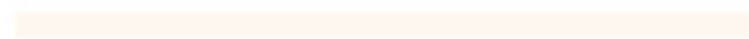
where q_e = amount of dye adsorbed (mg/g); C_e = equilibrium concentration (mg/L); K_F = indicator of adsorption capacity to be determined from intercept (L/mg); $\frac{1}{n}$ = adsorption capacity to be determined from slope (constant). For Linearised Freundlich model, the equation as stated below;

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

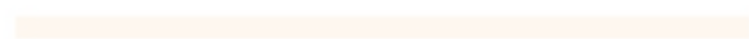
where q_e = amount of dye adsorbed (mg/g); C_e = equilibrium concentration (mg/L); K_F = indicator of adsorption capacity to be determined from intercept (L/mg); $\frac{1}{n}$ = adsorption capacity to be determined from slope (constant).



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CHAPTER 4

RESULT AND DISCUSSION

4.1 PREPARATION OF ADSORBENT

Raw oyster shells were collected from disposal site in Bachok, Kelantan. Before preparing oyster shells as adsorbent, there were few steps that need to be carried out as pre-treatment. Firstly, the shells was washed thoroughly with water, scrubbed clean and rinsed to remove residual meat and sediments, adhering dirt and organic residue. Next, the shells were air-dried in oven at 60°C for 24 hours to ensure complete dryness to remove moisture content within the shells. Besides that, drying also was carried out to eliminate the remaining organic material. Then, the oyster shells were crushed with mortar and pestle and were ground with grinder to obtain fine powders. The powdered raw oyster shell increases the surface area for adsorption process.

4.2 ADSORPTION STUDIES

4.2.1 CALIBRATION CURVE

Stock solution was prepared to construct MO calibration curve using 0.05 g of dye to 500 mL of distilled water to prepare 100 mg/L. Then, the stock solution of MO dye was diluted to eight different concentrations (0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 mg/L) obtain and were diluted with distilled water up to 50 mL using a 50 mL conical flask. All the concentrations of MO dye solutions were tested for their absorbance reading in wavelength of 465 nm using UV-visible spectrophotometer. Values obtained from the absorbance reading were used to construct MO calibration curve. Figure 4.1 showed the MO calibration curve measured at 465 nm at room temperature, 25°C. A linear relationship between the absorbance values and concentration was produced. When the dye concentration increase, the absorbance reading increases as well. A correlation coefficient, $R^2 = 0.9998$ was obtained from Figure 4.1.

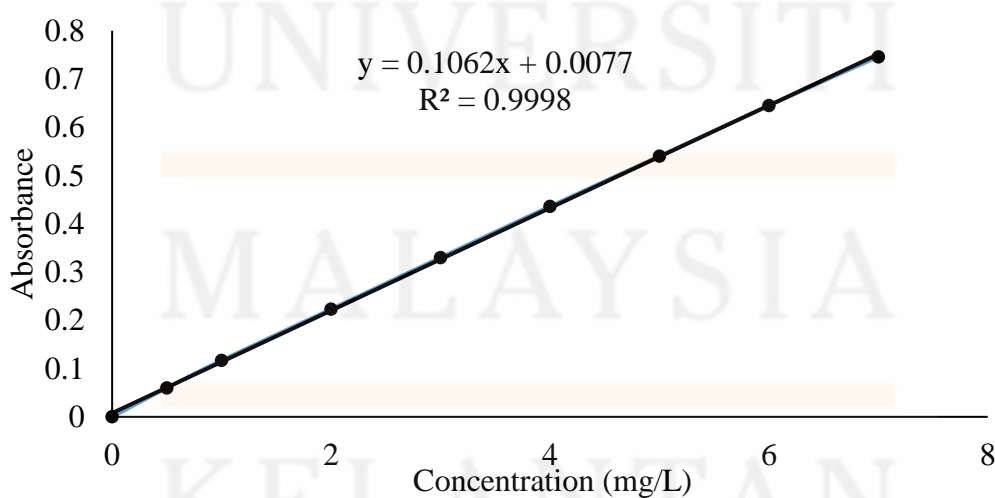


Figure 4.1: MO calibration curve measured at 465nm at room temperature (25°C)

4.2.2 EFFECT OF ADSORBENT SIZE

Particle size is an important parameter that can influence rate of adsorption. In order to study the effect of adsorbent size, the raw oyster shell (ROS) was prepared in powdered form by using blender. Then, to create different particle sizes, the powdered ROS was sieved into six different sizes which are 75 μm , 150 μm , 300 μm , 500 μm , 710 μm and 1000 μm . Amount of 0.5 g of powder from of each particle sizes were used to react with MO dye solution for 24 hours. Then, the solutions were filtered and absorbance reading was recorded by using UV-Spectrophotometer at 465 nm.

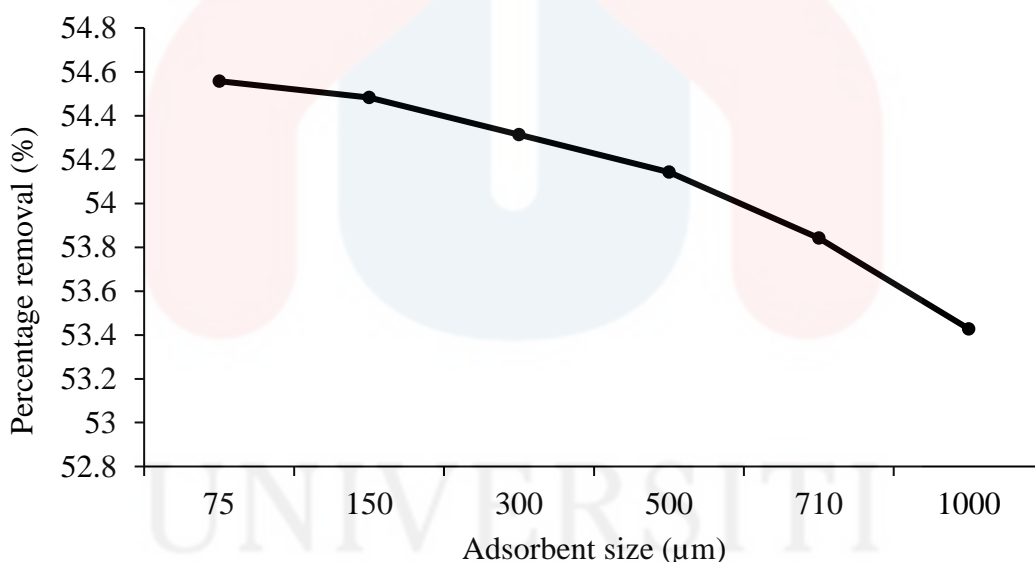


Figure 4.2: Effect of adsorbent size on MO dye removal, (concentration: 50 mg/L MO; volume: 100 mL; temperature: 25°C; adsorbent dosage: 0.5 g; contact time: 24 hours)

Based on Figure 4.2, the percentage of MO dye removal declined from 75 μm to 1000 μm . The highest percentage of MO dye removal was obtained at the smallest particle size whereas the lowest percentage of MO dye removal obtained at 1000 μm . Smallest

particle size shows the slightly highest percentage removal of MO dye which gave value of 54.56%. The largest particle size, 1000 μm records the least percentage of MO dye removal which was 53.43%. For particle size of 150 μm , 300 μm , 500 μm and 710 μm , they removed 54.48%, 54.31%, 54.14% and 53.84% MO dye, respectively.

Particle size of 75 μm able to remove highest percentage of MO dye because it has the largest surface area compared to other particle sizes. The number of the accessible sites increase when the micropores increase hence adsorption can take place rapidly. Besides that, rapid adsorption happen due to the presence of large number of smaller particles which provide the sorption system with larger surface area available for the dye adsorption (Krika & Benlahbib, 2015). From Figure 4.2, it can be concluded that as the adsorbent size increases, the efficiency decrease. The decrease in percentage of MO dye removal along the increment of particle sizes is because of reduction in surface area of adsorbent.

4.2.3 EFFECT OF ADSORBENT DOSAGE

To study the effect of adsorbent dosage on the adsorption efficiency of the ROS for removal of methyl orange dye, the experiment was carried out by varying the amount of adsorbent to be used from 0.1g to 2g.

