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MUAMMAR HAQIMI MOHD JASIN
17th April 2017

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LIST OF SYMBOL

	Symbol	Unit
A	Arrhenius factor	-
B_T	Constant for Temkin equation	-
C	Boundary layer	-
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
E	Mean free energy	J/mol
E_a	Arrhenius activation energy of adsorption	kJ/mol
k_1	Adsorption rate constant for the pseudo-first-order kinetic	1/hr
k_2	Adsorption rate constant for the pseudo-second-order	g/mg.hr
K_F	Freundlich isotherm constant	mg/g $(L/mg)^{1/n}$
K_L	Langmuir adsorption constant	L/mg
W	Mass of adsorbent	g
n_f	Constant for Freundlich isotherm	-
q_e	Amount of adsorbate adsorbed at equilibrium	mg/g
q_m	Adsorption capacity of Langmuir isotherm	mg/g
q_t	Amount of adsorbate adsorbed at time, t	mg/g
R	Universal gas constant	8.314 J/mol K
R^2	Correlation coefficient	-
R_L	Separation factor	-
t	Time	Min
T	Absolute temperature	K
V	Solution volume	L
ΔG^o	Changes in standard Gibbs free energy	kJ/mol
ΔH^o	Changes in standard enthalpy	kJ/mol
ΔS^o	Changes in standard entropy	kJ/mol

LIST OF ABBREVIATIONS

BG	Brilliant Green
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
DRS	Diffuse Reflectance Spectroscopy
FTIR	Fourier Transform Infrared
IUPAC	International Union of Pure and Applied Chemistry
rpm	Rotation per minute
SEM	Scanning electron microscopy
UV	Ultraviolet

FOTOKATALIS DIBANTU PENJERAP BERASASKAN AKRILIK UNTUK PENYINGKIRAN PEWARNA KATIONIK

ABSTRAK

Dalam kajian ini, penjerapan pewarna Brilian Hijau (BH) menggunakan tanah liat semulajadi diubah suai dengan memperkenalkan fotokatalis untuk penyingkirkan dan penyerosotan pewarna. Campuran titanium dioksida, bentonit dan polimer akrilik telah disediakan dengan kaedah salutan untuk berfungsi sebagai lapisan penjerap nipis. Formulasi bahan campuran ini telah dikaji selidik untuk mendapatkan nisbah yang optimum untuk proses penjerapan. Didapati nisbah yang terbaik ialah 0.2 g titanium dioksida, 0.3 g bentonit dan 1.5 g polimer akrilik yang mana 97% penyingkiran pewarna telah dicapai dalam masa 5 jam. Salutan penjerap dengan formulasi optimum ini dinilai dengan pencirian dan pencapaiannya. Pencirian salutan penjerap ini diuji dengan SEM, FTIR, DRS dan Zeta Berpotensi. Tambahan pula, pencapaian penjerap ini juga dikaji dengan menvariasikan kepekatan awal (50-200 mg/L) pewarna, kadar pH (3-11) dan suhu larutan (30 ^{o}C-70 ^{o}C). Data keseimbangan pewarna BH yang diperolehi sesuai dengan model Freundlich. Sementara itu, data kinetik terbaik diwakili oleh model pseudo second-order. Hasil kajian membongkarkan salutan penjerap ini berpotensi untuk teknologi rawatan air sisa masa depan.

PHOTOCATALYST ASSISTED ACRYLIC BASED ADSORBENT FOR CATIONIC DYE REMOVAL

ABSTRACT

In this study, adsorption of Brilliant Green (BG) dye using natural clay as adsorbent was being modified by inserting photocatalyst for colour removal and degradation. A coating formulation of titanium oxide, bentonite and acrylic polymer was prepared using a coating method which will act as thin adsorbent layer. The adsorbent layer was investigated to obtain the optimum ratio for adsorption process. It was found that the best ratio was 0.2 g of titanium oxide, 0.3 g of bentonite and 1.5 g of acrylic polymer where 97% of dye removal had been achieved in 5 hours. This adsorbent coating with the optimum ratio was further characterized and the performance evaluation was performed. Characterization of the adsorbent evaluated by SEM, FTIR, DRS and Zeta Potential. Furthermore, performance of the adsorbent was tested by varying the initial concentration (50-200 mg/L) of dye, solution pH (3-11) and temperature (30 ^{o}C-70 ^{o}C). The obtained equilibrium data for BG dye was best fitted by Freundlich model. Meanwhile, the kinetics data was best represented by the pseudo second-order model. The result revealed that this adsorbent coating has the potential for future wastewater technology.

