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Parametric and Adsorption Kinetic Studies of Methylene Blue Removal from Aqueous Solution Using Bornean Rambutan (*Nephelium lappaceum* L.) Skin

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In this study, methylene blue (MB) dye removal from water sample by adsorption onto rambutan skin, was examined. The adsorption studies using batch experiments were carried out under different parametric conditions of initial dye concentrations (3.0 mg/l – 15.0 mg/l), solution pH 2 – 12 and solution temperature 30°C – 60°C. MB adsorption uptake was found to increase with the increase in initial dye concentration and solution temperature and was also favourable at higher pH. Langmuir, Freundlich and Temkin isotherm models were used to examine the experimental isotherms and their corresponding constants. The equilibrium data obtained were best represented by Freundlich isotherm model with a high R^2 value of 0.898. The adsorption kinetic rates complied with the pseudo-second-order model indicated that chemisorption might be the rate-limiting step that controlled the overall adsorption process. Thermodynamic data analysis indicated that the adsorption process was endothermic in nature. The data presented above suggest that the rambutan skin could be an alternative low-cost biosorbent for the removal of cationic dye from textile industrial effluent.

Key words: Rambutan skin; methylene blue; adsorption; isotherm; kinetics

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Water pollution is a major environmental issue faced nowadays. Textile factories are located near rivers and lakes in order to source the cheap and abundant water. methylene blue (MB), which is a basic dye, normally used as a colouring agent in textile, pulp and paper, printing, cosmetics and food industries is released into these rivers and lakes without further treatment resulting in serious water pollution downstream. Annually, more than 100 000 types of commercially dyes with over 7×105 tones of dyestuff are produce and disposed after the industrial processes, resulting in water pollution This has led to a greater public perception in regards to water quality as the colour in wastewater is the first recognized signs of water pollution [1].

The discharge of MB contaminated wastewater into water bodies has resulted in increased toxicity and chemical oxygen demand (COD) of water sources. In addition, it reduces light penetration, resulting in a reduction of photosynthesis for aquatic plant life [2]. Although MB is not categorized as highly hazardous, it can still cause some harmful effects. Acute exposure to MB can cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans [3]. The complex molecular structure of dyes make them more stable but highly recalcitrant for removal from textile effluents before being discharged into water bodies [4].

Biological and chemical precipitations are commonly used to remove MB from textile effluents. However, these processes are effective and economical only in cases where the dye concentrations are relatively high [5]. Many treatment processes have been applied for the removal of dyes from wastewater such as: advanced oxidation processes [6–8], cation exchange membranes, precipitation process, solvent extraction, reverse osmosis and adsorption [9–12]. Among these methods, adsorption is the most widely used method due to its ease of operation, easy availability, high efficiency, relatively low cost of application in decolouration process and ability to treat dyes in concentrated forms [13].

Utilizing activated carbon to adsorb dyes from wastewater has been found to be superior to other techniques; however, the cost of activated carbons is relatively high, which limits its large scale application. Problems related to the carbon regeneration and difficulty in separation from the wastewater after use are the two major concerns of employing this adsorbent [14]. Many researchers have worked to search for cheaper substitutes which do not require further processing or only require drying process before usage such as fly ash, silica gel, wool wastes, agricultural wastes, wood wastes, and clay materials [5]. Agricultural wastes are the most common raw materials being researched for this purpose, as they are renewable, abundant, biodegradable and can be disposed efficiently [15]. Spent adsorbents can be ashed and used as fertilizer. This process will also eliminate the adsorbate in a single step process.

Rambutan skin which is a local agro-waste material is investigated in this work. Rambutan (*Nephelium lappaceum* L.) is a popular tropical fruit which belongs to *Sapindaceae* family [16] and can easily be sourced in Borneo. In Malaysia, due to the favourable soil and climate conditions, a rambutan tree may produce approximately 5000–6000 fruits with the total weight of 6 kg–70 kg [17]. Due to the high consumption of the rambutan's edible part including industrial cannery of its fruit for export, massive amount of the peel is disposed, causing a severe problem in the community as they gradually ferment and release off odours [16]. The conversion of rambutan peel into activated carbon has proven to be a cheap and effective adsorbent for wastewater remediation [17]. As rambutan skin contains cellulose and lignin groups as major constituents, it is possible for chemisorption to occur by the polar functional groups of lignin, which include alcohols, aldehydes, ketones, phenolic hydroxides and ethers, as these groups can significantly increase the affinity of the sorbent material towards organic molecules [18]. Hence, chemisorption can occur easily in the presence of rambutan skin due to the significant amount of lignin groups contained inside the rambutan skin.

In this study, we explored the direct use of the skin without complex and costly pretreatment steps and activation process for wasterwater remediation. The effectiveness of rambutan skin as MB adsorbent in aqueous solutions with parametric variables such as different dye concentration, temperature and pH were also determined. The equilibrium and kinetic data of the adsorption process were then analyzed to study the adsorption isotherms and kinetics of MB adsorption on the rambutan skin.

MATERIALS AND METHOD

Adsorbate

Methylene blue (MB), $C_{16}H_{18}ClN_3S{\cdot}3H_2O$, obtained from Aldrich, was used as an adsorbate without further purification. Stock solution was prepared by dissolving 1.0 g of methylene blue in 1 l of distilled water.

Preparation of the Biosorbent

Rambutan skin was obtained from the local market in Kota Kinabalu, Sabah, Malaysia. The rambutan skin collected was washed several times with distilled water to remove any adhering dirt and subsequently dried in an oven at 80°C overnight. The dried rambutan skin was ground and sieved to the size of 2–3 mm. Finally, the resulting product was stored in air-tight container for further use. No other chemical or physical treatments were applied prior to adsorption experiments.

Surface chemistry of the prepared rambutan skin powder was analyzed using Fourier Transform Infrared (FTIR) spectroscope (FTIR 2000, PerkinElmer) analysis to determine the surface functional groups, where the spectra were recorded from 4000 cm^{-1} to 400 cm^{-1}.

