STUDY OF ADSORPTION OF ACID VIOLET 7 DYE USING MAGNETIC ADSORBENT PREPARED FROM ONION PEEL

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by

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Nur Fauzana Sahul Hamid

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LIST OF SYMBOL

	Symbol	Unit
C_e	Equilibrium concentration of adsorbate	mg/L
C_o	Highest initial adsorbate concentration	mg/L
C_t	Dye concentration at time, t	mg/L
K_1	Adsorption rate constant for the pseudo-first-order kinetic	1/min
K_2	Adsorption rate constant for the pseudo-second-order	g/mg.min
K_F	Freundlich isotherm constant	mg/g $(L/mg)^{1/n}$
K_L	Langmuir adsorption constant	L/mg
W	Mass of adsorbent	g
n	Constant for Freundlich isotherm	-
q_e	Amount of adsorbate adsorbed at equilibrium	mg/g
q_t	Amount of adsorbate adsorbed at time, t	mg/g
Q_0	Maximum adsorption capacity	mg/g
R^2	Correlation coefficient	-
R_L	Separation factor	-
V	Volume of dye solution	L

LIST OF ABBREVIATIONS

AV7	Acid Violet 7
FTIR	Fourier Transform Infrared
OP	Onion peel
MOA	Magnetic onion peel adsorbent
rpm	Rotation per minute
SEM	Scanning electron microscopy
UV-Vis	Ultraviolet visible

KAJIAN PENJERAPAN ASID VIOLET 7 MENGGUNAKAN PENJERAP MAGNETIK DISEDIAKAN DARIPADA KULIT BAWANG

ABSTRAK

Biojisim magnet berliang merupakan bahan mesra alam penyahtoksik yang lebih cekap bila digunakan untuk membuang pewarna dan logam berat daripada larutan akueus. Penjerapan asid violet 7 (AV7) oleh penjerap magnetik kulit bawang merah (PMKBM) telah dikaji dalam proses kelompok. Kulit bawang merah (KBM) telah menjalani proses magnetik, dimana KBM telah direndam dalam larutan 1.0 mol/L besi (III) klorida hexahidrat dan dikacau selama lapan jam bagi menghasilkan PMKBM. Ciri-ciri fizikal dan kimia bagi PMKBM telah disiasat menggunakan spektrometer inframerah pengubahan Fourier (FTIR). PMKBM mengandungi kumpulan berfungsi logam oksida, kumpulan Si-O-Si, bengkok C-C dan benzena. Kesan kepekatan awal pewarna (20-150mg/L), masa kacau (0-60 minit), dos penjerap (0.2-1.5 g) dan kelajuan penggoncang (50-250 rpm) turut telah dinilai. Didapati bahawa model Langmuir adalah paling berpadanan untuk data garis sesuhu AV7 diterkapasiti penjerapan monolapisan 3.03 mg/g. Manakala, untuk analisa kinetik, didapati bahawa model pseudo-tertib-pertama adalah paling sesuai digunakan untuk menentukan mekanisme penjerapan AV7.

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STUDY OF ADSORPTION OF ACID VIOLET 7 DYE USING MAGNETIC ADSORBENT PREPARED FROM ONION PEEL

ABSTRACT

Magnetized porous biomass is an eco-friendly detoxification material which is highly efficient when used to remove dye and heavy metals from aqueous solutions. The adsorption of acid violet 7 (AV7) dye onto magnetic onion peel adsorbent (MOA) were investigated in a batch process. Onion peel (OP) undergoes magnetic process, where the OP was soaked into 1.0 mol/L Iron(III) chloride hexahydrate solution and stirred for eight hours to prepared MOA. The physical and chemical properties of MOA was investigated using Fourier transform infrared spectroscopy (FTIR). The MOA contained of metal oxide group, Si-O-Si group, C-C bending and benzene functional group. The effect of initial dye concentration (20-150mg/L), agitation time (0-60 minutes), adsorbent dosage (0.2-1.5 g) and shaker speed (50-300 rpm) were also evaluated through. The obtained equilibrium data for MB dye was best fitted by Langmuir model with monolayer adsorption capacity of 3.03 mg/g. Meanwhile, the kinetics data was best represented by the pseudo first-order model.

CHAPTER ONE

INTRODUCTION

1.1 Project Background

The increasing contamination of the environment is the main factor lead to environmental pollution such as air pollution, water pollution and soil pollution. Among the types of pollution, water pollution is the most important source that need to take care. Water is polluted by a variety of organic, inorganic, and biological pollutant around the world because of industries and urban life. Heavy metals and dyes are well known as water pollutants which are highly toxic, carcinogenetic and hazard. Wastewater producing from the industries are release without any treatment can cause the aquatic life die and the water no longer safe for human body and other living.

Adsorption is defined as the deposition of molecular species onto the surface of the adsorbent. The molecular species that gets adsorbed on the surface is known as adsorbate and adsorbent is the surface on which adsorption occurs. Adsorption is a spontaneous process at constant pressure and temperature. The Adsorbents Market report covers the major global markets including molecular sieves, activated carbon, silica gel, activated alumina and clay. It further divides the market on the basis of types, applications, and geography. The major material types within this market are molecular sieves and activated carbon (Dallas, 2014). The industry demands for adsorbents with larger surface area, high adsorption capacity and better service life. Adsorbents are the key materials used across different industries, such as oil and gas, water treatment, pharmaceutical, chemicals and petrochemicals.

Adsorption is widely used in removal of heavy metal and dyes from wastewater releasing by various sources and industries. Synthesized adsorbent using biomass or solid waste is more cheaper and eco-friendly. In this study, onion waste is used as the raw material is modified to form a magnetic onion peel adsorbent (MOA).