CHAPTER ONE

INTRODUCTION

1.1 Research background

Water pollution associated from wastewater containing synthetic dye originates from textile industries is a severe and weighty issue. The inappropriate disposal of coloured textile effluent to the environment may cause serious consequences. Several type of dyes have characteristics as toxic, mutagenic and even carcinogenic. Moreover, dyes usually have complex aromatic molecular structures and synthetic origin, which caused them to be more stable and hardly biodegradable. Hence, it gives bad effect to aquatic life as sunlight will be difficult to penetrate through (Gong et al., 2005).

Textile industry consists of complicated processes including bleaching, dyeing, printing and stiffening of textile product. The main pollutants came from the dyeing and finishing processes, which require a large amount of chemicals and eventually caused disposal problems. Textile industries generate huge volumes of contaminated wastewater, which cause serious problems for the natural ecosystem if discharged without proper treatment. In fact, a research showed that the industry consumed water up to 80–100 m^3/ton of finished textile and wastewater discharge with 115– 175 kg of COD/ton of finished textile (Savin and Butnaru, 2008).

Nevertheless, dyes are still broadly used in the industry because of their quickness in dyeing properties, bright colour, low energy consumption and smooth application techniques. The extensive use of dyes ends up with a bigger problem especially their coloured wastewater. The treatment of dye has becoming more challenging due to it's properties. In fact, even after series of treatments, colour may still remain in the effluent. Our naked eyes can detect dye with concentration as low as 0.005 mg/L, thus concentration above this limit is unacceptable (Santhy and Selvapathy, 2006).

The effort to treat dyes in textile industries continues to grow and many innovations have been made to tackle this problem. Traditional methods such as flocculation and coagulation have been improvised, while at the same time, new economical and effective methods are being explored and studied such as adsorption and membrane treatment. In this research, modification is intended to improve the reliability of desired method in term of effectiveness and economic measures.

1.2 Problem statement

In this research, the adsorption is carried out by using customize paint coating, which consists of bentonite and acrylic polymer as adsorbent. Despite of many advantages from this technique there is still some coverning drawbacks. From the previous study, applying paint based adsorbent has been proven to remove dye waste efficiently. However, after adsorption completed, the colour stains remained on the adsorbent, which limit the reusability of the adsorbent. Hence, by introducing photocatalyst in the coating formulation, it is believed could overcome the problem.

Photocatalyst has the potential to leave no dirt and contaminant from removal process thus give double advantages to clean the water and the adsorbent. Metal oxide has the suitable properties to be part of the photocatalytic system primarily able to absorb light to produce electron-holes pair and degrading dyes molecules in assisting the treatment process. In this study, Titanium Dioxide, TiO_2 was chosen as a photocatalyst since it has many beneficial features such as high chemical stability, high photocatalytic activity, relatively low cost, nontoxicity and high hydrophilicity (Nosrati et al., 2015).

1.3 Research objectives

The aim of the study is to produce a new adsorbent formula by using Bentonite as a natural sources and titanium dioxide as a photocatalyst to assist the color removal process. The specific study consists of the following objectives :

i. To formulate the acrylic based adsorbent coating with photocatalytic additives for dye removal.
ii. To evaluate the performance of photocatalyst assisted acrylic based adsorbent coating for dye removal.
iii. To study the isotherms for adsorption and photocatalysis processes

1.4 Scope of study

The focus of the study is on developing a thin adsorbent coating layer by painting bentonite, acrylic emulsion and titanium dioxide on a cotton cloth. The adsorbent coating is intended to remove Brilliant Green (BG), a cationic dye. The research work consists of 4 major parts. The first part focused on the formulation and testing the best formulation of the three components; namely titanium dioxide, bentonite and acrylic polymer, ranging from 0.1 to 1.5g. The components were painted on a cotton cloth and let to dry in an oven.

Part two looks into the characterization study where the optimized adsorbent coating formulation was characterized in order to observe the surface area, surface morphology, proximate content, elemental content and surface chemistry by using several analyzers; namely Scanning Electron Microscopic (SEM), Zeta Potential, Fourier Transform Infrared (FTIR) and Diffuse Reflectance Spectroscopy (DRS).

The last two parts touched on the adsorbent coating performance evaluation and isotherm study. Identification of coating performance were conducted to test the adsorption efficiency under various conditions. The performance is evaluated by manipulating several conditions in term of dye concentration (50-200 mg/L), solution temperature (30-70 ^oC) and pH effects (3-11). Lastly, the coating results were used in the equilibrium and kinetic studies in order to investigate the adsorption behaviour of BG onto the coating.

