Isotherms and Kinetics Studies on the Removal of Methylene Blue from Aqueous Solution by Gambir

K. S. Tong, A. Azraa, and M. Jain Noordin

***Abstract*—Gambir Indonesia was chemically modified into an adsorbent for the removal of methylene blue from aqueous solution. The surface morphology and functional groups of the adsorbent are characterized by using Scanning Electron Microscopy, Fourier Transform Infrared Spectrophotometry and surface area analysis. The solution pH of methylene blue and adsorbent dosage were optimized at pH 6.0 and 0.05 g, respectively. The isotherms studies showed that the adsorption experimental data was fitted well by Langmuir isotherm model. The adsorption capacity was found to be 149.3 mg/g. The pseudo-second-order equation has described well on the adsorption process of methylene blue onto gambir adsorbent.**

***Index Terms*—Langmuir, intraparticle diffusion, surface area, pseudo-second-order, Gibbs free energy.**

I. Introduction

Water pollution can be defined as any physical, chemical, or biological alteration in water quality that effected living organisms. Chemical industries and human communities are the example of point sources, which are mainly caused the pollution of surface waters like rivers, lakes and seas [1]. Dye is a common contaminant or pollutant compound that can be easily found in wastewater [2]. Dyes are applied in textile manufacturing, leather tanning, and paper production and food technology industries. Choy et al. [3] reported that the total dyes consumption of the textile industry alone is in excess of 107 kg year^{-1} and is estimated 90 % of this total ends up on fabrics industry. Dyeing wastewater discharged to natural receiving waters may bring unacceptable for public consumption [4]. Therefore, the wastewater treatment is desirable to overcome this problem. Methylene Blue is a kind of cationic dye (basic dye) contained of heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3SCl$. This dye generally classified as a basic dye and cationic species due to the presence of positively charge quaternary nitrogen atoms (as $–NR_3^+$, or $= NR_2^+$). These groups enhance solubility of dye in water due to their ionic characteristic [5].

There are many conventional methods that can remove dyes from its aqueous solution such as oxidative degradation by using chlorine or ozone, photo-degradation, and adsorption [6]. Among these, adsorption process is the most effective, fast and applicable. There are several types of adsorbent being applied in industrial wastewater such as activated carbon, silica gel and alumina [7]. However, these adsorbent has been restricted due to high cost and hardly decompose. Therefore, researchers are keen to investigate an alternative low cost and eco-friendly adsorbent.

Gambir is produced by boiling the young leaves of *Uncaria gambir*, pressing them to extract the juice and dried in a mold. Jain [8] had reported that the ethyl acetate extraction of gambir contained 87.33 % of catechin compound. This compound is capable to quench metal ions and formed complex.

The objective of the present study is to investigate the possible use of gambir as an alternative adsorbent material for the removal of methylene blue from aqueous solution. In addition, the adsorption experimental data was evaluated by Langmuir and Freundlich isotherms. Meanwhile, kinetic studies were calculated by using Lagergren-first-order, pseudo-second-order and intraparticle diffusion models.

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Authors are with Materials and Corrosion Laboratory, School of Chemical Sciences, Universiti Sains Malaysia, Gelugor, Pulau Pinang, Malaysia (email: lkstong@yahoo.com)

II. Materials and Methods

A. Preparation of Modified Gambir Adsorbent, MGA

The gambir was purchased from Medan, Indonesia. It was then ground and extracted with ethyl acetate. The chemically modified gambir adsorbent (MGA) was produced based on the modification of Stiasny reation [9]. 0.10 g of gambir extracts was added with 10 mL of distilled water, 2 mL of 37 % formaldehyde and 1 mL of 10 M HCl in a 50 mL round bottom flask with an attached condenser. The mixture was reflux for 1 hour at 90 ºC. After that, the mixture was filtered and washed with hot distilled water until the washing was approximately pH 4.0. The modified gambir adsorbent (MGA) was dried in an oven at 50 ^oC until a constant mass of MGA was obtained.

B. Characterization of MGA

The surface area analysis was carried out by using BET, Langmuir surface area and BJH pore size analysis methods.

MGA was analyzed with PerkinElmer System 2000 Fourier Transform Infrared Spectrometer (PerkinElmer FT-IR System 1600 model). The scanning wavelength of infrared was at 4000–400 cm^{-1}.