Effect of Initial Dye Concentration

In order to study the effect of initial dye concentration on the adsorption uptake, 25 ml of MB solutions with initial concentrations, C_i, of 3.0 mg/l–15.0 mg/l were prepared in a series of 250 ml Erlenmeyer flasks. The initial concentrations, C_i were analyzed by measuring the absorbance values using a Jasco V-530 (Uv-Vis) spectrophotometer at 664 nm and 586 nm. After that, 0.05 g of biosorbent (rambutan skin) was added into each Erlenmeyer flask and the flasks were then placed in an isothermal water bath shaker at constant temperature of 303 K. The mixture was stirred at a constant speed of 200 r.p.m. until equilibrium was attained. The final dye concentration (C_t) was measured and the amount of dye adsorbed, q_t (mg/g) was calculated using *Equation 1*:

$$q_t = (C_i - C_t)\left(\frac{V}{W}\right) \quad (1)$$

where C_i (mg/l) is the initial concentration of dye and C_t (mg/l) is the final concentration of dye. V is the volume of the dye solution (l) and W is the mass of the adsorbent used (g).

Effect of Solution Temperature

The effect of solution temperature on the adsorption process was examined at adsorption temperature of 30°C, 40°C, 50°C and 60°C. This was done by adjusting the temperature controller of the water bath shaker, while other operating parameters, such as solution pH and adsorption time were kept constant. The initial MB concentration, C_i was set constant at 6.0 mg/l.

The final dye concentration (C_t) was measured and the percentage removal of dye was calculated using *Equation 2*:

$$\% \text{ Dye removal} = \frac{C_i - C_t}{C_i} \times 100 \quad (2)$$

Effect of Solution pH

The effect of solution pH on the adsorption process was studied by varying the initial pH of the solutions from 2 to 12. The pH was adjusted using 0.1 M HCl and 0.1 M NaOH, and was measured using a pH meter. The initial dye concentration, C_i was fixed at 6.0 mg/l, with biosorbent dosage of 0.002 g/ml and the solution temperature was kept at 30°C. The final dye concentration (C_t) was measured and the percentage removal of dye was calculated using *Equation (2)*.

Adsorption Kinetic Studies

Adsorption kinetic experiments were performed by contacting 25 ml of Methylene Blue solution of different initial concentration ranging from 3.0 to 15.0 mg/l with 0.05 g of rambutan skin powder in a 250 ml Erlenmeyer flask at a temperature of 30°C. At fixed time intervals, the samples were extracted and analyzed.

RESULTS AND DISCUSSION

FTIR Analysis of Rambutan Skin

The FTIR spectra of the rambutan skin before and after adsorption are shown in Figure 1. The obtained spectra revealed that various functional groups are present on the surface of the rambutan skin sample. By comparing the spectra of the rambutan skin before and after adsorption, it was observed that there were some peaks that had shifted, while some had disappeared after undergoing the adsorption experiments. From Figure 1, the peak at 2994.08 cm^{-1} before adsorption, is attributed to the symmetric and asymmetric C-O stretching of aliphatic acids [16]. After the adsorption process, this peak has shifted to 2989.31 cm^{-1}

The peak at 1783.33 cm^{-1} before adsorption in Figure 1 is due to the asymmetric stretching vibrations of C=O group, which shifted to 1782.98 cm^{-1} after the adsorption process [16]. The peaks at 616.86 cm^{-1} and 500.47 cm^{-1} before adsorption were both attributed to the C-H group, diminished after the adsorption process [16]. Another peak at 562.72 cm^{-1} before adsorption in Figure 1 was also due to the presence of a C-H group but it had shifted to 563.20 cm^{-1} after the adsorption experiments.