CHAPTER TWO

LITERATURE REVIEW

2.1 Dyes

Dye is a coloured organic substance, usually soluble in aqueous solution and has affinity with the subtrate where it is being applied to. Dye can be classified into several ways, depending on the suitable classification (Djilani et al., 2015). There are classification according to the source of materials, chemical property, nuclear structure and even industrial classification. For the source of material, dye can be classified as natural and synthetic dye while for chemical property depends on the nature of dye chromophore. There are cationic dye, anionic dye and nonionic dye. Lastly, industrial classification is segregated according to the dyeing process ; acid, basic, direct and reactive dye (Ong et al., 2007). Table 2.1 shows the classification of dyes based on the method of applications in industrial processes

Table 2.1 : Dye application method classification (Lau and Ismail, 2009)

Class	Method of application	Characteristics	Type of fibres
Basic	Applied from acidic dye baths	Cationic, water soluble	Paper, polyester, modified nylon
Acid	From neutral to acidic dye baths	Anionic, water soluble	Wool, nylon, silk
Reactive	Covalently under influence of heat and pH	Anionic, water soluble	Cotton, wool, silk and nylon
Direct	Applied from neutral or slightly alkaline baths containing additional electrolytes	Anionic, water soluble	Cotton, rayon, nylon, leather

In this research, cationic dye is the focus of studies and evaluation. Cationic dye or also known as basic dye is a soluble dye, which ionizes into cationic ions in water. At molecular level, basic dye possesses amino group, which contributes to positive charge ions. As a result, cationic dye reacts with anionic compound/material (ionic bonding). Basic dye usually shows high brightness, high tinctorial strength. Usually the tinctorial strength are very high which less than 1 mg/L of the dye produces an obvious coloration and unlimited shade range (Anirudhan et al., 2009). Furthermore, cationic dye exhibits very good affinity towards silk, wool and synthetic anionic materials such as acrylic (Kiron, 2017). Brilliant green, methylene blue and crystal violet are examples of basic dye.

A huge amount of wastewater is discharged from different steps in the dyeing and finishing processes. This wastewater is normally high in colour pigments and contains build-up of dyes and chemicals, such as complex components, aerosols, high COD and BOD concentrations, and hard-degradation materials. For example, in a cotton mill, there are various steps involved in the textile processing in which each step discharge of some amount of pollutants as shown in Table 2.2.

Table 2.2 : Pollutants from dyeing processes (Babu et al., 2007)

Process	Compounds
Desizing	Sizes, enzymes, starch, waxes, ammonia
Scouring	Disinfectants and insecticides residues, NaOH, surfactants, soaps, fats, waxes, pectin, oils, sizes, anti-static agents, spent solvents, enzymes
Bleaching	H_2O_2,AOX, sodium silicate or organic stabilizer, high pH
	Metals, salts, surfactants, organic processing assistants, sulphide

2.1.1 Effect on health

Textile colorant makes the existance of metals in various classes of dye is very important. The discharge of these metals can cause severe adverse effect not only to the environmental eco-system but also to human health. Studies on animal has been conducted to observe the effect of these carcinogenic, mutagenic and genotoxic of dyes (Pang and Abdullah, 2013). Table 2.3 below shows heavy metals content in dyes.

Table 2.3 : Common metals presence in dyes (Pang and Abdullah, 2013)

Class	**Metals in dyes**
Basic	Copper, Lead, Zinc, Chromium
Acid	Copper, Lead, Zinc, Chromium, Cobalt
Reactive	Copper, Lead, Chromium
Direct	Copper, Lead, Zinc, Chromium

If human beings consume water containing dyes at a concentration as low as 1 mg/L, this can cause serious problems to human body (Malik et al., 2007). Dyes can lead to malfunction of kidneys, productive system, liver and brain and central nervous system (Kadirvelu et al., 2003). Furthermore, several dyes have characteristics as toxic, mutagenic and even carcinogenic type of wastes (Gong et al., 2005). Basic dye has been used as an adsorbate as it has been reported are known to be more toxic than the anionic dyes (Hao et al., 2000).

2.2 Treatment of dye wastewater

As mentioned earlier, the treatment of dye wastewater can be classified into 3 main methods namely; physical treatment, chemical treatment and biological treatment. Table 2.4 shows the summarized categories of these three treatments.

Table 2.4 : Effluent treatment methods (Kant, 2012)

Physical	**Chemical**	**Biological**
Sedimentation	Neutralization	Stabilization
Filtration	Reduction	Aerated Lagoon
Flotation	Oxidation	Trickling Filters
Coagulation	Catalysis	Activated Sludge
Reverse Osmosis	Electrolysis	Anaerobic Digestion
Solvent Extraction		Fungal treatment
Adsorption		Flocculation
Incineration		
Membrane Treatment		
Ion Exchange		

All these treatment methods have their own strengths and weaknesses in terms of operation as well as capital cost. Table 2.5 shows some advantages and limitations of the selected treatments. Physical treatment method is a treatment where including no gross chemical or biological changes and solely physical phenomena are used to treat wastewater. For example filtration process, it is a process where fluid is channel through a porous medium to remove matter held in a suspension. For membrane filtration method, there are limitations as the membrane has limited lifetime before fouling occur and require high pressure to channel the water through the membrane.