Leo Supra 50 VP Field Emission Scanning electron microscopy (Carl-Ziess SMT, Oberkochen, Germany) analysis was carried out to study the surface textures of MGA. The various elements present in MGA were determined by energy dispersive X-ray analyzer (Oxford Instruments Analytical, Bucks, UK, INCA-400 model)

The pH zero of point charge (pH_{pzc}) of the MGA was determined by using solid addition method [10] with slight modification.50.0 mL, 0.01 M KNO_3 solutions were prepared in Erlenmeyer flask. The pH initial ($pH_{initial}$) of these solutions were adjusted from pH 2.0 to 12.0 by adding 0.10 M HCl or 0.10 M NaOH solution. Then, 0.15 g of MGA was

added to each flask, stirred and the final pH (pH_{final}) of the mixture was measured after 24 hours. The graph ΔpH ($pH_{initial} - pH_{final}$) versus $pH_{initial}$ was plotted. The value of pH_{zpc} was determined from the curve that cuts the $pH_{initial}$ at which ΔpH become 0.

C. Adsorption Studies

The experiments were carried out by shaking (150 rpm) 0.05 g of MGA with 50 mL of aqueous solution of methylene blue in different conical flask at room temperature (30°C). At the end of pre-determined time interval the reaction mixtures were filtered out and analyzed for its dye concentrations using UV-vis spectrophotometer (Hitachi U2000 with 1 cm path length quartz cell). The adsorption experiments were also carried out to determine the solution pH of methylene blue (pH 2-10), adsorbent dosage (0.01-0.10 g), equilibrium time (10-360 min) and initial concentrations (25-300 mg/L) for maximum adsorption. All the investigations were carried out in triplicate to avoid the discrepancy in experimental results. The percentage of methylene blue adsorbed onto MGA was computed using the equation:

$$\%\ adsorption = \frac{C_0 - C_e}{C_0} x100\% \quad (1)$$

where C_i and C_e are the initial and equilibrium concentration of dye (mg/L) in the solution. Adsorption capacity was calculated by using the mass balance equation:

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (2)$$

where q_e is the adsorption capacity (mg/g), V is the volume of dye solution (L) and W is the weight of adsorbent (g).

III. Results and Discussion

A. Characterization of MGA

The surface are and pore diameter of MGA were determined. The BET surface area and Langmuir surface area were found to be 12.98 and 10.90 m^2/g, respectively by using the nitrogen adsorption method. According to the classification from International Union of Pure and Applied Chemistry (IUPAC), the pores are divided into three categories, micropores (diameter (d) < 20 Å), mesopores (20 Å < d < 500 Å) and macropores (d > 500 Å). The average pore diameter determined by Barrett-Joiner-Halenda (BJH) method was 100.80 Å, suggesting that MGA consists of mesopores.

The FTIR spectrum of MGA is shown in Fig. 1. The presence of broad peak at 3410 cm^{-1} is associated to the stretching of –OH group contained in catechin. The peak at 1615 cm^{-1} and 1521 cm^{-1} are corresponded to the aromatic -C=C- bond stretching. The formaldehyde in the preparation of MGA is undergoing polymerization process to form methylene bridges among catechin compounds [11]. Thus, peak at 1457 cm^{-1} in Fig. 1 has revealed the formation of methylene bridges. The peak observed from 1250 cm^{-1} to 1150 cm^{-1} is attributed to the aromatic C-O bond stretching of phenolic group and it is also assigned at 1115 cm^{-1}.

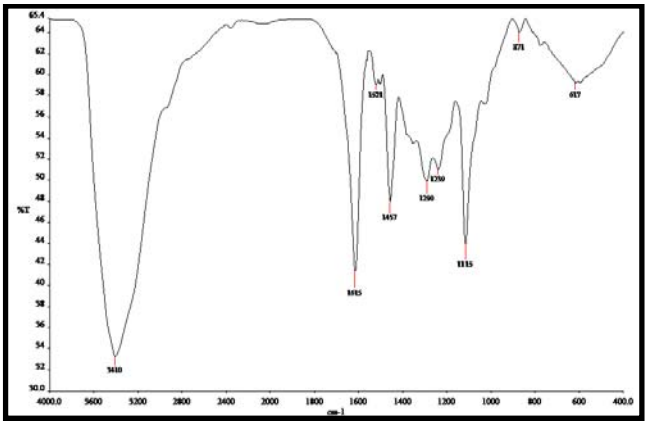

Fig. 1. FTIR spectrum of MGA.