1.2 Problem Statement

Dyes are coloured compounds which are widely used in textiles, printing, rubber, cosmetics, plastics, leather industries to colour their products results in generating a plenty amount of coloured wastewater. Commercially, more than 10,000 dyes are available with over 7×10^5 tonnes of dye stuff produced per year. Among various industries, textile industry ranks first in usage of dyes for colouration of fiber. Consequently, the amount of dyes discharged into waste stream by the textile industry worldwide are 1,000 tonnes per year or more (Marc et al, 1996).

Dyes has an adverse effect on all forms of life because of presence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, enzymes chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals all collectively make the textile effluent highly toxic (Kant, 2012). Discharged of wastewater contains of dyes into the natural streams cause the water pollution as dyes are soluble in water and produce very bright colours in water with acidic properties. Dyes absorb and reflect sunlight entering water and so can interfere with the growth of bacteria and hinder photosynthesis in aquatic plants which effect to the aquatic life, food web and human health. Therefore, various treatment systems have been accomplished to remove the dyes from wastewater before discharged to natural stream (Bharathi et al, 2013).

Adsorption is one of the treatment system to remove this component. Adsorption process is more efficient than other processes such as coagulation, oxidation and extraction. Moreover, magnetic adsorbent are simple to prepare, easy to produce from the waste biomass and it is cheap.

In this study, onion peel was modified as magnetic sorbent to remove acid violet 7 (AV 7) containing of wastewater. Onion peel is one of solid waste that produced from food processing industries and food seller where most of food in Malaysia use onion as their main ingredient. The amount of waste biomass that need to decompose can be reduced by convert it to a valuable material which will be a benefits for others. Therefore, this research will focus on the adsorption capability of magnetic sorbent prepared from onion peel as the raw material to remove AV 7.

In this study, the variables affecting the adsorption are focuses on the dye by adjust the concentration of dye, dosage of MOA, time and speed of shaker which should give an optimum adsorption result.

1.3 Research Objective

The objectives of this work are:

1. To study the adsorption removal of Acid Violet 7 (AV 7) dye by magnetic onion peel adsorbent (MOA).
2. To study the effect of MOA dosage, dye concentration, agitation time and speed variables on the adsorption of AV 7 dye by MOA.
3. To study the adsorption isotherm and kinetic model of MOA.

1.4 Scope of Research

This research focuses on the adsorption of AV 7 dye in wastewater using a type of adsorbent know as magnetic adsorbent prepared from onion peel and iron (III) chloride hexahydrate. Study about some parameters that will affect the dye adsorption. The parameters that involve are dye concentration, MOA dosage, agitation speed and time. Besides, study the characterization of the MOA and spent MOA using scanning electron microscopy (SEM), elemental analysis, Fourier transform infrared (FT-IR) and Ultraviolet–visible spectrophotometer (UV-Vis spectrophotometer). Besides, study about isotherm and kinetic studies, where for isotherm study using Langmuir and Freundlich isotherm to simulate the data and for kinetic using pseudo-first-order and pseudo-second-order model to evaluate the adsorption mechanism.

CHAPTER TWO

LITERATURE REVIEW

2.1 Dye

Dyes are coloured compounds which are widely used in textiles, printing, rubber, cosmetics, plastics, leather industries to colour their products results in generating a plenty amount of coloured wastewater. Wastewater containing dyes and heavy metal need to undergo pre-treatment before release to natural streams. This is because, in dyes presence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, enzymes chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals all collectively make the wastewater contaminated and highly toxic (Kant, 2012).

Acid violet 7 (AV 7) is a type dye used mainly in laboratory and dying industries. Commonly it used for wool, silk, polyamide fibre and leather, paper, soap, wood, medicine and cosmetics of dyeing, can also be used for the biological dyeing. AV 7 where it IUPAC name is 5-(Acetylamino)-3-[[4-(acetylamino) phenyl] azo]-4-hydroxy-2,7- naphthalenedisulfonic acid disodium salt. AV 7 dye is a sulfonated azo dye with molecular formula $C_{20}H_{16}N_4Na_2O_9S_2$ with molecular weight 566.47 g/mol. In visible light wavelength, violet has the shortest wavelength which is 380 nanometer. AV 7 dye is an raddishorange and odourless powder at room temperature and turn in dark red or orange solution when dissolved in water. It also slightly soluble in ethanol, acetone and soluble fibre element but insoluble in other organic solvents.

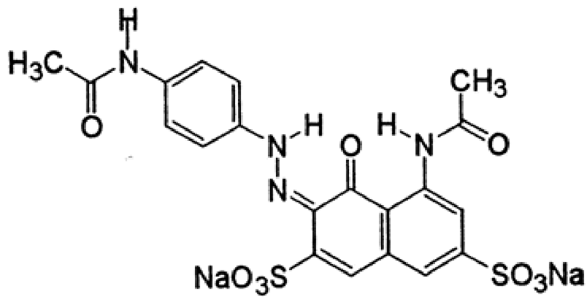

Figure 2.1: Structure formula of Acid Violet 7

AV 7 dye also has adverse effects on human health. It may be harmful to gastrointestinal causing muscle weakness and ataxia if accidentally swallowed the material. Beside, the dye also can cause eye irritation and lacrimation. AV 7 dye can causes skin irritation if absorbed by skin and respiratory tract irritation if inhaled. Moreover, causes chronic health effect which is cancer because of long term exposure of dye by inhalation, ingestion and absorbed on skin.

2.2 Adsorption

Adsorption is one of the treatment system that have been developed to remove colour and toxic from dye wastewaters. The advantages of adsorption process are possible regeneration at low cost, availability of known process equipment, sludge-free operation and recovery of the adsorbate (Kapdan and Kargi, 2002). Adsorption on commercial activated carbon is a very effective removal technique which produces effluents containing very low levels of dissolved organic compounds but it so expensive (Thio et al, 2017). Therefore, researchers come out with new adsorbent, magnetic separation which is more cheaper and efficient to removed dye in wastewater (Hameed, 2009).