Meanwhile, chemical treatment is method where chemicals are required to carry out some reactions for water improvement. Some disadvantages of chemical treatment are that it requires large amount of budget allocation. Furthermore, another drawback is that disposal problem due to production of sludge from this kind of treatment (Pang and Abdullah, 2013). Lastly for biological treatment technique, uses microorganism commonly bacteria to produce a stable end-product. Bacteria will degrade organic dyes using fixed or suspended growth systems to convert into carbon dioxide, water and other end-product. Nevertheless, this method is not very effective because dye has a characteristic of low biodegradability (Rafatullah et al., 2010).

Table 2.5 : Advantages and disadvantages of dye treatment (Babu et al., 2007, Crini, 2006)

Methods	Advantages	Disadvantages
Biodegradation	Rates of elimination by oxidizable substances about 90%	Low biodegradability of dyes
Coagulation - Flocculation	Elimination of insoluble dyes, simple and economically feasible	Production of sludge blocking filter
Adsorption	Effective in removing a wide variety of dyes	High capital costs
Reverse osmosis	Removal of all mineral salts, hydrolyzes reactive dyes and chemical auxiliaries	High pressure
Ozone treatment	Good decolorization	No reduction of the COD and short half-life (20 minutes)
Oxidation	Rapid and efficient	High operating cost and require the use of chemical
Photocatalysis	Mild operating condition	Effective for small capacity operation
Membrane filtration	Good permeate qualities	High pressure and limited lifetime of membrane before fouling occurs
Ion exchange	No adsorbents loss due to the capability of regeneration	Not applicable for wide range of dyes and high operating costs

2.3 Adsorption

Adsorption is a physical process where target pollutants such as dye accumulates on the surface/interface of the adsorbent. The adsorbed molecule on the surface is referred to as adsorbate. This process occurs when there is a different in properties of adsorbent than the bulk and simply there are 3 major steps in the adsorption process. The first step involves the adsorbate to diffuse from the major body of the stream to the external surface of the adsorbent particle. Next, the second step is where the adsorbate will migrate into the pores of the adsorbent within each adsorbent particle. These sites where most of the particles are attracted due to the availability of active sites and large surface area. Lastly, the third step is where the adsorbate adheres to the surface of the active sites and complete adsorption is achieved. Figure 2.1 shows the summary of how adsorption occurs.

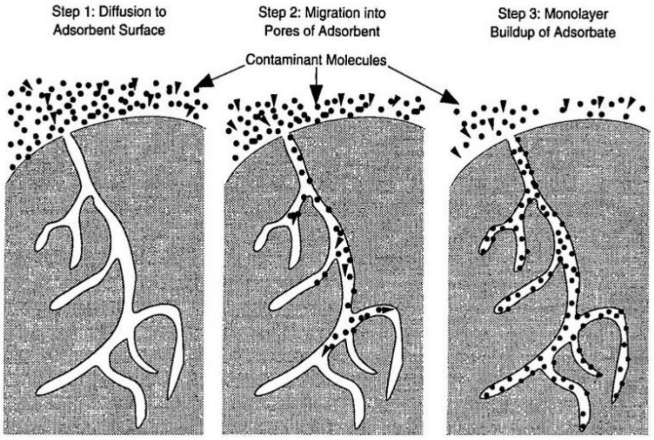


Figure 2.1: Adsorption mechanism

2.3.1 Types of adsorption

Adsorption can be classified into physisorption and chemisorption based on the nature of forces involved. Physisorption is a type of adsorption in which the adsorbate adheres on the surface of adsorbent only through weak Van der Waals interactions. There is no significant redistribution of electron density in either the molecule or at the surface of the substrate (Dąbrowski, 2001).

Meanwhile, chemisorption occurs when a molecule adheres to the surface of adsorbent through the formation of strong chemical or ionic bond. It involves the substantial rearrangement of electron density and due to the transformation of components in a chemical form, it is therefore irreversible. Additionally, this process can be influenced by several factors such as the interactions between adsorbate and adsorbent, nature of adsorbate, the surface area and pores structure of adsorbent, operating temperature and contact time (Dąbrowski, 2001). Table 2.6 depicts other comparisons between physisorption and chemisorption.