Fig. 2 shows the SEM-EDX micrographs of raw gambir and MGA. The surface morphology of raw gambir is smooth. Meanwhile the surface morphology of MGA is uniformed in size, highly pore structures, indicating that there is a good possibility for methylene blue to be trapped and adsorbed.

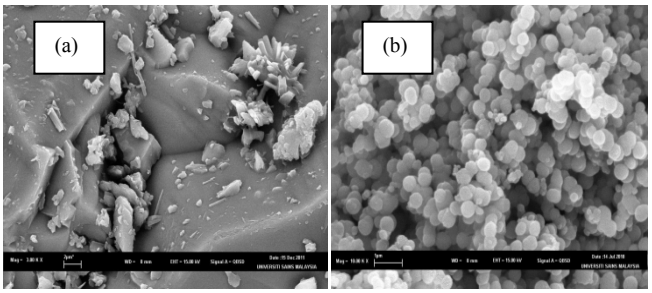

Fig. 2. SEM image of (a) gambir extracts and (b) MGA.

The pH_{pzc} of an adsorbent is a very important characteristic that determine the pH at which the adsorbent surface has net electrical neutrality. The pH_{pzc} of MAG was found to be 3.5 (Fig. 3).

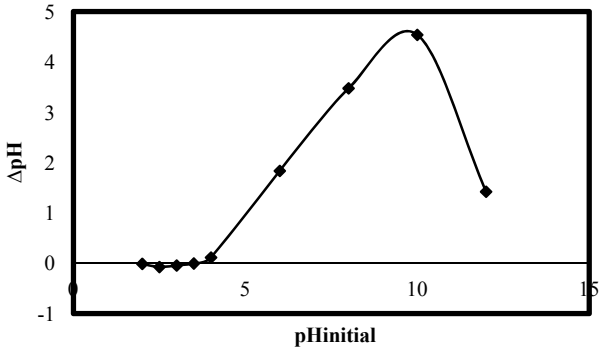

Fig. 3. The pH_{pzc} of MGA.

B. The Effect of Solution pH

The effect of pH on the adsorption of methylene on MGA has been studied by varying in the ranges of 2.0 to 10.0 as shown in Fig. 4. It can be observed that the uptake of methylene blue increased rapidly from 92.6 % to 98.5 % with the increasing of pH from 2.0 to 4.0. The MB dye uptake becomes slower as it had reached equilibrium condition at pH 6.0 (99.1 %) to pH 10.0 (99.4 %). At lower pH condition, MB solution contains high concentration of ion hydrogen (H^+) that is competing with MB ions for exchangeable active sites

on MGA surface. The MB adsorption is more favorable at higher pH condition due to the less competition of ions H^+ [12]. A similar investigation has been reported that the adsorption of MB dye is increased by increasing the solution pH [13, 14].

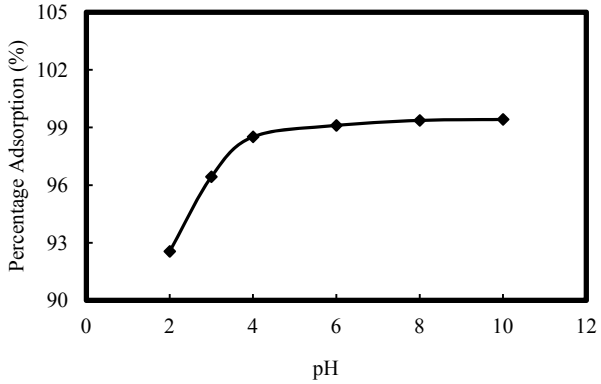

Fig. 4. Effect of pH on the adsorption of MB onto MGA.

C. Effect of Adsorbent Dosage

Adsorbent dosage is an important parameter because this factor determines the capacity of an adsorbent for a given initial concentration of the adsorbate [15]. It can be observed from Fig. 5, the adsorption percentage of MB on MGA was increased with the increasing of adsorbent dosage from 0.01 g (86.5%) until 0.10 g (99.6%). However, the adsorption capacity (q_e) presented the opposite trend. The increase of the removal rate of MB is due to the increase of adsorbent surface area and availability [16]. Meanwhile, the decrease of q_e from 216.3 mg/g to 24.9 mg/g is caused by the adsorption competition among the adsorbent and the split of concentration gradient [17].

