Equilibrium kinetic and isotherm studies of dye colour adsorption on the banana peel

A A A Bakar1, W N R W Mazlan1, I H Izaham1, N S Azizan1, K A M Ali1, and N M Daud1
1 School of Civil Engineering, College of Engineering, Universiti Teknologi MARA, Cawangan Pulau Pinang, Permatang Pauh Campus, 13500, Pulau Pinang, Malaysia.

E-mail: amalina.amirah@uitm.edu.my

Abstract. Textile, paper, rubber, plastics, leather, cosmetics, pharmaceuticals, and food industries extensively employ dyes. This study aims to determine the best equilibrium kinetic and isotherm model of dye colour adsorption using waste adsorbent. Methylene blue (MB) is a dye colour contaminant that can be removed from wastewater via adsorption due to its ease of usage and cost-effectiveness. This study employed banana peels (BPs), a low-cost and waste adsorbent, to remove MB from synthetic wastewater. A series of batch equilibrium adsorption studies investigated the effect of different dosages of 0.05 to 0.4 grams, contact time of 15 to 150 minutes, and agitation speed of 150 rpm. BPs dosage is added from 0.05 g to 0.4 g in 100 ml of Methylene Blue solution. The concentration of MB in the samples was determined using a HACH DR2800 Spectrometer. According to the kinetic study analysis, the adsorption of MB followed a pseudo-second order kinetic with an $R^2$ of 0.9934. Furthermore, the Freundlich model fit better than others based on the equilibrium isotherm investigation, with an $R^2$ of 0.7688. As a result, BPs can be used as an alternative waste adsorbent media for extracting dye colours from industrial effluent.

1. Introduction
Malaysia is experiencing immense physical development in achieving higher economic growth. However, it is still grappling with selecting the best waste management practices for industrial effluent discharges. The tremendous industrial developments in Malaysia have caused massive effluent discharges into water bodies, resulting in contaminated water sources, and affecting human health and the environment.

Dyes are primarily chemical compounds made up of two major components: chromophores, which provide colour, and auxochromes, which increase the dye's attraction for fibres [1]. Many industries, including dyestuff, textile, leather, printing, paper, and plastic, produce dye as a concomitant pollutant [2], [3]. Industrial effluent is one of the primary point-source water pollutions. Tahir [4] highlighted that almost 50% of water pollution generated from industrial effluent containing dye concentrations had been successfully reduced by utilising adsorbents such as activated carbon, peat, chitin, clay, etc. Methylene blue (MB) is a widely used cationic dye in the dyeing sector. MB is a harmful dye that can cause nausea, vomiting, eye injury, methemoglobinemia (blood disorder), profuse sweating, diarrhoea, gastritis in people exposed to it. Their effluent discharges are a severe cause of pollution. Even a tiny amount of dye in water can be poisonous and very noticeable. Therefore, removing MB from industrial effluent becomes extremely important for the environment [1,5]. Hence, dye pollution in wastewater must be treated with the appropriate approach.
Researchers have investigated numerous physical and chemical approaches to improve water quality, including ion exchange, membrane separation, solvent extraction, coagulation-flocculation, reverse osmosis and adsorption[1-2,4]. Compared to other methods, adsorption has the edge over other techniques since it can enhance cost and performance [3]. For decades, researchers have been using agricultural or biomass waste as an adsorbent, such as rice husk, tea waste, wheat bran, sugarcane baggase, sugar beet pulp, soya bean hulls, and clay, natural zeolite, sawdust, peanut shells, and fruits peels [6].

Bananas are a widely consumed fruit due to more than 130 countries grow bananas [7], making it one of the most significant crops on the earth. Banana (Musa Sapientum) cultivation is widespread in Malaysia, and it is the second most popular tropical fruit after durian. Banana peel (BPs) accounts for approximately 40% of the total weight of fresh bananas [3]. However, BPs contain unique carbohydrate content and an attractive low-cost precursor for effective adsorbents [3]. BPs will resolve environmental concerns as a crop residues precursor while simultaneously providing a high-value product from a low-cost feedstock.[8]. This study aims to determine the best equilibrium kinetic and isotherm model of MB adsorption using banana peel. Unlike the previous study, this study emphasises the potential use of untreated banana peel as a waste adsorbent.