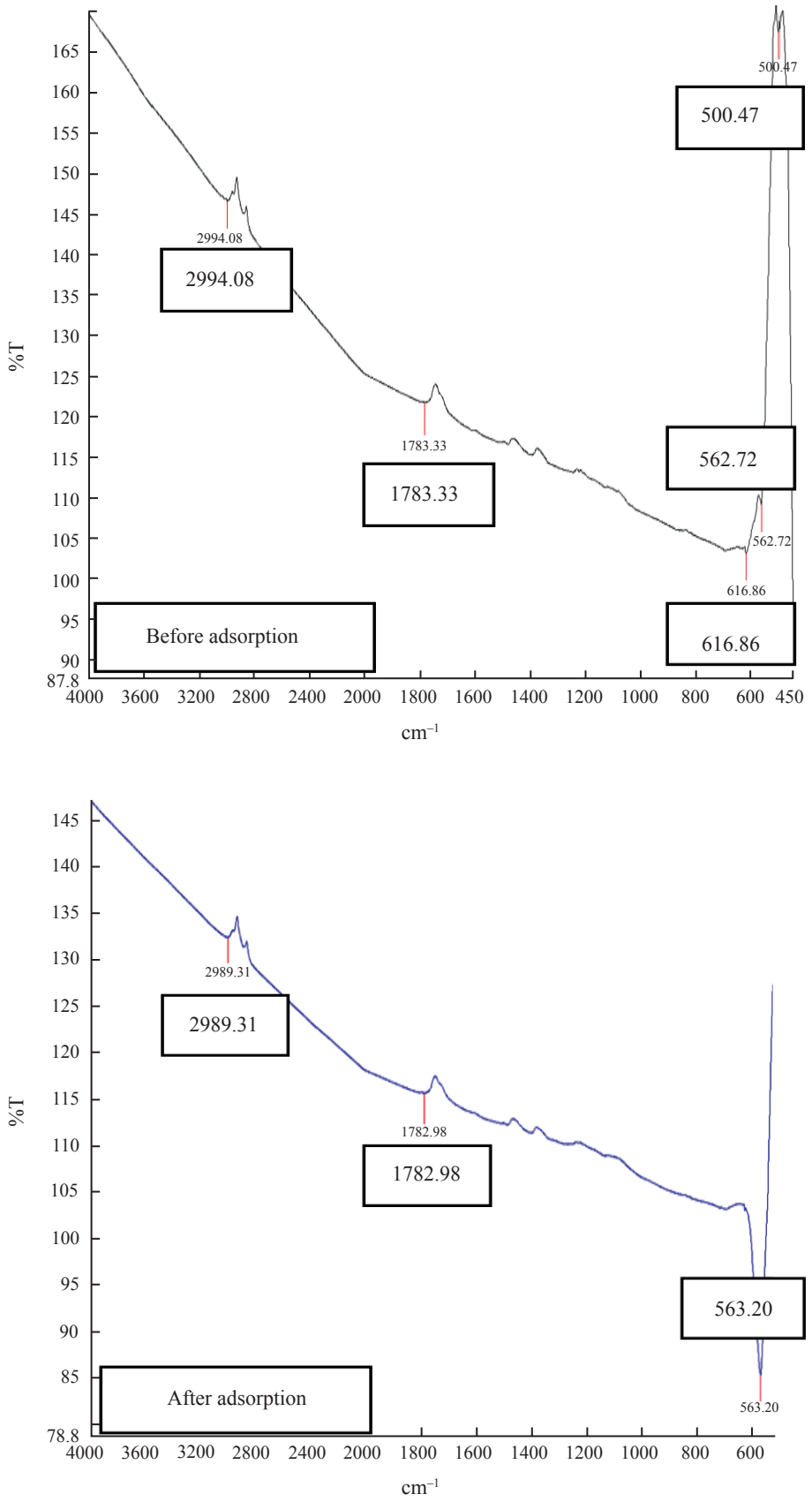

Figure 1. The FTIR Spectra of the rambutan skin before and after the adsorption process.

The detailed FTIR spectroscopic data are listed in Table 1. After the dye adsorption process, there is a shift in the positions of the C-O and C=O group peaks. This indicates that the MB molecules formed a temporary chemical bond with the C-O and C=O groups of the biosorbent. Therefore the changes in FTIR spectra confirmed the adsorption effect of MB with the functional groups of the biosorbent, which indicated the involvement of these functional groups on the surface of rambutan skin during and after the adsorption process.

Effect of the Initial Dye Concentration on the Adsorption Process

Figure 2 shows the effect of MB dye initial concentration on the dye uptake by the adsorbent at 30°C. It was observed that the MB dye adsorption rate was fast at initial stage, and then became slower until it reached the equilibrium state at around 60 min, where almost constant values were observed. At the equilibrium state, only a limited amount of dye could be further removed from the dye solution using the biosorbent.

This phenomenon was due to the fact that at the initial stage, a large number of the biosorbent surface sites were available for the adsorption of the MB molecules, but after most of the sites were occupied by these molecules, it was difficult to occupy the remaining surface sites due to the repulsion between the solute molecules of the solid and bulk phases.

Table 1. The FTIR Spectroscopic data of rambutan skin before and after MB adsorption process.

Frequency (cm^{-1})		Assignment
Before adsorption	After adsorption	
2994.08	2989.31	C-O stretching of aliphatic acids
1783.33	1782.98	C=O stretching
616.86	ND	C-H group
562.72	563.20	C-H group
500.47	ND	C-H group

*ND = Not detected

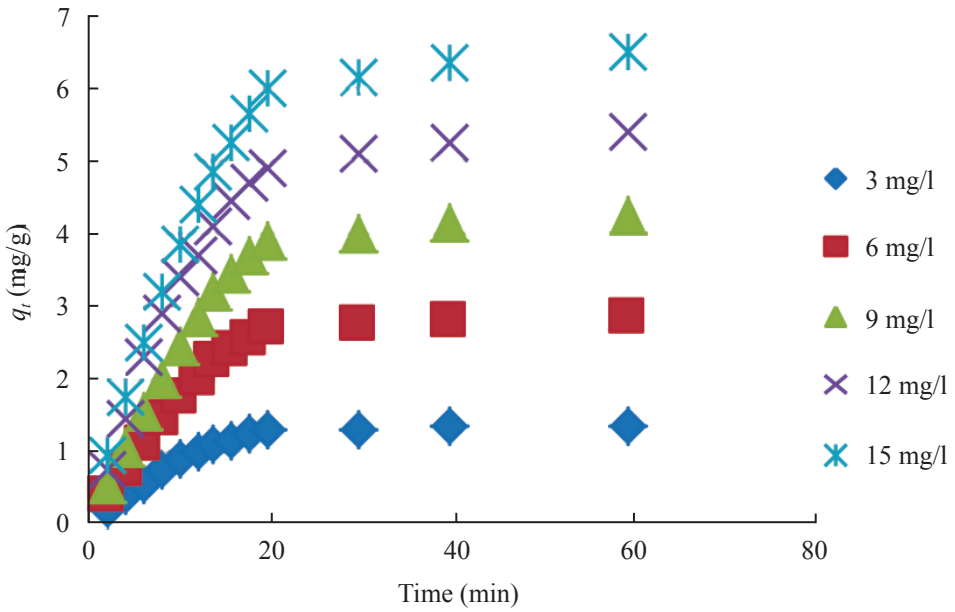

Figure 2. The effect of initial dye concentration on the adsorption capacity of the rambutan skin biosorbent.

An increase in the initial dye concentration led to an increase in the adsorption capacity of the dye on biosorbent, due to the increase in the driving force of the concentration gradient. The adsorption capacity at equilibrium increased from 1.344 mg/g to 6.506 mg/g, with an increase in the initial MB concentration from 3.0 mg/l to 15.0 mg/l.

Effect of the Solution Temperature on the Adsorption Process

The effect of the solution temperature on the MB dye adsorption was investigated at various temperatures, ranging from 30°C to 60°C. The graph in Figure 3 shows the effect of the solution temperature on the percentage removal of dye. The percentage removal of MB dye increased in proportion to the increase in solution temperature. The percentage removal of dye increased from 88.39% to 97.00%, when the solution temperature increased from 30°C to 60°C.

