Equilibrium Isotherms and Kinetic Studies of Removal of Methylene Blue Dye by Adsorption onto Miswak Leaves as a Natural Adsorbent

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ABSTRACT

In this research miswak leaves, agriculture wastes, available in large quantity in Saudi Arabia, was used as low-cost adsorbent for removing methylene blue (MB) dye. Equilibrium behavior of miswak leaves was investigated by performing batch adsorption experiments. The effects of [MB]₀, pH, contact time and adsorbent dose were evaluated. An alkaline pH (10.6) was favorable to the adsorption of MB dye. Adsorption isotherm models, Langmuir, Freundlich and Temkin were used to simulate the equilibrium data. Langmuir equation was found to have the highest value of R² compared with other models. Furthermore, it was found that miswak leaves have a high adsorptive capacity towards MB dye (200 mg/g) and show favorable adsorption of MB dye with separation factor (Rₛ < 1). In addition, pseudo-first-order, pseudo-second order and intra-particle diffusion were used to study the kinetics of MB adsorption onto miswak leaves. Adsorption process undergoes pseudo-second order kinetic as proved by the high value of R² and the low value of sum of squared error (SSE percentage). Results indicated that intra-particle diffusion is not the limiting step, and the adsorption process is spontaneous as indicated by the negative value of the ΔG.

Keywords: Miswak Leaves, Salvadora Persica, Methylene Blue, Adsorption Isotherms, Adsorption Kinetics

1. Introduction

Presence of many pollutants in water and wastewater has increased recently due to high increase in various industrial activities. Using dyes in many industries [1] such as textile, paper, plastics, leather, food and cosmetic, represent a large group of chemicals that get mixed in wastewater among many aqueous pollutants. In recent years, there is a dramatic increase in the annual production of different synthetic dyes representing more than 10,000 dyes [2]. Many azo dyes and their intermediates have toxic effects on environment and human health due to their carcinogenicity and visibility [3]. It was reported that incomplete degradation of dyes by bacteria in the sediment resulted in production of some carcinogenic and harmful amines [4]. In addition, presences of color substances in the water body may decrease the light transmission which decreasing the photosynthesis activity, leading to decrease growth of bacteria and hence decreasing the biodegradation of impurities in water [5]. Methylene blue dye (MB), is basic dye has been extensively used in textiles and printing industry, and it has been found as non-biodegradable dye. Therefore, it is essential that wastewater contaminated with MB dye to be given some treatments before discharge.

Many treatment techniques have been applied to a broad range of water and wastewater contaminated with dyes including physical- or chemical-treatment processes [6]. These include chemical coagulation/flocculation [7,8], ozonation, oxidation, photodegradation [9], ion exchange, irradiation, precipitation and adsorption. Several critical reviews on current treatment technologies were reported [10]. Many of these techniques are costly, required various tools and have limitations. It has been reported that the adsorption onto activated carbon, have proven to be the most efficient and reliable method for the removal many pollutants, including different dyes [7]. Although commercial activated carbon is very effective adsorbent, its high cost requires the search for alternatives and low-cost adsorbents [11]. Several low-cost adsorbents have been...
tested for removing dyes [12] including peat, pith, Orange peel, Indian Rosewood [11], cellulose based wastes, giant duckweed, banana pith and other agricultural by-products [12]. On the other hand, Salvadora persica (miswak or arak) is a common plant found widely in different areas in Jazan, Saudi Arabia in addition to other countries.

Miswak has been used by many Islamic communities as toothbrushes, and has been scientifically proven to be very useful in the prevention of tooth decay, even when used without any other tooth-cleaning methods [13,14]. However, roots of miswak only are used as a toothbrush and the rest of the plant such as leaves possibly remain as an agriculture waste. To make further use of the plant, the present study is an attempt to use miswak tree leaves, as nonconventional low-cost adsorbent for removal of MB dye from aqueous solution. The capacity of adsorbent for adsorbate is obtained by adsorption isotherm model, which is the equilibrium relationships between adsorbent/adsorbate systems.

In this study, three models (Langmuir, Freundlich [15-19], and Temkin [20,21]) have been used to describe the sorption process of MB onto miswak leaves. Furthermore, kinetics of MB adsorption onto miswak leaves will be investigated using a pseudo-first order [15], a pseudo-second order [22,23] and an intraparticle diffusion [15-24]. Linear regression analysis method will be used to determine the most fitted model and finding its parameters [25].