The adsorption kinetics and mechanism are determined by the physical properties of the adsorbent and solute molecule. The experimental data were implemented into different kinetic models, enabling analysis of the adsorption rate, modelling the process, and estimating the adsorbent/adsorbate interaction data. On the other hand, the isotherm analytical technique addresses the adsorption functions that link the quantity of adsorbate in the adsorbent. Numbers of adsorption isotherm models were applied, and better accuracy of adsorption rate was determined.

2. Methodology

2.1. Preparation of adsorbent and synthetic wastewater

2.1.1. Banana peel carbon. Banana peels (BPs) were collected from local fried banana stalls in Permatang Pauh, Penang, Malaysia. First, the BPs were dried out under the sunlight overnight. Next, BPs were rinsed with distilled water until discoloured and free from dirt like dust and soil. Next, the BPs were cut into small pieces and dried 24 hours in convection (Model: BINDER ED 720) with a temperature of ±109℃ to remove the moisture content, and the BPs weight is constant. The recommended size of BPs is at a range between 0.5 cm to 1 cm.

2.1.2. Methylene blue. 21.0 mg of Methylene blue (MB) powder was mixed with 1000 mL of distilled water to produce synthetic wastewater in a volumetric flask. For the preparation of MB stock, the initial concentration of MB stock was determined. Equation 1 is used to measure the concentration of Methylene blue powder for the preparation of MB stock:

\[ M_1 V_1 = M_2 V_2 \] (1)

where \( M_1 \) is the concentration in molarity (moles/litres) of the concentrated solution, \( V_1 \) is the volume of the concentrated solution number 1, \( M_2 \) is the concentration in molarity of the dilute solution (moles/litres), and \( V_2 \) is the volume of the dilute solution number 2. For this study, the initial Methylene blue water sample is in the range of 320 to 341 PtCo.

2.2. Batch Study

A batch adsorption study was used to test the ability of BPs in removing MB from synthetic wastewater. Several variables were examined in this batch study: (1) varied dosage and (2) varied contact time. In addition, the effect of varied dosage ranging from 0.50 g to 0.4 g and varied contact time ranging from 0 to 180 min at a speed of 150 rpm was investigated in this study.
2.2.1. Varied dosage. Methylene blue (MB) was removed in synthetic wastewater solution in various dosages, and the initial and final colouring was determined. The dosage of banana peel adsorbent added in the solution varied from 0.05 g, 0.1 g, 0.15 g, 0.2 g, 0.25 g, 0.3 g, to 0.4 g. Every 250 ml closed conical flasks were filled with seven varied dosages of banana peel adsorbent mixed with 100 ml of MB solution. For a control solution, the initial reading of MB synthetic solution is 320 PtCo. The shaking and settling times were set to 90 minutes and 60 minutes, respectively, and the reading for the final colour was recorded after settling time using the HACH DR2800 spectrophotometer. The optimum dosage which removed the highest MB percentage is determined.

2.2.2. Varied contact time. The removal of Methylene blue in synthetic wastewater by banana peel adsorbent was a time-controlled method. The method was assured by rapidly removing Methylene blue in synthetic wastewater by banana peel adsorbent at retention time ranging from 15 minutes to 180 minutes. For every seven conical flasks, the optimum dosages of banana peel adsorbent were used and let shake using an orbital shaker. The initial colour reading in all the beakers was set to 341 PtCo, and determined by using a HACH DR2800 spectrometer. The removal efficiency of the BPs can be expressed in Equation (2).

\[
\%\text{removal} = \left(\frac{C_i - C_f}{C_f}\right) \times 100
\]  

(2)

The adsorption capacity of banana peel adsorbent can be expressed in Equation (3).

\[
q_e = \left(\frac{C_i - C_f}{m}\right)V
\]

(3)

where \(C_i\) and \(C_f\) are the initial and final concentration of MB solution (mg/L), \(V\) is the volume of sample (L), and \(m\) is the mass of adsorbent (g).