Magnetized porous biomass is an eco-friendly material which is highly efficient to removed dyes from wastewater (Lingamdinne et al, 2016). Magnetized sorbent (MS) are excellent adsorbent for adsorption process. It is already widely used for removal of pollutants in water such as heavy metal ions and dyes. The main advantages of this technology consists in its capacity of treating large amount of wastewater within a short time and producing less contamination (Indira et al, 2010).

The practice of using conventional materials for dye removal in wastewater treatment has become a major concern for researchers in line with their environmental impact. The use of toxic materials in removal process contributed to the secondary pollution problems especially from their by-products. Researchers are always in a hunt for developing more suitable, efficient, cheap and easily available types of adsorbents, particularly from the waste materials. Agricultural waste materials have little or no economic value and often pose a disposal problem. The utilization of agricultural waste is of great significance (Paul et al, 1980).

There are many of researcher had studied on the efficiency of an adsorbent in removing of dyes and heavy metals. For example, synthesized a magnetic Fe_3O_4 core-shell (MFC) sorbent to enhance the efficiency of phosphate removal by phosphorus accumulating organisms (PAOs) (Liu, 2018), chitosan was cross-linked using glutaraldehyde in the presence of magnetite adsorbent was prepared for removal of Mo(VI) as molybdate anions from aqueous solution (Elwakeel et al, 2009), biochars derived from potassium (K)-rich feedstock such as banana peels and cauliflower leaves to remove heavy metal like copper (Cu(II)), cadmium (Cd(II)) and lead (Pb(II)) (Ahmad, 2018), MnO_x-coated rice straw biochar was synthesized through the reaction of rice straw biochar with $KMnO_4$ in aqueous solution, where it focused mainly on the evaluation of the sorbents for Pb(II) binding (Tan et al, 2018) and biosorbents from different fruit waste such as tomato waste and apple juice residue were prepared for removing of Pb(II) ion from the aqueous solution under optimized conditions (Heraldy et al, 2018).

Other than adsorption, there many more methods have been used for dyes removal, example, coagulation, oxidation, ion exchange and membrane. Coagulation is a chemical solution treatment technique typically applied prior to sedimentation and filtration to enhance the ability of a treatment process to remove particles. In coagulation, a chemical such as alum which produces positive charges was added to neutralize the negative charges on the particles in the wastewater. Then the particles will attracted to each other and stick together, forming larger particles which are more easily removed. Several type of chemical have been used for the coagulation recovery of dyes in wastewater (Sadri et al, 2010; Wen et al, 2007; Kasperchik et al, 2012).

Ion exchange is a specific chemical process in which unwanted dissolved ions such as magnesium are exchanged with other ions with a similar charge. The exchange process occurs between a solid (resin) and a liquid (water). In the process, the less desired compounds are swapped for those that are considered more desirable. These desirable ions are loaded onto the resin material. In the exchange of cations during water treatment, positively charged ions that come into contact with the ion exchange resin are exchanged with positively charged ions available on the resin surface and vice versa for anions exchange. Researcher used several types of ion exchange resin for dyes removal method in their study like used two anion exchangers, strong basic S6328a and weakly basic MP62 to remove dye (Karcher et al, 2002), used three anion exchange resins, weakly basic (Lewatit MonoPlus MP 62), intermediate (Lewatit MonoPlus MP

64), and strongly basic (Lewatit MonoPlus MP 500) for removal of Acid Orange 7 from the aqueous solutions and wastewater (Wawrzkiewicz, 2012), and used of two macroporous cation exchange resins, strongly acidic Purolite C145 and weakly acidic Purolite C107E to remove the dye Basic Blue 9 from an aqueous medium (Suteu et al, 2013).

2.3 Solid Waste

Onion is the largest production after the tomato with current annual production around 66 million tonnes. Over the past 10 years, onion production has increased by more than 25%. Lately, the demand for processed onions has been increase which has lead to an increase in waste production. Accordingly more than 500,000 tonnes of onion waste are produced annually in the European Union, mainly from Spain, UK and Holland. This is not included the waste produced in Asia, where most of the countries used onion as their main ingredient.

Onion waste present an environmental problem, since onion wastes are unsuitable for fodder in high concentrations neither organic fertilizer, because of onions strong aroma and rapid development of pungent chemical (Waldron, 2001). Therefore, in this study an adsorbent was synthesized by onion peel to remove dyes from wastewater and at same time to reduce the amount of onion wastes for disposal. Onion composition is variable and depends on cultivar, stage of maturation, environment, agronomic conditions, storage time and bulb section. Weight of onion contain of water, non-structural carbohydrates which include glucose, fructose and sucrose.

2.4 Batch Studies

Parameter study that involved four variable affecting the adsorption process, they are dye concentration, dosage of adsorbent which is known as MOA, time of agitation and speed of controlled shaker. Etim et al (2016) reported that the removal efficiency increase with the dosage of adsorbent. Besides, the removal efficiency decrease as the initial dye concentration increase (Etim et al, 2016; Megat et al, 2015)

Besides, isotherm study using linear Langmuir and Freundlich isotherm to simulate the experimental adsorption data. The obtained kinetic experimental data for the AV 7 was correlated using pseudo-first-order and pseudo-second-order kinetic model to evaluate the adsorption mechanism (Lingamdinne et al, 2016). The knowledge regarding adsorption kinetic can be studied in terms of the order of the rate constant (Gomez et al, 2007). Lodeiro et al (2006) reported that pseudo-first order model is similar to the diffusion expression attained for the case of diffusion through a boundary liquid film. Most researcher result shows the Freundlich adsorption isotherm and pseudo-second order kinetic model fitted the data better than Langmuir isotherm and pseudo-first order (Lingamdinne et al, 2016; Etim et al, 2016; Khattak et al, 2017).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Research Methodology Step

The overall experimental activities carried out in this study are presented in Figure 3.1.