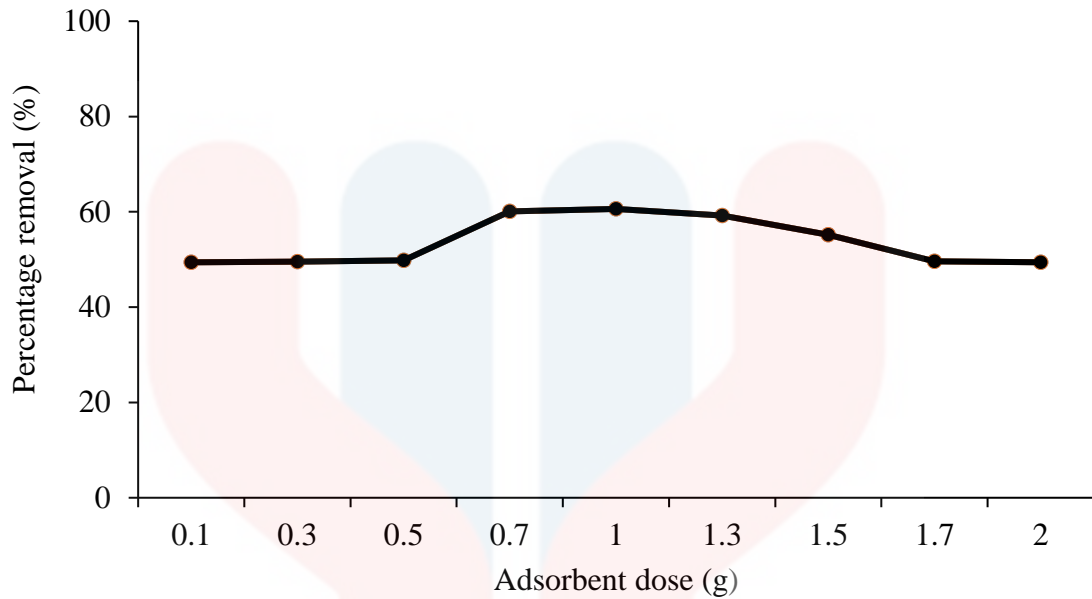


Figure 4.3: Effect of adsorbent dose on MO dye removal, (concentration: 50 mg/L MO; volume: 100 mL; temperature: 25°C; adsorbent size: 75 μm ; contact time: 24 hours)

Figure 4.3 showed percentage removal of MO dye increase with the increase in adsorbent dose from 0.1g to 1.0g. Increasing of adsorbent dosage increases the total number of active sites for adsorption of MO dye and cause difference in removal efficiency. However, the percentage of MO dye removal starts to decrease at adsorbent dose of 1.3 g to 2 g. This is because when adsorbent hits the optimum amount, the active sites may close with each other thus increase in unsaturation of adsorptive sites that can lead to the reduction of adsorption capacity (Teka & Enyew, 2014). Adsorbent dosage of 1.0 g was selected as the optimum adsorbent dosage because the adsorption has reached equilibrium hence resulting 60.60% of MO dye removal which gives the highest value compared to the other dosages. Hence, the optimum removal of MO dye can be obtained by using 1.0 g amount of adsorbent at 75 μm particle size.

4.2.4 EFFECT OF INITIAL DYE CONCENTRATION

The effect of initial dye concentration on MO dye adsorption was examined at eight concentration levels which were 10, 30, 50, 100, 150, 200, 250 and 200 mg/L. Figure 4.4 showed the graph of MO dye percentage removal with 1.0 g of adsorbent with 75 μ m particle size.

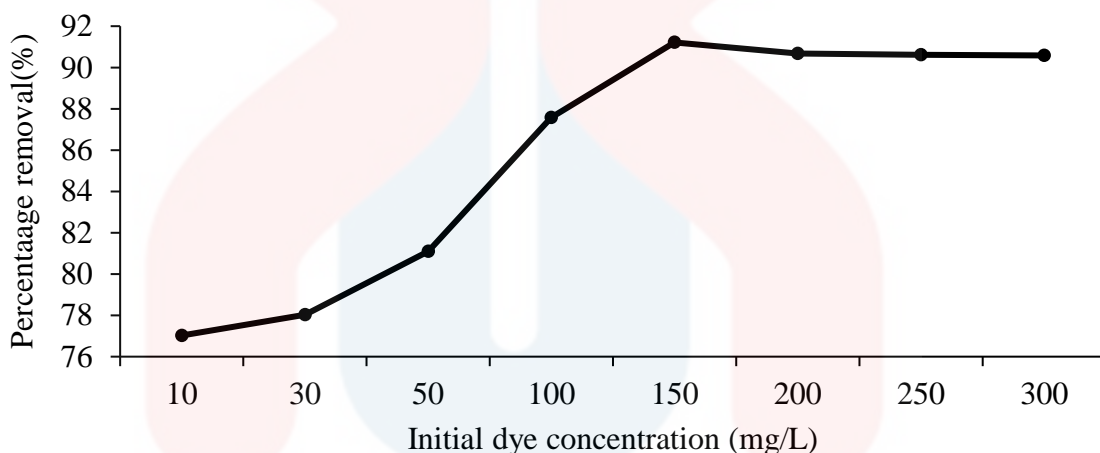


Figure 4.4: Effect of initial dye concentration on MO dye removal, volume: 100 mL; temperature: 25°C; adsorbent size: 75 μ m, adsorbent dose: 1.0 g, contact time: 24 hours)

Figure 4.4 shows that the percentage of MO dye removal increased from 77% to 91.2% with the increase in the initial dye concentration from 10 to 150 mg/L. At dye concentration of 10 mg/L, the least dye removal percentage of 77.02% was achieved. From observation, it was found that concentration of 150 mg/L was the optimum initial dye concentration as it gives the highest percentage of dye removal. When the initial dye concentration increases, the number of collisions between dye ions and the surface area

of oyster shell increases, which enhances the interaction between MO dye and adsorbent and increase the adsorption process. A necessary driving force was provided during higher initial concentration to overcome all resistances of the dye between the aqueous and solid phases, thus increasing the uptake (Krika & Benlahbib, 2015).

However, starting from concentration 200 mg/L, there was a slight reduction of percentage of dye removal which was 90.68%, followed by concentration 250 mg/L (90.62%) and 300 mg/L (90.59%). All active sites of the adsorbent were saturated with MO dye molecules which means that adsorption had reached equilibrium at 150 mg/L. As the adsorbent dosage was fixed, there is no more surface active sites available for adsorption so the percentage removal of dye start to decrease during this saturation point (Khani et al, 2011).

4.2.5 EFFECT OF CONTACT TIME

The effect of contact time was studied with interval of 1 hour to 9 hours using all the optimum parameters that were obtained from previous tests. Figure 4.5 shows the effect of contact time on MO dye removal. The percentage of MO dye removal was recorded in the range of 85.46% to 91.31%.

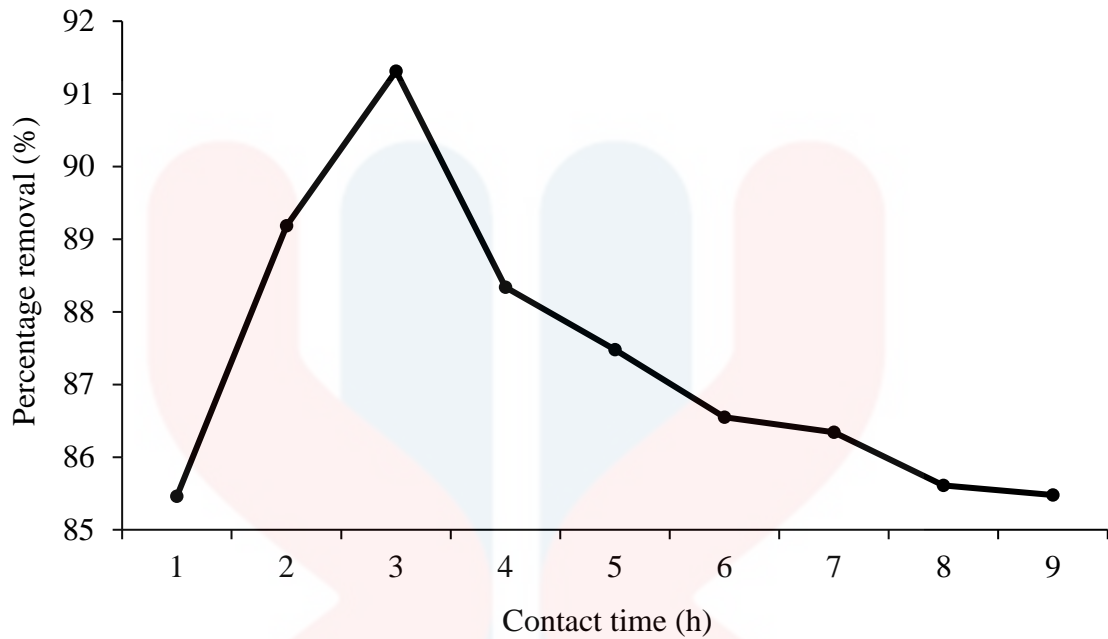


Figure 4.5: Effect of contact time on MO dye removal, volume: 100 mL; temperature: 25°C; adsorbent size: 75 μm , adsorbent dose: 1.0 g, initial dye concentration: 150 mg/L)

From Figure 4.5, it can be concluded that the MO adsorption rate is fast and rapid for the first 2 hours and reaches equilibrium at the third hour with the maximum percentage of MO dye removal of 91.31%. The results indicated that the rate of MO removal increase in reaction time until it reach a point where an equilibrium is achieved then, it progressively decreases with time. At the first two hours, the adsorption rate is extremely fast and quick because all the active sites were not occupied, and the competition among MO molecules is weak (Denizli et.al, 2004). Principally, MO will adsorb on the exterior surface until it saturated. Then, once the MO ions entered into the adsorbent pores, they were adsorb into the interior surface of the particles (Ma et. al, 2013). Nearly 3 hours was required to reach the equilibrium adsorption.

After 3rd until 9th hour, the percentage of MO dye removal continuously reduced slightly because the pores of adsorbent has been saturated with dye. Therefore, only slow adsorption happens because dye particles takes time to adsorb into adsorbent (Ma et. al, 2013). A total of 91.31% percentage of MO dye removal was managed to be obtained in the first 3 hours.