2.3. Kinetic study

Various kinetic models were tested to obtain information on the adsorbent's actions. The correlation coefficient (R²) determines the similarity between the values determined by the model and the experimental results [9]. A fairly high R² value points out that the model describes the kinetics of adsorption on adsorbent [9] successfully. The study of kinetics and the adsorption mechanism plays a significant role in designing an effective water treatment system [10].

2.3.1. Pseudo-first order. The kinetic Equation of the pseudo-first order reaction was created by Lagergren et al. [11]. This model is used to determine the adsorption in a liquid-solid system, which claimed that the adsorption rate is calculated by the number of unoccupied adsorptive sites [10]. The pseudo-first order kinetic equation is expressed in Equation (4).

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t
\]

(4)

Correspondingly, in the linear Equation of the kinetic model, \(q_e\) and \(q_t\) (mg/g) represent the removal capacities, and equilibrium, at a certain time [10]. The slope of \(\log (q_e - q_t)\) versus time, \(t\) helped to determine the value of the model's kinetic parameters, such as \(k_1\) (min⁻¹), \(q_{exp}\) (mg/g), \(q_{cal}\) (mg/g), and correlation coefficient, R².

2.3.2. Pseudo-second order. The Pseudo Second-Order kinetic model specified that the adsorption rate depends on the adsorbent and the molecules' solute sites and the formation of chemical bonds.
between the adsorptive site and the solute molecule is the rate-limiting step [10]. Therefore, the pseudo-second order kinetic Equation is expressed in Equation (5).

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t
\]

In the linearised mathematical expression of the model, its parameters are almost the same as the Pseudo First-Order kinetic model, where \(q_t\) and \(q_e\) (mg/g) represent the removal capacities and equilibrium at a certain time, and \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) represents the overall rate constant of the adsorption process, and it can be determined by the interception of plotting \(t/q_t\) versus time (t). Commonly, the linear Equation slope helped determine the value of the model's kinetic parameters such as \(q_{exp}\) (mg/g), \(q_{cal}\) (mg/g), and correlation coefficient, \(R^2\).

2.3.3. Elovich kinetic. The Elovich kinetic model, which is different from the Elovich isotherm model, is suitable for energetically heterogeneous solid surfaces with no lateral contact between adsorbate and adsorbent [10]. Therefore, it is another model that can be used in this study. The Elovich kinetic equation is expressed in Equation (6).

\[
q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t
\]

There are two parameters in the model's linear equation formula, where \(\alpha\) (mg/g/min) represents the initial rate coefficient for the adsorption. At the same time, it also represents the activation energy for chemical adsorption. The other one, \(\beta\) (g/mg), represents a coefficient that represents the rate of desorption. As usual, the linear Equation slope helped determine the value of the model's kinetic parameters and correlation coefficient, \(R^2\).

2.3.4. Intra-particle diffusion. The Intra-particle diffusion model expressed the function of adsorbate transfer from the aqueous solution to the adsorptive sites of the adsorbent. The model indicates that the total adsorption speed is regulated by the chemical or physical bond formed between the solute and the solid at interspatial solid sites. The Intra-particle diffusion kinetic equation is expressed in Equation (7).

\[
q_t = C + k_i t^{1/2}
\]

The values of constant parameter \(k_i\) can be obtained from the slope of the linear plot of \(q_t\) versus \(\sqrt{t}\) (time in minutes).

2.4. Equilibrium isotherm study

Isotherm models like Langmuir and Freundlich are commonly used in many previous studies. Still, in this study, another model, namely Temkin, is added to interpret the distribution of metal ions between phase liquid and phase solids in detail.

2.4.1. Langmuir isotherm. The Langmuir isotherm is effective for monolayer adsorption on a finite number of equal sides. It was the most widely used linear expression for studying the relationship between solute concentration in the liquid phase and solid phase under conditions of equilibrium [12]. The Langmuir isotherm equation is expressed in Equation (8).

\[
\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{Q_o \kappa_e C_e}
\]
According to Langmuir in 1918, in this isotherm, $C_e$ represents the equilibrium concentration of the resting MB in the solution (mg/L), while $q_e$ represents the removed amount of MB at equilibrium (mg/g). The values of constant parameters $Q_o$ and $b$ can be obtained from the slope and y-intercept of the linear plot of $C_e/q_e$ versus $C_e$.