Table 2.6 : Comparison between physical and chemical adsorptions (Ngulube et al., 2017)

Physisorption	Chemisorption
Weak intermolecular forces like van der Waals forces	Strong covalent bonding involving
Low enthalpy: $\Delta H < 20$ kJ/mol	High enthalpy: approximate 400kJ/mol
Multilayer adsorption	Monomolecular adsorption
Low temperature, constantly lower than the adsorbate critical temperature	High temperatures
Low activation energy	High activation energy
Reversible	Non-reversible
Non-selective surface attachment	Selective surface attachment

2.3.2 Advantages of adsorption

Recently, adsorption has been proven to be a better and effective method to remove dye in water due to several reasons and justifications. This method is an innovative and economical protocol in terms of performance and ease of operation (Asfaram et al., 2017). Furthermore, adsorption is becoming a preferred method due to its low cost, higher uptake capacity, greater selectivity, faster regeneration kinetics, less production of sludge and easy operation (Bu et al., 2016).

Adsorbent can be anything including activated carbon, bio-sorbent such as from chitosan and natural clay. Activated carbon is the most widely used adsorbent due to its effectiveness, versatility and capacity. Furthermore, activated carbon also has large porous surface area and manageable pore structure (Bello et al., 2013). However, despite of many advantages, activated carbon rises another problems. The application of activated carbon in some cases is very high cost in term of operation and regeneration problem in large scale operation.

2.4 Bentonite as adsorbent

Bentonite is classified as a natural clay material which has the potential as an effective adsorbent. It is actually a low price materials, abundant in nature and has high stability in term of chemical and physical over wide range of pH. Bentonite has a unique structure that enhances the adsorption of cationic or positively charge dye. It largely consist of montmorillonite, which shows lamellar structure where Si^{4+} will be partially replaced with Si^{3+} whereas Si^{3+} will be substituted by several heavy positive metal ions. This fact gives rise to the development of negative charges in the layers, which are balanced by the presence of Na^+, K^+ or Mg^+ cations strongly hydrated located in the interlayered space (Aguiar et al., 2017).

2.5 Photocatalyst

Photocatalyst is a catalyst that speeds up chemical reaction when photo or light energy is exerted on its surface which then produces electron-hole pair. This will induce chemical transformation of reactants involved, generate hole or reactive oxygen species such as -OH and O_2 radicals and surely degrade the organic pollutants existed (Siriwong et al., 2012, Khan et al., 2015). There are two types of photocatalytic reactions; homogeneous and heterogeneous photocatalyses. Homogeneous is a reaction where the reactant and catalyst are in the same phase while heterogeneous is vice versa. In this process, heterogeneous reaction is involved where the reactant (dye) is in liquid phases whereas catalyst is in solid. Some inportant features for photocatalytic system are the desired band gap, suitable morphology, high surface area, stability and reusability (Khan et al., 2015). Metal oxides are the most favourable photocatalyst used in industry. Metal such as titanium, vanadium, chromium, zinc, tin and cerium are suitable to be used as these metal can be induced by light to form positive holes. One example of photocatalyst is titanium dioxide, TiO_2, which is abundant in nature and very efficient to be used due to it's biocompability, exceptional stability in various condition and good ability to generate charge carrier when there is sufficient of light energy. In simple way, TiO_2 has high chemical stability when exposed to acidic or basic compound, nontoxic, relatively low cost and high oxidizing power (Nosrati et al., 2015).

2.6 Adsorption isotherm

Adsorption isotherm is a graphical depiction, then indicates how the adsorption molecules are distributed or spread between the liquid and solid phases when adsorption process comes in to an equilibrium state (Berrios et al., 2012). Therefore, it is important and useful as this isotherm can provide useful informations regarding to predict adsorption capacity and optimization. In this research, three adsorption isotherms namely; Langmuir, Freundlich and Temkin were conducted. Linear regression was used to determine the best-fitting isotherm and the correlation coefficient, R^2 is judged in order to compare the suitability of isotherm equations.

2.6.1 Langmuir isotherm

Among theoretical models, Langmuir isotherm is the simplest isotherm that has been widely used for the adsorption of solute from liquid solution. Few assumptions was in the application of isotherm, where; (i) it is a monolayer adsorption; (ii) all sites on the adsorbent are identical with equivalent energy; (iii) there is no interaction between the molecules adsorbed on the neighbouring sites; (iv) no further adsorption can take place once a particular site is occupied by a molecule and (v) adsorption energy is independent to the degree of occupation of an adsorbent's active sites (Gimbert et al., 2008). Theoretically, Langmuir model can be expressed as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2.1}$$

which can then be further rearranged in to:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \tag{2.2}$$

where,

C_e = Equilibrium concentration of adsorbate (mg/L),

q_e =Amount of adsorbate adsorbed at equilibrium (mg/g),

q_m =Monolayer adsorption capacity of the adsorbent (mg/g),

K_L =Langmuir adsorption constant (L/mg).

Therefore, a graphical plot of C_e/q_e against C_e gives a straight line with the slope of $1/q_m$ and intercept of $1/K_L q_m$. The adsorption coefficient can be determined from the slope and intercept of the straight line.