2. Experimental

2.1. Chemicals

All chemicals used in this study were of analytical-grade and used without further purification. Methylene blue (MB) or basic blue-9 is a monovalent cationic dye with a molecular formula of C16H18N3ClS (Mo. Wt. 319.85 g/mol), used as the model adsorbate in the present study to evaluate the efficiency of leaves Salvadora persica (miswak) as a natural adsorbent. The chemical structure of MB is shown in Figure 1. HCl, NaOH used to adjust the pH were purchased from BDH.

2.2. Adsorbent

Salvadora persica (miswak or arak) was used as a natural adsorbent. Salvadora persica plant is a member of the Salvadoraceae family. Leaves of miswak were collected from fields around El-Ardh area (Bathan) in Jazan, Saudi Arabia. Adsorbent was air dried and washed several times with distilled water, dried again then ground well and sieved.

2.3. Preparation of Dye Solutions

Methylene blue (MB) was used in this study as an environmental pollutant. Stock solutions (1000 mg/L) of MB dye were prepared by dissolving the required amount in distilled water. Batch experimental solutions were obtained by diluting the dye stock solutions in accurate different initial concentrations. Calibration curves were prepared by serial dilutions (1.0 to 10.0 mg/L).

2.4. Adsorption Studies

In batch adsorption experiments, certain amounts of miswak were added into several 10 mL bottles, each containing 5.0 mL solution of MB dye with [MB]₀ of 120 mg/L. Then the bottles were stirred at 800 rpm for 80 min using a magnetic stirrer at room temperature. Miswak in the samples was separated by centrifugation and the concentrations of dye at any time (t) were determined in the supernatant solutions. Adsorption isotherms were determined by introducing 0.005 g (1.0 g/L) miswak to respective 5.0 mL of different dye concentrations (16 - 150 mg/L) at room temperature.

2.5. Effect of Adsorbent Mass

To investigate the effect of adsorbent mass, different mass of miswak 0.005 to 0.015 g (1 - 3 g/L) was introduced to a number of glass tubes containing a specific volume of a fixed [MB]₀ at the same pH and room temperature. Concentrations of MB were measured at equilibrium.

2.6. Effects of Initial Dye Concentration (C₀) and Contact Time

To evaluate the effect of both contact time and adsorption kinetic, experiments were conducted at different periods using previously described system.

2.7. Analytical Methods

Standard solution of MB dye was used to obtain calibration curves. UV–vis spectrophotometer (APEL) was used for determining the concentrations of dye solutions. For each adsorption experiment, samples were withdrawn at interval times, and the adsorbate (miswak) was separated.
by the centrifuge. Then concentrations of residual dye solutions were measured by monitoring the absorbance changes at a wavelength of maximum absorbance ($\lambda_{\text{max}} = 665 \text{ nm}$) for MB dye. The amount of dye sorbed at any time, $q_t$, was calculated from:

$$q_t = \frac{V(C_0 - C_t)}{W}$$  \hspace{1cm} (1a)

At equilibrium, $q_e = q_e$ and $C_e = C_e$; therefore, the amount of sorbed dye, $q_e$, was calculated from

$$q_e = \frac{V(C_0 - C_e)}{W}$$  \hspace{1cm} (1b)

where $C_0$, $C_t$, and $C_e$ are the initial concentration, concentration at any time and equilibrium concentrations of dye solution (mg/L), respectively, $V$ is the volume of the solution (L), and $W$ is the mass of adsorbent (g) [26].

The dye removal percentage can be calculated as follows:

$$\text{Removal}\% = \left( \frac{C_0 - C_e}{C_0} \right) \times 100$$  \hspace{1cm} (2)

2.8. Equilibrium Isotherm Modeling

The experimental data at equilibrium between the amount of adsorbed dye ($q_e$) on the adsorbent (miswak) and the concentration of dye in solution ($C_e$) at a constant temperature and pH were used to describe the optimum isotherm model. The linear forms of Langmuir, Freundlich [15-19] and Temkin [20,21] equations (Table 1) were used to describe the equilibrium data. Applicability of these equations was compared by judging the correlation coefficients ($R^2$) [25].