2.4.2. Freundlich isotherm. The Freundlich isotherm was applied in this study to illustrate the nature of the interaction between the studied banana peel adsorbent and the addressed wastewater. The Freundlich isotherm equation is expressed in Equation (9).

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e$$

In this isotherm, $q_e$ represents an adsorbent equilibrium of methylene blue (mg/g), $C_e$ is the equilibrium concentration (mg/L), and $K_F$ and $n$ are parameters depending on the adsorbent capacity. The values of $K_F$ and $n$ can be obtained from the slope and y-intercept of the linear plot of $\log q_e$ versus $\log C_e$.

2.4.3. Temkin isotherm. The Temkin isotherm model is based on an empirical equation that includes a component indicating the adsorbent-adsorbed interactions [12-13]. The isotherm model assumes that adsorption heat is reduced linearly due to the adsorbent and adsorbent interactions in separate adsorption layers for all molecules [13]. A $q_e$ plot versus $\ln C_e$ allows the isotherm constants to be determined. The values of constant parameter $A_T$ and $b_T$ can be obtained from the slope and y-intercept of the linear plot of $q_e$ versus $\ln C_e$. The Temkin isotherm equation is expressed in Equation (10).

$$q_e = \frac{R_T}{b_T} \ln A_T + \frac{R_T}{b_T} \ln C_e$$

3. Result and Discussion

3.1. Effect of various dosages and contact time

The adsorption capacity was highest at the earlier stage of the experiment. At 0.05g of dosage, the adsorption capacity was at the highest with 222.00 mg/L. At a dosage of 0.3 g, the banana peel adsorbent gave the highest difference between the solution's initial and final colour of the solution with 53.2 mg/L of adsorption capacity. The dosage was able to remove 278 PtCo of methylene blue. Thus, the optimal percentage of synthetic solution methylene blue removal is 86.88%. The removal percentage began to decrease at 0.4 g of banana peel adsorbent. The high reactivity of the BPs was caused due to an increased surface availability at a high BPs concentration.

For every seven conical flasks, the optimum dosage of banana peel adsorbent of 0.3 g/100ml was used and let shake using an orbital shaker. At different agitating contact times, the adsorbent mixture with the synthetic wastewater significantly affected the methylene removal efficiency. The optimum percentage removal of methylene blue in synthetic wastewater by banana peel adsorbent was 86.22%, on a contact time of 150 minutes with total removal of 294 PtCo. Throughout the 15 minutes and 150 minutes of contact time, the adsorption of methylene blue by banana peel adsorbent increased steadily but dropped at 180 minutes. The obtained results were continued with the Kinetic and Isotherm study.

3.2. Kinetic study

The adsorption kinetics and mechanism are determined by the physical properties of the adsorbent and solute molecule. The experimental data were implemented into different kinetic models, enabling analysis of the adsorption rate, modelling the process, and estimating the adsorbent per adsorbate interaction data. Figure 1 shows the linear plots of adsorption kinetic models used in this study, such as the Pseudo-First Order, Pseudo-Second Order, Elovich, and Intra-particle Diffusion. These models are applied to describes the process by which contaminants are adsorbed.
Figure 1. The linear plot of adsorption kinetic models

The value of all the model's kinetic constant parameters, linear Equation that has the value of slope (m), y-intercept (c), and correlation coefficient (R²), were tabulated in Table 1.