4.2.6 EFFECT OF pH

The effect of pH solution on the MO dye removal was investigated by varying pH in the range of 3 to 11, with initial dye concentration of 150 mg/L and 3 hours contact time. The adsorption was performed at room temperature. As shown in Figure 4.6, the percentage of MO dye removal decreases from 91.64% to 83.09% as the pH increases.

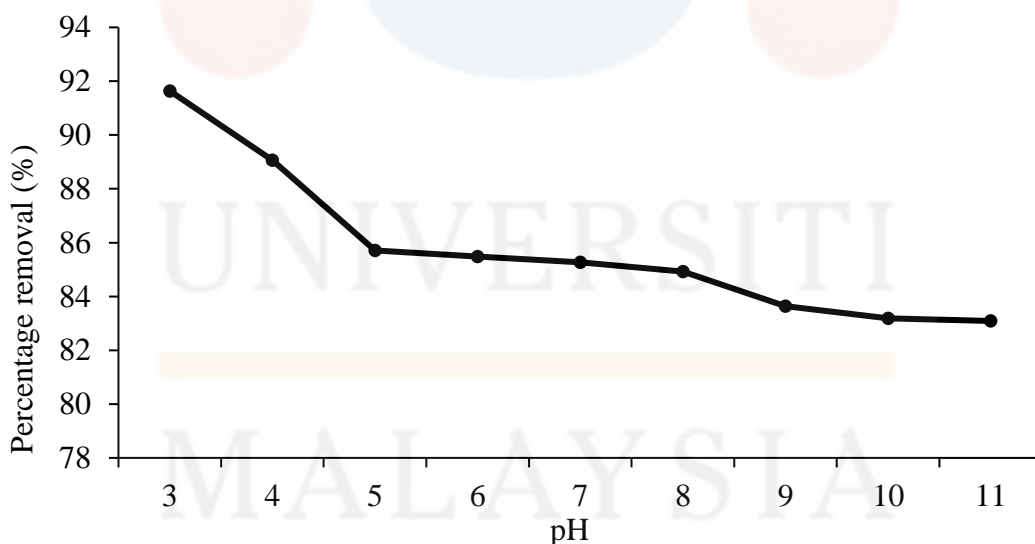


Figure 4.6: Effect of pH on MO dye removal, volume: 100 mL; temperature: 25°C; adsorbent size: 75 μm, adsorbent dose: 1.0 g, initial dye concentration: 150 mg/L, contact time: 3hours)

The pH of solution is one of other important parameter that control adsorption efficiency by influencing surface charge of the adsorbent and dissociation of functional groups on the active sites of the adsorbent (Bazrafshan et.al, 2013). The maximum percentage of MO dye removal was achieved in acidic region at pH 3 and the minimum adsorption of MO dye was identified in pH 11 providing the MO dye removal percentage of 83.09%. In strong acidic condition, MO occurs as quinonoid form which gives red colour while in alkaline solution, it forms as benzenoid which gives yellow colour (Hosseini et.al, 2011).

At low pH, higher adsorption attain because of protonation properties of adsorbent. This happen due to the higher hydrogen ion concentration in acidic solution and negative charges at internal pores surface that are neutralised. Besides, there is also new development of some adsorption sites which provides surface with positive charges in order for anionic MO dye which contains negatively charged sulfonate group ($\text{SO}_3^- \text{Na}^+$) to get adsorbed. Hence, the increase of electrostatic attractions between negatively dye molecules and positively charged adsorption sites caused an increasing in dye adsorption (Zhao et.al, 2014).

There is decreasing of dye removal along the increase of pH (pH 4-6) because the adsorbent protonation was delayed and there is reduction in electrostatic attraction. However, the involvement of other physical forces such as hydrogen bonding and van der Waals force help adsorbent to still adsorb MO molecule (Zhao et.al, 2014).

Based on Figure 4.6, the percentage of MO dye removal decreases in alkaline solution (pH 8-11) because the presence of $-\text{OH}$ ions that compete with MO anionic dye molecules. There are electrostatic repulsive interaction between the negatively charged

adsorbent surface and anionic dye that contribute to the low adsorption process thus reducing the percentage removal of MO dye in alkaline solution (Mahmoud et.al, 2014).

4.2.7 EFFECT OF AGITATION SPEED

The other important parameter that was studied in this project is agitation speed as it can influence the adsorption phenomena by affecting the solute distribution in bulk solution and external boundary film formation (Umer et al., 2012). The effect of agitation speed on adsorption was investigated by varying the agitation speeds between 90 rpm to 170 rpm with 3 hours contact time each. Figure 4.7 presented the corresponding values of percentage of MO dye removal with different agitation speed which are 90 rpm, 110 rpm, 130 rpm, 150 rpm and 170 rpm.

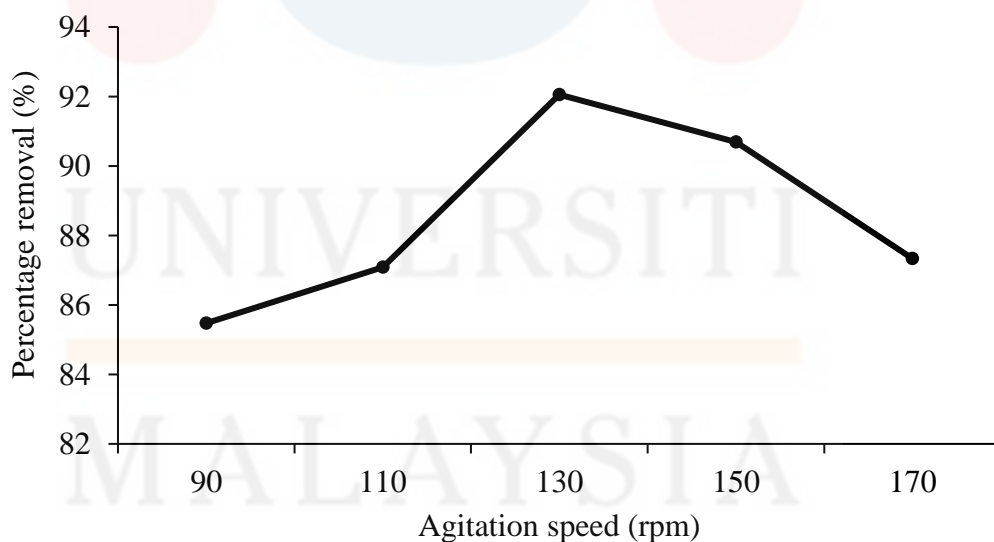


Figure 4.7: Effect of agitation speed on MO dye removal, volume: 100 mL; temperature: 25°C; adsorbent size: 75 μm, adsorbent dose: 1.0 g, initial dye concentration: 150 mg/L, contact time: 3 hours, pH: 3)

Based on Figure 4.7, there was slight increase of dye percentage removal when agitation speed increase from 90 rpm to 130 rpm. The least percentage removal was obtained during 90 rpm speed which is 85.47%. The value increased to 87.08% and 92.05% with 110 rpm and 130 rpm, respectively. Agitation speed of 130 rpm is the state where adsorption capability reaches maximum and can be considered as the optimum agitation speed. However, there is declination of dye removal starting from 150 rpm onwards.

Some explanation could answer the trend of the graph. Agitation speed seemed to affect the rate of adsorption between 90 rpm to 130 rpm because external diffusion and pore diffusion influence the adsorption kinetic control. The increase of agitation speed causes the increase of adsorption rate. This is supported by the fact that the effect of speed and turbulence cause the decreasing in boundary layer thickness to mass transfer around adsorbent particle which will eventually increase the adsorption of MO dye (El-Latif & Ibrahim, 2010). The maximum percentage removal was achieved at 130 rpm which is 92.05% and there was no significant increase in percentage removal of dye beyond this point. Besides, 130 rpm was an optimum speed that sufficient enough to provide available surface binding sites for MO dye uptake (El-Latif et al., 2010).

At higher agitation speed which are 150 rpm and 170 rpm, the percentage of dye removal decreases due to increase of kinetic energy for both adsorbate and adsorbent particles in which they will collide with each other rapidly and cause the detachment of adsorbate molecules that were bound loosely (Jamil et al., 2011). Besides, the decrease in percentage of dye removal is also because of unsystematic random collision between particles which cause adsorbent (powdered oyster shell) and adsorbate (methyl orange dye) have less contact time to make bond (Umer et al., 2012).

4.2.8 EFFECT OF AGITATION TIME

The other important factor that affects efficiency in adsorption process is agitation period. By using the optimum parameters that have been obtained from previous tests, the effect of agitation time has been studied. The optimum agitation time was studied by agitating 100 mL of aqueous solution containing 150 mg/L of MO dye with 1.0 g of adsorbent of 75 μm sizes in constant agitation speed of different agitation time in intervals of 15min to 75min.