Since the adsorption percentage increased when the solution temperature was increased, the system was considered to be endothermic. Such phenomenon could be explained by the increased mobility of the MB molecules in tandem with a rise in solution temperature. This behaviour implied a kinetically controlling biosorption process. As the solution temperature increased, more MB molecules would acquire sufficient energy from the solution to undergo an interaction with the active sites on the biosorbent surface. In addition, increasing the solution temperature also increased the rate of diffusion of MB molecules across the external boundary layer of the biosorbent particles due to the decrease in the solution viscosity.

Effect of Solution pH

Figure 4 shows the graphical result of the effect of solution pH on the adsorption of MB. As shown in Figure 4, the percentage removal of MB increased gradually, when the solution pH increased from pH 2 to pH 12. The adsorption of MB on rambutan skin was favourable at higher pH. The percentage removal of MB dye increased from 63.71% to 93.76%, with the increase of pH from pH 2 to pH 12.

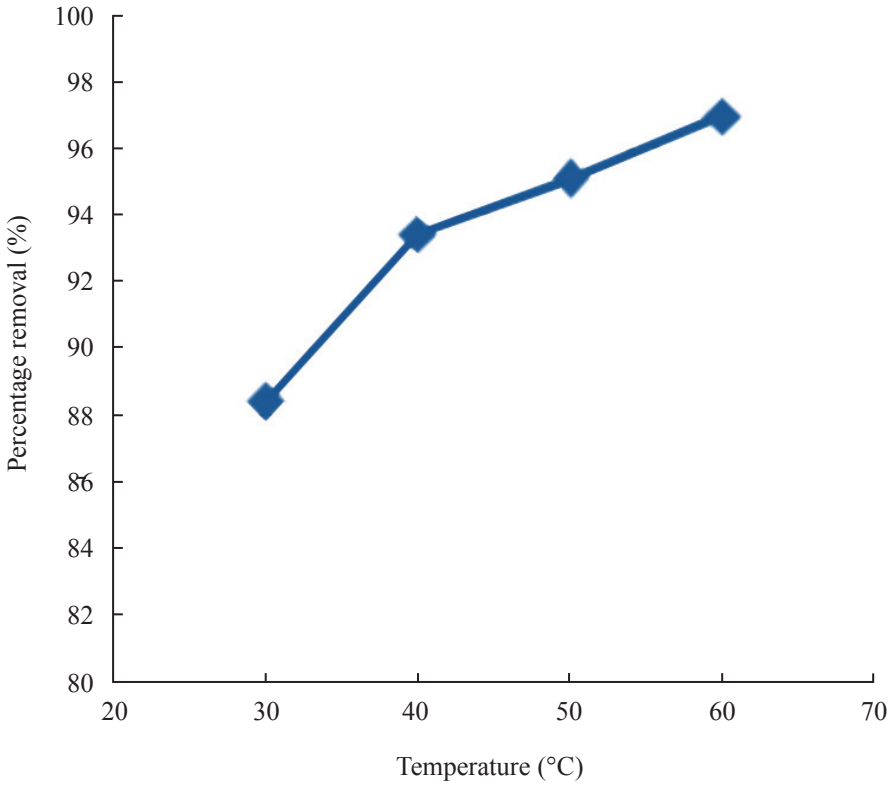

Figure 3. The effects of the solution temperature on MB dye adsorption percentage.

The adsorption of MB dye by rambutan skin adsorbent is unfavourable at low pH because at lower pH, the number of negatively charged adsorbent sites decreased, while the number of positively charged surface sites increased. This condition was unfavourable for the adsorption of positively charged MB dye cations due to electrostatic repulsion. The presence of excess H^+ ions competing with MB dye cations for the adsorption sites on the rambutan skin might also decrease the adsorption of MB dye cations at acidic pH. As the pH value increases, the percentage removal of MB dye increases gradually, due to the significant change in polarity, where the number of negatively charged active sites increased and more MB cations were able to bond to the adsorption active sites of the rambutan skin.

Adsorption Isotherm

The adsorption isotherm indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [18]. The time required to attain this equilibrium state is termed the equilibrium time, and the amount of dye adsorbed at equilibrium reflects the maximum adsorption capacity of the adsorbent under the operating conditions [18]. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model for the adsorption of MB using rambutan skin. The Langmuir, Freundlich, and Temkin models were used to examine the data derived from the adsorption of MB by the biosorbent.

Langmuir model is based on the assumption that adsorption energy is constant and independent of the surface coverage where the adsorption occurs on localized sites with no interaction between the adsorbate molecules and that maximum adsorption occurs when the surface is covered by a monolayer of adsorbate [16]. The linear form of Langmuir isotherm Equation is given as:

$$\frac{C_e}{C_e} = \frac{1}{Q_O K_L} + \frac{1}{Q_O} C_t \qquad (3)$$

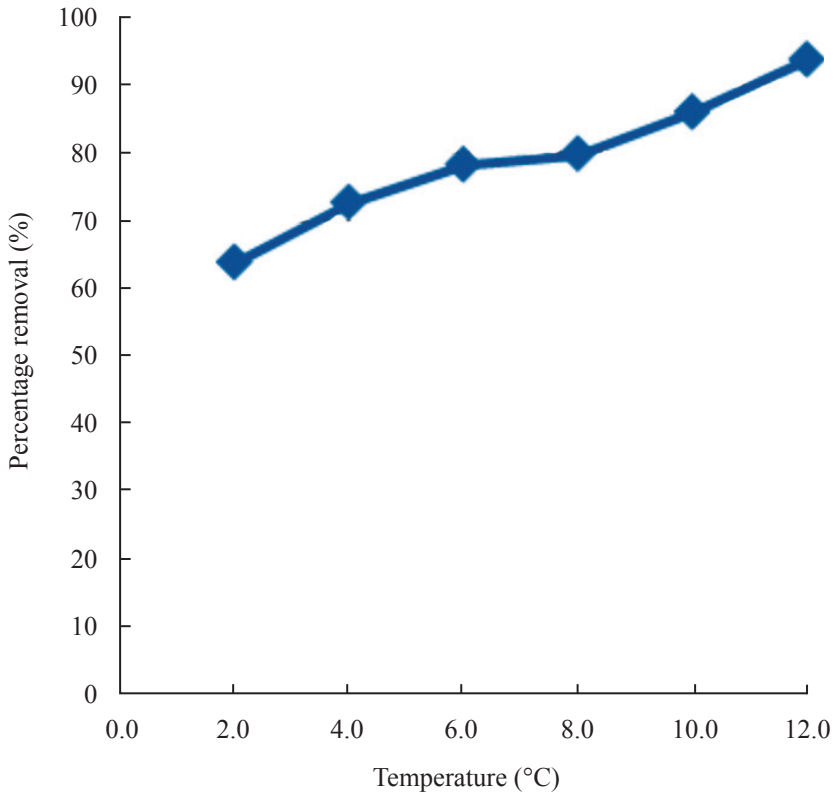

Figure 4. The effect of solution pH on the percentage of MB dye removal.

Where, C_e is the equilibrium concentration of the MB dye (mg/l), q_e is the amount of MB adsorbed per unit mass of the rambutan skin (mg/g), Q_o is the Langmuir constant related to adsorption capacity (mg/g), and K_L is the Langmuir constant related to rate of adsorption (l/mg).

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L), defined by:

$$R_L = \frac{1}{(1 + K_L C_O)} \qquad (5)$$

where C_0 is the highest initial solute concentration (mg/l).

In order to find the value of R^2, Q_0 and K_L for the Langmuir isotherm for the adsorption of MB on rambutan skin, the graph of C_e/q_e against C_e is plotted as shown in Figure 5.

Freundlich model is an empirical Equation based on adsorption on a heterogeneous surface or surface supporting sites of varied affinities [16]. In the case of the adsorption of MB dye on the rambutan skin biosorbent, Freundlich model is represented by the well known logarithmic form of Equation given as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (5)$$

where K_f and n are the Freundlich constants with n as a measure of the deviation of the model from linearity of the adsorption and K_f indicates the adsorption capacity of the adsorbent. In general, n>1 suggest that adsorbate is favorably adsorbed on the adsorbent.

In order to find the value of R^2, n and K_f for the Freundlich isotherm for the adsorption of MB on rambutan skin, the graph of log q_e against log C_e is plotted as shown in Figure 6.

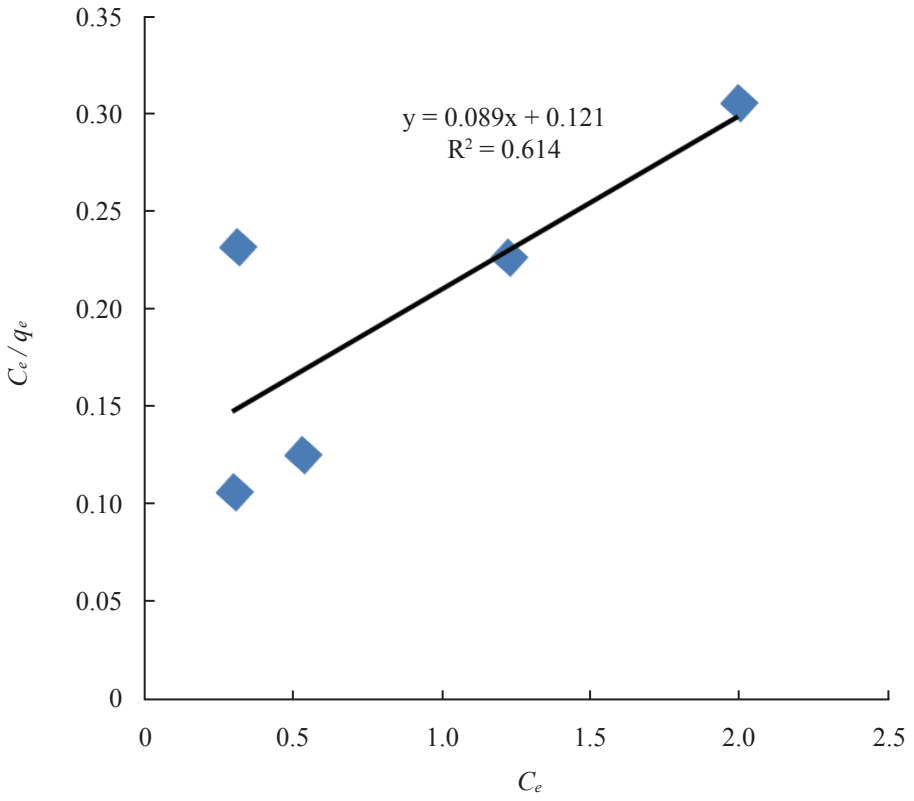

Figure 5. The graph of Langmuir isotherm for MB dye adsorption onto rambutan skin biosorbent.