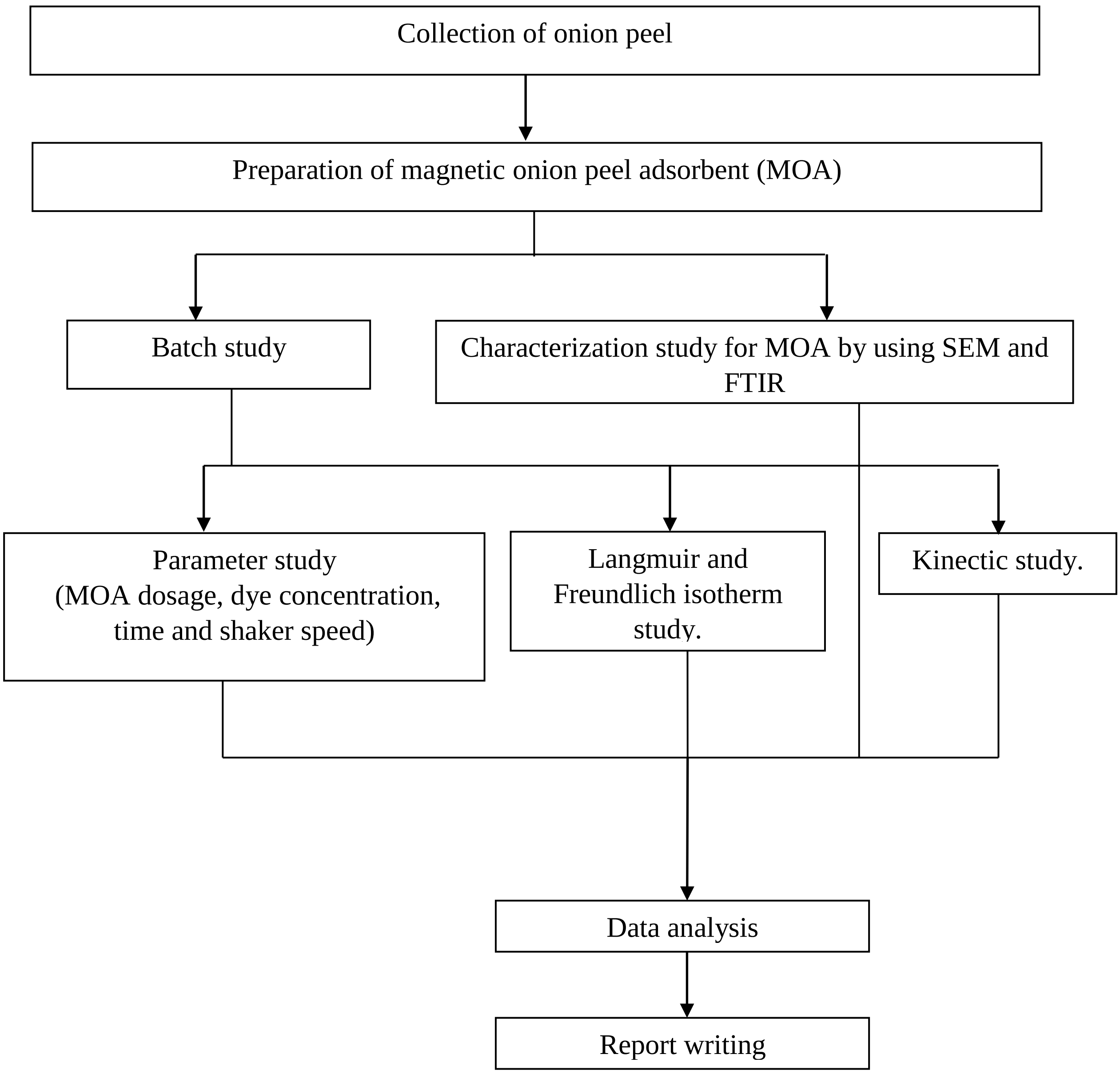

Figure 3.1: Schematic flow diagrams of experimental activities.

3.2 Preparation of MOA

Onion peel are collected from food seller around Parit Buntar, Perak, Malaysia area. The onion was washed with deionised water in order to clean it from any impurities. It was cut in small size, dried and then ground it to fine powder. Then boil the onion peel to remove the colour compound. Onion peel was collected by filtration and put into 1.0 mol/L Iron(III) chloride hexahydrate solution. The onion peel was soak and stirred for eight hours for magnetization process. After that, the magnetized onion peel was separated using external magnet. The magnetized onion peel was washed with distilled water and dried in vacuum oven at 45^0C, the resultant product know as magnetic onion peel adsorbent (MOA).

3.3 Preparation of AV7 Dye Solution

A stock solution of 1000 mg/L AV 7 was prepared each time adsorption experiment were conducted. A mass of 0.25 g AV 7 was dissolved in a 250 mL beaker with distilled water before transfer into a 500 mL volumetric flask. The stock solution was then diluted to 100 mg/L which are analyzed using UV-VIS Spectrophotometer.

3.4 Batch Studies

In general, adsorption experiments were done by adding 0.2 g of MOA into 25 mL AV 7 solutions in 100 mL beakers with different initial concentrations. The mixture was agitated using controlled shaker at specific time, speed 250 rpm and temperature

30^0C. After adsorption, the solutions are filtered and filtrates were analysed by using a UV-VIS Spectrophotometer. The effect of the shaker speed on adsorption of AV 7 at constant MOA dosage, shaking time, dye concentration are carried out in the speed range of 50 -300 rpm. The effect of adsorbent dosage was evaluated by varying the initial weight of MOA in the range of 0.2-1.5 g.