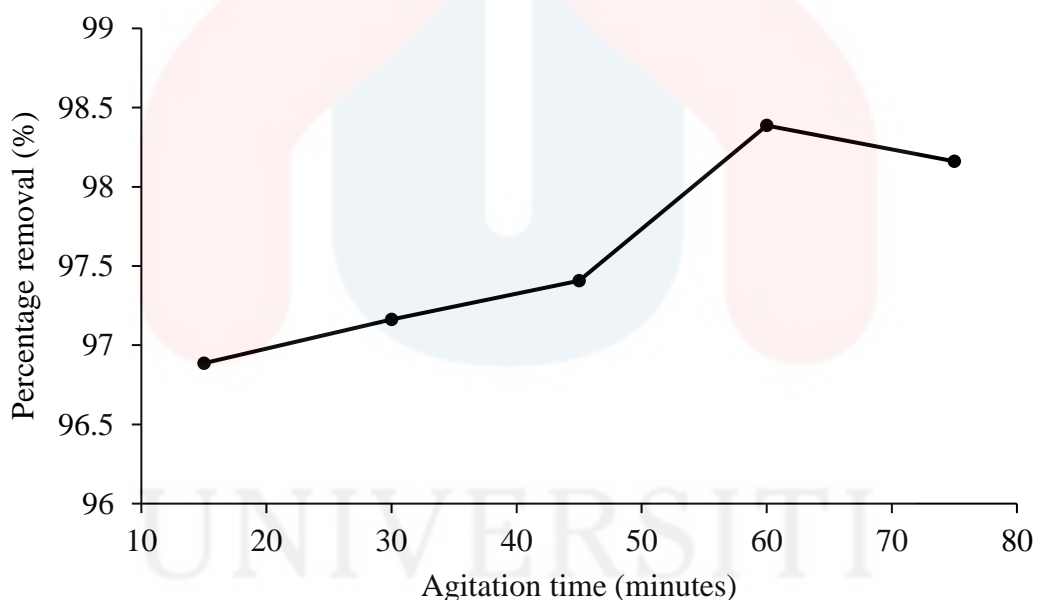


Figure 4.8: Effect of agitation time on MO dye removal, volume: 100 mL; temperature: 25°C; adsorbent size: 75 μm , adsorbent dose: 1.0 g, initial dye concentration: 150 mg/L, contact time: 3 hours, pH: 3, agitation speed: 130 rpm)

Based on the result shown in Figure 4.8, it shows that removal efficiency increase significantly from first 15 minute until 60 minute and shows a slight decrease to the

minute of 75. Therefore, 1 hour was found to be the most suitable and optimum agitation period for adsorption of MO dye. The percentage of MO dye removal increase from 96.89% to 98.39% and then decrease to 98.16% at minute of 75. The rate of percentage removal increases in the first 60 minutes indicating the fact that adsorbent provides adequate amount of surface area for dye adsorption.

When time increases, rapid adsorption happens and surface area of adsorbent become limited for adsorption as the reaction has reach equilibrium. Based on Yadla, Sridevi and Lakshmi (2012), this phenomena happen when adsorbate forms a thin layer called monomolecular that cover over the adsorbent surface which cause adsorbent capacity to adsorb decreases. The highest percentage of MO dye removal was obtained after 60 minutes of stirring in orbital shaker and beyond this optimum time, the rate changes is insignificant. Therefore, the optimum parameters for MO dye adsorption is using 1.0 g of 75 μ m of adsorbent particle size with initial dye concentration of 150 mg/L in acidic condition of pH 3 in 130 rpm agitation speed for 1 hour.

4.3 ADSORPTION ISOTHERM

Adsorption isotherms represents the interaction between adsorbents and adsorbate and describe information on the nature of the solute-surface interaction. It is crucial to identify the adsorption system design and the parameters attained from each different models as those parameters useful by giving great significance and value on surface properties of adsorbent and its affinity towards adsorbate (Ahmaruzzaman, 2012). For the purpose of analysis such as to predict maximum adsorption capacity of adsorbent, it is a need to understand partition of adsorbate molecules between solid and liquid phases under equilibrium condition (Kebir et al., 2014). Therefore, few isotherm equations have been

developed and the most commonly used isotherm are Langmuir and Freundlich. These two most popular isotherm were analysed in this study to understand the adsorption equilibrium.

4.3.1 LANGMUIR ISOTHERM MODEL

The Langmuir model is recognised based on the monolayer coverage of adsorbate over a homogenous adsorbent surface. An assumption related to Langmuir is that the adsorption process is monolayer in nature which that it happen at specific homogenous sites on the adsorbent surface. There is no further adsorption process can take place on same site where dye molecule has occupies or in other word is no stacking of adsorbed molecules. (Wang et al., 2015). Linearized Langmuir isotherm equation was commonly used in study. The values of q_{\max} and K_L were determined from the linear plot and their values are present in Table 4.1.

Table 4.1 presents the isotherm parameters and the correlation coefficients of this model where the values of q_{\max} and K_L were determined from the linear regression using Equation 3.4 as in section 3.7.3. Figure 4.9 represent Langmuir adsorption isotherm on the effect of adsorbent size on the removal of MO dye followed by Figure 4.10, 4.11, 4.12, 4.13, 4.14, 4.15 which represent effect of adsorbent dosage, initial dye concentration, contact time, pH, agitation speed and agitation time, respectively. Langmuir isotherm model displays a linear plot of C_e/q_e which shows coverage on the monolayer surface.

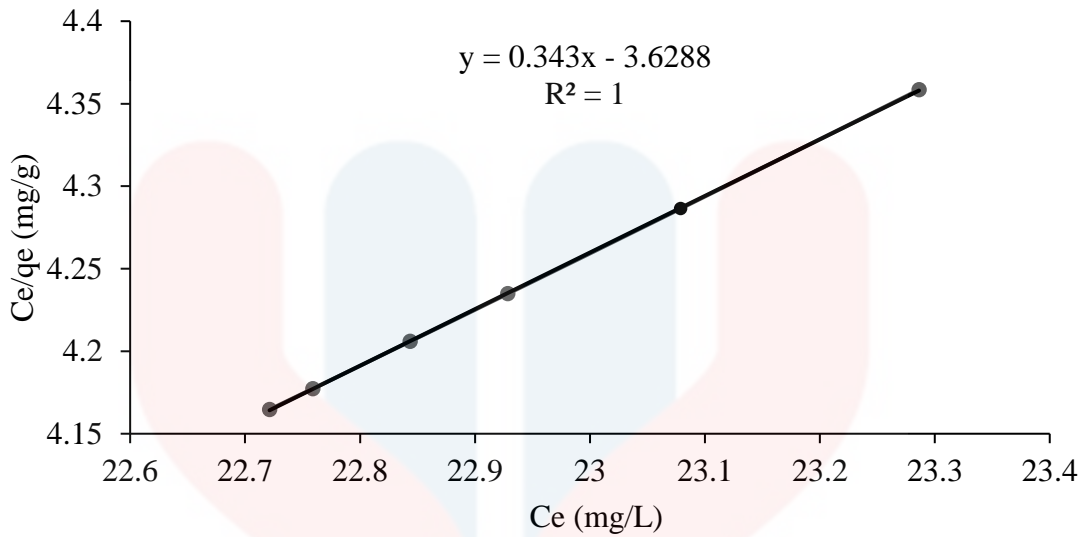


Figure 4.9: Plot of Langmuir isotherm for effect of adsorbent size on removal of MO

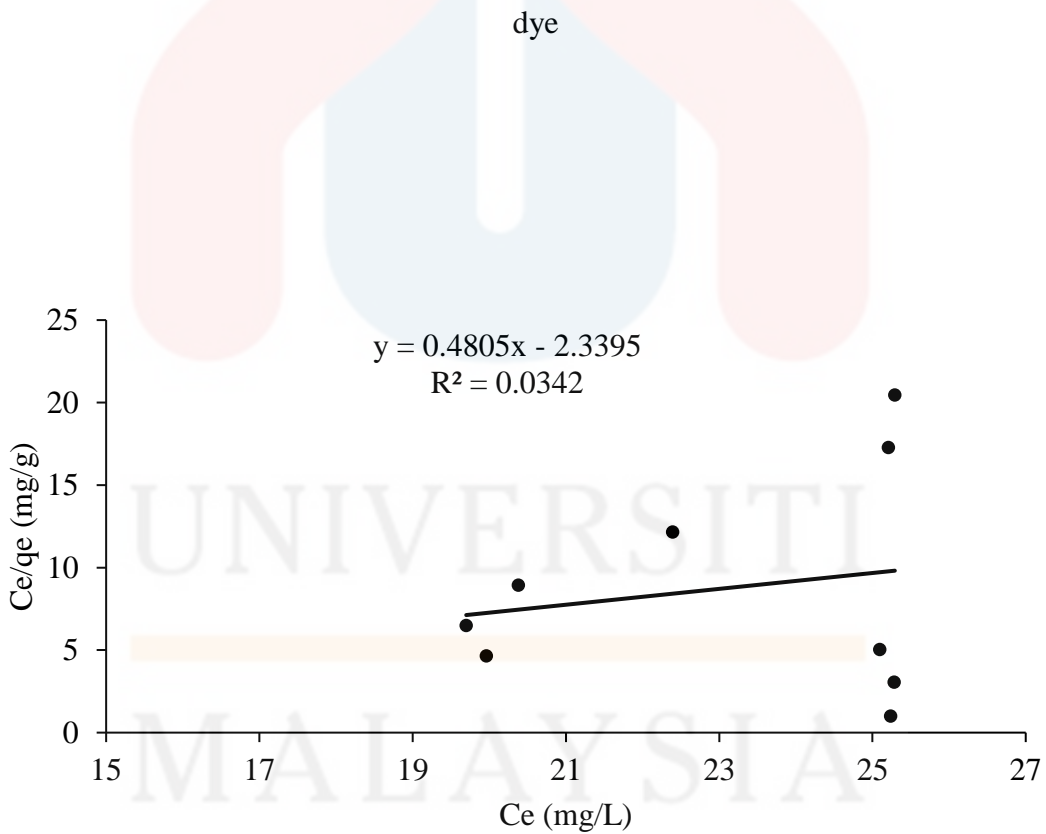


Figure 4.10: Plot of Langmuir isotherm for effect of adsorbent dose on removal of MO