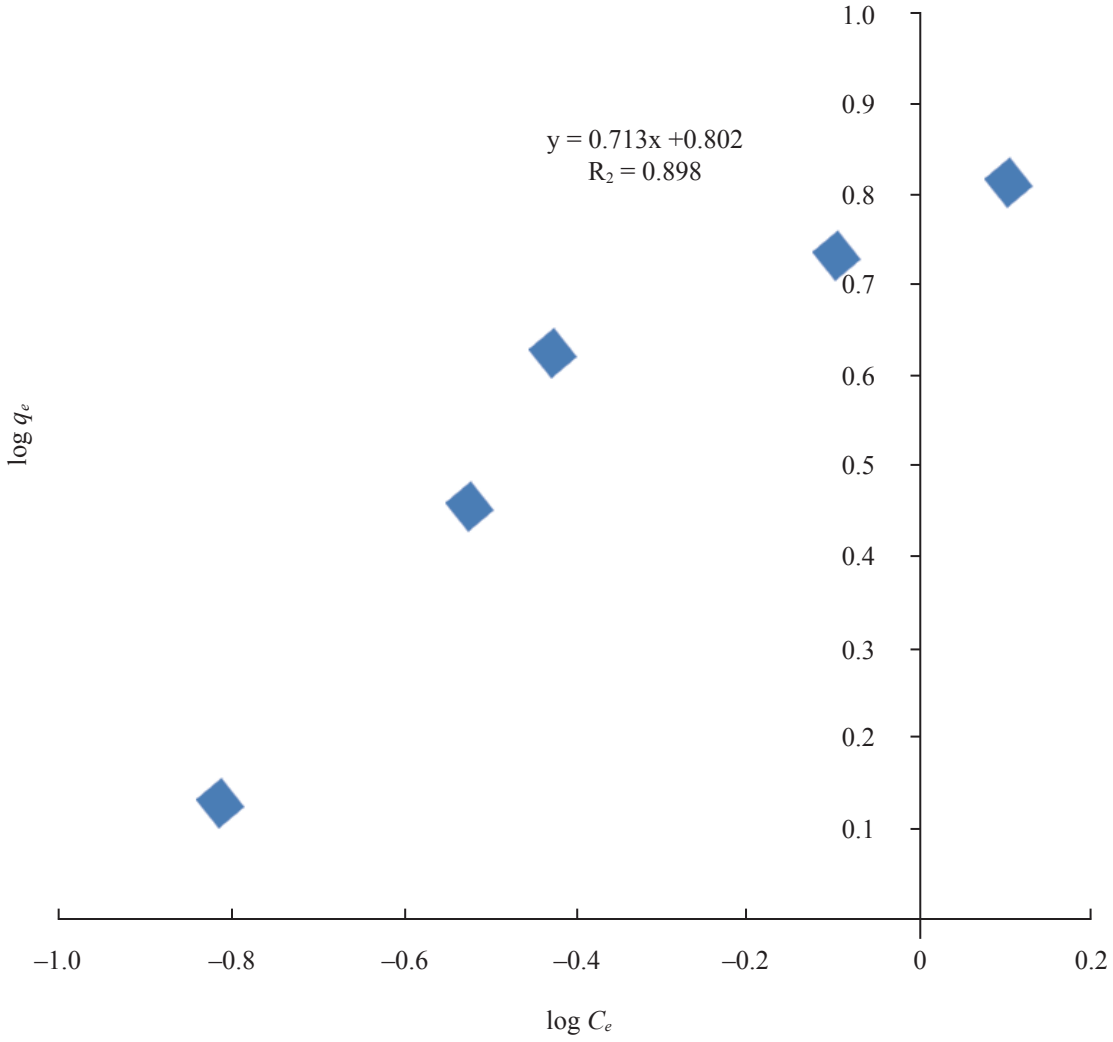

Figure 6. The graph of Freundlich isotherm for MB dye adsorption onto rambutan skin biosorbent.

Temkin isotherm assumes that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbent-adsorbate interaction and the adsorption is characterized by a uniform distribution of binding energies [16]. Temkin model is expressed as:

$$q_e = \left(\frac{RT}{b}\right) \ln (A_T C_e) \qquad (6)$$

where $RT/b = B$ (J/mol), is the Temkin constant related to heat of sorption whereas A (1/g) is the equilibrium binding constant corresponding to the maximum binding energy. R (8.314 J/mol.K) is the universal gas constant and T *(K)* is the absolute solution temperature.

In order to find the value of R^2, A_T and B for the Temkin isotherm for the adsorption of MB on rambutan skin, the graph of q_e against ln C_e need to be plotted. The graph is shown in Figure 7.

Table 2 summarizes all the constants and correlation coefficient, R^2 values obtained from the three isotherm models applied for the adsorption of MB dye on the rambutan skin biosorbent. On the basis of the R^2 value, Freundlich isotherm seemed to represent the equilibrium adsorption data with a better fit as compared to the other isotherms. The reason is because the R^2 value for the Freundlich isotherm (0.898) is higher than that of Langmuir (0.614) and Temkin isotherms (0.819). This