Table 1. Data collected from the adsorption kinetic models

| Model              | Kinetic parameters | Data from linear plot |
|--------------------|--------------------|-----------------------|
|                    | \(q_{\text{exp}}\) (mg/g) | \(q_{\text{cal}}\) (mg/g) | Difference | m   | c   | R²  |
| Pseudo First Order | \(k_1\) (1/min)    | 0.0186                | 98         | 90.3231 | 7.6769 | 0.0081 | 1.9558 | 0.9825 |
|                    | \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) | 0.00031               | 98         | 117.7563 | -19.7563 | 0.0085 | 0.3371 | 0.9934 |
| Pseudo Second Order|                   |                       |            |        |        |        |
| Elovich Kinetic    | \(\beta\)          | 26.316                | \(\alpha\) | 1.89 x 10\(^{15}\) | -       | -      | 0.038 | 1.4609 | 0.9881 |
|                    | \(C\)               | 1.6967                | \(k_i\)    | 0.1465 | 1.6967 | 0.9627 |
| Intraparticle Diffusion |                |                       |            |        |        |        |

Table 1 shows that the Pseudo-Second Order gives greater compatibility than any other kinetic models, with the R², \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)), \(q_{\text{exp}}\) (mg/g), and \(q_{\text{cal}}\) (mg/g) of 0.9934, 0.00031, 98, and 117.7563. The R² value obtained in this study means that the data is 99.34% accurate, and the adsorption capacity of 98 mg/g, almost similar to the theoretical adsorption capacity \(q_{\text{cal}}\), 117.7563 mg/g. It indicates that the adsorption rate depends on the adsorption sites of both adsorbent and solute molecules and the difference between the number of sites occupied and the available adsorbent sites at equilibrium relative to the
square product. The rate-limiting step is the formation of chemical bonds between the adsorptive site and solute molecule.

3.3. Isotherm study

Since the adsorption process involves more than one component, an equilibrium and interaction between the components are created [14]. Isotherm analytical approach discusses the adsorption functions that connect the amount of adsorbate in the adsorbent. Figure 2 shows the linear plots of adsorption isotherm models used in this study, such as the Langmuir, Freundlich and Temkin. These models are applied to interpret the distribution of metal ions between phase liquid and phase solids in detail.

![Figure 2. The linear plot of adsorption kinetic models](image)

All the model's constant parameters, linear Equation that has the value of slope (m), y-intercept (c), and correlation coefficient ($R^2$), were tabulated in Table 2.

| Model   | Constant parameter | Linear Equation                        | $R^2$  |
|---------|--------------------|----------------------------------------|--------|
| Langmuir | $Q_0$              | $y = 0.0036x + 0.4333$                 | 0.672  |
|         | $b$                |                                        |        |
| Freundlich | $K_F$, $n$         | $y = 0.5157x + 1.0569$                | 0.7688 |
| Temkin | $A_T$, $b_T$       | $y = 66.25x - 174.81$                 | 0.7187 |

The Freundlich isotherm model is the best fit compared with other models, with the $R^2$ and n values of 0.7688 and 1.0569. The $R^2$ value obtained in this study means that the data is 76.88% accurate, and the n value is more than 1. Due to that, the degree of non-linearity between concentration and adsorption of the solution is a favourable and beneficial condition (n > 1). n>1 also means that the adsorbent's solid
surfaces, on which each adsorptive site has unique bond energy and a stronger binding site physically occupied first by solute molecules, forming multilayer.

4. Conclusion
From all the models applied in this study, it is concluded that the Pseudo Second-Order kinetic model produced the highest correlation coefficient value, $R^2$ with the value of 0.9934, which is very close to 1. It means that the model has 99.34% of kinetic adsorption accuracy, and the kinetic adsorption study is best fitted with the Pseudo Second-Order model. For the adsorption equilibrium isotherm study, the Freundlich isotherm model produced the highest correlation coefficient $R^2$, with a value of 0.7688. It means that the model has 76.88% of adsorption accuracy, and the adsorption study is best fitted with the Freundlich model. It is conceivable that the final MB (between 18.11mg/L to 18.24mg/L) obtained from the batch study comply with the Environmental Quality (Industrial Effluent) Regulations 2009. Thus, BPs can be employed as a natural waste adsorbent to remove Methylene Blue from industrial effluent because it is environmentally safe, cost-effective, and readily available.

Acknowledgement
The authors are grateful to the Research Management Institute and the School of Civil Engineering, College of Engineering, Universiti Teknologi MARA Cawangan Pulau Pinang (UiTMPP) for their support and assistance in completing the study this work. Although they may not agree with all of the interpretations of results in this research, we thank our colleagues from UiTMPP, who gave insight and knowledge that substantially aided us in completing this work.