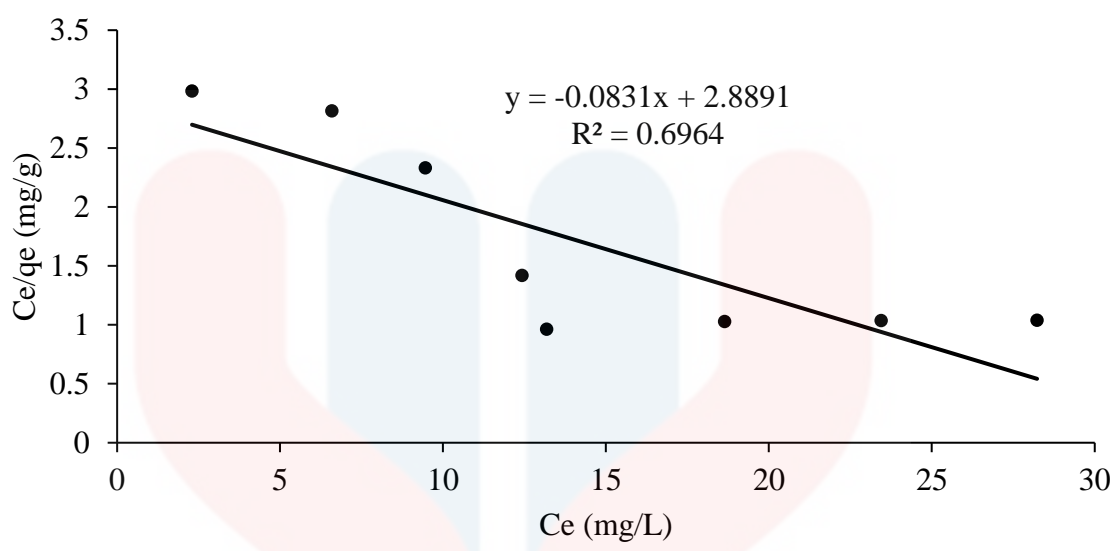


Figure 4.11: Plot of Langmuir isotherm for effect of initial dye concentration on removal of MO dye

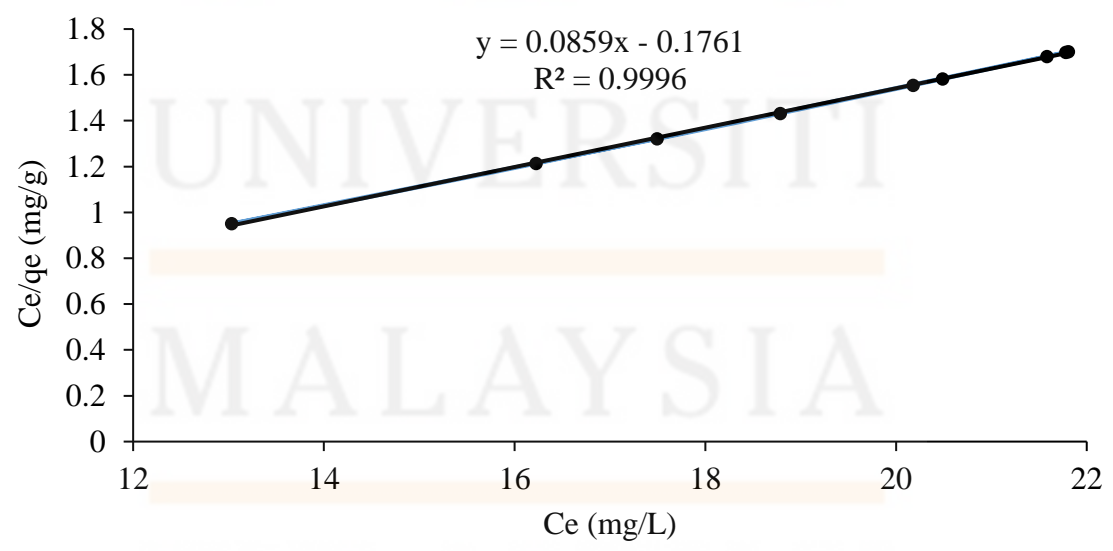


Figure 4.12: Plot of Langmuir isotherm for effect of contact time on removal of MO dye

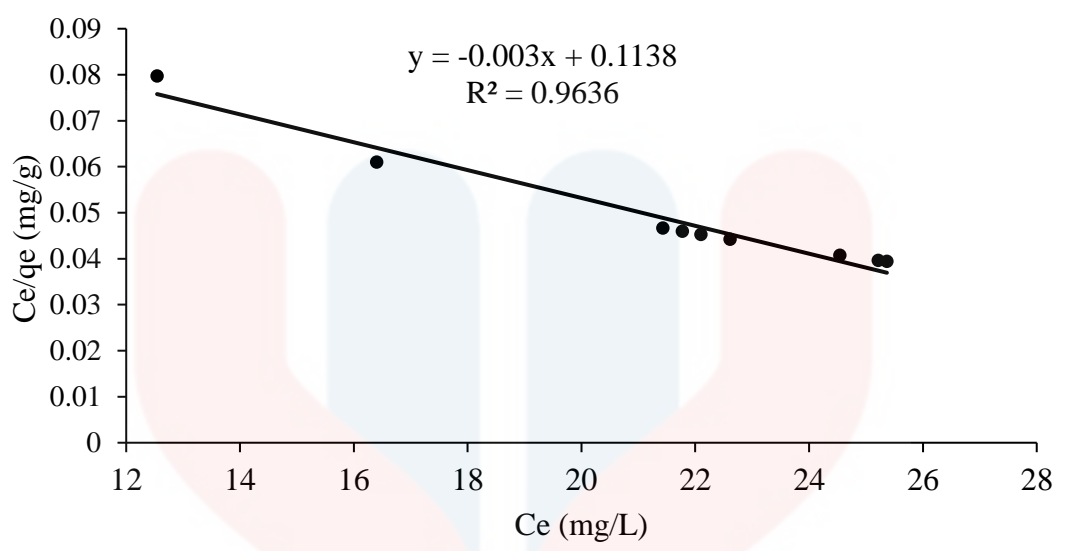


Figure 4.13: Plot of Langmuir isotherm for effect of pH on removal of MO dye

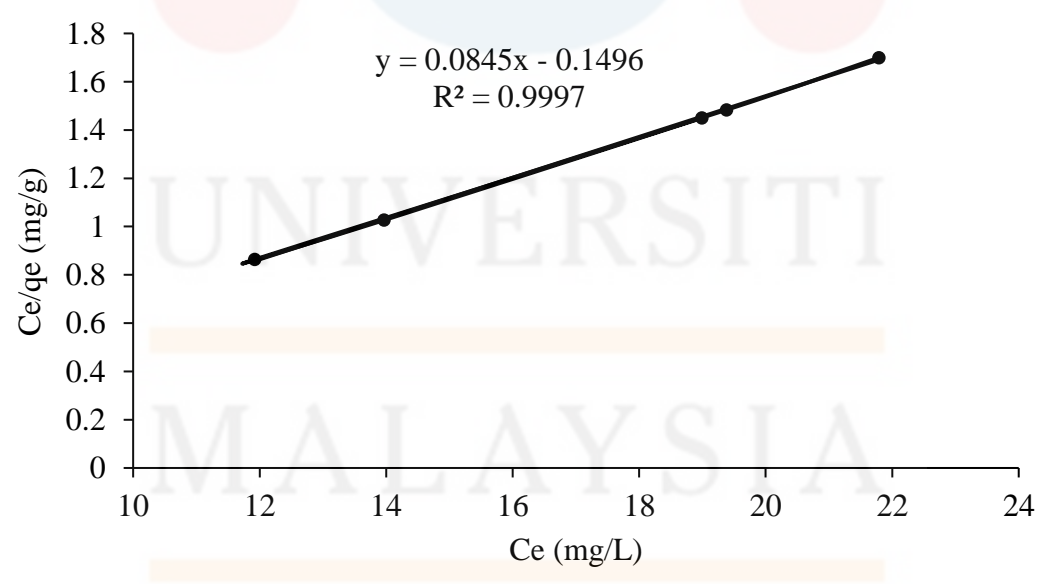


Figure 4.14: Plot of Langmuir isotherm for effect of agitation speed on removal of MO dye