The percentage removal (%) of AV 7 was calculated by using Equation 3.1:

$$\text{Removal (\%)} = \frac{(C_o - C_e)}{C_o} \times 100 \tag{3.1}$$

where *Co* is the initial concentration of AV 7 (mg/L) and *Ce* is the final concentration of AV 7 (mg/L). For kinetics study and effect of agitation time, a weight of 0.2 g of MOA was added into 25 mL (100 mg/L) AV 7 solutions. The initial pH of AV 7 was fixed at pH 4 and agitated at different time intervals (0-60 min).

The amount of AV 7 adsorbed, q_e (mg/g) was calculated by using Equation 3.2:

$$q_e = \frac{(C_o - C_e)V}{w} \tag{3.2}$$

where *Co* and *Ce* are the concentrations of AV 7 before and after adsorption (mg/L), respectively. *V* is the volume of AV 7 used (L) and w is the weight of the MOA (g). Each adsorption experiment was conducted until a steady-state reached.

3.5 Adsorption Isotherm and Kinetic Studies

Langmuir and Freundlich are used to fit the experimental data. The best-fitted isotherm can be determined through the value of correlation coefficient; R^2 which is closest to the unity. The Langmuir isotherms were employed to simulate the experimental data which expressed as Equation 3.3:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{K_L\, Q_0} \tag{3.3}$$

where Q_0 (mg/g) is the maximum adsorption of AV 7 and K_L is the Langmuir equilibrium constant. The Q_0 and K_L can be determined by plotting graph C_e/q_e against C_e.

The Freundlich isotherm as Equation 3.4:

$$\log q_e = \frac{\log C_e}{n} + \log K_F \tag{3.4}$$

Here the K_F and n are the Freundlich equilibrium constant. The K_F and n value can be determined by plotting graph log q_e against log C_e.

For kinetic studies, pseudo-first-order and pseudo-second-order models are used in this study. By applying the above models, the correlation coefficient, R^2 can be determined (Megat, 2015). The pseudo-first-order and pseudo-second-order are expressed in Equation 3.5 and 3.6 respectively:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \tag{3.5}$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2\, {q_e}^2} \tag{3.6}$$

where the K_1 and K_2 are the rate constant of the pseudo-first and second-order.

3.6 Characterization and Analysis.

The characterization is focused on quantitative analysis using elemental analysis, qualitative using FTIR and optical using SEM in order identify the morphology (texture) and pore structure and active sites of MOA. All of the analysis are carried out at School of Chemical Engineering, Universiti Sains Malaysia.

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometer (UV-Vis) refers to adsorption spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. UV-Vis spectrophotometer is used in the quantitative determination of concentrations of the adsorbate in the solutions of transition metal ions and highly conjugated organic compounds.

The scanning electron microscope (SEM) use a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology, chemical composition, and crystalline structure and orientation of materials making up the sample. Application of the SEM is used to generate high-resolution images of shapes of objects (SEI) and to show spatial variations in chemical compositions, acquiring elemental maps or spot chemical analyses using Energy-Dispersive X-Ray Spectroscopy (EDX). The SEM is also widely used to identify phases based on qualitative chemical analysis and/or crystalline structure (Swapp).

Elemental analysis is the measurement of certain elements (typically a weight percent) within a sample. Elemental analysis can be measured qualitatively and quantitatively. Qualitative analysis determine which elements exist in a sample such as carbon and hydrogen. While, quantitative analysis is the determination of the atom or weight percentage of each element present. A variety of techniques used for this purpose, including mass spectrometry, X-ray fluorescence spectrometry, atomic absorption, inductively coupled plasma techniques, and instrumental neutron activation analysis. There are also many different experiments for determining elemental composition. The most common type of elemental analysis is for carbon, hydrogen, and nitrogen (CHN analysis).

Fourier Transform Infrared Spectroscopy, also known as FTIR Analysis or FTIR Spectroscopy, is an analytical technique used to identify organic, polymeric, and inorganic materials. FTIR spectroscopy is a technique that is used to find an infrared spectrum of absorption, emission or photoconductivity of solid, liquid or gas. The FTIR analysis method uses infrared light to scan test samples and observe chemical properties. This technique is used to assess a sample purity and is highly reliable to determine base polymer composition, additives, and organic contaminants. FTIR analysis is crucial in analyzing structure and composition information on the functional groups present in the samples. The functional groups present in the samples were investigated using FTIR spectroscopy.

CHAPTER FOUR

RESULT AND DISCUSSION

4.1 Experimental Design.

4.1.1 Standard Curve

Standard curve also known as calibration curve is a general method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of known concentration. Figure 4.1 shows the calibration curve of absorbance against AV7 dye concentration. The absorbance increased with an increase in AV7 dye concentration. The absorbance was measured at different AV7 dye concentration in the range of 50 mg/L to 250 mg/L. The absorbance high at 0.942, when the concentration of AV7 dye high at 200 mg/L. This relationship shows, absorbance are directly proportional to the concentration of AV7 dye. Hence, the absorbance of AV7 dye was highly depended on the concentration of AV7 dye. The calibration curve was plotted to determine the final concentration of AV7 dye regarding to the absorbance of the dye after it immersed with MOA.