2.8.1. Langmuir Isotherm

The Langmuir isotherm model is used to predict the sorption of aqueous compounds onto a solid phase [15, 19]. This mechanistic model assumes that a monolayer of adsorbed material (in liquid, such as MB) is adsorbed over a uniform adsorbent surface (a flat surface of solid phase, such as miswak leaves) at a constant temperature and that the distribution of the compound between the two phases is controlled by equilibrium constant. Hence at equilibrium both rates of adsorption and desorption are equal. The Langmuir equation is derived as:

$$q_e = \frac{q_mK_mC_e}{1 + K_mC_e}$$

where $q_m$ (the maximum capacity of adsorption, mg/g,) and $K_L$ (a constant related to the affinity of the binding sites, L/mg,) are the Langmuir isotherm constants. Both $q_m$ and $K_L$ will greatly impact the conclusions made about the experimental data and can be determined by a simple method of equation optimization by linear regression [25]. That is to transform the isotherm variables to a linear form and then to apply the linear regression analysis of known $C_e$ and $q_e$ values as described by Line-weaver-Burk (Langmuir-II).

2.8.2. Freundlich Isotherm

Freundlich isotherm model [15,19] is assuming that the adsorption process takes place on a heterogeneous surface. The Freundlich exponential equation is given as:

$$q_e = K_F C_e^{1/n}$$  \hspace{1cm} (4)

where $K_F$ ((L/mg) is an indicator of the adsorption capacity and $1/n$ is the adsorption intensity and indicates both the relative distribution of energy and the heterogeneity of the adsorbent sites. The linear form is derived by taking the log of the terms as shown in Table 1.

2.8.3. Temkin Isotherm

Temkin isotherm model (Equation (5)) was used also to test the adsorption potential of miswak leaves to MB dye. This model is taking into account the effects of indirect adsorbate/adsorbate interactions on the adsorption process. Furthermore, the model is assuming that the heat of adsorption ($\Delta H_{ads}$) of all molecules in the layer decreased linearly by increase the coverage. The linear form of Temkin is given as follows:

$$q_e = \frac{RT}{b_f} \ln(K_T) + \frac{RT}{b_f} \ln C_e$$  \hspace{1cm} (5)

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Nonlinear form</th>
<th>Linear form</th>
<th>Plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir-II</td>
<td>$q_e = \frac{K_mC_e}{1 + K_mC_e}$</td>
<td>$\frac{1}{q_e} = \left( \frac{1}{K_mC_e} \right) + \left( \frac{1}{q_m} \right)$</td>
<td>$\frac{1}{q_e}$ VS. $\frac{1}{C_e}$</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$q_e = K_F C_e^{1/n}$</td>
<td>$\log q_e = \log K_F + \frac{1}{n} \log C_e$</td>
<td>$\log q_e$ VS. $\log C_e$</td>
</tr>
<tr>
<td>Temkin</td>
<td>$q_e = \frac{RT}{b_f} \ln(K_T C_e)$</td>
<td>$q_e = \frac{RT}{b_f} \ln K_T + \frac{RT}{b_f} \ln C_e$</td>
<td>$q_e$ VS. $\ln C_e$</td>
</tr>
</tbody>
</table>
where, $R$ is common gas constant (0.008314 kJ/mol K), $T$ is the absolute temperature (K), $1/b_T$ is the Temkin constant related to the heat of sorption (kJ/mol) which indicates the adsorption potential (intensity) of the adsorbent and $K_T$ (L/g) is Temkin constant related to adsorption capacity. The liner plots of $q_e$ versus $\ln C_e$ enable to determine the constants $1/b_T$ and $K_T$ from the slope and intercept respectively.