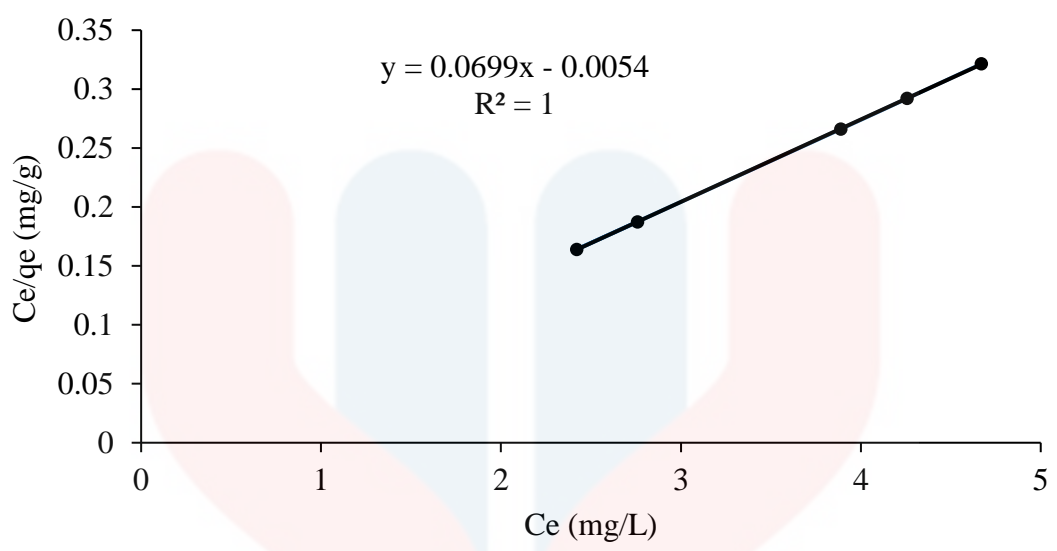


Figure 4.15: Plot of Langmuir isotherm for effect of agitation time on removal of MO dye

Table 4.1: Values of constants for Langmuir adsorption model.

Parameters	q_{max} (mg/g)	K_L (L/mg)	R^2
Adsorbent size	2.9155	-0.0945	1
Adsorbent dosage	2.0812	-0.2054	0.0342
Initial dye concentration	-12.0334	-0.0288	0.6964
Contact time	11.6414	-0.4878	0.9996
pH	-333.33	-0.0264	0.9636
Agitation speed	11.8343	-0.5648	0.9997
Agitation time	14.3062	12.9444	1

The best fit of isotherm was chosen dependent on the highest correlation coefficient (R^2) value (closer to unity) which depicts the fitness of the isotherm to the experimental data. According to Table 4.1, the value of R^2 for parameter adsorbent size and agitation time were 1 respectively. This shows that both of this parameter fit well Langmuir isotherm. The value of q_{\max} and K_L for adsorbent size is -0.0945 L/mg and 2.9155 mg/g, respectively while for agitation time is 12.9444 L/mg and 14.3062 mg/g, respectively. To study the behaviour of adsorption, it can be observed that the K_L value which is the Langmuir constant indicate the strength of adsorption bond. The higher the K_L value, the strong the adsorption bond. In this study, agitation time has higher K_L and q_{\max} value compared to adsorbent size. Hence, agitation time was chosen as the best plot of Langmuir isotherm for removal of MO dye (Aljeboree, Alkaim & Dujaili, 2014).

4.3.2 FREUNDLICH ISOTHERM MODEL

The Freundlich isotherm is an empirical equation predicting the adsorption process occur on a heterogeneous surface sites through a multilayer adsorption mechanism and adsorption capacity is related to the concentration of dye at equilibrium. There are various adsorption-binding sites with different energies of adsorption and some of them are non-identical (Wang et al., 2015). Figure 4.16 represent Freundlich adsorption isotherm on the effect of adsorbent size on the removal of MO dye followed by Figure 4.17, 4.18, 4.19, 4.20, 4.21, 4.22 which represent effect of adsorbent dosage, initial dye concentration, contact time, pH, agitation speed and agitation time, respectively. The values of unknown was obtained by using formula from Equation 3.6 as in section 3.7.4. Through the linear plot of $\log q_e$ versus $\log C_e$ obtained, we can calculate the values of n

and K_f for each parameters by using the intercept. Table 4.2 presents value of equilibrium constants.

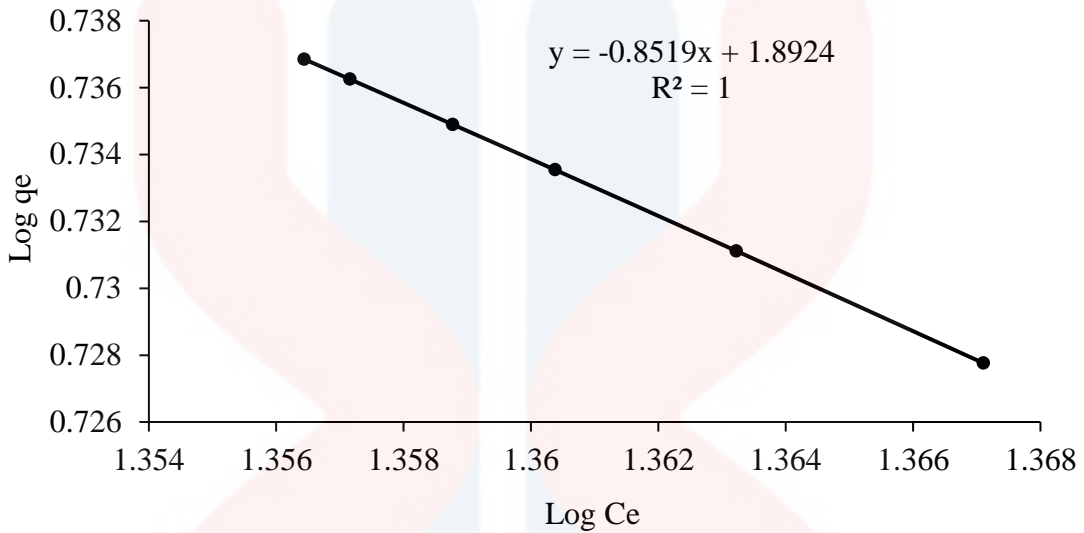


Figure 4.16: Plot of Freundlich isotherm for effect of adsorbent size on removal of MO dye

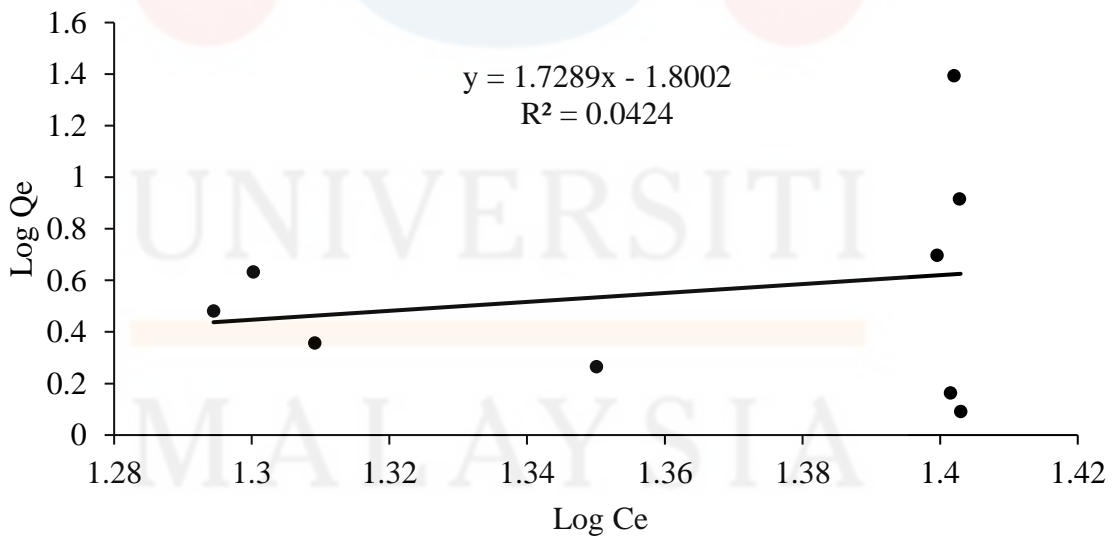


Figure 4.17: Plot of Freundlich isotherm for effect of adsorbent dose on removal of MO dye

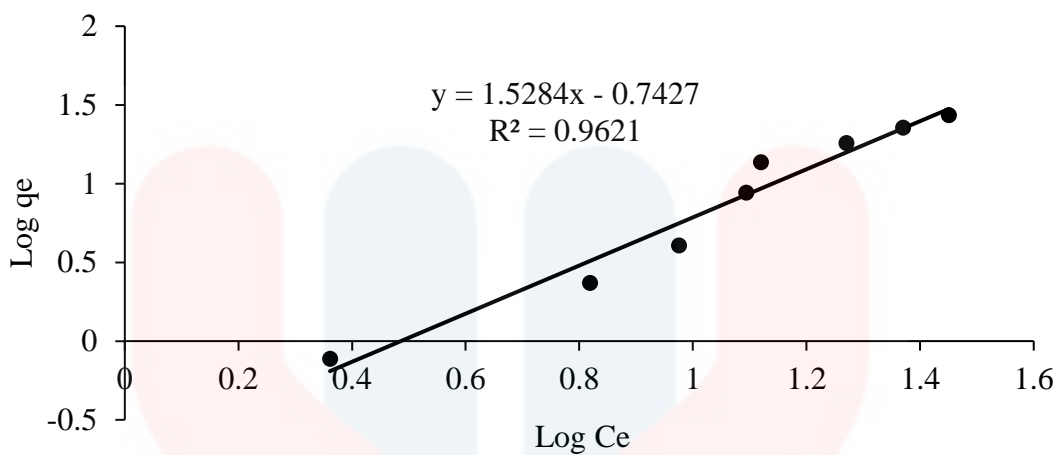


Figure 4.18: Plot of Freundlich isotherm for effect of initial dye concentration on removal of MO dye