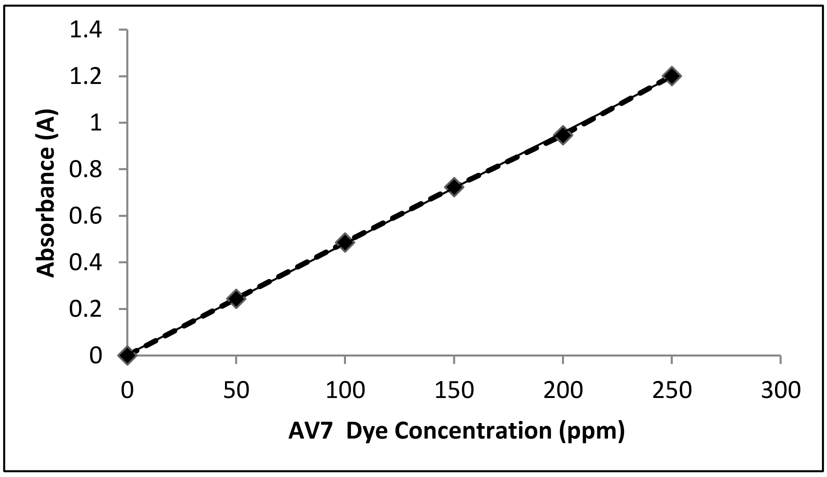

Figure 4.1: Calibration curve for AV7

4.1.2 Effect of Agitation Time

Agitation time is one of the parameter that investigated in this study. It was investigated with constant MOA dosage, initial AV7 dye concentration and shaker speed at 0.2g, 100 mg/L and 250 rpm respectively. The amount of AV7 dye adsorbed was found to increase with the agitation time before attaining equilibrium as shown in Figure 4.2. At initial 30 minutes, the adsorption process was rapid then become slowly until it closely approached equilibrium. This was due to the large number of active sites available for adsorption process at initial stage. As the agitation time longer, it become difficult for the AV7 dye to occupy the remaining number of active sites because of the repulsive force between solute molecules on the MOA and the aqueous phases, thus the adsorbance capacity of dye become consistent (Lingamdinne et al., 2016). Besides, it consist of two phases, which know as an initial rapid phase and a slow second phase (Megat et al, 2015). The initial phase occurred rapidly was related to exterior surface adsorption. The second phase was steady state before the adsorption achieved equilibrium.

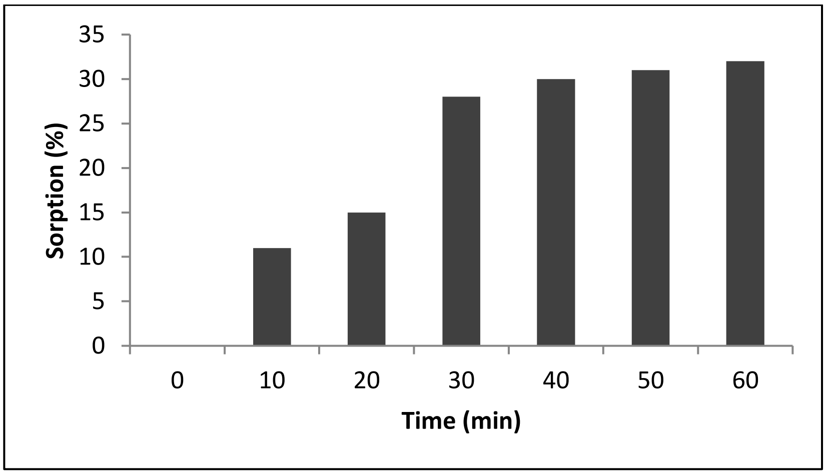

Figure 4.2: Effect of the agitation time on the sorption removal of AV7 dye by MOA

4.1.3 Effect of Shaker Speed

Speed of shaker is important in order to get the effective mixing rate for higher removal efficiency. The effect of shaker speed on the adsorption of AV7 was investigated by fixed other parameters like MOA dosage, initial AV7 dye concentration and agitation time at 0.2 g, 100 mg/L and 20 minutes respectively. Figure 4.3 shows, the dye removal was rapid before 100 rpm but become relatively slow until speed 250 rpm then suddenly at 300 rpm the removal decreased to 12.3%. This was due to the higher speed of shaker that produced vortex which reduced the contact efficiency between adsorbate and adsorbent thus difficult for the dye to occupy the vacant surface site of MOA. The optimum removal efficiency of AV7 dye was determined at speed 250 rpm. Hence, further investigations was carried out at shaker speed of 250 rpm.

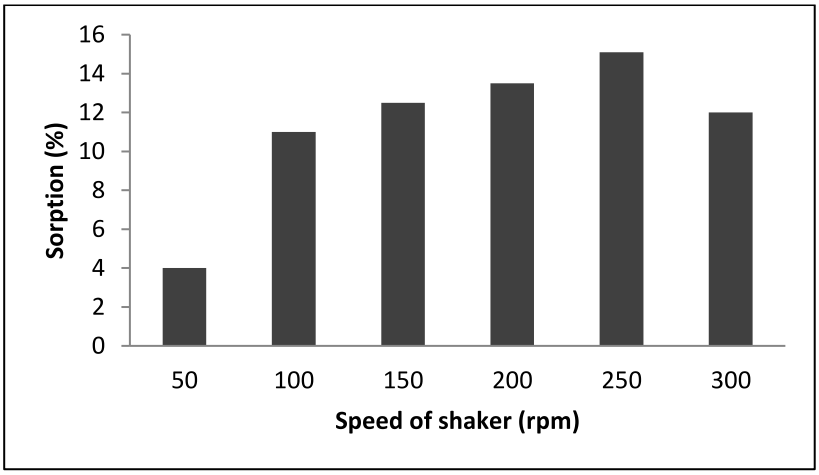

Figure 4.3: Effect of the shaker speed on sorption removal of AV7 dye by MOA

4.1.4 Effect of MOA Dosage.

The adsorbent dose is an important parameter in this study because it determines the capacity of adsorbent for a given initial concentration of dye solution. The effect of MOA dosages 0.2 g, 0.4 g, 0.6 g, 0.8 g, 1.0 g and 1.5 g on the adsorption of AV7 was investigated by contacting 25 mL of AV7 dye solution with an initial AV7 dye concentration of 100 mg/L, for 20 minutes of agitation time and shaker speed of 250 rpm. The sorption removal of AV7 dye increased with the MOA dosages up to 1.0 g MOA as shown in Figure 4.4. due to the availability of active site on MOA (Etim et al, 2016; SenthilKumar et al, 2010). The optimum removal efficiency for AV7 was determined at MOA dosage of 1.0g, at which the sorption removal of AV7 is 62%. While, at 1.5g of MOA the sorption removal decrease due to the excess impurities leave in the filtrate after the adsorption.