3. Results and Discussion

3.1. Effects of Initial Dye Concentration ($C_0$) and Contact Time

A miswak leaves dosage of 0.005 g (1.0 g/L) was added to 0.005 L of different concentrations (16 - 150 mg/L) of MB dye solution. Experiments were conducted at a temperature of 303 K for 80 min to test the effect of initial concentration and contact time on the adsorption process. The results (Figure 2) indicated that the adsorption of MB dye onto miswak increases as $[MB]_0$ increased. At the first 10 min of the adsorption process, as $[MB]_0$ increased by 9.4 times (from 16 to 150 mg/L), the adsorbed amount ($q_t$) onto miswak leaves increased 6.5 times (from 6.2 to 40.0 mg/g). Also, as the contact time increased to 30 min, $q_t$ increased by about seven times (from 9.01 to 62.13 mg/g). Therefore, the adsorption of MB dye was very rapid during the first 10 min, and increased gradually during the second 20 min until reached equilibrium at 30 min. The results showed that the uptake of MB dye by miswak leaves depends on $[MB]_0$ and contact time. This is because $[MB]_0$ act as the driving force that increases the mass transfer of MB dye from aqueous solution onto the surface of miswak leaves. During the adsorption process, solutions with different initial concentrations possibly will reach equilibrium at different times. This may be due to the time required for the dye molecules to encounter the boundary layer effect, then diffuse to the surface of the adsorbent and finally diffuse to the porous structure of the adsorbent [27]. Therefore, solutions with low initial concentration (16 mg/L) reached equilibrium first at about 30 min, while solutions with high initial concentration of 150 mg/L takes longer time and reached equilibrium at 60 min. To ensure complete equilibrium of the data, adsorption samples were collected at 80 min. It was noted that as $[MB]_0$ dye increased from 16 to 150 mg/L, the removal % at equilibrium decreased by 25% (from 55.78 to 41.79%). This may be because the constant number of available sites in miswak leaves is easily saturated by the increase of $[MB]_0$, which would lead to a decrease in the removal percentage of MB dye. Other researchers reported similar trend [28,29]. Furthermore, Figure 2 indicated that the increase in $[MB]_0$ from 120 to 150 mg/L led to slight improve in the adsorption capacity of MB onto miswak leaves. Consequently, 120 mg/L of MB was chosen as an optimum $[MB]_0$ for further experiments.

3.2. Effect of Solution pH on Dye Removal

Experiments were conducted at 120 mg/L $[MB]_0$, 1.0 g/L miswak leaves dose, and 80 min contact time at 303 K, to study the effect of solution pH on the equilibrium adsorption capacity ($q_e$) of MB dye onto miswak leaves as shown in Figure 3. It is indicated that $q_e$ of MB dye reaching a maximum in a basic medium and decreased by decreasing the pH values in the acidic medium. The $q_e$ of MB dye in a basic medium (at the pH range of 10.6 to 12.0) reached 60.9 mg/g and become about 13.54 at pH 2.8. Therefore, further adsorption experiments were performed at pH 10.6 as an optimum pH value. The variations in the pH values from acidic to alkaline medium would affect the adsorption rate because both the degree of ionization of dye molecules and the surface properties of the adsorbent (miswak leaves) would vary. It is previously reported that the adsorption process increased by increasing the electrostatic attraction [2]. Thus anionic dyes (dye$^-$) are favorably adsorbed by the adsorbent at
lower pH values due to the presence of H⁺ ions, while adsorption of cationic dyes (dye⁺) are favorably adsorbed at higher pH values, which led to increase the presence of OH⁻ ions as a result of an increase the electrostatic attraction in each case [2]. Therefore, performing the adsorption in the basic medium, at pH 10.6, would increase the negative charge on the adsorbent surface causing an increase in the electrostatic attraction between cationic dye molecules (MB dye⁺) and the surface of miswak leaves, hence increasing the adsorption rate of MB dye. On the other hand, the presence of high concentration of H⁺ ions in the acidic medium at pH 2.8 would make them compete effectively with cationic dye molecules (MB dye⁻) causing a decrease in the amount of dye adsorbed. These results can be further proven by opposite behaviour shown for the adsorption of anionic dyes such as methyl orange (MO) onto Lapindo volcanic mud (LVM) [30]. It was found that the highest adsorption capacity was obtained at pH 3. In addition, a similar trend was shown by the adsorption of some metal cations onto different adsorbents [31,32].