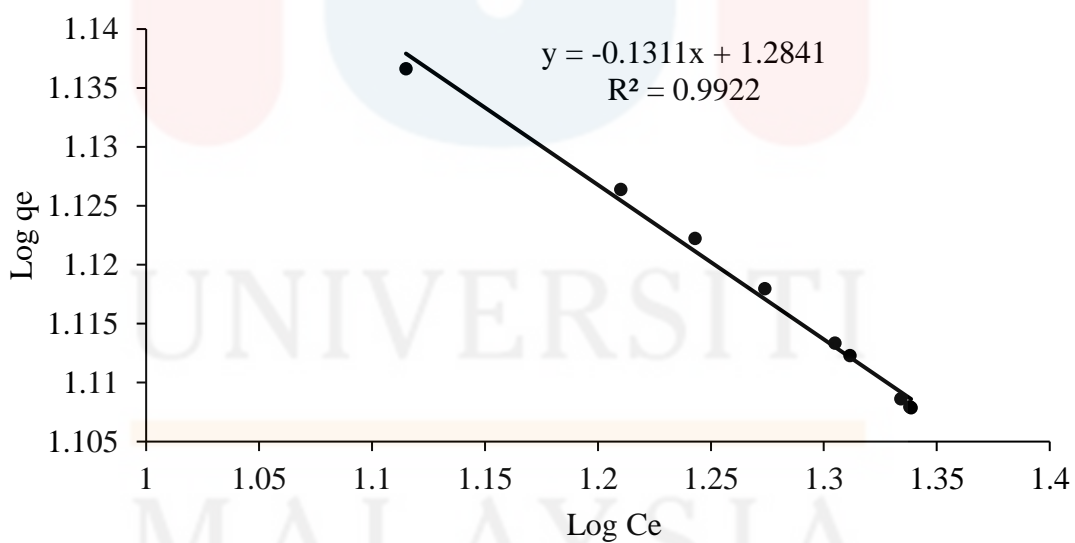


Figure 4.19: Plot of Freundlich isotherm for effect of contact time on removal of MO dye

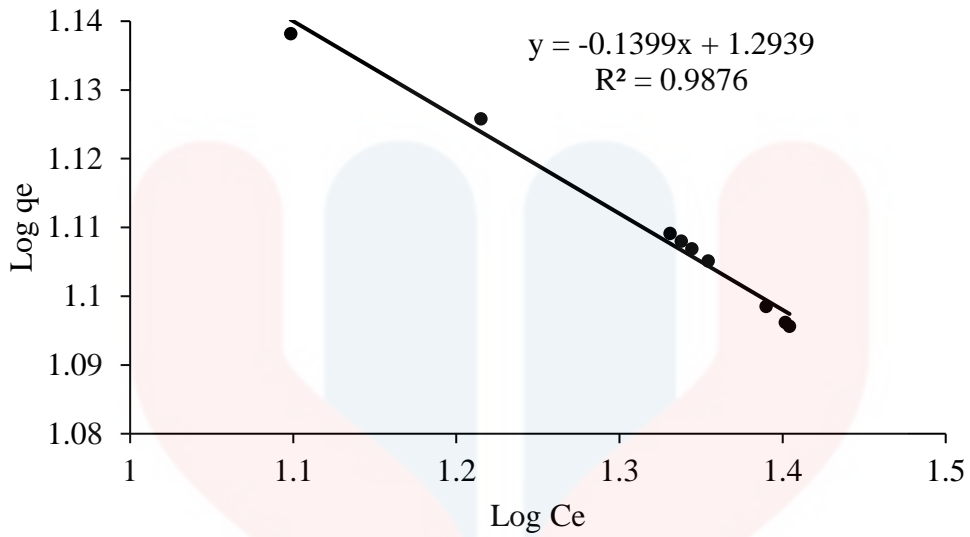


Figure 4.20: Plot of Freundlich isotherm for effect of pH on removal of MO dye

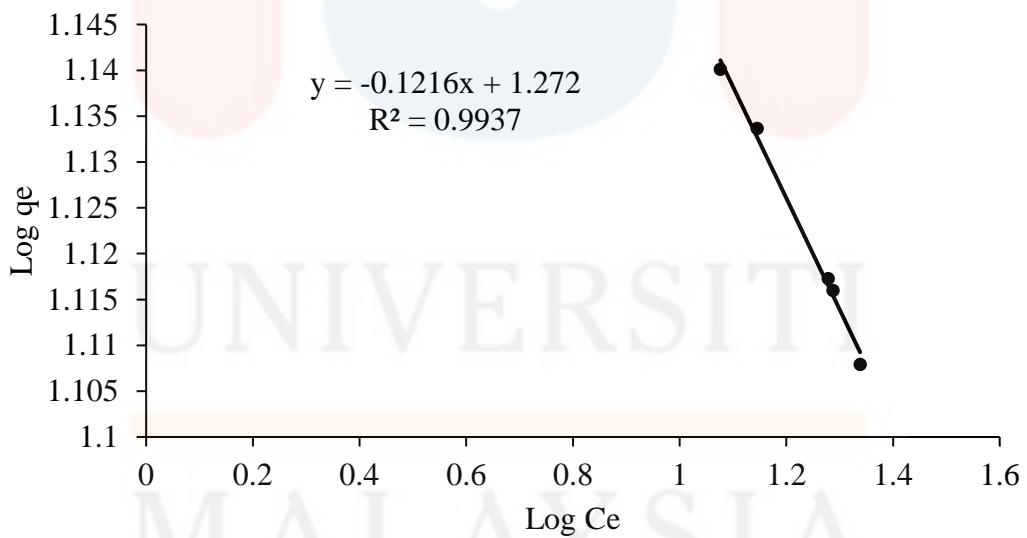


Figure 4.21: Plot of Freundlich isotherm for effect of agitation speed on removal of MO dye

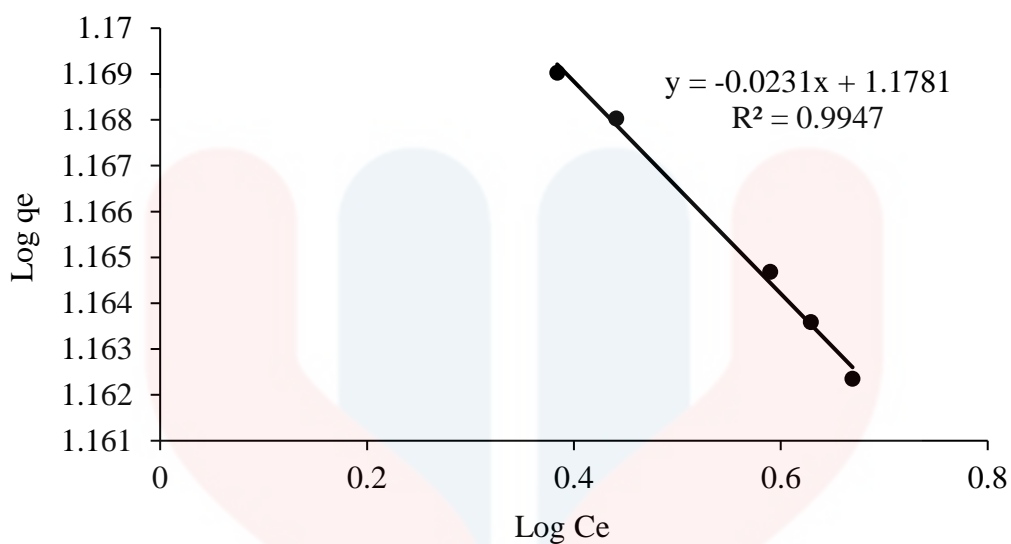


Figure 4.22: Plot of Freundlich isotherm for effect of agitation time on removal of MO dye

Table 4.2: Values of constants for Freundlich adsorption model

Parameters	n	K _f (L/mg)	R ²
Adsorbent size	-1.1738	78.0549	1
Adsorbent dosage	0.5784	0.0158	0.0424
Initial dye concentration	0.6543	0.1808	0.9621
Contact time	-7.6278	19.2353	0.9922
pH	-7.1480	19.6743	0.9876
Agitation speed	-8.2237	18.7068	0.9937
Agitation time	-43.29	15.0695	0.9947

Based on Table 4.2, correlation coefficient, R^2 of agitation time is 0.9947, where the values of n and K_f for agitation time are -43.29 and 15.0695 L/mg respectively. Higher K_f indicates higher maximum capacity. Besides, it can be analysed that the value of n represents the nature of adsorption. The obtained n value was less than one which describes unfavourable adsorption. Generally, $n > 1$ illustrates that adsorbate is favourably adsorbed on an adsorbent. Beside, $1/n$ is a measure of intensity of adsorption which also can be used to analysed the nature of adsorption. If the value of $1/n$ higher, the adsorption is considered as favourable (Aljeboree et al., 2014).