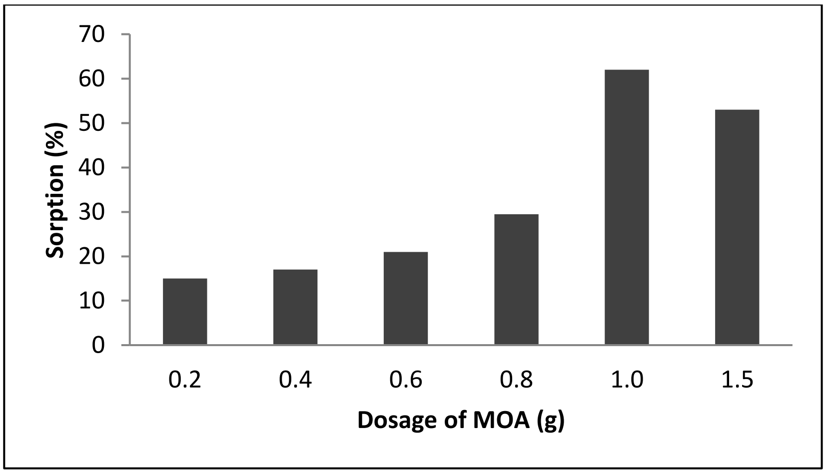

Figure 4.4: Effect of MOA dosage on sorption removal of AV7 dye

4.1.5 Effect of Initial AV7 Dye Concentration

Initial amount of AV7 dye concentration will highly effect the removal percentage of dye. The effect was depends on the relation of the dye concentration and the available active sites on an adsorbent surface. The effect of initial AV7 dye concentration was studied with different concentration of dye which are 20, 40, 60, 80, 100 and 150 mg/L with constant MOA dosage of 0.2 g, agitation time for 20 minutes and shaker speed of 250 rpm. The sorption removal of AV7 decreased with an increase in initial AV7 dye concentration as shown in Figure 4.5. This is because as the initial dye concentration increased, the available active sites are decreasing, due to increase in the loading capacity of the adsorbent which made the adsorbent surface saturated.

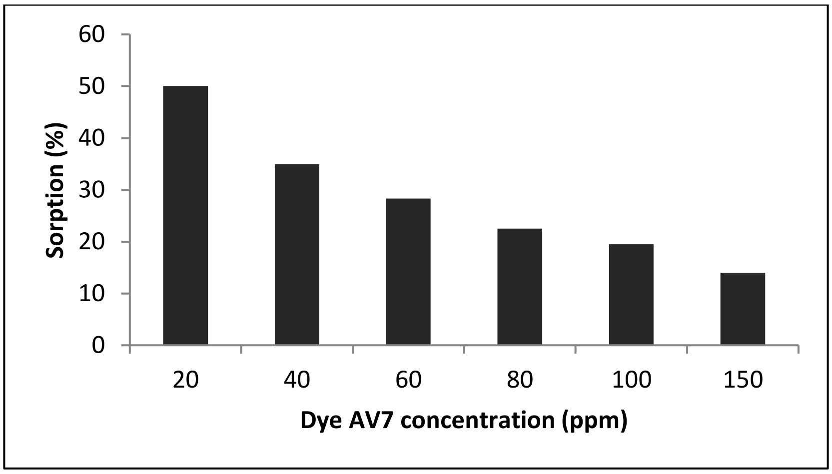

Figure 4.5: Effect of initial AV7 dye concentration on sorption removal of AV7 dye by MOA

4.2 Adsorption Isotherms Studies

Adsorption isotherm provides important models in the description of adsorption behaviour. It describes how the adsorbate interacts with the adsorbent and offers explanation for the mechanism of the adsorption process. When the adsorption reaction reaches equilibrium state, the adsorption isotherm can indicate the distribution of adsorbate molecules between the solid phase and the liquid phase (Tan et al, 2008). Information on adsorption mechanism and surface properties of an adsorbent can be obtained from different models of isotherm. Therefore, Langmuir and Freundlich model are used to investigate the behaviour of MOA for AV7 adsorption. The adsorption isotherm was studied at different initial AV7 concentration in the range of 50 mg/l to 200 mg/l at room temperature and within 30 minutes.

4.2.1 Langmuir Isotherm

The Langmuir isotherm constants, Q_0 and K_L are determined from the slope and intercept of the linear curve of C_e/q_e against C_e as listed in Table 4.1. From Table 4.1, the correlation coefficient, R^2 value obtained for Langmuir isotherm model (0.9991) is higher than Freundlich. The Langmuir isotherm model fitted the data better compared to Freundlich isotherm model with monolayer adsorption capacity of 3.034 mg/g. The value of separation factor, R_L, 0.868, indicates the adsorption of AV7 onto MOA was favourable. The adsorption occurs at specific homogenous sites within the MOA which knows as monolayer adsorption.