References
[1] F Kallel, F Chaari, F Bouaziz, F Bettaieb, R Ghorbel and S E Chaabouni 2016 Sorption and desorption characteristics for the removal of a toxic dye, methylene blue from aqueous solution by a low cost agricultural by-product J. Mol. Liq. vol. 219 pp. 279–288 doi: 10.1016/j.molliq.2016.03.024
[2] A H Hashem, E Saied and M S Hasanin 2020 Green and ecofriendly bio-removal of methylene blue dye from aqueous solution using biologically activated banana peel waste Sustain. Chem. Pharm. vol. 18 no. July p. 100333 doi: 10.1016/j.scp.2020.100333
[3] D Yu, L Wang and M Wu 2018 Simultaneous removal of dye and heavy metal by banana peels derived hierarchically porous carbons J. Taiwan Inst. Chem. Eng. vol. 93 pp. 543–553 doi: 10.1016/j.jtice.2018.08.038
[4] T Ahmad and M Danish 2018 Prospects of banana waste utilisation in wastewater treatment: A review J. Environ. Manage. vol. 206 pp. 330–348 doi: 10.1016/j.jenvman.2017.10.061.
[5] S Gautam and S H Khan 2016 Removal of methylene blue from waste water using banana peel as absorbent Int. J. Sci. Environ. vol. 5 no. 5 pp. 3230–3236
[6] A Ali 2017 Removal of Mn(II) from water using chemically modified banana peels as efficient adsorbent Environ. Nanotechnology, Monit. Manag. vol. 7 pp. 57–63 doi: 10.1016/j.enmm.2016.12.004
[7] A Ali, K Saeed and F Maboood 2016 Removal of chromium (VI) from aqueous medium using chemically modified banana peels as efficient low-cost adsorbent Alexandria Eng. J. vol. 55 no. 3 pp. 2933–2942 doi: 10.1016/j.aej.2016.05.011
[8] A H Jawad, R A Rashid, M A M Ishaq and K Ihsan 2018 Adsorptive removal of methylene blue by chemically treated cellulosic waste banana (Musa sapientum) peels J. Taibah Univ. Sci. vol. 12 no. 6 pp. 809–819 doi: 10.1080/16583655.2018.1519893
[9] F Aydin Temel and A Kuleyin 2016 Ammonium removal from landfill leachate using natural zeolite: kinetic, equilibrium, and thermodynamic studies Desalin. Water Treat. vol. 57 no. 50 pp. 23873–23892 doi: 10.1080/19443994.2015.1136964
[10] S I Siddiqui, G Rathi and S A Chaudhry 2018 Acid washed black cumin seed powder preparation for adsorption of methylene blue dye from aqueous solution: Thermodynamic, kinetic and
isotherm studies *J. Mol. Liq.* vol. 264 pp. 275–284 doi: 10.1016/j.molliq.2018.05.065

[11] M Rezakazemi and S Shirazian 2019 Lignin-chitosan blend for methylene blue removal: Adsorption modeling *J. Mol. Liq.* vol. 274 pp. 778–791 doi: 10.1016/j.molliq.2018.11.043.

[12] A Savran, N Selçuk, Ş Kubilay and A Kul 2017 Adsorption Isotherm Models for Dye Removal by Paliurus spinachristi Mill. Fruits and Seeds in a Single Component System *IOSR J. Environ. Sci. Toxicol. Food Technol.* vol. 11 pp. 18–30 doi: 10.9790/2402-1104021830

[13] M Tanzifi *et al.* 2017 Artificial neural network optimisation for methyl orange adsorption onto polyaniline nano-adsorbent: Kinetic, isotherm and thermodynamic studies *J. Mol. Liq.* vol. 244 pp. 189–200 doi: 10.1016/j.molliq.2017.08.122.

[14] M A Al-Ghouti and D A Da'ana 2020 Guidelines for the use and interpretation of adsorption isotherm models: A review *J. Hazard. Mater.* vol. 393 no. November 2019, p. 122383 doi: 10.1016/j.jhazmat.2020.122383.