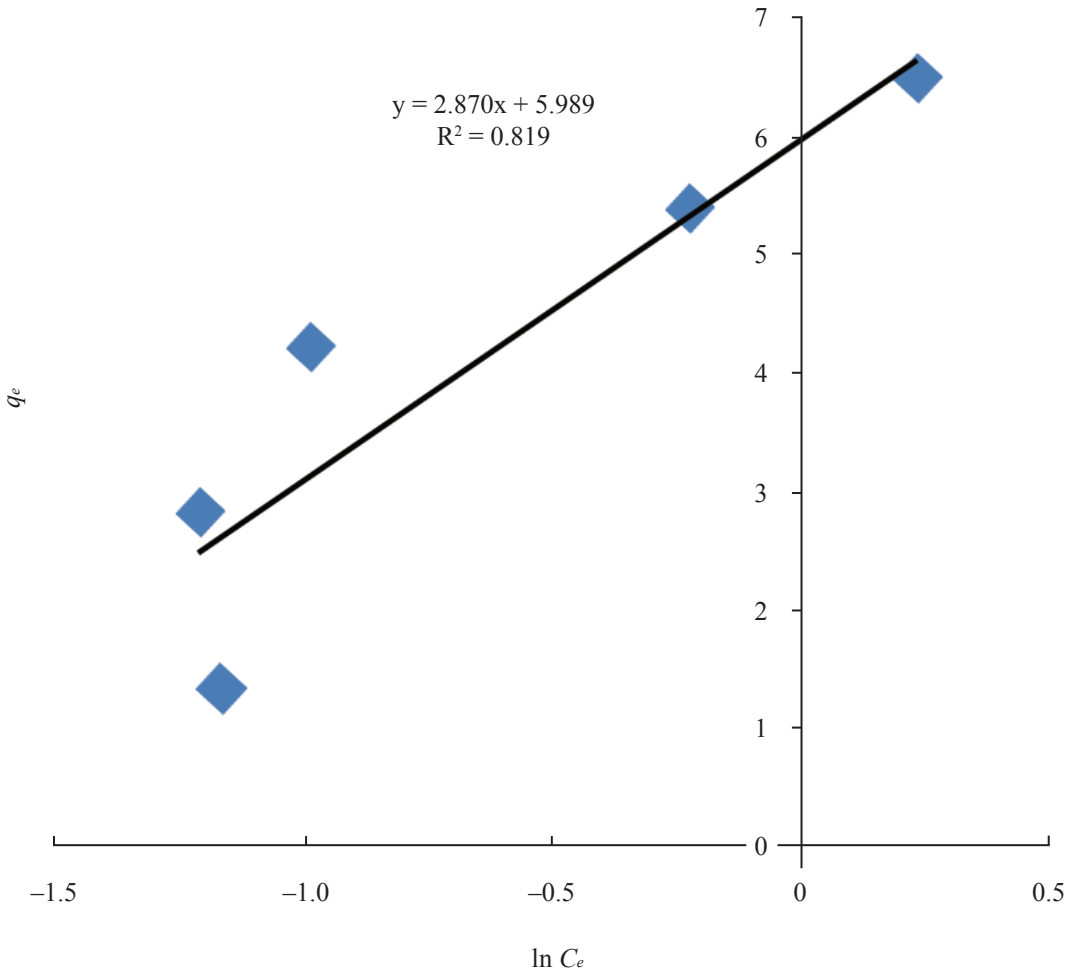

Figure 7. The graph of Temkin isotherm for MB dye adsorption onto rambutan skin biosorbent.

Table 2. The adsorption isotherm parameters for adsorption of MB using rambutan skin at temperature 30°C.

Isotherm	Isotherm constants
Langmuir isotherm	
Q_0 (mg/g)	11.24
K_L (L/mg)	0.735
R^2	0.614
Freundlich isotherm	
K_f	6.339
1n	0.713
R^2	0.898
Temkin isotherm	
A_T	8.059
B	2.870
R^2	0.819

explains the heterogeneous nature of the rambutan skin surface. The value of n is greater than unity, suggesting that MB dye is favourably adsorbed by the biosorbent. Maximum adsorption capacity of the rambutan skin is 11.24 mg/g at the temperature of 30°C.

Adsorption kinetics

The study of adsorption kinetics describes the solute uptake rate which controls the residence time of adsorbate uptake at the solid/solution interface [18]. In order to analyze the adsorption kinetics of MB dye onto rambutan skin, two kinetic models were applied to analyze the experimental data. These two models are pseudo-first-order and pseudo-second-order kinetic models.

The pseudo-first-order kinetic model is widely used to predict the adsorption kinetics and is defined as:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

where q_e and q_t (mg/g) are the amounts of adsorbate adsorbed at equilibrium and at any given time, t (min), respectively. k_1 (min^{-1}) is the adsorption rate constant. In order to determine the suitability of the pseudo-first-order kinetic model, a graph of ln (q_e–q_t) versus t is plotted as shown in Figure 8.

The pseudo-second-order Equation predicts the behaviour over the whole range of adsorption process and is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_z q_e^z} + \frac{1}{q_e} t \quad (8)$$

Where, k_2 (g/mg.h) is the rate constant of second-order adsorption. In order to determine the suitability of the pseudo-second-order kinetic model, a graph of t/q_t versus t is plotted as shown in Figure 9.

By comparing the two graphical charts in Figures 8 and 9, it was observed that the correlation coefficients (R^2) for pseudo-second-order model were in the range of 0.953 to 0.972, which were higher than the R^2 values of the pseudo-first-order ($0.909 < R^2 < 0.972$), which indicated a better fit for the pseudo-second-order kinetic model. Hence, the adsorption process of MB dye using rambutan skin as biosorbent followed the pseudo-second-order kinetic model. Moreover, this also suggested that chemisorption might be the rate-limiting step that controled the overall adsorption process.

CONCLUSION

This study showed that rambutan skin was a promising biosorbent to be used in the removal of MB from aqueous solutions over a wide range of concentrations. This biosorbent could be effectively employed as an alternative adsorbent to replace activated carbon in removing MB dye with the added benefit of it being cheaper. Adsorption of MB was found to increase with the increase in initial MB dye concentration. The adsorption of MB dye was also found to increase in proportion to the solution temperature, due to the endothermic nature of the adsorption system. As the pH of the aqueous solutions increased, the adsorption of MB increased as well. The equilibrium data were best described by the Freundlich isotherm model due to the heterogeneous nature of the rambutan skin surface. Maximum adsorption capacity of the rambutan skin was 11.24 mg/g. The rate of adsorption of MB dye was found to follow the pseudo-second-order kinetic model with correlation of $0.953 < R^2 < 0.972$. The overall result demonstrated that rambutan skin could be economically feasible to replace activated carbon as an alternative adsorbent for the removal of MB dye from aqueous solutions. The spent biosorbent could be ashed and used as fertilizer as it a plant residue. This will in turn also destroy the adsorbate, reducing the need for any further treatment and cost.