2.6.2 Freundlich isotherm

Freundlich isotherm is an empirical equation normally used for a non-ideal sorption such as adsorption that involves heterogeneous sorption (Tan et al., 2007). It stated that the heat of adsorption decreases in logarithmic magnitude with increasing extent of adsorption, indicating that the adsorption sites are distributed exponentially with respect to the adsorption energy. This isotherm is used for multilayer adsorption with the interaction between adsorbed molecules (Gimbert et al., 2008).

Theoretically, Freundlich model can be expressed as:

$$q_e = K_F \, C_e^{\frac{1}{n_F}} \tag{2.3}$$

which can then be further rearranged to:

$$\ln q_e = \frac{1}{n_F} \ln C_e + \ln K_F \tag{2.4}$$

where,

q_e = Amount of adsorbate adsorbed per unit mass of adsorbent (mg/g),

$1/n_F$ = Adsorption intensity,

C_e = Equilibrium concentration of the adsorbate (mg/L),

K_F = Freundlich isotherm constant (mg/g (L/mg) $^{1/n}$).

Therefore, a graph of ln q_e against ln C_e gives a straight line with the slope of $1/n_F$ and intercept of ln K_F. From the slope of graph, the value of $1/n_F$ measures the adsorption intensity or surface heterogeneity. When the value of adsorption intensity is close to 0, it indicates that the system become more heterogeneous. Meanwhile, with the value lower than 1, it shows a normal Langmuir isotherm. Meanwhile, if the value above 1, it shows that the system is from cooperative adsorption. Additionally, from the intercept of graph, the value of K_F can be determined. Generally, K_F is a constant related to the bonding energy of a system. It is the adsorption or distribution coefficient that represents the quantity of dye adsorbed onto adsorbents for a unit equilibrium concentration.

2.6.3 Temkin isotherm

The Temkin isotherm assumes that the heat of adsorption decreases linearly rather than logarithmic due to the indirect interactions between adsorbate and adsorbent. The heat of adsorption of all molecules in each layer decreases linearly with coverage. Comparing with Langmuir parameters, Temkin model gives higher equilibrium constants (Fil et al., 2012). Theoretically, Temkin model can be expressed as (Thilagavathy and Santhi, 2014):

$$q_e = \left(\frac{RT}{b}\right) \ln(A_t\, C_e) \tag{2.5}$$

which can then be further rearranged to:

$$q_e = B \ln C_e + B \ln A_t \tag{2.6}$$

where,

q_e = Amount of adsorbate adsorbed at equilibrium (mg/g),

R = Universal gas constant (8.314 J/mol K),

T = Absolute temperature (K),

A_t = Equilibrium binding constant (L/mg),

C_e = Equilibrium concentration of adsorbate (mg/L),

B = RT/b = Constant related to the heat of adsorption (L/mg).

Therefore, a graph of q_e versus ln C_e gives a straight line with the slope of B and intercept of $B \ln A_t$.

2.7 Kinetic study

Adsorption kinetic is often studied to understand the mechanism of adsorption process. The kinetic data was evaluated to understand the dynamics of the adsorption process. The adsorbate will undergo different stages from moving from bulk to adsorbent surface area. In this study, two kinetic models were used which includes the pseudo-first-order and pseudo-second-order models.

2.7.1 Pseudo-first-order model

Pseudo-first-order model was used to describe the adsorption rate based on the adsorption capacity and its differential equation can be expressed as:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \tag{2.7}$$

where,

q_t = Amount of adsorbate adsorbed at time t (mg/g),

k_1 = Pseudo-first-order rate constant of adsorption (1/hr),

q_e = Amount of adsorbate adsorbed at equilibrium (mg/g).

By integrating the above equation with boundary layer condition of $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, a linear equation can be obtained as below:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2.8}$$

A graph of ln $(q_e\text{-}q_t)$ against t gives a straight line with the slope of $-k_1$ and intercept of ln q_e. This model assumes that the rate of change of solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid uptake with time.

2.7.2 Pseudo-second-order model

Pseudo-second-order model is based on the adsorption capacity onto a solid phase, which is used to predict the behavior over the entire studied range. It involves the valency forces through sharing or exchange of electrons during the adsorption process (Ho and McKay, 1999). The differential equation can be expressed as:

$$\frac{dq_t}{dt} = k_2 (q_e - q)^2 \tag{2.9}$$

where,

q_t = Amount of adsorbate adsorbed at time t (mg/g),

k_2 = Pseudo-second-order rate constant of adsorption (g/mg.h),

q_e = Amount of adsorbate adsorbed at equilibrium (mg/g).

which can then be further rearranged to:

$$\frac{dq_t}{(q_e - q_t)^2} = k_2 dt \tag{2.10}$$

By integrating the above equation with boundary layer condition of $t = 0$ to $t = \mathrm{t}$ and $q_t = 0$ to $q_t = \mathrm{q_t}$, a linear equation can be obtained as below:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{2.11}$$

A graph of t/q_t against t gives a straight line with the slope of $1/q_e$ and intercept of $1/k_2 q_e^2$.