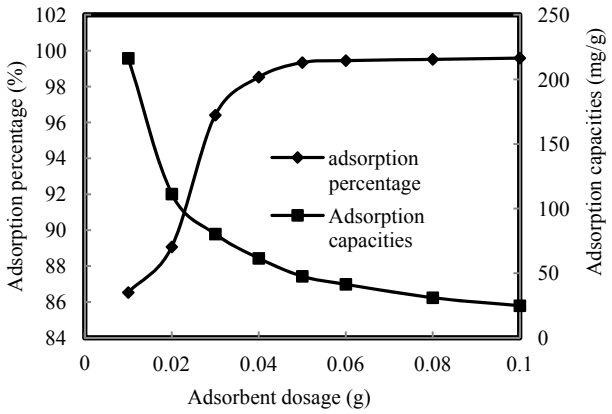

Fig. 5. Effect of adsorbent dosage.

D. Effect of Initial Concentrations and Contact Time

The influence of contact time on the adsorption of MB onto MGA was studied at initial concentrations of 50 and 100 mg/L. The result of the MB adsorption by MGA is shown in Fig. 6. The development of surface charged for solid interface can be explained through the effect of contact time. Fig. 6 has showed that the adsorption rate of MB onto MGA was increased rapidly at the initial stage and became slower as it reached near the equilibrium condition. The initial concentration of MB plays an important role as a given adsorbent dosage can be adsorbed only a fixed amount of adsorbate [18]. Obviously, the more concentrate the effluent, the smaller the volume of effluent that a given adsorbent can be purified. The fractional adsorption is low in high concentration is due to dyes that present in lower concentration adsorption medium could interact with the adsorption sites, in order to obtain a higher adsorption yields. Hence, at higher concentration, lower adsorption yields were observed because of the saturation of the adsorption sites [19].

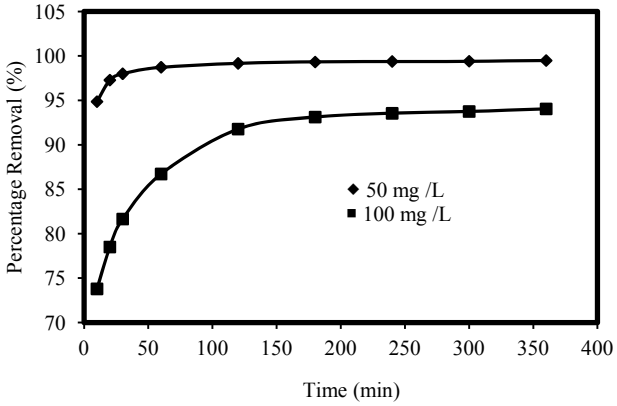

Fig. 6. Effect of contact time on initial concentration.

E. Isotherms Studies

Isotherms studies have described the adsorption mechanisms, surface properties and the affinity of adsorbent towards adsorbate [20]. The distribution of adsorption molecule between the adsorbate (liquid phase) and the adsorbent (solid phase) is constant at equilibrium due to the amount of adsorbate being adsorbed is equal to the amount of adsorbate being desorbed from the adsorbent [21]. Thus, it is important to fit the adsorption experimental data into an appropriate isotherm model. Therefore, Langmuir and Freundlich isotherms were used to evaluate the relationship between the amount of dye adsorbed at equilibrium (adsorption capacity) and the concentration of dye at equilibrium state.

The Langmuir isotherm is based on the assumption that all adsorption sites are equivalent and adsorption at an active sites is independent of whether the adjacent active sites is occupied or not [22]. Langmuir isotherm [23] is represented by the following linear equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)$$

where C_e (mg/L) is the dyes concentration at equilibrium, q_e (mg/g) is the dyes adsorption capacity at equilibrium, K_L (L/mg) is the Langmuir constant related to the adsorption energy, and q_m (mg/g) is the adsorption capacity. The Langmuir constants q_m and K_L were determined from the slope and intercept of the plot and their values are listed in TABLE 1.

The essential features of Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant called separation factor on equilibrium parameter (R_L), which is defined by the following relationship [24]:

$$R_L = \frac{1}{1+K_L C_o} \quad (4)$$

where K_L is the Langmuir constant and C_o (mg/L) is the highest dye concentration. The value of R_L indicates the type of the isotherm to be either unfavorable (R_L>1), linear (R_L=1), favorable (0<R_L<1) or irreversible (R_L=0). As shown in Table 1, the calculated value of R_L was found between 0.02 and 016. This implies that the adsorption of MB on MGA is favorable under the conditions used in this study.