ACKNOWLEDGEMENTS

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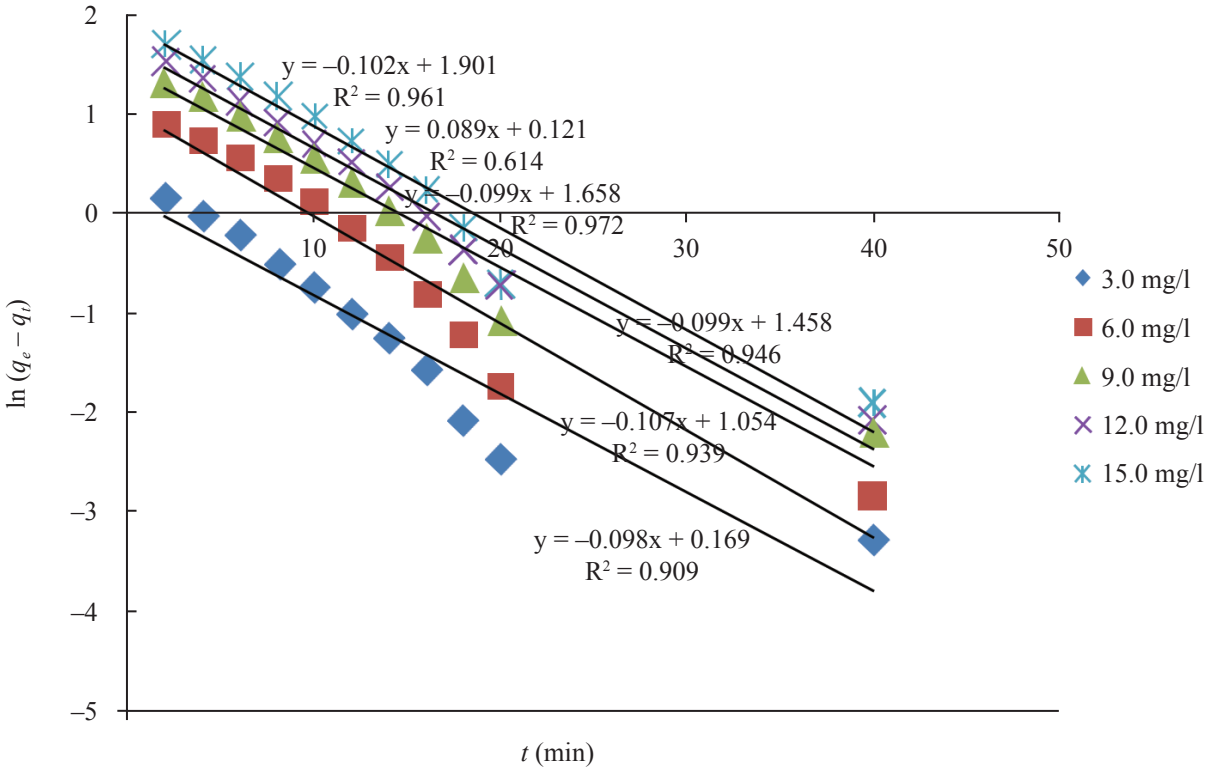

Figure 8. The pseudo-first-order kinetic model for MB dye adsorption onto rambutan skin biosorbent.

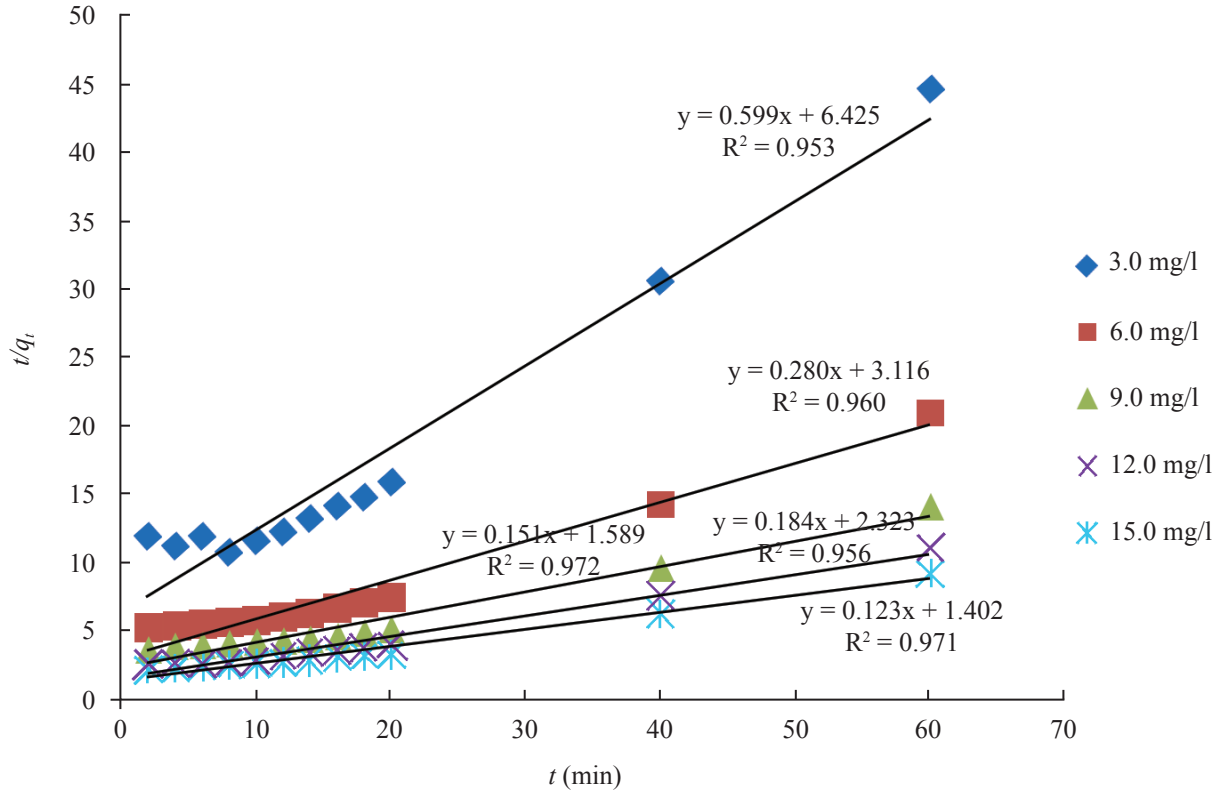

Figure 9. The pseudo-second-order kinetic model for MB dye adsorption onto rambutan skin biosorbent.

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