2.8 Thermodynamics study

2.8.1 Adsorption thermodynamics

Thermodynamic parameters are used to indicate the energy transformation in an adsorption process. It is assumed that entropy change is the driving force in an isolated system (Amin, 2009). In this study, three thermodynamic parameters are evaluated in order to characterize the adsorption process due to the transfer unit mole of solute from solution onto the solid-liquid interface. They include: (i) standard enthalpy change ($\Delta H°$); (ii) standard entropy change ($\Delta S°$); and (iii) standard free energy change ($\Delta G°$). The value of $\Delta H°$ and $\Delta S°$ can be calculated by using the following equation:

$$\ln k_L = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{2.12}$$

where,

k_L = Langmuir adsorption constant (L/g),
$\Delta S°$ = Changes in standard entropy (kJ/mol K),
R = Universal gas constant (8.314 J/mol K),
$\Delta H°$ = Changes in standard enthalpy (kJ/mol),
T = Absolute solution temperature (K).

Therefore, by plotting a graph of ln k_d against $1/T$, the values of both $\Delta H°$ and $\Delta S°$ from the slope and intercept of the graph can be determined. Fundamentally, a positive $\Delta H°$ value indicates that an adsorption process is endothermic in nature while a negative value represents exothermic reaction. As for $\Delta S°$, a positive value shows the increment in randomness at the solid/solution interface that occurs in the adsorption process besides reflecting the affinity of the adsorbent toward the adsorbate (Bello et al., 2013). Additionally, the change in standard Gibbs energy, $\Delta G°$ can be calculated using the following relation with a negative $\Delta G°$ value indicates that an adsorption process is a spontaneous process at the study temperature and vice versa.

$$\Delta G° = \Delta H° - T\Delta S° \tag{2.13}$$

As the nature of adsorption is determined by the magnitude of activation energy, E_a, Arrhenius equation has been applied to determine either the process is physical or chemical. Normally, physisorption process has activation energy ranging from 5 to 40kJ/mol. On the other hand, for chemisorption process, the activation energy is in range from 40 to 800 kJ/mol. As shown in the following relationship, Arrhenius equation can be represented by:

$$ln\ k_2 = \ln A - \frac{E_a}{RT} \qquad (2.14)$$

where,

k_2 = Rate constant obtained from pseudo-second-order kinetic model (g/mg h)

A = Arrhenius factor,

E_a = Arrhenius activation energy of adsorption (kJ/mol),

R = Universal gas constant (8.314 J/mol K),

T = Absolute temperature (K).

Therefore, by plotting a graph of lnk_2 against $1/T$, we are able to determine the values of E_a from the slope of the graph, - E_a/R.

CHAPTER 3

MATERIALS AND METHODS

The overall experiment activities are illustrated in the flow chart as shown in Figure 3.1