3.3. Effect of Adsorbed Amount

At constant [MB]₀ (120 mg/L), different amounts of miswak (0.5 to 3.0 g/L) were added to dye solutions (0.005 L) to study the effect of miswak leaves amount on MB dye adsorption. Results in Figure 4 shows that the adsorption capacity of MB dye in the first stage increased rapidly with the increase in the adsorbent dose then increased slowly with the further increase in the adsorbent dose. It can be seen that at 1.0 g/L of the adsorbent dose, the adsorption capacity of the dye reached the most at 60.90 mg/g. Then an increase in the dose of miswak leaves from 1.0 to 3.0 g/L resulted only in about 0.7 mg/g more to reach 61.8 mg/g. Thus 1.0 g/L of miswak leaves was chosen as the optimum dose and used in the further experiments. The increase in adsorption capacity of MB dye with the increase in the amount of miswak leaves up to 1.0 g can be assigned to the increase in both the surface area and the adsorption sites to MB dye molecules [23,33]. The adsorption of methylene blue and indigo carmine dye onto different adsorbents such as grass waste, rice husk ash, and bamboo-based activated carbon respectively [23,29,33] was reported with a similar trend.

3.4. Isotherms for the Sorption Process

3.4.1. Langmuir isotherms

Linear fit of Langmuir-II for the adsorption of MB onto miswak leaves at 30°C is shown in Figure 5. The value of qm, Kᵢ, and R² are presented in Table 2. The results indicated that linear form of Langmuir-II model shows the minimal deviation from the fitted equation as indicated by the high value of R² as 0.999. It was proposed that when the value of R² is greater than 0.89, the adsorption data would follow the Langmuir model [2]. Furthermore, the value of qm which is the measure of the maximum adsorption capacity of miswak leaves for MB dye was calculated as 200 mg/g (Table 2). Representing the experimental data by Langmuir isotherm indicates both the homogeneous nature of miswak leaves surface and the formation of monolayer coverage of MB dye molecule at its outer surface [23]. Other researchers reported similar observations for the adsorption of different dyes onto activated carbon prepared from various sources. Adsorption of acid orange 10 dye [34], direct dyes [35] and Congo red dye [36] onto activated carbon prepared from bagasse, sawdust and coir pith respectively.
3.4.1.1. Separation Factor
Separation factor \( R_L \), is a dimensionless constant \([21, 23]\), and it is a good characteristic of the Langmuir isotherm. \( R_L \), can be expressed in the following equation:

\[
R_L = \frac{1}{1 + K_L C_0}
\]

(6)

where \( C_0 \) (mg/L) is the highest [MB]0 and \( K_L \) (L/mg) is Langmuir constant. The value of \( R_L \) indicates the shape of the isotherm to be either linear (\( R_L = 1 \)), unfavourable (\( R_L > 1 \)), favourable (\( 0 < R_L < 1 \)), or irreversible (\( R_L = 0 \)). Thus the \( R_L \) values between 0 and 1 indicate favourable adsorption. Plot of \( R_L \) versus \( C_0 \) of MB at 30°C is shown in Figure 6. The \( R_L \) values were in the range of 0.500 to 0.904, which is less than unity, indicating that the adsorption of MB onto miswak leaves is a favourable process, and the data fits Langmuir isotherm model. Accordingly, miswak leaves is a good adsorbent for MB dye.

3.4.2. Freundlich Isotherm
Equilibrium adsorption data of MB dye onto miswak leaves was tested with Freundlich isotherm model. The linear plot of Freundlich isotherm at 303 K (Figure 7) is employed to determine the intercept value of \( K_F \) and the slope \( 1/n \) along with \( R^2 \) (Table 2). Although, the value of \( R^2 \) (0.993) of Freundlich is slightly lower than the value of \( R^2 \) (0.999) of Langmuir-II isotherm. The value of \( 1/n \) (indicative of favorability) is 0.85, which is close to the unity and indicates the favorability of the adsorption process [5]. Therefore, Freundlich model is still a good model to describe the adsorption data.

3.4.3. Temkin Isotherms
In addition, Temkin adsorption isotherm was chosen to fit with the equilibrium adsorption data. The linear plot of the Temkin isotherm at 303 K is illustrated in Figure 8. The parameters, \( K_T \) and \( b_T \) of the Temkin equation have been calculated for MB dye (Table 2). Due to the low value of both adsorption capacity, \( K_T \), (0.161 L/g) and the value of \( R^2 \) (0.95), the data of equilibrium isotherms of MB onto miswak is poorly described by the Temkin model. On the other hand, comparison of maximum monolayer adsorption capacity \( (q_m) \) of MB onto various adsorbents obtained in the literature is presented in Table 3 in order to compare the efficiency of miswak leaves. It can be seen that miswak leaves are very effective adsorbent for cationic dyes such as MB with a relatively large adsorption capacity of 200 mg/g when compared with some other adsorbents.