The linear form of the Freundlich equation [25]:

$$logq_e = logK_F + \frac{1}{n} logC_e \quad (5)$$

where C_e (mg/L) is the dyes concentration at equilibrium, q_e (mg/g) is the amount of dyes adsorbed at equilibrium, K_f and n are Freundlich constants. The value of n gives an indication of how favorable the adsorption process. The plot of ln q_e versus ln C_e gives straight lines with slope, 1/n and intercept, K_f, respectively.

From TABLE I, it is observed that the experimental data of MB adsorption was followed by Langmuir isotherm with correlation coefficient 0.99. The monolayer adsorption capacity for the adsorption of MB was found to be 149.3 mg/g. The value of 1/n was in between 0.1 and 1.0 confirmed the heterogeneity of the adsorbent, indicating that the bonding of MB and MGA is strong [26].

TABLE I: REGRESSION PARAMETERS FOR THE ADSORPTION ISOTHERMS.

Isotherms	Parameters	Values
Langmuir	q_m, mg/g	149.3
	K_L, L/mg	0.21
	R_L	0.02-0.16
	R^2	0.99
Freundlich	K_F, mg/g	52.4
	1/n	0.22
	R^2	0.91

F. Kinetics Studies

Adsorption is a physicochemical process that involves mass transfer of a solute from liquid phase to the adsorbent surface. Three of the most widely used kinetic models, i.e. Lagergren-first-order equation, pseudo-second-order equation and intraparticle diffusion equation were used to research the adsorption kinetic behavior of MB onto MGA. The best fit model was selected based on the linear regression correlation coeffiecient values (R^2). The Lagergren-first-order kinetic equation is described as [27]:

$$\log(q_e - q_t) = logq_e + \frac{k_1}{2.303} t \quad (6)$$

where k_1 (1/min) is the rate constant of Lagergren-first-order kinetic model.

A linear form of pseudo-second-order model is expressed as [20]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

where k_2 (mg/g min) is the rate constant. The q_e and q_t (mg/g) are the amounts of MB adsorbed at equilibrium and time (t), respectively.

The intraparticle diffusion equation is showed as below:

$$q_t = K_d t^{0.5} \quad (8)$$

where K_p (mg g^{-1} $min^{-0.5}$) is the intra-particle diffusion rate constant. All the parameters of kinetics models are listed in TABLE II. As can be seen in TABLE II, the correlation coefficient, R^2 of pseudo-second-order kinetic model were greater than 0.99 for both 50 and 100 mg/L MB solution. Therefore, its calculated q_e values were agreed with the experimental q_e values, implying that the adsorption kinetic of MB is well described by pseudo-second-order model.

TABLE II: PARAMETERS OF KINETIC MODELS FOR THE ADSORPTION OF MB ON MGA.

Kinetic Models	MB	
	50 mg/L	100 mg/L
q_e exp (mg/g)	49.6	91.8
Lagergren-first-order		
q_e cal (mg/g)	2.9	22.5
k_1 (1/min)	4.63×10^{-2}	2.53×10^{-2}
R_2	0.97	0.99
Pseudo-second-order		
q_e cal (mg/g)	49.8	93.5
k_2 (g/mg min)	4.49×10^{-2}	3.19×10^{-2}
R^2	0.99	0.99
Intraparticle diffusion		
K_d (mg/g $min^{0.5}$)	0.3	2.42
R^2	0.79	0.96

From Table II, it can be seen that the pseudo-second order kinetic rate constants decreased with the increasing of initial MB concentrations. This is due to the competition for the adsorbent active sites are increased at higher concentration, and consequently the adsorption rate will become slower [11]. Meanwhile, the intraparticle diffusion shows that the adsorption process of MB is more efficient at high concentration (100mg/L) with K_d value, 2.42 mg/g $min^{-0.5}$.

IV. CONCLUSIONS

On the basis of the experimental results of this investigation, several conclusions can be drawn:

- The characterization has showed that MGA consisted mesopres structure and pH_{pzc} was found to be 3.5.
- The solution pH of MB and adsorbent dosage of MGA for the adsorption process were optimized at pH 6.0 and 0.05g, respectively.
- The Langmuir isotherm was well fitted to the adsorption data with monolayer adsorption capacity of 149.3 mg/g.

- The adsorption kinetic of the experimental data was well presented by pseudo-second-order kinetic model.
- The data from this study has suggested that MGA is a potential eco-friendly and low-cost adsorbent which might able to apply on the adsorption of dyes from aqueous solution.

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