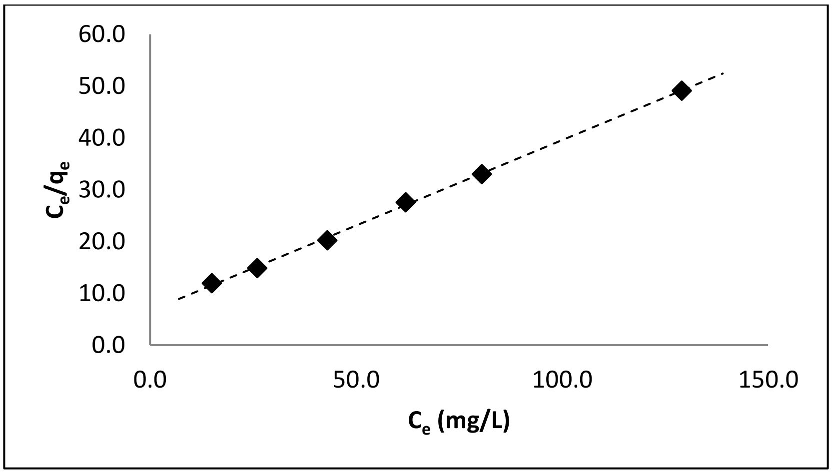

Figure 4.6: Langmuir isotherm for AV7 dye adsorption

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4.2.2 Freundlich Isotherm

The Freundlich isotherm model is the adsorption at the heterogenous sites with interaction between adsorbed molecule. The linear curve of log q_e versus log C_e was plotted to calculate the value of Freundlich constants, K_F and n as listed in Table 4.1. K_F shows adsorption capacity while n is the adsorption intensity. The value of n was 2.978, which in the range as good adsorption with R^2 value of 0.9322.

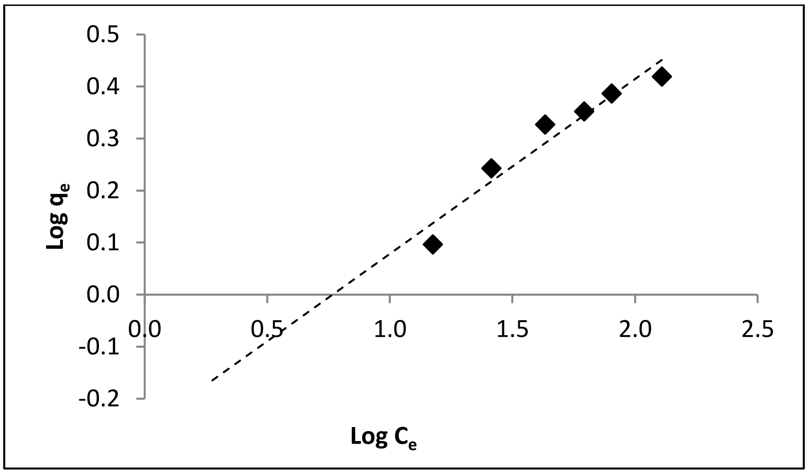

Figure 4.7 : Freundlich isotherm for AV7 dye adsorption

Table 4.1: Isotherm parameters for AV7 dye adsorption onto MOA.

Langmuir				Freundlich		
Q_o (mg/g)	K_L (L/mg)	R^2	R_L	K_F (mg/g (L/mg)$^{1/n}$)	n	R^2
3.034	0.049	0.999	0.868	0.553	2.978	0.932

4.3 Adsorption Kinetics Studies

The pseudo-first order model rate constant, K_1 and q_e values were determined from the intercept and slope of the linear plot of log (q_e-q_t) versus t as shown in Figure 4.8.

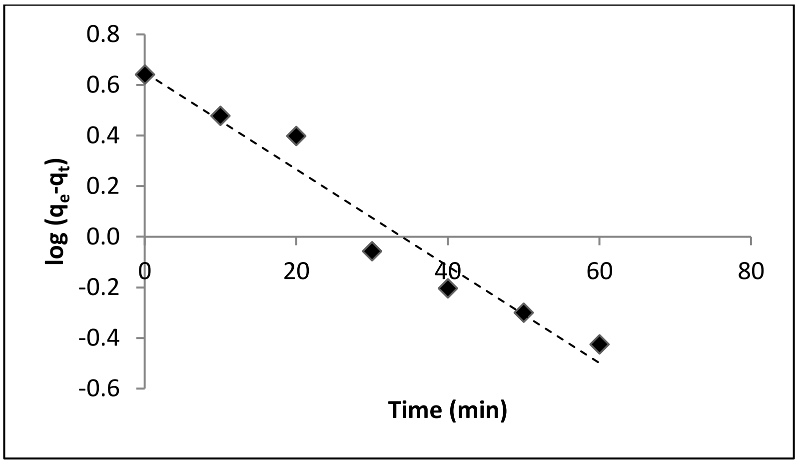

Figure 4.8: Pseudo-first order kinetic plot for the adsorption of AV7 by MOA

The pseudo-second order model is based on the adsorption capacity and it can be used to predict chemisorption processes. The pseudo-second order model rate constant, K_2 and q_e values were determined from the intercept and slope of the linear plot of t/q_t versus t as shown in Figure 4.9.

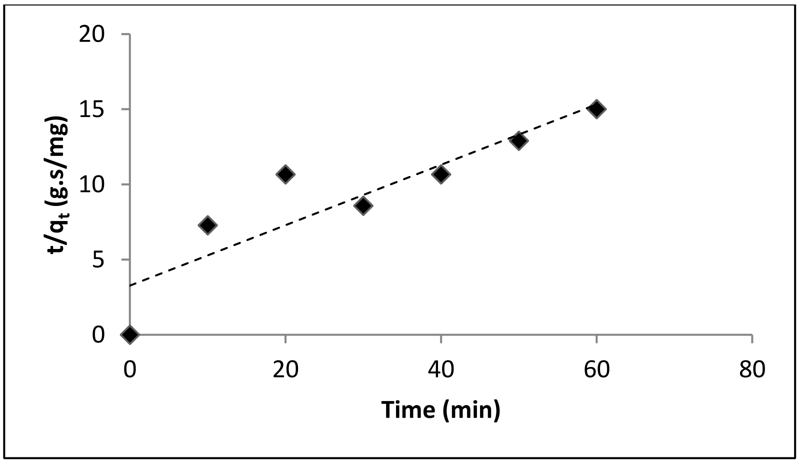

Figure 4.9: Pseudo-second order kinetic plot for the adsorption of AV7 by MOA