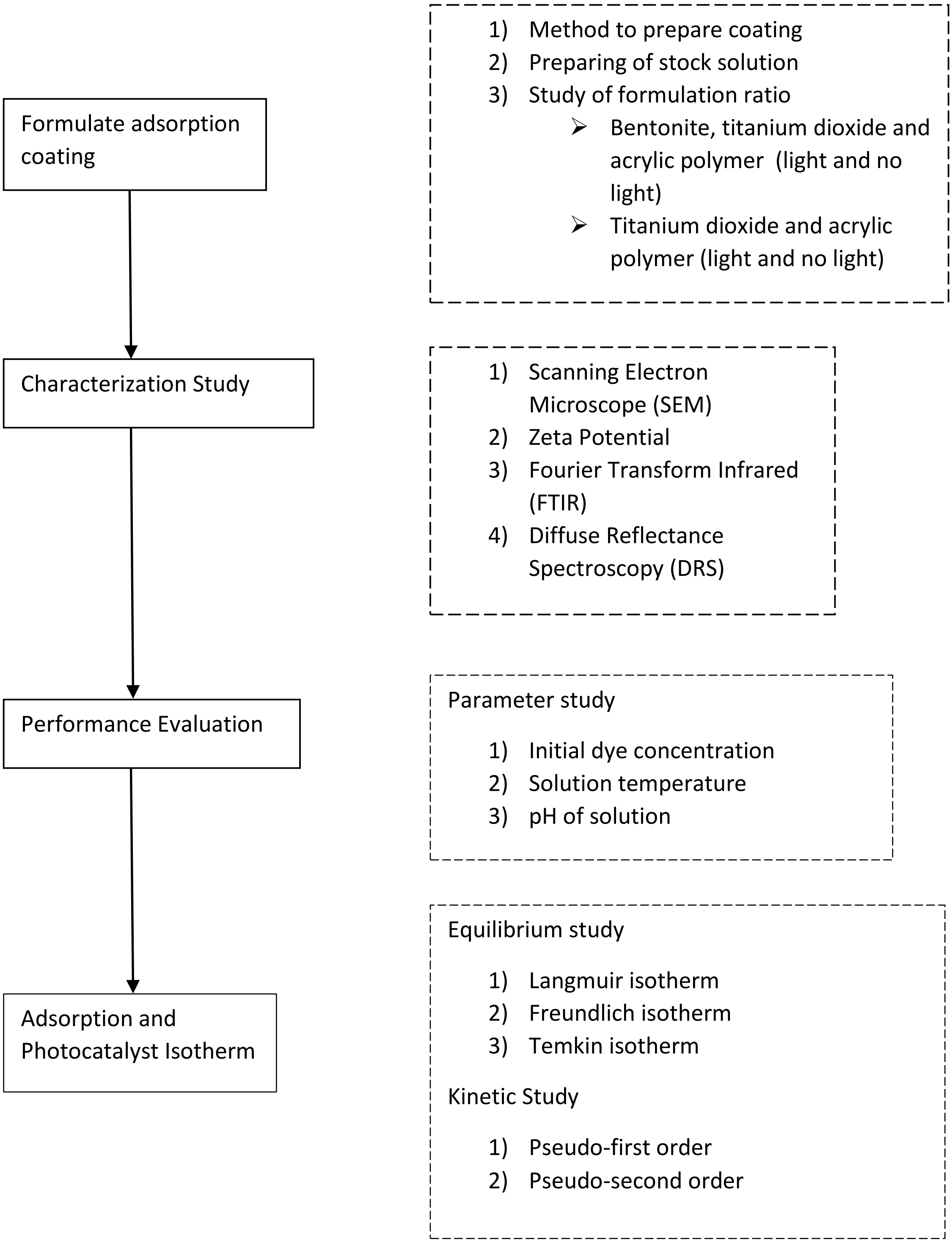


Figure 3.1 : Flow chart for the experimental activities

3.1 Materials

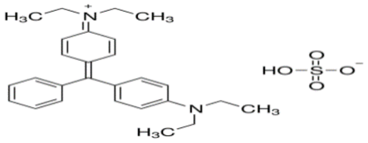
In this study, combination of bentonite act as adsorbent, acrylic emulsion as binder and titanium oxide as photocatalyst for coating. The chemicals used were listed as shown in Table 3.1 below:

Table 3.1: List of materials used

Chemicals/Materials	**Characteristics**	**Purpose**	**Supplier**
Bentonite	Powder form	Adsorbent	Sigma Aldrich Sdn Bhd
Acrylic Polymer	Liquid	Binder	Sigma Aldrich Sdn Bhd
Titanium Dioxide	Powder form	Photocatalyst	Sigma Aldrich Sdn Bhd
Hydrochloric acid	Liquid	pH adjustment	Merck, Germany
Sodium Hydroxide	Liquid	pH adjustment	Merck, Germany
Brilliant Green	Powder form	Adsorbate	Sigma Aldrich Sdn Bhd
Distilled Water	Liquid	Solvent	

Brilliant Green (BG) as an adsorbate. All of these were supplied by Sigma-Aldrich (M) Sdn. Bhd, Malaysia. BG properties were summarized in Tables 3.2.

Table 3.2: Brilliant Green Properties

Properties	
Common name	Brilliant Green (BG)
IUPAC name	4-[[4-(diethylamino)phenyl]-phenylmethylidene]cyclohexa-2,5-dien-1-ylidene]-diethylazanium;hydrogen sulfate
Other name	Ethyl Green, Basic green
Molecular formula	$C_{27}H_{34}N_2O_4S$
Molecular weight	482.63 g/mol
CAS number	633-03-4
Maximum wavelength, λ_{max}	625nm
Chemical structure	

3.2 Equipment and Instrumentation

3.2.1 Preparation of Adsorbent coating

As mentioned earlier, the coating is consist of 3 components namely bentonite, acrylic polymer and titanium dioxide with addition of distilled water. The components were painted on a (5 X 20 cm) cotton cloth by using paint brush. The cloth was then dried by using oven (Model Memmert 600, Germany) at 60 ^{o}C for at least 8 hours to remove all the water presence in the coating. This is to prevent any peeled off of the adsorbent coating. See Figures 3.2 and 3.3.