To identify the best isotherm model, a comparison between two isotherms model was made. It obviously can be seen that the correlation coefficient, R^2 of agitation time for Langmuir isotherm model is 1 which is unity compared to the correlation coefficient, R^2 of agitation time in Freundlich model which is 0.9947. Thus, it can be stated that experimental data more suited to Langmuir isotherm compared to Freundlich isotherm model. The Langmuir model was found to represent the isotherm data better which gives 14.3062 mg/g maximum adsorption capacity and Langmuir constant of 12.9444 which is better than Freundlich. By that means, it can be concluded that monolayer adsorption had happen at specific homogenous site of adsorbent in which all adsorption sites are equally probable in this adsorption process. The maximum adsorption capacity of ROS for the removal of MO dye was found to be 14.3062 mg/g. These prove that ROS could be considered as an effective and economical substitute of commercial adsorbent.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

An awareness about environmental protection has been increased globally. These days, the technologies are changing quickly due to industrialisation and its practices that contribute to pollution and producing lot of waste. For the similar mission, potential waste has been proven to be utilised becoming an effective adsorbent for removal of pollutants in environment especially water sources.

Based on the finding, this study has successfully prepared and produced raw oyster shell for adsorption of MO dye. In adsorption study, there were seven parameters that have been conducted. They were adsorbent size, adsorbent dosage, initial dye concentration, contact time, pH, agitation speed and agitation time. Each of these parameters are very important in order to determine and provide the best and optimum condition for adsorption process to take place so that maximum adsorption can be achieved and give out higher percentage of MO dye removal. The highest percentage of MO dye removal in this study was found to be 98.39% that perform well in optimum condition of 75 μm adsorbent size with 1.0 g dose in 150 mg/L initial dye concentration at pH of 3 in 130 rpm agitation speed of orbital shaker at 1 hour. Percentage of MO dye

removal increases along the parameters proving that adsorption efficiency increase as well when the condition for adsorption to take place getting more optimum. Orbital shaker was used to reduce the time consumption during adsorption and it gave positive result when the contact time can be reduced from 3 hours to 1 hour after process of agitation.

Based on the analysis of two different isotherm models, adsorption data follow the orders of Langmuir adsorption isotherm very well which proving that MO adsorption process on ROS was monolayer adsorption that happened at specific homogeneous sites on the adsorbent. The maximum adsorption capacity was found to be 14.3062 mg/g. Linear correlation regression at 1 shows it fits all the equilibrium data into the isotherm model.

There are few recommendations that can be carried out to improve the outcome of this study. Firstly, the oyster shell could be treated with chemical in order to increase the surface area and adding porosity so that adsorption can rapidly occur. For instance, treat the powdered oyster shell to make it slurry by soaking it into 0.1 M H_2SO_4 as acid activate the oyster shell (Olalekan et al., 2016). Besides, the shell can be turn into activated carbon or biochar in order to increase surface area so that adsorption can easily take place. To produce an activated carbon, charcoal undergoes some process to increase the porosity. This will make the activated carbon to have immense surface area which can perform adsorption process as its best. The kinetic properties of activated carbon is associated with particle size and pore structure significantly. There were many studies have been conducted recently that use activated carbon as adsorbent. Wide range of industrial application used activated carbon including wastewater treatment, gas and air cleaning, water filters, chemical purification process and many more (Agrawal, Vairagade & Kedar, 2017).

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APPENDIX



Figure A1: Oyster shells were collected

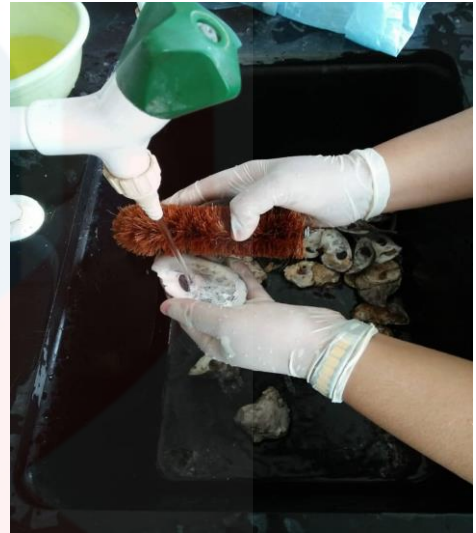


Figure A2: The shells were washed



Figure A3: The shells were sun-dried



Figure A4: Oven-drying



Figure A5: Crushing processing



Figure A6: Grinding process



Figure A7: Powdered oyster shell

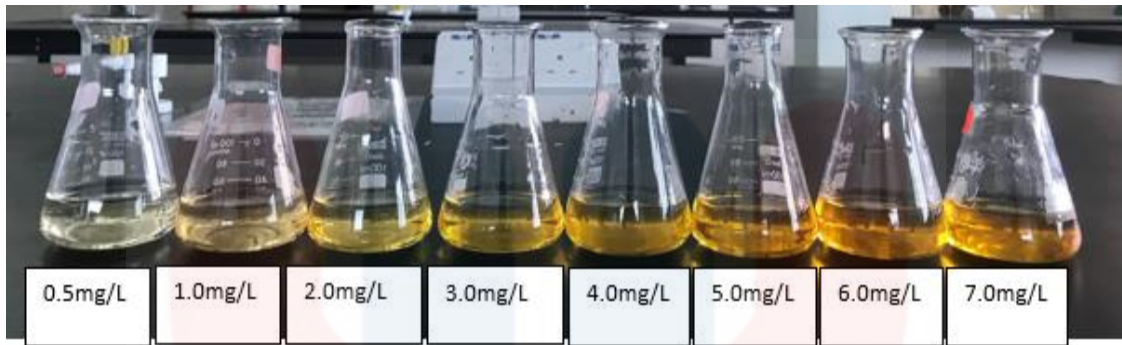


Figure B1: Dilution of Methyl orange for calibration curve

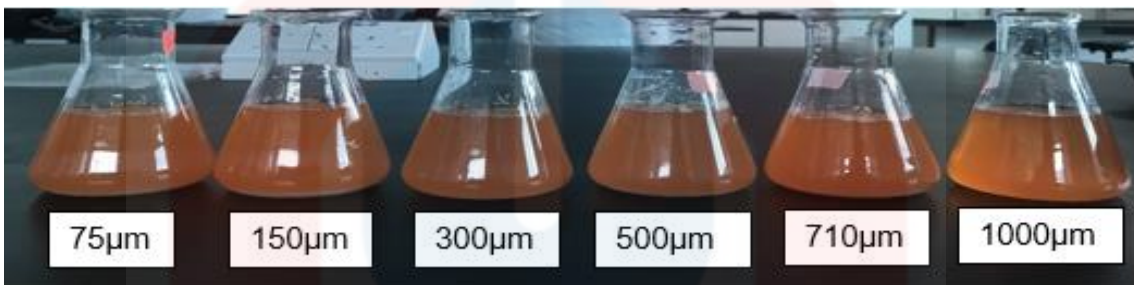


Figure B2: MO dye with different adsorbent sizes before 24 hours



Figure B2(i): MO dye with different adsorbent sizes after 24 hours

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Figure B3: MO dye with different adsorbent dosage before 24 hours



Figure B3(i): MO dye with different adsorbent dosage after 24 hours



Figure B4: MO dye with different initial dye concentration before 24 hours



Figure B4(i): MO dye with different initial dye concentration after 24 hours



Figure B5: MO dye before contact time



Figure B5(i): MO dye after contact time

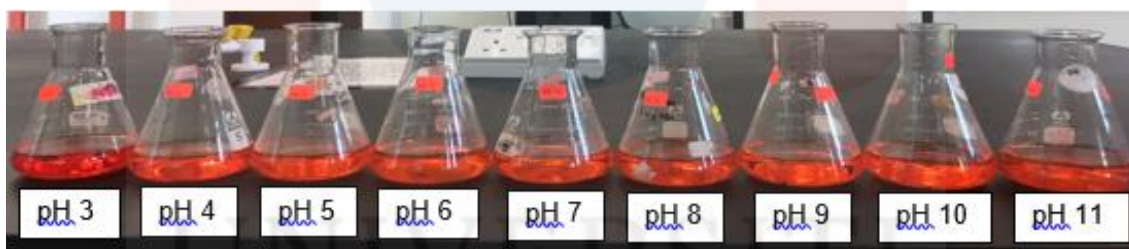


Figure B6: MO dye in different pH solution with adsorbent before 3 hours



Figure B6(i): MO dye in different pH solution with adsorbent after 3 hours



Figure B7: MO dye with adsorbent before put in orbital shaker

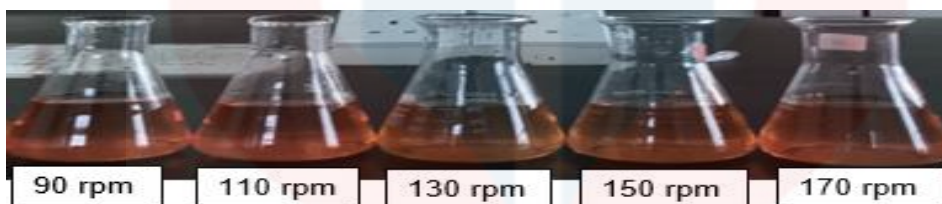


Figure B7(i): MO dye with adsorbent after put in orbital shaker



Figure B8: MO dye with adsorbent before agitation time



Figure B8(i): Colour changes of MO dye with different agitation time at 130 rpm



Figure B9: The colour changes of MO dye after going through membrane filtration