3.5. Adsorption Kinetics
In order to study the adsorption of MB onto miswak leaves and to interpret the results, experimental data obtained were fitted into different kinetic models such as the pseudo-first-order [15], the pseudo-second order [22, 23] and an intraparticle diffusion [15,24].

![Figure 6. Plot of separation factor versus [MB] i (T = 303 K, miswak dosage = 1.0 g/L, [MB] i = 16 - 150 mg/L, pH i = 10.6, V' = 0.005 L).](image)

![Figure 7. Freundlich isotherm (T = 303 K, miswak dosage = 1.0 g/L, [MB] i = 16 - 150 mg/L, pH i = 10.6, V' = 0.005 L).](image)

![Figure 8. Temkin isotherm (T = 303 K, miswak dosage = 1.0 g/L, [MB] i = 16 - 150 mg/L, pH i = 10.6, V' = 0.005 L).](image)
Table 3. Comparison of the maximum monolayer adsorption of MB onto various adsorbents.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$q_m$ (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Miswak leaves</td>
<td>200</td>
<td>This study</td>
</tr>
<tr>
<td>Natural Jordanian tripoli</td>
<td>16.6</td>
<td>[1]</td>
</tr>
<tr>
<td>Banana peel</td>
<td>20.8</td>
<td>[15]</td>
</tr>
<tr>
<td>Orange peel</td>
<td>18.6</td>
<td>[15]</td>
</tr>
<tr>
<td>Activated carbon prepared from oil palm shell</td>
<td>243.90</td>
<td>[37]</td>
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<tr>
<td>Activated furniture (850°C)</td>
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<td>[38]</td>
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<tr>
<td>Activated tyres (850°C)</td>
<td>130</td>
<td>[38]</td>
</tr>
<tr>
<td>Activated sewage char (800°C)</td>
<td>120</td>
<td>[38]</td>
</tr>
<tr>
<td>Pyrolysed furniture</td>
<td>80</td>
<td>[38]</td>
</tr>
<tr>
<td>Bamboo-based activated carbon</td>
<td>454.2</td>
<td>[23]</td>
</tr>
<tr>
<td>Pineapple leaf powder (PLP)</td>
<td>294.26</td>
<td>[39]</td>
</tr>
</tbody>
</table>

3.5.1. Pseudo First-Order Equation

The rate constant of adsorption is determined from the pseudo first-order equation given by Langergren and Svenska (1898) [15], which expressed as follows:

$$ \log(q_e - q_t) = \log q_e - \left( \frac{k_1}{2.303} \right) t $$

where $q_e$ and $q_t$ are the amounts of the MB adsorbed (mg/g) at equilibrium and at time $t$ (min), respectively, and $k_1$ is the rate constant adsorption (min$^{-1}$).

Values of $k_1$ and $q_e$ were calculated from the slope and the intercept of the plots of $\log(q_e - q_t)$ versus $t$ respectively at different concentrations (Figure 9). The results in Table 4 show that the values of $R^2$ were low and the experimental $q_e$ values do not agree well with the calculated values. This shows that the adsorption of the MB onto miswak is not first-order kinetics.

3.5.2. Pseudo-Second-Order Rate Equation

Equation of pseudo second-order based on equilibrium adsorption [22-23] can be expressed as:

$$ \frac{d(q_e - q_t)}{dt} = k_2 (q_e - q_t)^2 $$

or

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

where, $k_2$ (g/mg·min) is the adsorption rate constant of pseudo second-order adsorption rate. The value of $q_e$ and $k_2$ can be from the slope and intercept of the plot of $\frac{t}{q_t}$ versus $t$ respectively. The results in Figure 10 show linear plots for all different initial concentrations studied with very high values of $R^2$ (Table 4) in addition to the good agreement between experimental and calculated values of $q_e$. Therefore, the adsorption of MB onto miswak is greatly represented by the pseudo second-order kinetics. Moreover, adsorption process of MB onto different natural adsorbents such as a pineapple leaf powder (PLP) undergoes second-order kinetics [40].

3.5.3. Intraparticle Diffusion Study

In order to investigate the mechanism of the MB adsorption onto miswak, intra-particle diffusion based mechanism was studied. It is proposed that the uptake of the adsorbate (MB dye) by the adsorbent (miswak leaves) varies almost proportionately with the square root of the contact time ($t^{1/2}$). Weber and Morris [15,24] proposed the most-widely applied intra-particle diffusion equation for sorption system as:

$$ q_t = k_{ad} t^{1/2} $$

where, $q_t$ is the amount of MB dye adsorbed per unit mass of adsorbent (mg/g) at a time $t$ and $k_{ad}$ the intra-particle diffusion rate constant (mg/g·min$^{-1/2}$). The
Table 4. Adsorption kinetic parameters for the adsorption process (miswak dosage = 1.0 g/L, [MB] = 16 - 150 mg/L, T = 303 K, pH 10.6 and V = 0.005 L).

<table>
<thead>
<tr>
<th>[MB]₀ (mg/L)</th>
<th>qₑ,exp (mg/g)</th>
<th>qₑ,cal (mg/g)</th>
<th>k₁ (min⁻¹)</th>
<th>R²</th>
<th>SSE</th>
<th>qₑ,cal (mg/g)</th>
<th>k₂ (g/mg·min⁻¹)</th>
<th>R²</th>
<th>SSE</th>
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<td>16</td>
<td>8.93</td>
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<td>0.901</td>
<td>47.71</td>
<td>66.67</td>
<td>0.0023</td>
<td>0.991</td>
<td>5.16</td>
</tr>
<tr>
<td>150</td>
<td>62.69</td>
<td>84.14</td>
<td>-0.1497</td>
<td>0.937</td>
<td>49.50</td>
<td>71.43</td>
<td>0.0025</td>
<td>0.994</td>
<td>7.82</td>
</tr>
</tbody>
</table>

Units used for the above terms are as follow: [MB]₀ (mg/L), qₑ (mg/g), k₁ = min⁻¹, SSE = %, k₂ = g/mg·min⁻¹.

3.6. Validity of Kinetic Models

The applicability of both pseudo-first order and pseudo-second order models for the adsorption of MB onto miswak were verified at different [MB]₀ using the sum of squared error (SSE, percentage ) equation [23] given by:

\[
SSE = \sqrt{\frac{(qₑ,exp - qₑ,cal)^2}{N}}
\]

where, \(N\) is the number of data points used in the linear plot of each model. The validity of these models was compared by judging the low value of \(SSE,\%\) which indicates the better fit. The values of \((SSE,\%)\) obtained for the two models listed in Table 3. It is indicated that...
the pseudo-second-order kinetic model yielded the lowest $SSE,\%$ values (0.535 to 7.819). Whereas, the first-order model led to very high values of $SSE,\%$ (1.87 to 49.50). This agrees with the previous values of both $R^2$ and $q_{e,exp}$ obtained earlier for the pseudo-second order (Table 3) to further prove the suitability of the pseudo-second-order kinetic to describe the adsorption process of MB onto miswak leaves. Also, a similar trend was reported for the adsorption of MB onto bamboo-based activated carbon [23].

3.7. Standard Free Energy Change ($\Delta G^\circ$)

Standard free energy ($\Delta G^\circ$) can be calculated from the following equations [2]:

$$\Delta G = -RT \ln K_C \quad (12)$$

$$K_C = \frac{q_e}{C_C} \quad (13)$$

where, $T$ is the temperature (K), $R$ is gas constant (kJ/mol K), $K_C$ (L/g) is the standard thermodynamic equilibrium constant, $q_e$ is the amount of adsorbed MB dye per unit mass of miswak leaves at equilibrium (mg/g) and $C_C$ is the equilibrium aqueous concentration of MB. The Gibbs free energy change ($\Delta G^\circ$) is negative indicating that the adsorption process of MB onto miswak is spontaneous.

4. Conclusions

The adsorption of MB dye onto miswak leaves was studied. Among the three different isotherm models, the equilibrium data was best fitted with the Langmuir-II equation. The equilibrium capacities based on the Langmuir analysis was 200 mg/g which is comparable with different adsorbents used for the adsorption of MB dye. Also, the equilibrium data can be modeled by Freundlich isotherm model. The adsorption of MB was favored by miswak leaves with value of RL less than unity. Furthermore, the adsorption process is spontaneous follows pseudo-second order kinetics and the mechanism involved more than one process. The present work revealed that the miswak leaves are a promising material for the removal of MB dye from aqueous solutions.

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REFERENCES


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